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Preface

The chapters in this and its two companion volumes deal with an aspect of transition metal chemistry which is fundamental to the application of ligand field theory. The change from a high spin to a low spin ground state which occurs for a particular metal ion when the ligand field is progressively strengthened is one of the most important aspects of the theory. When this occurs within a particular complex merely by the application of some external perturbation without any change in chemical composition a most remarkable and fascinating situation arises – electronic spin crossover or spin transition, the subject of these volumes. As will be evident from the various chapters, the situation is realised in a surprisingly large number of instances and its detection is feasible by application of a great variety of techniques. The perturbations which can instigate a change in spin state, initially confined to a variation in temperature or pressure, now include irradiation with visible light, X-rays and radioactive sources as well as application of a magnetic field.

Spin crossover has been investigated by chemists almost since the beginning of the application of the ideas of ligand field theory. It offers a very diagnostic means of testing many aspects of the theory and its study has revealed features of importance in the understanding of the mechanism of a range of reactions of transition metal complexes – e.g. substitution, electron transfer, racemisation and photochemical processes. But its relevance goes beyond this and it is no longer the exclusive domain of chemists. Biochemists and biologists have long had a strong interest in the phenomenon since its role in, for example, the function of certain haem systems is crucial. Similarly its relevance to earth scientists, arising principally from the pressure dependence, has become widely recognised. Because of the remarkable ways in which spin crossover is manifested in solid substances it has attracted the attention of solid-state scientists and it provides a highly responsive probe for the investigation of cooperative phenomena in solids. Thus physicists, theoreticians and others have become attracted to the topic and much of the recent progress in the field can be ascribed to highly effective interdisciplinary collaborations. A further driving force for both a broader and a deeper interest in spin crossover is the recognition that the spin crossover

phenomenon has potential application in switching, sensing, memory and other devices. Hence materials scientists are also now making important contributions to the field. It is particularly noteworthy that spin crossover research has recently been incorporated into the program of the biannual International Conference on Molecular Magnetism (ICMM) with a continually growing participation from researchers in the field. Related to this is the recent establishment by the German Science Foundation of a *Priority Program* on Molecular Magnetism involving some 50 projects, a quarter of which are directly concerned with spin crossover.

The interest in the practical aspects of spin crossover, together with the discovery of the light-induced spin changes first reported in the early 1980s, the latter also opening up a totally new approach to the study of fundamental aspects of the phenomenon, have resulted in a remarkable, almost exponential, growth in the literature devoted to the field. This growth has been stimulated too by the remarkable advances in techniques, particularly in structure determination. The importance of understanding the structural consequences of a spin state change was recognised early but it was rare, up until the 1980s, to have both spin states characterised structurally. With the improvement in equipment and advances in computing it has become feasible to monitor much more closely the structural changes which occur throughout the course of a transition, even for a transition induced by a change in pressure or by irradiation. Synchrotron radiation sources too have become more widely available and valuable structural information has been provided by application of these, particularly for those systems which are not amenable to X-ray crystallography. The net result is that complex, yet beautifully inter-locked networks containing spin crossover centres have now been characterised and structural details can provide the basis for the understanding of the actual nature of the spin transition in the solid species. An impetus of a different kind has been responsible for much of the increased activity in the field in recent years. In 1998 a four year research program titled "Thermal and Optical Switching of Molecular Spin States" (TOSS) was established by the European Union, involving ten leading research groups. The results of the efforts of the groups in this program are evident in much of the material covered in the following chapters.

The field of spin crossover is now obviously a very broad one and in these volumes an attempt has been made to present as comprehensive a treatment of the topic as feasible. Over the years there have been many reviews devoted to aspects of the phenomenon of spin crossover, and a few of these have attempted to give a relatively broad treatment. As the literature and the scope of the topic have grown so markedly in recent times, it has become unrealistic to cover the whole area in a single review article. The range of topics covered in the present volumes takes in the most important modern aspects of the spin crossover field and should provide a sound basis for the understanding of the occurrence of the phenomenon and its multi-faceted

manifestation. It is hoped that it will stimulate further interest in the area. An overall perspective introduces the first volume of the series (volume 233) and this is followed by the ligand field basis for the occurrence of spin crossover. The emphasis in the subsequent chapters, extending into volume 234, is on the nature of the systems in which the phenomenon is observed. This is followed in volumes 234 and 235 by consideration of some fundamental specific phenomena associated with spin crossover and the techniques applied to monitor them. Theoretical aspects are presented in volume 235 which concludes with a discussion of the practical applications of spin crossover, thereby pointing the way to the likely future emphasis of research in the area.

The authors have been drawn from a truly international source and we thank them for their willingness to contribute so enthusiastically to the volumes. Their patience and cooperation, together with those of the staff at Springer, have lightened the burden of our own efforts in bringing the project to fruition. Among the names of authors of the chapters in these volumes, those of two of the most prominent contributors to the field of spin crossover are conspicuously absent – Edgar König and Olivier Kahn. While König, a real pioneer and leader in the field for about thirty years, has been pursuing other interests in an active retirement, sadly Kahn died suddenly in 1999 while his activity in the field was at its peak. The rich legacy of the contributions of both of them to the field of spin crossover is reflected in the extent to which their names appear in the reference lists of many of the chapters of these volumes.

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March 2004

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Time-Resolved Relaxation Studies of Spin Crossover Systems in Solution

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Abstract This chapter focuses on the kinetics of spin-state relaxation, primarily in iron(II) complexes in solution. Initial work carried out during the 1970s and early 1980s by chemical relaxation methods is briefly reviewed, followed by a more detailed account of the laser photoperturbation technique and the photophysics which underpin this approach, now widely adopted as the method of choice for spin crossover relaxation studies in solution. The use of time-resolved vibrational spectroscopy as an alternative to conventional spectrophotometric probing of the spin crossover relaxation process is described. The results of variable temperature and pressure studies on a variety of spin crossover complexes are also considered, particularly with reference to strategies for the control of spin state lifetimes through design of ligand structures.

Keywords Spin crossover · Dynamics · Kinetics · Ultrafast spectroscopy · Photoperturbation · Photophysics · Activation parameters · Time-resolved vibrational spectroscopy

List of Abbreviations

b(bdpa)	<i>N,N'</i> -Bis(benzyl)- <i>N,N'</i> -bis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine
bpy	2,2'-Bipyridine
btpa	<i>N,N,N',N'</i> -Tetrakis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine
CT	Charge transfer
dpa	Bis(2-pyridylmethyl)amine
HB(pz) ₃	Hydrotris(pyrazolyl)borate
HS	High spin
ISC	Intersystem crossing
LF	Ligand field
LFP	Laser flash photolysis
LIESST	Light induced excited spin state trapping
lpp[9]aneN ₃	<i>N</i> -(6-Methyl-2-pyridylmethyl)- <i>N',N''</i> -bis(2-pyridylmethyl)-1,4,7-triazacyclononane
LS	Low spin
metpen	<i>N</i> -Methyl- <i>N,N',N'</i> -tris(2-pyridylmethyl)-1,2-diaminoethane
MLCT	Metal-to-ligand charge-transfer
phen	1,10-Phenanthroline
phenmethoxa	3-(1,10-Phenanthrol-2-yl)-5-methyl-1,2,4-oxadiazole
pic	2-Picolylamine
ppa	<i>N</i> ² -(Pyridylmethyl)picolinamidine
ptz	1-Propyltetrazole
pyBimH	2-(2'-Pyridyl)benzimidazole
pyimH	2-(2-Pyridylimidazole)
Sal ₂ trien	Bis(salicylaldiminato)triethylenetetramine
SCO	Spin crossover
TA	Transient absorption
terpy	2,2',6',2''-Terpyridine
tp[10]aneN ₃	<i>N,N',N''</i> -Tris(2-pyridylmethyl)-1,4,7-triazacyclodecane
tpchxn	Tetrakis(2-pyridylmethyl)-trans-1,2-cyclohexanediamine
tpen	Tetrakis(2-pyridylmethyl)ethylenediamine
tppn	Tetrakis(2-pyridylmethyl)-1-methyl-1,2-propanediamine
tptMetame	1,1,1-Tris((<i>K</i> -(2-pyridylmethyl)- <i>N</i> -methylamino)methyl)ethane
tptn	<i>N,N,N',N'</i> -Tetrakis(2-pyridylmethyl)-1,3-diaminopropane
tren(py) ₃	Tris(2-pyridylmethyliminoethyl)amine
TRIR	Time resolved infra red
TR ³	Time resolved resonance Raman
T	Relaxation time

1**Introduction**

The phenomenon of spin-state crossover in Fe(III) complexes has been known for some 70 years [1] and in the case of Fe(II) systems for about 40 years [2]. The first direct measurements on the intramolecular kinetics of spin-state relaxation (in an Fe(II) complex) were not reported until 1973

with the appearance of a paper by Beattie et al. on the complex bis(hydrotris(pyrazolyl)borate)iron(II), $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ using a laser heating temperature jump relaxation technique [3]. It is interesting to note at the outset of this chapter on time-resolved relaxation studies of SCO complexes in solution that this first paper carried the title 'Rate of intersystem crossing between ^1A and ^5T states of an Fe(II) complex in solution', underscoring the photophysical significance of the spin state relaxation phenomenon. As was pointed out by Beattie in a 1988 review, investigation of the dynamics of spin equilibria provides a convenient means of probing intersystem crossing (ISC) processes, under ground electronic state conditions [4]. ISC is of course an inherent part of the photophysics of excited states where other competitive deactivation pathways occur. In the case of a spin equilibrium, the states of differing multiplicity (singlet, quintet in the case of Fe(II) and doublet, sextet in the case of Fe(III)) are, in general, both accessible under ambient conditions. It turns out that photophysics assumes a quite central role in spin crossover dynamics. This is so for quite fundamental reasons, as will be discussed later, but is also connected with the fact that at the experimental level, the most generally applicable method of investigating the relaxation kinetics in SCO complexes employs laser flash photolysis (LFP), whereby photoperturbation of the spin equilibria is brought about photo-physically, as discussed below.

It is not too surprising that much of the earlier, as well as ongoing work on spin crossover systems has concentrated on the solid state, since many of the potentially useful properties of SCO systems depend ultimately on the cooperative phenomena which are associated with the solid phase. Nevertheless, studies in dilute solution continue to be of central importance in the spin crossover field, permitting study of the fundamental intramolecular processes in the absence of intermolecular effects. An understanding of spin crossover dynamics in solution is also relevant to an understanding of the role or participation of spin crossover in natural systems, particularly in heme proteins [3, 5] Some further discussion of this aspect is presented later.

2

Methods Employed for Investigating the Relaxation Kinetics of Spin Crossover Complexes in Solution

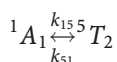
The field was comprehensively reviewed in 1988 [4] and since then there have been several accounts addressing more specific aspects of the relaxation dynamics [6].

The techniques employed are dictated by the range of relaxation rate constants exhibited by SCO systems in solution, which typically fall in the range 10^6 – 10^8 s^{-1} for Fe(II) spin crossover complexes at ambient temperature,

while for Fe(III) complexes the corresponding rate constants may be an order of magnitude higher [7, 8]. For Co(II) SCO systems, no precise determinations of relaxation rate constants have been reported but ultrasonic absorption studies (see below) point to spin-equilibrium relaxation times of less than 2 ns [9]. Consequently, methods with time resolution in the microsecond to nanosecond range or shorter have been employed. The majority of investigations have utilised one of the following techniques:

1. Laser Raman temperature-jump
2. Ultrasonic relaxation
3. Photoperturbation

The temperature-jump and ultrasonic relaxation techniques have both played an important part in the development of our current knowledge of the kinetics of SCO systems in solution. In the broad field of fast reactions in solution, they are the most widely known and used techniques of a group which come under the general heading of “chemical relaxation methods” as originally developed in the 1950s in the group of Manfred Eigen at the Max Planck Institute für Physikalische Chemie, Göttingen [10]. Relaxation methods in general work on the principle of a system at equilibrium being disturbed, either by a pulsed, single perturbation (e.g. a temperature-jump) or by an oscillating perturbation (such as an ultrasonic wave). In the former case, following the pulse, the system relaxes towards the new equilibrium position (e.g. characterized by the raised temperature), with a relaxation time which is a function of the forward and back rate constants of the reactions involved in setting up the equilibrium: e.g.



for which the relaxation time is given by

$$1/\tau = k_{15} + k_{51}$$

In the ultrasonic technique, the equilibrium under investigation is perturbed by a periodic signal generated by an ultrasonic wave which is absorbed by the sample. For a single relaxation process the absorption maximizes at a frequency which is the inverse of the relaxation time of the perturbed equilibrium. This is a rather simplified summary of what is in practice an involved relaxation method. Due to the considerable technical difficulties involved in its practical use, coupled with an inherent lack of specificity with respect to the chemical equilibrium being probed, the method never gained wide acceptance as a broadly applicable method in the spin crossover field. Lack of chemical specificity however proved not to be a serious drawback in practice for SCO studies, as is evident from the pioneering studies of Beattie et al. using the method, which provided important kinetic informa-

tion in the crucial early stages of developing an understanding of the kinetics of spin crossover systems [11–13].

A general restriction which applies to the chemical relaxation methods just referred to is that the system under study must be at equilibrium. This is not the case with photoperturbation method 3), essentially a laser flash photolysis-based approach, where it was recognised from the outset of its use [14] that it could be applied to the study of spin interconversion dynamics in a wide range of complexes and in a variety of solvents. Indeed it is the photoperturbation method which has proven to be the most widely applicable technique for the investigation of spin crossover kinetics in solution. Moreover, the introduction [15, 16] of picosecond and subpicosecond lasers to the area has not only extended the range of relaxation times which can be studied at readily accessible temperatures but has also enabled the photophysical processes which underpin this photoperturbation method to be probed in more detail later.

2.1

The Laser Flash Photolysis (Photoperturbation) Technique

McGarvey and Lawthers were the first to apply a photoperturbation technique to investigation of the relaxation kinetics in several Fe(II) spin crossover systems [14], a study which had its origins in earlier investigations by an analogous photo perturbation approach to the relaxation of configurational equilibria in Ni(II) complexes [17]. For the complexes $[\text{Fe}(\text{biz})_3]^{2+}$, $[\text{Fe}(\text{ppa})_2]^{2+}$ and $[\text{Fe}(\text{pyimH})_3]^{2+}$ they showed that irradiating within the metal-to-ligand charge-transfer (MLCT) band of the low spin isomer caused ground state depletion followed by a recovery to equilibrium [14]. In the case of the $[\text{Fe}(\text{ppa})_2]^{2+}$ complex, it was also possible to observe a transient absorbance increase at monitoring wavelengths in the range 270–330 nm, providing more direct evidence for restoration of the spin equilibrium as shown by the grow-in of the high-spin ($^5\text{T}_2$) isomer. In effect, what the LFP method amounts to is a photophysically-induced concentration-jump perturbation of the spin equilibrium, in that irradiation within absorption bands of the low-spin isomer results ultimately in an ‘over population’ of the HS isomer and the perturbed spin equilibrium then relaxes to its original position. The relaxation times were found to vary with temperature but were independent of monitoring wavelength and concentration. Although the effect was initially demonstrated in Fe(II) complexes, it was later shown by the same group to be equally applicable to Fe(III) SCO systems [18].

Subsequent to these first reports of LFP studies of Fe(II) SCO complexes in solution, Decurtins et al. observed that a crystal of hexa-1-propyltetrazole-iron(II) tetrafluoroborate could be converted by irradiation to the ^5T state and that this state had a relaxation time of several days at cryogenic

temperatures [19]. This phenomenon, termed LIESST (Light Induced Excited Spin State Trapping) has obvious photophysical parallels with the LFP approach under discussion here and is dealt with in much greater detail elsewhere in this book (Hauser II).

The underlying principle of the photoperturbation technique is that the MLCT state initially populated by irradiation quickly decays to the high spin (HS) state ($^5T_2$). The initial studies utilised an irradiation wavelength of 530 nm, lying within the intense MLCT ($t_{2g} \rightarrow \pi^*$) absorption band of the low-spin isomer, resulting in ground state depletion within the excitation laser pulse risetime, followed by a recovery of the ground state absorption which was assigned to relaxation of the spin-state equilibrium. Although a non-radiative MLCT $\rightarrow$ LF process with a rate coefficient $\geq 10^9 \text{ s}^{-1}$ was implied by the results presented in the initial paper [14], formation of the high-spin ($^5T_2$) state could only be inferred at that time (with the possible exception of the $[\text{Fe}(\text{ppa})_2]^{2+}$ complex) and it is from the later picosecond and subpicosecond work of McCusker et al. that a more complete photophysical picture has emerged [15, 16, 20], as discussed in more detail in the section immediately following this one.

An important check to apply at the outset of the application of the LFP method to SCO kinetics was a comparison of the derived spin-state relaxation times with those determined by other methods. Excellent agreement was obtained across a range of systems, as exemplified in Table 1 which compares the spin crossover relaxation times for several complexes measured by the LFP method with the values measured by other techniques. Additionally, the efficacy of the LFP approach has been tested by demonstrating that the SCO relaxation kinetics in a variety of Fe(II) complexes were independent of both excitation and probe wavelengths over the wavelength span of the MLCT $\leftarrow ^1A_1$ transition of the low-spin isomer [21].

LFP has been the technique of choice for the majority of SCO relaxation studies reported in the more recent literature, as some representative data in Table 2 illustrate.

Table 1 Relaxation times obtained for Fe(II) and Fe(III) complexes using different techniques (all relaxation times measured at 298 K)

System	Method	Lifetime	Ref
Fe(HB(pz) ₃) ₂	Raman temperature jump	32 ± 10 ns	3
	Ultrasonic relaxation	33 ± 0.7 ns	11
[Fe((py)imH) ₃] ²⁺	Raman temperature jump	48 ± 8 ns	8
	Photoperturbation	50 ± 3 ns	14
Fe(Sal ₂ trien) ⁺	Ultrasonic relaxation	5.33 ± 0.05 ns	12
	Photoperturbation	5 ± 1 ns	18

Table 2 Selected relaxation times for some spin crossover complexes

System	Solvent	Temp/K	Lifetime	Ref
[Fe(tpen)] ²⁺	Water	290	18±2 ns	15
[Fe(tptn)] ²⁺	Water	^c	1.6±0.1 ns	15
[Fe(bpy) ₃] ²⁺	Water	^c	676±30 ps	15
[Fe(phen) ₃] ²⁺	Water	^c	687±30 ps	15
[Fe(tptMetame)] ²⁺	Propionitrile/butyronitrile (4:5)	227	20 ns	29
[Fe(terpy) ₂] ²⁺	Water	190	23±2 ns	20
[Fe(tpchxn)] ²⁺	Methanol	255	53.1 ns	30
			153 ns	
[Fe(tpchxn)] ²⁺	Methanol	280	61.8 ns	30
[Fe(btpa)] ²⁺	Methanol	295	70 ns	31
			1750 ns	
[Fe(tp[10]aneN ₃)] ²⁺	Acetonitrile	298	<30 ns ^a	32
[Co(terpy) ₂] ^{2+b}	Water	293	<2 ns	9

^a Biphasic process; relaxation time given for fast process only^b Measured by ultrasonic relaxation (all others measured using photoperturbation technique)^c Not given

2.2

Probing the Mechanism of Photoconversion

The discovery [14] that low-spin/high-spin inter-conversion in SCO complexes could be achieved photochemically represented a significant breakthrough for a number of reasons. In addition to the important technological ramifications that may arise out of the LIESST effect, photo-induced SCO provided researchers with access to the well-developed tools of time-resolved laser spectroscopy for studying the dynamics of the SCO phenomenon. Moreover, in addition to being interesting in their own right, SCO systems can at the same time provide a unique platform for detailed studies of the photophysics of transition metal complexes in general. The observation that MLCT excitation of a low-spin Fe(II) complex results in the formation of the ⁵T₂ state immediately raises mechanistic questions. In a formal sense this conversion is a highly forbidden ΔS=2 transition (albeit non-radiative), so the fact that photo-induced SCO happens at all is, on the surface, rather surprising. From a quantum mechanical perspective, it is clear that intermediate spin states (e.g. S=1 state(s) for Fe(II)) must play a role in the conversion, since spin-orbit coupling between wavefunctions differing by two spin quanta is vanishingly small. One could envisage this role to be one of simple mixing of the requisite wavefunctions (e.g. singlet mixes with triplet, which in turn mixes with the quintet), or by invoking the ΔS=1 manifold as comprising distinct intermediates in the relaxation mechanism.

Initial models describing the photophysics of SCO tended toward the latter picture, which was based on ideas from the far more mature field of or-

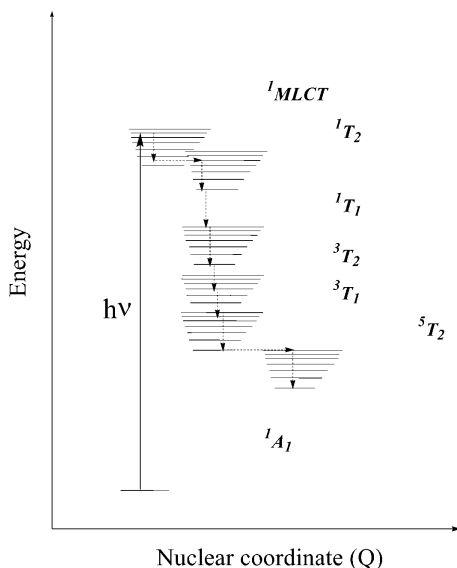


Fig. 1 Cascade model for formation of the $^5T_2$ excited state of an Fe(II) complex following $^1A_1 \rightarrow ^1MLCT$ excitation. This picture assumes $k_{\text{vib}} \gg k_{\text{IC}} \gg k_{\text{ISC}}$ (see text for details)

ganic photochemistry. In this context, one considers the relative rates of various processes based on the nature of that process. Vibrational relaxation (k_{vib}), which can be defined as structural relaxation on a given electronic potential energy surface, should occur on the time scale of the relevant vibrations of the molecule (ca. 10^{12} s^{-1}). The two electronic processes involved in SCO, namely internal conversion and intersystem crossing, are distinguished by their allowedness with respect to conservation of spin angular momentum: internal conversion (k_{IC}) would therefore be considered to occur at a faster rate than intersystem crossing (k_{ISC}). The picture that evolves from these assumptions when applied to the electronic states relevant for a Fe(II) SCO complex (for which most of the mechanistic work has been carried out) is shown in Fig. 1.

This model is the one typically invoked to describe photo-induced conversion from the $^1A_1$ to the $^5T_2$ state [6a].

The first experimental data suggesting that Fig. 1 is misleading if not incorrect were actually published prior to McGarvey and Lawthers' pioneering work. In 1983, Netzel and co-workers published a picosecond time-resolved absorption study of the excited-state dynamics of $[\text{Fe}(\text{bpy})_3]^{2+}$ [22]. Although not a SCO compound, the lowest-energy excited state of $[\text{Fe}(\text{bpy})_3]^{2+}$ is also the $^5T_2$ state and therefore presents in electronic terms a strict analogy to the SCO systems we are considering here [23]. In addition to some dynamic information, Netzel reported a quantum yield for formation of the

lowest-energy excited state of 1.0 ± 0.05 , i.e., *the $^5T_2$ state is formed with unit efficiency following $^1A_1 \rightarrow ^1MLCT$ excitation.* This remarkable result is in agreement with a previous, albeit somewhat less precise value reported by Sutin and co-workers several years earlier [24]. More recently, Hauser has reported a quantum efficiency near unity for $[\text{Fe}(\text{2-pic})_3]^{2+}$ in the solid-state at 11 K [25].

What makes these quantum yield data difficult to reconcile with Fig. 1 is the fact that all of the electronic states that are populated in the cascade mechanism prior to forming the $^5T_2$ state, i.e. the ^1MLCT , $^1T_2$, $^1T_1$, $^3T_2$ and $^3T_1$ states, are expected to have significant electronic coupling to the ground state. Population of the $^1T_2$ and $^1T_1$ states presents a particularly interesting situation: relaxation from either of these states back to the ground state is spin-allowed, whereas continuation in the cascade involves intersystem crossing steps. Differences in energy gaps between states and vibronic coupling are certainly mitigating factors in the overall mechanism of $^5T_2$ state formation. It is nevertheless quite striking that despite all of the more electronically viable pathways back to the ground state, reformation of the $^1A_1$ state proceeds exclusively through the $^5T_2$ level.

The mechanism of $^5T_2$ formation has been examined directly by several groups. In 1991, Hauser published a superb low-temperature single-crystal study of the spectroscopy of $[\text{Fe}(\text{ptz})_6]^{2+}$ [26]. One key point for the purposes of the present discussion is that formation of the $^5T_2$ state was observed following excitation into all four ligand-field states (i.e. $^1T_2$, $^1T_1$, $^3T_2$ and $^3T_1$). The viability of the $^1A_1 \rightarrow ^3T \rightarrow ^5T_2$ conversion pathway was taken as evidence of its role as an intermediate in the mechanism of SCO. Since the focus in this chapter is on solution phase studies, we shall defer any further discussion of solid-state work to a separate chapter.

Solution phase investigations of SCO systems on ultrafast time scales were first reported by Hendrickson and co-workers in 1992 and 1993 [15, 20]. These studies employed sub-picosecond transient absorption spectroscopy on $[\text{Fe}(\text{tpen})]^{2+}$, a low-spin compound whose $^5T_2$ energy places it on the upper edge of the SCO regime ($\Delta E_0 \approx 500 \text{ cm}^{-1}$). The important result from this study was what was *not* observed, i.e. the lack of a rise time corresponding to formation of the $^5T_2$ state. One caveat that should be entered here is that the spectral probe region for the sub-picosecond measurements was limited to the visible. Given the weak absorption characteristics of the $^5T_2$ state, the absorbance difference spectrum between the $^1A_1$ and $^5T_2$ states in this region is very similar to the loss of $^1A_1$ absorption alone. Since the latter will always occur instantaneously following excitation, the lack of any dynamics whatsoever is not absolutely conclusive. Nevertheless, the data strongly suggest that the $^5T_2$ state is formed within the time resolution of the experiment ($< 700 \text{ fs}$). Similar results were found for several other low-spin Fe(II) complexes, including $[\text{Fe}(\text{bpy})_3]^{2+}$, suggesting that such ultrafast formation of the $^5T_2$ state is a general feature of the photophysics of Fe(II)

polypyridyls. These initial studies were expanded upon by Monat and McCusker using $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$, a molecule whose energetics closely resemble those of $[\text{Fe}(\text{tpen})]^{2+}$ [16]. With improved time resolution of ca. 100 fs, these workers were able to resolve dynamic spectral shifts associated with the formation of the $^5\text{T}_2$ state. This moderates to a large extent the concerns raised above in the earlier work by Hendrickson and confirms their main conclusion, i.e. that the $^5\text{T}_2$ state is formed extremely rapidly ($\tau \sim 300$ fs). These newer data also reveal additional dynamics attributed to vibrational relaxation in the $^5\text{T}_2$ state with a time constant of 8 ± 2 ps.

Information concerning dynamics associated with the initially formed charge-transfer state was also revealed through the work of Monat and McCusker. In particular, by monitoring spectral changes in regions where the difference spectra for the ligand-field and charge-transfer states are of opposite sign (i.e. the LF states yield a bleach feature, whereas the CT state(s) yield an absorption) it was determined that depopulation of the charge-transfer manifold occurs with $\tau = 80 \pm 20$ fs. All of these time constants are expected to vary with pump wavelength, but the overall trends will likely remain intact. We can now view with greater clarity the quantum yields cited previously: since the rate of $^5\text{T}_2$ formation is $> 10^{12} \text{ s}^{-1}$, any other relaxation pathway back to the ground state would have to have a rate of at least 10^{11} s^{-1} in order to compete with $^5\text{T}_2$ formation and thus drop the quantum yield below unity. This in itself is not easy to understand given conventional photophysical models such as those discussed above, but the experimental data are nonetheless very compelling in this regard.

The preceding discussion suggests that a significant revision of the model presented in Fig. 1 for the mechanism of photo-induced SCO is necessary; a model more consistent with the available data is given in Fig. 2.

This diagram is obviously quite vague in certain ways, but this is as much detail as the available data will support. There is a distinct kinetic process corresponding to conversion from the charge-transfer to ligand-field manifolds. Beyond that, there is no evidence to suggest that any electronic state other than the $^5\text{T}_2$ is involved in photo-induced SCO for Fe(II), at least in the form of distinct intermediates along the lines suggested by Fig. 1. It is probably not correct to state that the $^1\text{MLCT}$ state converts directly to the $^5\text{T}_2$ state, nor is it correct to invoke any of the ^3T states as intermediates in the sense that they must be formed from the singlet manifold in order to proceed on to the $^5\text{T}_2$. The most reasonable picture may be one that involves extensive mixing among all of the excited ligand-field states that lie between the $^1\text{MLCT}$ and $^5\text{T}_2$ states. Qualitatively, one could envisage a process involving an initial conversion from the charge-transfer state (most likely the non-thermalized $^1\text{MLCT}$) to the ligand-field manifold of states. The picture within the ligand-field manifold is much less clear but probably involves a barrierless potential slope in which the wavefunction continuously evolves in its character from something approximating a singlet to that of the $^5\text{T}_2$ state (a

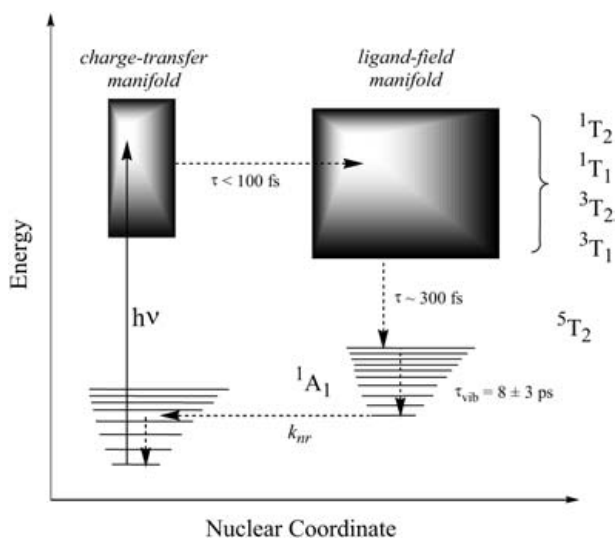


Fig. 2 Proposed mechanism for photo-induced spin conversion in Fe(II) spin crossover complexes

similar model has recently been put forward by Okada and co-workers to describe the $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ intersystem crossing in $[\text{Ru}(\text{bpy})_3]^{2+}$ [27]). To go beyond this admittedly coarse picture of photo-induced SCO, what is required at this point (in addition to more extensive ultrafast spectroscopic data on a wider range of SCO systems) is a theoretical analysis of the SCO conversion, along the lines of Bixon and Jortner's original treatment [28], that accounts for the information recently gleaned from ultrafast experiments.

2.3

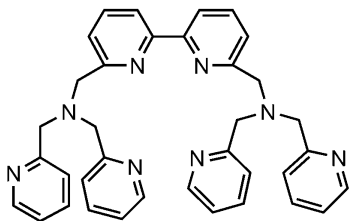
Probing the Relaxation Kinetics

Spectrophotometric detection has been by far the most common approach to the matter of probing the relaxation kinetics, for both laser temperature-jump and LFP investigations. It provides a straightforward method of following the HS $\rightarrow$ LS relaxation. The spectra of LS Fe(II) complexes in the visible region tend to be dominated by MLCT transitions. Since the HS state has only weak absorbance in the visible region, the kinetics of the relaxation of the spin equilibrium are generally (but not exclusively, v.i.) probed by monitoring the recovery of the absorbance in this region, following laser-induced bleaching.

As has been pointed out by Hendrickson, McCusker et al. [20], the ambiguity in assigning excited states from excited state absorption spectra alone is a potential drawback of conventional LFP methods. However, through a

careful study of one representative SCO Fe(II) complex, $[\text{Fe}(\text{tpen})](\text{ClO}_4)$, coupled with parallel investigations of other, exclusively low-spin, Fe(II) polypyridyl complexes, these workers succeeded in demonstrating rather conclusively that formation of the $^5\text{T}_2$ state is the general outcome of $^1\text{MLCT} \leftarrow ^1\text{A}_1$ excitation of low-spin Fe(II) complexes [20], (see above). An important part of the evidence was location of an isosbestic point between transient absorption and bleach signals, as had also been seen for one of the Fe(II) complexes in the originally reported LFP study of SCO [14].

However, electronic absorption spectra in solution are often broad and relatively featureless. Vibrational spectra are potentially more structure-specific. Both infrared and Raman spectroscopy have been used to an appreciable extent [33, 34] in the characterization of SCO complexes and Raman in particular is increasingly being used to assess the vibrational contribution to the entropic driving force of spin equilibria [35]. Recently Kaizaki et al. have monitored SCO equilibria by variable temperature Raman spectroscopy and found that the LIESST effect may be induced by the excitation laser, making it difficult to obtain a true LS spectrum at low temperatures [36]. However, the use of time-resolved vibrational spectroscopy to examine SCO dynamics has remained unexplored until a recent study in which time-resolved resonance Raman (TR^3) spectroscopy on the nanosecond timescale has been employed [37], to investigate the SCO complex of Fe(II) with the potentially octadentate ligand, btpa. The structure of the btpa ligand is shown below.



The primary requirement for the successful application of TR^3 spectroscopy is an appropriate choice of probe wavelength in resonance with vibronic transitions of the transient species of interest [38], which for SCO complexes will be the high- and low-spin isomers. Because the absorption in the near-UV-visible spectral region of many SCO complexes tends to be dominated by the low-spin isomers, a probe wavelength of 321 nm was chosen for the study of $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$, lying within the $\pi\text{-}\pi^*$ absorption band of the bipyridyl backbone of the btpa ligand. An important feature of this choice of monitoring wavelength was that it rendered possible the investigation of vibrational modes of *both* LS and HS isomers, through coupling to spin-state-dependent dihedral angle changes of the bipyridyl ligand backbone, with consequent subtle changes in the resonance Raman enhancement of bipyridyl modes between the two spin states [37, 39]. Examples of TR^3 spectra

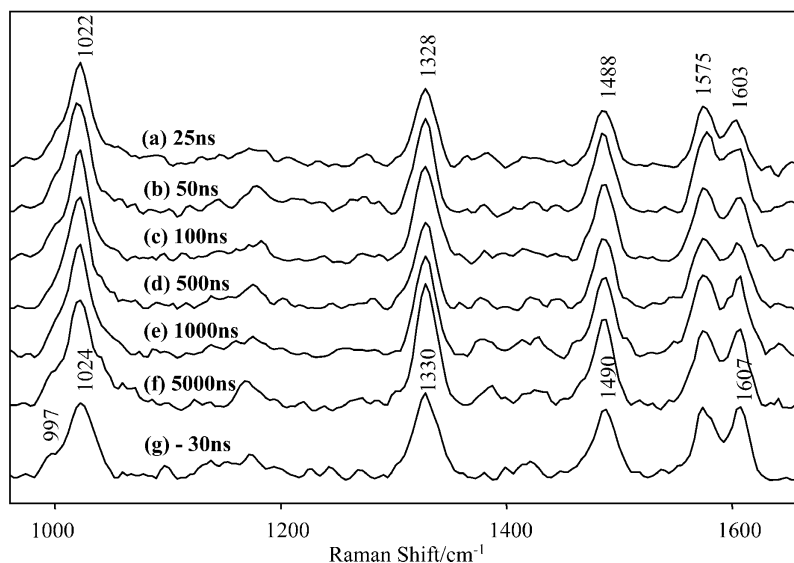


Fig. 3 Time-resolved resonance Raman spectra recorded on nanosecond timescales for $[\text{Fe}(\text{btppa})](\text{PF}_6)_2$ in MeCN. Pump wavelength 354.7 nm; probe 321 nm

recorded at this probe wavelength are shown in Fig. 3, from which it proved possible to extend investigations of the relaxation kinetics for this complex, previously demonstrated by conventional spectrophotometric monitoring to be biphasic, with fast ($k_{\text{HL}}=2.5 \times 10^7 \text{ s}^{-1}$ at 295 K) and slow ($k_{\text{HL}}=3.7 \times 10^5 \text{ s}^{-1}$ at 295 K) steps [31]. The latter are discussed further later.

It is worthwhile to devote some space here to explain in a little more detail the basis of the analysis of the TR^3 spectra and to indicate how data of structural and kinetic significance can be extracted from such spectra.

At a negative time delay of -30 ns in Fig. 3, i.e. where the probe pulse encounters the sample *in advance* of the pump pulse so that the ground electronic state of the complex is being probed prior to excitation, the spectrum contains vibrational features attributable to both the HS and LS forms, reflecting the ground state equilibrium. In the spectra recorded at a series of positive pump-probe time delays close examination reveals that small but significant shifts in the positions of several bands occur with change in time delay. Scaled subtractions of the short time delay and negative time delay spectra reveal representative HS and LS spectra and highlight the shifts more clearly, making it possible to pick out vibrational features characteristic of both spin states. The shifts are small but readily discernible, as is apparent for instance in the pairs of (LS, HS) bands at $(1607 \text{ cm}^{-1}, 1597 \text{ cm}^{-1})$ and $(1333 \text{ cm}^{-1}, 1327 \text{ cm}^{-1})$. Using the normal coordinate analysis described by Kincaid et al. [40] for the ground and excited state resonance Raman

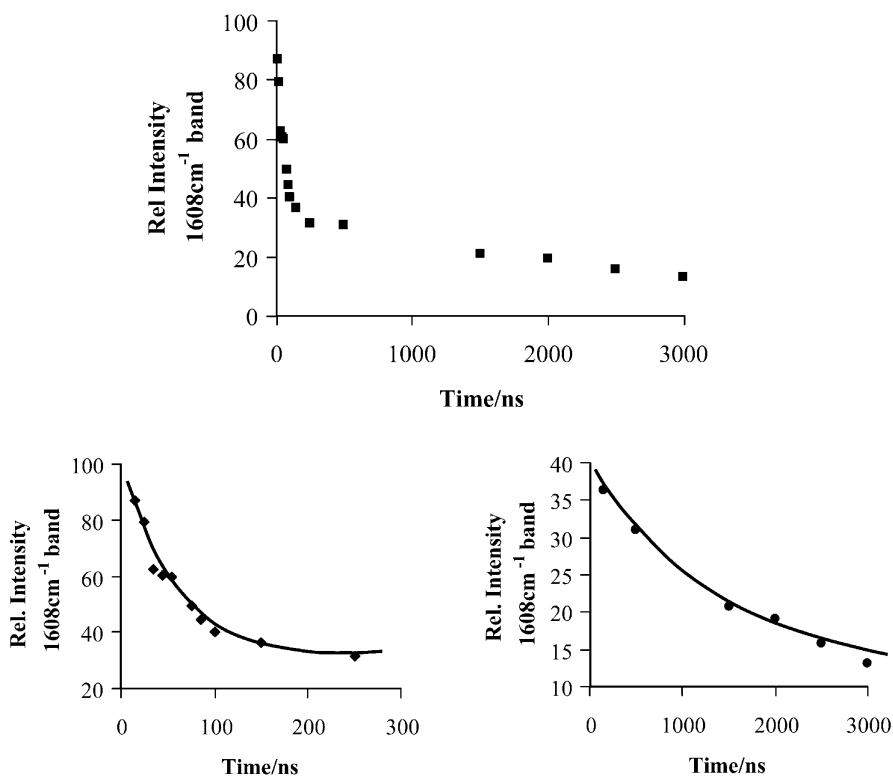


Fig. 4 Kinetic plots derived from the TR³ spectra in Fig. 3

spectra of [Ru(bpy)₃]Cl₂ as a qualitative guide, the modes corresponding to these bands can be taken to involve ring stretching vibrations of the bipyridyl moiety. There is virtually no dihedral angle change accompanying the spin crossover changes in the [Fe(btpa)]³⁺ complex [41]. The 1330 cm⁻¹ feature can be assigned as an inter-ring stretching mode, by analogy with the [Ru(bpy)₃]Cl₂ example [40] and the observed small reduction in frequency of this band for HS compared to LS is also in accord with the low dihedral angle change [37].

The kinetics plots, derived from the TR³ data by plotting the relative intensity of the 1607 cm⁻¹ LS band as a function of time delay, are shown in Fig. 4 and the biphasic nature of the decay is evident, with slow and fast components as indicated and in good agreement with the data derived from the conventional spectrophotometric measurements [31]. Plotting the relative intensity of the 1333 cm⁻¹ LS feature gave equivalent results. Interestingly, in the analogous complex with the bipyridyl replaced by 1,10-phenanthroline, which also exhibited biphasic SCO relaxation, the amplitude of the fast process was too small for easy measurement by conventional spectro-

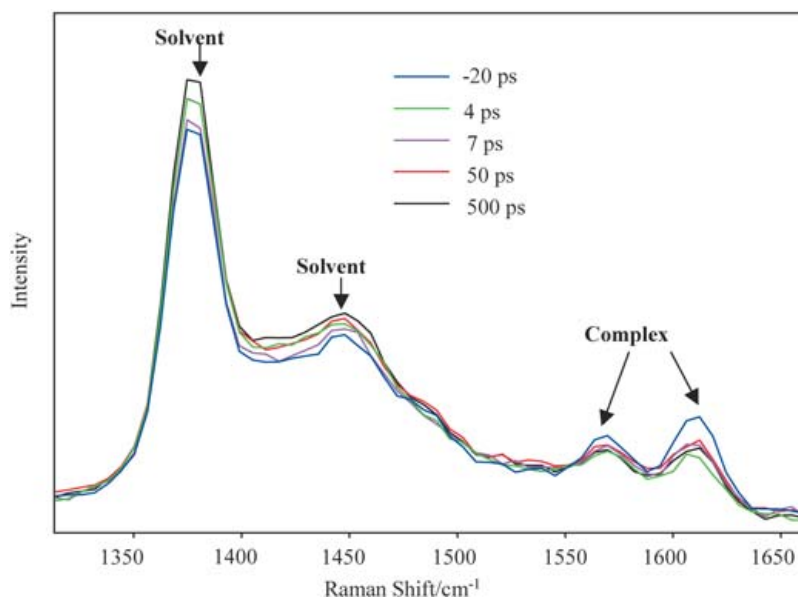


Fig. 5 Picosecond TR³ study of [Fe(btpa)](PF₆)₂ in MeCN

photometry and kinetic analysis of the fast step was more readily realised using the TR³ technique [39].

Measurements by TR³ spectroscopy on these systems have also recently been extended to the picosecond timescale [42]. Some representative TR³ spectra recorded on picosecond timescales for [Fe(btpa)](PF₆)₂ in acetonitrile are shown in Fig. 5. Due to uncertainty broadening of the Raman bands (the laser excitation pulse duration for these studies was ca. 4 ps) subtle shifts in band frequencies are not observable but there are clear changes in overall band intensities as a function of pump-probe time delay, as well as changes in relative intensities. Notable in Fig. 5 is the fact that changes in solvent vibrational band intensities occur in the opposite direction to intensity changes in vibrational features of the complex, indicating that structural effects involving the complex are occurring and that inner filtering due to increased transient absorption created by the pump laser cannot account for the changes. Closer analysis [39] of Fig. 5 suggests an early process, complete in 20 ps or less, possibly pointing to vibrational relaxation in the initially formed ⁵T₂ state, analogous to the early dynamics noted in the picosecond transient absorption studies of Monat and McCusker on Fe(II) SCO complexes [16] and attributed also to vibrational cooling in the high-spin state. Further time-resolved vibrational studies, perhaps using time-resolved infrared (TRIR) techniques, will be required to more fully evaluate any such comparisons.

Time-resolved infrared (TRIR) spectroscopy, already well established as a technique in the general area of metal complex and organometallic photochemistry and photophysics throughout the time range μs -ps, has not so far been applied to study of SCO dynamics. However, a recent report [43] by picosecond TRIR of MLCT excited state relaxation in Cr(0) complexes points to its promise in the SCO field also, particularly since the technique enables vibrational modes of complexes to be directly probed without the requirement for resonance with vibronic transitions, as is the case with the TR³ method.

3

The Influence of Temperature and Pressure on SCO Dynamics in Solution

The early studies of SCO kinetics in solution using the laser temperature-jump and ultrasonic relaxation techniques included variable temperature measurements, but only over limited temperature ranges [4]. The photoper-turbation method allows the kinetics to be studied over a wide range of temperatures. This facility has proved to be important in several respects. Using both the Arrhenius and Eyring equations [4, 44] (see later comments concerning the appropriateness of using these equations in the context of SCO relaxation), activation parameters have been assembled for a range of SCO complexes [21, 44, 45]. One of the most significant early outcomes of the applicability of the LFP method for studying SCO dynamics over wide temperature ranges was the experimental confirmation by Xie and Hendrickson of the non-adiabatic nature of the high-spin-low-spin relaxation, in which studies over the temperature range 300–4.2 K in polystyrene matrices demonstrated temperature independence of the relaxation rate at low temperatures and thus evidence of quantum mechanical tunnelling [46]. Significantly, they were also able to demonstrate that even at higher temperatures in the range 140–300 K, quantum mechanical tunnelling still contributes substantially to the spin interconversion rate. This and subsequent studies by Hauser and colleagues [47, 48] clearly pointed to the non-adiabatic character of the spin interconversion, supporting the earlier theoretical description of spin-state conversion in solution in terms of a radiationless, non-adiabatic multiphonon process [28].

Nevertheless, the Arrhenius and Eyring equations do provide a useful basis for consideration of the temperature-variation of the of the HS→LS relaxation, especially in the context of mechanistic considerations. This is well illustrated by variable temperature investigations of $^5\text{T}_2 \rightarrow ^1\text{A}_1$ ISC in a series of Fe(II) polypyridyl complexes, which explored empirical correlations between activation parameters and ligand structure [21]. A significant conclusion from this study was that a symmetric iron-ligand stretching mode might not always be the dominant reaction coordinate for the spin crossover

Table 3 Activation parameters for quintet→singlet spin crossover in Fe(II) complexes in solution

Complex	Solvent	$\Delta H_{51}^{\#}$ kJ mol ⁻¹	$\Delta S_{51}^{\#}$ J mol ⁻¹ K ⁻¹	Ref
[Fe(dpa) ₂] ²⁺	Methanol	2	-	21
[Fe(tpMetame)] ²⁺	Propionitrile/ butyronitrile	6±1	-75±12	29
[Fe(btpa)] ^{2+a}	Methanol	15.5	-	31
[Fe(btpa)] ^{2+a,b}	Methanol	27.5	-	31
[Fe(tpchxn)] ²⁺	DMF	34.4±1.2	2±5	44
	Acetonitrile	1.8±0.4	-102±6	44
	Methanol	9.72	-68.1	30
[Fe(metpen)Cl] ²⁺	Methanol	8.7±0.6	-90±3	60
[Fe(lpp[9]aneN ₃)] ²⁺	Methanol	9.4±0.6	-63.5±2	45
[Fe(tpen)] ²⁺	Methanol	7.23	-76.5	21
[Fe(tp[10]aneN ₃)] ^b	Acetonitrile	20.1	-94.4	32

^a Arrhenius equation^b Slow process

and that torsional modes could also play a role. The possible role of torsional modes in the SCO reaction coordinate has its origins in a suggestion by Purcell [49], further discussed by Toftlund [50], that synchronous enantiomerisation and spin-state isomerisation could be energetically favourable via a pseudorotational mechanism. If torsional motion is blocked, a higher energy pathway for SCO may result. Support for the importance of twisting modes also comes from consideration of the relative magnitudes of the activation barriers for spin crossover in complexes with ligands where promotion or inhibition of twisting modes had been designed into the structures [29, 32, 44, 45]. Table 3, which summarises activation parameters, $\Delta H_{51}^{\#}$ and $\Delta S_{51}^{\#}$, for the quintet→singlet crossover for several such systems, illustrates the point. For instance, [Fe(dpa)₂]²⁺ has a low value of $\Delta H_{51}^{\#}$ suggesting that the tridentate dpa ligand poses no constraint on a twisting motion [21]. By contrast, the larger value obtained for [Fe(lpp[9]aneN₃)]²⁺ suggests that the twisting mode is more unfavourable, perhaps due to steric interactions within the ligand [45].

One of the other practical advantages of the LFP technique for studying SCO kinetics is that the pulsed laser excitation source can be readily coupled to conventional static pressure vessels, enabling variable pressure studies and hence the derivation of activation volumes for the spin change [51, 52]. Experimentally determined activation volumes, $\Delta V_{\text{obs}}^{\#}$, will consist of 'intrinsic' (involving bond expansion or contraction) and 'solvational' contributions, $\Delta V_{\text{obs}}^{\#} = \Delta V_{\text{int}}^{\#} + \Delta V_{\text{solv}}^{\#}$. Measurements on a number of complexes with varying ligand structures and in several solvents gave activation volumes for quintet→singlet relaxation, $\Delta V_{51}^{\#}$, derived from the slopes of the

Table 4 Activation volumes for $^5T_2 \rightarrow ^1A_1$ spin crossover in Fe(II) complexes

Complex	Solvent	$\Delta V_{51}^\# \text{ cm}^3 \text{ mol}^{-1}$	References
[Fe(pyimH) ₃] ²⁺	Acetone	-5.4 ± 0.3	51
	Acetonitrile	-5.4 ± 0.3	51
[Fe(pyBimH) ₃] ²⁺	Acetone	-4.9 ± 0.4	51
	Acetonitrile	-6.4 ± 0.3	51
[Fe(phenmethoxa) ₂] ²⁺	Acetone	-8.4 ± 2.0	52
[Fe(ppa) ₂] ²⁺	Acetone	-6.1 ± 0.5	44
[Fe(tppn)] ²⁺	DMF	-9 ± 3	44
	Acetonitrile	-5.6 ± 0.7	44
[Fe(tpchxn)] ²⁺	DMF	$+5.7 \pm 2.0$	44
	Acetonitrile	-6.1 ± 1.2	44

semilog plots of the reciprocal SCO relaxation times, τ^{-1} , against pressure according to the equation

$$RT(\ln \tau^{-1}/dP) = -\Delta V_{51}^\# - K_{15}\Delta V^0/(1 + K_{15})$$

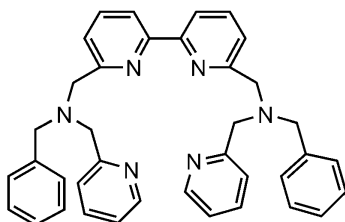
where $K_{15}=k_{15}/k_{51}$ is the spin equilibrium constant at atmospheric pressure and ΔV^0 is the molar volume for the spin equilibrium. Table 4 illustrates activation volumes calculated for the HS-LS conversion in several Fe(II) complexes [44]. The resultant values covered a remarkably narrow range, centred around $-5 \text{ cm}^3 \text{ mol}^{-1}$, taken to indicate a primarily intrinsic contribution to $\Delta V_{51}^\#$, associated with contraction of the Fe-N bond in the activation step from the high-spin state [33]. The reaction volume, ΔV^0 and the activation volume $\Delta V_{15}^\#$ for the reverse LS $\rightarrow$ HS step are markedly solvent-dependent. The overall conclusion is that the volume of the transition state is located approximately midway between the HS and LS states [45, 51].

4

Use of Ligand Structure to Control Spin-State Lifetimes

The influence of ligand structure (rigidity etc.) on spin-state interconversion kinetics had been recognised since the earliest studies on spin crossover dynamics [4] but it is in more recent work, primarily emanating from the ligand design strategies developed by Toftlund et al. [45] that more systematic investigations along such lines have been initiated. Such approaches have been successful in creating ligand structures resulting in considerably slower relaxation rates in the complexes concerned and in some instances have also uncovered other interesting features in the kinetics. One of the strategies has been to investigate ligand structures designed to couple the spin crossover to conformational changes in the molecule [32]. The Fe(II) complex with the hexadentate ligand tp [10]aneN₃ based upon the 10-membered

macrocycle, triaza cyclodecane, with pendant pyridyl arms exhibited biphasic relaxation kinetics in acetonitrile solution [32], involving both fast and slower steps attributed to a spin change, strongly coupled to conformational change in the molecule via radial (Fe-N) bond length changes. Another striking example is encountered in the case of the Fe(II) complex with the potentially octadentate ligand, btpa, referred to earlier [31]. The ligand has a bipyridyl backbone and four pendant pyridyl arms, (Structure 1, above), of which only two are directly coordinated to the Fe(II) centre. Again, the relaxation kinetics were characterised by biphasic behaviour, with fast and slow steps, the latter being the slowest light-induced relaxation reported so far for an Fe(II) SCO complex in solution. Significantly, the observed relaxation rate constants for both the fast and slow steps were the same in three different solvents [31]. For the complex with the analogous ligand b(bdpa) in which the two non-coordinating pyridyl groups are replaced by benzyl groups, single-exponential relaxation kinetics were observed with rate constants in the expected range for a single-step SCO relaxation and essentially identical to those measured for the fast step in the complex with btpa, suggesting that the fast step is due to the direct $^5T_2 \rightarrow ^1A_1$ SCO relaxation in the case of both complexes, with metal-ligand bond lengthening as the primary reaction coordinate. The structure of the b(bdpa) ligand is shown below.



The biexponential behaviour has been attributed to the potentially octadentate nature of btpa with a rearrangement of the pendent pyridyl arms being postulated as the additional process [31]. The apparent Arrhenius activation energy for this slow step, $27.5 \text{ k J mol}^{-1}$, is approximately twice that of the fast step, indicative of a geometric rearrangement beyond that of metal-ligand bond lengthening. While the fact that the kinetics were essentially unaltered when the bipyridyl was replaced by phenanthroline, suggested that twisting of the bpy backbone could be eliminated as a crucial step [31], evidence that some flexing of the more rigid phen backbone in this case may still accompany spin crossover is provided by the TR^3 spectra, in which a feature near 1313 cm^{-1} changes position between LS and HS states, similar to that seen for the equivalent inter-ring $\text{C}=\text{C}$ stretching mode at 1330 cm^{-1} in the TR^3 spectra for the corresponding btpa complex [39].

The $[\text{Fe}(\text{btpa})](\text{PF}_6)_2$ complex also exhibits intriguing behaviour when embedded in Nafion film [39]. Irradiation results in formation of a HS form (characterised by resonance Raman spectroscopy) which remains trapped

for several hours at room temperature, apparently due to the Nafion environment impeding rearrangement of the pyridyl arms. The recovery shows approximately exponential behaviour [39].

5

Spin Conversion in Biological Systems

In 1974 Beattie and West used a temperature-jump technique based upon joule heating to establish a lower limit of 5×10^{-6} s for the HS $\leftrightarrow$ LS relaxation time in ferric myoglobin [53]. Wilson, Sutin et al. subsequently studied the same system, taking advantage of the superior time resolution of the laser Raman temperature jump technique [54]. The structural changes which accompany the spin transition in natural systems may involve elongation of the axial bonds and a displacement of the central iron atom out of the porphyrin plane. Although the protein environment surrounding the iron atom might be expected to influence the kinetics, it appeared in this instance at least that the rate constants of $>10^7$ s $^{-1}$ obtained were not significantly different from those in synthetic inorganic compounds [55, 56], pointing to the utility of studies of the relaxation kinetics of synthetic SCO compounds as models of natural systems. Spin conversion rates in heme proteins may however vary over a wide range, from 10^{-9} s in fluid solution to 10^3 s in highly viscous media, reflecting spin equilibria involving normal first coordination sphere iron-ligand rearrangement in the case of the fastest rates or extensive protein-solvent reorganization for the slowest conversion rates [5].

6

Concluding Remarks

From a practical standpoint, one of the most notable successes of solution phase relaxation studies has been that of demonstrating ligand design as a successful strategy for controlling the ISC barrier. The LFP method has become well established as the primary technique for investigation of SCO dynamics in fluid media, enabling studies over extensive ranges of both temperature and pressure. Mechanistic questions remain regarding details of the underlying photophysical steps involved in the mechanism of photoper-turbation. Their fuller elucidation will require ultrafast spectroscopic investigations on a wider range of SCO complexes, especially taking advantage of recent advances in the techniques of ultrafast vibrational spectroscopy [57–59]. Additional insight offered by theoretical work will also be required, building upon the earlier studies of Bixon and Jortner [28].

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Pressure Effect Studies on Spin Crossover and Valence Tautomeric Systems

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Abstract In the present review chapter we discuss the results of investigations of the influence of hydrostatic pressure (up to 1.2 GPa) on the spin transition behaviour in coordination compounds of 3d transition metal ions. The systems under investigation are mononuclear spin crossover compounds of iron(II) and chromium(II), dinuclear complexes of iron(II) exhibiting coexistence of intramolecular antiferromagnetic coupling and thermal spin crossover, and 1D, 2D and 3D polynuclear spin crossover complexes of iron(II). Results from studies of the effect of pressure on coordination compounds exhibiting thermally induced electron transfer with subsequent spin state changes are also presented and discussed. It is demonstrated that pressure effect studies are very helpful

in elucidating the mechanism of cooperative dynamic electronic structure phenomena accompanied by significant volume changes. Application of hydrostatic pressure serves as a tool for modifying the ligand field strength in a controlled manner.

Keywords Spin crossover · Pressure · Phase transitions · Hysteresis · Elastic interactions

List of Abbreviations and Symbols

ST	Spin transition
SCO	Spin crossover
HS	High spin
LS	Low spin
X_M	Molar magnetic susceptibility
$T_{1/2}$	Temperature at which 50% of the “ST-active” molecules change the spin state
T_c	Critical temperature of spin transition
$\Delta T_{1/2}$	Hysteresis width of spin transition
P	Pressure
$P_{1/2}$	Pressure at which 50% of the “ST-active” molecules change the spin state
P_c	Critical pressure of spin transition
Y_{HS}	HS molar fraction
$Y_{HS}(T)$	HS molar fraction as a function of temperature
Y_{LS}	LS molar fraction
Y^G	Grüneisen parameter
Y_0	Eshelby constant
H	Magnetic field
ZFS	Zero field splitting
ΔS	Entropy difference between the HS and LS states
ΔH	Enthalpy difference between the HS and LS states
Γ	Parameter accounting for intermolecular interactions
K	Bulk modulus
V	Volume
ΔV	Molecular volume change between HS and LS species
$f_{int}(Y, T)$	Free energy of intermolecular interaction
G	Gibbs free energy
ΔF_{HL}	Change of the (Helmholtz) free energy due to spin transition
Δ_s	Energy shift of the lattice upon interaction with the reference lattice
Π^*	Reduced pressure
k_B	Boltzmann constant
2-pic	2-(Aminomethyl)pyridine
pyz	1-Pyrazolyl
pz	Pyrazine
phen	1,10-Phenanthroline
ptz	1- <i>n</i> -Propyl-tetrazole
depe	1,2-Bis(diethylphosphino)ethane
PM-Bia	(<i>N</i> -(2'-Pyridylmethylene)-4-aminobiphenyl
bipy	2,2'-Bipyridine
PM-Aza	(<i>N</i> -(2'-Pyridylmethylene)-4-azophenylaniline
mtz	1-Methyl-tetrazole

abpt	4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
bt	2,2'-Bithiazoline
phy	1,10-Phenanthroline-2-carbaldehyde-phenylhydrazone
5-NO ₂ -sal-N(1,4,7,10)	5-NO ₂ -Salicylaldehyde-1,4,7,10-tetraazadecane
bpym	2,2'-Bipyrimidine
4-R-trz	4-Substituted-1,2,4-triazole
hyptrz	4-(3'-Hydroxypropyl)-1,2,4-triazole
hyetrz	4-(2'-Hydroxy-ethyl)-1,2,4-triazole
4,4-bipy	4,4'-Bipyridine
azpy	4,4'-Azopyridine
btr	4,4'-Bitriazole
btre	1,2-Bis(1,2,4-triazol-4-yl)ethane
bpb	1,4-Bis(4-pyridyl-butadiyne)
btzb	1,4-Bis-(tetrazol-1-yl)butane-N1,N1'
py	Pyridine
bpe	<i>trans</i> -1,2-Bis(4-pyridyl)ethylene
cat	Catecholato
sq	Semiquinonato
phendiox	9,10-Dioxophenanthrene
cth	<i>dl</i> -5,7,7,12,14,14-Hexamethyl-1,4,8, 11-tetraazacyclotetradecane

1 Introduction

The first experiments to study the effect of applied pressure on the spin crossover (SCO) phenomenon date back more than 40 years and have been performed in solution by Ewald et al. with a family of Fe(III) dithiocarbamate complexes [1]. It was soon realised that the temperature dependent thermal equilibrium between $^2T_2 \leftrightarrow ^6A_1$ states is strongly influenced by pressure. The low spin (LS) $^2T_2$ state has a smaller molecular volume than the high spin (HS) $^6A_1$ state and becomes favoured as pressure increases. König [2] pointed out that the strong dependence of the ligand-field strength on the metal-donor atom distances and the resulting large difference in metal-ligand bond lengths between the two spin states leads to the change of entropy, which is the genuine driving force for the thermal spin transition. Indeed, the underlying reason for the pressure influence on the spin transition process is the large difference in the metal-donor atom bond lengths, $\Delta r_{HL} = r_{HS} - r_{LS} \approx 0.1$ and 0.2 Å, for Fe(III) and Fe(II) spin crossover molecules, respectively. A schematic representation of the pressure influence on the LS and HS potential wells of Fe(II) is shown in Fig. 1: application of pressure increases the relative vertical displacement of the potential wells; the additional minor relative horizontal displacement of the potential wells due to a slight decrease in bond length accompanying an increase in pressure has been neglected. Increasing the pressure favours the LS state of the molecule,

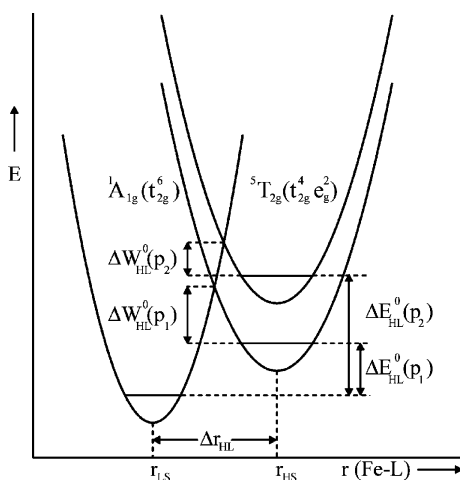


Fig. 1 Schematic representation of the pressure influence ($p_2 > p_1$) on the LS and HS potential wells of Fe(II)

thus shifting the spin transition to higher temperatures because pressure increases the zero point energy difference ΔE_{HL}^0 by the work term $p\Delta V_{HL}^0$ and decreases the activation energy ΔW_{HL}^0 , favouring the LS state.

Although the spin crossover phenomenon is essentially a property of the isolated complex molecule due to the competition between the dependence of the ligand-field strength on the metal-ligand bond length and the electron-electron repulsion, external perturbations such as pressure may effectively influence the spin crossover properties. Moreover, the application of pressure to compounds with thermal SCO is a powerful tool in investigations of thermodynamic characteristics and microscopic aspects of the mechanism for the spin transition in molecular compounds. Systematic and detailed studies of the concerted action of temperature and pressure variation on SCO compounds have only recently become possible with the development of special hydrostatic pressure cells in conjunction with various physical techniques such as magnetic susceptibility, optical and Mössbauer measurements, EXAFS and vibrational spectroscopy. The earlier, significant publications [3–13] cited in the review article [14] published in 1994 refer to results obtained using mainly a Mössbauer high pressure cell. Much progress has been made since then, including the pressure studies in liquid solution discussed in detail in Chap. 21, due to the availability of modern equipment. In the following we shall discuss significant results of pressure effect studies in the solid state on SCO systems published during the last decade. Among them are mononuclear SCO systems of iron(II) and chromium(II), dinuclear complexes of iron(II) exhibiting a fascinating interplay between thermal SCO and antiferromagnetic coupling, and polymeric 1D, 2D

and 3D SCO compounds of iron(II). Examples for temperature dependent valence tautomerism involving electron transfer and concomitant spin state changes have also been studied under pressure and will be discussed in this contribution.

2 Experimental Methods

In most SCO coordination compounds the molecular and lattice structures can be relatively easily disrupted by shear deformations, which always occur when applied pressure is not hydrostatic. The role of crystal defects which may be caused by the non-hydrostatic nature of the pressure is of importance, too. Experiments with mechanically treated polycrystalline SCO compounds have confirmed that with increasing milling the residual HS fraction increases, the transition curves become broader and hysteresis loops widen and flatten out [15]. Comparison of the results from pressure effect studies of the same compound with non-hydrostatic [16] and hydrostatic conditions [17] has shown that non-hydrostatic pressure of ~ 0.1 GPa can significantly deform the transition curve (partial suppression of the SCO process).

A large number of publications deal with investigations of the effect of pressure on SCO systems using a high pressure cell in conjunction with Mössbauer spectroscopy. For optimal performance the cell should be constructed with windows made of hard material which is transparent to γ -radiation. Gas (e.g. He, Ar) or liquid (e.g. silicone oil) is generally used as the pressure-transmitting medium. Such a hydrostatic gas pressure cell operating up to ~ 0.2 GPa was applied in Mössbauer experiments on $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic=2-(aminomethyl)pyridine) [12]. A newly developed Mössbauer pressure cell made of hardened beryllium bronze and equipped with windows made of B_4C and using silicone oil as the pressure transmitting medium has been described in [18]. It was designed for measurements up to 1.5 GPa in the temperature range 2–350 K. The diamond anvil cell (DAC) technique is used for measurements of Mössbauer spectra up to ≈ 5 GPa [19]. Pressure calibration is accomplished by focusing a blue or green laser on a small chip of ruby within the pressure medium of the DAC. The major disadvantages of this cell for Mössbauer spectral studies are the small capacity of the sample holder, requiring the use of isotopically enriched samples, and the non-hydrostatic pressure. For instance, one cannot exclude that the non-hydrostatic nature of the pressure is responsible for the unusual partial LS $\rightarrow$ HS transformation in $\text{Fe}[\text{HB}(\text{pz})_3]_2$ (pz=1-pyrazolyl) observed at pressures above 4 GPa [9, 19].

Transparency of diamonds to photons over a wide energy range from infrared to X-rays enables wide application of the DAC technique. A pressure cell with a beryllium gasket between two diamonds, containing a hole

of ~ 0.3 mm diameter for encapsulating a sample with a liquid as pressure-transmitting medium, provides hydrostatic pressure conditions up to 1.0 GPa. It has proven to be a very efficient device for X-ray diffraction studies and is being employed by several groups in X-ray crystal structure determinations of SCO compounds under pressure [20–22]. Successful application of high-pressure X-ray absorption spectroscopy to the study of spin crossover phenomena in several Fe(II) and Co(II) tris(pyrazolyl)borate complexes has also been reported [23, 24].

A pressure effect study with infrared spectroscopy of several thiocyanato and isocyanato complexes of Fe(II) showed that the spin transitions occurred below 1.0 GPa [25]. The application of Raman spectroscopy for samples under high pressure was recently reported [26]. In this study, pressure-induced hysteresis at room temperature was found for spin crossover polymers of formula $\{\text{Fe}(\text{pz})[\text{M}(\text{CN})_4]\} \cdot 2\text{H}_2\text{O}$ (pz=pyrazine and M=Ni, Pd, Pt). An experimental set-up for temperature- and pressure-dependent optical absorption spectroscopy was reported in [27]. A helium gas pressure cell for pressures up to 0.1 GPa has been described in conjunction with a closed-cycle He refrigerator, allowing variable temperatures between 15 and 300 K. Hydrostatic He pressure was created by a two-membrane pneumatic compressor. This installation has been successfully used to study several iron(II) SCO systems where comparatively low external pressures induced significant changes in the thermodynamic equilibrium as well as in the relaxation dynamics discussed in detail in Chap. 17. A low-temperature helium pressure chamber operating in the pressure range up to 0.16 GPa for optical reflectivity studies is described in [28]. This apparatus is particularly useful for the study of spin crossover processes occurring in thin layers or on the surface of solid SCO materials.

Magnetic susceptibility measurements on SCO compounds at elevated pressures are possible with a hydrostatic high pressure cell made of hardened beryllium bronze and using silicone oil as a pressure-transmitting medium [17, 29]. The cell has the following characteristics: range of pressure up to ~ 1.3 GPa, accuracy of pressure determination ± 0.025 GPa. The sample holder is ~ 1 mm in diameter and 5–7 mm in length and operates in the temperature range of 1.5–400 K. Because of the small weight and the negligible magnetic background, the cell can be used in Foner-type and SQUID magnetometers. The pressure is calibrated using the superconducting transition temperature of high purity tin.

3

Effect of Pressure on Mononuclear Spin Crossover Systems

Most of the SCO compounds of iron(II) consist of mononuclear FeN_6 core complex molecules held together in the crystal lattice by non-covalent inter-

actions. They display a wide range of spin crossover behaviour from gradual to abrupt transitions with and without thermal hysteresis [14]. In the following we shall discuss results of pressure effect studies on SCO systems displaying both gradual and abrupt transitions with and without hysteresis and of pressure induced spin crossover in a compound that does not undergo thermal SCO at ambient pressure.

3.1

Effect of Pressure on $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ Polymorph II

$[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ ($\text{X}=\text{S}, \text{Se}$) are the first and still among the most thoroughly studied SCO systems of iron(II) [30] (Fig. 2a). Fisher and Drickamer [31] investigated the effect of pressure on the spin transition behaviour of this system using the Mössbauer effect. Their results demonstrated not only the expected increase of $\text{HS} \rightarrow \text{LS}$ conversion with increasing pressure at a given temperature, but even a partial reverse $\text{LS} \rightarrow \text{HS}$ transformation above a certain threshold of pressure. Subsequent studies of Adams et al. [4] and Pebler [5] did not confirm the reverse $\text{LS} \rightarrow \text{HS}$ process, raising the question of whether the conditions in the experiments carried out by Fisher and Drickamer were hydrostatic. The first magnetic susceptibility measurements under pressure on the title compound have been carried out by Usha et al. [7]. All the results obtained in these studies provided the evidence for $\text{HS} \rightarrow \text{LS}$ conversion under pressure, the reported values of the pressure $P_{1/2}$ for 50% spin state conversion at room temperature ranging between 0.6 and 1.2 GPa. König et al. have demonstrated the existence of two crystallographic modifications of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [30]. Polymorph I undergoes an almost complete thermal spin transition, whereas in polymorph II a fraction of HS molecules of ca. 17% is retained at low temperatures. A possible reason for the range of $P_{1/2}$ values indicated above is that the studies were carried out with different polymorphs. While in [4] the actual polymorph that was investigated is not specified, in [5] and [31] the experiments were carried out on polymorph II. The non-hydrostatic nature of the pressure in the experiments using diamond anvil cells could also contribute to the discrepancy in $P_{1/2}$ values. X-ray diffraction on a single crystal of polymorph II did not reveal a change of the space group, neither during the thermal spin crossover nor under pressure up to 1.3 GPa [32b]. Despite the existence of detailed structural knowledge, several important thermodynamical features of the spin transition in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II under pressure have not been explored up to now. A very recent magnetic susceptibility study under pressure [33] is described in the following.

The $\chi_M T$ vs T curves measured at different pressures for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II are shown in Fig. 2b. At ambient pressure the transition curve is extremely steep with $T_{1/2}=177$ K. The presence of a narrow temperature hysteresis and the value of residual HS fraction ($\cong 17\%$) are in

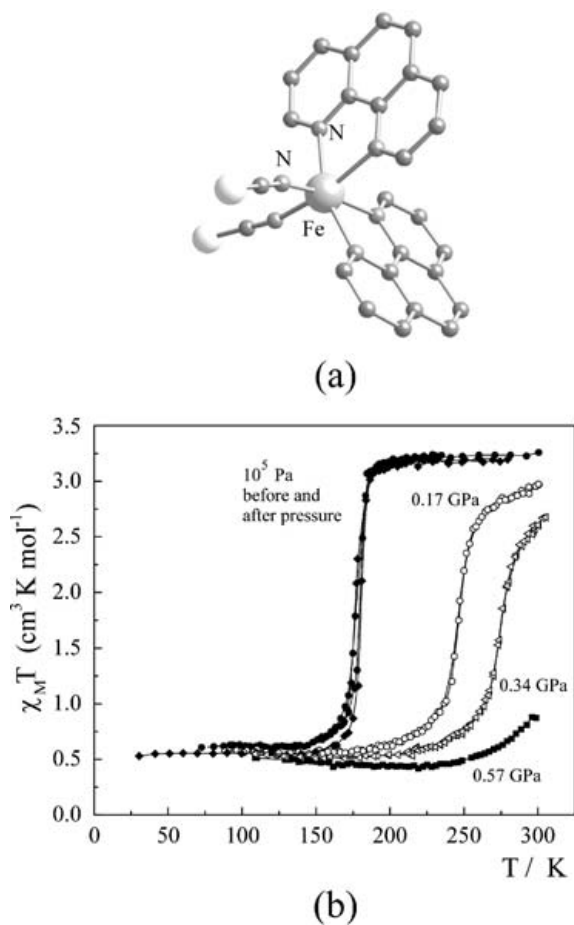


Fig. 2 **a** Molecular structure. **b** $\chi_M T$ vs T curves at different pressures for [Fe(phen)₂(NCS)₂] polymorph II

agreement with published data [32a]. As the pressure is increased, the transition curve is displaced to higher temperatures with an average dependency of 220 K/GPa. With the application of pressure the narrow hysteresis loop disappears and the transition curves become gradual. At pressures around 0.6 GPa the sample is mostly in the LS state up to room temperature, however, the residual HS fraction below the transition remains essentially unaltered. This observation is in line with results found in [32b], viz. conservation of the space group during the spin crossover transition under pressure up to 1.3 GPa and the structure being a decisive factor for the completeness of the spin transition in [Fe(phen)₂(NCS)₂]. It should be noted that usually a complete spin transition is accomplished under hydrostatic pressure. A pro-

gressive diminution of the pressure influence on the transition temperature ($\frac{\partial T_{1/2}}{\partial P} = 410 \text{ K/GPa}$ at 0.17 GPa, 180 K/GPa at 0.34 GPa, 150 K/GPa at 0.57 GPa) points at the presence of a steric barrier, which can be a possible factor preventing a complete HS $\rightarrow$ LS transformation in polymorph II of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. In fact, π -interactions between $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ units are found within the (*a*, *b*) layers and, more precisely, these interactions are oriented in the *b* direction [22]. The pressure dependence of the lattice parameters *a*, *b* and *c* reveals a significant discontinuity for *a*, but quasi-linear behaviour for *b* and *c*. The discontinuity along *a* seems to be related to the spin state change, as a similar effect has been observed in the dilatation experiments [22]. Finally, a comparison between the evolution of the unit cell volume and the $\chi_M T$ product under pressure clearly shows the correlation between the magnetic and structural properties for this compound.

The interpretation of the influence of pressure on the thermodynamic parameters of the HS $\leftrightarrow$ LS transition in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in the frame of a phenomenological mean-field description [34] is given below. This compound appears to be ideal for this purpose, because of the proven absence of a structural phase transition in both temperature and pressure variation.

3.2

Spin Crossover Under Pressure in $[\text{CrI}_2(\text{depe})_2]$

The first thermal spin crossover in chromium(II) compounds was reported by Halepoto et al. in 1989 [35] and is considered in Chap. 13. The compound *trans*-bis[1,2-bis(diethylphosphino)ethane]di-iodochromium(II) ($[\text{CrI}_2(\text{depe})_2]$) (Fig. 3a) exhibits a very sharp $^3T_{1g}$ (*S*=1) $\leftrightarrow$ ^5E_g (*S*=2) spin transition with $T_{1/2}=169$ K without noticeable thermal hysteresis at ambient pressure. A magnetic susceptibility study under pressure shows a progressive increase of $T_{1/2}$ and a decrease of the transition steepness with increasing pressure (Fig. 3b) [33]. Application of pressure of ca. 0.8 GPa transforms the compound entirely to the low-spin state at ambient temperature. Qualitatively, one can interpret this pressure effect on the basis of mean-field theory [34]. In mean field approximation the pressure dependence of the spin transition temperature obeys the Clausius-Clapeyron relation:

$$\frac{\partial T_{1/2}}{\partial P} = \frac{\Delta V}{\Delta S_{HL}} \quad (1)$$

This relation reflects the scaling of the transition temperature $T_{1/2}$ and the volume change ΔV . Figure 4 shows the plots of $T_{1/2}$ vs pressure for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II and $[\text{CrI}_2(\text{depe})_2]$. For the latter compound strong non-linearity contrasts the almost linear dependence for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. A detailed interpretation of this is not possible without the knowledge of the thermal and pressure dependences of the ele-

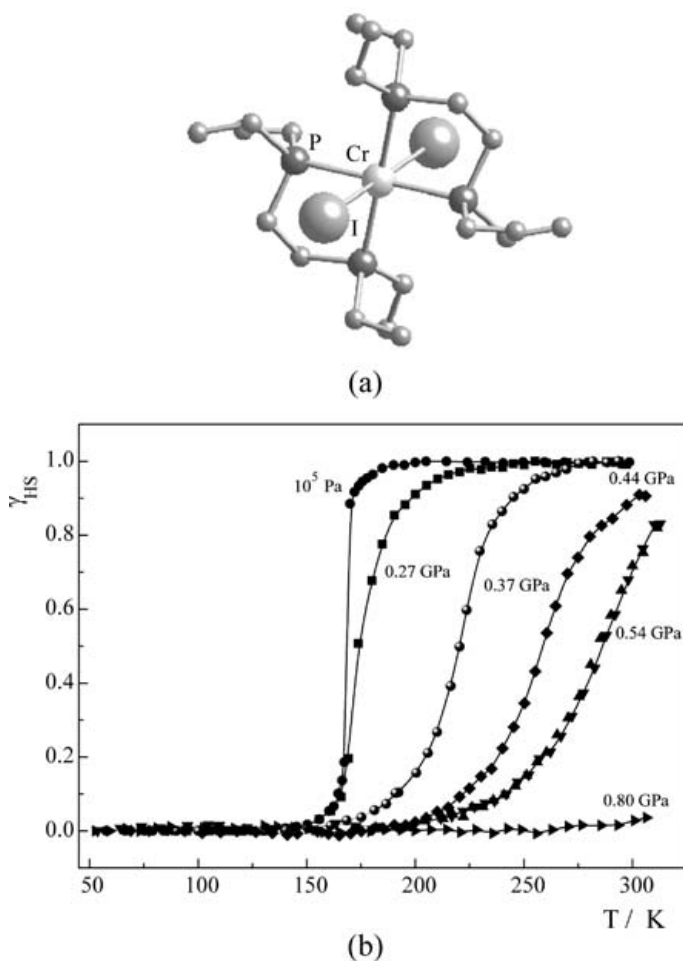


Fig. 3 a Molecular structure. b $\gamma_{\text{HS}}(T)$ curves at different pressures for $[\text{CrI}_2(\text{depe})_2]$

mentary cell volume of $[\text{CrI}_2(\text{depe})_2]$, as has been accomplished for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [22]. However, it looks as though the elementary cell volume of $[\text{CrI}_2(\text{depe})_2]$ hardly changes across the spin transition in the pressure range up to ~ 0.3 GPa, similar to the findings in X-ray studies on $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after LIESST at ambient pressure [36]. The reason may be found in the different compressibilities of the large iodide ions as compared to the smaller and harder phosphorus donor atoms in the CrP_4I_2 core. Application of low pressure seems to reduce mainly the volumes of the iodide ions leaving the Cr-P donor atom distances essentially unchanged. The influence of pressure on $T_{1/2}$ in the present case seems to start above a certain threshold when the Cr-P bond lengths are noticeably

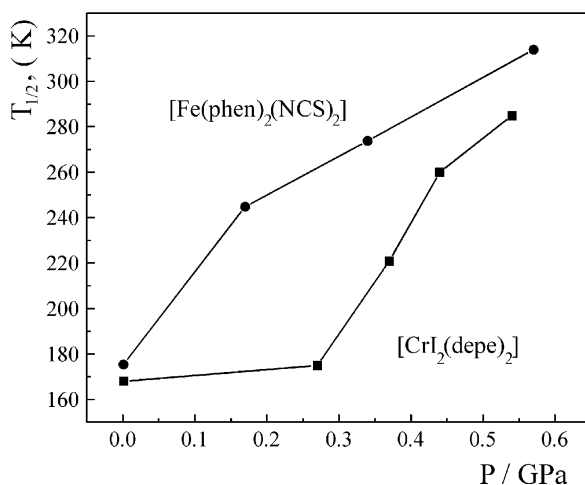


Fig. 4 Plot of $T_{1/2}$ vs P for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{CrI}_2(\text{depe})_2]$ [33]

altered by pressure. A quantitative interpretation of the influence of pressure on the spin crossover behaviour of $[\text{CrI}_2(\text{depe})_2]$, particularly the pressure dependence of the transition temperature $T_{1/2}$, is only possible with a detailed crystallographic study of the compound under variable pressure and at variable temperatures.

3.3

Effect of Pressure on the Spin Transition in $[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{PM-Pea})_2(\text{NCS})_2]$

In Fig. 5 are depicted the plot of γ_{HS} vs T at different pressures for the complex $[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$ (PM-Bia = N -(2'-pyridylmethylene)-4-amino-bi-phenyl) together with the molecular structure [37]. At atmospheric pressure an almost complete and unusually abrupt transition (within 1–2 K) is observed with hysteresis of 5 K width. When the pressure is increased to ca. 0.60 GPa, the transition temperature $T_{1/2}$ is shifted upwards and the width of the hysteresis loop is reduced. At higher pressures the hysteresis width reaches approximately 25 K. At 1 GPa, the spin transition is more gradual and the hysteresis width diminishes slightly. Further increase of pressure around 1.3 GPa has no further effect. The formation of this large hysteresis for $P > 0.6$ GPa is totally reversible, as illustrated by the identical data obtained at atmospheric pressure before (open squares) and after (filled circles) the application of hydrostatic pressure up to 1.26 GPa. This points at the formation of a new crystallographic phase at elevated pressure, denoted as phase II; whereas the one observed at low pressure is denoted as phase I [37]. The transition behaviour in the 0.6–0.8 GPa range reflects the presence

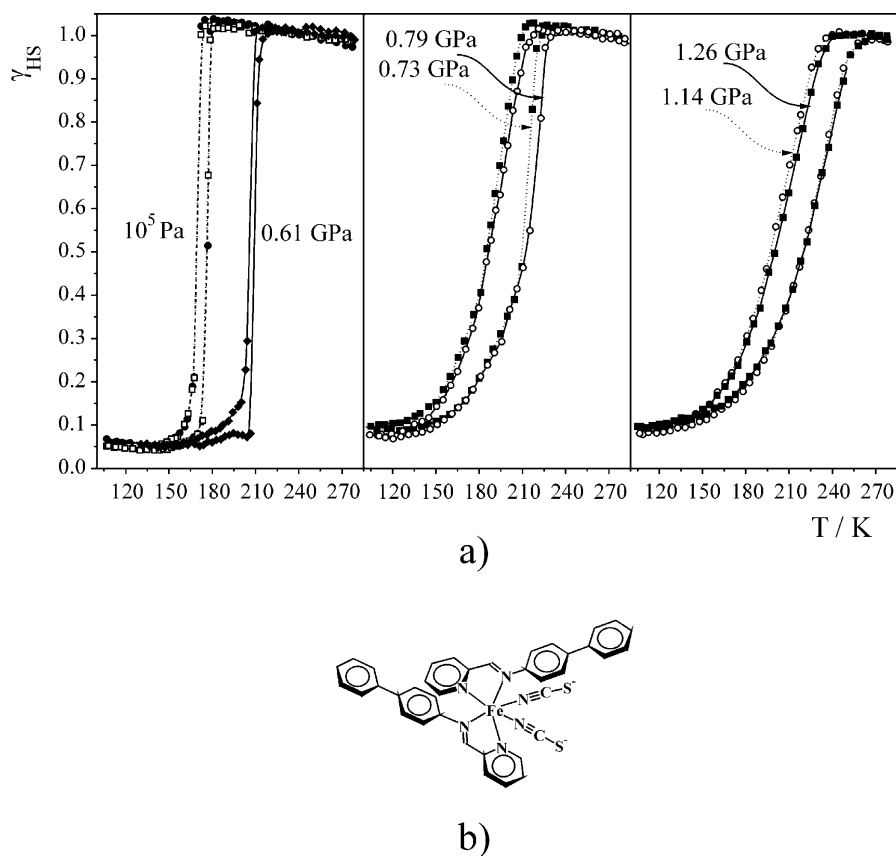
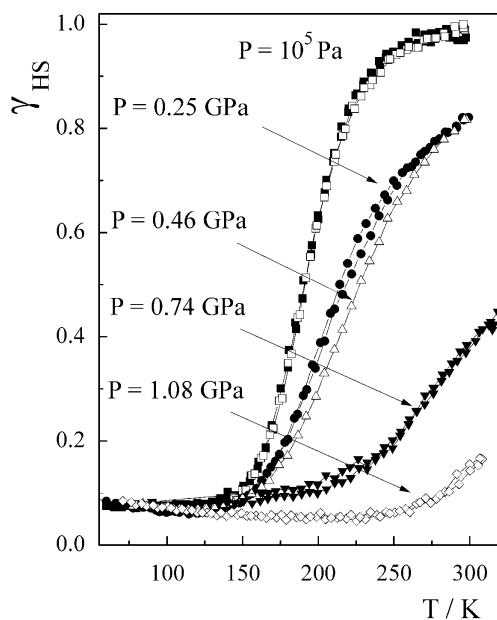


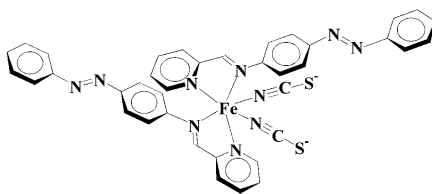
Fig. 5 **a** Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$. **b** Molecular structure [37]

of a mixture of the original phase I and the pressure-induced phase II. Both phases show the typical features of first-order transitions. The observation that the hysteresis becomes much broader in the pressure-induced phase II lends support to the conclusion that in the new phase II the spin transition is accompanied by a crystallographic phase change. Also, it seems that the strength of the cooperative interactions between the spin state changing molecules has no direct influence on the hysteresis width. The steepness of the transition curves, which is a measure of the cooperativity, is reduced in the pressure-induced phase II, but the hysteresis width is approximately ten times larger than in phase I. The spin crossover process in phase I of $[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$ is not accompanied by a change of the space group, which is Pccn above and below $T_{1/2}$.

For the mononuclear compound $[\text{Fe}(\text{PM-Aza})_2(\text{NCS})_2]$ (PM-aza = $(N-(2'$ -pyridyl-methylene)-4-(azophenyl)aniline) [37], γ_{HS} at ambient pressure de-



a)



b)

Fig. 6 **a** Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{PM-Aza})_2(\text{NCS})_2]$. **b** Molecular structure [37]

creases continuously with decrease in temperature which corresponds to a gradual and complete spin transition (Fig. 6). An increase of pressure shifts the transition temperature upwards and decreases the slope of the transition curve. The pressure dependence of $T_{1/2}$ is linear, the slope of the $T_{1/2}$ vs P straight line, $dT_{1/2}/dP=160 \text{ K GPa}^{-1}$, is very close to that observed for the mononuclear compounds $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic=2-picolyamine) [12] and $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ [41] where $dT_{1/2}/dP=150$ and 176 K GPa^{-1} , respectively. This pressure influence on gradual transitions can be qualitatively interpreted on the basis of the phenomenological theory of phase transitions in spin crossover systems [12] which predicts the observed changes in the slope of the transition curve and in $T_{1/2}$.

3.4

The Spin Transition in $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ with Non-Equivalent Metal Centres

A pressure effect study was carried out on the mononuclear complex $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ (mtz=1-methyl-tetrazole) [38] in which the iron(II) ions occupy two non-equivalent crystallographic sites A and B with population ratio 1:1 [36]. At ambient pressure only site A molecules undergo thermal spin transition, whereas the molecules in the lattice site B remain in the HS state down to 4.2 K [39]. The ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ above ~ 160 K, however, show only one quadrupole doublet typical of iron(II) in the HS state. This obviously indicates that the two sites A and B are only minutely different in energy. Poganiuch et al. [40] have shown that at low temperatures the ground state of iron(II) in both sites can be converted by light into long-lived metastable spin states: the LS state of A site molecules to HS with green light, this process being called $\text{LIESST}(\text{LS} \rightarrow \text{HS})_{\text{A}}$, and the HS state of B site molecule to LS with red light, denoted as $\text{LIESST}(\text{HS} \rightarrow \text{LS})_{\text{B}}$.

Figure 7 shows the temperature dependence of the HS fraction γ_{HS} at different pressures derived from susceptibility measurements. At ambient pressure $T_{1/2} = 75$ K, in accordance with previous measurements [40]. The absence of thermal hysteresis and the value of the residual HS fraction of $\sim 50\%$ also agree with published data [40]. At pressures of ca. 0.14 GPa, the slope of the transition curve decreases and the transition shifts to higher temperatures. One should notice that this pressure strongly modifies the spin transition process associated with A site molecules and does not change the spin state of B site molecules. This correlates with observations made in an X-ray study [36] where practically no change of volume during $\text{LIESST}(\text{HS} \rightarrow \text{LS})_{\text{B}}$ was found. According to the Clausius-Clapeyron relation (Eq. 1), if $\Delta V = 0$ the effects of external pressure will be minimal. However,

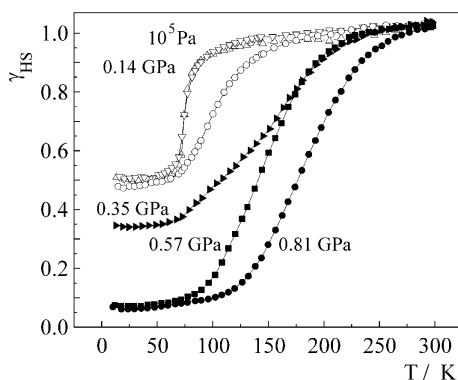


Fig. 7 Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$

higher pressure of 0.35 GPa not only shifts the part of the curve associated with A site molecules upwards, but also causes partial spin transition of B site molecules which is clearly seen in the lowering of $\gamma_{HS}(T)$ in the low temperature region. Pressure of 0.57 GPa switches the rest of B site molecules from HS to LS and the spin transition in $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ becomes nearly complete. The highest applied pressure of 0.81 GPa generates a gradual transition curve with $T_{1/2} \sim 180$ K.

3.5

Pressure-Induced Spin Transition in $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ Polymorph B

Figure 8 shows the temperature dependence of the $\chi_M T$ product for $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ polymorph B (abpt=4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) at different pressures and a picture of the molecular structure [41]. At room temperature and at atmospheric pressure the complex is high spin. As the temperature is lowered, $\chi_M T$ practically remains constant and the sharp decrease of $\chi_M T$ at temperatures below 25 K is caused by zero-field splitting of the HS iron(II) ions. This behaviour remains as pressure is increased up to 0.44 GPa, where an incomplete thermal spin crossover appears around $T_{1/2}=65$ K. It is reasonable to assume that the slow kinetics blocks the HS $\leftrightarrow$ LS equilibrium, due to the low temperatures involved in the spin transition of $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ below 0.44 GPa. A relatively sharp spin transition takes place at $T_{1/2}=106$, 152 and 179 K, as pressure increases to 0.56, 0.86 and 1.05 GPa, respectively. The pressure dependence of $T_{1/2}$ is nearly linear and similar to that observed for $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [12]. The application of hydrostatic pressure to $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ has once more demonstrated the possibility of inducing thermal spin crossover in an HS compound by altering the ligand field strength in a controlled manner and thereby shifting the ΔE_{HL} parameter (see Fig. 1) from negative to positive values.

3.6

The Influence of Hydrostatic Pressure on the Hysteresis Width in $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$

Mössbauer studies on the first-order spin transition in $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ and $[\text{Fe}(\text{phy})_2](\text{ClO}_4)_2$ under pressure [16] revealed an increase of the hysteresis widths with increasing pressure contrary to the expectation from mean field theory [34]. In these experiments, samples were pressed between two disks of boron carbide using a tin metal gasket. Such a pressure cell construction does not guarantee hydrostatic pressure conditions so that the unexpected increase of the width of the hysteresis loop could be connected with a large uniaxial component of applied stress. The observed irreversible changes of the residual HS fraction at low temperatures in $[\text{Fe}(\text{phy})_2](\text{ClO}_4)_2$ indicated

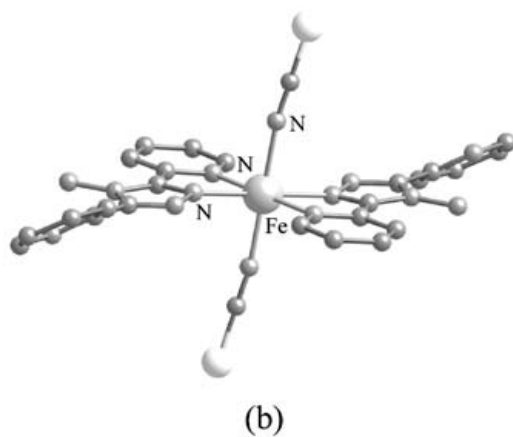
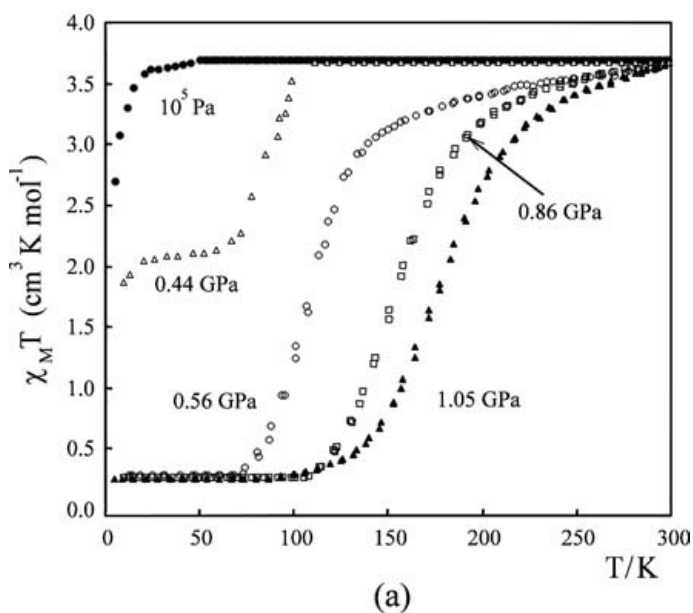


Fig. 8 **a** $\chi_M T$ vs T curves at different pressures. **b** The molecular structure for $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ [41]

the formation of defects in polycrystalline samples as a consequence of non-hydrostatic conditions. In order to confirm the reported unexpected increase of the width of the hysteresis loop under pressure the spin transition in this compound has been re-investigated under hydrostatic pressure using the pressure cell for magnetic susceptibility measurements [17]. The results are displayed in Fig. 9.

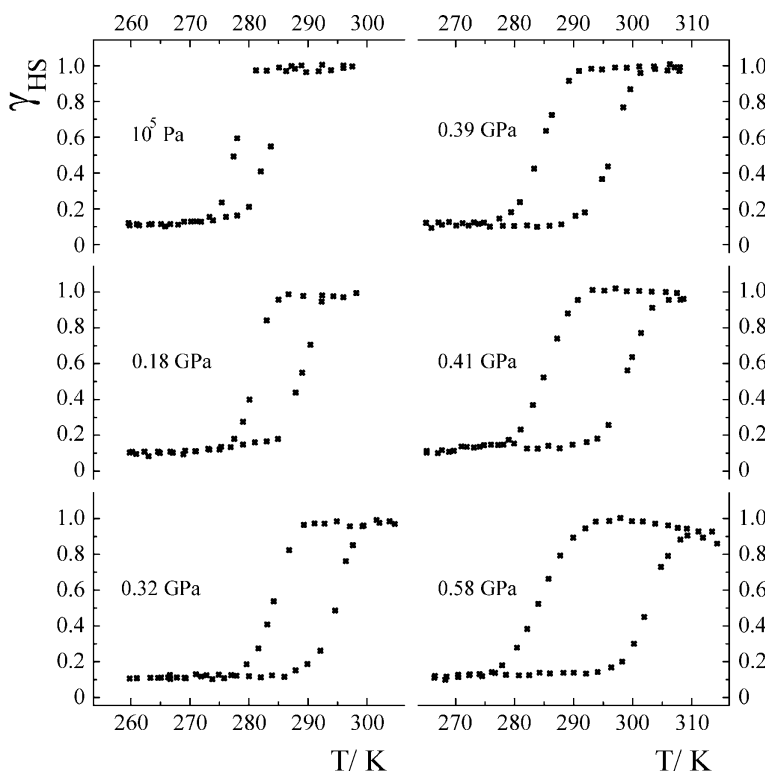


Fig. 9 Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ [17]

In Fig. 10 the measured transition temperatures $T_{1/2\downarrow\uparrow}$ and the mean value $T_{1/2} = 1/2(T_{1/2\downarrow} + T_{1/2\uparrow})$ are plotted vs pressure together with the data obtained by König et al. [16] by Mössbauer spectroscopy. Up to 0.12 GPa, both sets of data agree well. The straight lines are linear regressions in the range up to 0.39 GPa and 0.44–0.58 GPa. Below 0.39 GPa the average temperature $T_{1/2}$ increases by 30 K GPa^{-1} (broken line in Fig. 10) and the hysteresis width $\Delta T_{1/2}$ increases. The discontinuity of $T_{1/2\uparrow}$ around 0.41 GPa possibly indicates a pressure-induced crystallographic phase transition. The temperature $T_{1/2\uparrow}$ remains constant whereas $T_{1/2\downarrow}$ decreases slightly with increasing pressure.

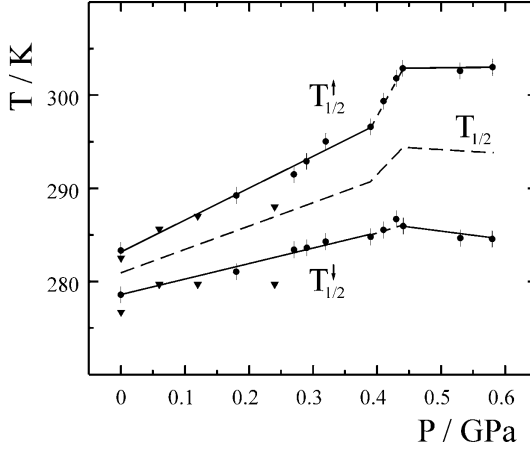


Fig. 10 Transition temperatures $T_{1/2\downarrow\uparrow}$ and the mean value $T_{1/2}=1/2(T_{1/2\downarrow}+T_{1/2\uparrow})$ for $[\text{Fe}(\text{phen})_2](\text{BF}_4)_2$ are plotted vs pressure. The *triangles* represent the measurements of König et al. [16] (adapted from [17])

4 Theoretical Description of the Pressure Effect in Isotropic Spin Crossover Compounds

On thermodynamical grounds, thermally induced spin crossover is described in terms of Gibbs free energy within the regular solution theory [3, 12, 14, 17]. The pressure effect on the spin crossover behaviour is determined by the magnitude of the volume change of the unit cell per spin crossover complex, ΔV , and by the intermolecular interaction free energy $F_{\text{int}}(\gamma, T)$. The change of the Gibbs free energy at an external pressure P is given by

$$\Delta G = \gamma \Delta F_{\text{HL}} + F_{\text{int}}(\gamma, T) - TS_{\text{mix}}(\gamma) + \gamma P \Delta V \quad (2)$$

where γ is the fraction of HS molecules and ΔF_{HL} the change of the free energy due to the spin transition. The mixing entropy is given by

$$S_{\text{mix}}(\gamma) = -k_B [\gamma \ln \gamma + (1 - \gamma) \ln (1 - \gamma)] \quad (3)$$

Following [34], the energy shift Δ_s and the interaction constant Γ in the serial expansion of the interaction energy yield

$$F_{\text{int}}(\gamma, T) = \Delta_s \gamma - \Gamma \gamma^2 \quad (4)$$

The change of the free energy may be expressed as

$$\Delta F_{\text{HL}}(T) = \Delta H(T_{1/2}) - \Delta S_{\text{HL}} T \quad (5)$$

Here, $\Delta H(T_{1/2})$ and ΔS_{HL} are the changes of the enthalpy and the entropy at ambient pressure. Under the condition that the lattice is in thermal equilibrium,

$$(\partial \Delta G / \partial \gamma)_{T,p} = 0 \quad (6)$$

Finally, the pressure influence on the spin crossover is described by the equation of state

$$T = (\Delta H(T_{1/2}) + \Delta_s + P\Delta V - 2\gamma\Gamma) / \left(k_B \ln \frac{1-\gamma}{\gamma} + \Delta S_{HL} \right) \quad (7)$$

Applying Eq. (7) to the data of the magnetic susceptibility measurements under pressure for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ several important thermodynamical features have been derived. Assuming, according to [34], Δ_s being independent of temperature, one can extract the volume changes ΔV per spin cross-over complex. The resulting average change of the unit cell volume of $134 \text{ \AA}^3$ is comparable with the value of $119 \text{ \AA}^3$ found in the structural study of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II under pressure [22]. The slight difference may be attributed to a possible pressure influence on the energy shift Δ_s . With increasing pressure the transition curves become more gradual (Fig. 2b). It can be understood, considering the so-called reduced pressure introduced by Köhler et al. [12]:

$$\Pi^* = \frac{\Delta F_{HL}(T) + \Delta_s + P\Delta V}{\Gamma} \quad (8)$$

which characterizes the type of the spin crossover transition [12]. A first order transition with hysteresis is expected to occur at temperatures

$$T_{1/2} < T_c = \frac{\Gamma}{2k_B} \quad (9)$$

if $\Pi^*(T_c) < 1$; the spin transition is of continuous type if $\Pi^*(T_c) > 1$. At $P = 10^5 \text{ Pa}$ the reduced pressure is $\Pi^* = 0.62$. As a consequence, a first-order transition with a very steep transition curve is observed. One can estimate that at an external pressure $P \geq 0.05 \text{ GPa}$ the parameter Π^* exceeds 1, giving rise to gradual transitions. The observation of smooth transition curves at $P \geq 0.17 \text{ GPa}$ confirms this conclusion.

A detailed thermodynamical treatment of the spin transition under the influence of external pressure was reported for $[\text{Fe}(\text{ptz})_6](\text{PF}_6)_2$ (ptz = 1-*n*-propyltetrazole) [27]. This compound shows a rather steep transition with strong cooperativity, but without hysteresis. The interaction constant $\Gamma = 101 \text{ cm}^{-1}$ was found to be very close to the critical value above which hysteresis solely due to the cooperative effects is expected. In contrast to the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II, the interaction constant was found

to be pressure independent presumably because of the comparatively low pressure applied in this study.

The increase of the hysteresis width with increasing pressure in $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ contradicts the expectation following from the phenomenological mean field theory of phase transitions in SCO compounds [34]. In the frame of this approach the pressure dependence of the spin transition temperature given by the relation (1) predicts an increasing transition temperature with increasing pressure. Furthermore, the mean field approach predicts a decrease of the hysteresis width and of the slope of the transition curve with increasing pressure [7, 12, 34c]. The hysteresis vanishes at a critical pressure, and at even higher pressures the transition transforms to the gradual type belonging to the overcritical region of the phase diagram. A shift of the transition temperature and a decrease of the slope of the gradual transition were observed in $[\text{Fe}(\text{2-pic-ND}_2)_3]\text{Cl}_2\text{EtOD}$ [12]. The data were obtained by Mössbauer measurements under hydrostatic pressures up to 0.15 GPa using a helium gas pressure cell. The expected decrease of the width of the hysteresis loop with increasing pressure was observed in $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ [42]. However, the above-mentioned pressure effects on the spin transition in $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ and also in $[\text{Fe}(\text{PM-Pea})_2(\text{NCS})_2]$ [37], are not in line with a mean field approach [34]. The parallel shift of the two-step transition curve and the behaviour of the hysteresis width (Fig. 11) observed for the SCO compound $[\text{Fe}(\text{5-NO}_2\text{-sal-N}(1,4,7,10))]$ under pressure [43] also cannot be adequately described by this theory.

A possible explanation for increasing hysteresis width under applied pressure was suggested by Das and Ghos [44], who discussed the Landau expansion of the free energy density with third- and fifth-order couplings between

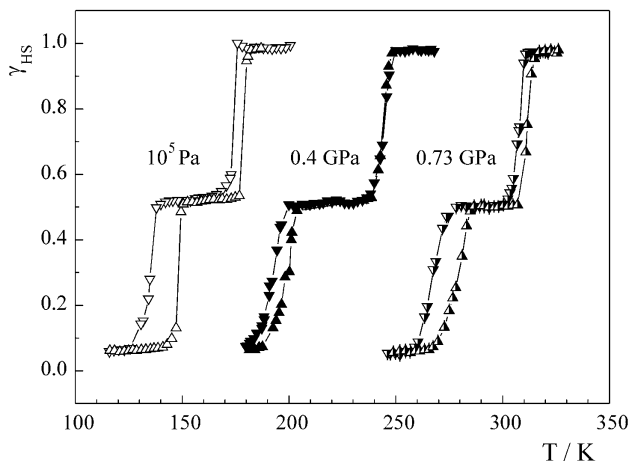


Fig. 11 Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{5-NO}_2\text{-sal-N}(1,4,7,10))]$ (adapted from [43])

elastic strains and the order parameter of the phase transition. However, this theory cannot be mapped on the free energy of a spin crossover system, because it contains, on the one hand, no linear term of the order parameter which is the dominant one in the free energy of a spin crossover system, and on the other hand no direct coupling exists between the pressure and the order parameter. The direct coupling is given by the experimental fact that there is a volume change of the crystal proportional to the fraction of molecules of either spin states. The mean field approach by Köhler et al. [12] neglects all indirect couplings of the pressure to the order parameter, which was chosen to be the fraction γ_{HS} of HS molecules.

In order to describe the pressure effect on hysteresis and the scope of the above-mentioned experimental features of spin transitions, the mean field approximation of the free energy for spin crossover compounds has been extended [17]. For the interpretation of the interaction constants on the basis of elasticity theory the indirect coupling of pressure to the order parameter through the pressure dependence of the bulk modulus has been taken into account [45].

Using the theoretical considerations of [17] and taking into account only the linear terms in the expansion of the difference of the free energies of HS and LS states around T_c (Eq. 4) the following expressions for the pressure derivatives of the transition temperature $dT_{1/2}/dP$ and hysteresis width $d\sqrt{\Delta T_{1/2}}/dP$ have been derived:

$$\frac{dT_{1/2}}{dP} = (2\gamma^G + 1) \frac{T_c}{K} \left(\frac{A}{\sigma_c} + \frac{T_{1/2}}{T_c} \right) \quad (10)$$

$$\frac{d\sqrt{\Delta T_{1/2}}}{dP} = (2\gamma^G + 1) \frac{\sqrt{T_c}}{K} \left(\tau_c A + \frac{1}{2} \sqrt{\frac{\Delta T_{1/2}}{T_c}} \right) \quad (11)$$

The quantity A is a function of physical parameters of the compounds:

$$A = \frac{3\gamma_0 - 1}{2\gamma_0} \frac{K}{2\gamma^G + 1} \frac{\Delta V}{2k_B T_c} + \frac{\Delta_s - 2k_B(T_c + \sigma_c T_{1/2})}{2k_B T_c} \quad (12)$$

where $\tau_c = \frac{d\sqrt{\Delta T_{1/2}^*}}{d\Pi^*}$ depends on the reduced hysteresis width $\Delta T_{1/2}^* = \frac{\Delta T_{1/2}}{T_c}$ and the reduced pressure Π^* (Eq. 8). Equations (10) and (11) show that the derivatives $dT_{1/2}/dP$ and $d\sqrt{\Delta T_{1/2}}/dP$ are linear functions of the variable A, which depends on $T_{1/2}$ and T_c , on the molecular volume change between HS and LS species ΔV , the dimensionless parameter σ_c which is the entropy change S_{HL} divided by $2k_B$, and the ratio $K/(2\gamma^G + 1)$, where K is the bulk modulus, γ^G the Grüneisen parameter and γ_0 is the Eshelby constant [46]. Thus one can conclude that the different behaviour of $T_{1/2}$ and $\Delta T_{1/2}$, even the unexpected decrease of $T_{1/2}$ and also the increase of $\Delta T_{1/2}$ with increas-

ing pressure, is explained by the different values of the parameter A . The calculated values of the parameter A , the boundaries of changes of $T_{1/2}$ and $\Delta T_{1/2}$ for several spin crossover compounds are presented in [47].

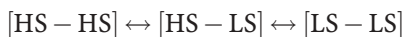
Summarizing, the increase of the widths of the hysteresis in $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ with increasing pressure can be described in mean field theory of spin transitions if the dependence of the bulk modulus K on pressure is introduced. The parameters entering the theory have values comparable to those found in other spin crossover compounds, thus exhibiting a consistent picture. This theory qualitatively describes the behaviour of $T_{1/2}$ and $\Delta T_{1/2}$ under pressure but does not always give realistic values for the physical parameters of the investigated iron(II) compounds. To clarify the reasons for such discrepancies, further investigations on SCO compounds with a systematic definition of the above mentioned experimental parameters K , Δ_s , γ^G , etc., are necessary.

5

Effect of Pressure on Dinuclear Spin Crossover Systems

Closely associated with the goal of designing and preparing new multifunctional materials [48], the idea of combining different electronic properties, like magnetic exchange and spin transition, in the one system emerged. One of the steps along this line aimed to afford a multi-property material began with the class of 2,2'-bipyrimidine (bpym)-bridged iron(II) dinuclear compounds discussed in Chap. 7 of this review series [49].

A remarkable feature of the spin crossover process in several dinuclear iron(II) compounds is a plateau in the two-step transition curve. These macroscopic steps, also detected by means of Mössbauer spectroscopy and calorimetric measurements, were interpreted in terms of a microscopic two-step transition between the three possible spin pairs of each individual dinuclear molecule [50]:



The pressure dependence of the thermal variation of $\chi_M T$ has proved to be a useful diagnostic probe to show that the formation of [HS-LS] spin pairs is not fortuitous but that they are the preferentially formed species in the dinuclear-type complexes [51]. The stabilisation of the [HS-LS] mixed-spin pair results from a synergistic effect between intramolecular and cooperative intermolecular interactions. It is shown also that application of external hydrostatic pressure can help to unravel features of this whole class of compounds, which usually can be revealed by variation of chemical composition. Further, the interplay between the antiferromagnetic coupling and spin transition has been studied under hydrostatic pressure [52].

From the analysis of the results of the pressure experiments, it is inferred that the plateau originates from successive ST in the two metal centres, leading first to the formation of relatively stable [HS-LS] pairs and then, above a critical pressure, to the formation of [LS-LS] pairs on further lowering of the temperature. The intermolecular interactions between [HS-LS] pairs lead to domains that contribute to the stability of the crystal lattice. Indeed, in the absence of intermolecular interactions, the increase of pressure should decrease the amount of the HS fraction. These experimental data underline the role of intermolecular interactions, particularly short range interactions competing with omnipresent long-range interactions, in the stabilisation of the hypothetical “chequerboard-like” structure consisting of [HS-LS] units as proposed by Spiering et al. [12] for mononuclear SCO compounds exhibiting a two-step transition.

6

Effect of Pressure on 1D, 2D and 3D Polymeric Spin Crossover Systems

During the last decade many efforts have been undertaken in order to synthesise and characterize one- two- and three-dimensional spin crossover systems [22, 53 and references therein]. These are discussed in Chap. 9. In the following we shall discuss the pressure studies carried out on several kinds of such materials with the aim to arrive at a deeper insight in the co-operative interactions in polymeric SCO systems. The potential for practical applications is well recognised for such systems displaying strong cooperativity together with associated thermochromic effects.

6.1

1D Spin Crossover Systems

The first one-dimensional (1D) polymeric spin crossover compound, which was reported by Lavrenova et al. [54] and re-investigated by Kahn and co-workers [55, 56], belongs to the family of $[\text{Fe}(4\text{-R-trz})_3](\text{anion})_2 \cdot x\text{H}_2\text{O}$ (4-R-trz=4-substituted 1,2,4-triazole). In this system the iron atom is triple-bridged by triazole ligands through the nitrogen atoms occupying the 1- and 2-positions and defining a linear chain (Fig. 12a). The ST behaviour depends on the substituent in position 4, the counterion and the non-coordinating solvent molecules. Some of these compounds show very abrupt spin transitions close to room temperature and with thermal hysteresis of width up to 35 K. Studies of the effect of pressure on the spin transition in some members of this family of complexes reveal remarkable features relevant to possible practical applications.

The system $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate}) \cdot \text{H}_2\text{O}$ where hyptrz=4-(3'-hydroxypropyl)-1,2,4-triazole [57] shows a very steep and complete ST

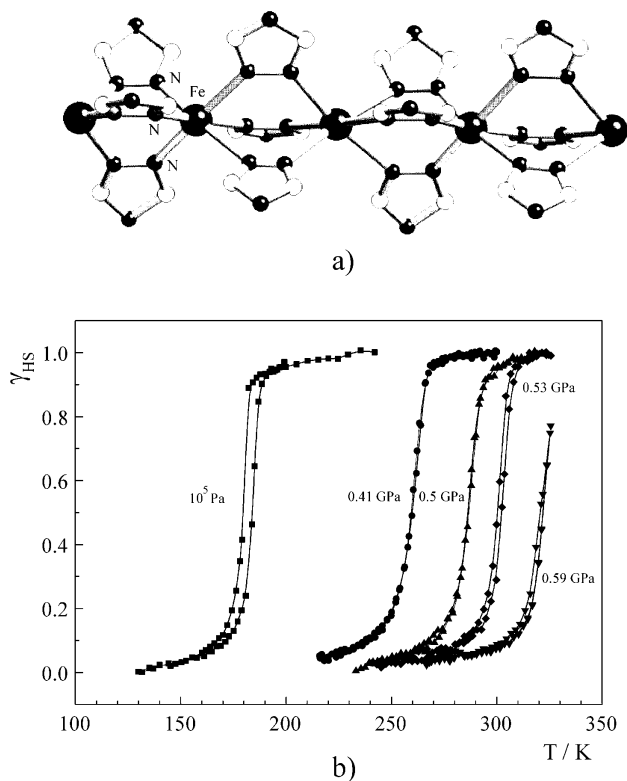


Fig. 12 **a** Structure of the polymeric $[\text{Fe}(\text{triazole})_3]_n^{2n+}$ spin crossover cation deduced from EXAFS data [56]. **b** Plot of γ_{HS} vs T at different pressures for $[\text{Fe}(\text{hyprtrz})_3](4\text{-chlorophenylsulfonate})\cdot\text{H}_2\text{O}$ [57]

around 180 K with a thermal hysteresis of 6 K as evidenced by magnetic susceptibility measurements at ambient pressure (Fig. 12b). Applying pressure induces a shift of the transition curve to room temperature and even higher. Unusual, however, is that this shift is parallel, as generally one observes a flattening of the transition curves with increasing pressure. Furthermore, it is interesting that the width of the hysteresis loop behaves non-monotonically with increasing pressure. Figure 13 shows the pressure dependence of the LS fraction, γ_{LS} , at 290 K. A very sharp HS→LS transition is observed at room temperature around ~0.6 GPa which is accompanied by an easily detectable colour change from white to deep purple. This feature could be used for applications such as pressure sensors or displays.

Similar pressure studies have been performed on $[\text{Fe}(\text{hyetrz})_3](4\text{-chlorophenylsulfonate})$ [58] leading to the same type of behaviour for the $\chi_M T$ vs T curves under pressure (Fig. 14). Moreover, the thermal hysteresis width, 10 K, was practically independent of pressure. The strength of the

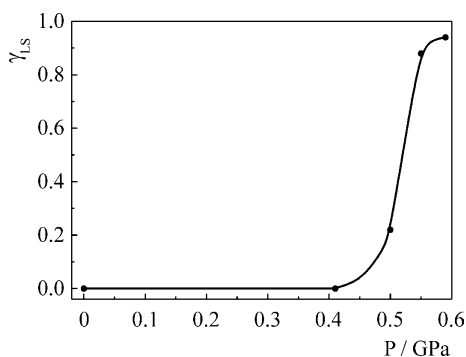


Fig. 13 Pressure dependence of the LS fraction, γ_{LS} , for $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})\cdot\text{H}_2\text{O}$ at 290 K [57]

cooperativity, however, apparently is not altered. The experimental results suggest that the hysteresis originates not only from intra-chain but also from inter-chain interactions. The pressure influence is more pronounced in these systems than in mononuclear compounds. Thus the $dT_{1/2}/dP$ slopes are found as 240 and 230 K GPa^{-1} for $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})\cdot\text{H}_2\text{O}$ and $[\text{Fe}(\text{hyetrz})_3](4\text{-chlorophenylsulfonate})$, respectively, compared to 150 K GPa^{-1} reported for $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\cdot\text{EtOH}$ [12], 176 K GPa^{-1} for $[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$ and finally 160 K GPa^{-1} for $[\text{Fe}(\text{PM-Aza})_2(\text{NCS})_2]$.

Another class of one-dimensional spin crossover systems concerns the complexes of formula $[\text{Fe}(\text{L})(\text{bt})(\text{NCS})_2]\cdot\text{bt}$ where L=4,4'-bipyridine (4,4'-bipy) [59], 4, 4'-azopyridine (azpy) [60], bt=2,2'-bi-thiazoline. As de-

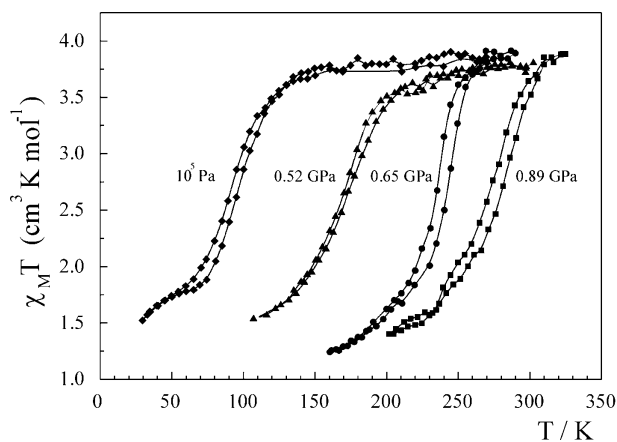


Fig. 14 Plot of $\chi_{\text{M}}T$ vs T at different pressures for $[\text{Fe}(\text{hyetrz})_3](4\text{-chlorophenylsulfonate})$ [58]

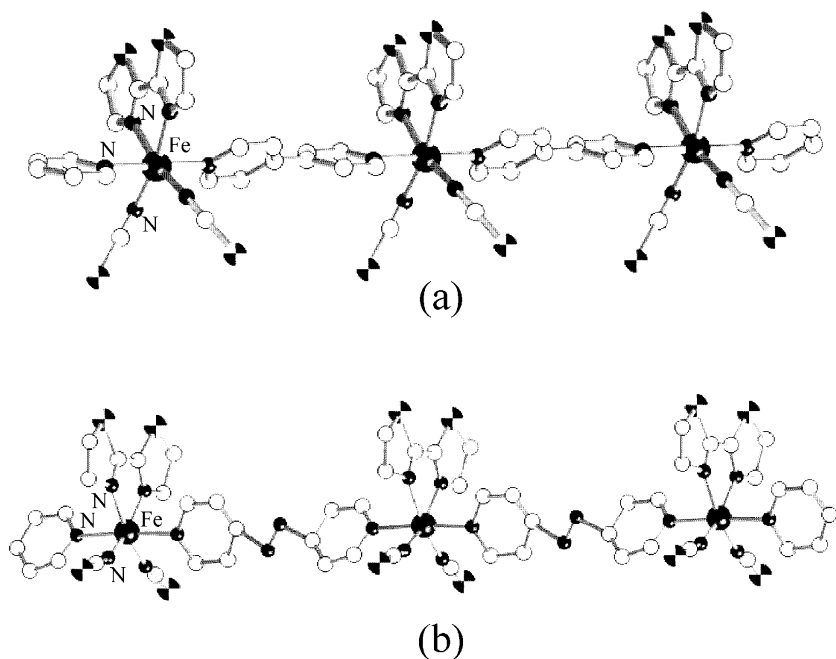


Fig. 15a,b Views of the chains: **a** $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$; **b** $[\text{Fe}(\text{azpy})(\text{bt})(\text{NCS})_2]\cdot\text{bt}$ (adapted from [59, 60])

picted in Fig. 15, these compounds consist of parallel linear chains defined by *trans*-4,4'-bipy or *trans*-azpy linked to iron(II) ions. For $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$ the crystal structure is made up by crystallographically independent parallel chains associated with slightly different $[\text{FeN}_6]$ cores (see Fig. 15). In the case of $[\text{Fe}(\text{azpy})(\text{bt})(\text{NCS})_2]\cdot\text{bt}$ only one Fe(II) crystallographic site was found. The equatorial plane is defined by two nitrogen atoms of one bt ligand and two thiocyanate groups in *cis* position for both complexes. The coordination octahedron of the iron(II) is strongly distorted in both cases.

The magnetic behaviour of these derivatives shows that a very incomplete spin transition occurs in $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$, while $[\text{Fe}(\text{azpy})(\text{bt})(\text{NCS})_2]\cdot\text{bt}$ is paramagnetic in the whole range of temperatures at atmospheric pressure. The incomplete character of the spin transition in $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$ is a consequence of the low temperatures at which the conversion takes place. For temperatures lower than ca. 70 K the kinetics of the HS→LS process becomes very slow and quenches the spin transition. Moreover, this behaviour can be understood considering the simple Ising-like model [59]. In Fig. 16a are depicted the $\chi_M T$ vs T curves at different pressures for $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$. It is remarkable that the incomplete-

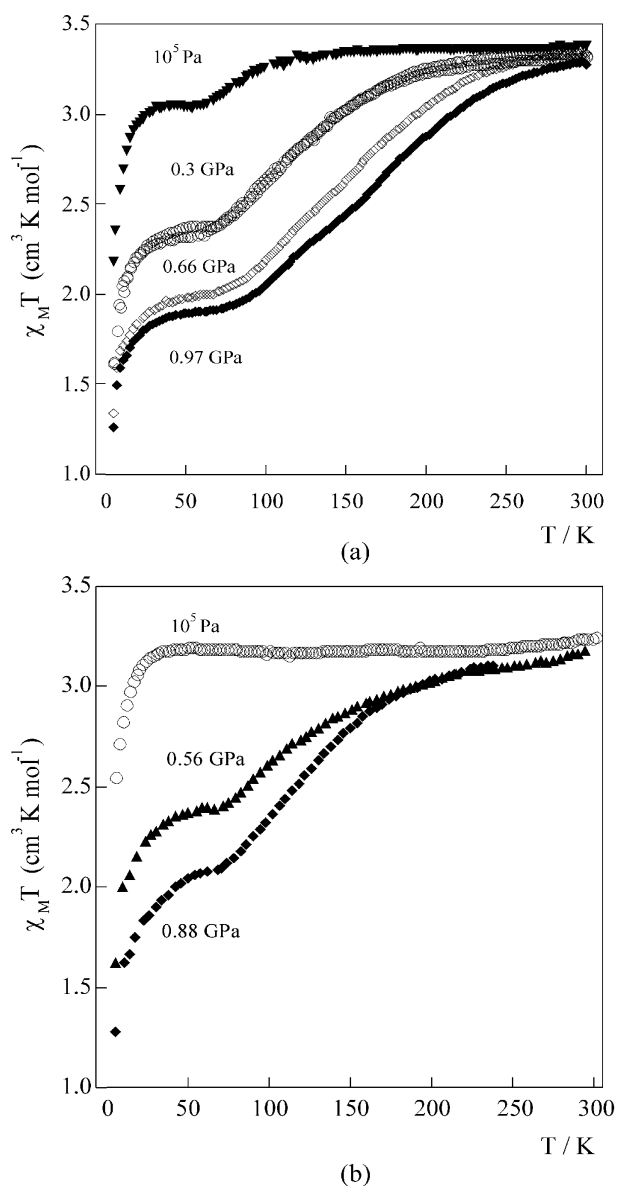


Fig. 16a,b $\chi_M T$ vs T curves at different pressures for: **a** $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$; **b** $[\text{Fe}(\text{azpy})(\text{bt})(\text{NCS})_2] \cdot \text{bt}$ (adapted from [60])

ness of the spin transition persists even at 0.97 GPa where the percentage of HS molecules deduced from the molar susceptibility value at 60 K is 52%. Kinetic effects seem to be responsible for the incomplete HS $\rightarrow$ LS conversion below 70 K for all applied pressures. The decrease of the magnetic suscepti-

bility below 50 K is due to ZFS (zero field splitting) of the iron(II) ions remaining in the HS state. $T_{1/2}$ moves upwards with increasing pressure and at $P > 0.66$ GPa the spin state conversion curve is in accord with a Boltzmann distribution between ground LS and excited HS states. In fact, the experimental transition curves at all pressures can be fairly well fitted with a Boltzmann function. As shown in Fig. 16b, the pressure studies on $[\text{Fe}(\text{azpy})(\text{bt})(\text{NCS})_2] \cdot \text{bt}$ reveal $\chi_M T$ vs T behaviour similar to that observed for $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$, but the influence of pressure is somewhat less pronounced regarding the completeness of the spin transition. This could be explained considering the lower field strength at the iron(II) nuclei in comparison with $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$.

A particular example of pressure induced spin crossover behaviour in 1D systems is the compound $[\text{Fe}(\text{bpym})(\text{NCS})_2]$ [51]. The magnetic behaviour shows that at ambient pressure this complex is HS in the whole range of temperature (Fig. 17b). As in the dinuclear analogue $[\text{Fe}(\text{bpym})(\text{NCS})_2]_2\text{bpym}$ [49–52] the magnetic behaviour is dominated by intramolecular magnetic exchange mediated by the bpym bridge, which extends along the 1D system (Fig. 17a). However, $[\text{Fe}(\text{bpym})(\text{NCS})_2]$ undergoes noticeable thermal spin transition at pressures much higher than in the case of $[\text{Fe}(\text{bpym})(\text{NCS})_2]_2\text{bpym}$. As can be seen in Fig. 17b, the curve measured at 0.98 GPa shows no indication of spin crossover; at 1.18 GPa, however, there is a one-step partial spin transition between 100 and 150 K leading to 50% of LS species. The significantly higher pressures required to trigger the spin transition in $[\text{Fe}(\text{bpym})(\text{NCS})_2]$ compared to $[\text{Fe}(\text{bpym})(\text{NCS})_2]_2\text{bpym}$ are rather surprising in view of their molecular structures. The average Fe–N bond distances can be considered the same in both compounds (2.180 and 2.179 Å for $[\text{Fe}(\text{bpym})(\text{NCS})_2]_2\text{bpym}$ and $[\text{Fe}(\text{bpym})(\text{NCS})_2]$, respectively), and consequently, the ligand field strength is expected to be very similar in both compounds. So, the difference in sensitivity to pressure should be attributed to different packing of active SCO centres in the crystal lattice.

A microscopic model describing the role of hydrostatic pressure on spin crossover in one-dimensional systems was developed by Klokishner et al. [61]. The system Hamiltonian includes long- and short-range interactions and takes into account external pressure. Long-range interactions are shown to arise from the coupling of the electronic states of the Fe(II) ion to the full symmetric strain. Short-range interactions are also introduced in the model. The short-range interactions of a crossover molecule with two nearest neighbours in the chain is only considered. It is shown that the competition between the short- and long-range interactions in 1D systems determines the type and the temperature of the spin transitions and, where relevant, the width of the hysteresis loop.

The model describes successfully the main features of the pressure effect in 1D spin crossover systems. It has been proved that when short-range interactions exceed significantly the long-range interactions, the width of the

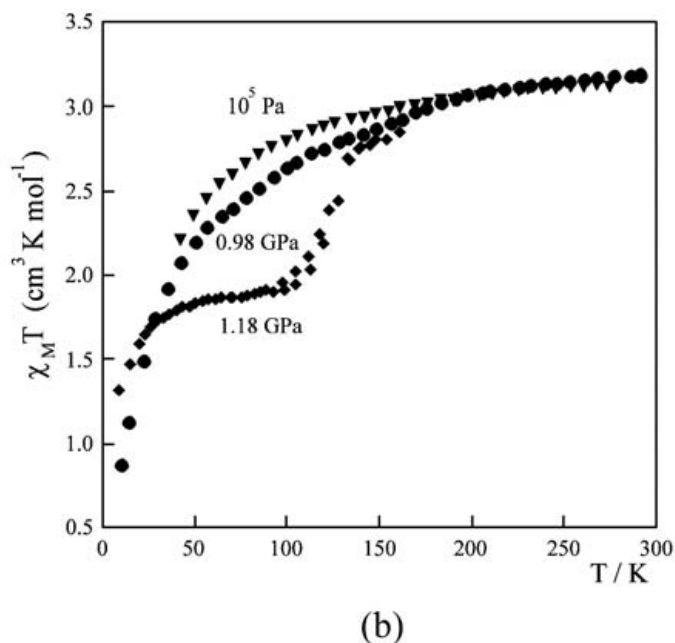
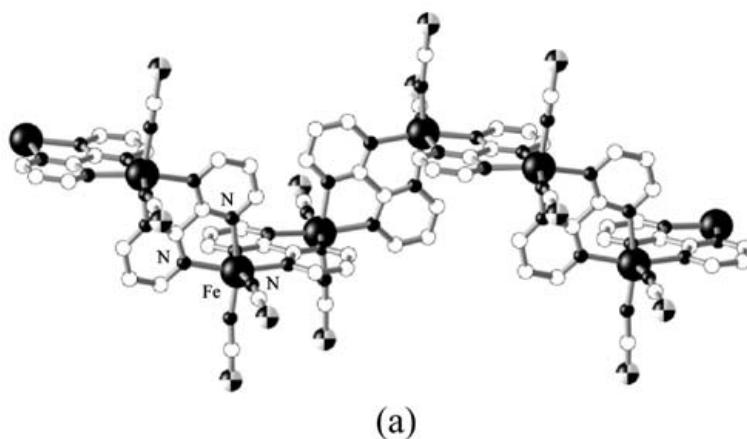


Fig. 17 a Molecular structure of the polymeric complex $[\text{Fe}(\text{bpym})(\text{NCS})_2]$. b $\chi_M T$ vs T curves at different pressures for $[\text{Fe}(\text{bpym})(\text{NCS})_2]$ [51]

hysteresis loop is only slightly influenced by pressure, whereas the mean value of the transition temperature increases significantly with pressure increase. Thus pressure studies of 1D systems provide information about the strength of short- and long-range interactions.

6.2

2D Spin Crossover Systems

Only a relatively small number of two-dimensional (2D) spin crossover compounds has been reported in the literature up to now and most of them belong to the series $[\text{FeL}_2(\text{NCS})_2] \cdot n\text{S}$ where L is a bis-monodentate ligand. One member of this family was prepared by Haasnoot from L=4,4'-bitriazole (btr) [53a,b]. The N2,N4 and N1,N1' bridging modes of btr ligands lead to a 2D layered compound of composition $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ (see Chap. 9 for the structure). In this system, the iron(II) ions are surrounded by four nitrogen atoms belonging to the triazole rings, and two thiocyanate anions fill the apical positions of the compressed octahedron. The layers are interconnected by means of van der Waals forces and weak hydrogen bonds involving the non-coordinating water molecules.

At atmospheric pressure, the title compound displays an abrupt ST at low temperature with hysteresis [62], this latter behaviour being probably due to a crystallographic phase transition [63]. Where, as is likely in this instance, both a spin transition and a crystallographic phase transition occur, the pressure dependence of both phenomena can be followed, and in the most favourable cases a decoupling can be observed between them [64]. In Fig. 18 the magnetic response of the material in the form of $\chi_M T$ vs T at different pressures is illustrated. The main features observed with increasing pressure are: i) the spin transitions in both cooling and warming modes become less abrupt and are shifted towards higher temperatures; ii) the hysteresis width decreases and finally disappears at ca. 1 GPa, where the system unexpectedly shows a considerable stabilisation of the HS state under pressure; iii) after pressure release the hysteresis is essentially restored, but a considerable amount of HS fraction remains in the low temperature region, which finally relaxes (after 175 h at room temperature) to a steady value of ~30%.

These findings demonstrate that it is possible to induce a complete LS→HS conversion by applying hydrostatic pressure to an iron(II) ST material. This result is entirely unexpected since the normal effect of an increase in pressure is to stabilise the low spin state. The appearance of the HS state under pressure was earlier observed on LS iron(II) complexes by Mössbauer spectroscopy and, as stated before, was probably due to non-hydrostatic conditions [9, 31, 65]. The possibility of converting LS to HS by applying pressure was theoretically considered by Kambara [66]. He proposed that the HS state can be stabilised by increasing the intramolecular coupling strength by pressure, since the molecular displacements with E_g symmetry can couple only with the HS state. The experimentally observed pressure dependence of the HS fraction for the present compound cannot be described by this model, probably because the cooperative interactions that are relevant in the present case were not considered in this theory.

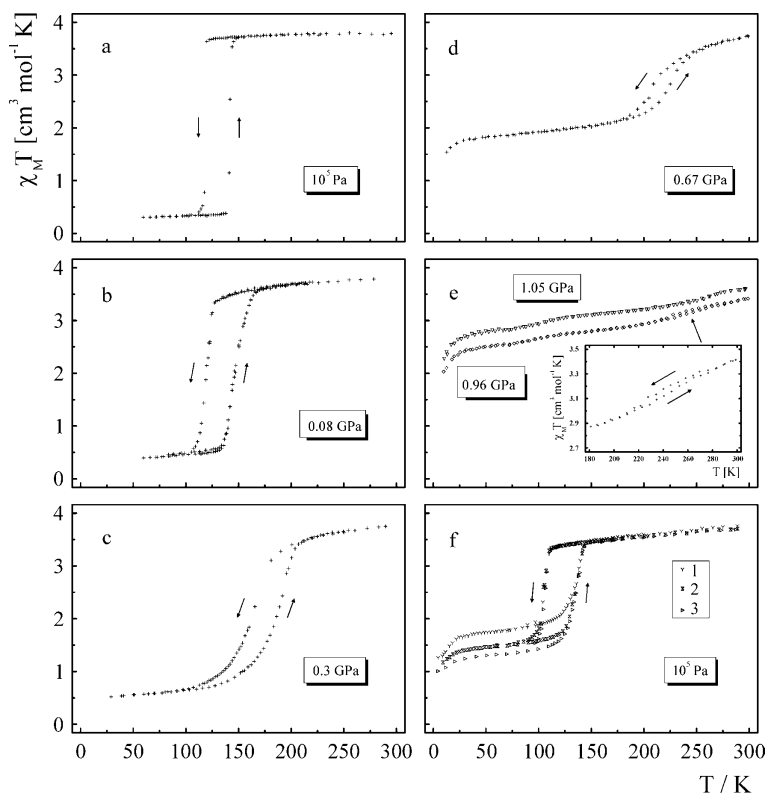


Fig. 18 $\chi_M T$ vs T curves at different pressures for $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ [62]

The complex $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ possesses unusual ST characteristics: a wide hysteresis loop with sharp ST occurring at low temperatures. Although the ligand field strength ($10Dq=11600 \text{ cm}^{-1}$) [67a] is at the lower limit of the range where spin crossover is expected [14], the system $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ does undergo spin crossover. We therefore assume that the ST is probably triggered by a crystallographic phase transition, in contrast to $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ where the ST triggers the crystallographic phase transition [67]. It is noteworthy that the isostructural compound $[\text{Fe}(\text{btre})_2(\text{NCS})_2]$ with $\text{btre}=1,2\text{-bis}(1,2,4\text{-triazol-4-yl})\text{ethane}$ remains HS even at 1.2 GPa [68]. Its crystal structure does not reveal any hydrogen bonds in contrast to that of $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$. This might play a decisive role in the appearance of the structural phase transition and thus of the spin crossover behaviour in the latter compound.

The role of a structural change is considered to be the main factor in the stabilisation of the HS state under pressure in $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$. We assume that a structural phase transition probably governs the ST in the pres-

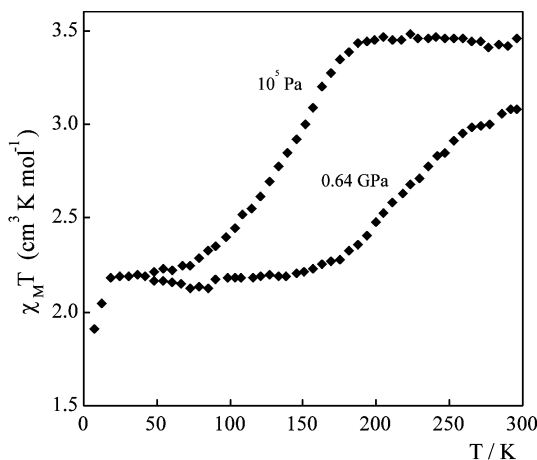


Fig. 19 $\chi_M T$ vs T curves at different pressures for $[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5 \text{ MeOH}$

ent case. We aim to clarify this behaviour further by X-ray measurements at variable temperatures and pressures and to establish the phase diagram of $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ in order to specify the variety of structural modifications induced by pressure.

The spin transition in $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, neat or diluted in a Ni-homologue, has been recorded using optical reflectivity in the pressure range up to 0.16 GPa [69]. The observed variation of the transition temperature with pressure was higher in comparison with magnetic susceptibility measurements. It is likely that this discrepancy originates from the different SCO behaviour on the surface as compared to the bulk.

Real and co-workers have reported on a new 2D spin crossover system formulated as $[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5 \text{ MeOH}$ (bpb=1,4-bis(4-piridyl)butadiyne) which consists of two different arrays of nets. Two crystallographically independent iron sites (Fe1 and Fe2) define the nodes of the nets [70]. The structure is described in detail in Chap. 9. In Fig. 19 are depicted the $\chi_M T$ vs T curves for $[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5 \text{ MeOH}$ at two different pressures [60, 71]. At 0.64 GPa 50% of the transition is still retained but $T_{1/2}$ is shifted towards room temperature. The continuous character of the spin transition becomes more pronounced and a LS fraction at 300 K is inferred from the value of $\chi_M T$ at this temperature. Further increase of pressure, even up to 1.14 GPa, has no further effect. This indicates a barrier to spin change at the Fe2 site and the concomitant change in volume which presumably cannot be accommodated in this highly interlocked network structure.

6.3

3D Spin Crossover Systems

Only a few 3D polymeric SCO systems have been synthesised and structurally characterised [72, 73]. Most of these systems possess perchlorate as counterions, and due to the danger in working with these under pressure, no pressure studies have been carried out so far. A new series of 3D spin crossover compounds has been obtained by extension of the $\{[\text{Fe}(\text{py})_2[\text{M}(\text{CN})_4]]$ 2D system where py=pyridine and M is Ni(II), Pd(II) or Pt(II) [53f]. Replacement of the py ligand by pz (pyrazine) in the 2D system affords the new family of 3D compounds $\{[\text{Fe}(\text{pz})_2[\text{M}(\text{CN})_4]] \cdot 2\text{H}_2\text{O}$. The molecular structure is illustrated in Chap. 9. In this new structure the pz ligand bridges the iron atoms of consecutive sheets achieving a pillaring of the 2D sheets by vertical columns of the pz bridge to give the 3D structure. These compounds undergo strong cooperative spin transition with 20–40 K wide hysteresis loops at ambient pressure. Molnar et al. have recorded the solid-state Raman spectra at room temperature as a function of pressure [26]. The studies show a reproducible pressure induced hysteresis loop at room temperature for the Ni derivative. For the Pd and Pt complexes, the spin state change occurs between 0.18 and 0.35 GPa, respectively, and competes with a pressure-induced structural transformation.

Concurrently with the synthesis of these polymers, Real and co-workers [53c] have investigated the suitability of the $[\text{Ag}(\text{CN})_2]^-$ anion for the synthesis of new 3D spin crossover systems. Using 4,4'-bipy and bpe (bispyridyl-ethylene) as bridging ligands they have succeeded to synthesise two new 3D molecular architectures with interesting magnetic response under hydrostatic pressure. The structures are also discussed in Chap. 9 and described fully in [53c]. The average Fe–N bond length in $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ is 0.011(9) Å greater than that for $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ in the high spin state. Despite this small difference, the former complex is HS in the whole range of temperatures studied while the latter (single crystal form) undergoes thermal spin transition at ambient pressure accompanied by a large thermal hysteresis. Figure 20 illustrates the $\chi_M T$ vs T curves at different pressures for $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ and $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ (microcrystalline powder form). The thermal spin conversion induced under pressure for $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ takes place without thermal hysteresis, being similar to that observed for $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ in the crystalline form. When the pressure is increased, a continuous and incomplete spin transition is observed which is shifted upwards to higher temperatures. Furthermore, the low temperature HS residual fraction decreases. Finally, at ca. 0.6 GPa the spin transition disappears and the system is stabilised in the LS state at all temperatures studied. The $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ system exhibits thermal spin transition at ambient pressure but only in half the iron (II) centres. The sharp decrease of $\chi_M T$ after the plateau arises from the ZFS of the remaining

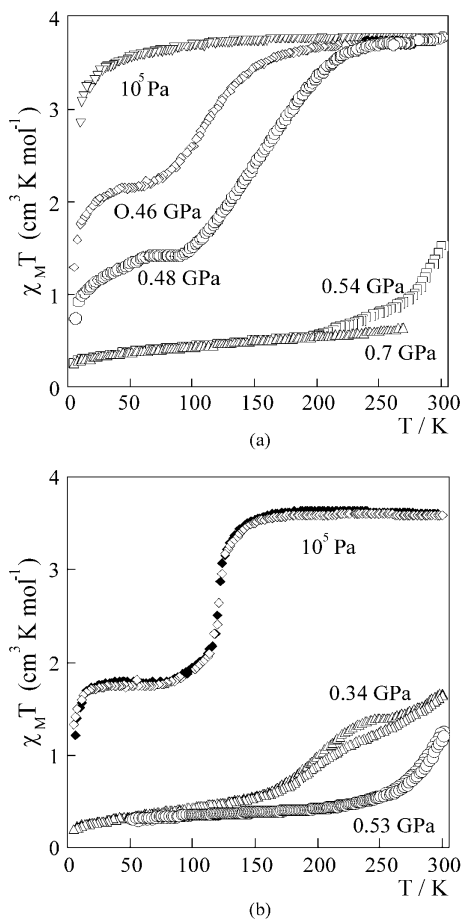


Fig. 20a,b $\chi_M T$ vs T curves at different pressures for: **a** $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$; **b** $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ [53c]

iron(II) ions in the HS state. The spin crossover behaviour in this system turns out to be very susceptible to pressure. As seen in Fig. 20 pressure of only ca. 0.5 GPa seems to be sufficient to stabilise the system in the LS state. The plot of $\chi_M T$ at 300 K vs P for $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ (Fig. 21) shows the unusual discontinuous character of the pressure-induced spin transition at room temperature. Although no hysteresis is observed, the extreme sensitivity of $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ and $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$ to pressure at 300 K suggests the occurrence of strong cooperativity in the 3D network.

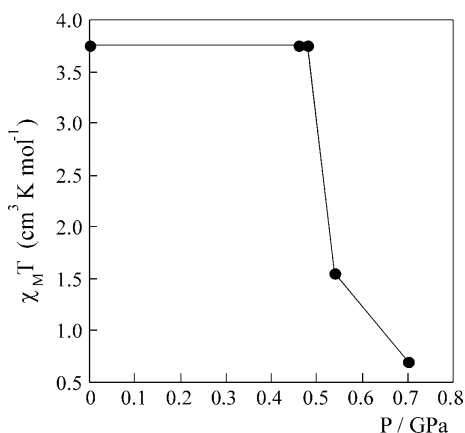


Fig. 21 Plot of $\chi_M T$ vs P at 300 K for $\{\text{Fe}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ [53c]

7

Effect of Pressure on Valence Tautomeric Systems

7.1

O-Dioxolene Adduct of a Cobalt-Tetraazamacrocyclic Complex

The phenomenon of temperature-induced valence tautomerism in cobalt complexes has been well established in the literature [74]. In these systems, a thermally induced intramolecular one-electron transfer takes place between the catecholato ligand and the LS cobalt(III) acceptor with a spontaneous change in spin state from Co(III) ($S=0$) to Co(II) ($S=3/2$), converting thereby the catecholato to the semiquinonato ligand with $S=1/2$. The equilibrium between the two valence tautomers with different total spin states, viz. $S=0$ and $S=2$, respectively, can be easily followed by magnetic susceptibility measurements. The phenomenon resembles very much the thermal spin transition process in iron(II) compounds and is considered in detail in Chap. 14.

We have investigated the influence of pressure on the temperature dependence of the valence tautomeric interconversion between the catecholato (cat) and semiquinonato (sq) forms, $[\text{Co}^{\text{III}}(\text{L})(\text{cat})]^+ \leftrightarrow [\text{Co}^{\text{II}}(\text{L})(\text{sq})]^+$, in the system $[\text{Co}(\text{cth})(\text{phendiox})]\text{PF}_6 \cdot \text{H}_2\text{O}$ (cth=dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; phendiox=9, 10-dioxophenanthrene) [75]. It has been inferred from crystal structure determination that the volume of the unit cell shrinks by more than 4% on going from the paramagnetic (HS) $[\text{Co}^{\text{II}}(\text{L})(\text{sq})]^+$ species to the diamagnetic (LS) $[\text{Co}^{\text{III}}(\text{L})(\text{cat})]^+$ species, which is far more than can be accounted for by thermal contraction. Thus it is clear that the magnetic properties of this valence tautomeric system must be pressure dependent. Indeed, as shown in Fig. 22, the transition temperature increases and the transition becomes more gradual with increasing pressure.

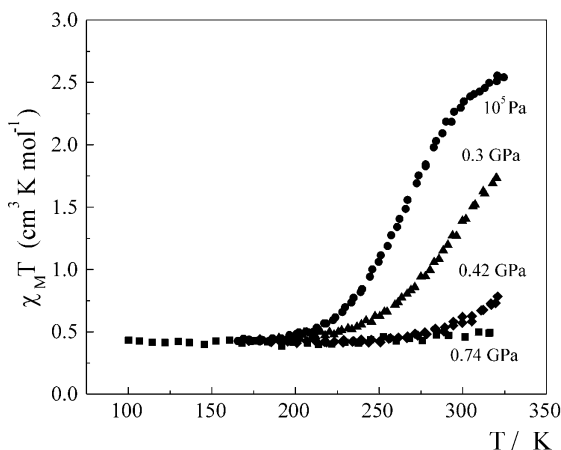


Fig. 22 $\chi_M T$ vs T plots at different pressures for $[\text{Co}(\text{CTH})(\text{phenidiox})]\text{PF}_6 \cdot 1.5\text{CH}_2\text{Cl}_2$ [75]

When the pressure reaches 0.74 GPa, the compound is practically diamagnetic at room temperature [75]. These findings are very similar to those from pressure effect studies on SCO compounds as described above. After appropriate calibration, i.e. taking the $\chi_M T$ values for different pressure values at a given temperature, such valence tautomeric systems appear to be suited for application in pressure sensors [75].

7.2

A Prussian Blue Analogue

A remarkable influence of pressure on the magnetic properties has been found in molecular magnets based on Prussian Blue type compounds of the general formula $\text{Co}_4[\text{Fe}(\text{CN})_6]_3$.

In 1996, Hashimoto and co-workers found a photoinduced magnetisation effect (PIM) in a cobalt-iron Prussian blue analogue [76]. This phenomenon was explained as being due to the presence of diamagnetic $\text{Co}^{3+}(\text{LS})\text{--Fe}^{2+}(\text{LS})$ pairs and a photo-induced electron transfer from Fe^{2+} to Co^{3+} through the cyanide bridge to produce $\text{Co}^{2+}(\text{HS})\text{--Fe}^{3+}(\text{LS})$ magnetic pairs [77]. Since the discovery of PIM, much effort has been devoted to the explanation of the appearance of diamagnetic pairs and their role in the PIM process. Introducing alkali metal cations in the tetrahedral sites of the *fcc* structure of $\text{Co}_4[\text{Fe}(\text{CN})_6]_3$ leads to a “chemically” induced electron transfer from cobalt(II) to iron(III) resulting in stable diamagnetic $\text{Co}^{3+}\text{--Fe}^{2+}$ pairs. In studying $\text{K}_{0.1}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7} \cdot 18\text{H}_2\text{O}$ (hereafter $\text{K}_{0.1}\text{Co}_4\text{Fe}_{2.7}$) showing no spontaneous $\text{Co}^{2+}(\text{S}=3/2)\text{--Fe}^{3+}(\text{S}=1/2) \rightarrow \text{Co}^{3+}(\text{S}=0)\text{--Fe}^{2+}(\text{S}=0)$ process, we found a pressure-induced charge transfer taking place in the paramagnetic $\text{Co}^{2+}\text{--NC--Fe}^{3+}$ units, leading to diamagnetic $\text{Co}^{3+}\text{--NC--Fe}^{2+}$ units [18].

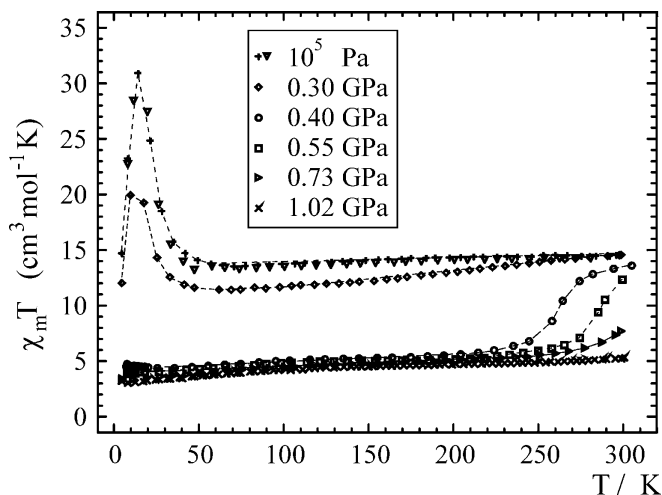


Fig. 23 Temperature dependence of $\chi_M T$ for $\text{K}_{0.1}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7} \cdot 18\text{H}_2\text{O}$ at different pressures. Measurements at 10^5 Pa after release of pressure confirm the reversible behaviour of $\chi_M T$ vs T [18]

The $\chi_M T$ vs T plots of the $\text{K}_{0.1}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7} \cdot 18\text{H}_2\text{O}$ sample measured at ambient and under applied hydrostatic pressure are displayed in Fig. 23. At ambient pressure the compound shows antiferromagnetic interaction and a ferrimagnetic ordering below $T_C \cong 6$ K. This magnetic behaviour remains unaltered as pressure is increased up to 0.3 GPa. Drastic changes are observed as the pressure reaches 0.4 GPa. At this pressure in the temperature range $200 \text{ K} < T < 300 \text{ K}$, a strong decrease of the $\chi_M T$ product is observed and at low temperature the long range magnetic ordering disappears. When the pressure is increased further, the pressure-induced feature in the magnetic behaviour above 200 K shifts to higher temperatures with a rate $\cong 170 \text{ K/GPa}$. At 1.02 GPa, the $\chi_M T$ value varies between 3 and $5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ in the temperature range 4.2–300 K.

^{57}Fe Mössbauer spectroscopy confirmed the pressure-induced $\text{Co}^{2+}(S=3/2) - \text{Fe}^{3+}(S=1/2) \rightarrow \text{Co}^{3+}(S=0) - \text{Fe}^{2+}(S=0)$ charge transfer in $\text{K}_{0.1}\text{Co}_4\text{Fe}_{2.7}$. At ambient pressure and 4.2 K the magnetically split Mössbauer spectrum proves the existence of magnetic ordering in $\text{K}_{0.1}\text{Co}_4\text{Fe}_{2.7}$ below 16 K (Fig. 24a). The spectrum with an average hyperfine field $\langle H \rangle = 164(2) \text{ kOe}$ and isomer shift $\delta = -0.07(2) \text{ mm/s}$ corresponds to 100% of Fe^{3+} in the $S=1/2$ spin state. At a pressure of 0.3 GPa, in addition to the magnetically split spectrum, a diamagnetic $\text{Fe}^{2+}(S=0)$ component, a singlet with isomer shift $\delta = -0.015(2) \text{ mm/s}$, appears (Fig. 24b) and is the only iron species present at pressures exceeding 0.4 GPa (Fig. 24c).

The joint study of the magnetic properties and hyperfine interactions by Mössbauer spectroscopy under pressure in $\text{K}_{0.1}\text{Co}_4\text{Fe}_{2.7}$ and other related

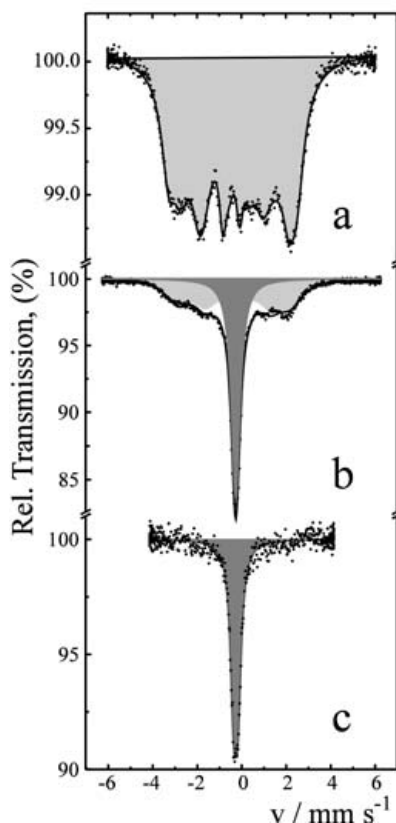


Fig. 24a–c Mössbauer spectra of $\text{K}_{0.1}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7} \cdot 18\text{H}_2\text{O}$ recorded at 4.2 K and different pressures: **a** ambient pressure; **b** 0.3 GPa; **c** 0.4 GPa. Shaded subspectra correspond to: $\text{Fe}^{2+}(\text{S}=0)$ (dark grey), $\text{Fe}^{3+}(\text{S}=1/2)$ (light grey) (adapted from [18])

Prussian blue analogues [18] gives clear evidence of pressure-induced electron transfer $\text{Co}^{2+}(\text{S}=3/2)-\text{NC}-\text{Fe}^{3+}(\text{S}=1/2) \rightarrow \text{Co}^{3+}(\text{S}=0)-\text{NC}-\text{Fe}^{2+}(\text{S}=0)$. Application of hydrostatic pressure provides a method of “tuning” the ligand field strength and enables one to determine the charge states in this important class of compounds.

8 Conclusion

Results of pressure effect studies in solid state on spin crossover and valence tautomeric systems using hydrostatic pressure cells and magnetic susceptibility and Mössbauer effect measurements have been presented and dis-

cussed. It has been demonstrated that the application of pressure provides important information on thermodynamical properties and on the driving force of thermal spin transition in SCO compounds. Analysing the evolution of the spin transition curve obtained under pressure it is possible to extract, along with the changes of enthalpy and entropy, the change of the volume of the unit cell ΔV upon spin conversion as well as the behaviour of the interaction constant Γ . It was also shown that application of pressure is a powerful tool to investigate the role of the structure and the interplay between spin transition and structural phase transition. Changes of the molecular volumes play a significant role in the cooperative interactions in solid compounds exhibiting dynamical electronic structures such as in spin crossover and valence tautomeric systems. It has been found that application of pressure is an elegant method of changing the ligand field strength and thereby modifying the spin transition behaviour in a controlled manner. Application of hydrostatic pressure to mono-, oligo- and polynuclear SCO systems has yielded results which are, on the one hand, quite expected like the stabilisation of the LS state due to its smaller molecular volume as compared to that of the HS state. On the other hand, some unexpected features in the SCO behaviour have been unravelled under pressure and await quantitative theoretical interpretation. There are, for instance, the two types of pressure influence: (i) the shape of the ST curve remains essentially unchanged, but the transition is shifted to higher temperatures under pressure; (ii) the relatively steep ST curve at ambient pressure becomes more and more gradual, stabilising the LS state and shifting $T_{1/2}$ upwards, as pressure increases, until the HS state entirely disappears. In both cases it is, of course, the molecular volume change ΔV_{HL} that tends to stabilise the LS state under pressure. However, there must be other factors, most probably arising from special lattice properties (hydrogen bonding, π - π stacking, packing effects), which are held responsible for the cooperative interactions between the spin state changing molecules and also contribute to the pressure-induced changes of the SCO behaviour. By the same token, it is believed that the unexpected stabilisation of the HS state and gradual diminishing of the hysteresis with increasing pressure have their origin in particular lattice properties. Clearly, theoretical progress in understanding such unexpected pressure effects will only be possible with data from crystal structure determination under applied pressure and, of course, variable temperature.

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The Spin Crossover Phenomenon Under High Magnetic Field

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Abstract The effect of high magnetic fields, static and pulsed, on the SCO phenomenon is described in detail, based on the results obtained by a number of different research groups. The experimental results gained from optical and magnetization techniques under magnetic field, and their interpretation are described. The contribution of theoretical models of the thermodynamic, microscopic, static, and dynamic properties, to the understanding of the effect of high magnetic fields on SCO is outlined.

Keywords Spin transition · Spin crossover · Magnetic field · Relaxation · Metastability · Dynamics · Ising-like models · Thermodynamics

List of Abbreviations

S	Spin
SCO	Spin crossover
T _{1/2}	Spin transition temperature
LS	Low-spin

HS	High-spin
T	Tesla
K	Kelvin
B	Magnetic field
btr	4',4'-Bis(1,2,4-triazole)
phen	1,10-Phenanthroline
γ_{HS}	High-spin fraction
k_{B}	Boltzmann constant ($1.38066 \times 10^{-23} \text{ J K}^{-1}$)
J	Cooperative interaction parameter
PMF	Pulsed magnetic field
μ_{B}	Bohr magnetron
$\text{H}_2(\text{fsa})\text{en}$	<i>N,N'</i> -Ethylene bis(3-carboxysalicylaldimine)
Py	Pyridine
(pyrrol) ₃ tren	Trianionic Schiff base
N_{A}	Avogadro constant
μ_0	Induction constant

1

Introduction

In some transition metal complexes, a change of electronic state (SCO: spin crossover) from a low-spin (LS) to a high-spin (HS) state can be induced by changing the temperature or the pressure, or by light irradiation [1–5]. Due to the influence of both short and long range intermolecular interactions [6], the crossover may occur abruptly, as a function of temperature, leading to a first-order phase transition, and may exhibit hysteresis [1, 4, 7–10]. Typical examples are provided by Fe(II) surrounded by six N atoms, such as in the well-known complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [1, 11, 12] or $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ [13, 14] and their metal-diluted species [15, 16].

The $\text{LS} \rightleftharpoons \text{HS}$ switching is usually detected by Mössbauer spectroscopy (the LS and HS states show different quadrupole interactions and isomer shifts), or by magnetic susceptibility (for Fe(II), the spin states are $S=0$ (LS) and $S=2$ (HS)) [1, 2, 4], or optical techniques (the optical properties are different in the LS and HS states) [8, 17].

For spin crossover complexes the possibility of switching between the HS and LS states can be achieved by a thermal, optical, pressure or magnetic perturbation [5, 19, 20] see also [21–23].

Application of a static magnetic field stabilizes the HS state, with a downward shift of the transition temperature $T_{1/2}$, the shift being a quadratic function of the intensity of the applied field [24–26]. Sasaki and Kambara [27] have first proposed a theoretical model of the effect of a magnetic field based on cooperative Jahn-Teller interaction and predicted the effect of large fields (20–100 T).

2

Static and Pulsed Magnetic Field Experiments

The first conclusive experimental study was carried out by the Gütlich group on $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [5] with a static magnetic field of 5.5 T obtained with a superconducting coil in a Faraday balance [24]. This study showed a shift of -0.12 K in $T_{1/2}$ which has been interpreted within the framework of the thermodynamical model based on the Gibb's free energy including the magnetic contribution of the HS state and neglecting the contribution of the diamagnetic LS state. J. Lejay et al. [25] investigated the very gradual spin conversion of cobalt complexes under a static field of 20 T, and observed a shift of the spin transition temperature of ~ -0.6 K. The effect has been analyzed with the same thermodynamical model [24]. Recently, Garcia et al. [28] have studied the gradual but more abrupt spin conversion of $[\text{Mn}(\text{pyrrol})_3\text{tren}]$ under 23 T static magnetic field. An observed shift of ~ -1.6 K was reported, together with a quadratic dependence of the transition temperature shift versus magnetic field, according to the law: $T_{1/2} \text{ (K)} = 43.7 - 0.003 B^2$ (B in Tesla).

In order to increase the rather small effects so far reported, it was of interest to use pulsed magnetic fields, which may reach high values, typically ~ 60 T at the present time.

However, the main obstacle to using pulsed fields was finding a technique suitable for the detection of the spin state fractions under pulsed field conditions, since it is not feasible to measure the magnetic properties directly. The experiment has been made possible by the use of optical reflectivity detection, as described in [17] (see also [18, 21, 29, 30] for recent developments of this method). In 2000 [20], we reported the first study of the effect of a high magnetic pulsed field (32 T) on the spin crossover in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, leading to an irreversible partial triggering of the spin crossover. An increase of the HS fraction by $\sim 15\%$ was induced. The irreversible process was obviously limited by the kinetic nature of the experiment. Later, by using metal-diluted complexes $[\text{Fe}_x\text{Ni}_{(1-x)}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ under 32 T pulsed field we observed a clear correlation between the cooperativity of the thermal transition and the dynamics of the triggering process [21, 22].

3

Review of the Existing High Magnetic Field Systems

Due to the high power required, of the order of 20 MW, static fields in excess of 30 T are available only at a limited number of facilities [31] (NHMMFL-Tallahassee, GHMFL-Grenoble, University of Nijmegen, TML-Tsukuba, HFLSM-Sendai). An alternative solution to attaining high fields is the gener-

ation of pulsed magnetic fields as pioneered by P. Kapitza in Cambridge in 1924 [32]. The idea is to induce a pulse of current into a pre-cooled coil, such that the temperature increase does not exceed a desired value chosen in order to avoid any damage to the coil. The most common way to generate non-destructive pulsed fields in the 30–60 T range is to discharge a capacitor bank into the resistive coil. This type of facility is currently operating in several laboratories worldwide; for a complete review see [33] and references cited therein. For most of the facilities the typical pulse duration is of the order of a few ms (5–10 ms).

The pulsed field facility at LNCMP (Toulouse) [34] produces fields up to 60 T with a pulse duration in the one second range [35], sometimes described as “quasi-static”.

Fields above 100 T (referred to as Megagauss) are obtained by using systems in which either the magnet alone or the magnet together with the sample are blown up during the experiment. With the capacitor-driven single turn coil technique, also called semi-destructive, fields of 300 T with a pulse duration of 3 μ s may be reached. The Humboldt Magnetic Field Centre in Berlin [36] and Tokyo University [37] are presently running such facilities. Even higher magnetic fields can be generated by an explosive-driven flux compression technique allowing optical and magnetization experiments in the 10 MG range with a few μ s, the absolute record being 2800 T obtained at the Russian Federal Nuclear Centre (VNIIEF) [38]. The experiments presented below were performed at the LNCMP. Pulsed magnetic fields up to 32 T were generated by the discharge (up to 1.25 MJ) of a capacitor bank (25,000 μ F) into a resistive copper coil immersed in liquid nitrogen. The wave form of the increasing field is a quarter of a sine wave and the maximum is reached in 75 ms, the magnetic field then decreases to 0 in 1.3 s following an exponential law due to crowbar diodes [35] inserted in the circuit, see Fig. 1.

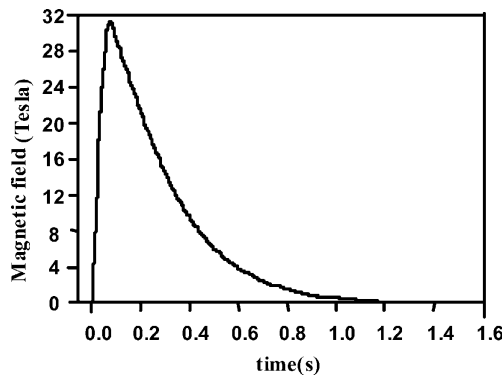


Fig. 1 Time dependence of the applied magnetic field pulse (after [20])

4 Optical Detection Under Magnetic Field

The HS fraction of molecules (γ_{HS}) is determined by reflectivity measurements [17, 18, 29] using a low-power, 5-mW He-Ne laser with $\lambda=632.8$ nm, for example (see Fig. 2). The radiation reaches the sample through one branch of a split stack of optical fibers. The reflected intensity (I_r) is measured at the output of the other branch by a Si PIN photodiode.

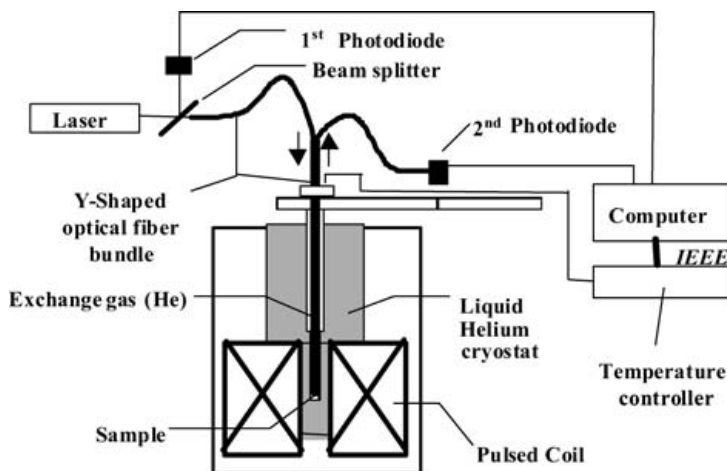


Fig. 2 Schematic representation of the experimental set-up allowing optical reflectivity detection of the $\text{LS} \rightleftharpoons \text{HS}$ transition under high pulsed magnetic field (after [21, 22])

In order to account for the effects of laser intensity fluctuations, a fraction of the incident light intensity (I_0) is simultaneously recorded with the same type of detector. According to previous studies [17, 18], if the wavelength of the laser source is well chosen the ratio I_r/I_0 varies nearly linearly as a function of the proportion of HS molecules.

The sample (ca. 15 mg) is a microcrystalline powder enclosed in a cylindrical holder made of insulating matter. The temperature is stabilized by using a self-control system (Lakeshore system for example).

5 Pulsed Magnetic Field Experiments

5.1 [Fe(phen)₂(NCS)₂]

In the absence of a magnetic field, the fraction of [Fe(phen)₂(NCS)₂] molecules in the high spin state γ_{HS} is determined by reflectivity measurements

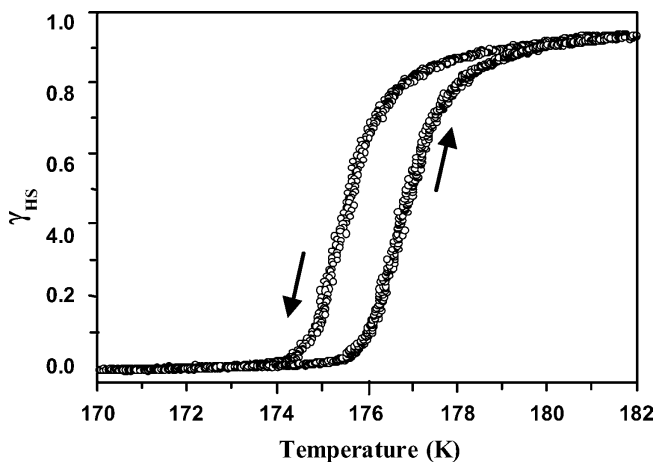


Fig. 3 Thermal hysteresis loop of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ detected by optical reflectivity in the absence of an external magnetic field (after [20]). Total sweeping time 80 min

(as described in the optical reflectivity measurement in the previous section and as shown in Fig. 2). The fraction was recorded vs either temperature or magnetic field. The thermal variation of the high spin fraction $\gamma_{\text{HS}}(T)$ obtained by reflectivity, in the absence of an external magnetic field, in the cooling and heating mode is shown in Fig. 3. Using a low sweep rate

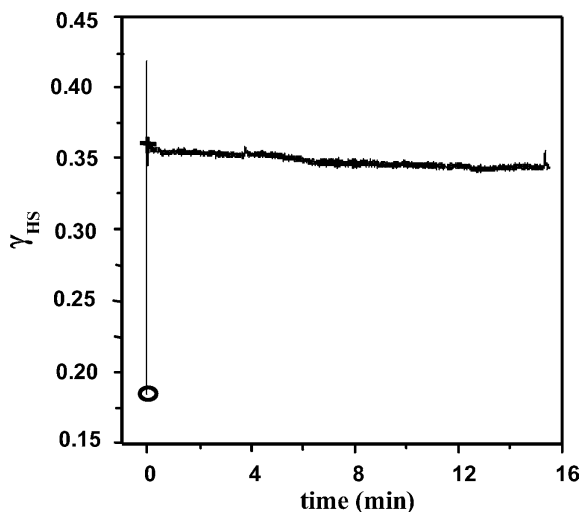


Fig. 4 A typical pulsed field experiment, showing the irreversible jump of the HS fraction (top curve) of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. An open circle and a cross show the initial and the final states, respectively (after [20])

($5 \times 10^{-3} \text{ K s}^{-1}$) a hysteresis loop width of $\sim 1.3 \text{ K}$ is obtained in agreement with magnetic measurements [12, 39].

A typical field-induced irreversible jump in the optical signal indicating a sizeable triggering of the phase transition is shown in Fig. 4. The magnetic field pulse (the maximum intensity of 32 T is reached in $\sim 75 \text{ ms}$), was applied at $T=176.1 \text{ K}$, for an initial state of the sample belonging to the ascending branch of the hysteresis loop (heating mode). The irreversible character of the field-induced effect is evident from its observation over a rather long time ($\sim 15 \text{ min}$), which shows the stability of the optical signal intensity once the jump has taken place.

Several experiments for various initial states along the ascending and descending branches of the thermal hysteresis loop showed systematic differences in the corresponding field-induced effects. The results are plotted in Figs. 5 and 6. These effects have been discussed in [20–23].

In Fig. 5, two typical time dependence plots of the optical response to the applied magnetic field, are selected, revealing the transient regimes during and immediately after the pulse. The response curves are compared to the time dependence of the field, (excitation of the system), and exhibit sizeable delays between the maximum field value and the maximum value of the optical response. The existence of such delays between excitation and response indicates the kinetic character of the experiment. In other words, the time

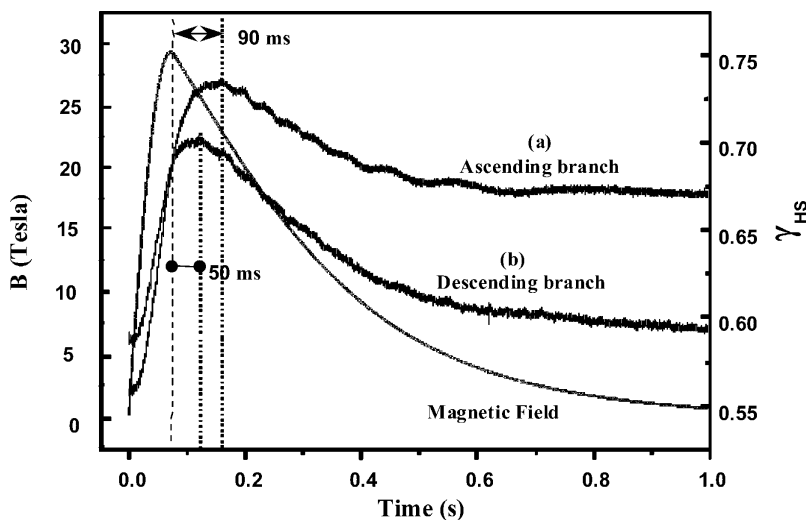


Fig. 5 $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$: the time-dependence for two typical responses, for initial states, with nearly the same population, belonging to the ascending (a) and descending (b) branches of the thermal hysteresis loop. The time-dependence of the magnetic field pulse is also shown, for comparison (after [20])

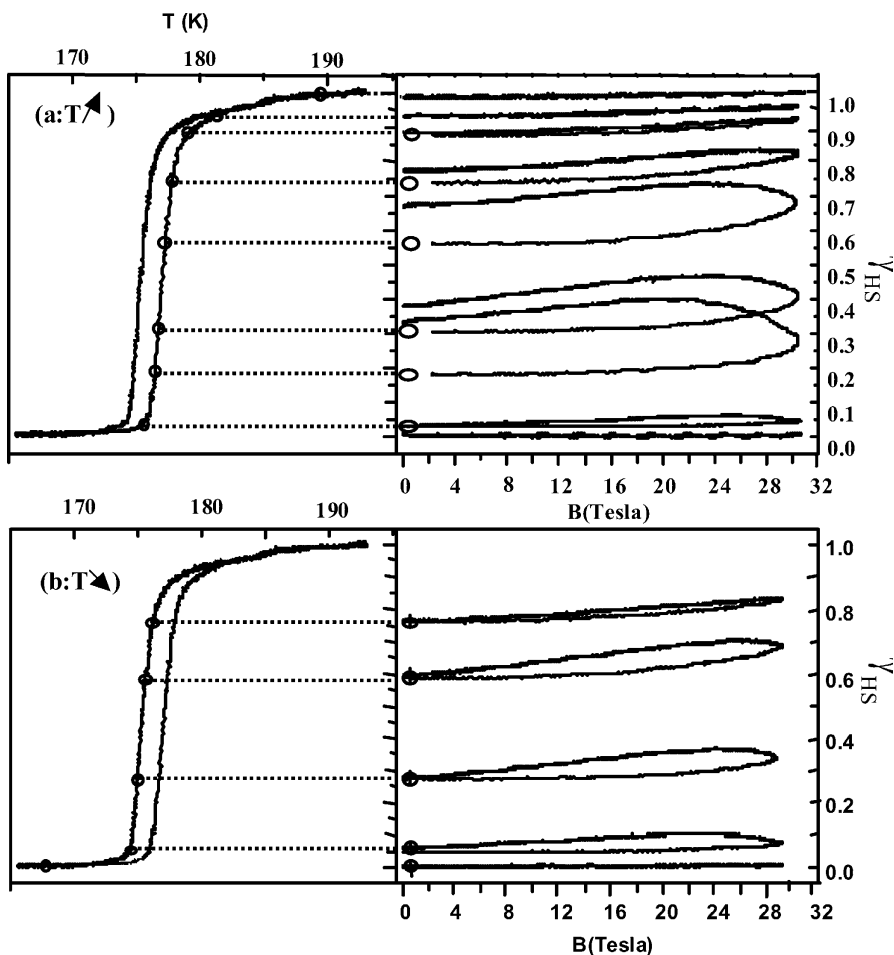


Fig. 6 High magnetic field effect on the thermal variation of the high-spin fraction in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (after [20])

scale of the field-induced transformation and the rise-time of the applied magnetic field (75 ms) are in the same time window.

An important point emerges from the data shown in Fig. 5. For the *ascending* (or *descending*) branch, the field-induced effect was *irreversible* (or *reversible*). In other words, in the ascending branch we succeed to trigger the “first-order” (in the non-equilibrium meaning) magnetic field induced spin transition. In addition, the time delays for the maximum values observed are markedly different: 90 and 50 ms, respectively.

The complete set of data is better displayed using response (γ_{HS}) vs excitation (B) plots as shown in Fig. 6a,b. The phase shift between the signals

endows the curve with an hysteretic aspect. According to its reversible or irreversible character, the loop appears closed or open, respectively.

The data collected in Fig. 6 confirm the close correlation between the presence of reversibility (or irreversibility) in γ_{HS} and the choice of the initial state in the descending (or ascending) branch of the thermal hysteresis loop. A correlation also has been observed between the magnitude of the effect ($\delta\gamma_{\text{HS}}/B_{\text{max}}$) and the slope of the transition curve $\partial\gamma_{\text{HS}}/\partial T$. It also appears from Fig. 6 that the delay value depends on the initial HS fraction. For some of the curves, when the loop is narrow, the quadratic dependence of the effect upon the applied field is clearly observed.

5.2

$[\text{Fe}_x\text{Ni}_{(1-x)}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$

In order to investigate the correlation between the kinetic effects (delay) and cooperativity, high magnetic field experiments have been performed [21] with the mixed-complex series $[\text{Fe}_x\text{Ni}_{(1-x)}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$ where cooperativity is controlled by the relative concentration, x , of the spin crossover active species in the system. The mixed complex is thus a diluted system with less effective interactions between the iron sites, see [5, 16] and references cited therein. With these complexes, the generic effects of a magnetic field previously evidenced with $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, i.e., irreversible (or reversible) triggering in the ascending (or descending) branch, and kinetic effects, were also obtained, as shown in Fig. 7.

The experimental values of the delay between magnetic excitation and response, measured on the ascending branch, for the compounds studied so far, now are used to discuss the kinetic aspect of the magnetic triggering. Indeed it is clear that the spin switching dynamics are governed by the barrier energy of the *metastable state*. In the present case, the LS $\rightarrow$ HS energy barrier associated with the magnetic triggering is expected to be macroscopic, and the barrier energy should be tightly correlated to the strength of interactions in the system, in addition to further physical quantities, usually considered in theoretical models (see for example [42–45]), such as the strength of the vibronic coupling, intramolecular vibration frequencies, energy gap between the spin states, the range of steric interactions and temperature. We have considered in Fig. 8a possible correlation with the cooperative character of the system, expressed as the ratio of the interaction parameter and transition temperature values. It is well known that, in mean-field approaches, the first-order transition only occurs above the threshold value $J/k_{\text{B}}T_{1/2}=1$, and this approximately is the case of the most diluted sample, the hysteresis loop of which is very narrow (a basic introduction to the Ising-like model involving J can be found below). The main issues of Fig. 8 are (i) the data obtained with the series $[\text{Fe}_x\text{Ni}_{(1-x)}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$ follow the expected trend, i.e., the larger the

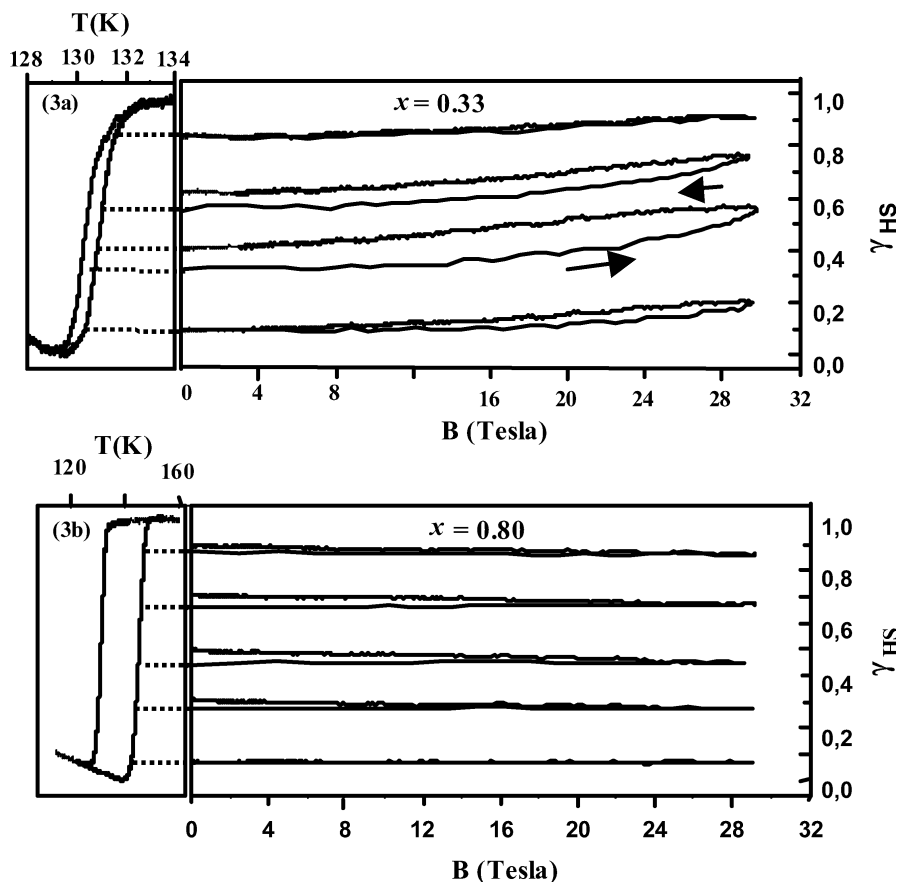


Fig. 7 $[\text{Fe}_x\text{Ni}_{(1-x)}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$: variation of the HS molecular fraction versus temperature (*left panels*) and vs magnetic field applied at different temperatures on the $T \uparrow$ branch (*right panels*) for $x=0.33$ (3a) (after [21]) and $x=0.8$ (3b) (after [22])

interaction parameter, the slower the dynamics and (ii) the single value obtained for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ agrees with the same trend. It is suggested that the dynamics of the magnetic spin triggering is mainly governed by the interaction strength, for a given type of spin crossover units (for instance iron(II)). However, the role of the denticity of the ligand (e.g., mono- bi- tri-dentate), which has been recently shown [46] to be of major importance for the lifetime of the metastable HS state, remains to be investigated systematically.

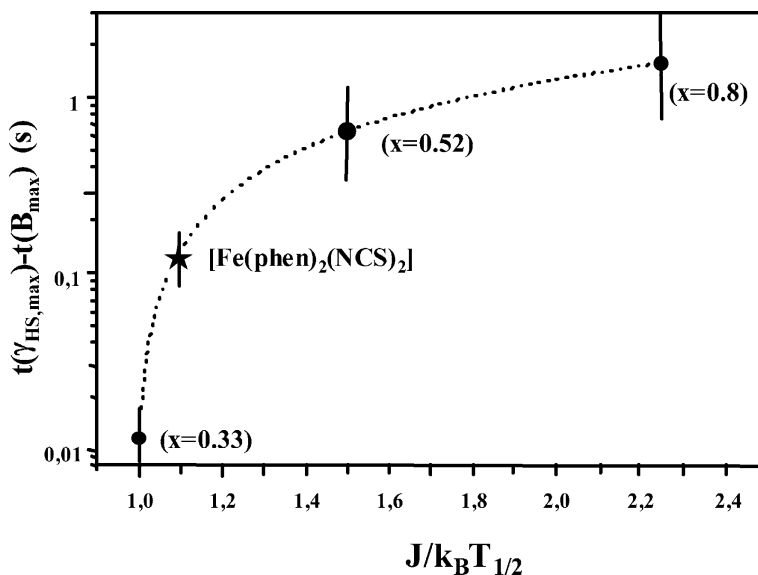


Fig. 8 Plot of the available values of the magnetic triggering delay, i.e., the time separation between $B^{\max}(t)$ and $\gamma_{HS}^{\max}(t)$ on the $T \uparrow$ branch, measured in the present work, for the same initial value $\gamma_{HS}^0 = 0.4$, vs the "cooperative character" of the transition. The latter is quantitatively expressed through the ratio of the mean field interaction parameter and the transition temperature: $J/k_B T_{1/2}$. The *dotted line* is a guideline (after [22])

5.3

$[Co(H_2(fsa)_2en)py_2]$

The studies presented above, together with the theoretical analyses reported in a further section, led to the conclusion that the kinetic nature of the experiment was responsible for the incompleteness of the magnetic triggering. Therefore, we investigated the compound $[CoH_2(fsa)_2en)py_2]$, which also exhibits an abrupt spin crossover, but possesses a lower energy barrier between the two states ($S=1/2$, $S=3/2$) [40]. Compared to the Fe(II) complexes, the smaller energy barrier in the case of the Co(II) complex may be due, as reported for Fe(III) complexes [41], to a smaller Huang-Rhys factor, resulting from a smaller difference between the metal-ligand bond distances in the LS and HS states.

The spin transition between the paramagnetic high-spin and low-spin electronic states of $[Co(H_2(fsa)_2en)py_2]$ under a pulsed and intense magnetic field (32 T) has been probed by optical reflectivity. In the absence of perturbation, as shown in Fig. 9, a thermal hysteresis loop ($\Delta T_{1/2} = 19.4$ K, average $T_{1/2} = 126$ K) was detected [23] confirming the cooperative character of the system as reported previously from magnetic measurements [40].

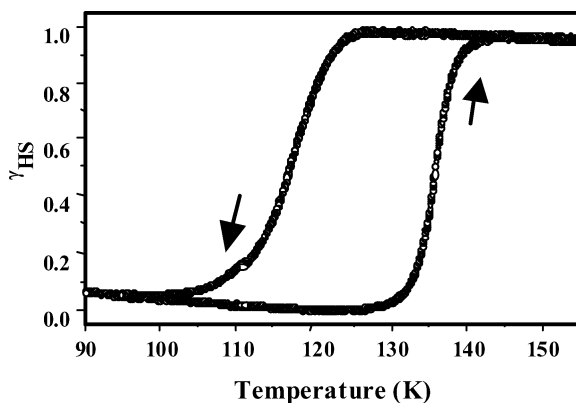


Fig. 9 Thermal hysteresis (high spin fraction (γ_{HS}) vs temperature) of $[\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py}_2)]$, obtained by reflectivity measurements after [23]

Applying a magnetic field of 32 T in the ascending branch of the hysteresis loop, as shown in Fig. 10, leads to an irreversible and quasi-complete $S=1/2 \rightarrow S=3/2$ transition [23]. The maximum triggering reaches $\sim 60\%$. The measured delays between $B^{\text{max}}(t)$ and $\gamma_{\text{HS}}^{\text{max}}(t)$ are quite small with respect to those of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, according to the flat character of the return branch of the irreversibility loops. As expected, the triggering is clearly more efficient with an energy barrier of ~ 620 K [40] (this system) than in the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ where the maximum triggering was only 15% for an energy barrier of ~ 1050 K [12].

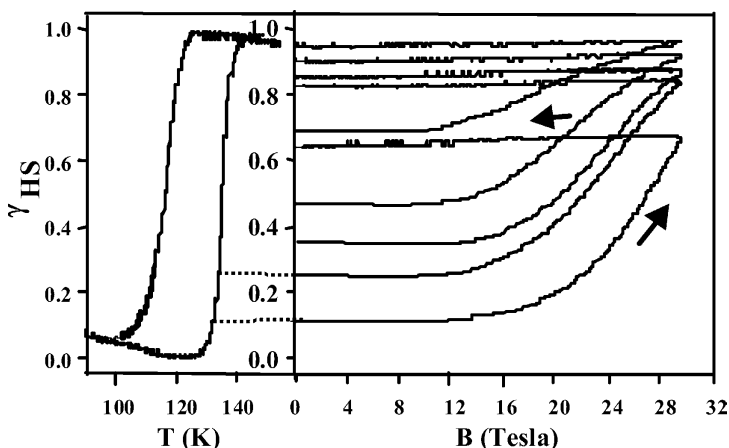


Fig. 10 Set of isotherms $\gamma_{\text{HS}}(B)$ showing the irreversible (and quasi-total) triggering effect on the HS fraction in $[\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py}_2)]$ (after [23])

6 Theoretical Approaches

6.1 Thermodynamic Approach

The analytical expression for the field dependence of the spin transition temperature is obtained from the magnetic free-energy expression (written in terms of molar quantities) [20, 24, 25]:

$$\begin{aligned}\Delta G &= G_{HS} - G_{LS} \\ &= \Delta H(0) + (\chi_{HS} - \chi_{LS})\mu_0 H^2/2 + p\Delta V - T\Delta S(0) - B\Delta M \\ B\Delta M &= (\chi_{HS} - \chi_{LS})B^2/\mu_0\end{aligned}$$

leading to

$$\Delta G = \Delta H(0) + p\Delta V - T\Delta S(0) - (\chi_{HS} - \chi_{LS})B^2/2\mu_0 \quad (1)$$

$\Delta H(0)$, $\Delta S(0)$ refer to the properties of the system in the absence of an external field. In the following, the pressure effect is neglected since there is no applied pressure, and the spin transition temperature is deduced from $\Delta G=0$ as

$$\begin{aligned}T_{1/2}(B) &= \Delta H(0)/\Delta S(0) - (\chi_{HS} - \chi_{LS})B^2/2\mu_0\Delta S(0) \\ &= T_{1/2}(0) - (\chi_{HS} - \chi_{LS})B^2/2\mu_0\Delta S(0)\end{aligned} \quad (2)$$

Taking into account the paramagnetic properties of the spin crossover systems, and substituting $T_{1/2}$ for temperature in the Curie law, Eq. (2) becomes for spin states 0, 2:

$$T_{1/2}(B) = T_{1/2}(0) - Ng^2S(S+1)(\mu_B B)^2/6k_B\Delta H(0) \quad (3)$$

where μ_B is the Bohr magneton, g the Landé factor, and k_B the Boltzmann constant. Equation (3) can also be obtained by a canonical approach of two-level systems, as previously reported in [20, 28] and takes the following form, for spin states 0, 2, with $g=2$ (spin-only):

$$T_{1/2}(B) = T_{1/2}(0) - 4(\mu_B B)^2/k_B\Delta(0) \quad (4)$$

Thus, the equilibrium temperature $T_{1/2}$ undergoes a negative magnetic field-induced shift:

$$\delta T_{1/2}(B) = T_{1/2}(B) - T_{1/2}(0) = -4(\mu_B B)^2/k_B\Delta(0) \quad (5)$$

In a first approach, we considered that the hysteresis loop was shifted as a whole by the presently calculated $\delta T_{1/2}$. This negative shift of the transition

temperature can also be considered through the magnetic field effect on the energy gap $\Delta(0)$ between the LS and the HS states. Indeed, the applied field B reduces the energy gap, which becomes in the applied field

$$\Delta(B) = \Delta(0) - 4(\ln r)(\mu_B B)^2 / \Delta(0) \quad (6)$$

with $\Delta(0) = \Delta H(0)/N_A$ the energy gap of the two-level systems and r the effective degeneracy ratio of the spin states (including vibrational contributions).

In the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [12] for which the calorimetric measurements give $\Delta(0) \sim 1050$ K, an applied field B of 32 T leads to a calculated temperature shift $\delta T_{1/2} \cong -1.8$ K.

As expected, the negative sign of $\delta T_{1/2}$ is in agreement with a stabilization of the HS state through its coupling to the magnetic field. It should be noted, comparing $|\delta T_{1/2}|$ with the width of the hysteresis loop (1.3 K, see Fig. 3), that the triggering of the SCO of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ by a pulsed field of 32 T

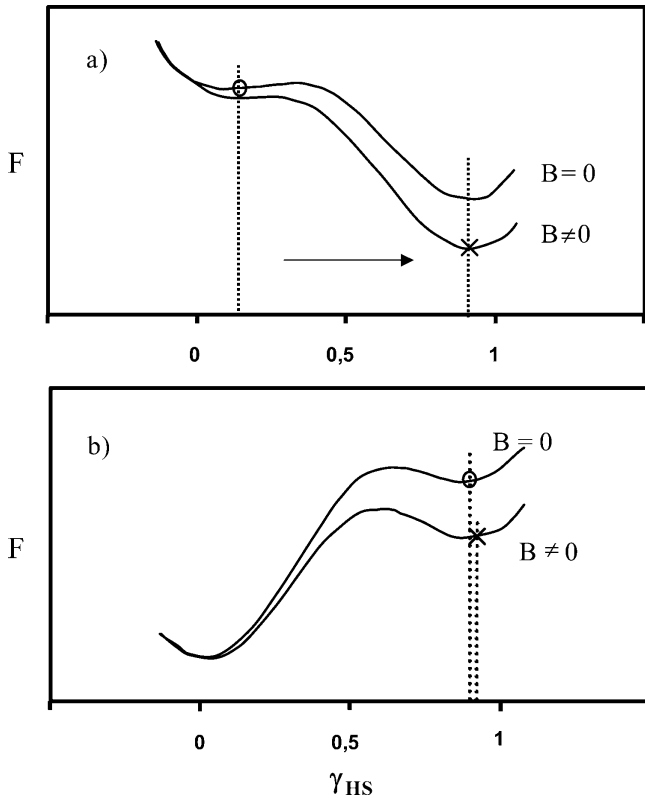


Fig. 11a,b The Landau free-energy (F) associated with a first-order transition, for a system close to instability, in: **a** the ascending branch, $T > T_{1/2}$; **b** the descending branch, $T < T_{1/2}$, of the thermal hysteresis loop in the presence and absence of a magnetic field. Open circles and crosses show initial and final states, respectively (after [20])

is expected to be complete. Figures 4–6 show, however, that only 15% of the molecules are converted. This effect was interpreted [20, 22] as a consequence of the dynamics of the spin crossover process which was later modeled [23] by using an Ising-like treatment [42] (see next section).

The irreversible aspects of the process can be qualitatively understood on the basis of the (Landau) free-energy schemes associated with the first-order transitions; see Fig. 11. If we assume that the sample is made up of independent crystallites, with a distribution of transition temperatures, the field mainly acts on the crystallites which initially are close to a metastable state, as shown in Fig. 11 in the ascending branch of the hysteresis loop, Fig. 11a, the field destabilizes these states, and triggers the transition; in contrast, in the descending branch, Fig. 11b, the field stabilizes these states, and the effect is reversible.

6.2

Ising-Like Model and Its Dynamical Extension

From the microscopic theoretical viewpoint, a cooperative spin crossover solid in a magnetic field B can be described by an extended Ising-like model [42], for which the Hamiltonian is written as [23, 43, 44]

$$\begin{aligned} \hat{H} = & \frac{\Delta(0) - kT \ln g_+ / g_-}{2} \sum_i \hat{\sigma}_i - \sum_{i \neq j} \hat{\sigma}_i \hat{\sigma}_j \\ & - g_L \mu_B \hat{S}_z^H B \sum_i \frac{\hat{\sigma}_i + 1}{2} - g_L \mu_B \hat{S}_z^L B \sum_i \frac{1 - \hat{\sigma}_i}{2} \end{aligned} \quad (7)$$

In this specific Hamiltonian, the HS and LS states are associated with the eigenvalues $+1$ and -1 , respectively, of the fictitious spin operator $\hat{\sigma}$ with their respective different degeneracies g_+ and g_- ($r = g_+ / g_-$). $\Delta(0)$ is the energy difference $E(\text{HS}) - E(\text{LS})$ for isolated molecules. In the mean-field approximation, the model is formally equivalent to the regular solution model treated in the Bragg-Williams approximation, with the simple correspondence $z k_B J = 2R\Gamma$ between their specific interaction parameters (z = number of involved neighbors). The last two terms of Eq. (7) are the Zeeman contribution in the HS and LS states, respectively, where μ_B is the Bohr magneton, g_L the Landé factor and $\hat{S}_z^{H,L}$ is the magnetic spin momentum operator corresponding to the HS and LS states. In the absence of a magnetic field, the transition temperature $T_{1/2}$, obtained for equal populations of HS and LS states, is given by $T_{1/2} = \Delta(0) / (k_B \ln r)$. Under a static magnetic field B , such that $g_L \mu_B < k_B T_{1/2}$, the shift of the transition temperature $\delta T_{1/2}$ is expected to be

$$\delta T_{1/2} = - \frac{g_L^2 \mu_B^2 B^2}{24 k_B \Delta(0)} [(2S_H + 1)^2 - (2S_L + 1)^2] \quad (8)$$

where S_H, S_L are the values of the true spin.

In the case of $[\text{Co}(\text{H}_2\text{fsa})\text{enpy}_2]$ for which $S_H=3/2$, $S_L=1/2$, $\Delta(0)=700$ K [40], under a magnetic field of 32 T one obtains $\delta T_{1/2} = -\frac{2(\mu_B B)^2}{k_B \Delta(0)} \approx -4.9^\circ \text{K}$.

Now we consider the non-equilibrium properties of the full Hamiltonian (Eq. 7) in which elastic and magnetic interactions are included. As known from the non-equilibrium statistical mechanics, such extension requires a stochastic description based on the master equation formalism [43, 44]. The master equation gives the time evolution of the probability $P(\sigma_1, \sigma_2, \dots, \sigma_N; t)$ of finding the spin system in the configuration $(\sigma_1, \sigma_2, \dots, \sigma_N)$. It is important here to recall that the spin operator $\sigma_i = \pm 1$ represents the occupations of the respective states HS and LS. Thus, a configuration denoted in terms of spins as $(+1, -1, +1, +1, \dots)$ corresponds in terms of spin transition molecules to the electronic configuration $(\text{HS}, \text{LS}, \text{HS}, \text{HS}, \dots)$. The time dependence of the probability $P(\sigma_1, \sigma_2, \dots, \sigma_N; t)$ is then given by the following equation:

$$\frac{d}{dt}P(\{\sigma\}; t) = \sum_j W_j(-\sigma_j)P(\{\sigma\}_j; -\sigma_j; t) - \sum_j W_j(\sigma_j)P(\{\sigma\}_j; \sigma_j; t) \quad (9)$$

$\{\sigma\}_j$ denotes the configuration of all spins except σ_j . $W_j(\sigma_j)$ are the transition rates of the spin flip $\sigma_j \rightarrow -\sigma_j$, induced by the thermal bath, which are constrained to obey the condition of microscopic detailed balance [23].

The average value of the “magnetization” at time t is obtained by calculating the expectation value of the fictitious spin σ_j , given by $\langle \sigma_j \rangle = \sum_{\{\sigma\}} \sigma_j P(\sigma_1, \sigma_2, \dots, \sigma_N; t)$. Knowing that the “fictitious magnetization” is directly related with to HS fraction by $\gamma_{\text{HS}} = \frac{1+\langle \sigma \rangle}{2}$, it becomes possible to express the time evolution equation of the high spin fraction using the present formalism.

Due to the existence of a vibronic energy barrier between the HS and LS states at the molecular level, as shown in Fig. 12, the convenient dynamics

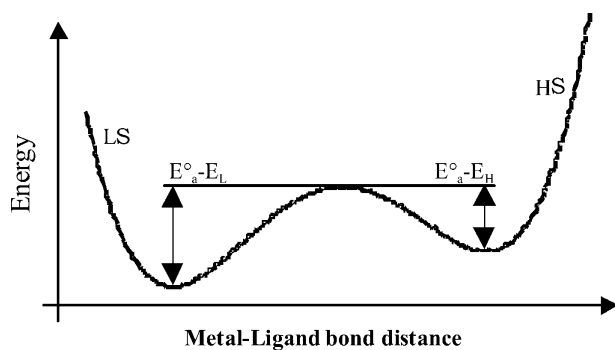


Fig. 12 Vibronic intramolecular energy barrier E_a^D for a SCO system. E_H and E_L are the energies of the HS and LS states, respectively (after [23])

for the SCO problem at high temperature is based on an Arrhenius-like process [45]. Let us denote by E_a^0 the energy barrier between the HS and LS states when they have the same energy, by E_H and E_L their respective energies, and by $W(H \leftrightarrow L)$ the transition rates between the two states. Therefore, $W(H \rightarrow L) \propto e^{-\beta(E_a^0 - E_H)}$, and consequently the general form of the rate transition can be written as $W_j(\sigma_j) = \frac{1}{2\tau_0} e^{-\beta(E_a^0 + \sigma_j E_j)}$ in which $1/\tau_0$ defines the individual spin flip rate between the two states, and $E_j = -\frac{\Delta(0)}{2} + 2\frac{(\mu_B B)^2}{kT} + \frac{kT}{2} \ln \frac{g_+}{g_-} + J \sum_i \sigma_i$.

Inserting this form of transition rates in the master Eq. (9), we may calculate the temporal evolution of the “fictitious magnetization” $m = \langle \sigma_j \rangle$. In the mean-field approximation [43], we obtain the following non-linear differential equation for the HS fraction of molecules $\gamma_{HS} = (1+m)/2$:

$$\frac{d\gamma_{HS}}{dt} = -\frac{2}{\tau_0} \gamma_{HS} e^{-\beta \varepsilon^+} e^{-2\beta q J \gamma_{HS}} + \frac{2}{\tau_0} (1 - \gamma_{HS}) e^{-\beta \varepsilon^-} e^{2\beta q J \gamma_{HS}}$$

$$\text{with } \varepsilon^\pm = \pm E_a^0 \mp \frac{\Delta(0)}{2} \mp qJ \pm \frac{kT}{2} \ln 2 \frac{g_+}{g_-} \pm 2 \frac{(\mu_B B(t))^2}{kT} \quad (10)$$

To compare qualitatively the present model to the experimental results, Eq. (10) was resolved in the ascending and descending branches of the thermal hysteresis loop, for the magnetic pulse represented in Fig. 2. The results obtained in the case of relatively rapid thermal relaxation are reported in Fig. 13 for the heating branch. They lead to the following conclusions: (i) this model is qualitatively in good agreement with the experimental behav-

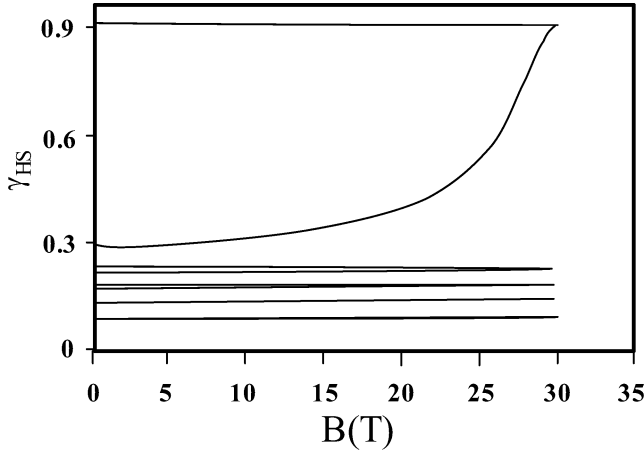


Fig. 13 Calculated HS fraction as a function of the pulsed magnetic field B in the ascending branch of the hysteresis loop (after [23])

ior; (ii) it clearly shows that the non-reversible variation of the high-spin fraction is well reproduced and the amplitude $\delta\gamma_{\text{HS}}$ of the irreversibility depends on the initial state, as found in the experiments. In the same way, the reversible character of the evolution of the HS fraction under a pulsed magnetic field is also found when the pulse is applied in the descending branch of the hysteresis loop.

In addition, this approach shows that the efficiency of the $LS \rightarrow HS$ triggering depends on various parameters, including the frequency $1/\tau_0$ of the individual spin flip, the strength of the vibronic coupling (from which the energy barrier E^a_0 originates), and the transition temperature $T_{1/2}$. Indeed, the same magnetic pulse applied to $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [20] produces a jump in the HS fraction 60% weaker than that obtained with $[\text{Co}(\text{H}_2(\text{fsa})\text{en})\text{py}_2]$. These results are in very good agreement with the expected shifts in transition temperature, $\delta T_{1/2} = -1.9$ K for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and -4.9 K for $[(\text{Co}(\text{H}_2(\text{fsa})\text{en})\text{py}_2)]$, respectively. The influence of the energy gap, closely associated with the transition temperature value, according to Eq. (4), is prominent. A second factor of particular importance for the iron(II) complexes, compared to cobalt(II) or iron(III) spin crossover complexes, is the slower relaxation between the spin states, due to the stronger vibronic coupling between the spin states and the larger change in metal-ligand bond length [41].

It is also noteworthy that, as an immediate consequence of the fast dynamics, the non-linear effects of the interactions are hidden in $[\text{Co}(\text{H}_2(\text{fsa})\text{en})\text{py}_2]$, while they are visible in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. An additional experimental factor may be the inhomogeneous state of the sample, namely a distribution of transition temperatures characterized by a smoothing of the edges of the thermal hysteresis loop [4]. Then, the triggering effect is expected to take place at different temperatures for the different crystallites, so as to smear out the response of the system to the magnetic excitation.

To summarize, the efficiency of the PMF on the triggering of the spin crossover process can be based on a few essential points: (i) the magnetic triggering occurs only in the ascending branch of the thermal hysteresis loop; (ii) the kinetics of the magnetic triggering are mainly governed by the strength of the vibronic coupling responsible for the energy barrier between the spin states; (iii) additional factors such as intermolecular interactions, the energy gap between the spin states and macroscopic homogeneity of the sample are also relevant factors. Future experimental work might take advantage of additional magnetic facilities allowing variation in the rise-time of the magnetic field. From the theoretical point of view, the static and dynamic effects observed are well reproduced by the extended Ising-like model including the magnetic field effect.

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The Role of Molecular Vibrations in the Spin Crossover Phenomenon

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Abstract The prominent role of intra- and inter-molecular vibrations in the spin cross-over phenomenon is outlined, based on the results obtained by the spin crossover community. The experimental results gained from various techniques (IR, Raman, X-ray diffraction, heat capacity, Mössbauer spectroscopy, synchrotron radiation techniques, etc.) and their interpretation are described. The contribution of theoretical models (thermodynamic and Ising-like electro-vibrational models) to the understanding of the relationship between the relative energies of the high-spin and low-spin states and molecular vibrations, especially when the high-spin and low-spin energy levels are close to each other, is stressed.

Keywords Spin crossover · Spin-state equilibrium · Vibrational properties · Molecular vibrations · Lattice dynamics · Mass effect · Isotope substitution · IR and Raman spectroscopy · Synchrotron radiation techniques · Ising-like microscopic model · Ising-like electro-vibrational model · Macroscopic thermodynamic model

List of Abbreviations and Symbols

4,4'-bipy	4,4'-Bipyridine
bpp	2,6-Bis(pyrazol-3-yl)pyridine
bpy	2,2'-Bipyridine
bpym	2,2'-Bipyrimidine
bt	2,2'-Bithiazoline
btr	4,4'-Bis-1,2,4-triazole
bzimpy	2,6-Bis(benzimidazol-2'-yl)pyridine
DFT	Density functional techniques
EXAFS	Extended X-ray absorption fine structure
f_{LM}	Lamb-Mössbauer factor
FTIR	Fourier transform infrared spectroscopy
HB(pz) ₃	Hydrotris(1-pyrazolyl)borate
H ₂ B(pz) ₂	Dihydrobis(pyrazolyl)borate
HS	High-spin
LIESST	Light induced excited spin state trapping
LS	Low-spin
3-MeO,5-NO ₂ -sal-N(1,10)NMe(4,7)	1,10-Bis(3-methoxy,5-nitro-salicylaldimine) -1,4-diaza-7,10-bis(methylaza)decane
NFS	Nuclear forward scattering
NIS	Nuclear inelastic scattering
5-NO ₂ -sal-N(1,4,7,10)	1,10-Bis(5-nitro-salicylaldimine) -1,4,7,10-tetraazadecane
phen	<i>o</i> -Phenanthroline
2-pic	2-Picolylamine
ptz	1-Propyltetrazole
PVDOS	Partial vibrational density of states
py	Pyridine
pz	Pyrazine
SCO	Spin crossover
Θ_D	Debye temperature
tpa	Tris(2-pyridylmethyl)amine
tptMet	1,1,1-Tris{[<i>N</i> -(2-pyridylmethyl)- <i>N</i> -methylamino] -methyl}ethane
TRIM	4'-(4-Methylimidazole-2'-(2''-imidazolylmethyl) imidazole

1

Introduction

Since its discovery some 70 years ago [1, 2], the thermally induced spin crossover (SCO) from a low-spin (LS) state at low temperature to a high-spin (HS) state at higher temperature has been comprehensively studied by

numerous experimental techniques. Most SCO materials being iron complexes, ^{57}Fe Mössbauer spectroscopy has been extensively used to investigate the SCO phenomenon.

Since ferrous SCO materials largely predominate over the ferric ones, this chapter will focus on iron(II) SCO complexes which are octahedral, and where the number of anti-bonding e_g electrons increases from 0 to 2 upon $\text{LS}(t_{2g}^6)$ to $\text{HS}(t_{2g}^4 e_g^2)$ crossover.

The significant weakening of the six Fe^{II} -ligand bonds resulting from the above-mentioned increase in anti-bonding electrons upon $\text{LS} \rightarrow \text{HS}$ crossover is responsible for the modification of the crystal structure upon SCO which has been described in detail for many Fe^{II} complexes based mainly on X-ray diffraction and to a lesser extent on EXAFS (extended X-ray absorption fine structure) data [3, 4]. It is well documented that the SCO is always accompanied by important changes in the coordination environment of the transition metal (metal-ligand bond lengths and angles) and consequently by a modification of the crystal volume. For example, in Fe^{II} complexes including nitrogen ligands, the six Fe-N bond lengths increase on average by 0.2 Å upon $\text{LS} \rightarrow \text{HS}$ crossover, yielding an approximate increase of up to 5% in the unit cell volume. Obviously, such large structural changes must have important effects on the vibrational properties of SCO molecules and on lattice dynamics of SCO solids. Indeed, the elastic properties (acoustic modes) and vibrational spectra (optical modes) are usually very different in the two spin-states.

Since the LS and HS states differ predominantly in the metal-ligand distance, the reaction coordinate is often assumed to be approximately equivalent to the totally symmetric normal coordinate. In a simple harmonic approximation the two potential curves (LS and HS ground states) correspond thus to two parabolas along this normal coordinate (Fig. 1). The HS potential well is located at a larger metal-ligand distance, while the energy gap between the bottom of the wells must fall within the range of thermal energies

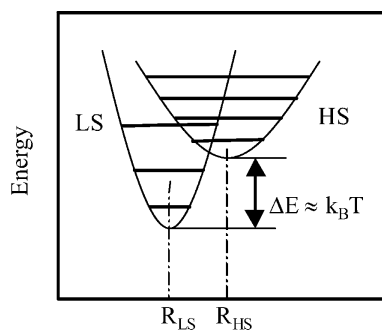


Fig. 1 Schematic potential energy diagram for a transition metal ion in the HS and LS state

for occurrence of the SCO phenomenon. One can note that the curvature of the parabolas and the distance separating the vibrational levels are both larger in the LS state. This is because the LS vibrational frequencies (i.e., force constants) are higher ($\omega_{\text{LS}} > \omega_{\text{HS}}$). In the solid state, this difference in force constants leads to a more rigid LS lattice which is reflected in its higher Debye temperature.

2

Vibrational Spectra and Vibrational Properties

From the beginning of SCO research, vibrational spectra have been used as a complement to other physical methods (e.g., Mössbauer spectra, magnetic susceptibility measurements) to follow the spin-state crossover and to gain more insight into the properties of these compounds. In most cases variable temperature mid-IR or far-IR techniques have been employed [5, 6] while Raman spectroscopy has become only recently a well established technique for the characterization of the SCO phenomenon [7–11]. It is worth noting that IR spectroscopy of SCO complexes is complicated by the fact that the SCO is very sensitive to mechanical treatments (grinding, milling, pressure, etc.); hence samples usually cannot be processed as pellets, but only as nujol mulls. Raman spectroscopy has the advantage that, frequently, little or no sample preparation is involved. On the other hand, highly colored samples can cause difficulties due to laser heating effects and a careful choice of the excitation wavelength is mandatory [7]. For example, in the case of

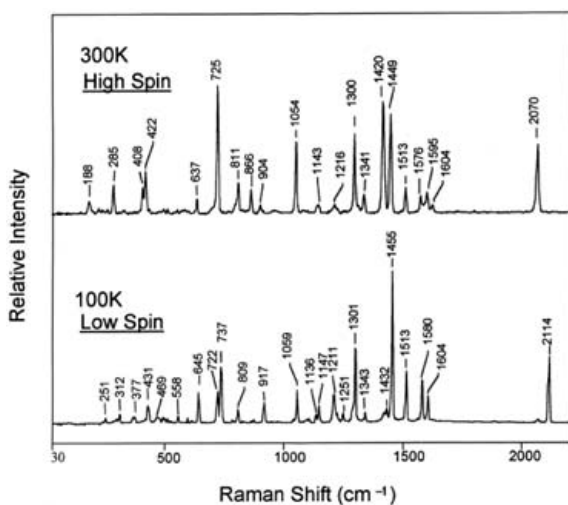


Fig. 2 Raman spectra of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in the HS (300 K) and LS (100 K) states [7]

[Fe(phen)₂NCS₂] which is deep violet in the HS state, clean Raman spectra may only be obtained with a red (~632 nm) excitation wavelength. Comparison of the 100 K (LS state) and room temperature (HS state) Raman spectra of Fig. 2 clearly indicate that vibrational modes are shifted of upon SCO.

2.1

Internal Ligand Modes as Diagnostic Tools

In a majority of cases, vibrational spectra have been used only as a diagnostic tool to identify a change in spin-state. Although the best choice would apparently be to observe metal-ligand modes, their assignment is often not straightforward, and thus internal ligand modes are more often probed. One of the most convenient probes is the C-N stretch of NCX ligands, which exhibits a large frequency shift upon LS $\rightleftharpoons$ HS SCO (typically 40 cm⁻¹). The convenient feature of these modes is that they lie in a spectral region (~2100–2200 cm⁻¹) largely free of interfering absorptions: the frequency shift has been explained in [6]. By plotting the HS and LS area fractions of C-N stretching bands as a function of temperature a spin-transition curve can be obtained. Zilverentant et al. [12] have shown that the spin transition in the complex [Fe(btr)₂(NCS)₂] $\cdot$ H₂O can be followed in a quantitative manner provided careful normalization of the IR spectra with an internal reference is carried out. Other ligand vibrations such as the α -diimine stretches show also significant frequency shifts that can be used to identify spin equilibria [13]. For more examples, see the reviews by Gütllich [5] and Toftlund [6].

2.2

Metal-Ligand Vibrations

In view of the particular importance of metal-ligand vibrations with regard to the SCO mechanism, the paucity of available data concerning these modes is somewhat surprising. The first detailed study aimed at assigning metal-ligand vibrational modes in SCO compounds was carried out by Takamoto and Hutchinson [14–17] using metal isotope substitution on [Fe(phen)₂(NCS)₂] and related compounds. They assigned a shift of Fe-N(phen) and Fe-N(NCS) stretching frequencies from 220 cm⁻¹ (HS) to 375 cm⁻¹ (LS) and from 252 cm⁻¹ (HS) to 530 cm⁻¹ (LS), respectively. The validity of this latter assignment has been questioned and the low-frequency spectra of this compound have been reassigned recently [18, 19]. Table 1 summarizes the available data on metal-ligand stretching frequencies in SCO compounds. The large frequency shifts between the HS and LS states are a noteworthy feature. To obtain some idea of the expected frequency changes, Jung et al. [20] compared the Fe-N stretching force constants for iron(II) in very weak ([Fe(NH₃)₆]²⁺) and very strong ([Fe(CN)₆]⁴⁻) ligand fields. From these lim-

Table 1 Fe-N stretching frequency changes upon SCO in iron(II) compounds

Compound	Fe-N stretching frequencies (cm ⁻¹)		$\omega_{\text{LS}}/\omega_{\text{HS}}$	Ref
	HS state	LS state		
[Fe(X-bzimpy) ₂](ClO ₄) ₂ (X=H, OH, Cl)	220, 215, 212	436, 436, 436	2.0–2.1	23
[Fe(X-bzimpyH ₋₁) ₂] (X=H, OH, Cl)	229, 217, 213	440, 436, 435	1.9–2.0	24
[Fe(ptz) ₆](BF ₄) ₂	167, 231	261/279, 412	1.6, 1.8	25
[Fe(phen) ₂ (NCS) ₂]	220, 252	368, 376	1.7, 1.5	18
[Fe(phen) ₂ (¹⁵ N ¹³ CS) ₂]	220, 248	368, 374	1.7, 1.5	19
[Fe(phen) ₂ (NCSe) ₂]	218	363	1.7	14
[Fe(bpy) ₂ (NCS) ₂]	235	384	1.6	16
[Fe(HB(pz) ₃) ₂]	223, 258	400, 434	1.8, 1.7	26
[Fe(CH ₃ O-phen) ₃](ClO ₄) ₂ ·H ₂ O	227, 237	341, 352	1.5	27
[Fe(tpa)(NCS) ₂]	241, 242, 284	344, 375, 424	1.5	22
[Fe(pz)(M(CN) ₄) ₂ ·2H ₂ O (M: Ni, Pd, Pt)	231, 223, 226	394, 390, 402	1.7–1.8	11
[Fe(py) ₂ (M(CN) ₄)] (M: Pd, Pt)	217, 221	383, 395	1.8	11

iting force constant values, they found ~ 1.8 as the maximum $\omega_{\text{LS}}/\omega_{\text{HS}}$ frequency ratio in a simple harmonic approach. The data in Table 1 show, somewhat unexpectedly, that the experimental $\omega_{\text{LS}}/\omega_{\text{HS}}$ frequency ratios are often close to this rather crude limit for the Fe-N stretching frequencies of SCO compounds. This apparent concurrence needs further examination. In this respect, the recent progress in normal coordinate and DFT calculations on SCO compounds represents a promising platform for further consideration [21, 22].

2.3

Versatility of Vibrational Spectroscopy

A considerable advantage of IR and Raman spectroscopy is their wide versatility with regard to the type of perturbation that may be used to induce SCO (in addition to change in temperature, variation in pressure, light, magnetic field, etc. can also be easily implemented). Pressure-induced SCO was investigated by Ferraro et al. [28] on several complexes using a diamond anvil cell in conjunction with IR spectroscopy and recently by Molnár et al. using high-pressure Raman spectroscopy [29]. Light-induced excited state spin trapping (LIESST) of [Fe(phen)₂(NCS)₂] and its methyl-substituted analogues has been detected by variable temperature FTIR measurements in which the C-N stretching frequency was probed [30]. The LIESST effect arose in this instance as a result of irradiation with the low power 632.8 nm He-Ne laser used for calibration of the FTIR spectrometer. However, this method uses a limited radiation source and Suemura et al. [31] showed that laser Raman spectroscopy with excitation radiation of various wavelengths and variable power could be used advantageously to study the LIESST effect.

The main advantage (but also the drawback) of this technique is that it uses a unique light source for LIESST excitation and detection of spin states. Raman and IR spectroscopy have also been used to study the structure of the LIESST phase. Recently, Tayagaki et al. [32, 33] reported Raman and IR spectra of the complex $[\text{Fe}(\text{2-pic})_3\text{Cl}_2]\cdot\text{EtOH}$ in the HS, LS, and LIESST phases. Interestingly, their results suggest that the structure of the LIESST phase is different from the thermally induced HS phase in this complex. It is also worth noting that Raman and IR spectroscopy allow investigation of the SCO phenomenon with high spatial [34] and temporal [35] resolution, leading to a better understanding of the microscopic mechanisms.

2.4

Vibrational Properties and Debye Model

Due to the lack of fully assigned vibrational data, the vibrational properties are often discussed on the basis of the Debye model, which assumes a simplified phonon spectrum based on a single parameter, the Debye temperature (Θ_D). Although applicability of the Debye model to transition metal complexes with complicated lattices consisting of different atoms is rather limited, knowledge of Θ_D provides general information on the lattice dynamics of such systems [36]. Values of Θ_D for both the HS and LS phases can be derived from the temperature dependence of the specific heat, or from the measurement of elastic properties. However, Debye temperatures have been generally estimated from the recoilless fraction of temperature-dependent Mössbauer spectra, i.e., from the Lamb-Mössbauer factor (f_{LM}) [37]. Then, in addition to the question of the general applicability of the Debye model, further problems arise due to thickness effects and an increased effective mass of the ^{57}Fe nucleus in covalent complexes. Numerous Mössbauer studies revealed in general approximately a 10% diminution of Θ_D on going from the LS to the HS state [20, 37–40]. The present state of the art in Mössbauer spectroscopy accounts for an "effective" mass, m_{eff} , for the Mössbauer atom, larger than the atomic value, and depending on the strength of the metal-ligand bonds. The actual expression of the Lamb-Mössbauer factor depends on the product $(m_{\text{eff}})^{1/2} \Theta_D$, i.e., it involves both the lattice effect ($\Theta_D^{(\text{LS})} > \Theta_D^{(\text{HS})}$) and the bond strength effect ($m_{\text{eff}}^{(\text{LS})} > m_{\text{eff}}^{(\text{HS})}$). However, the thermal dependence of the isomer shift only depends on m_{eff} and finally enables lattice and bond strength effects to be disentangled. Recent results [41, 42] suggest that the bond strength effect plays the prominent role at the spin-transition temperature. A typical ratio $m_{\text{eff}}^{(\text{LS})}/m_{\text{eff}}^{(\text{HS})} \sim 1.2$ would explain as well the Lamb-Mössbauer factor change usually observed upon SCO.

2.5

Investigation of Lattice Dynamics with Synchrotron Radiation Techniques

Following recent progress in the development of synchrotron radiation sources and techniques, valuable new tools are now available for the investigation of lattice dynamics in spin-crossover solids. For example, nuclear forward scattering (NFS) has been used to determine f_{LM} factors in the SCO compound $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ [22]. The advantage of this method over classical Mössbauer spectroscopy is that the derived f_{LM} factors are more accurate. Nuclear inelastic scattering (NIS) has also been applied to several iron(II) SCO compounds [21, 22, 43, 44]. In comparison with NFS, NIS provides a complete energy spectrum of the absorption probability and allows one to extract the frequencies of those normal modes that involve significant mean-square displacement of the iron center. In other words, a partial vibrational density of states (PVDOS) related to the iron-ligand core of the molecule can be extracted from NIS data. Such PVDOS were extracted for the complexes $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ [21], $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$ [45], and $[\text{Fe}(\text{tptMet})](\text{ClO}_4)_2$ [44]. For the latter complex, the high energy resolution (0.65 meV) enabled detection of individual vibrational modes and observation of a shift of the metal-ligand stretches from 30 meV (HS) to 40 and 46 meV (LS) upon SCO. Compared to IR or Raman spectroscopy which detects only vibrations in the center of the Brillouin zone, NIS has also the advantage of summing over the entire Brillouin zone. Finally, it should be mentioned that f_{LM} factors have also been extracted from temperature dependent EXAFS data for some SCO compounds [46, 47].

3

Role of Vibrations in the SCO Mechanism

3.1

Heat Capacity Measurements and Entropy Data:

A First Assessment of the Role of Vibrations in the Mechanism of SCO

The primary driving force governing the temperature induced SCO phenomenon is the increase in entropy (ΔS) upon LS to HS transition. Since several recent reviews are available on heat capacity measurements and entropy data [48, 49, chapter Sorai], here we recall only that experimental values of ΔS for octahedral iron(II) complexes range from 35 to 80 $\text{JK}^{-1} \text{mol}^{-1}$. On the basis of heat capacity measurements on the complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, Sorai and Seki [50] were the first to stress the role of vibrations as a prominent contributor to the entropy change accompanying SCO. In fact, the experimentally determined total entropy change associated with the spin transition ($\Delta S=48.8 \text{JK}^{-1} \text{mol}^{-1}$) is much larger than the electronic contribu-

tion (ΔS_{el}), the latter amounting to $R\ln(2S+1)=13.4 \text{ JK}^{-1} \text{ mol}^{-1}$ (a bare ~28%). They concluded that the remainder must be attributed to vibrational contributions. Concerning the vibrational modes involved, they proposed that the predominant contribution should arise from the metal-ligand stretching and deformation modes, with minor additional contributions from other intra or intermolecular modes.

3.2

First SCO Models Accounting for the Role of Vibrations

Zimmerman and König [36, 48] proposed the first Ising-like microscopic model [51–53] taking into account vibrations in the description of the SCO phenomenon. They assumed that the free energy of the pure HS and LS phases could be described by the Debye model separately, i.e., each phase is characterized by its Debye temperature ($\Theta_D(\text{LS})$, $\Theta_D(\text{HS})$). They found that the vibrational contribution to the free energy includes two terms: one contributing to the free energy of the HS state, and the other one contributing to the interaction term. This model including vibrations, irrespective of their intra- or intermolecular nature, gave better agreement with experimental observations than a purely electronic model and—more importantly—was able to account for the entropy changes observed upon SCO. Additionally, their model indicated that the phonons must make a certain contribution to the cooperativity (interaction term) in SCO solids. This can be qualitatively understood as follows. Upon LS to HS transition the crystal volume increases. Coupled to the anharmonicity of the oscillator potentials, this volume increase leads to lower oscillator frequencies and, in turn, to higher vibrational entropy. However, the estimation of the magnitude of this effect is extremely difficult and this contribution to the interaction is generally neglected with respect to the usual lattice pressure effect [4].

A more sophisticated model explicitly including vibrations has been developed by Kambara [54]. However, this vibronic model, based on the coupling of the electronic state with both a lattice strain and intramolecular vibrations, has been scarcely used for the interpretation of experimental data, probably due to the extensive calculations required.

Spiering et al. [55] have developed a vibrational extension of the macroscopic thermodynamic model of Slichter and Drickamer [56]. This sophisticated model was used for studying the effect of the lattice expansion on HS-LS crossover.

3.3

Intramolecular Vibrations and the Ising-Like Electro-Vibrational Model [57]

In spite of their limitations, the early models reported above have succeeded in accounting for the predominantly vibrational origin of ΔS , thus giving

new impetus to the idea that characterization of the vibrational properties of the HS and LS isomers should be a central aim. Here, a question immediately arises as to which vibrational modes are primarily involved. In the case of ferrous SCO compounds, the increase in antibonding e_g electrons upon an $LS(t_{2g}^6) \rightarrow HS(t_{2g}^4 e_g^2)$ transition significantly weakens the metal-ligand bonds. Thus, the vibrational modes most affected by the change in spin-state are the metal-ligand stretching and bending frequencies. Unfortunately, spectroscopic data on which to base consideration of the contributions from different vibration modes are rather scarce and incomplete. Moreover, vibrational spectra even from a variety of sources (Raman, IR, neutron or nuclear inelastic scattering) may not necessarily provide the complete vibrational spectrum. For these reasons, theoretical treatments incorporating vibrational effects must inevitably rely on various approximations.

The effect of intramolecular vibrations on the SCO of independent molecules has been studied by Bousseksou et al. [58] within the framework of the two-level Ising-like model [59], involving a set of harmonic oscillators. Each two-level molecule is associated with p harmonic oscillators having two possible frequencies, ω_{LS} and ω_{HS} .

For each oscillator, of frequency ω_i , the vibrational partition function is written:

$$z_i(\omega_i, T) = 1 / [\exp(\hbar\omega_i/kT) - 1] \quad (1)$$

The contribution of oscillator (i) to the total entropy is then derived from the free energy expression ($F_i = -kT \ln z_i$; $S_i = -\partial F_i / \partial T$):

$$S_i(\omega_i, T) = \hbar\omega_i/2T \tanh(\hbar\omega_i/2kT) - k \ln[2 \sinh(\hbar\omega_i/2kT)] \quad (2)$$

The total entropy of the system is calculated by summing up the contributions of the considered vibrational modes. The decrease in frequencies upon $LS \rightarrow HS$ crossover results in an entropy increase, expressed by

$$\Delta S(T) = S_{HS}(T) - S_{LS}(T) \quad (3)$$

The entropy change upon SCO expressed by Eq. (3) is usually referred to the equilibrium temperature. The reason is obvious in the case of a steep transition; in the case of a progressive conversion, ΔS usually depends little on T , except for the case of almost iso-energetic spin-states [58] for which the Vant'Hoff plot departs appreciably from linearity.

It is worth analyzing the role of frequency in Eqs. (3) and (4). Obviously, the contribution to ΔS depends on the frequency change upon SCO. In the low-frequency approximation [58], it is roughly proportional to the *relative* change in frequency upon spin conversion:

$$\Delta S_{LF} = R \ln(g_{HS}/g_{LS}) + pR \ln(\omega_{LS}/\omega_{HS}) \quad (4)$$

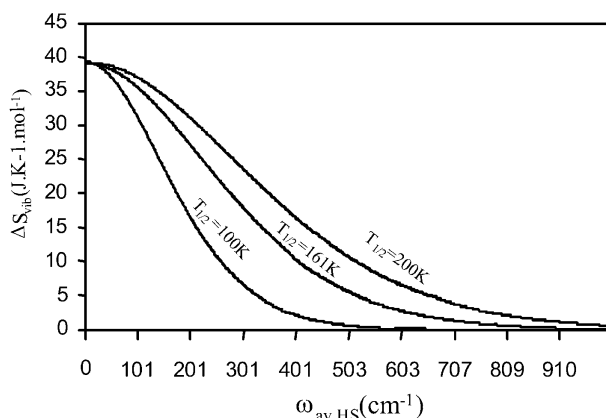


Fig. 3 Vibrational contribution to the entropy change upon LS→HS crossover for different values of the equilibrium temperature ($T_{1/2}$) and with $\omega_{LS}/\omega_{HS}=1.1$

where p is the number of oscillators, g_{LS} , g_{HS} the electronic degeneracy of the corresponding spin state. It is worth mentioning that the latter expression can be interpreted in terms of the ratio of density of states, since the density of states of an harmonic oscillator is merely $1/D\omega$. Thus an ‘effective degeneracy’ of electro-vibrational origin can be associated with each spin-state [58, 60].

The frequency dependence of the contribution of a given mode to the total entropy change, calculated according to Eqs. (2) and (3), is shown in Fig. 3. The higher the frequency, the less the mode contributes to $\Delta S(T)$; in other words, the low frequency approximation (Eq. 4) overestimates the vibrational contributions to the entropy change with respect to the correct expression, Eq. (2).

Also, the electronic degeneracies to be considered are, in general, only the spin degeneracies, with the ratio $(2S+1)_{HS}/(2S+1)_{LS}=5/1$ in the case of iron(II). This corresponds to the frequently encountered situation of an almost complete quenching of the orbital momentum (lifting of the orbital degeneracies by the ligand field).

In most cases, as a first approach, the low frequency ($\hbar\omega \ll k_B T$) approximation (LF) may be used. Then, the problem is reduced to that of a set of two-level molecules with additional degeneracies (i.e., with a larger g_{HS}/g_{LS} degeneracy ratio) compensating for intramolecular vibrations.

In the case of high frequencies ($\hbar\omega \gg k_B T$), the only noticeable effect is a decrease of the energy gap between the LS and HS states, resulting in a decrease of the equilibrium temperature, $T_{1/2}$.

In the general case ($\hbar\omega \approx k_B T$), computations have been performed with the simplifying assumption of an average, 15-fold degenerate, vibrational mode (corresponding to the (3 N-6) metal-ligand vibrational modes in a

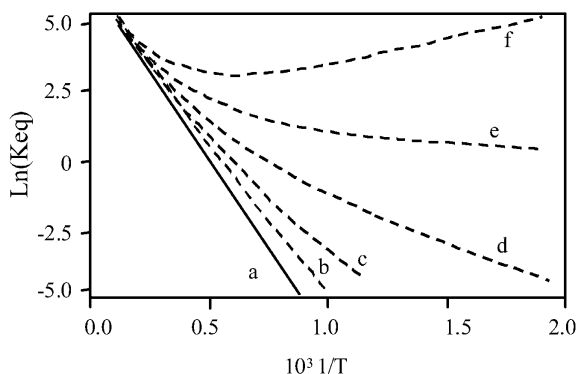


Fig. 4 Thermal variation of the equilibrium constant, computed in the absence of cooperativity with the Ising-like electro-vibrational model with $\hbar\omega=72$ (a), 143 (b), 215 (c), 286 (d), 357 (e), 428 (f) cm^{-1} . The computed values for situations from (a) to (e) are: $T_{1/2}=204.7, 194.3, 174.9, 140.0$ K; $\Delta S(T_{1/2})=63.0, 59.7, 53.1, 40.0$ $\text{J K}^{-1} \text{mol}^{-1}$; $\Delta C_p(T_{1/2})=2.0, 8.1, 18.7, 31.7$ $\text{J K}^{-1} \text{mol}^{-1}$. The *full line* represents the limiting behavior in the low-frequency approximation, computed with $g_{\text{HS}}/g_{\text{LS}}=2189$ [61], leading to $\Delta S(T_{1/2})=\Delta S^\circ=64$ $\text{J K}^{-1} \text{mol}^{-1}$ [58]

regular coordination octahedron). Figure 4 shows the results (thermal variation of the equilibrium constant) obtained with the average frequency ratio $\omega_{\text{LS}}/\omega_{\text{HS}}=1.5$, leading as a first (LF) approximation to $S_{\text{LF}}(T_{1/2})=64$ $\text{J K}^{-1} \text{mol}^{-1}$, in good agreement with literature data. The electronic degeneracy ratio was considered as the spin-only value (see above).

3.4

Mass Effect

H/D or $^{14}\text{N}/^{15}\text{N}$ isotope effects have been studied in the case of a few spin-crossover complexes: $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\cdot\text{Et}$, $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\cdot\text{Met}$ [4, 62] and $[\text{Fe}(5\text{-NO}_2\text{-sal-N}(1,4,7,10))]$ [63]. From magnetic susceptibility and Mössbauer measurements a significant stabilization of the LS state was inferred, i.e., the spin transitions are shifted towards higher temperatures by as much as 15 K. The stabilization of the LS state due to isotope substitution was qualitatively interpreted by considering the mass effect on the zero point electro-vibrational levels. The effective force constants, averaged over the 15 valence vibrations of an octahedral iron atom, larger for the LS than for the HS state, are expected to decrease proportionally upon isotope substitution. Figure 5 shows the variation of the transition temperature as a function of the LS vibrational frequency calculated with the Ising-like electro-vibrational model [58]. It can be seen that an upward shift of $T_{1/2}$ is associated with a proportional lowering of the ω_{LS} and ω_{HS} vibrational frequencies (higher reduced mass: decreased vibrational contribution) [60]. The Ising-like electro-

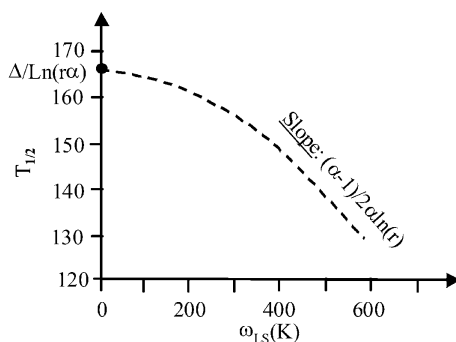


Fig. 5 Thermal variation of the equilibrium temperature $T_{1/2}$ as function of the averaged intra-molecular vibrations of the LS state with the ratio $\alpha = \omega_{LS}/\omega_{HS} = 3$ [60]

vibrational model (in the case of high frequencies) is thus appropriate for consideration of the mass effect. However, as mentioned in [4] and [63] a change in ligand field strength may also result from isotope substitution, especially when hydrogen bonds are involved, possibly yielding an additional contribution to the $T_{1/2}$ shift.

A similar effect has been observed with the two-step SCO compounds $[\text{Fe}^{\text{II}}(\text{bt})(\text{NCX})_2]_2\text{bpym}$ (bt=2,2'-bithiazoline, X=S,Se, bpym=2,2'-bipymiridine) [64] where the increase in the value of $T_{1/2}$ upon substitution of Se for S can be mainly attributed to the decrease in ΔS due to the change in low-frequency intramolecular vibrations (Se/S mass effect). In this case, other factors may contribute, in particular the expected higher ligand field strength of NCSe vs NCS could make a contribution to the higher $T_{1/2}$ value.

3.5

Recent Studies Clarifying the Role of Metal-Ligand Vibrations

The Raman spectra of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ have been analyzed [7] using the assumption of an average frequency representative of the idealized FeN_6 octahedron. An average frequency ratio of 1.32–1.37 was obtained in good agreement with the result (1.5) of recent DFT calculations on the same compound [8, 65]. Using this value, the estimated vibrational contribution from the coordination core was obtained as $20 \text{ JK}^{-1} \text{ mol}^{-1}$. This result supports the proposition of Sorai and Seki [50] that the intramolecular vibrations represent a prominent contribution to the overall entropy change.

The inherent limitations of the average frequency approach have been addressed by summing the entropy terms associated with the distinct vibrational modes of the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [8] and $[\text{Fe}(\text{phen})(\text{H}_2\text{B}(\text{pz})_2)_2]$ [10] complexes. For the latter complex, the entropy change associated with the 15 normal vibrational modes of the FeN_6 pseudo-octahedron has been estimated from the measured spectra as $\Delta S_{\text{vib}} = 36 \text{ JK}^{-1} \text{ mol}^{-1}$, and the total entropy

change is $\Delta S = \Delta S_{\text{vib}} + \Delta S_{\text{el}} = 49 \text{ JK}^{-1} \text{ mol}^{-1}$. In comparison, a value of $49 \pm 3 \text{ JK}^{-1} \text{ mol}^{-1}$ was obtained from calorimetric measurements.

A group of highly-symmetric coordination polymers of formulae $[\text{Fe}(\text{py})_2(\text{M}(\text{CN})_4)]$ and $[\text{Fe}(\text{pz})(\text{M}(\text{CN})_4)] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$), displaying comparatively clear-cut low frequency vibrational spectra, has recently been studied by using a similar approach [11]. Another important feature of these SCO compounds was their high $T_{1/2}$ values: as a consequence, they closely satisfy the high-temperature limit, which enables compensatory weighting, within acceptable error limits, for any undetected modes. The results indicate that alongside a major contribution from the metal-ligand vibrations ($\sim 60\%$) other intra- and intermolecular vibrations can make non-negligible contributions as well ($\sim 40\%$).

3.6

Almost Iso-Energetic LS and HS Levels: SCO Modulated by Molecular Vibrations

SCO systems characterized by a low equilibrium temperature $T_{1/2}$, i.e., a small energy gap, Δ_0 , between the LS and HS states of the isolated two-level molecule, are expected to have energy profiles essentially determined by their vibrational frequencies: this type of situation may lead to a change in nature of the ground state. Molecular vibrations may thus exert a prevailing effect on the SCO of such molecules.

The thermal variation of γ_{HS} has been computed with the Ising-like electro-vibrational model [58] for situations close to the critical Δ_0 value, with use of the complete set of intramolecular vibrations that the authors had estimated for Fig. 2. This situation corresponds to $\Delta_{\text{eff}} = \Delta_{\text{elec}} - \Delta \sim 0$, with $\Delta \sim \hbar(\omega_{\text{LS}} - \omega_{\text{HS}})/2$, i.e., almost iso-energetic LS and HS ground states. This is illustrated by the asterisk-labeled curve ($\Delta \sim 700 \text{ cm}^{-1}$) in Fig. 6 where the

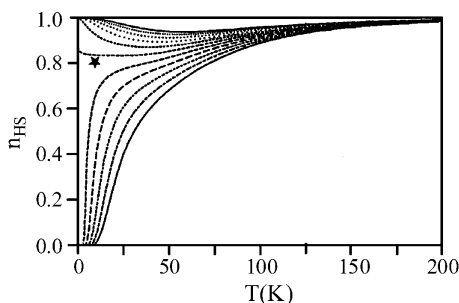


Fig. 6 Thermal variation of the HS fraction, computed close to the critical situation, with the same vibrational data as for Fig. 4: $\omega_{\text{LS}}/\omega_{\text{HS}} = 1.3$, $p = 15$, and Δ ranging from 664 to 736 cm^{-1} . The critical value is ca. 700 cm^{-1} (asterisk-labeled curve) [58]

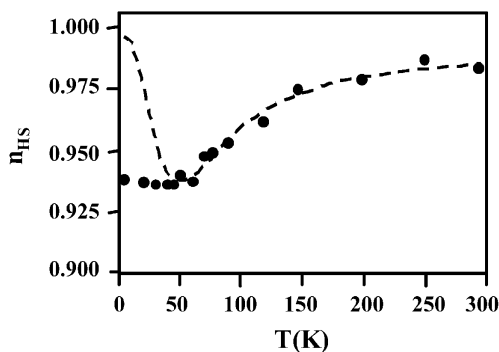


Fig. 7 Least-squares fit of the conversion data for $[\text{Fe}(\text{TRIM})_2]\text{F}_2$ to the Ising-like electro-vibrational model. The fit was performed in the 50–300 K equilibrium domain [66]

thermal variation of γ_{HS} is shown for Δ values ranging from 664 to 736 cm^{-1} .

$[\text{Fe}(\text{TRIM})_2]\text{F}_2$ [66] was the first reported SCO compound for which fitting of the thermal variation of γ_{HS} with the Ising-like electro-vibrational model pointed to nearly iso-energetic LS and HS ground states. The parameter values resulting from the fit (shown in Fig. 7) of the high temperature range ($T > 50$ K) of the experimental $\gamma_{HS}(T)$ data ($\Delta = 254$ cm^{-1} , $\omega_{LS} = 166$ cm^{-1} , $\omega_{LS}/\omega_{HS} = 1.297$) lead to a HS ground state.

An energy level scheme is drawn in Fig. 8, showing that the HS ground state is ~ 43 K (30 cm^{-1}) below the first low-lying LS state. This small energy difference between the HS and LS lowest states is the reason why the SCO is

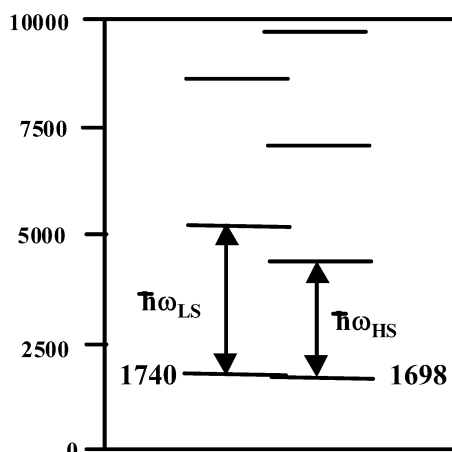


Fig. 8 Lower levels of the electro-vibrational energy scheme obtained with the parameter values resulting from the fit in Fig. 7 [66]

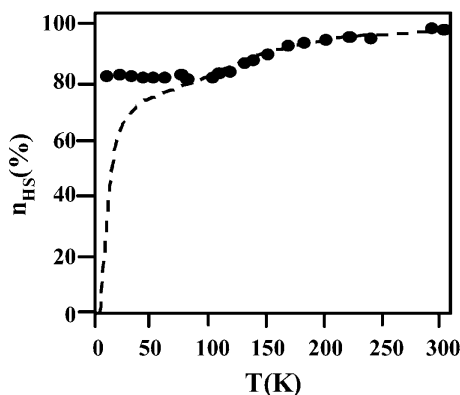


Fig. 9 Least-squares fit of the conversion data for $[\text{Fe}^{\text{II}}(3\text{-MeO},5\text{-NO}_2\text{-sal-N}(1,10)\text{NMe}(4,7))]$ to the Ising-like electro-vibrational model. The fit was performed in the 50–300 K equilibrium domain [67]

no longer controlled by the electronic gap, thus leading to a thermal variation of γ_{HS} controlled by population of the vibrational levels.

Additional examples of compounds where the SCO is controlled by molecular vibrations have recently been reported.

$[\text{Fe}^{\text{II}}(3\text{-MeO},5\text{-NO}_2\text{-sal-N}(1,10)\text{NMe}(4,7))]$ experiences an incomplete (17%) and progressive (70–240 K temperature range) SCO [67]. A theoretical approach based on the Ising-like electro-vibrational model [58] fits the $\gamma_{\text{HS}}(T)$ variation with an energy gap $\Delta=1645\text{ cm}^{-1}$ between the lowest LS and HS states, an average vibration frequency $\omega_{\text{LS}}=518\text{ cm}^{-1}$ and an average $\omega_{\text{LS}}/\omega_{\text{HS}}$ ratio of 1.724 (fit shown in Fig. 9). The above parameter values enabled the authors to compute the energies of the electro-vibrational levels: the ground state is LS, and the first excited level is HS with an energy only $\sim 13\text{ cm}^{-1}$ higher than the LS ground state. With such a small energy difference, the lowest LS and HS states are essentially iso-energetic, and the thermal dependence of the system arises solely through population of vibrational states.

The thermal variation of the HS fraction for the polymeric compounds $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCX})_2]$ ($\text{X}=\text{S}, \text{Se}$) is gradual and incomplete (12% ($\text{X}=\text{S}$), and 20% ($\text{X}=\text{Se}$)) with onset temperatures as low as 60 K [68]. Their $\gamma_{\text{HS}}(T)$ variation has been fitted (Fig. 10) using the Ising-like electro-vibrational model [58]. The parameters resulting from the fit of the experimental SCO data ($\Delta=597\text{ cm}^{-1}$, $\omega_{\text{LS}}=382\text{ cm}^{-1}$ ($\text{X}=\text{S}$) and 365 cm^{-1} ($\text{X}=\text{Se}$), $\omega_{\text{LS}}/\omega_{\text{HS}}=1.22$) lead to a LS ground state. This LS ground state is $\sim 65\text{ cm}^{-1}$ ($\text{X}=\text{S}$), 86 cm^{-1} ($\text{X}=\text{Se}$), below the first low-lying HS state. The ca. $1.05\omega_{\text{LS}}(\text{X}=\text{S})/\omega_{\text{LS}}(\text{X}=\text{Se})$ ratio is close to the ca. $1.04\sqrt{(\text{Se}/\text{S})}$ molar mass ratio, thus illustrating a mass effect in a SCO compound otherwise characterized by the unusual situation of almost iso-energetic HS and LS states.

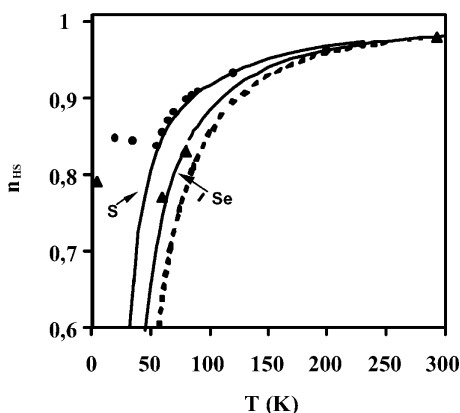


Fig. 10 Thermal variation of the high-spin molar fraction, γ_{HS} , deduced from Mössbauer spectroscopy, circles: $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCS})_2]$; triangles $[\text{Fe}(4,4'\text{-bipy})(\text{bt})(\text{NCSe})_2]$. Solid lines correspond to the fit obtained by using the Ising-like electro-vibrational model. The dashed line is the $\gamma_{\text{HS}}(T)$ curve calculated with the Δ and $\omega_{\text{LS}}/\omega_{\text{HS}}$ parameters obtained for $X=\text{S}$ and a theoretical $\omega_{\text{LS}}(X=\text{Se})$ value such that $\omega_{\text{LS}}(X=\text{S})/\omega_{\text{LS}}(X=\text{Se})$ is in the 1.04 $\sqrt{(\text{Se}/\text{S})}$ molar mass ratio [68]

4

Conclusion and Prospects

The role of molecular vibrations as a primary contributor to the entropy change accompanying SCO, initially suggested by Sorai and Seki from the results of heat capacity measurements [50], has been fully confirmed by all subsequent approaches including vibrational spectroscopy [7–11], SCO models accounting for the role of molecular vibrations [36, 48, 54, 55, 58], and DFT calculations [8, 65]. While most results point to the prominent contribution of metal-ligand vibrations [7–10], some recent data indicate that other intra- and intermolecular (lattice) vibrations can make significant contributions as well [11]. However, their relative contributions are not yet clearly evaluated. This is an important question that needs further investigation, especially in order to clarify the role of long range interactions with respect to cooperativity. Synchrotron-Mössbauer and modern Raman techniques, and multi-temperature crystallographic studies associated with detailed DFT calculations open up promising new prospects in this exciting research area.

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Isokinetic and Iseoquilibrium Relationships in Spin Crossover Systems

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Abstract A thorough statistical mechanical analysis of sources of variations and correlations in ΔE^0 and ΔS^0 of spin crossover equilibrium in the solid state is given. Attention has been brought to possible contributions of vibrations and rotations towards the entropy of reaction. In the ideal approximation, isoequilibrium relationships (IER) can be observed due to variations in the intermediate-frequency vibrational modes (θ_{vib} lying within the experimental range of temperatures). Such IER are characterised by high or infinite T_{iso} . Cases of isoequilibrium temperatures lying within the experimental range or below cannot be explained in the approximation of an ideal crystal. These (and actually all known) types of IER are explained by invoking non-ideality within the models of binary and triple molecular interactions. A stochastic model of chemical kinetics applied to isokinetic relationship (IKR) in spin crossover explains cases of IKR characterised by positive T_{iso} . Negative T_{iso} can arise from concerted variations in parameters separately determining activation energy and entropy. IKR and IER are versatile tools in identifying reactions which follow a common mechanism.

Keywords Spin crossover · Isoequilibrium relationship · Isokinetic relationship

List of Abbreviations and Symbols

α_1, α_2	Dissimilarity coefficients of a spin transition compound
ϵ	Electronic energy per molecule
$\Delta\epsilon$	Difference in electronic energies per molecule
γ_{HS}, γ_{LS}	Fraction of a spin crossover compound being in high spin or low spin state
$\eta_1, \eta_2, \dots, \eta_n$	Parameter which can be varied in a reaction series
$\sigma_l(t)$	Time-dependent density of the reactants within the discrete levels l
ω	Frequency ($\nu 2\pi$) in cm^{-1}
Φ	Balance of free energies in an equilibrium mixture
$\theta = h\nu_{vib}/k_B$	Vibrational frequencies in Kelvin
ν	Vibrational frequencies in Hz
ζ	Mole fraction of spin crossover compound in mixed complex
a_i	Efficiency parameter for chemical reactivity
D_A, D_B	Splitting of the free energy levels of the low spin or high spin complex
ΔE^0	Standard energy of spin crossover
ΔE_∞	Standard energy change of spin crossover compound in a matrix of solvent
ΔE_{solv}	Standard energy change of solvent due to SCO
E_a	Activation energy
E_{el}	Electronic energy per mol
ΔE_{ex}	Excess energy of mixing
ΔE_{inf}	Formal standard energy of spin crossover at infinite dilution ($\Delta E_{inf} = \Delta E_\infty + \Delta E_{solv}$)
$\Delta E^\#$	Activation energy (kinetic data)
F	Helmholtz free energy
ΔF_∞	Standard free energy change of spin crossover compound in a matrix of solvent
ΔF_{ex}	Excess of free energy of mixing
ΔF_{inf}	Formal standard free energy of spin crossover at infinite dilution ($\Delta F_{inf} = \Delta E_\infty + \Delta E_{solv}$)
ΔF_{solv}	Standard free energy change of solvent due to SCO
g	Degeneracy factor
$g(l)$	Source term for particles
h	Planck constant
ΔH^0	Standard enthalpy of spin crossover (of a reaction)
IER	Isoequilibrium relationship
IKR	Isokinetic relationship
k^0	Composition independent part of the reaction rate constant
k	Rate constant
K	Equilibrium constant
k_B	Boltzmann constant
m	Mass
n	Number of molecules
N	Number of atoms in a molecule
N_L	Avogadro number
P_{lm}	Transition probability per collision for the transition from reactant level m to l
Q_v	Vibrational contribution towards equilibrium constant
R	Gas constant

$R(l)$	Continuous probability function describing the probability of transition of molecules between level $l-1$ and l
r	Radius of a molecule
ΔS^0	Standard entropy of spin crossover (reaction)
$\Delta S^\#$	Activation entropy (kinetic data)
ΔS_∞	Standard entropy change of spin crossover compound in a matrix of solvent
T_{iso}	Isoequilibrium or isokinetic temperature
u	Potential hindering molecular or internal rotation ('restraining potential')
u_{ex}	Excess energy of mixing per molecule
U	Potential (lattice) energy
V	Volume
x_A, x_B	Mole fractions of LS (A) and HS (B) species in a reaction mixture
y_A, y_B	Relative efficiencies of the first substitution in the surroundings of LS(A) and HS(B) molecules
z	Partition function
z_{fr}	Partition function of the free rotation
z_r	Rotational partition function
z^{vib}	Vibrational partition function
z_{int}	Partition functions for internal degrees of freedom (of a molecule)
Z	Collision number

1 Introduction

Isokinetic and isoequilibrium relationships (IKR and IER) have been found to be of high applicability to the investigation of similarities and differences in the chemical reactivity within related series of reactions [1]. Theoretical descriptions of these two formally similar phenomena employ completely different approaches: statistical thermodynamics are made use of in the investigation of IERs [2] whereas non-equilibrium thermodynamics are applicable to IKRs [3]. We have therefore separated the present chapter into two parts, one of which is concerned exclusively with the equilibrium phenomenon (IER) and the other with the dynamical one (IKR). Formal conditions for observation of these phenomena are, however, common and are considered here.

Isokinetic and isoequilibrium relationships appear as a distinct intersection of a series of Arrhenius or respective van't Hoff plots at a single point. A linear correlation exists between ΔE^0 and ΔS^0 ($\Delta E^\#$ and $\Delta S^\#$ for kinetic data)¹ in such reaction series. These phenomena are usually observed in sys-

¹ As has been shown [4] for reactions in the condensed state at constant pressures up to 10 bar the Helmholtz free energy can be used as a thermodynamic potential instead of the Gibbs free energy. This provides a convenient way of comparing experimental and theoretical values because the Helmholtz free energy is easily calculated employing statistical mechanical formulae. We are using therefore standard internal energy (ΔE^0) and not standard enthalpy (ΔH^0) of reaction or activation. For the sake of brevity we also call internal energy just energy (hence the standard energy ΔE^0).

tematic studies of *variations of chemical reactivity*. Although a reaction mixture can be modified in a large number of ways, two general types of *systematic study* are quite common, namely those involving modifications of either the reactant or the solvent.

Studies involving modification of reactants may be 'remote' or 'direct' with respect to the reaction centre. In practice, modification is often achieved by the introduction of *substituents* into reactant molecules. From the point of view of statistical thermodynamics chemical reactivity is determined by electronic, vibrational, rotational and translational partition functions. Modifications of reactants should therefore be characterised by the changes in electronic energy and degeneracy (experimentally determined by optical spectroscopy), vibrational frequencies (IR spectroscopy), moments of inertia (IR spectroscopy), molecular mass and volume. All these parameters can also be estimated for model molecular structures employing quantum mechanical calculations. These simulations provide a valuable tool for estimating possible effects in such reaction series.

Spin crossover presents a perhaps unique case of a solid-state equilibrium to which a strict formalism of statistical thermodynamics is fully applicable both in ideal and non-ideal approximations. We shall therefore characterise modifications by parameters relevant to partition functions as listed above.

It is in practice impossible to independently vary a single molecular parameter. For example, by varying a substituent in a reactant we change the molecular mass, electronic energy, number and frequencies of vibrational modes, rotational modes (inertia moments) determining molecular free energy, hence the value of the equilibrium constant in the ideal approximation. The variation of a substituent also changes the molecular radius, electric dipole moment, and electronic polarisability determining the strength of molecular interactions, and hence the non-ideality terms of the law of mass action in non-ideal approximations. In a reaction series we always have a vector of varied parameters $\{\eta_1, \eta_2, \dots, \eta_n\}$. A perfectly designed systematic study must therefore minimise all parametrical sensitivities, $\partial \Delta E^0 / \partial \eta_i$ and $\partial \Delta S^0 / \partial \eta_i$, for all but one varied molecular parameters by a careful choice of the mode of modification. In such cases a simple physical interpretation of the isoequilibrium or isokinetic relationship is possible.

Another approach is to assume that a linear correlation exists between variations of different parameters (η_i, η_k) determining the value of the equilibrium constant in a reaction series:

$$d\eta_i = a_i d\eta_k \quad (1)$$

The coefficient a_i depends on how variations of chemical reactivity are effected (unfortunately this depends on an arbitrary decision of an experimentalist!). The interpretation of an IER and an IKR therefore becomes dif-

ficult. However, by applying a well-founded formalism of statistical thermodynamics one can analyse any given case of IER (IKR) in spin crossover.

An intersection of several van't Hoff plots means that the equilibrium constant at a certain temperature is independent of the parameters (η_i), the variation of which brings about the observed changes in ΔE^0 and ΔS^0 . Mathematically this can be written as

$$d(R \ln K) = \sum_i \left(\frac{\partial \Delta S^0}{\partial \eta_i} - \frac{1}{T_{iso}} \frac{\partial \Delta E^0}{\partial \eta_i} \right) d\eta_i = 0 \quad (2)$$

in which T_{iso} is the isoequilibrium temperature. It is highly improbable that a random variation of several independent parameters η_i in a reaction series results in the same T_{iso} .

One possibility for the observation of an IER (IKR) is that only one parameter (η_k) is varied in a reaction series, i.e. all parametrical sensitivities but one are minimised. The condition at Eq. (2) is then transformed into

$$\frac{\partial \Delta S^0}{\partial \eta_k} d\eta_k - \frac{1}{T_{iso}} \frac{\partial \Delta E^0}{\partial \eta_k} d\eta_k = 0 \quad (3)$$

$$d\Delta S^0 - \frac{1}{T_{iso}} d\Delta E^0 = 0 \quad (4)$$

which leads to a linear relationship between ΔS^0 and ΔE^0 , *provided that none of the partial derivatives in Eq. (3) is zero*. This means that the varying parameter must contribute towards both the standard energy and the standard entropy of reaction. The isoequilibrium (isokinetic) temperature is then the ratio of the parametric sensitivities of ΔE^0 and ΔS^0 :

$$T_{iso} = \frac{\partial \Delta E^0}{\partial \eta_k} \bigg/ \frac{\partial \Delta S^0}{\partial \eta_k} \quad (5)$$

The isoequilibrium temperature is thus informative with respect to the relationships controlling ΔS^0 and ΔE^0 .

Another possibility for an isoequilibrium (isokinetic) relationship is that several parameters in a reaction series vary in a concerted manner, according to Eq. (1). Such a possibility must be very common, at least when parameters are varied over a narrow range. In such a case Eq. (2) is transformed into

$$\sum a_i \frac{\partial \Delta S^0}{\partial \eta_i} - \frac{1}{T_{iso}} \sum a_i \frac{\partial \Delta E^0}{\partial \eta_i} = 0 \quad (6)$$

This condition can be fulfilled provided *none of the sums* is zero. An intersection of van't Hoff plots may then be observed but *the isoequilibrium temperature does not reflect exclusively the parameters of a reaction mixture*.

It includes also the coefficients a_i which are *strongly dependent on the mode of collecting experimental data*²:

$$T_{iso} = \sum a_i \frac{\partial \Delta E^0}{\partial \eta_i} \bigg/ \sum a_i \frac{\partial \Delta S^0}{\partial \eta_i} \quad (7)$$

The relationship between ΔS^0 and ΔE^0 in this case is also linear: by multiplying Eq. (6) by $d\eta_k$, we transform sums into complete differentials of ΔS^0 and ΔE^0 , thus obtaining Eq. (3), which yields upon integration a linear relationship

$$\Delta S^0 = \frac{1}{T_{iso}} \Delta E^0 + Const \quad (8)$$

This shows that the experimental set-up plays an important role in studies of IERs and IKRs. There is in addition the problem of the statistical reliability of either the linearity of Eq. (8) or the intersection point.

Earlier theories of IKR/IER concentrated mostly on the interpretation of kinetic data assuming that an IER is a direct consequence of an IKR in direct and reverse reactions. However, it is difficult to highlight parameters in kinetic equations that are to cancel out in order to achieve the required independence of the equilibria involved in the reaction mechanism. It is more relevant to derive directly the description of the IER from the laws of chemical equilibria. This will be done in the first part of the present paper using the formalism of statistical thermodynamics.

2 The IER in Spin Crossover

According to the above an IER can be observed in a reaction series with concerted variations of ΔE^0 and ΔS^0 . The question arises then, what kind of concerted changes in ΔE^0 and ΔS^0 *may be expected* when molecules participating in a spin equilibrium are modified?

A spin equilibrium can be studied over a wide range of temperatures in the crystalline state without the solid undergoing crystallographic phase transitions. Spin crossover is often observed at low temperatures making the assumption of an ideal crystal to be at least approximately correct. The experimental observation of the intersection of transition curves at a single point (to be considered below) is highly significant and suggestive of IER with an isoequilibrium temperature in the experimental range.

² It is even possible that for each parameter either $\partial \Delta S^0 / \partial \eta_i$ or $\partial \Delta E^0 / \partial \eta_i$ is zero but the sums in Eqs. (6) and (7) will be non-zero. This case corresponds to a *pseudo-correlation* arising from the multidimensionality of variables.

In the following we first analyse theoretical possibilities of IER in spin crossover arising from (i) variations of parameters of an isolated molecule (ideal approximation) and (ii) variations of parameters of molecular interactions.

2.1

Statistical-Mechanical Model of IER in Spin Crossover

Spin crossover is commonly represented as a chemical equilibrium between LS (A) and HS (B) isomers:



Neglecting the effects of molecular interactions (the approximation of an ideal crystal) the free energy of the reaction mixture (Eq. 9) can be written as

$$F = n_A F_A + n_B F_B + k_B T (n_A \ln n_A + n_B \ln n_B) \quad (10)$$

in which the last term represents the mixing entropy. The composition of the reaction mixture can be found from the condition of chemical equilibrium, namely $dF/dn_A=0$, or $dF/dn_B=0$. Free energies of molecules of one kind, (A) can be written as

$$F_A = -k_B T \ln z_A = -k_B T \ln \left[\left(\frac{2\pi m_A k_B T}{h^2} \right)^{\frac{3}{2}} \times V \times g_A e^{-\frac{\epsilon_A}{k_B T}} \times \prod_i^{m_{int}} z_{Aint} \right] \quad (11)$$

in which n_A is the number of molecules A, z_A is the partition function, m_A is the mass, g_A is the degeneracy factor, ϵ_A is the electronic energy³ and z_{Aint} are partition functions for internal degrees of freedom of the molecule of the type A.

The *electronic partition function* $g_{A(B)} \exp(-\epsilon_{A(B)}/k_B T)$ undergoes a change corresponding to $g_B=5$ (or 15 if involving orbital degeneracy in a perfect octahedron) $g_A=1$ and $\Delta\epsilon=0-40$ kJ/mol, i.e., $0-3000$ cm⁻¹ according to experimental data.

The change in *translational degrees of freedom* during a spin transition only includes an increase in volume (masses of molecules are not changed). This increase can be quite large (up to 5%) due to longer bond distances in HS spin complexes [5] originating, e.g., in Fe(II), from the presence of two electrons in e_g antibonding orbitals.

For a molecule composed of N atoms there are $m_{int}=3N-6$ *internal degrees of freedom*. In the solid state they are usually reduced to *hindered rotational oscillations* (rocking, wagging or twisting vibrations). The partition

³ Electronic energy contains also a contribution from mean molecular field considered as static in the approximation of ideal crystal.

function for a hindered rotational oscillation in the potential field u (*re-restraining potential*) can be written as [6]

$$z_{rhind} = \left(\frac{2\pi I k_B T}{h^2} \right)^{1/2} \left(\frac{2\pi k_B T}{u} \right)^{1/2} e^{\frac{u}{k_B T}} = z_{fr} \left(\frac{2\pi k_B T}{u} \right)^{1/2} e^{\frac{u}{k_B T}} \quad (12)$$

in which I is the moment of inertia of the rotating unit and z_{fr} is the partition function for free rotation. Note that in this respect variation of restraining potential *via* the expansion of a HS molecule causes a considerable change in the partition function for hindered rotation. The critical field corresponding to a transfer from rotation to oscillations is [6] $u_{crit} = k_B T/4$. Simple calculations show that rotations of polar groups are converted into rotational oscillations below 200 K.

Spin transition also affects considerably the frequencies of vibrations in spin crossover compounds. The *vibrational partition function* can be written as

$$z_i^{vib} = \left[2 \sinh \frac{\theta_i}{2T} \right]^{-1} \quad (13)$$

Metal-donor atom stretching vibrations change their frequencies from ca. 200 cm^{-1} in the HS state to ca. 400 cm^{-1} in the LS state. Internal vibrations of ligands in the range of 1000–2000 cm^{-1} change their frequencies by ca. 20 cm^{-1} [7].

Taking into account the properties of partition functions explained above, the free energy of a LS molecule in the state of an ideal crystal can be written as

$$F_A = -k_B T \ln \left[z_{Atr} V_A \times g_A \exp \left(-\frac{\epsilon_A}{k_B T} \right) \times \prod_{i=1}^l \left(2 \sinh \frac{\theta_i^{Avib}}{2T} \right)^{-1} \times \prod_{i=1}^m z_{Ari} \left(\frac{2\pi k_B T}{u_{Ai}} \right)^{1/2} \exp \left(\frac{u_{Ai}}{k_B T} \right) \right] \quad (14)$$

in which ϵ is the electronic energy, l and m are numbers of vibrational and rotational degrees of freedom affected by spin crossover, u_i is the re-restraining potential acting on the i -th rotational degree of freedom. The law of mass action for Eq. (9) can then be obtained from the condition $dF/dn_B = 0$ as

$$\ln K = -\frac{\epsilon_B - \epsilon_A}{k_B T} + \sum_{i=1}^m \left(\frac{u_{Bi} - u_{Ai}}{k_B T} \right) + \sum_{i=1}^l \ln \frac{\sinh \frac{\theta_i^A}{2T}}{\sinh \frac{\theta_i^B}{2T}} + \ln \frac{V_B g_B}{V_A g_A} + \frac{1}{2} \sum_{i=1}^m \ln \frac{u_{Ai}}{u_{Bi}} \quad (15)$$

Terms linearly dependent on T^{-1} yield standard energy, whereas terms independent of T yield standard entropy. The vibrational term in Eq. (15) generally contributes towards both ΔE^0 and ΔS^0 . However, when vibrational frequencies are low ($\theta/T \ll 1$) $\sinh x$ approaches its argument and Eq. (15) is reduced to

$$\ln K_{low} = -\frac{\varepsilon_B - \varepsilon_A}{k_B T} + \sum_{i=1}^m \left(\frac{u_{Bi} - u_{Ai}}{k_B T} \right) + \sum_{i=1}^l \ln \frac{\theta_i^A}{\theta_i^B} + \ln \frac{V_B g_B}{V_A g_A} + \frac{1}{2} \sum_{i=1}^m \ln \frac{u_{Ai}}{u_{Bi}} \quad (16)$$

yielding a linear van't Hoff plot. These conditions are fulfilled for lattice vibrations having frequencies in the range $\theta=30$ – 100 K ($\theta_A/\theta_B=1.1$) as well as for rotational oscillations at moderately low temperatures. *Low-frequency vibrations* (including rotational oscillations) contribute ca. $lR \ln(\theta_A/\theta_B)$, towards the standard entropy. The average change in frequency may be ca. 10%; the number of such degrees of freedom can be ca. 10–20. The contribution of low frequency vibrations (rotational oscillations) may thus reach $20R \ln 1.1 \cong 1.9 R$ which is virtually the same as the volume/degeneracy term of $R \ln(1.3 \times 5)$ namely $1.9 R$.

Low-frequency vibrations do not contribute directly towards the standard energy of spin crossover which is controlled by the difference in electronic energies of HS and LS molecules plus some contribution from *restraining potentials*. In the approximation of electrostatic interactions restraining potentials are inverse functions of the square of ion-dipole distances. Assuming these distances to be changed during spin crossover by ca. 10–20% the term $u_{HS} - u_{LS}$ can be estimated as ca. $0.3 |u|$ ($|u|$ being of the order of magnitude of 8–40 kJ/mol) per hindered rotation. In a similar manner restraining potentials contribute approximately (0.1–0.2) mR towards standard entropy.

For *high vibrational frequencies* affected by spin crossover ($\theta/T \gg 1$, $z_v \approx \exp(-\theta/2T)$) Eq. (15) also yields a linear van't Hoff plot:

$$\ln K_{high} = -\frac{\varepsilon_B - \varepsilon_A}{k_B T} + \sum_{i=1}^m \left(\frac{u_{Bi} - u_{Ai}}{k_B T} \right) + \sum_{i=1}^l \frac{\theta_i^A - \theta_i^B}{2T} + \ln \frac{V_B g_B}{V_A g_A} + \frac{1}{2} \sum_{i=1}^m \ln \frac{u_{Ai}}{u_{Bi}} \quad (17)$$

Equation (17) shows that high-frequency vibrations (internal vibrations in ligand molecules, $\theta > 1000 \text{ cm}^{-1}$; $\theta_A - \theta_B \cong 10$ – 30 K) contribute towards the standard energy alone. This contribution depends on the extent to which vibrations are affected by spin crossover. The highest change is apparently 300 K, i.e. ca. 2.4 kJ/mol per oscillator. The number of such oscillators being ca. 10 this contribution is comparable with the difference in electronic energies. The contribution from restraining potentials can also be significant:

$\Delta u = mRT(1 - (r_{HS}/r_{LS})^2)$. Standard entropy in such cases is determined by the volume/degeneracy term with possible contributions from restraining potentials.

Spin crossover is often studied in the range of temperatures where some of the most affected vibrational frequencies (metal-ligand stretching vibrations about 200 cm^{-1}) are partially excited. Under these conditions van't Hoff plots might be non-linear. Indeed non-linear Van't Hoff plots corresponding to Eq. (15) are observed for metal-diluted systems such as $[\text{Fe}_x\text{Zn}_{1-x}(2\text{-pic})_3]\text{Cl}_2\cdot\text{ethanol}$ [8].

2.2

IER in Spin Crossover Arising from Intra-Molecular Correlations

Two types of IER can be distinguished, viz.:

- Those arising from variation of a single parameter contributing towards both ΔE and ΔS (e.g. variations of FIR, MIR vibrations *or* the number of such modes (l))
- Those originating from concerted variations of parameters separately determining ΔE^0 and ΔS^0 (e.g. variations of electronic energy *and* low-frequency vibrations).

Modifications of a ligand in a spin crossover compound may *change the number of oscillators* affected by spin crossover. If it is assumed that these oscillators have identical frequencies, one obtains a series of van't Hoff plots shown in Fig. 1A simulated according to Eq. (15). When investigated over a limited range around some temperature they appear as a set of straight lines intersecting at one point in the region of negative temperatures (Fig. 1B).

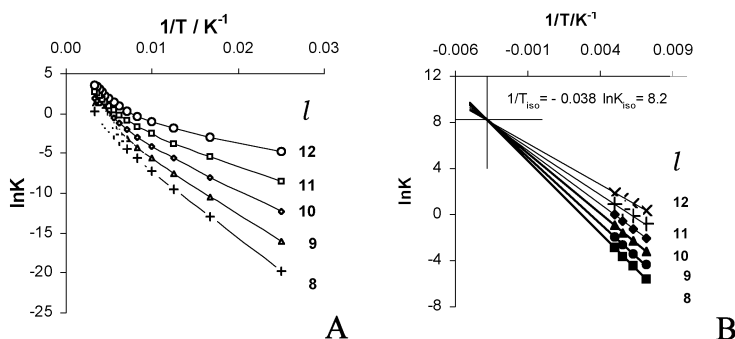


Fig. 1A,B Van't Hoff plots of a model system ($E_{HS}-E_{LS}=17.47\text{ kJ/mol}$, $\theta_B=300\text{ K}$, $\theta_A=600\text{ K}$, $V_{HS}/V_{LS}=1.1$, $g_{HS}/g_{LS}=5$, $u_{HS}=104.5\text{ kJ/mol}$, $u_{LS}=73\text{ kJ/mol}$, $m=6$): **A** with varying number (l) of vibrational degrees of freedom affected by spin crossover; **B** approximations of these data in a limited range around a constant temperature

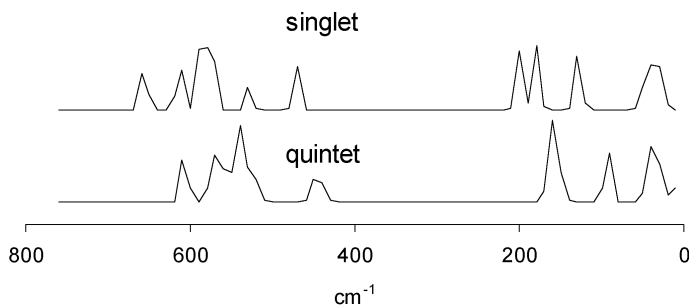


Fig. 2 Spectra of vibrations computed from the data on the normal mode analysis of the model ion $[\text{Fe}(\text{NH}_3)_6]^{2+}$ in singlet and quintet states (Hyperchem5) assuming each normal mode to be a Gaussian function with $\sigma=5 \text{ cm}^{-1}$

More realistic models must take into account parallel variations of electronic energy and vibrational frequencies.

One can calculate the vibrational contributions from a *complete set* of θ as

$$\ln Q_v = \sum_{i=1}^l \ln \sinh \frac{\theta_i^A}{2T} - \sum_{i=1}^l \ln \sinh \frac{\theta_i^B}{2T} \quad (18)$$

in which l is the total number of internal degrees of freedom $l=m_{\text{int}}$. Such sets of frequencies can be obtained for simple model structures using quantum mechanical calculations.

Figure 2 shows the ‘spectra of vibrations’ of $[\text{Fe}(\text{NH}_3)_6]^{2+}$ in HS and LS states obtained using the program Hyperchem5. The amplitudes in these spectra reflect the number of vibrations in a given frequency range. All frequencies were non-imaginary, i.e. all internal rotations were converted into rotational oscillations by interactions with the field of the central ion. Both low- (FIR) and intermediate- (MIR) frequency vibrations are affected by spin transition.

The *vibrational contributions* to the equilibrium constant ($\ln Q_v$) increase approximately linearly with T^{-1} equivalent to a negative standard energy of reaction of -5.016 kJ/mol . Variation of the $E_{\text{HS}}-E_{\text{LS}}$ in a model complex possessing such a set of vibrations yields a series of non-linear van’t Hoff plots that can be approximated by straight lines intersecting at infinite isoequilibrium temperature. Such behaviour is usually called ‘isoentropic’ [1].

Modification may consist in substituting one of the hydrogens in NH_3 by a methyl group. Such a modification introduces new vibrational/rotational modes and must therefore change both the standard energy and the standard entropy of reaction. Within the methyl group hydrogens can be substituted by halogens without introducing new vibrational modes but only changing electronic energies and vibrational (rotational) frequencies.

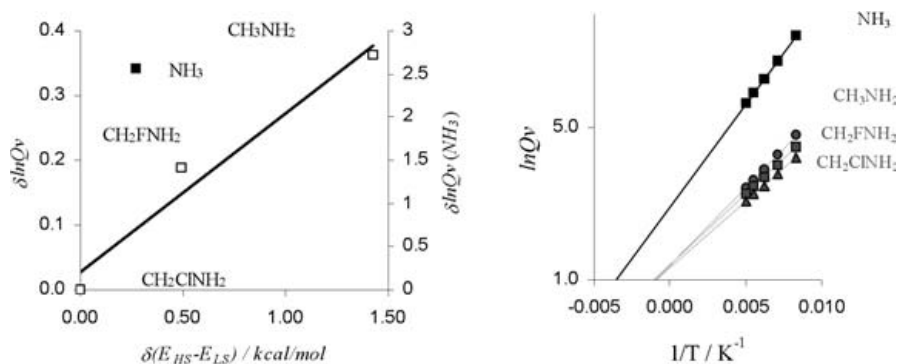


Fig. 3 Correlation between variations of electronic energy in the series $[\text{Fe}(\text{XCH}_2\text{NH}_2)_6]^{2+}$, $\text{X}=\text{H}, \text{F}, \text{Cl}$ and corresponding variations of the vibrational contributions ($\ln Q_v$) at $T=200 \text{ K}$. The *right-hand graph* shows an isoequilibrium relationship arising from this correlation

The temperature dependence of the vibrational contribution to the equilibrium constant obtained from the quantum mechanical normal mode analysis of $[\text{Fe}(\text{NH}_3)_6]^{2+}$ and $[\text{Fe}(\text{NH}_2\text{CH}_2\text{X})_6]^{2+}$ ($\text{X}=\text{H}, \text{F}, \text{Cl}$) yield (contrary to what might be expected) a smaller vibrational contribution in $[\text{Fe}(\text{NH}_2\text{CH}_2\text{X})_6]^{2+}$ than in $[\text{Fe}(\text{NH}_3)_6]^{2+}$. This means that frequencies of some of new vibrational/rotational modes decrease with the HS $\rightarrow$ LS transition in contrast to those of the most affected metal-ligand vibrations. Although the change (upon a transition) of these new frequencies is small their large number causes the observed negative effect. Therefore, the larger the numbers of internal degrees of freedom in ligands, the less predictable are the spin crossover parameters (see below). The substitution in the methyl group by halogens does not change the number of vibrational modes but brings about correlated changes of electronic energy and vibrational frequencies. It yields isoequilibrium relationships (Fig. 3) with $T_{iso}=10540 \text{ K}$ (calculated from the slope of ΔS^0 vs ΔE^0 dependence). These results show that isoequilibrium relationships in spin crossover can be observed in reaction series with a constant number of vibrational modes.

Modification of intra-molecular parameters thus brings about correlated changes of ΔE^0 and ΔS^0 characterised by very high (or negative) isoequilibrium temperatures. Cases of isoequilibrium temperatures lying within or below the experimental range cannot be explained by variations of intra-molecular parameters (i.e. in the approximation of an ideal crystal).

2.3

IER in Spin Crossover Originating from Intermolecular Interactions

For reactions in the condensed state one has to take into account interaction between molecules of reactants and products as well as interactions with molecules in the direct molecular surrounding. Among the various approximations of spin crossover in non-ideal systems such as the model of elastic interactions [5] or the quantum mechanical model employing Ising-like Hamiltonians [9], the model of classical correlations [10] is best adapted to the description of isoequilibrium relationships in spin crossover.

This model is based on the assumption that a spin transition perturbs the state of molecules in the nearest neighbourhood of the transformed one. The expanding HS molecule increases the potential energy of neighbouring molecules via repulsive interactions of closed electron shells of ligands. Also, the energy of electrostatic interactions between polar parts of such molecules is changed as well as the energy of interactions with counter-ions.

Taking into account just two nearest neighbours along a coordinate a given molecule, let us say A, may then have three different values of free energy (partition function) depending on the nature of its neighbours (AAA, AAB and BAB); see Fig. 4. Assuming the crystal to be isotropic and coordinates to be independent allows one to sum the free energy over three coordinates. The free energy of an equilibrium mixture of HS and LS molecules is calculated as quasi-additive with molecular free energies (F_A , F_B) dependent on composition:

$$F_A = x_A^2 F_{AAA} + 2x_A x_B F_{AAB} + x_B^2 F_{BAB} \quad (19)$$

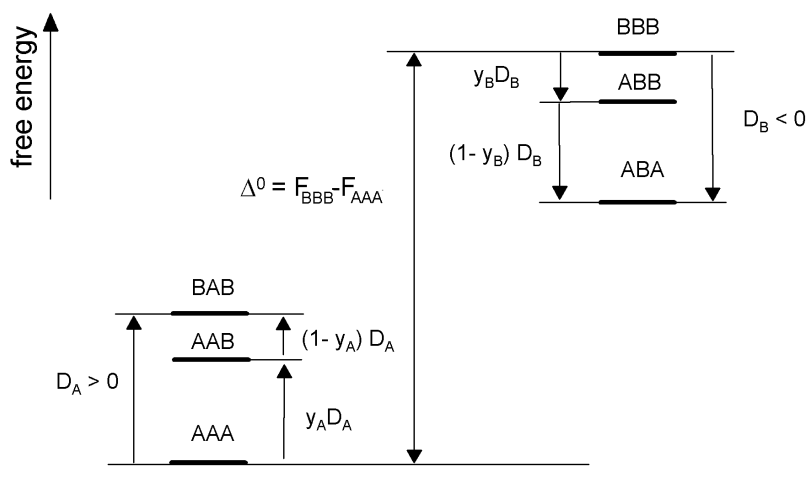


Fig. 4 Free energy level diagram taking into account interactions with two nearest neighbours

$$F_B = x_A^2 F_{ABA} + 2x_A x_B F_{ABB} + x_B^2 F_{BBB} \quad (20)$$

Free energies of molecules in given surroundings F_{x_Ay} , F_{x_By} can be written via partition functions similarly to molecular free energies in the ideal approximation (Eq. 14) as

$$F_{x_Ay} = -k_B T \ln \left[z_{Atr} V_A g_A \exp \left(-\frac{\epsilon_{x_Ay}}{k_B T} \right) \prod_{i=1}^l \left(2 \sinh \frac{\theta_i^{x_Ay vib}}{2T} \right)^{-1} \cdot \prod_{i=1}^m z_{Ari} \left(\frac{2\pi k_B T}{u_i^{x_Ay}} \right)^{1/2} \exp \left(\frac{u_i^{x_Ay}}{k_B T} \right) \right] \quad (21)$$

Translational and rotational (free rotation) partition functions, z_{tr} , z_r can be considered as independent of the nature of surroundings. The electronic energies ϵ , vibrational frequencies θ and restraining potentials u are dependent on the nature of nearest neighbours. Orbital degeneracy might probably be changed by distortions of the crystal field caused by a spin crossover in the nearest neighbourhood.

It has been shown [10] that the free energy of a binary equilibrium mixture under the conditions specified above can be expressed via the splittings of the free energy levels of low-spin and high-spin complexes (D_A , D_B) and relative efficiencies of the first substitution in the coordination sphere (y_A , y_B ; see Fig. 4) as

$$F = x_A^3 [(1 - 2y_A)D_A - (1 - 2y_B)D_B] + x_A^2 [(1 - 4y_B)D_B - 2(1 - y_A)D_A] + x_A (D_A + 2y_B D_B - \Delta^0) + F_{BBB} + Nk_B T [x_A \ln x_A + (1 - x_A) \ln (1 - x_A)] \quad (22)$$

In this,

$$D_A = F_{BAB} - F_{AAA}; \quad D_B = F_{ABA} - F_{BBB}; \quad \Delta^0 = F_{BBB} - F_{AAA} \quad (23)$$

$$y_A = \frac{F_{AAB} - F_{AAA}}{D_A}; \quad y_B = \frac{F_{ABB} - F_{BBB}}{D_B} \quad (23a)$$

Parameters D_A , D_B consist of two parts: the energy term $D_{AE} = E_{BAB} - E_{AAA}$ and entropic term $D_{AS} = T(S_{BAB} - S_{AAA})$. The law of mass action is then obtained from the condition $dF/dn_A = 0$ as

$$3x_A^2 [(1 - 2y_A)D_A - (1 - 2y_B)D_B] + 2x_A [(1 - 4y_B)D_B - 2(1 - y_A)D_A] + D_A + 2y_B D_B - \Delta F + Nk_B T \ln \frac{x_A}{1 - x_A} = 0 \quad (24)$$

in which $\Delta F = F_{BBB} - F_{AAA}$. The last line in Eq. (24) represents a quasi-ideal law of mass action in which molecular interactions contribute towards standard energy and standard entropy. The upper line shows the composition-

dependent non-ideality terms originating from triple and binary interactions.

When the effects of the surroundings are additive: $y_A=y_B=1/2$ the first non-ideality term is zero and Eq. (24) is reduced to

$$(1 - 2x_A)(D_B + D_A) - \Delta F + Nk_B T \ln \frac{x_A}{1 - x_A} = 0 \quad (25)$$

This equation is an analogue of that arising from the model of binary interactions (see, e.g. [6]) and used by Slichter and Drickamer [11] to explain the phenomenon of the abrupt crossover:

$$(1 - 2x_B) \Gamma + \Delta G^0 = k_B T N \ln \frac{1 - x_B}{x_B} \quad (26)$$

in which Γ is the so-called *interaction parameter*, a *measure of the cooperativity*, a non-ideality parameter also called *interchange energy* and *excess energy of mixing*. The complete identity of Eqs. (25) and (26) is achieved when the entropic part of the *excess free energy of mixing* ΔF_{ex}

$$\Delta F_{ex} = D_A + D_B = F_{BAB} - F_{AAA} + F_{ABA} - F_{BBB} \quad (27)$$

is assumed to be zero. The excess free energy of mixing in the developed formalism thus reflects an algebraic sum of the effects of surroundings on the partition function of HS and LS molecules. The excess entropy of mixing reflects the effects of spin crossover in the nearest surroundings of a given molecule on its electronic degeneracy, volume and low-frequency vibrations.

This formalism predicts various kinds of isoequilibrium behaviour due to variations in the excess (non-ideality) parameters (e.g., achieved by modifi-

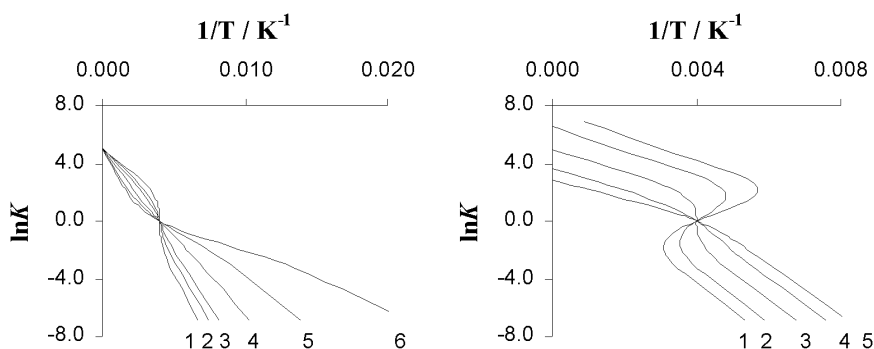


Fig. 5 Van't Hoff plots simulated for a model system ($\Delta E=10.55$ kJ/mol, $\Delta S=41.8$ J/mol/ $^{\circ}\text{K}$) with variable excess parameters. *Left hand graph* corresponds to $\Delta S_{ex}=0$ and variable $\Delta E_{ex}=4.18$ (1), 2.6125 (2), 1.672 (3), -0.836 (4), -3.344 (5) and -5.852 (6) kJ/mol. *Right hand graph* corresponds to $\Delta E_{ex}=4.18$ kJ/mol and variable $\Delta S_{ex}=20.9$ (1), 12.54 (2), 0 (3), -12.54 (4), -20.9 (5) J/mol/ $^{\circ}\text{K}$

cation of molecular periphery). Simulation of transition curves with constant ΔF and variable non-ideality parameters, ΔE_{ex} and ΔS_{ex} , yields a series of van't Hoff plots intersecting at the *spin transition temperature* (Fig. 5). When studied over a limited range of temperatures or values of $\ln K$, spin crossover yields van't Hoff plots that can be approximated by straight lines which, when extrapolated, intersect at one point. The isoequilibrium temperature in such a case is strongly dependent on the mode of distributing experimental points along T^{-1} scale. Expressions for isoequilibrium temperature in such cases can be found in [2].

2.4

Comparison with Experimental Data

The most striking instance of the intersection of transition curves at one point (Fig. 6) has been observed in a compound 'modified' by different modes of preparation, dilution by a non-crossover analogue and physical processing [12]. This shows the sensitivity of spin crossover towards molecular interactions and long-range order.

Among other methods of modification, dilution is the most easily controlled and quantified. The dilution effectively 'shields' species in equilibrium from each other whereas on the other hand it introduces solute-solvent interactions. According to the model described in the previous section the law of mass action for diluted systems can be written as [2]

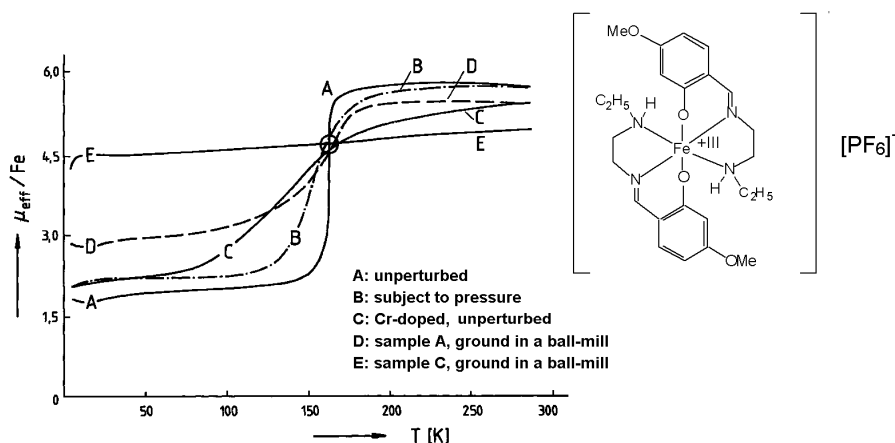


Fig. 6 Spin crossover curves for $[\text{Fe}(\text{3-OCH}_3\text{-SalEen})_2]\text{PF}_6$ subjected to processes changing the number of defects: A: unperturbed; B: subject to pressure; C: Cr-doped, unperturbed; D: sample A ground in a ball-mill; E: sample C, ground in a ball-mill (adapted from [12])

$$\zeta(1 - 2\gamma_{LS})\Delta F_{ex} - \zeta\Delta F - (1 - \zeta)(\Delta F_{\infty} + \Delta F_{solv}) + RT\ln\left(\frac{\gamma_{LS}}{1 - \gamma_{LS}}\right) = 0 \quad (28)$$

in which $\zeta = x_A + x_B$ is the mole fraction of the spin crossover compound in solution and $\gamma_{LS} = x_A/\zeta$ is the degree of conversion of HS species into LS species. Among the parameters entering this law of mass action the free energies ΔF_{ex} and ΔF characterise binary equilibrium in the undiluted spin crossover solid. The free energy change for the spin crossover compound in the matrix of solvent S is denoted as

$$\Delta F_{\infty} = F_{SBS} - F_{SAS} \quad (29)$$

The formal standard free energy at infinite dilution also contains a contribution from solvent molecules:

$$\Delta F_{solv} = F_{BSB} - F_{ASA} \quad (30)$$

i.e. the free energy change of a solvent molecule due to the spin crossover in its neighbourhood. This parameter is thus an analogue of the excess free energy.

It is impossible to estimate ΔF_{∞} and ΔF_{solv} separately from experimental data by a fitting procedure. One can, however, make a reliable guess concerning their relationship to ΔF and ΔF_{ex} . For example, when the solvent molecules are similar to those of the spin crossover compound (as it is in cases of dilution by diamagnetic analogues), $|\Delta F_{solv}| \cong \Delta F_{ex}$, whereas ΔF_{∞} must be close to ΔF . The law of mass action then becomes

$$\Phi = \zeta(1 - 2\gamma_{LS})\Delta F_{ex} - \zeta\Delta F - (1 - \zeta)(\alpha_1\Delta F + \alpha_2\Delta F_{ex}) + RT\ln\left(\frac{\gamma_{LS}}{1 - \gamma_{LS}}\right) = 0 \quad (31)$$

in which α_1 and α_2 are coefficients accounting for the dissimilarity of the spin crossover compound and its diamagnetic analogue. According to the model of repulsive interactions (leading to the diagram of free energy levels in Fig. 4), $\alpha_2 \cong 1$ if the solvent molecule resembles the LS isomer and $\alpha_2 \cong -1$ if it is similar to the HS isomer [2]. The coefficient α_1 approximately equals 1 in both cases. Equation (31) predicts the intersection of transition curves corresponding to different grades of dilution when $\partial\Phi/\partial\zeta = 0$. (Coordinates of the isoequilibrium point can be obtained by graphical or numerical solution of two equations arising from this condition).

For solid solutions of spin crossover compounds in their analogues ($\alpha_1 \cong 1$) the degree of conversion over which isoequilibrium conditions prevail is either very small ($\alpha_2 = 1$, $\gamma_{LSiso} \approx 0$) or very large ($\alpha_2 = -1$, $\gamma_{LSiso} \approx 1$). This corresponds to the 'whisk broom' patterns of van't Hoff plots in Fig. 7.

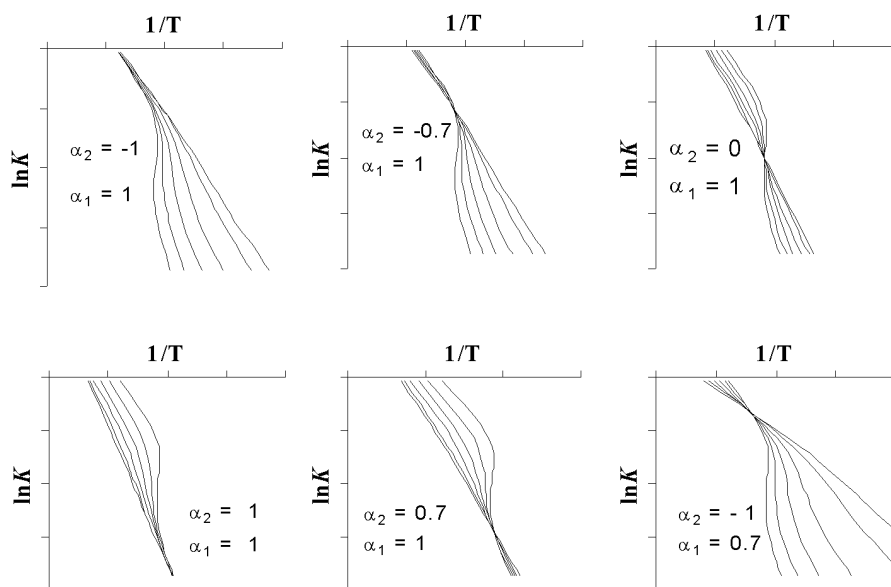


Fig. 7 Series of van't Hoff plots suggestive of isoequilibrium behaviour in a model system characterised by: $\Delta E=6.27$ kJ/mol, $\Delta S=29.26$ J/mol $^{\circ}$ K, $\Delta E_{ex}=2.09$ kJ/mol, $\Delta S_{ex}=0$. Plots in each series correspond to $\zeta=1, 0.8, 0.6, 0.4, 0.2$ and 0.1 . Types of isoequilibrium behaviour are determined by coefficients α_1 and α_2 (Eq. 31) shown in the graphs

The intersection of van't Hoff plots at $\gamma_{LS} \approx 1/2$ is possible when the diluting agent strongly differs from the spin crossover compound. If such a solvent only affects molecular interactions but leaves the parameters of spin crossover unchanged then γ_{HS} of an intersection point with $\alpha_1=1$ and $\alpha_2=0$. (such as shown in Fig. 6) This means that $\Delta F_{solv}=0$, i.e. the free energy of solvent molecules, is unaffected by spin crossover in their nearest neighbourhood. For normal molecules such an independence is hardly to be expected. However, for vacancies (defects) in a crystal lattice the free energy change may indeed be considered as zero. The IER in $[\text{Fe}(\text{3-OCH}_3\text{-SalE-en})_2]\text{PF}_6$ modified by external pressure and grinding in a ball mill (Fig. 6) belongs most probably to this type.

The parameters of Eq. (31) can be estimated with good precision by non-linear regression of experimental data obtained over a wide range of dilution. Figure 8 shows the results of the fitting of data on spin crossover in $[\text{Fe}_y\text{Zn}_{1-y}(\text{ptz})_6](\text{BF}_4)_2$ to Eq. (31). Experimental data are only suggestive of the isoequilibrium behaviour: the precision of the experimental determination of the conversion degree in the range of $\gamma_{HS} \rightarrow 1$ is poor and does not allow a direct determination of the isoequilibrium temperature. Theoretical transition curves approximating the whole set of data intersect, however, in one point.

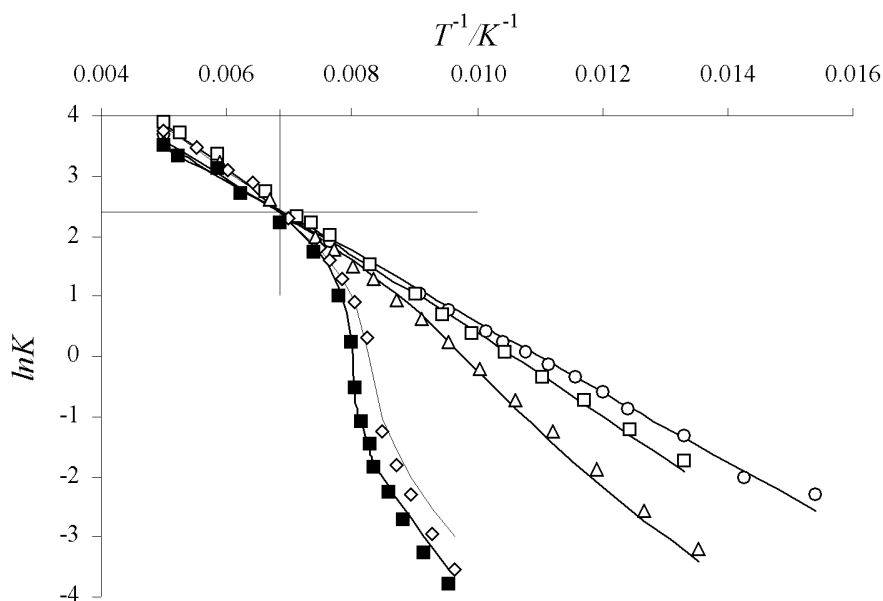


Fig. 8 Theoretical van't Hoff plots (*lines*) describing experimental data on spin crossover in metal-diluted $[\text{Fe}_y\text{Zn}_{1-y}(\text{ptz})_6](\text{BF}_4)_2$ [13]

Estimates of the parameters of Eq. (31) obtained by non-linear regression of experimental data of spin crossover in $[\text{Fe}_y\text{Zn}_{1-y}(\text{ptz})_6](\text{BF}_4)_2$ [13] and result in $\Delta E = 7.49 \pm 0.012$ kJ/mol, $\Delta S = 59.8 \pm 0.08$ J/mol/K, $\Delta E_{\text{ex}} = 1.98 \pm 0.025$ kJ/mol, $\Delta S_{\text{ex}} = 0$ J/mol/K, $\alpha_1 = 0.88 \pm 0.02$, $\alpha_2 = -0.91 \pm 0.02$, $\gamma_{\text{LSiso}} = 0.92$ and $T_{\text{iso}} = 146$ K. The regression error (with respect to γ_{HS}) ± 0.017 .

The amount of available data on IER in spin crossover in the solid state is limited because molecular interactions are strong and may lead to phenomena such as the abrupt spin crossover, hysteresis and two-step spin crossover that overshadow any possible IER.

A systematic study of the variation of Fe(II) complexes with halogenated ethyl-tetrazoles ($[\text{Fe}(\text{teeX})_6](\text{BF}_4)_2$, X=I, Br, Cl, F) yields a striking variety of the shapes of transition curves [14]. Although the modifications of the ligands in this series are remote from the donor atom, the effect on the shape of the transition curve is very strong. Thus a gradual SCO in $[\text{Fe}(\text{teeI})_6](\text{BF}_4)_2$ and $[\text{Fe}(\text{teeBr})_6](\text{BF}_4)_2$, a two-step SCO in $[\text{Fe}(\text{teeCl})_6](\text{BF}_4)_2$, and an incomplete SCO in $[\text{Fe}(\text{teeF})_6](\text{BF}_4)_2$ are observed (Fig. 9).

Spin crossover in the $[\text{Fe}(\text{teeCl})_6](\text{BF}_4)_2$ compound was found to be sensitive towards the mode in which a compound was obtained: a well crystallised sample of $[\text{Fe}(\text{teeCl})_6](\text{BF}_4)_2$ shows a two-step spin crossover with a well defined wide plateau whereas that obtained by fast precipitation only exhibits a very narrow plateau or a deflection point.

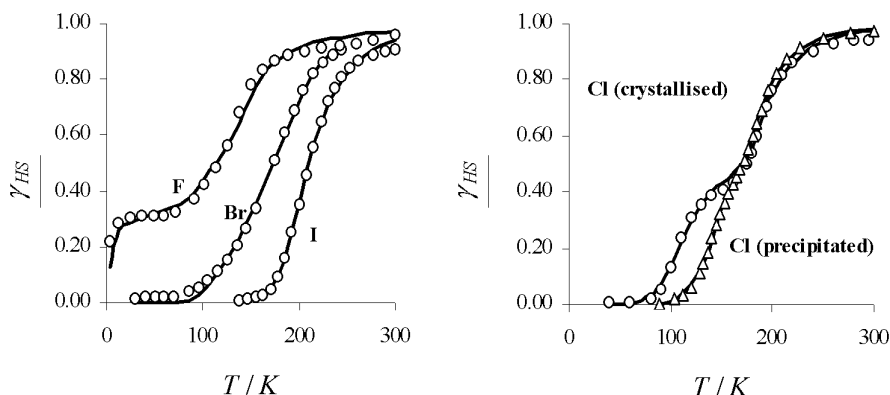


Fig. 9 Transition curves for SCO in Fe(II) complexes with halogenated ethyltetrazoles: $[\text{Fe}(\text{teeX})_6](\text{BF}_4)_2$, $\text{X}=\text{F}$, Cl , Br , I . Solid lines are theoretical curves of the model of ordering

The two-step spin crossover is a critical phenomenon (as indicated by peaks of heat capacity [15]) connected with the formation of regular structures with interchanging HS and LS molecules [2]. The two-step spin crossover is qualitatively predicted within the approximation of binary interactions also taking into account *ordering*. The quantitative description requires taking into account triple interactions [10].

As shown in [14b] all these transition curves can be described with approximately equal precision by (i) the model of ordering in the approximation of triple molecular interactions [10] or by (ii) a quasi-chemical model similar to that suggested in [16]. Theoretical transition curves of the model of ordering are shown in Fig. 9.

According to the *model of ordering* all variations of the shape of transition curves originate from regular changes in the energy of ligand-ligand interactions. The ligand-ligand interactions can be satisfactorily approximated by electrostatic dipole-dipole interactions of CX fragments of ethyl chains of ligands belonging to neighbouring molecules. The *quasi-chemical model* considers molecular interaction as a chemical reaction characterised by certain stoichiometry. The energy of molecular interactions is represented by the energy difference of the species in equilibrium. These species can be virtual or real isomers arising from changes in molecular distances. These models represent thus two limiting cases of weak and strong molecular correlations.

Behind these fascinating transformations of the shape of transition curves one easily misses an intersection of van't Hoff plots in Fig. 10. (Curves corresponding to the well-crystallised $[\text{Fe}(\text{teeCl})_6](\text{BF}_4)_2$ and to $[\text{Fe}(\text{teeF})_6](\text{BF}_4)_2$ fall out of the general pattern.) A common point of intersection indicates that despite the variety of shapes the observed changes

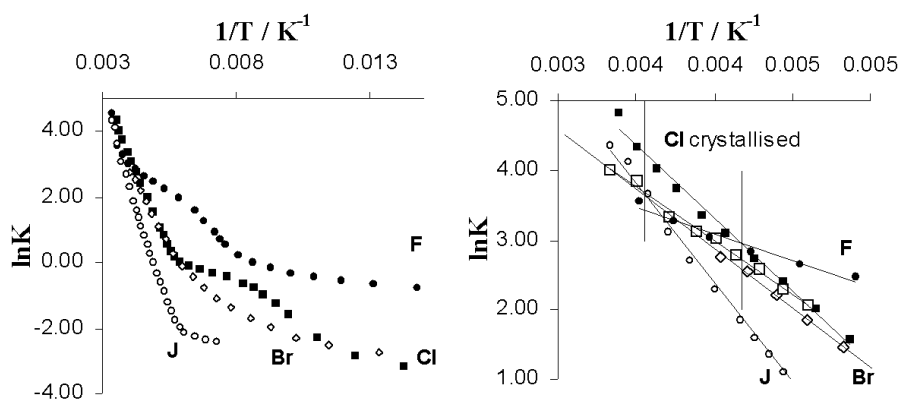


Fig. 10 Van't Hoff plots for SCO in Fe(II) complexes with halogenated ethyltetrazoles: $[\text{Fe}(\text{teeX})_6](\text{BF}_4)_2$, $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$. The *right hand graph* shows that these plots intersect at $T_{\text{iso}}=278 \text{ K}$ and at 239 K

must be caused by a systematic variation of one parameter or of a small number of correlated parameters.

Accordingly, two intersection points of van't Hoff plots separate the investigated compounds into two groups: well-crystallised $[\text{Fe}(\text{teeCl})_6](\text{BF}_4)_2$ and $[\text{Fe}(\text{teeF})_6](\text{BF}_4)_2$ belong apparently to systems with strong correlations whereas other studied complexes are systems with weak correlations.

The variation of the length of the alkyl chain of alkyl-tetrazole ligands in $[\text{Fe}(\text{ntz})_6](\text{BF}_4)_2$ (n being the number of carbon atoms in a chain) also yields a wide variety of the spin crossover behaviour [17].

As Fig. 11 depicts, the spin transition temperature T_{SC}^4 increases with increasing chain length of complexes with ligands between 1 tz and 5 tz. Presumably caused by structural reasons [17], the spin transition temperature decreases abruptly from 5 tz to 6 tz followed again by an increase up to 8 tz. At longer chain lengths structural changes can only be more gradual. The next decrease of T_{SC} takes place between 8 tz and 12 tz. For longer chain lengths the series is not complete and does not allow further interpretation. Beside the spin transition temperature, the general shape of the spin transition curves is also very different. While 1 tz and 2 tz show an incomplete transition, because of two unequivalent iron positions in the lattice [18, 19], the 3 tz has an abrupt spin transition with a hysteresis caused by strong cooperative effects. On the other hand, ligands with longer chains exhibit a more gradual spin transition (4 tz, 5 tz...).

Interestingly, the isoequilibrium investigation connects all of the mentioned compounds, except the most extensively studied $[\text{Fe}(\text{3tz})_6](\text{BF}_4)_2$

⁴ T_{SC} describes the spin transition temperature, where 50% of the complexes, which can undergo a spin transition, are in the high spin or low spin state respectively. This enables also the comparison of spin transitions which are not complete.

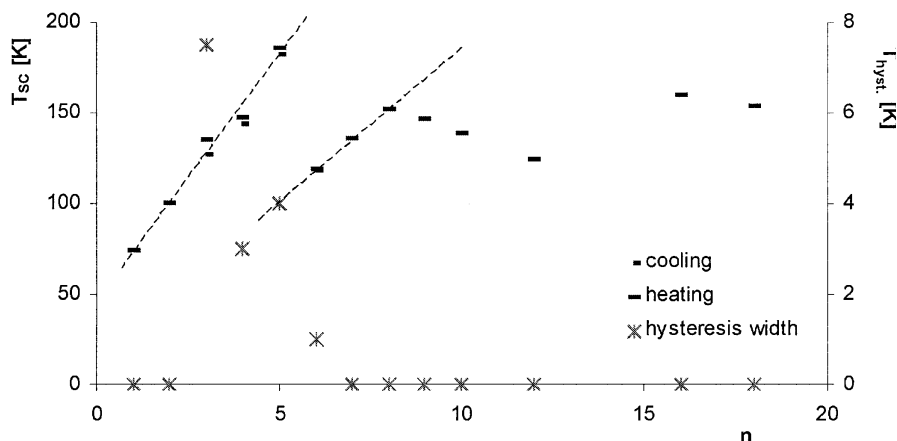


Fig. 11 Overview of the spin crossover properties of $[\text{Fe}(\text{ntz})_6](\text{BF}_4)_2$ describing different behaviour. E.g. T_{sc} increases approximately linearly from complexes with 1 tz to 5 tz as ligands. After an abrupt decrease, probably due to structural changes in the structure between 5 tz and 6 tz, an increase is again observed. Possibly hysteresis occurs as well. The dashed lines are guides for the eyes

[17]. Figure 12 shows a point of intersection at T_{iso} of approximately 330 K. This indicates that one mechanism is valid for all these compounds. The differences in the qualitative (shape of the curve and completeness of the spin transition) and quantitative spin transition leads to thermodynamic differences, but keep the isoequilibrium relationship intact. As mentioned above, $[\text{Fe}(3\text{tz})_6](\text{BF}_4)_2$ does not fit to this trend, leading to the conclusion that its spin transition mechanism is governed by a different mechanism, which most likely can be assigned to its known strongly pronounced cooperative effects accompanying the spin transition in this system. This underlines the usefulness of IKR and IER as a tool to visualise mechanistic or structural differences in various dynamic processes.

Liquid solutions of spin crossover compounds are extremely diluted ($\zeta \ll 1$); therefore, excess free energy does not change the shape of the transition curve. Neither does ΔF contribute towards the equilibrium constant in solution. The observed variations in experimental ΔF^0 originate from variations of $\Delta F_{\text{inf}} = \Delta F_{\text{solv}} + \Delta F_{\infty}$. If an isoequilibrium relationship is observed, the variations of ΔE_{inf} and ΔS_{inf} must be linearly correlated.

Figure 13 shows van't Hoff plots of spin crossover in solutions of $[\text{Fe}(\text{py})\text{imH}_3](\text{BPh}_4)_2$ and $[\text{Fe}(\text{py})\text{bzimH}_3](\text{BPh}_4)_2$ in two different solvents ($\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ 1:4 and acetone).

The change in ΔF produced by the modification of the ligand (filled and open symbols in Fig. 13) is ca. twice as large as the change produced by modification of the solvent. According to the above, the observed changes in ΔE^0 and ΔS^0 originate from variations of $\Delta F_{\text{inf}} = \Delta F_{\infty} + \Delta F_{\text{solv}}$. When the ligands in a complex are modified, ΔF_{∞} (standard free energy of spin crossover

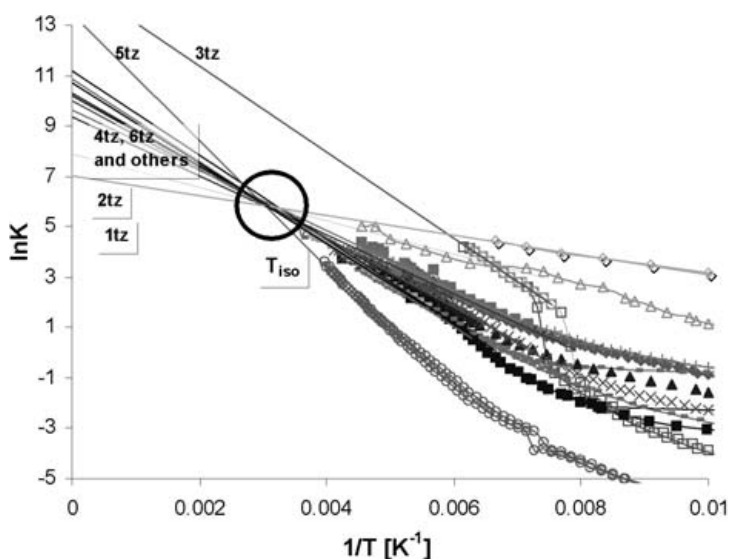


Fig. 12 Iseoquilibrium investigations show an intersection point for all complexes $[\text{Fe}(\text{ntz})_6](\text{BF}_4)_2$ with $n=1, 2, 4-8, 12, 16$ which indicate one mechanism to be valid for all their spin transitions. The system $[\text{Fe}(3\text{tz})_6](\text{BF}_4)_2$ does not intersect, due to strong cooperative effects

in the solution) is expected to change due to changes in electronic energy (ΔE_∞) and vibrational frequencies (ΔS_∞) of the spin crossover molecule.

Ligand modification also changes the energy of intermolecular interaction and, to a smaller extent, its entropy (small changes in the low-frequency

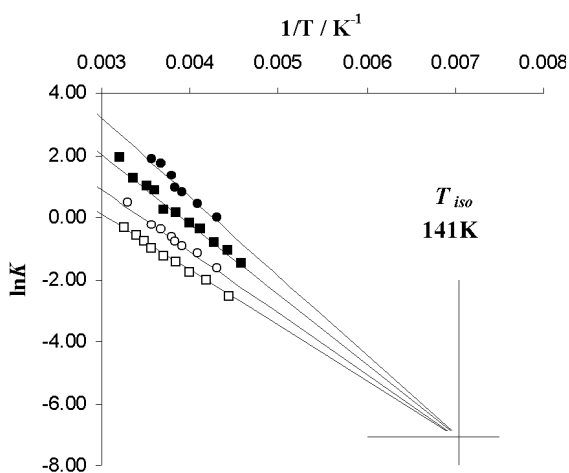


Fig. 13 Iseoquilibrium relationship observed in solutions of $[\text{Fe}(\text{py})\text{imH}]_3(\text{BPh}_4)_2$ (filled circles and squares) and $[\text{Fe}(\text{py})\text{bzimH}]_3(\text{BPh}_4)_2$ (open circles and squares) in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ 1:4 (circles) and acetone (squares) [20]

vibrations). In agreement with experimental results the total effect on ΔF_{solv} must be smaller than on ΔF_{∞} because solvent-solute interactions are weak.

Under such conditions $\Sigma \partial \Delta E^0 / \partial \eta_i$ and $\Sigma \partial \Delta S^0 / \partial \eta_i$ (Eq. 6) are non-zero, and one must expect two van't Hoff plots to intersect at T_{iso} either above or below the experimental range. Experimental data show that the isoequilibrium temperature is low and positive corresponding to parallel variations of ΔE_{∞} and ΔS_{∞} . When the solvent is changed the observed variation of ΔF_{inf} mainly originates from the variations of ΔF_{solv} (solvent-solute interactions that may cause variations of ΔF_{∞} are weak). Experimental van't Hoff plots are shifted by solvent variations so as to be almost parallel. This means that changes in ΔF_{solv} are mainly entropic, reflecting the variations in the number of degrees of freedom and molecular volume of solvent molecules.

Variation in the number/frequency of high-frequency vibrations (affected by spin crossover in the neighbourhood of a solvent molecule) contributes towards the energy term apparently in parallel with variations in ΔE_{solv} caused by the modification of the ligand. This yields the intersection of two pairs of van't Hoff plots at a single point.

The parameters of isoequilibrium relationships are thus useful in the analysis of non-ideality effects, especially when the reaction can only be studied over a narrow range of degrees of conversion (for example, in the liquid state where phase changes limit the available range of temperatures). When the whole transition curve can be obtained, the data can be analysed directly according to the general equation of the law of mass action.

3 Isokinetic Relationships in Spin Crossover

3.1 Stochastic Model of IKRs

In Kramer's theory [21] of rate constants the reactant molecules become activated through their interaction with other molecules of the molecular surrounding, which acts as a constant-temperature "heat-bath". After a random-walk of spin crossover species over discrete energy levels they reach, at the highest point of the barrier, a point of no return. The number of molecules crossing over this barrier in unit time (crossing rate) constitutes the chemical reaction rate. Figure 14 and Eq. (32) explain this in some detail:

$$\begin{aligned} \frac{d\sigma_l(t)}{dt} = Z \left[- \sum_{l < m} P_{ml} N^- \sigma_l(t) + \sum_{l < m} P_{ml} N_m^+ \sigma_l(t) \right. \\ \left. + \sum_{m < l} P_{lm} N_{lm}^+ \sigma_m(t) + \sum_{m > l} P_{lm} N^- \sigma_m(t) \right] \end{aligned} \quad (32)$$

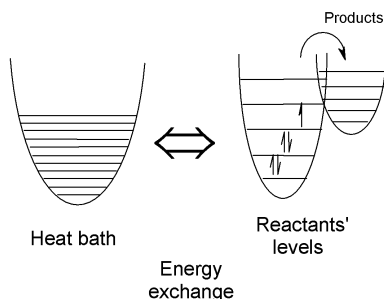


Fig. 14 General reaction pathway where the reactants distributed in a potential well with a point of no return (i.e. a reaction barrier) coupled to a heat-bath storing energy in vibrational levels

In this σ_l represents the time-dependent density of the reactants with the discrete levels l . The P_{lm} are the transition probabilities per collision for the transition from m to l (with $P_{0,-1}=0$), Z is the collision number and N_{lm}^+ is the number of heat bath molecules which have “sufficient energy” to be excited from a given level l to a higher level m ($m>l$) and N^- is the number of heat-bath molecules able to absorb the energy released when reactant molecules relax from m to l (m,l).

In the long-time limit, equilibrium should be reached as represented by

$$\frac{d\sigma_l(t)}{dt} = 0 \quad (33)$$

This yields the condition

$$N_{lm} = \exp\left(\frac{\Delta E}{k_B T}\right) N_{ml} \quad (34)$$

which (with ΔE representing the energy difference between two heat-bath energy levels) represents a Boltzmann distribution for the heat-bath. A non-equilibrium approach is to be applied to the reactant distribution providing that reactants are able to exchange energy with their molecular surroundings.

Equation (32) can be rewritten in the form of a Langevin equation, by assuming l to be continuous and therefore allowing for a change from a *difference* equation to a *differential* equation, namely:

$$\frac{\partial \sigma(t)}{\partial t} = \frac{\partial}{\partial l} R(l) \left[\frac{\partial \sigma}{\partial l} + \frac{1}{k_B T} \frac{\partial}{\partial l} \omega(l) \sigma \right] + g(l) \quad (35)$$

In this $g(l)$ represents a source term for particles, so that a steady-state solution of the Master Eq. (35) can be obtained under the condition of large barriers with a point of no return at the energy barrier, and connected with

a surrounding heat-bath. It has been assumed that during a reaction a non-equilibrium steady-state distribution of reactant particles is present so that the solution of the differential equation at Eq. (35) takes the form [21–24]

$$k = \phi(s_N) \left[\int_0^{s_N} dl \exp \left(-\frac{h}{k_B T} \int_0^l \omega l'' dl'' \right) \int_0^{s_N} dl' \frac{1}{P(l')} \exp \cdot \right. \\ \left. \cdot \left(\frac{1}{k_B T} \int_0^{s_N} \omega(l'') dl'' \right) \phi(l') \right]^{-1} \quad (36)$$

This integral may be solved by partial integration and thereupon yields, assuming that the energy barrier is much larger than $k_B T$, the following simplified form:

$$k \cong A_0 \frac{h\nu}{k_B T} P_{s_N, s_N-1} \exp \left(-\frac{s_N h\nu}{k_B T} \right) \quad (37)$$

The terms A_0 , $s_N h\nu$, T and P_{s_N, s_N-1} represent a constant involving mainly the collision number, the energy barrier height, and the temperature of the molecular surroundings of the reactants (i.e. the heat-bath) and the quantum mechanical probability of a transition between the reactant level s_{N-1} to the highest reactant level (i.e. the point of no return) s_N , respectively.

The problem of understanding the IKR is at this point transferred to the problem of the quantum-mechanical transition probability P_{s_N, s_N-1} [25]. When using, like McCoy [23], or Kramers [26], the Landau-Teller transition probabilities [27] which are based on a translational energy exchange between a non-vibrating particle (i.e. a member of the heat-bath) and an harmonic vibrator, isoentropic behaviour is found. In condensed phases, however, it must be assumed that the heat-bath mainly contains energy stored in the form of vibrational degrees of freedom. This situation refers to that given in Fig. 14. Note that the (molecular) structure of the heat-bath is not included in its required properties.

The appropriate transition probabilities for a vibrational-vibrational energy transfer are calculated in [25] and shown to yield

$$P_{lm} = l e^{\frac{v}{\omega}} \quad (38)$$

where a resonance condition

$$vm = \omega l \quad (39)$$

is included, meaning that energy is exchanged with the highest probability at equal energies (m represents the number of the heat-bath level, v the associated frequency, and the resonance condition is given in its form for a har-

monic oscillator; ω , l refer to the respective parameters of the reactant system). Using this, the following form of the rate constant is found:

$$k \cong A_0 s_N \left(\frac{h\omega}{k_B T_{\text{exp}}} \right)^2 \exp \left[-s_N \left(\frac{\omega}{\nu} - \frac{h\omega}{k_B T_{\text{exp}}} \right) \right] \quad (40)$$

in which ν represents a vibrational heat-bath frequency predominantly active in the energy exchange with the reactants. From this the IKR follows immediately.

Formally, the isokinetic or isoequilibrium relationship corresponds to the condition

$$\left. \frac{d \ln k(\eta)}{d\eta} \right|_{T_{\text{iso}}^{-1}} = 0 \quad (41)$$

manifesting that, at the isokinetic point, the rate or equilibrium constant does not depend on the variable parameter η . If, for example, we consider the reactants, the parameter η from Eq. (41) may be identified with the frequency ω of vibrations along the reaction coordinate. Then

$$\left[\frac{\partial \ln k(\omega)}{\partial \omega} \right]_{T_{\text{iso}}} = 0 \quad (41a)$$

Applying this condition to Eq. (34) a relation is found between T_{iso} and the vibrational frequency predominantly exchanging energy with the reactants present in their molecular surroundings:

$$\frac{1}{RT_{\text{iso}}} = \frac{1}{E} + \frac{1}{N_L h\nu} \quad (42)$$

in which h is Planck's constant, N_L is the Avogadro number and ν is the predominantly active heat-bath frequency. The first right-hand term is associated with collision activation and may be neglected for reaction series in the condensed phase where vibrational activation is predominant. In this case:

$$\frac{1}{RT_{\text{iso}}} = \frac{1}{N_L h\nu} \quad (43)$$

should be valid. This means that, in whatever form the members of the series are represented, they exhibit the same rate at T_{iso} or show a minimum in selectivity at this temperature. It might be significant for this approximation that in the gas phase, where the energy exchange occurs by individual collisions, the experimental results show $1/T_{\text{iso}}$ values near zero, i.e. isentropic behaviour is observed. At T_{iso} the dependence upon η vanishes from the rate equations and the members of the reaction series cannot therefore be identified by means of their rate constants, i.e. they exhibit *isoselective behaviour*. It should be pointed out that the relationship at Eq. (43) has been

shown to be valid for a large number of reaction series in solution. The characteristic frequency can be found in the far-IR-spectra of the solvents used in the respective IKR [28]. Obviously, the given theoretical description might be applied to spin crossover dynamics, as long as the potential surface does not change significantly and as long as $E_a > k_B T$, a requirement which might become important with tunnelling processes.

3.2

Isokinetic Relationships in Spin Crossover Dynamics

The HS→LS relaxation kinetics for Fe complexes in solutions in polar solvents have been studied by Hendrickson and co-workers [29]. The complexes were synthesised from hexadentate Schiff base condensates of varying numbers (a total of 3) of moles of different aldehydes (mepy: 6-methyl-2-pyridinecarboxaldehyde, and py: 2-pyridinecarboxaldehyde) and one mole of amine (tren: tris(2-aminoethyl)amine). These ligands provide therefore the ligand-defined variations within the first coordination sphere of Fe. Three types of kinetic spin crossover correlations have been investigated arising from variations of (i) composition of the first coordination sphere, (ii) solvent and (iii) concentration.

Quite a good isokinetic relationship is observed for variations of the composition of the first coordination sphere yielding $T_{iso} \approx 300$ K (Fig. 15a). This isokinetic temperature can be related to weak absorptions in acetone observed around 200 cm^{-1} and representing the heat bath frequencies (Eq. 43).

The variation of the concentration of $[\text{Fe}(\text{py})_3\text{tren}]^{2+}$ in acetone solutions also results in an apparent IKR ($T_{iso} \approx 230$ K, Fig. 15b). Obviously the above theory does not account for this IKR. However, the reaction coordinate of

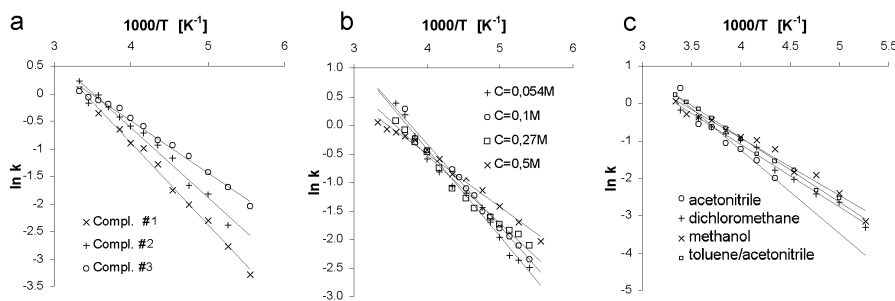


Fig. 15 a Arrhenius plots for HS-LS relaxation kinetics in $[\text{Fe}(\text{mepy})_{3-x}(\text{py})_x\text{tren}](\text{ClO}_4)_2$ in a series of complexes dissolved in acetone: $x=1$ (#1); $x=2$ (#2); $x=3$ (#3). b Arrhenius plots for HS-LS relaxation kinetics in acetone solutions of $[\text{Fe}(\text{py})_3\text{tren}](\text{ClO}_4)_2$ of varying concentration. c Arrhenius plots for HS-LS relaxation kinetics in $[\text{Fe}(\text{mepy})_2(\text{py})\text{-tren}](\text{ClO}_4)_2$ dissolved in different solvents [29]

spin transitions is associated with the metal-donor atom stretching vibrations and torsional modes (see above and [30]) occurring in the first coordination sphere. The effect of concentration was explained as arising from ion association, which results in a change in the ligand field strength (about 300 cm^{-1} would account for the observed effect) and/or vibrational mass.

Activation parameters for the spin crossover dynamics of $[\text{Fe}(\text{mepy})_2(\text{py})\text{tren}](\text{ClO}_4)_2$ have been found to be significantly dependent on the solvent. However, no single mechanism has been suggested for this effect. Neither do we observe a good IKR in the series of Arrhenius plots with varying solvents (Fig. 15c). Solvent effects include both the association and solvation phenomena; therefore there is no observable IKR. The dilution of acetonitrile by toluene brings about a large change in activation energy, which indicates an increase in the ion association effects.

Spin transition rates in Fe(III) complexes are significantly higher than in complexes of Fe(II). A study of HS $\rightarrow$ LS relaxation rates [31] of complexes of Fe(III) of different nature and in different matrices revealed a correlation between activation energy and the logarithm of the pre-exponential factor yielding an isokinetic temperature of 234 K. This is close to the mean spin transition temperature, 231 K, in this series; see Table 1. The significance of this, however, must be treated with caution as the apparent close agreement might be due to statistical artefacts.

In metal-diluted complexes of Fe(II) the relaxation kinetics is single-exponential but the temperature dependences are non-Arrhenius type with predominantly temperature independent tunnelling ($k(T\rightarrow 0)$) at low temperatures. This contribution increases with increasing energy gap between HS and LS states which reveals itself in the correlation between $\ln k(T\rightarrow 0)$

Table 1 Activation energies, pre-exponential factors and spin crossover temperatures in solid and liquid solutions of Schiff base complexes of Fe(III) [32]

Complex	E_a/cm^{-1}	A/s^{-1}	$T_{1/2}/\text{K}$
Fe(III)			
$[(\text{In}/\text{Fe})\text{Sal}_2\text{tr}]\text{PF}_6$	735	3.40×10^9	120
$[\text{FeSal}_2\text{tr}]\text{PF}_6$ in KBr	748	1.80×10^9	130
In PN/BN ^a	1254	4.20×10^{10}	250
In H ₂ O	1733	8.10×10^{11}	305
In methanol	1738	1.50×10^{11}	290
In methanol	1578	2.80×10^{11}	290
In acetone	3301	5.30×10^{15}	280
$[\text{Fe}(\text{acpa})_2]\text{PF}_6$ in KBr	709	7.00×10^8	190
$[\text{Fe}(\text{bzpa})_2]\text{PF}_6$	880	2.60×10^8	220
$[\text{Fe}(\text{bzpa})_2]\text{PF}_6$ in PN/BN ^a	1280	4.40×10^8	240
Fe(II)			
$[(\text{Mn}/\text{Fe})\text{pic}_3]\text{Cl}_2\cdot\text{methanol}$	1120	2.00×10^8	118

^a Propionitrile/butyronitrile

Table 2 Transition temperatures $T_{1/2}$, activation energies E_a , pre-exponential factors A and low temperature tunnelling rate constants for intersystem crossing rates in some Fe(II) compounds [33]

	$T_{1/2}$ K	E_a cm^{-1}	A s^{-1}	k ($T \rightarrow 0$) s^{-1}
$[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$	95	1100	5×10^7	$\sim 5 \times 10^{-7}$
$[\text{Mn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2 \cdot \text{methanol}$	118	907	2×10^8	2.5×10^{-7}
$[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_6](\text{PF}_6)_2$	210	837	5×10^8	1.4×10^{-7}
$[\text{Zn}_{1-x}\text{Fe}_x(\text{py})_6](\text{PF}_6)_2$	>350	640	1×10^9	4×10^2
$[\text{Zn}_{1-x}\text{Fe}_x(\text{bipy})_3](\text{BF}_4)_2$	Low spin	364	2×10^9	6×10^5

and transition temperature ($T_{1/2}$). Kinetic data of various diluted spin cross-over complexes of Fe(II) reported in [33] are shown in Table 2. These data reveal a well-pronounced correlation between $\ln A$ and E_a yielding a negative isokinetic temperature of -292 K, apparently arising from ‘anti-compensation’, i.e. opposite concerted variations of activation energy and pre-exponential factor.

A certain empirical rule is established for spin crossover relaxation kinetics called the *inverse energy gap rule* [5]. According to this rule, the higher the difference in energies of HS and LS states (energy gap), the lower the activation energy of relaxation. If we consider the activation barrier as arising from the intersection of potential energy surfaces, the higher the energy of HS (and hence $T_{1/2}$), the lower will be the potential barrier for relaxation. The frequencies of vibrations of a high spin state in such a potential well determining the entropic part of activation free energy also decrease. Therefore, the observed negative T_{iso} reflects indirectly correlations in this reaction series that are not connected with the origin of the inverse energy gap law and correlations between E_a and $1/T_{1/2}$, Fig. 15c.

In non-diluted solid spin crossover systems the relaxation from the HS to the LS state is very often non-exponential with a considerable self-acceleration due to cooperative interactions. Such kinetics can be described by the following equation [35]:

$$k(\gamma_{HS}) = a_0 \exp(-k^0(T) \exp(a(T)(1 - \gamma_{HS}))) \quad (44)$$

The coefficient $a(T)$ is then responsible for self-acceleration caused by these interactions. The temperature dependence of the parameters in Eq. (44) was determined for a series of solvates: $[\text{Fe}(\text{dppen})_2\text{X}_2]\text{nSolv}$, where $\text{X} = \text{Cl}^-$ or Br^- , $\text{Solv} = \text{CHCl}_3$ or CH_2Cl_2 (dppen=diphenylphosphine ethylene). The complex $[\text{Fe}(\text{dppen})_2\text{X}_2](\text{CHCl}_3)_2$ relaxes exponentially ($a(T) = \text{const} = 1$) whilst other complexes show self-acceleration of the relaxation to the low spin state. Arrhenius plots for these systems do not show IKR and thus there is no single parameter variation in this series.

4 Conclusions

The statistical mechanical analysis of the phenomenon of spin crossover in the condensed phase given in this paper shows that isoequilibrium relationships can arise from two sources: (i) the concerted variations of parameters determining ΔE^0 and ΔS^0 and (ii) the effects of molecular interactions (non-ideality). Changes in vibrational frequencies play a considerable role in the IER of the first type contributing to both ΔE and ΔS of spin crossover. The role of molecular interactions can be evaluated using the formalism of excess thermodynamic functions in the approximation of triple interactions. The stochastic model successfully explains isokinetic relationships observed in spin crossover.

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Nuclear Resonant Forward and Nuclear Inelastic Scattering Using Synchrotron Radiation for Spin Crossover Systems

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Abstract The nuclei in the center of atoms undergoing spin crossover can serve as spectators which via their emitted radiation provide information about the microscopic mechanisms governing the process. Conventional Mössbauer spectroscopy has proven its usefulness in this respect. Application of nuclear resonant scattering of synchrotron radiation opens new possibilities in various ways: Nuclear resonant forward scattering (NFS) makes studies of very small samples, e.g., in pressure cells or as single crystals, feasible and yields results of the Lamb-Mössbauer factors with high accuracy, while nuclear inelastic scattering (NIS) has initiated a novel field of vibrational spectroscopy. Examples and results of these methods will be given in the following chapter.

Keywords Spin crossover · Nuclear resonance · Molecular vibrational modes · Density functional theory

1 Introduction

Synchrotron radiation, which was originally not more than a nuisance for high-energy physicists, has developed into an indispensable source for a series of spectroscopies. This has also become true in the field of nuclear resonant absorption and scattering where only nuclear sources were available before the problem of energy and time discrimination of synchrotron radiation had been solved. Now not only nuclear resonant forward scattering of synchrotron radiation has evolved as a widely used tool for the study of hyperfine interactions but also, quite unexpectedly, nuclear inelastic scattering offers an enormous scientific potential in the field of vibrational spectroscopy.

After a short explanation of these two methods examples for their applications to spin crossover studies will be given in the following.

2 Experimental Methods

2.1 Nuclear Resonant Forward Scattering

Nuclear resonant forward scattering (NFS) is an elastic and coherent scattering process, i.e., it takes place without energy transfer to electronic or vibronic states and is delocalized over many nuclei. This scattering is sensitive to the nuclear environment, similar to conventional Mössbauer transmission experiments. Therefore, the time-differential spectra of nuclear forward scattering provide precise data on hyperfine frequencies and relative isomer shifts. The time-differential intensity of nuclear resonant forward scattering by a nuclear state of width $\Gamma_0 = \hbar/\tau_0$, which is subject to an electric quadrupole splitting $|\Delta E_Q| = \hbar \cdot \Delta\omega$ with $|\Delta E_Q| \gg t_{\text{eff}}\Gamma_0$ can be approximated by [1]

$$I_{\text{fwd}}(t) \sim \frac{\Gamma_0}{\Delta E_\gamma} \cdot \frac{t_{\text{eff}}}{t/\tau_0} \cdot \exp(-t/\tau_0 - \sigma_{\text{el}} n d) \\ \times J_1^2 \left(\sqrt{0.5 t_{\text{eff}} t / \tau_0} \right) \cdot \cos^2 \left(\frac{1}{2} \Delta\omega t + \frac{t_{\text{eff}} \Gamma_0}{8 \hbar \Delta\omega} \right) \quad (1)$$

with ΔE_γ being the bandwidth of the incoming radiation and σ_{el} the electronic absorption cross-section. The exponential decay is modulated by the square of a Bessel function of first order giving rise to so-called dynamic beats. The positions of their minima and maxima can be determined with high accuracy and give thus exact information about the effective thickness of the sample:

$$t_{\text{eff}} = d n f_{\text{LM}} \sigma_0, \quad (2)$$

which appears in the argument of J_1 . Because the geometric thickness of the sample d , the number of Mössbauer nuclei per unit volume n and the nuclear absorption cross-section at resonance σ_0 are in general very well known, the Lamb-Mössbauer factor f_{LM} can be determined with high accuracy without the necessity to take into account corrections due to background and source properties as in conventional Mössbauer spectroscopy.

2.2

Nuclear Inelastic Scattering

In contrast to NFS, nuclear inelastic scattering (NIS) takes place with vibronic energy transfer and is localized on a particular nucleus so that it proceeds incoherently. This method allows to excite the nuclei several meV apart from the resonance energy, if and only if the energy difference between the incident beam and this resonance energy corresponds to the energy of a phonon in the lattice which might be either created or annihilated. NIS is therefore suitable for complementary investigations of molecular vibrations because it aims at the Mössbauer nucleus alone and allows to extract those normal modes that are connected with a considerable mean-square displacement (msd) of the Mössbauer nucleus. By this means it provides information on the partial phonon density of states (PDOS) with an energy resolution on the order of meV.

2.3

Instrumentation

Nuclear inelastic scattering exploits the special features of synchrotron radiation as high collimation of the X-ray beam and its pulsed time structure. A typical experimental set-up of this technique as it is installed at the Nuclear Resonance beamline, ID 18, of the European Synchrotron Radiation Facility (ESRF) in Grenoble/France is shown in Fig. 1 [2]. A monochromatic beam of X-rays with about one eV bandwidth is prepared by the standard beam-line equipment, among them the undulator and the high-heat-load pre-monochromator being the most important items. Further monochromatiza-

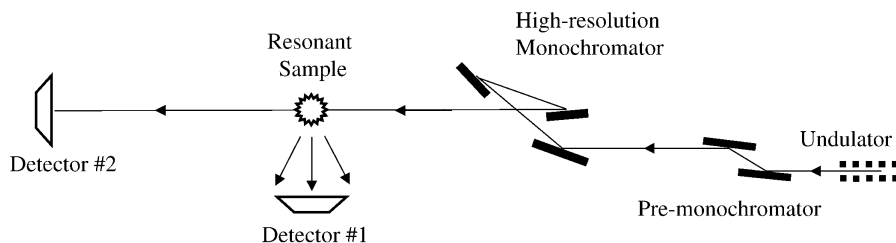


Fig. 1 Scheme of the experimental setup for nuclear resonant scattering

tion down to $\sim$ meV bandwidth is achieved with the high-resolution monochromator.

The beam of X-rays, the energy of which is close to the resonance energy of the nuclear transition, irradiates a sample and excites the resonant nuclei. The radiation which results from nuclear de-excitation has to be distinguished from other (prompt) photons, which pass through the sample without interaction or which are scattered by the electrons. This is achieved utilizing the time distribution of the scattered radiation. The yield of nuclear scattering is delayed due to the finite lifetime of the nuclear excited state, whereas the electronic scattering is essentially prompt on that time scale. Fast electronics is synchronized with the revolutions of the electron beam in the storage ring and counts only the events between the pulses of incident radiation. Thus only the delayed quanta which result from nuclear scattering are detected.

Nuclear scattering is counted by two avalanche photo diode (APD) detectors. The first detector (#1 in Fig. 1) is located close to the sample. It counts the quanta scattered in a large solid angle. The second detector (#2) is located far away from the sample. It counts the quanta scattered by the nuclei in forward direction. These two detectors follow two qualitatively different processes of nuclear scattering. Being scattered inelastically, the photon acquires a certain phase shift and, therefore, is no longer coherent with the incident radiation. If the phase shift is random for various nuclei, the scattering is spatially incoherent over the nuclear ensemble, and the scattered photon may be associated with some individual nucleus. The products of de-excitation of the single nucleus are emitted in a large solid angle as spherical waves (neglecting the polarization effects). Thus the first detector monitors the energy spectrum of inelastic excitation via counting the incoherent scattering of radiation by individual nuclei. In addition to incoherent scattering of primary radiation, the first detector may also collect delayed atomic fluorescent radiation resulting from internal conversion. This contribution is a dominant one, for instance, for the most important Mössbauer isotope of ^{57}Fe . The two channels have identical dependencies on the energy of incident radiation.

With the same setup also NFS can be measured by monitoring the intensity as a function of the delay time by the second detector, which is mounted in forward direction beyond the sample.

3 Materials

We have investigated the two iron(II) complexes $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ (where “tpa”=tris(2-pyridylmethyl)amine) [3] and $[\text{Fe}(\text{tp}t\text{Metame})](\text{ClO}_4)_2$ (where

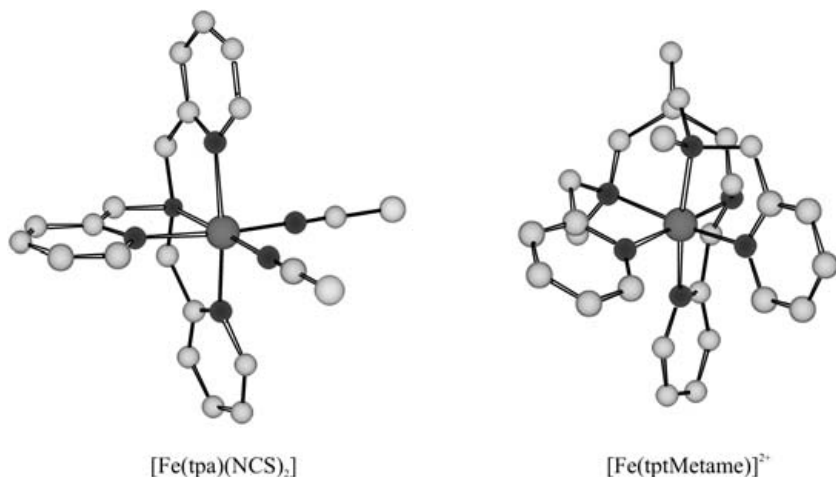


Fig. 2 Geometry of the two spin crossover complexes under study. The hydrogen atoms are not shown for clarity

“tptMetame”=1,1,1-tris((*N*-(2-pyridylmethyl)-*N*-methylamino)methyl)ethane [4] (Fig. 2).

In [Fe(tpa)(NCS)₂] the iron(II) is octahedrally coordinated by six nitrogens. The complex shows a temperature-induced spin-state transition accompanied by a hysteresis from the paramagnetic high-spin ($^5T_{2g}$, $S=2$) to the diamagnetic low-spin ($^1A_1$, $S=0$) phase. SQUID measurements show that above the spin transition the measured effective moment $\mu_{\text{eff}}=5.35 \mu_B$ is larger than expected from the “spin-only” value $\mu_{\text{so}} \approx 4.9 \mu_B$ for $S=2$ of a ferrous high-spin complex. The same behavior had been reported earlier for similar compounds and was attributed to orbital contributions [5]. In the low-spin phase $\mu_{\text{eff}}=1.1 \mu_B$ was measured. The deviation of the effective moment for the low-spin phase from zero is due to an incomplete transition as shown by the data obtained from conventional Mössbauer measurements (Table 1).

The iron(II) complex [Fe(tptMetame)](ClO₄)₂ exhibits a temperature-induced spin transition at 180 K as reflected by the temperature dependence of the effective magnetic moment (Fig. 3). This compound is particularly attractive for spin crossover studies because rather big single crystals (belonging to the monoclinic space group $P2_1/n$) can be grown. X-ray diffraction measurements have shown that all four molecules in the unit cell have the same orientation of their threefold symmetry axis (C_3), namely parallel to the crystallographic *a* axis. This gives the opportunity to perform an angular-resolved spectroscopy of the hyperfine fields as well as of the vibrational modes.

Table 1 Fractions, quadrupole splittings ΔE_Q and isomer shifts δ for $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ obtained by conventional Mössbauer spectroscopy. HS_2 denotes the second high-spin state besides HS, which can be neglected at higher temperatures but has to be taken into account at low temperatures

T (K)		Fraction (%)	ΔE_Q (mm s ⁻¹)	δ (mm s ⁻¹)
4.2±0.1	LS	98.0±1.0	0.41±0.01	0.49±0.01
	HS	1.0±0.5	2.46±0.15	1.11±0.15
	HS ₂	1.0±0.5	3.00±0.15	1.11±0.15
77±0.5	LS	99.0±1.0	0.40±0.01	0.47±0.01
	HS	0.5±0.5	2.75±0.15	1.11±0.15
	HS ₂	0.5±0.5	2.80±0.15	1.11±0.15
130±0.5	LS	4.0±0.5	0.34±0.15	0.47±0.15
	HS	95.5±1.0	2.51±0.01	1.09±0.01
	HS ₂	0.5±0.5	2.60±0.15	1.09±0.15
200±0.5	LS	1.0±0.5	0.34±0.15	0.52±0.15
	HS	98.5±1.0	2.32±0.01	1.05±0.01
	HS ₂	0.5±0.5	2.30±0.15	1.05±0.15

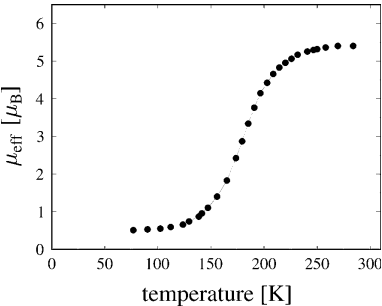


Fig. 3 The effective magnetic moment in units of Bohr magnetons μ_B of $[\text{Fe}(\text{tpt-Metame})](\text{ClO}_4)_2$ as a function of temperature (data taken from [4])

4
Measurements

4.1
Nuclear Resonant Forward Scattering

4.1.1
[Fe(tpa)(NCS)₂]

The time evolution of nuclear forward scattering by $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ has been measured at ID18, ESRF Grenoble/France in hybrid-bunch mode as a function of temperature in the range from 35 K to 290 K with a time resolution better than one nanosecond (see Fig. 4). The simulations by means of

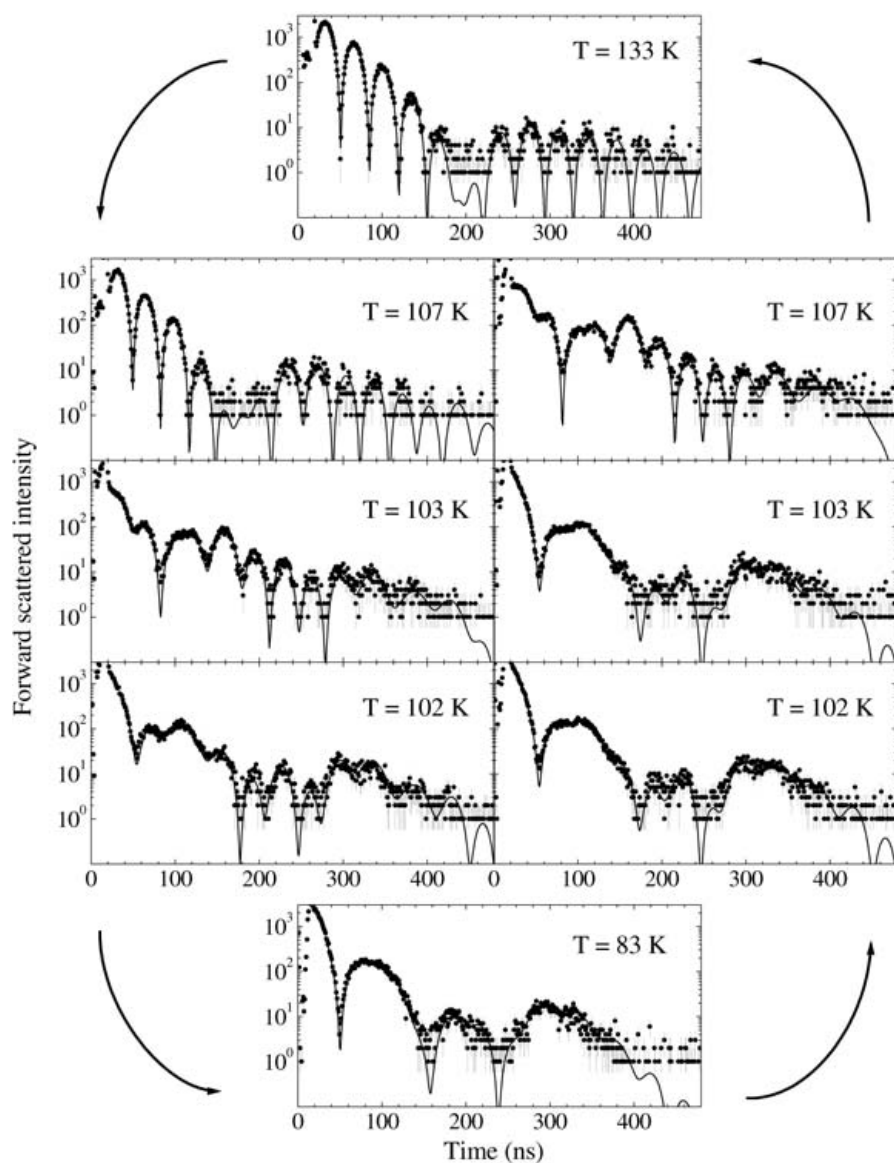


Fig. 4 Time evolution of the NFS intensity by $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ for various temperatures around the high-spin to low-spin transition taken in the order as indicated by the arrows. The points give the measured data and the curves are results from calculations described in the text [3]

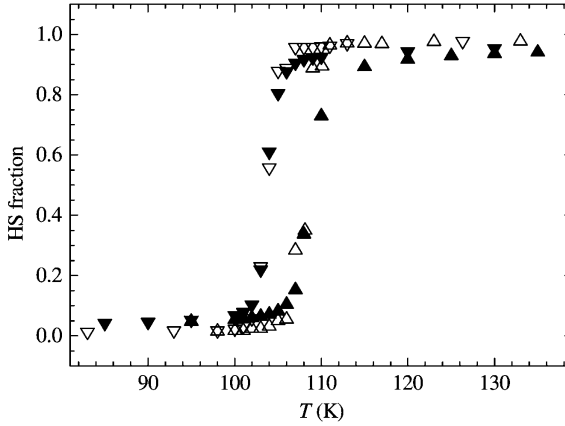


Fig. 5 High-spin fraction of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ in the region of the transition temperature measured by SQUID (*solid triangles*) and NFS (*open triangles*). The values derived during a temperature scan with increasing (decreasing) temperature are marked by *up triangles* (*down triangles*) [3]

theoretical NFS spectra have been performed using the CONUSS program package [6].

The measurements yield a temperature dependence of the fraction of molecules in the high-spin state which is in agreement with the data previously obtained using SQUID (Fig. 5).

The Lamb-Mössbauer factors f_{LM} (Fig. 6) show a pronounced decrease with increasing temperature caused by elevating the population of vibrational states. An abrupt drop of the Lamb-Mössbauer factor exactly at the spin crossover temperature is attributable to the softening of the iron-ligand vibrational modes as it has been observed by NIS and will be explained in more detail below.

If the NFS pattern is to be calculated for a sample which contains more than one kind of scatterers, it has to be decided whether the superposition of the outgoing waves has to be performed coherently or incoherently. Longitudinal scattering is always coherent, because there is no path-length difference for nuclei located along the X-ray beam. The transversal coherence length $L_{\text{c,trans}}$, however, has to be taken into account. It is given by the expression

$$L_{\text{c,trans}} = \frac{\lambda}{2\pi} \cdot \frac{1}{\sigma_{\theta}} \text{ with } \sigma_{\theta} = \sqrt{\left(\frac{s_0}{S}\right)^2 + \left(\frac{\sigma_d}{D}\right)^2} \quad (3)$$

where s_0 is the diameter of the source and σ_d that of the detector, while S denotes the distance between source and scatterer and D between scatterer and detector [7]. If one discards the contribution of s_0/S because of the large

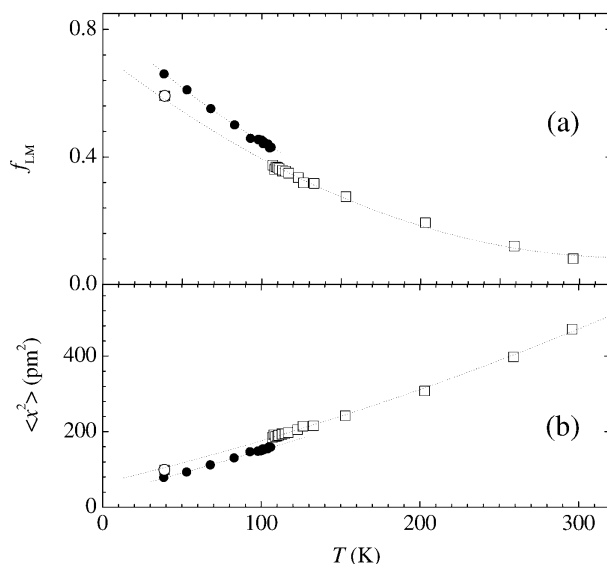


Fig. 6 Temperature dependence of the Lamb-Mössbauer factor of f_{LM} and of the mean-square displacement $\langle x^2 \rangle$ of the iron in $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ [3]

distance S , one calculates for the transversal coherence length $L_{c,\text{trans}} \approx 3$ nm, if for D about 1 m and for σ_d about 5 mm are assumed.

In the case of Fe(II) complexes which exhibit spin transition, either induced by temperature, by pressure or by light, it is well-known, that the form of the transition curve and the width of the hysteresis are determined by the degree of cooperativity. In order to describe these features theoretically it is necessary to know whether the intermolecular interactions are long or short ranging. By means of NFS this question can in principle be addressed by making use of effects of the transversal coherence length in order to estimate the size of the spin domains which possibly form in the transition region.

The sample of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ enriched with 20% ^{57}Fe which was studied in the present work had the form of a powder with a particle size of about $2 \mu\text{m}$. If these particles were composed of domains with a diameter $\gg 3$ nm, this fact would manifest itself by an incoherent scattering process. The time dependent NFS, which was registered at 108 K (Fig. 7) where the ratio of low-spin to high-spin iron is about 1:1, can satisfactorily be explained by a purely coherent superposition of the outgoing waves as it is done in Fig. 4. The conclusion is, however, not unequivocal because the sample was 0.5 mm thick, so that the longitudinal coherence predominates since many particles lie along the forward scattering pathway. In order to arrive at a conclusive result the measurements ought to be performed with a smaller ratio σ_d/D on

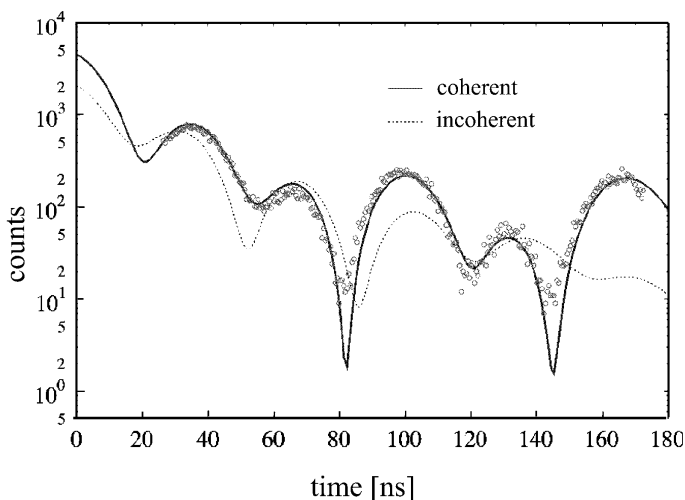


Fig. 7 Time dependent NFS of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ taken at 108 K. The curves represent comparison of a coherent vs incoherent superposition of the scattering from 50% low-spin and 50% high-spin iron(II) characterized by their corresponding quantum beat pattern. The effective thickness of the sample was $t_{\text{eff}}=18$

a much thinner sample. Such an experiment would require a sample with 100% enriched ^{57}Fe and a much higher beam intensity.

4.1.2

$[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$

As will be shown in the forthcoming chapter, the change of the vibrational spectra of $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ when going from the high-spin to the low-spin state by lowering the temperature has been well documented by means of NIS. This raises the question whether a pressure-induced transition to the low-spin phase affects the vibrational modes in the same way. However, the size of samples which can be accommodated by pressure cells is rather limited so that it is very time consuming to collect sufficient statistics in a conventional Mössbauer spectrometer. Nevertheless such measurements have proven feasible. It is, however, preferable to perform such studies by means of NFS because here full use can be made of the advantages of the small beam size of less than 1 mm^2 . We have therefore performed a series of NFS measurements on $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ in a pressure cell of the kind as described in [8] in order to find out which minimum pressure has to be applied to achieve a complete transition into the low-spin phase. It has been found out that a value of 1.7 GPa will suffice [9].

4.2

Nuclear Inelastic Scattering

4.2.1

[Fe(tpa)(NCS)₂]

NIS spectra were also recorded at ESRF. The 6-GeV electron storage ring was operated in 16-bunch mode. The incident beam was monochromatized by a Si(111) double-crystal pre-monochromator to a bandwidth of 2.5 eV. The actual measurements on [Fe(tpa)(NCS)₂] were performed with two different sets of high-resolution monochromators (HRM). In the inset in Fig. 8 the data obtained with an energy resolution of $\Delta E_\gamma = 1.7$ meV are reproduced. Contributions in the measured spectra with an energy defect ($E - E_0 < 0$) account for annihilation and with an energy excess ($E - E_0 > 0$) for creation of vibrations in the molecular complex. At low temperatures only low-energy phonon states are occupied (2.5 meV corresponds to approximately 30 K) and therefore annihilation of phonons is insignificant in this temperature region. Hence, at low temperatures ($T = 13$ K in Fig. 8) the broadening of the central peak is slightly asymmetric. Creation of phonons, however, is possible at all vibrational energies of the complex under study. At elevated temperatures, i.e., at $T = 293$ K in Fig. 8 when only the HS phase is present, a symmetric broadening of the inelastic data around the resonance energy E_0 and weak peaks at about ca. -30 and $+30$ meV are observed.

In order to achieve higher statistics in the most interesting region up to 100 meV above the resonance energy, the measurements have also been per-

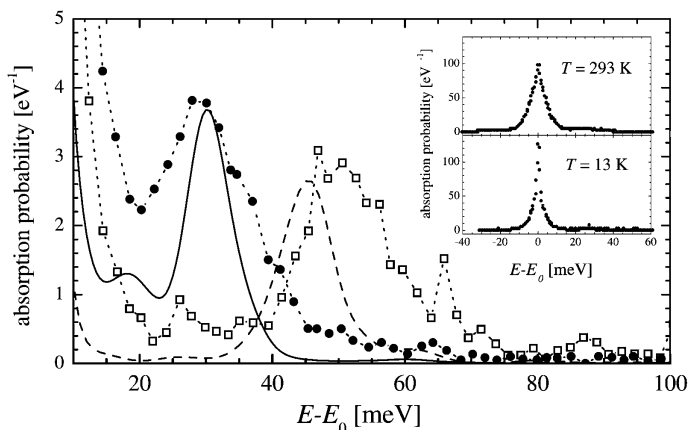


Fig. 8 NIS spectra of [Fe(tpa)(NCS)₂] taken from the LS phase (*open squares*) and from the HS phase (*closed circles*) are shown in the main panel together with results from DFT calculations [11]. In the *inset* measurements of the central peak with an energy resolution of 1.7 meV at two different temperatures as indicated are reproduced [3]

formed with an energy resolution of $\Delta E_\gamma = 6.4$ meV (data shown in the main panel of Fig. 8). The measured NIS spectra of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ exhibit an inelastic peak at 30 meV in the HS state and at 50 meV in the LS state. The LS spectrum exhibits another rather small peak at 66 meV, which is not seen in the HS spectrum. The linewidth (12–15 meV) of the inelastic peaks observed at 30 meV (HS) and at 50 meV (LS) is by far broader than the resolution of the HRM and the linewidth of the central peak which was 7.2 meV. Assuming that these peaks are attributed to only one individual molecular vibration, the observed broadening might be caused by either (i) strong dispersion of the optical phonon branch that corresponds to this molecular mode, or (ii) damping of this mode (i.e., dissipation of the energy of this mode into other vibrational modes due to anharmonicity) which leads to a very short lifetime of this mode (<1 ps). Neither of the two explanations can be strictly ruled out in the case of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$. However, experimental data for similar spin crossover complexes as $[\text{Fe}(\text{bpp}_2)][\text{BF}_4]_2$ (where “bpp” = 2,6-bis(pyrazol-3-yl)pyridine) [10] and $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ shown in the next section do not exhibit such a broadening. The NIS measurements for $[\text{Fe}(\text{bpp}_2)][\text{BF}_4]_2$ at different temperatures have revealed that the linewidth of the observed peaks is roughly temperature independent. Instead, if the linewidth would be caused by damping, a significant temperature dependence would be expected. Therefore we conclude that the two peaks (HS and LS) most likely are a superposition of two or more individual peaks.

Simulations of the inelastic part of the NIS spectra on the basis of DFT calculations [11] can reproduce the group of peaks around 50 meV for the LS state and around 30 meV for the HS state. These peaks correspond to normal modes involving predominantly Fe-N bond stretching. Due to the almost octahedral environment of the iron center three out of six Fe-N stretching modes are invisible in NIS spectra. Those modes transform according to the A_{1g} and E_g representations of the ideal octahedron and therefore do not contribute to the mean-square displacement (msd) of the iron nucleus. Only the remaining three modes which transform according to the T_{1u} representations can be observed in NIS spectra. These three modes, with calculated energies of 29.1, 30.1, and 35.3 meV for the HS state and 42.8, 46.6, and 52.6 meV for the LS state, give rise to prominent peaks in the simulated NIS spectra of both the LS and HS isomer of $[\text{Fe}(\text{tpa})(\text{NCS})_2]$.

Considerable contributions to the calculated absorption probability also arise from N-Fe-N bending modes in the range from 3 to 20 meV. These modes cannot be identified in the experimental spectra because they are superimposed by modes originating from the acoustical phonons which give much larger contributions to the experimental NIS spectra than the optical phonon branch does.

According to the normal-mode analysis the low-intensity peak at 66 meV in the measured NIS spectrum must be assigned to a mode which has predominantly N-C-S bending character and to some extent Fe-N stretching

character. The mixed character of this mode is due to interactions between Fe-N stretching and N-C-S bending modes, which are close in energy in the LS isomer. The calculated N-C-S bending modes of the HS isomer do not show any admixture of Fe-N stretching modes because of the relatively large energy gap of about 30 meV between these modes. Correspondingly, the NIS spectrum of the HS isomer does not exhibit a peak at the respective energy.

IR measurements on several spin-crossover complexes with a central $[\text{FeN}_6]$ octahedron have indicated a remarkable increase of the Fe-N bond stretching frequencies from about 25–30 meV in the HS state to about 50–60 meV in the LS state. For the complex studied here, Fe-N bond stretching frequencies of 59.5 and 66.0 meV were reported from IR measurements of the LS isomer [12]. NIS is a valuable alternative to IR and Raman spectroscopy, as it easily extends below 35 meV which is difficult to reach by IR, and, in addition, allows one to identify definitely the Fe-N stretching modes, whereas the IR and Raman spectra are rather complex in this energy region making an unambiguous assignment of these modes very difficult.

In summary, the measured NIS spectra of the LS isomer as well as the DFT calculations suggest, that the IR line attributed previously to an Fe-N bond stretching mode of the LS isomer [12] should be assigned to a bending mode of the NCS group instead. As a result, the frequency shift of the Fe-N stretching mode upon spin crossover is about 40% smaller than assumed earlier. Nevertheless, the suggested predominance of mode softening in the high-spin phase giving rise to an entropy gain as major cause for the phase transition appears to be verified explicitly.

4.2.2

$[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$

The fact that relatively large single crystals are available and that all molecules in the unit cell have their threefold symmetry axis oriented parallel to the crystallographic a axis make the complex $[\text{Fe}(\text{tptMetame})](\text{CO}_4)_2$ an especially attractive candidate for NIS studies. Under these conditions the peaks in the NIS spectra of molecular vibrations obtained from different orientations of the crystal with respect to the X-ray beam could be assigned by comparison with the results from density functional (DFT) calculations (see [13]).

The new high-resolution monochromator [14] at the beamline ID-18 of ESRF with an energy resolution of 0.65 meV allowed one for the first time to detect individual intra-molecular vibrational modes of a single-crystalline spin crossover complex. The measurements were performed with single crystals which had the form of 2 mm long needles with ~ 0.2 mm thickness. The sample was mounted in a closed-cycle cryostat and cooled down to 30 K to reach the LS state. The first spectrum was recorded with the needle axis, which is also the threefold symmetry axis C_3 , perpendicular to the wave vector k of the X-ray beam, two more spectra were recorded after rotating the

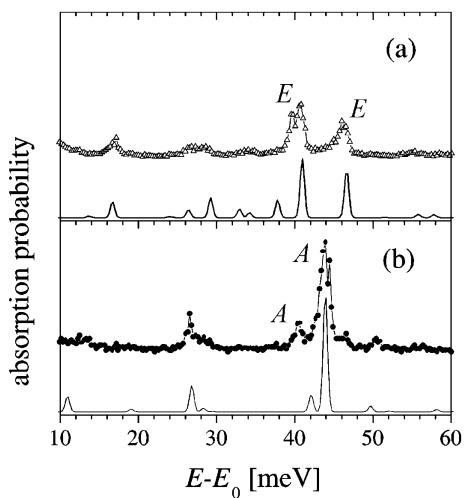


Fig. 9a,b NIS spectra of $[\text{Fe}(\text{tptMetame})][\text{ClO}_4]_2$ measured at 30 K. The direction of the incident beam was: (a) $k \perp a$; (b) $k \parallel a$. The solid lines are the results of DFT calculations [15]

crystal around the needle axis by 45° each time. These three orientations yielded identical spectra as expected due to the symmetry of the molecules; their summation is shown in Fig. 9a. Before recording the fourth spectrum the needle axis was mounted parallel to the wave vector k of the X-ray beam. The resulting spectrum (Fig. 9b) is clearly different from the previous (Fig. 9a). In addition, a significant shift of the peaks to lower energy is observed in the spectrum of the HS isomer that was recorded at room temperature (Fig. 10).

The LS isomer with $k \perp a$ exhibits two dominant peaks at 40 and 46 meV as well as several smaller peaks in the range from 10 to 40 meV (Fig. 9a). With $k \parallel a$ one dominant peak appears at 44 meV accompanied by several smaller peaks with energies below 40 meV (Fig. 9b). The HS isomer for $k \perp a$ shows one dominant peak at 30 meV and a smaller peak at 20 meV (Fig. 10), both being broader than those observed for the LS isomer. For the interpretation of the experimental spectra DFT calculations were performed for the HS and LS isomers of the $[\text{Fe}(\text{tptMetame})]^{2+}$ cation in vacuo using the B3LYP [15].

Considering an ideal $[\text{FeN}_6]$ octahedron there exist six Fe-N bond-stretching modes which transform according to the A_{1g} , E_g , and T_{1u} irreducible representations of the point group O_h . The *gerade* modes A_{1g} and E_g , are not connected with a displacement of the iron nucleus, and thus only the three *ungerade* T_{1u} bond-stretching modes can be detected by NIS. Actually, the first coordination sphere of the iron in the $[\text{Fe}(\text{tptMetame})]^{2+}$ cation has to be regarded as a distorted $[\text{FeN}_6]$ octahedron. Because of the lower symmetry the vibrational T_{1u} term is split into an A and a doubly degenerate E

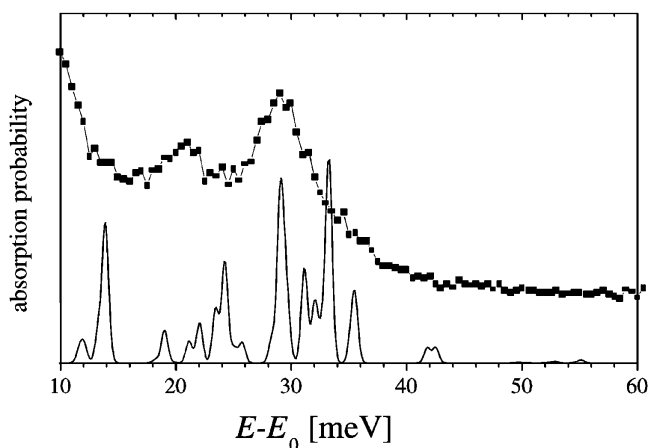


Fig. 10 NIS spectra of $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ measured at room temperature. The direction of the incident beam was $k \perp a$. The solid lines are the results of DFT calculations [15]

term. In this case all six bond-stretching modes are visible by NIS: two pairs of doubly degenerate E modes are connected with a displacement of the iron nucleus within the equatorial plane and are visible if k lies within this plane that is perpendicular to the threefold symmetry axis (Fig. 9a). The remaining two A modes are connected with a displacement of the iron nucleus along the molecular symmetry axis (Fig. 9b). The smaller peak at 41 meV corresponds to the nearly fully symmetric breathing mode where the iron nucleus participates only slightly in the vibration.

The calculated iron modes in the HS and the LS isomer are in an overall agreement with the experimental spectra with the exception of the acoustic contributions which are not included in the molecular model. The acoustic part, however, extends only up to 5 meV and is roughly the same for the HS and the LS. As far as the recorded NIS spectra of $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ are concerned they support the assumption that upon the transition into the HS phase essentially a softening of the iron-ligand bond stretching and bending modes takes place, which causes an entropy gain as driving force for spin crossover.

5 Summary

The application of nuclear resonance methods to the study of spin crossover compounds has strong impact on their understanding. It has been shown that from nuclear resonant forward scattering the Lamb-Mössbauer factors

can be derived precisely, which provides global information on the dynamics of these systems. Nuclear inelastic scattering aims at details of these dynamics and allows one to extract those normal modes from the complex vibrational spectrum of spin crossover complexes in which the iron center takes part with a considerable mean-square displacement. With the help of the iron partial density of vibrational states, which has been derived from nuclear inelastic scattering, the mode softening when passing from the low-spin to the high-spin state has been visualized. Thus it has been proven that the gain in vibrational entropy is the major driving force for the spin transition. By monitoring the NIS spectra of a single crystal of $[\text{Fe}(\text{tp}^{\text{t}}\text{Metame})](\text{ClO}_4)_2$ the individual asymmetric modes of vibration of a molecular crystal have been measured for the first time and assigned properly to the normal modes calculated by DFT.

It is expected that tiny differences in the vibrational spectra of temperature-induced and pressure-induced spin transition will become observable. Further on, it may be possible by optimizing the experimental conditions to estimate the size of spin clusters in spin crossover complexes, a question whose answer is eagerly awaited by theoreticians.

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Heat Capacity Studies of Spin Crossover Systems

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Abstract As the spin crossover phenomena occurring in O_h symmetry involve a transfer of electrons between the e_g and t_{2g} orbitals, the metal-to-ligand bond distances change remarkably. This brings about a drastic change in the density of vibrational states, mainly the metal-ligand skeletal vibrational modes. Thus, the transition entropy due to the spin crossover involves a dominant contribution from the non-electronic vibrations in addition to the contribution from a change in the spin multiplicity. It is concluded that a coupling between the electronic states and the phonon system plays a fundamental role in the spin crossover occurring in the solid state. Heat capacity is a physical quantity containing contributions from all kinds of molecular degrees of freedom. Consequently calorimetry is a suitable experimental tool to help elucidate the mechanism involved in spin crossover phenomena.

Keywords Spin crossover · Heat capacity · Entropy · Phase transition · Domain model

List of Abbreviations and Symbols

phen	1,10-Phenanthroline
LS	Low spin
HS	High spin
2-pic	2-Aminomethylpyridine or 2-picolylamine
solv	Solvated molecule
DTA	Differential thermal analysis
acpa	Hacpa= <i>N</i> -(1-acetyl-isopropylidene) (2-pyridylmethyl) amine
depe	1,2-Bis(diethylphosphino)ethane
3EtO-salAPA	3EtO-salAPAH is the Schiff base condensed from 1 mol of 3-ethoxysalicylaldehyde with 1 mol of <i>N</i> -aminopropylaziridine
<i>S</i>	Molar entropy
<i>H</i>	Molar enthalpy
<i>G</i>	Molar Gibbs energy
<i>R</i>	Gas constant

C_p	Molar heat-capacity under constant pressure
T	Temperature
$T_{1/2}$	Spin transition temperature
γ_{HS}	High-spin fraction
K	Equilibrium constant
μ_{eff}	Effective magnetic moment

1

Introduction

The first experimental evidence for thermal spin crossover in iron(II) complexes $[\text{Fe}(\text{NCX})_2(\text{phen})_2]$ ($\text{X}=\text{S}$ or Se ; $\text{phen}=1,10\text{-phenanthroline}$) was reported in 1967 by König and Madeja [1]. They gave a reasonable interpretation for the unusual magnetic behavior of such complexes reported first by Baker and Bobonich [2] in 1964. Since the spin crossover phenomenon is principally based on a change in the quantum state of the electron spin, many researchers believed that the dominant driving force leading to temperature-induced spin crossover transition would be a change in the spin multiplicity. However, in 1974, Sorai and Seki [3, 4] measured heat capacities of the spin crossover Fe(II) complexes $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ and $[\text{Fe}(\text{NCSe})_2(\text{phen})_2]$ for the first time, and their results showed that this interpretation was not correct.

As reproduced in Fig. 1, we found a phase transition for $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ at 176.29 K with an entropy change of $\Delta S=(48.8\pm0.7) \text{ J K}^{-1} \text{ mol}^{-1}$.

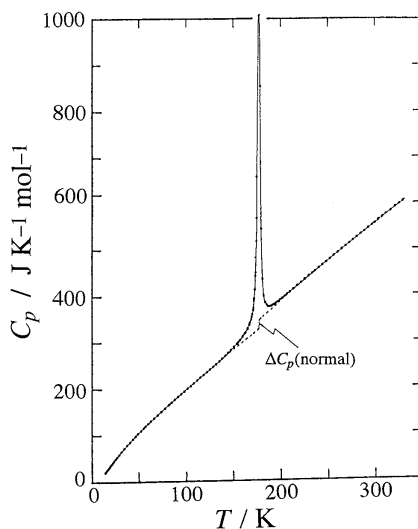


Fig. 1 Molar heat capacity of $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$. Broken curves indicate the normal heat capacities [3, 4]

This entropy value is extremely large in comparison with the entropy gain, $\Delta S = R \ln 5 = 13.38 \text{ J K}^{-1} \text{ mol}^{-1}$, expected for a conversion from the low-spin (LS) state $^1A_{1g}$ to the high-spin (HS) state $^5T_{2g}$. It should be remarked here that the change in the orbital degeneracies between the LS and HS states does not generally contribute to the entropy gain at the spin crossover transition because the orbital degeneracy, if any, has been lifted by the Jahn-Teller distortion to give a non-degenerate orbital in the resultant lower symmetry. Strictly speaking, therefore, the distorted ligand field is not genuine octahedral O_h but is tetragonal D_{4h} or has even lower symmetry.

As the spin crossover involves a transfer of electrons between the e_g and t_{2g} orbitals, the metal-to-ligand bond distances change remarkably, being about 0.02 nm shorter in the LS state than in the HS state. This brings about a drastic change in the density of vibrational states, mainly the metal-ligand skeletal vibrational modes [5]. Thus, the transition entropy involves a big contribution from the non-electronic vibrations and the lattice heat capacity exhibits a discontinuity at the transition temperature. As seen in Fig. 1, for the complex $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ a jump of $\Delta C_p(\text{normal}) = 18.7 \text{ J K}^{-1} \text{ mol}^{-1}$ is observed. Based on variable-temperature IR spectroscopy, we could interpret the excess entropy beyond the contribution from the spin multiplicity and the heat capacity jump at the transition temperature in terms of the phonon contribution. We concluded that the temperature-induced spin crossover is an entropy-driven phenomenon and coupling between the electronic states and the phonon system plays a fundamental role in the spin crossover transition occurring in the solid state [4]. This concept has long since been accepted.

Subsequently, we have developed calorimetric studies for a variety of spin crossover systems, in which the spin transition takes place either abruptly or gradually, and these studies have revealed many important aspects inherent in the spin crossover phenomena [6]. In this chapter, those thermodynamic studies on spin crossover complexes containing Fe(II) and Fe(III) ions are described.

2

Heat Capacities of Iron(II) Picolylamine Complexes

2.1

Influence of Solvate Molecule

The spin transition temperature 176.29 K for $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ is drastically shifted to 231.26 K for $[\text{Fe}(\text{NCSe})_2(\text{phen})_2]$, in which a sulfur atom of the monodentate ligand NCS, remote from the central iron atom, is replaced by a selenium atom. As mentioned above, since the spin crossover is an entropy-driven phenomenon, the spin transition temperature is principally deter-

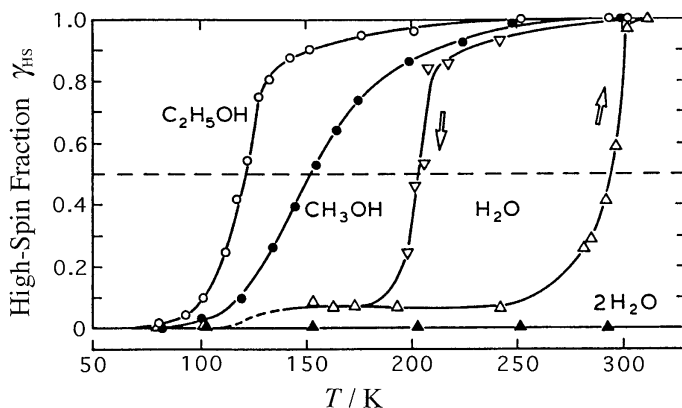


Fig. 2 Temperature dependence of the high-spin area fraction γ_{HS} in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot (\text{solv})$ [$\text{solv} = \text{H}_2\text{O}$ ((empty triangles), (empty upside down triangles)), $2\text{H}_2\text{O}$ (filled triangles), CH_3OH (filled circles), $\text{C}_2\text{H}_5\text{OH}$ (empty circles)] [9]

mined by compensation of the energy difference caused by a change in the ligand-field strength with the entropy term $T\Delta S$ mainly originating in the phonon system. This is the reason for the large shift of spin transition temperature. In such a way, the spin crossover behavior in the solid state is sensitively influenced by chemical and physical factors [7].

The $\text{Fe}(\text{II})$ spin crossover complexes $[\text{Fe}(\text{2-pic})_3]\text{X}_2$ (2-pic=2-amino-methyl-pyridine, termed 2-picolyamine; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) reported by Renovitch and Baker [8] are appropriate materials for probing various chemical influences. The magnetic behavior of this series of complexes markedly depends upon the anion, even though the anion is not coordinated to the central iron atom. In the course of ^{57}Fe Mössbauer spectroscopic studies, we found that the complex prepared from solution always led to a compound having solvate molecule(s) such as $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot (\text{solv})$ ($\text{solv} = \text{H}_2\text{O}, 2\text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{C}_2\text{H}_5\text{OH}$) [9]. The solvate molecule was found to be stoichiometrically incorporated in the crystal lattice [10–17]. As shown in Fig. 2, the temperature dependence of the high-spin fraction γ_{HS} determined on the basis of ^{57}Fe Mössbauer spectroscopy [9] was significantly different among these solvate complexes. When the solvate molecule is ethanol, the spin state transformation occurs rather abruptly. For the methanol solvate crystal, the spin crossover proceeds gradually over a wide temperature region. On the other hand, for the monohydrate the spin crossover was reported to be associated with broad hysteresis. If we simply define the spin transition temperature as the temperature at which γ_{HS} becomes 0.5, it is 295 K on heating for the monohydrate, while it is 204 K on cooling. In contrast to this, the dihydrate remains low-spin unless partial dehydration occurs. A noticeable influence of the non-coordinating solvate molecule $\text{C}_n\text{H}_{2n+1}\text{OH}$ on spin crossover behav-

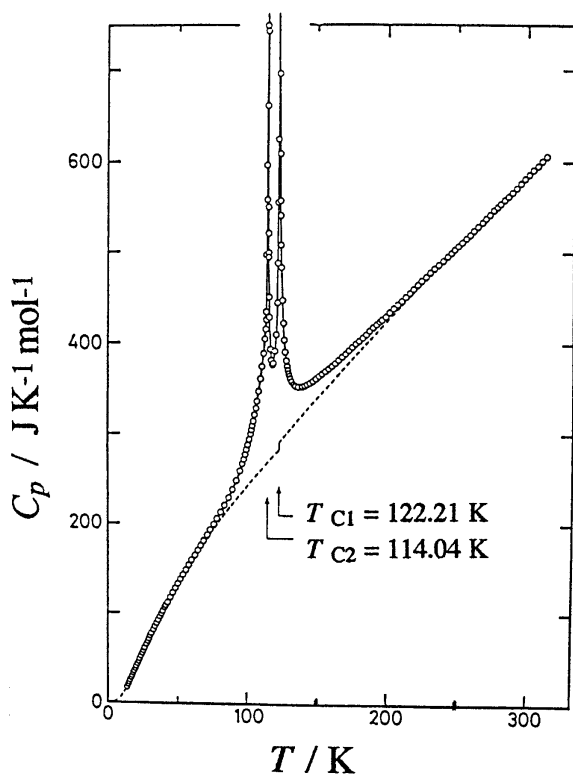


Fig. 3 Molar heat capacity of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$. Broken curves indicate the normal heat capacities [18]

ior is seen in the drastic change in the transition temperature with the number of carbon atoms n : 121.5 K for $n=2$, 153 K for $n=1$, and 295 K for $n=0$. This is accounted for in terms of a combined action of both the hydrogen-bond formation between the ligand and the intervening solvent molecule and a change in the relevant phonon system caused by different packing geometry and/or some crystallographic change.

In order to elucidate the spin crossover behavior of these complexes from energetic and entropic viewpoints, we measured their heat capacities by adiabatic calorimetry. Figure 3 shows the temperature dependence of the molar heat capacity of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ [18]. This complex exhibited two heat capacity peaks due to phase transitions at 114.04 K and 122.21 K. As the peak temperatures agree with the spin transition temperature estimated from the Mössbauer spectra, these two peaks are closely related to the spin crossover event. The observation of double peaks accords with the re-investigation of Mössbauer spectroscopy and earlier magnetic susceptibility measurements by Gütlich and his collaborators [19] showing that a two-step

spin conversion in the crossover region occurs at 114.0 K and 120.7 K. Sasaki and Kambara [20] suggested a theoretical model for the two-step spin crossover assuming a sublattice structure for the HS and LS complexes, between which a quasi “antiferromagnetic” interaction is assumed. Real et al. [21] also supported the short-range antiferromagnetic interactions as the source of step-like spin crossover. A recent interpretation by Spiering et al. [22, 23] is based on a short-range interaction which is present in addition to the long-range elastic interaction between the spin-changing molecules. A two-step spin crossover phenomenon has been found in other complexes; one recent example is seen in *tris*(4,4'-bis-1,2,4-triazole)iron(II) diperchlorate [24].

The broken curves drawn in Fig. 3 give the normal heat capacities determined by an effective frequency distribution method [25]. Integration of the excess heat capacity beyond the normal heat capacity curves with respect to T and $\ln T$ gives the enthalpy gain ΔH and the entropy gain ΔS due to the phase transition, respectively. The observed ΔS was $50.6 \text{ J K}^{-1} \text{ mol}^{-1}$, which is much larger than the entropy gain $R \ln 5$ ($=13.4 \text{ J K}^{-1} \text{ mol}^{-1}$) due to the change in the spin manifold from singlet (LS state) to quintet (HS state). The X-ray structural study [11, 14] revealed that the ethanol solvate molecule is disordered over three sites with occupancies in the ratios 3:2:2 in the HS phase. This dynamic reorientation contributes $9.0 \text{ J K}^{-1} \text{ mol}^{-1}$ [$= -R(3/7) \ln(3/7) - 2R(2/7) \ln(2/7)$] to the entropy. The remaining entropy 28.2 ($=50.6 - 13.4 - 9.0$) $\text{J K}^{-1} \text{ mol}^{-1}$ was accounted for in terms of the phonon entropy mainly due to the six fundamental skeletal vibrational modes of the $[\text{FeN}_6]$ core [18].

When the ethanol solvate molecule is substituted by methanol, the resultant crystal $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$ exhibits quite different spin crossover behavior. As illustrated in Fig. 4, this complex gives rise to a broad heat capacity peak centered around 150 K [26]. The entropy gain due to the anomaly is $59.5 \text{ J K}^{-1} \text{ mol}^{-1}$, which is of the same order of magnitude as that of the ethanol solvate complex ($50.6 \text{ J K}^{-1} \text{ mol}^{-1}$). As is now widely accepted, temperature-induced spin-crossover phenomena are classified into two principal types: one is the so-called “*abrupt type*” in which the spin state conversion between LS and HS states takes place within a narrow temperature range less than about 10 K and the other is the “*gradual type*” in which the spin crossover proceeds over a wider temperature range than 100 K. The spin crossover complex $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$ corresponds to the gradual type. Regardless of the type of spin crossover, the transition entropy largely exceeds the spin entropy due to the change in the spin manifold. The factor governing the abruptness is the degree of cooperativity associated with the spin state conversion. This subject will be discussed later.

Based on ^{57}Fe Mössbauer spectroscopy, we reported that the mono-hydrate complex $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ exhibits a spin crossover at 204 K on cooling and at 295 K on heating, manifesting a large thermal hysteresis loop

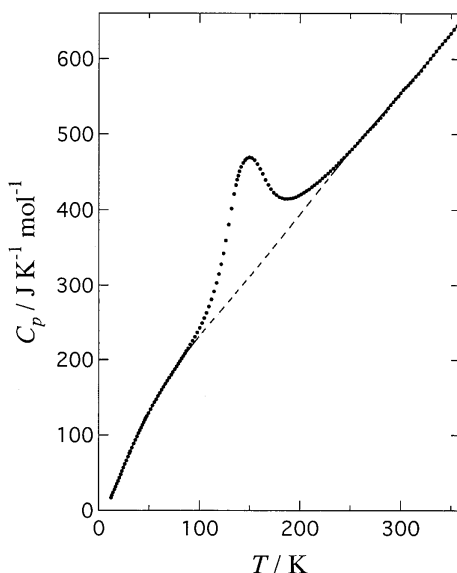


Fig. 4 Molar heat capacity of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$. Broken curve indicates the normal heat capacity [26]

of width about 90 K [9]. In order to confirm this, we recorded its thermogram by DTA (differential thermal analysis). As the result, it turned out that the thermal hysteresis is not genuine but only apparent. The cooling DTA-run for the as-grown sample always gave rise to an exothermic peak at 199 K and the immediately succeeding heating run showed an endothermic peak at 211 K, while no anomaly was observed around 295 K. This thermal behavior is quite different from that previously derived from Mössbauer spectroscopy [9]. Since the elemental analysis for C, H, and N agreed well with the calculated values, it was not likely that the different spin crossover behavior originated in differences in chemical purity. In order to resolve this anomaly we measured precisely the heat capacity of the sample by use of an adiabatic calorimeter [27].

The sample was first cooled from room temperature to 10 K. In the course of cooling, an exothermic peak due to a transition from the high-temperature HS-phase to the LS-phase was detected at 200 K. The heat capacity measurement was started for the specimen thus cooled. Although a heat capacity peak originating in the phase transition from the LS-phase to the HS-phase was actually observed around 220 K, the magnitude of this peak depended on the nature of the heat treatment applied to the specimen. When the sample was annealed around 200 K, the more or less metastable LS-phase was stabilized to the stable LS-phase with evolution of heat and, as a result, the phase transition at 220 K disappeared. Instead, as shown in

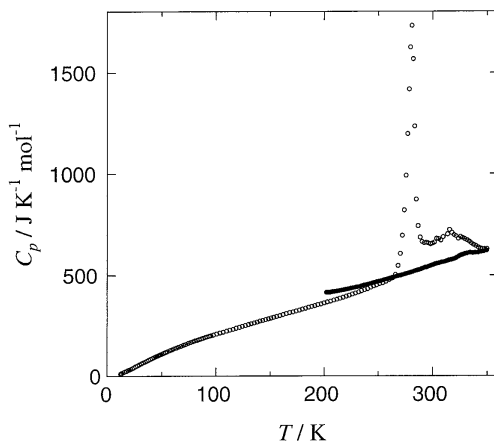


Fig. 5 Molar heat capacity of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{H}_2\text{O}$. Empty circles denote the data determined in the stable phases, while filled circles correspond to the undercooled HS-phase [27]

Fig. 5, a large heat capacity peak arising from the transition from the stable LS-phase to the stable HS-phase was observed at 280 K. This phase transition was accompanied by a broad hump centered at 320 K. The enthalpy and entropy gains due to the spin transition at 280 K and the hump at 320 K are $\Delta H = 17.1 \text{ kJ mol}^{-1}$ and $\Delta S = 59.4 \text{ J K}^{-1} \text{mol}^{-1}$. The relationships between these phases are schematically shown in Fig. 6. The phase transition at 280 K was always supercooled to about 200 K (path: $A \rightarrow B \rightarrow C \rightarrow D$) and the super-

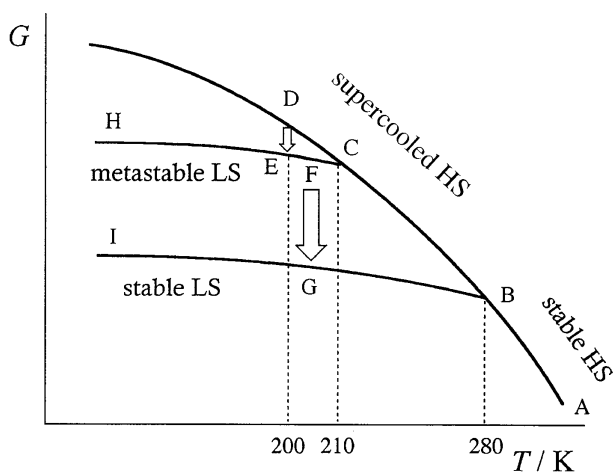


Fig. 6 Gibbs energy relationship between various LS and HS phases realized in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{H}_2\text{O}$

cooled HS-phase was transformed to the metastable LS-phase around 200 K (path: D→E). When the heating rate is high, this phase was transformed to the supercooled HS-phase at 210 K (path: E→F→C→B→A). However, when the specimen was treated slowly around this temperature region, the metastable LS-phase was stabilized to the stable LS-phase around 200 K (path: F→G). The heat capacity measurement for the specimen thus treated reflects the abrupt spin transition (and possible accompanying structural change) at 280 K [path: (I)→G→B→A]. The data shown by open circles in Fig. 5 correspond to the heat capacities for the stable phases determined along the path I→G→B→A, while the data shown by solid circles imply the heat capacities for the supercooled HS-phase along the path D→C→B→A. This new finding of the existence of the metastable LS-phase by the present calorimetric study [27] clarifies the cause of the apparent thermal hysteresis loop spanning 204 K and 295 K found in the earlier Mössbauer experiment [9]. In that experiment the cooling rate was such that the HS-phase was supercooled (beyond B) down to ca. 200 K. As the time for recording a Mössbauer spectrum (usually several hours) is much longer than the annealing time, the sample relaxed near 200 K from the metastable to the stable LS-phase (path F→G). Thus the cooling branch of the HS-fraction derived from the Mössbauer spectra as a function of temperature followed the path A→B→C→D→E→F→G→I. When the sample was heated, the Mössbauer measurements recorded always the stable LS-phase following the path I→G→B. At 280 K (B) the transition from the stable LS to the stable HS phase occurred. Thus the path I→G→B→A in the heating mode is followed in both the Mössbauer and heat capacity experiments. It is likely that at B there is both a spin change and a lattice structural change.

2.2

Influence of Metal Dilution

On the basis of precise heat capacity measurements, we have suggested that the spin transitions in $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ and $[\text{Fe}(\text{NCSe})_2(\text{phen})_2]$ are cooperative phenomena proceeding via significant coupling between the electronic state and the phonon system and that the spin conversion occurs simultaneously in a group of molecules forming a “cooperative domain” [3, 4]. For a more complete understanding of this picture of cooperative spin transitions, studies on solid solutions in which spin crossover complexes are diluted with non-crossover complexes were expected to provide useful clues. Renovitch and Baker [8] briefly reported that the chloride salt of the iron complex diluted with 85 mol% of the zinc complex, $[\text{Fe}_{0.15}\text{Zn}_{0.85}(\text{2-pic})_3]\text{Cl}_2$, exhibits magnetic behavior similar to that of the pure iron complex. In the light of this finding, we performed a Mössbauer effect study for the solid solutions $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ ($x=0.2, 0.6, 0.8, 1.0$) [28]. The spin transition temperature $T_{1/2}$ defined by the area fraction of the Mössbauer

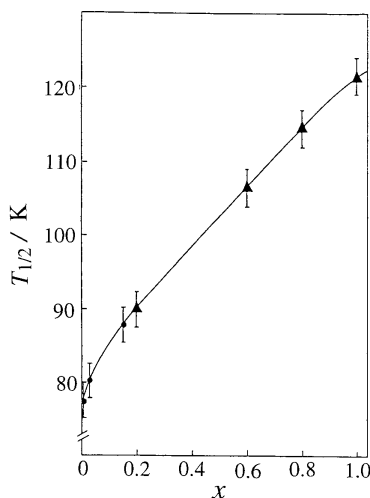


Fig. 7 Concentration dependence of the spin transition temperature ($T_{1/2}$) for $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$. (filled triangles): Sorai et al. [28], (filled circles): Gütlich et al. [29]

spectra was 121.5 K, 114.5 K, 106.5 K, and 90.0 K for the systems with $x=1.0$, 0.8, 0.6, and 0.2, respectively. A linear relation between $T_{1/2}$ and x was obtained as

$$T_{1/2}(x)/\text{K} = 40x + 82.$$

Gütlich et al. [29] extended the Mössbauer study to more diluted solid solutions having $x=0.15$, 0.029, and 0.0009. As reproduced in Fig. 7, the concentration dependence of the spin crossover temperature is almost linear and the extrapolated value of $T_{1/2}(x \rightarrow 0)$ is ca. 80 K. As discussed later, this concentration dependence originates in the phonon-assisted mechanism inherent in the spin crossover transition.

Figure 8 illustrates the excess heat capacity ΔC_p for the spin crossover transition in $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ ($x=0.66$, 0.85, 0.93, 1.00) [30]. The temperature interval of the two-step transition and the peak intensities are diminished as x is decreased. The disappearance of the step at $x \approx 0.85$ is in accordance with observations of Köhler et al. based on Mössbauer and magnetic susceptibility measurements [31]. The averaged transition temperature follows closely the equation given above. As listed in Table 1, the observed entropy gains $\Delta S(x, \text{obsd.})$ are well reproduced by the following contribution:

$$\Delta S(x)_{\text{calc}} = x(R \ln 5 + R \ln 3 + 28.24 \text{ JK}^{-1} \text{ mol}^{-1}).$$

The first term on the right hand side of the equation corresponds to the entropy due to the change in the spin manifold, the second term stands for

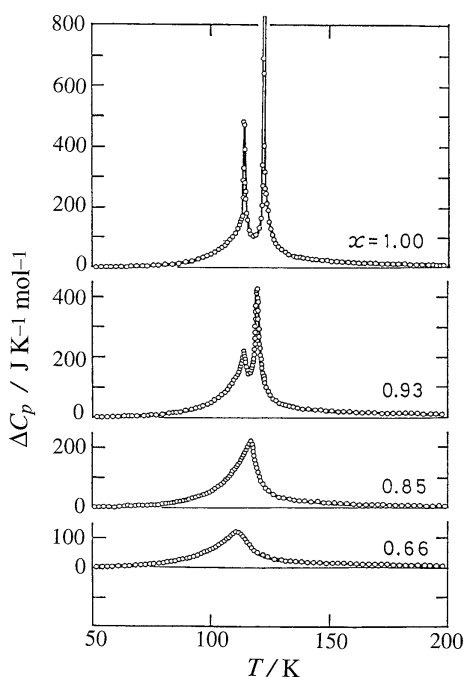


Fig. 8 Concentration dependence of the excess heat capacities arising from the spin crossover transition for $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ ($x=0.66, 0.85, 0.93, 1.00$) [30]

the configurational entropy of the ethanol solvate molecule, and the third term gives the phonon entropy due to the change in metal-ligand bond lengths. It is of great significance that both the transition temperature $T_{1/2}$ and the entropy gain $\Delta S(x)_{\text{calc}}$ show linear concentration dependence over the whole range of x . This strongly suggests that the spin crossover takes place by long-range interactions communicated through normal modes of lattice vibration [28].

Table 1 The entropy gain ΔS due to the spin crossover transition in $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ [30]

x	$\Delta S(x, \text{obsd})$	$\Delta S(x, \text{calcd})$
	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$
1.00	50.6	50.8
0.93	48.2	47.2
0.85	42.4	43.1
0.66	33.3	33.5
0.00	0.00	0.00

Similar studies on the metal dilution were made by Jakobi et al. [32, 33] for partially deuterated complexes $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic-ND}_2)_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OD}$ ($x=1.00, 0.91, 0.78, 0.68, 0.60, 0.46$) on the basis of DSC measurements and for $[\text{Fe}_{0.73}\text{Zn}_{0.27}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ based on measurements made using a relaxation microcalorimeter [34].

3

Cooperative Domain Model for Spin Crossover

As widely recognized, spin-crossover transformations can phenomenologically assume two limiting cases: one is the so-called abrupt type in which the spin-state transformation takes place abruptly within a narrow temperature range of a few Kelvin and the other is the gradual type in which the spin-crossover occurs gradually over a wide temperature range, typically greater than 100 K.

The first calorimetric measurement of the gradual type was made for the iron(III) spin crossover complex $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ [$\text{Hacpa}=\text{N}-(1\text{-acetyl-iso-propylidene}) (2\text{-pyridylmethyl}) \text{ amine}$] [35]. This complex shows fast electronic relaxation between ${}^2\text{T}_{2g}$ ($S=1/2$) and ${}^6\text{A}_{1g}$ ($S=5/2$) in comparison with the ${}^{57}\text{Fe}$ Mössbauer lifetime (10^{-7} s). As reproduced in Fig. 9, an unusually broad heat capacity peak ranging from 120 K to 280 K was observed. The

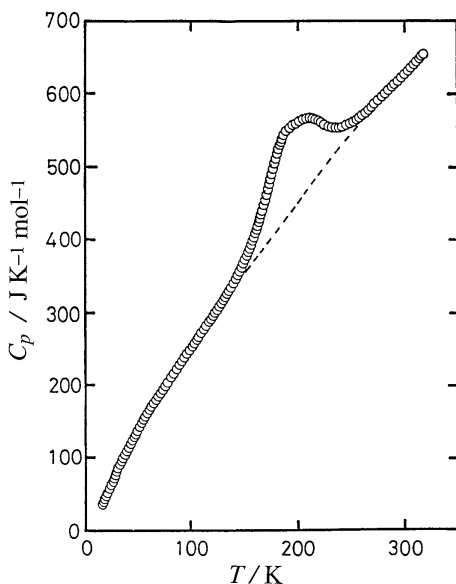


Fig. 9 Molar heat capacity of $[\text{Fe}(\text{acpa})_2]\text{PF}_6$. The *broken curve* stands for the normal heat capacity [35]

Frenkel Theory of Heterophase Fluctuations in Liquids

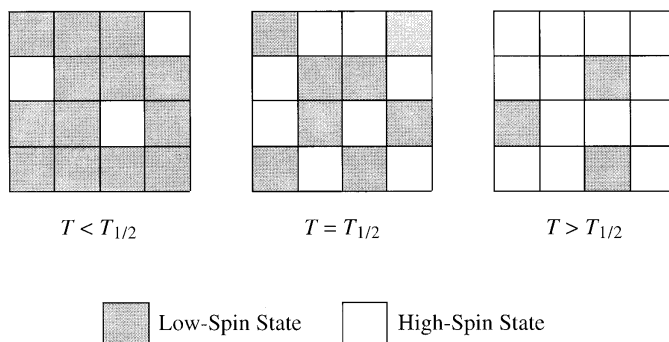


Fig. 10 Schematic drawing of the domain model. The crystal lattice is considered to consist of domains of uniform size containing equal numbers of spin-crossover complexes. $T_{1/2}$ is the transition temperature at which the number of LS domains becomes equal to that of HS domains

enthalpy and entropy arising from the spin crossover phenomenon were 7.03 kJ mol^{-1} and $36.2 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The entropy gain was well accounted for in terms of the sum ($37.7 \text{ J K}^{-1} \text{ mol}^{-1}$) of the contributions from the change in the spin manifold $R \ln(6/2)$ ($=9.1 \text{ J K}^{-1} \text{ mol}^{-1}$) and from a change in the skeletal normal modes of vibration detected by IR and Raman spectra ($28.6 \text{ J K}^{-1} \text{ mol}^{-1}$). To elucidate the reason for the gradual spin state conversion, Sorai and Seki [4] proposed in 1974 a simple domain model based on the Frenkel theory [36] of heterophase fluctuations in liquids. As schematically shown in Fig. 10, this model assumes that a crystal lattice consists of non-interacting domains with uniform size containing n complexes and that the spin state conversion in each domain takes place simultaneously. This assumption of independent domains is obviously a consequence of the nucleation-and-growth mechanism inherent in the first-order phase transition. As the number n is decreased, the heat capacity peak due to the spin crossover becomes broader and the cooperativity of the transition becomes weaker. When n takes the extreme value of unity, the system simply corresponds to a chemical equilibrium described by the van't Hoff scheme. Evidence for the existence of such domains was obtained for $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ based on EPR measurements in 1990 by Doan and McGarvey [37]. The number of complexes n in a domain estimated for $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ on the basis of this model was only five, which makes a sharp contrast to 95 and 77 found for the abrupt type complexes $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$ and $[\text{Fe}(\text{NCSe})_2(\text{phen})_2]$ [4], respectively, and 2000 for $[\text{CrI}_2(\text{depe})_2]$ [depe =1,2-bis(diethylphosphino)ethane] [38]. In the case of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$, the excess heat capacity ΔC_p is well reproduced by

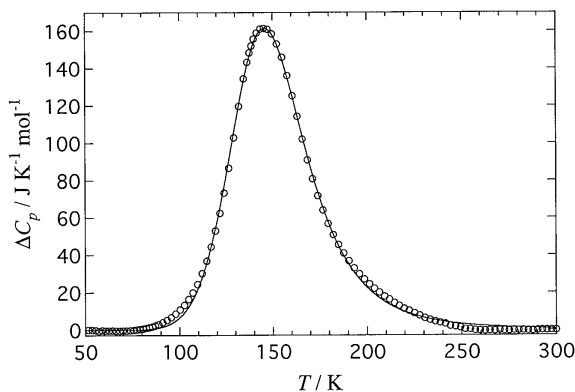


Fig. 11 Excess heat capacity arising from the spin crossover in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$ [26]

the domain model with $n=1.5$ (Fig. 11) [26]. This small number of complexes per domain implies that the cooperativity in this complex is extremely weak or absent.

A homologous series of iron(III) complexes $[\text{Fe}(\text{3EtO-salAPA})_2]\text{ClO}_4 \cdot (\text{solv})$ ($\text{solv} = \text{C}_6\text{H}_6$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, or $o\text{-C}_6\text{H}_4\text{Cl}_2$) provides us with an interesting example of the gradual type spin crossover, where 3EtO-salAPAH is

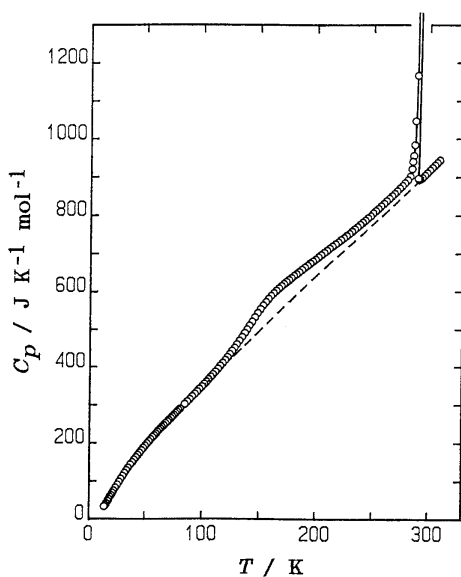


Fig. 12 Molar heat capacity of $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{Br}$. The broken curve indicates the normal heat capacity [6, 43]

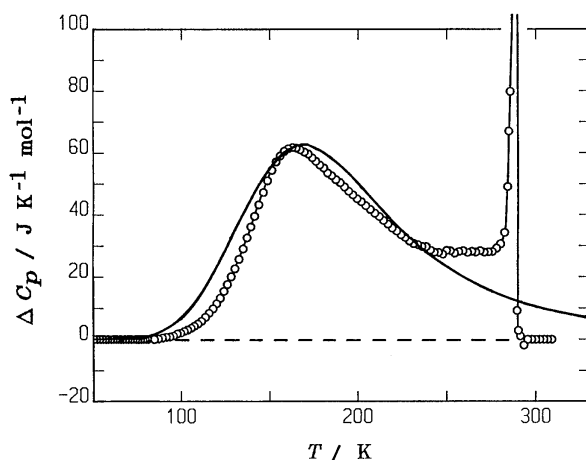


Fig. 13 Excess heat capacity of $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{Br}$. The *solid curve* represents the theoretical curve based on the van't Hoff equation with $\Delta H = 8.21 \text{ kJ mol}^{-1}$ and $\Delta S = 42.7 \text{ J K}^{-1} \text{ mol}^{-1}$, while the observed values are $\Delta H = 7.99 \text{ kJ mol}^{-1}$ and $\Delta S = 40.4 \text{ J K}^{-1} \text{ mol}^{-1}$ [6, 43]. The *solid line* connecting the observed points shown by *empty circles* is given merely to assist clarity

the Schiff base condensed from 1 mol of 3-ethoxysalicylaldehyde with 1 mol of *N*-aminopropylaziridine. The effective magnetic moments [39] of these complexes indicate very gradual spin-state transformation over a wide temperature region. In accordance with this feature, the complexes show very broad heat capacity anomalies [40–43]. Figure 12 shows the temperature dependence of the molar heat capacity of the bromobenzene solvate complex. As is expected from the temperature dependence of the magnetic moment [39, 40], a very broad heat capacity anomaly is observed for this complex, centered around 165 K. A peak at 288.3 K originates in the structural change detected by X-ray diffraction analysis [40]. Excess heat capacity of $[\text{Fe}(\text{3EtO-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{Br}$ beyond the normal value is shown in Fig. 13. The thermodynamic quantities associated with the broad anomaly and the phase transition at 288.3 K are $\Delta H = 7.99 \text{ kJ mol}^{-1}$ and $\Delta S = 40.4 \text{ J K}^{-1} \text{ mol}^{-1}$. Of the observed entropy gain, the contribution from the change in the spin manifold is only $R \ln(6/2) = 9.13 \text{ J K}^{-1} \text{ mol}^{-1}$. As in the case of other spin crossover complexes, the main part of the remaining entropy can be accounted for in terms of the phonon entropy and a small contribution from the structural change.

Let us consider here the cooperativity inherent in the spin-state interconversion. In a dilute solution of spin-crossover complexes, the equilibrium between HS and LS states is governed by the Boltzmann distribution function. In the solid state, however, the existence of intermolecular interactions leads to a more or less cooperative nature of the spin crossover. We consider

now a system in which LS and HS species are in thermal equilibrium. When the HS fraction is γ_{HS} , the LS fraction becomes $(1-\gamma_{\text{HS}})$. The equilibrium constant K is defined by the following equation:

$$K = [\gamma_{\text{HS}}] / [1 - \gamma_{\text{HS}}].$$

The high-spin fraction γ_{HS} can be derived from the experimental magnetic moment μ_{eff} based on the equation

$$\mu_{\text{eff}}(\text{exptl})^2 = \gamma_{\text{HS}} \cdot \mu_{\text{eff}}(\text{HS})^2 + (1 - \gamma_{\text{HS}}) \mu_{\text{eff}}(\text{LS})^2.$$

By substituting the HS fraction γ_{HS} in K with the values determined by this equation, one can determine the value of K as a function of temperature. A plot of $\ln K$ against $1/T$ for the present complex provided a straight line. This indicates that the spin crossover can be described by a simple equilibrium scheme, corresponding to the van't Hoff equation:

$$\ln K = -\Delta G/RT = -\Delta H/RT + \Delta S/R,$$

where ΔG is the Gibbs energy difference between the HS and LS states, ΔH the enthalpy difference, and ΔS the entropy difference. A least-squares fitting procedure gave $\Delta H = 8.21 \text{ kJ mol}^{-1}$ and $\Delta S = 42.7 \text{ J K}^{-1} \text{ mol}^{-1}$. These values are very close to the values determined calorimetrically: $\Delta H = 7.99 \text{ kJ mol}^{-1}$ and $\Delta S = 40.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

The excess heat capacity arising from such an equilibrium system can be derived from the following equation:

$$\Delta C_p = d(\gamma_{\text{HS}} \cdot \Delta H) / dT = (\Delta H)^2 \exp(-\Delta H/RT + \Delta S/R) / \{RT^2 [1 + \exp(-\Delta H/RT + \Delta S/R)]^2\}.$$

The observed heat capacity anomaly of $[\text{Fe}(\text{3EtO-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{Br}$ is compared with the calculated value in Fig. 13. The former is given by empty circles while the latter is given by the solid curve. The broad anomaly centered around 165 K can be satisfactorily reproduced by the van't Hoff equation. In other words, the gradual type spin-state transformation in the present complex occurs as a simple equilibrium scheme without any significant cooperativity. That the spin crossover can proceed non-cooperatively rationalizes the experimental result described above that the iron spin-crossover complex highly diluted with the zinc analogue $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ ($x=0.0009$) still exhibits a spin-state conversion as seen by Mössbauer spectroscopy [29].

4 Concluding Remarks

Heat capacity is a physical quantity containing contributions from all kinds of molecular degrees of freedom according to the Maxwell-Boltzmann distribution. This is in contrast with various spectroscopies in which a particular nuclide and/or particular modes are selectively sensed. In other words, thermodynamic measurements are not restricted by any selection rules or other selectivity. Consequently calorimetric studies are applicable to a wide range of materials and phenomena.

Modern research tends to be greatly specialized in an individual field of study. Therefore, better understanding of materials and/or natural phenomena would be achieved by employing experimental techniques which make complementary contributions to experiments leading to microscopic aspects and to those leading to macroscopic aspects. The application of calorimetry to the study of the spin crossover phenomenon has indeed complemented studies by other techniques and has provided a solid experimental basis to a theoretical understanding of the phenomenon.

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Elastic Interaction in Spin Crossover Compounds

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Abstract The derivation of the Gibbs free energy of a spin crossover system in terms of the mean field approximation of the interacting molecules involves an interaction constant and an energy term which are together proportional to the fraction of spin changing molecules and of the order of 10^2 cm^{-1} for concentrated mononuclear compounds. Using the concept of elastic dipole defects for the spin crossover molecules, which change their size and the shape on going from one spin state to the other, the contributions of long range elastic interactions to the interaction constant and the energy shift are calculated. The right order of magnitude of these quantities, their ratio and their proportionality to the fraction of spin changing molecules is well reproduced by approximating the crystal to a homogeneous isotropic elastic medium. A further contribution originates from the dependence of the elastic constants on the deformation of the crystal. This is treated using the Grüneisen approximation. The origin of large short range interactions observed in one- and two-dimensional networks is briefly discussed. The results for the compounds which were studied in some detail and the applied dipole concept are presented.

Keywords Elasticity · Elastic dipole · Elastic interaction · Point defects · Infinite range interaction

List of Abbreviations and Symbols

A_{ij}	General interaction tensor
k_B	Boltzmann constant
s_{mix}	Mixing entropy per molecule
$\Delta f_{HI}(T)$	Free energy difference $f_{HS}(T) - f_{LS}(T)$ per molecule
Δ	Energy separation between HS and LS states
Δ_{image}	‘Image’ contribution to Δ
Δ_{elect}	Electronic energy contribution to Δ
Δ_{elast}	Elastic energy contribution to Δ
e	Elastic energy per molecule
e_{self}	Elastic self energy per molecule
e_α	Elastic energy of defect type $\alpha=HS, LS, M$
E_{d_int}	Elastic energy of direct interaction
E_{self}	Total elastic self energy
$e_{self, M}^\alpha$	Elastic self energy of defect type α and strain component M
ε_{ik}	Deformation (strain) tensor; Cartesian coordinates ($i=x, y, z$)
ε_M	Spherical coordinates ($M=-2, 1, \dots, 2$)
ε_M	Spherical coordinates, real components ($M=-2c, 1c, 0, 1s, 2s$)
$F(T, \gamma_{HS})$	Free energy of an ensemble of N molecules
$f_\alpha(T)$	Free energy per molecule of molecules in the α -states
γ_{HS}	Fraction of molecules in the HS state
Γ	Interaction constant
Γ_{image}	‘Image’ contribution to the interaction
γ_0	Eshelby constant
γ_G	Grüneisen constant
HS	High spin
K	Bulk modulus
K_0	$K(V_0)$ at volume V_0
LS	Low spin
P_i	General elastic dipole tensor at lattice site i
P^α	Elastic dipole tensor of α -molecules ($\alpha=HS, LS, M$)
σ	Poisson ratio
$V(T)$	Volume of the crystal containing N molecules
V_0	Volume of the crystal at temperature $T=T_0$
v_m	Crystal volume per molecule (V/N)
v_0	Volume provided by the crystal for a molecule
v_α	Volume taken by α -molecules ($\alpha=HS, LS, M$)
$V(R), W(R)$	Average tensors of direct interaction
x	Concentration of spin changing molecules
$Y_{km}(\theta, \phi)$	Spherical harmonics
Z_α	Partition function of molecules in the α -states ($T, \alpha=HS, LS$)

1

Introduction

The fraction γ_{HS} of isolated non-interacting spin crossover molecules in the HS state is determined by the Boltzmann population. The approximation is used that the molecule has only HS and LS states thermally populated and all other vibronic spin states are sufficiently high in energy so that their thermal population is negligible. In this case the fraction γ_{HS} can be expressed by the partition functions $Z_\alpha(T)$ of the $\alpha=HS$ and LS states:

$$\gamma_{HS}(T) = \frac{Z_{HS}(T)}{Z_{HS}(T) + Z_{LS}(T)} \quad (1)$$

The HS fraction γ_{HS} can be measured using different methods [1-3]. Defining the corresponding free energies $f_\alpha = -k_B T \cdot \ln Z_\alpha(T)$ of an ensemble of molecules in the HS and LS state, the difference $\Delta f_{HL}(T) = f_{HS}(T) - f_{LS}(T)$ of the free energies per complex molecule is directly obtained from $\gamma_{HS}(T)$:

$$\Delta f_{HL}(T) = -k_B T \cdot \ln \left(\frac{\gamma_{HS}(T)}{1 - \gamma_{HS}(T)} \right) \quad (2)$$

The difference $\Delta f_{HL}(T)$ of the free energies can be changed by embedding the spin crossover molecules in different host matrices of the corresponding metal compounds with $M=Zn, Co$. The explanation for the observed energy shift is the work term arising from the increase of the metal-to-donor atom bond length on going from LS to the HS state of the molecule. This results in an overall expansion of the molecule against the elastic forces of the lattice.

The free energy F of an ensemble of N molecules diluted in different systems is that of a binary mixture of HS and LS molecules with mixing entropy $s_{mix} = -k_B(\gamma_{HS} \ln \gamma_{HS} + (1 - \gamma_{HS}) \ln(1 - \gamma_{HS}))$:

$$F(T, \gamma_{HS}) = N\gamma_{HS}f_{HS} + N(1 - \gamma_{HS})f_{LS} - TNs_{mix}(\gamma_{HS}) + N\Delta\gamma_{HS} \quad (3)$$

The minimum of $f(T, \gamma_{HS})$ with respect to γ_{HS} leads to the Boltzmann population of Eq. 1. The energy shift Δ per molecule accounts for different host matrices. In the case of the picolylamine complex $[Fe(pic)_3]^{2+}$ the values of Δ range from a few to ca. 10^3 cm^{-1} [1]. The number N drops out of the equations if the free energy per molecule $f = F/N$ is considered.

There are several examples [4-6] of mixed crystal series of mononuclear compounds where a simple extension of the free energy by an interaction term $-x\Gamma\gamma_{HS}^2$ gives a satisfying description of the transition curves $\gamma_{HS}(T)$ over the whole concentration range $0 < x \leq 1$ of spin crossover molecules:

$$f(T, \gamma_{HS}) = \gamma_{HS}\Delta f_{HL} - Ts_{mix}(\gamma_{HS}) + x\Delta\gamma_{HS} - x\Gamma\gamma_{HS}^2 \quad (4)$$

The energy shift $x\Delta$ and the interaction constant $x\Gamma$ are proportional to the concentration x . The free energy of the LS state $f_{LS}(T)$ has been omitted in Eq. (4) as terms independent of γ_{HS} do not contribute to the transition curve. When the free energy difference $\Delta f_{HL}(T)$ for the highly diluted case $x \rightarrow 0$ is known there are only two parameters, Δ and Γ , remaining to describe the $\gamma_{HS}(T)$ curves for the whole mixed crystal series. The origin of these two parameters and their dependence on the crystal properties is the topic of this contribution.

Three different kinds of molecules in mixed crystals, the spin changing molecules in two spin states HS and LS and the molecules with other metal centers M, yield six types of pair interactions: (HS,HS), (HS,LS), (HS,M), (LS,LS), (LS,M), (M,M) depending on the distance between the interacting species, while Eq. (4) has only one interaction constant $x\Gamma$. As the interaction energy is proportional to γ_{HS}^2 , it is interpreted as the interaction between HS molecules in the mean field approximation. Below we consider general two-center-interactions in the mean field approximation, in order to throw some light on the description with only one interaction constant.

The changes of size and shape of the molecules on going from the LS to the HS state necessarily induce strain fields in the crystal. The deformation of the crystal has been shown for several examples to be proportional to the fraction of molecules in the HS state [5, 7, 8]. With application of the concept of elastic point dipoles [9] contributions to the interaction constant are calculated by approximating the crystal to a homogeneous isotropic medium. Elasticity theory is structured such that the interaction is calculated by several independent steps. The theory starts with an infinite medium. Then the consequence of the free surface of the finite medium is considered. Closed solutions are available only for a spherical surface. The treatment of the point defects and their elastic fields by expansion in spherical harmonics allows a further separation of the whole problem. The spherical part which is the volume change by the defect and the second rank tensor which describes the change of shape separates the problem further. Correspondingly, later sections deal with the independent contributions to the interaction.

The dependence of the elastic properties on the deformation of the crystal, especially the volume change, leads to another source of interaction between the spin changing molecules. However, this turns out to be difficult to estimate as discussed below. Two examples which were studied to considerable extent by applying the theoretical results are given later.

2

Mean-Field-Approximation of Two Center-Interactions

Any interaction energy between two interacting objects at lattice sites i and j in the crystal can be expressed by an expansion series which is a sum of

terms $\mathbf{P}_i \mathbf{A}_{ij} \mathbf{P}_j^\dagger$, where $\mathbf{P}$ and $\mathbf{A}$ are generally tensors of increasing rank. The object at site i has the property $\mathbf{P}_i$. $\mathbf{A}_{ij}$ depends on the distance between sites i, j . In the case of exchange interaction between two magnetic ions with spin S_i and S_j , for instance, the spin represents the property and $\mathbf{A}_{ij}$ the exchange integral of the electron wavefunctions. If s-electrons dominate, the tensor $\mathbf{A}_{ij}$ reduces to a scalar. The general case is a $(2S_i+1)(2S_j+1)$ matrix for $\mathbf{A}_{ij}$. In elasticity theory the interaction energy of point defects is considered. The quantities $\mathbf{P}$ and $\mathbf{A}$ are second and fourth rank tensors, respectively. $\mathbf{P}_i \mathbf{A}_{ij} \mathbf{P}_j^\dagger$ describes the interaction between two elastic dipoles. As in Ising systems of spin $S = \frac{1}{2}$, the quantities $\mathbf{P}$ in a spin crossover system have two values $\mathbf{P}^{HS}$ and $\mathbf{P}^{LS}$ for the HS and LS states, respectively. Both kinds of molecules (HS and LS) are described by point defects implying a misfit of the molecules to the lattice. The misfit of a molecule to its own lattice is not experimentally accessible. Even if, e.g., the HS molecule fits perfectly to the lattice, the LS molecule will not.

The interaction energy between all molecules is the double sum:

$$E = \frac{1}{2} \sum_{i \neq j} \mathbf{P}_i \mathbf{A}_{ij} \mathbf{P}_j^\dagger \quad (5)$$

The difference of point defect tensors $\mathbf{P}^{HS} - \mathbf{P}^{LS}$ can be obtained from the deformation of the crystal on going from the LS to the HS state and the elastic constants of the crystal [10], as will be described later. In order to deal with measurable quantities the general double sum of Eq. (5) is rearranged by introducing the tensor difference $\mathbf{P}^{HL} = \mathbf{P}^{HS} - \mathbf{P}^{LS}$. The sum over all lattice sites N ($i, j = 1, \dots, N$) is split by summing separately over the sites N_{HS}, N_{LS} in the HS and LS state, respectively, with indices i_{HS}, i_{LS} . In Eq. (6) the three sums corresponding to interactions between (HS,HS), (HS,LS), and (LS,LS) molecules is expressed by three new sums:

$$\begin{aligned} E &= \frac{1}{2} \sum_{i_{HS} \neq j_{HS}} \mathbf{P}_{i_{HS}}^{HS} \mathbf{A}_{i_{HS}j_{HS}} \mathbf{P}_{j_{HS}}^{HS\dagger} + \sum_{i_{HS}j_{LS}} \mathbf{P}_{i_{HS}}^{HS} \mathbf{A}_{i_{HS}j_{LS}} \mathbf{P}_{j_{LS}}^{LS\dagger} + \frac{1}{2} \sum_{i_{LS} \neq j_{LS}} \mathbf{P}_{i_{LS}}^{LS} \mathbf{A}_{i_{LS}j_{LS}} \mathbf{P}_{j_{LS}}^{LS\dagger} \\ &= \frac{1}{2} \sum_{i_{HS} \neq j_{HS}} \mathbf{P}_{i_{HS}}^{HL} \mathbf{A}_{i_{HS}j_{HS}} \mathbf{P}_{j_{HS}}^{HL\dagger} + \sum_{i_{HS} \neq j} \mathbf{P}_{i_{HS}}^{HL} \mathbf{A}_{i_{HS}j} \mathbf{P}_j^{LS\dagger} + \frac{1}{2} \sum_{i \neq j} \mathbf{P}_i^{LS} \mathbf{A}_{ij} \mathbf{P}_j^{LS\dagger} \end{aligned} \quad (6)$$

In the derivation of this equation the equality $\sum \mathbf{P}_{i_{HS}}^{LS} \mathbf{A}_{i_{HS}j_{LS}} \mathbf{P}_{j_{HS}}^{HS\dagger} = \sum \mathbf{P}_{i_{HS}}^{HS} \mathbf{A}_{i_{HS}j_{LS}} \mathbf{P}_{j_{HS}}^{LS\dagger}$ has been used. The first term has the shape of an interaction between all sites which are in the HS state, however, the interacting property is not that of a HS molecule but the difference of the point defect tensors of the HS and LS molecules. The third term, which runs over all lattice sites ($i, j = 1, \dots, N$) with $\mathbf{P}^{LS}$ attached to each site, is a constant contributing

only to the energy reference level. The second double sum involves the interaction energies of the difference tensor at each HS site with a background of LS point defects at all other sites in the crystal. For an ‘infinite’ crystal this energy does not depend on the individual HS site (i_{HS})—the case of equivalent sites of the unit cell is considered— so that this term is proportional to the number of sites in the HS state. Such a term represents an energy shift between the HS and the LS states.

In the case of mixed crystal systems containing, in addition to the spin crossover molecules, molecules containing the metal ion M , there are six interaction terms which have to be rearranged. The energy shift is the same, but the interaction between sites in the HS state and metal sites M with the quantities $\mathbf{P}^{HL}$ and $\mathbf{P}^{ML} = \mathbf{P}^M - \mathbf{P}^{LS}$, respectively, have to be considered. $\mathbf{P}^{ML}$ is also experimentally accessible by comparison of the unit cells of the pure HS and LS compound with the one containing only M . The interaction energy is written as

$$E = \frac{1}{2} \sum_{i_{HS} \neq j_{HS}} \mathbf{P}_{i_{HS}}^{HL} \mathbf{A}_{i_{HS}j_{HS}} \mathbf{P}_{j_{HS}}^{HL\dagger} + \sum_{i_{HS}j_M} \mathbf{P}_{i_{HS}}^{HL} \mathbf{A}_{i_{HS}j_M} \mathbf{P}_{j_M}^{ML\dagger} + \sum_{i_{HS} \neq j} \mathbf{P}_{i_{HS}}^{HL} \mathbf{A}_{i_{HS}j} \mathbf{P}_j^{LS\dagger} \\ + \frac{1}{2} \sum_{i_M \neq j_M} \mathbf{P}_{i_M}^{ML} \mathbf{A}_{i_Mj_M} \mathbf{P}_{j_M}^{ML\dagger} + \sum_{i_M \neq j} \mathbf{P}_{i_M}^{ML} \mathbf{A}_{i_Mj} \mathbf{P}_j^{LS\dagger} + \frac{1}{2} \sum_{i \neq j} \mathbf{P}_i^{LS} \mathbf{A}_{ij} \mathbf{P}_j^{LS\dagger} \quad (7)$$

The last three terms in Eq. (7) obviously do not change if the number N_{HS} of molecules in the HS state and/or the indices i_{HS} of molecular sites in the HS state change and therefore represent a constant energy shift.

In the mean field or Bragg Williams approximation each site interacts with the average property attributed to all other sites. The average of $\mathbf{P}$ of a fraction x of spin changing molecules of which a fraction γ_{HS} is in the HS state is given by $\bar{\mathbf{P}} = x(\gamma_{HS}\mathbf{P}^{HS} + (1 - \gamma_{HS})\mathbf{P}^{LS}) + 1(1 - x)\mathbf{P}^M$. Starting with Eq. (5),

$$E = \frac{1}{2} \sum_{i \neq j} \mathbf{P}_i \mathbf{A}_{ij} \mathbf{P}_j^\dagger = \frac{1}{2} \sum_i \mathbf{P}_i \left(\sum_{j \neq i} \mathbf{A}_{ij} \right) \mathbf{P}_i^\dagger \quad (8)$$

For an ‘infinite’ lattice with all sites being equivalent the sum over j does not depend on the index i . With the abbreviation $\mathbf{A}_\Sigma = \sum_j \mathbf{A}_{ij}$ and the use of $\bar{\mathbf{P}} = x(\gamma_{HS}\mathbf{P}^{HS} + (1 - \gamma_{HS})\mathbf{P}^{LS}) + 1(1 - x)\mathbf{P}^M$, Eq. (8) becomes $N\bar{\mathbf{P}} = \sum_i \mathbf{P}_i$ where the superscript MF standing for ‘Mean Field’ has been added. In the following Eq. (9) the average $\bar{\mathbf{P}}$ is inserted:

$$E^{MF} = N \frac{1}{2} \left[x^2 \gamma_{HS}^2 \mathbf{P}^{HL} \mathbf{A}_\Sigma \mathbf{P}^{HL\dagger} + x(1 - x) \gamma_{HS} (\mathbf{P}^{HL} \mathbf{A}_\Sigma \mathbf{P}^{ML\dagger} + \mathbf{P}^{ML} \mathbf{A}_\Sigma \mathbf{P}^{HL\dagger}) + x \gamma_{HS} (\mathbf{P}^{HL} \mathbf{A}_\Sigma \mathbf{P}^{LS\dagger} + \mathbf{P}^{LS} \mathbf{A}_\Sigma \mathbf{P}^{HL\dagger}) + ((1 - x) \mathbf{P}^{ML} - \mathbf{P}^{LS}) \mathbf{A}_\Sigma ((1 - x) \mathbf{P}^{ML\dagger} - \mathbf{P}^{LS\dagger}) \right] \quad (9)$$

Typically the energy correction $e=E^{MF}/Nx$ per spin changing molecule is considered where the energy terms independent of γ_{HS} are dropped as constant energy shifts:

$$e = \frac{1}{2} \left[x \mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger} \gamma_{HS}^2 - x (\mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{ML\dagger} + \mathbf{P}^{ML} \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger}) \gamma_{HS} + (\mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{M\dagger} + \mathbf{P}^M \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger}) \gamma_{HS} \right] \quad (10)$$

The square of the HS fraction γ_{HS} has been loosely associated an interaction between HS sites, or HS-HS interaction. Rewriting this expression according to Eq. (11) justifies the consideration of a HS-LS interaction, since the product $\gamma_{HS}(1-\gamma_{HS})$ of HS and LS fraction is part of the interaction energy and the term proportional to the HS fraction has changed accordingly:

$$e = \frac{1}{2} \left[x \mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{LH\dagger} \gamma_{HS}(1-\gamma_{HS}) + x (\mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{HM\dagger} + \mathbf{P}^{HM} \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger}) \gamma_{HS} + (\mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{M\dagger} + \mathbf{P}^M \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger}) \gamma_{HS} \right] \quad (11)$$

Strictly speaking, the interaction constants $\frac{1}{2} \mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{HL\dagger} = -\frac{1}{2} \mathbf{P}^{HL} \mathbf{A}_{\Sigma} \mathbf{P}^{LH\dagger}$ have not only opposite signs, but must differ in their absolute values by a factor of 2. The reason is that double counting of interaction paths between LS and HS sites does not occur. It is obvious from these considerations that the phrases, *HS-HS interaction* and *HS-LS interaction*, attached to the interaction energy do not meet the true physical background, which takes into account the interactions between all lattice sites.

The phenomenologically introduced interaction energy for mixed crystal systems

$$e = -x\Gamma\gamma_{HS}^2 + x\Delta\gamma_{HS} + \Delta_{HL}\gamma_{HS}$$

represents the general expression in mean field theory. The coefficients of $x\gamma_{HS}^2$, $x\gamma_{HS}$, and γ_{HS} are interpreted by Eq. (10).

3 Elastic Interaction Between Spheres

In this section the molecules are approximated by spheres of volumes v_{HS} , v_{LS} and v_m . The misfit of the molecules to the crystal lattice is expressed by $v_{\alpha}-v_0$, where $\alpha=LS,HS,M$ and the volume v_0 represents the volume fitting to the lattice site, i.e., the volume provided by the lattice for its molecules. In the case of an isotropic and homogeneous medium the elastic energy needed to extend or shrink the volume v_0 to that of v_{α} given by [9]

$$e_\alpha = \frac{1}{2}K(\gamma_0 - 1) \frac{(v_\alpha - v_0)^2}{v_0} - \frac{1}{2}K\gamma_0(\gamma_0 - 1) \frac{(v_\alpha - v_0)^2}{V} \quad (12)$$

The isotropic and homogeneous elastic medium is described by two elastic constants, the bulk modulus K and the Poisson ratio $0 \leq \sigma \leq \frac{1}{2}$. Eshelby introduced the constant $\gamma_0 = 3(1-\sigma)/(1+\sigma)$ (Eshelby constant) the meaning of which will be given later. The volume V is the volume of the crystal, so that V/v_0 is of the order of Avogadro's number. Both energy contributions in Eq. (12) depend on the square of the volume misfit, so that the sign of the misfit is irrelevant in this context.

The second term vanishing in an infinite medium corrects for the effect of a free surface of the crystal. It is interpreted as the volume work against an image pressure on the surface of the crystal. The image pressure is the result of the volume change of the crystal Δv_α upon incorporation of v_α :

$$\Delta v_\alpha = \gamma_0(v_\alpha - v_0) \quad (13)$$

which is larger by the factor $1 \leq \gamma_0 \leq 3$ [9] than the misfit volume $v_\alpha - v_0$. The additional volume change $\Delta v_\alpha - (v_\alpha - v_0) = (\gamma_0 - 1)(v_\alpha - v_0)$ is formally attributed to a pressure $p_I = -K(\gamma_0 - 1)(v_\alpha - v_0)/V$. The second term is then the integral of $p_I \gamma_0 dv$, where dv is the volume changing from v_0 to v_α inside the crystal and $\gamma_0 dv$ the change observed at the surface of the crystal on which the image pressure acts:

$$\begin{aligned} \int_{v_0}^{v_\alpha} p_I \gamma_0 dv &= -K\gamma_0(\gamma_0 - 1) \left(\frac{1}{2}v^2 - v_0 v \right) \Big|_{v_0}^{v_\alpha} \\ &= -\frac{1}{2}K\gamma_0(\gamma_0 - 1)(v_\alpha - v_0)^2 / V = \frac{1}{2}p_I \Delta v_\alpha \end{aligned} \quad (14)$$

Pressure is independent of the location on the surface, as assumed for the integration of Eq. (14), only for spherical symmetry, i.e., a spherical defect at the center of a spherical crystal. Eshelby, however, could show that Δv_α remains valid irrespective of the shape of V and the position of the defect. For a homogeneous distribution of defects over the volume V the pressure is again independent of their location on the surface. The pressure is positive, when ions with $v_\alpha < v_0$ are incorporated, and negative for larger volumes $v_\alpha > v_0$. This effect is used for the creation of positive or even negative pressures by replacing atoms in the crystal with smaller or larger foreign atoms. The term "chemical pressure" is therefore in use. Although small for one defect, for one mole of defects (in spin crossover compounds every metal lattice site is treated as a defect) the pressure adds up to a finite entity which acts on all defects. For N sites in a crystal (defects in an isotropic homogeneous elastic medium) the total elastic energy is not simply the sum of e_α , but becomes

$$E = \frac{1}{2}K(\gamma_0 - 1) \sum_{i=1}^N (v_i - v_0)^2 / v_0 - \frac{1}{2}K\gamma_0(\gamma_0 - 1) \left[\sum_{i=1}^N (v_i - v_0) \right]^2 / V \quad (15)$$

The second term, the energy correction due to the free surface, does not sum the squares of the misfits $v_i - v_0$ but squares the sum of the misfits. The simple proof by complete induction gives a good insight into the mechanism of the interaction. Calculating the volume work of the N+1 defect, two contributions have to be added, the work against the image pressure p_I^N of N defects already present and the integration for the N+1 defect:

$$\begin{aligned} E = & \frac{1}{2}K(\gamma_0 - 1) \sum_{i=1}^{N+1} (v_i - v_0)^2 / v_0 - \frac{1}{2}K\gamma_0(\gamma_0 - 1) \left[\sum_{i=1}^N (v_i - v_0) \right]^2 / V \\ & - K(\gamma_0 - 1) \left[\sum_{i=1}^N (v_i - v_0) \right] / V \cdot \gamma_0(v_{N+1} - v_0) \\ & - \frac{1}{2}K\gamma_0(\gamma_0 - 1)(v_{N+1} - v_0)^2 / V \end{aligned} \quad (16)$$

Collecting the three energy terms gives just the square of the sum of N+1 defects which proves the validity of Eq. (15).

If the sums in Eq. (15) are expressed by the fraction x and γ_{HS} ,

$$\begin{aligned} \frac{1}{N} \sum_{i=1}^N (v_i - v_0)^2 &= x[\gamma_{HS}(v_{HS} - v_0)^2 + (1 - \gamma_{HS})(v_{LS} - v_0)^2] \\ &\quad + (1 - x)(v_M - v_0)^2 \\ \frac{1}{N} \sum_{i=1}^N (v_i - v_0) &= x[\gamma_{HS}(v_{HS} - v_0) + (1 - \gamma_{HS})(v_{LS} - v_0)] \\ &\quad + (1 - x)(v_M - v_0) \end{aligned} \quad (17)$$

the elastic energy per spin crossover molecule (Eq. 15 divided by Nx) can be rearranged as follows (terms independent of γ_{HS} are omitted):

$$\begin{aligned} e = & \frac{1}{2}K(\gamma_0 - 1)(v_{HS} + v_{LS} - 2v_0)v_{HL}/v_0\gamma_{HS} - x\frac{1}{2}K\gamma_0(\gamma_0 - 1)v_{HL}^2/v_m\gamma_{HS}^2 \\ & - xK\gamma_0(\gamma_0 - 1)v_{HL}v_{LM}/v_m\gamma_{HS} - K\gamma_0(\gamma_0 - 1)v_{HL}(v_M - v_0)/v_m\gamma_{HS} \end{aligned} \quad (18)$$

In analogy to differences of properties, differences of volumes, which are the actual properties of each lattice site here, are written as $v_{HL} = v_{HS} - v_{LS}$ and $v_{LM} = v_{LS} - v_M$. The volume per metal site of the crystal is $v_m = V/N$.

Comparing with the phenomenological free energy of Eq. (4) the interaction constant and the energy shift, both proportional to x are interpreted as ($v_{ML} = -v_{LM}$):

$$\begin{aligned} \Gamma(x) &= x\frac{1}{2}K\gamma_0(\gamma_0 - 1)v_{HL}^2/v_m \\ \Delta(x) &= xK\gamma_0(\gamma_0 - 1)v_{HL}v_{ML}/v_m \end{aligned} \quad (19)$$

The first and fourth terms in Eq. (18) linear in γ_{HS} are energy shifts which are absorbed in the energy separation Δf_{HL} in Eq. (4) between the HS and LS energy levels of the molecule. Note that ν_0 is absent from $\Gamma(x)$ and $\Delta(x)$. Thus all parameters can be experimentally determined. $\gamma_0\nu_{HL}$ is the volume increase on going from the LS to the HS state, which has been determined by variable-temperature structure determination. $\gamma_0\nu_{ML}$ is obtained by comparison of the unit cell volumes of the metal compound and the Fe compound in the LS state at the same temperature. K and γ_0 are accessible as elasticity constants. If typical values are used the derived interaction constant is an order of magnitude too small. This discrepancy was evident already when this theory was applied for the first time to the mixed crystal series $[Fe_xZn_{1-x}(picolyamine)_3]Cl_2 \cdot EtOH$ [4]. The bulk modulus which is needed to account for the magnitude of the interaction constant Γ was about $5 \times 10^{10} \text{ Nm}^{-2}$, which is an order of magnitude larger than can be expected for these types of molecular crystals.

4

Elastic Dipoles

The anisotropic lattice deformation accompanying the spin transition is described by a Cartesian tensor ε with components ε_{ik} ($i=x,y,z$), which for convenience of transformation, is expressed with respect to a spherical basis. The trace of the Cartesian ε -tensor is the relative volume change of the lattice:

$$\begin{aligned}\varepsilon_s &= \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \\ \varepsilon_0 &= \frac{1}{\sqrt{6}}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}) \\ \varepsilon_{\pm 1} &= \mp(\varepsilon_{xz} \pm \varepsilon_{yz}) \\ \varepsilon_{\pm 1} &= \frac{1}{2}(\varepsilon_{xx} - \varepsilon_{yy}) \pm i\varepsilon_{xy}\end{aligned}\quad (20)$$

The ε_M are transformed by the Wigner rotation matrix $D_{MM'}^2(\alpha, \beta, \gamma)$ with Euler angles $\bar{\beta} = (\alpha, \beta, \gamma)$. The complex numbers are avoided by use of another basis:

$$\begin{aligned}\varepsilon_0 &= \frac{1}{\sqrt{6}}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}) \\ \varepsilon_{1c} &= \sqrt{2}\varepsilon_{xz} \\ \varepsilon_{1s} &= \sqrt{2}\varepsilon_{yz} \\ \varepsilon_{2c} &= \frac{1}{\sqrt{2}}(\varepsilon_{xx} - \varepsilon_{yy}) \\ \varepsilon_{2s} &= \sqrt{2}\varepsilon_{xy}\end{aligned}\quad (21)$$

The tensor components are evaluated from the deformation of the unit cell due to the spin transition. Several examples have been studied [7, 8, 11, 12]. Taking these deformations as uniform throughout the crystal which is approximated to a homogeneous medium, the origin of the deformation is traced back to elastic point dipole tensors $\mathbf{P}$ with components P_s, P_M where ($M=s, -2, -1, \dots, +2$ or $M=s, 0, 1c, 1c, 2c, 2s$) which have the dimension of an energy:

$$\begin{aligned} P_s &= K\nu_m \varepsilon_s \\ P_M &= \frac{3}{2} K\nu_m (\gamma_0 - 1) \varepsilon_M \end{aligned} \quad (22)$$

For example, the P_s component is closely related to the volume change at a lattice site introduced above by $P_s^\alpha = K\gamma_0(\nu_\alpha - \nu_0)$. If there is only one molecule per unit cell, then Eq. (22) defines unequivocally an elastic point dipole at the center of the unit cell. If, however, the unit cell contains n equivalent sites, which are related to each other by symmetry transformations, then only few components of P_M are accessible. The rotational part of the symmetry transformations may be describes by Euler angles $\bar{\beta}^i = (\alpha^i, \beta^i, \gamma^i)$ ($i = 2, \dots, n$) with respect to one chosen site denoted by 1. The dipole tensors P_M^i of the point defects at site $i=2, \dots, n$ have the components (complex basis)

$$\begin{aligned} P_M^i &= \sum_{M'} P_{M'}^1 D_{M'M}^2(\bar{\beta}^i) \\ P_s^i &= P_s^1 \end{aligned} \quad (23)$$

The spherical part P_s^1 is, of course, the same for equivalent sites. Each dipole tensor causes a strain field, the sum of these fields gives the deformation of the crystal observed by X-ray measurement. This fact is expressed by Eq. (24):

$$\sum_i^n P_M^{HL,i} = K\nu_m \frac{3}{2} (\gamma_0 - 1) \varepsilon_M^{HL} \quad (24)$$

4.1

Self Energy of Elastic Dipoles

The first term in Eq. (12) which is proportional to the square of the volume change of the inclusion and inversely proportional to the volume provided by the lattice for the inclusion represents the elastic self energy stored in an infinite medium. This equation has been generalized for an arbitrary change of shape. For the general dipole in an isotropic medium the self energy e_{self} outside the radius of the volume ν_0 is given by (i.e., [13]):

$$e_{self} = \frac{1}{2} \frac{(\gamma_0 - 1)}{\gamma_0^2} \frac{1}{Kv_0} \left(P_s^2 + \frac{1}{15} \frac{(3\gamma_0^2 + 4\gamma_0 + 5)}{(\gamma_0 - 1)^2} \sum_M P_M P_M^* \right) \quad (25)$$

(The conjugate complex superscript $(*)$ can be dropped if the real basis is taken). If all sites in the lattice are equivalent, P_s can be replaced by the strain field e_s and in the case of a fraction γ_{HS} of the fraction x of spin changing molecules the first term in Eq. (25) gives the same dependence on γ_{HS} as Eq. (18). This term contains the sum of the volume changes $\varepsilon_{HS} + \varepsilon_{LS}$, which is not accessible as the reference volume provided by the lattice cannot be measured. In the case of more than one equivalent site in the unit cell some components of the tensor $\mathbf{P}$ remain hidden, apart from the fact that their values are also not measurable. This means that a calculation or even an estimation of the self energy is not possible. On the other hand, the temperature dependence of this energy contribution may influence to a large extent the spin transition curve. By thermal expansion of the lattice the volume v_0 provided by the lattice will increase with increasing temperature and also the shape of the space for the molecule will change, whereas the thermal expansion of the molecule itself is much smaller and can be neglected. Since the value of the self energy can be positive or negative, the energy separation, the sum of electronic and elastic energies, may decrease or increase with temperature.

4.2

Interaction of Elastic Dipoles by Image Pressure

The stress field, specifically the image pressure, a result of the free surface, is the sum of the stress fields of all defects and affects all dipoles the same way independent of their location in the crystal. Therefore the interaction energy caused by the image pressure (stress field) is expressed by average tensor components [10]:

$$E_{image} = -\frac{1}{2} N \frac{(\gamma_0 - 1)}{\gamma_0} \frac{1}{Kv_m} \left(\bar{P}_s^2 + \frac{2}{15} \frac{(2\gamma_0 + 1)}{(\gamma_0 - 1)^2} \sum_M \bar{P}_M \bar{P}_M^* \right) \quad (26)$$

According to Eq. (24) the average of the dipole tensor components $\bar{P}_M = \sum_i x \left(\gamma_{HS} P_M^{HS,i} + (1 - \gamma_{HS}) P_M^{LS,i} \right) + (1 - x) P_M^{M,i}$ (the case of the same concentration x and HS fraction γ_{HS} at all equivalent lattice sites i is implied) are proportional to the strain tensor components ε_M . In order to obtain the elastic energy e_{image} per spin changing site the total elastic energy E_{image} is divided by Nx . In the following equation terms independent of γ_{HS} are omitted and we obtain

$$e_{image} = -x \frac{1}{2} Kv_m \frac{(\gamma_0 - 1)}{\gamma_0} \left((\varepsilon_s^{HL})^2 + \frac{3}{10} (2\gamma_0 + 1) \sum_M (\varepsilon_M^{HL})^2 \right) \gamma_{HS}^2$$

$$\begin{aligned}
& -xKv_m \frac{(\gamma_0 - 1)}{\gamma_0} \left(\epsilon_s^{HL} \epsilon_s^{LM} + \frac{3}{10} (2\gamma_0 + 1) \sum_M \epsilon_M^{HL} \epsilon_M^{LM} \right) \gamma_{HS} \\
& -Kv_m \frac{(\gamma_0 - 1)}{\gamma_0} \left(\epsilon_s^{HL} \epsilon_s^M + \frac{3}{10} (2\gamma_0 + 1) \sum_M \epsilon_M^{HL} \epsilon_M^M \right) \gamma_{HS}
\end{aligned} \quad (27)$$

A comparison of this equation with Eq. (18) above allows the recognition of the spherical part of the interaction energy. The interaction constant Γ_{image} and the energy shift Δ_{image} , proportional to the concentration of the spin changing sites, now have extensions which are the second additive terms within the brackets:

$$\begin{aligned}
\Gamma_{image} &= x \frac{1}{2} K v_m \frac{(\gamma_0 - 1)}{\gamma_0} \left((\epsilon_s^{HL})^2 + \frac{3}{10} (2\gamma_0 + 1) \sum_M (\epsilon_M^{HL})^2 \right) \\
\Delta_{image} &= x K v_m \frac{(\gamma_0 - 1)}{\gamma_0} \left(\epsilon_s^{HL} \epsilon_s^{ML} + \frac{3}{10} (2\gamma_0 + 1) \sum_M \epsilon_M^{HL} \epsilon_M^{ML} \right)
\end{aligned} \quad (28)$$

It turns out that these anisotropic contributions can be an order of magnitude larger than the spherical one, so that the magnitudes already compare with experimental values as will be discussed later.

If the molecule containing the metal ion M is of the size of the molecule in the HS state ($\epsilon^M = \epsilon^{HS}$) then $\Delta_{image} = 2\Gamma_{image}$ and for molecules of the size of the spin crossover molecules in the LS state $\Delta_{image} = 0$. This behavior is true for all elastic contributions discussed in the following and is a consequence of the mean field approximation.

5 Direct Interaction

In elasticity theory the interaction energy of point defects is split into two contributions which are the image part (a consequence of a free surface), which readjusts according to the distortion inside the medium by the defect, and a direct interaction also present in an infinite medium. The direct interaction between spherical point defects in an isotropic medium vanishes, whereas interactions between non-spherical defects and also those between spherical and non-spherical defects remain. These decrease with the third power of the distance and depend on their relative orientations.

A general solution for the interaction energy of point defects at arbitrary positions $\mathbf{R}^a$ and $\mathbf{R}^b$ in an infinite isotropic medium was derived by Hirsekorn and Siems [14]. They also calculated the image interaction between two defects by a free surface of spherical shape. Using their solution, Eq. (27) can be obtained by integrating the image interaction between arbitrary defects homogeneously distributed over a sphere. For the calculation of the interaction

of randomly distributed point defects of HS, LS and M-type we will start from the special case of two defects on the z-axis as given by Shuey and Beyeler [13].

5.1

Two Elastic Dipoles

The elastic energy expression of two arbitrary dipole defects P_M^a and P_M^b ($M = s, -2, -1, \dots, 2$) in an isotropic homogeneous medium separated by a distance R (Shuey and Beyeler [13]) is given by

$$E_{d,int}^\infty = \frac{1}{4\pi R^3} \frac{1}{K\gamma_0} \left(\sqrt{6}(P_0^a P_s^b + P_0^b P_s^a) + 2\frac{\gamma_0 + 1}{\gamma_0 - 1} P_0^a P_0^b \right. \\ \left. - \frac{2}{\gamma_0 - 1} (P_1^a P_1^{b*} + P_{-1}^a P_{-1}^{b*} - (P_2^a P_2^{b*} + P_{-2}^a P_{-2}^{b*})) \right) \quad (29)$$

One dipole is at the origin of the coordinate system and the second on the z-axis at $z=R$. One observes that the product $P_s^a P_s^b$ is missing. Spherical point defects do not interact in an isotropic homogeneous medium. Further, the interaction decreases with the third power of distance R (dipole-dipole interaction), which means that there is no convergence when summing (integrating) over all dipoles in a large (infinite) medium as $\int^R r^{-3} dr r^2 d\Omega \propto \ln R$ diverges. It follows that this so-called direct interaction has long range behavior and is therefore well treated by the mean field approximation. The sum over all dipoles becomes finite only because of their angular dependence. Eq. (29) has to be generalized to an arbitrary site at (R, θ, ϕ) in the crystal. This is done in the following equation [15]:

$$E_{d,int}^\infty(\mathbf{R}) = \sum_M P_M^a V(\mathbf{R})_M P_s^b + P_M^b V(\mathbf{R})_M P_s^a + \sum_{MM'} P_M^a W(\mathbf{R})_{MM'} P_{M'}^{b*} \quad (30)$$

where the components of the tensors $V(\mathbf{R})$ and $W(\mathbf{R})$ are defined as

$$V(\mathbf{R})_M = \frac{1}{K} \frac{1}{\gamma_0} V(\mathbf{R})_M^2 \\ W(\mathbf{R})_{MM'} = \frac{1}{K} \frac{2}{7\gamma_0(\gamma_0 - 1)} (-2(\gamma_0 + 2) W(\mathbf{R})_{MM'}^2 + 3(\gamma_0 + 3) W(\mathbf{R})_{MM'}^4) \quad (31)$$

These depend on the elastic constants K and γ_0 and tensor expressions calculated by the position of defect b :

$$\begin{aligned}
V(\mathbf{R})_M &= \frac{1}{R^3} \sqrt{\frac{3}{10\pi}} Y_{2,M}^*(\theta, \phi) \\
W(\mathbf{R})_{MM'}^2 &= \frac{1}{R^3} \frac{1}{2} \sqrt{\frac{7}{2\pi}} \begin{pmatrix} 2 & 2 & 2 \\ M & -MM' & -M \end{pmatrix} (-1)^M Y_{2,M-M'}^*(\theta, \phi) \\
W(\mathbf{R})_{MM'}^4 &= \frac{1}{R^3} \frac{1}{6} \sqrt{\frac{35}{2\pi}} \begin{pmatrix} 2 & 2 & 2 \\ M & -MM' & -M \end{pmatrix} (-1)^M Y_{4,M-M'}^*(\theta, \phi)
\end{aligned} \tag{32}$$

The $Y_{km}(\theta, \phi)$ are the spherical harmonics. The even values of k in Eq. (32) guarantee that the interaction does not depend on interchanging defects a and b (inversion of vector $\mathbf{R}$)

For a concise representation the sum over components of the tensors in Eq. (30) is replaced by a vector-matrix notation:

$$E_{d,int}^\infty(\mathbf{R}) = \mathbf{P}^a \mathbf{V}(\mathbf{R}) P_s^b + \mathbf{P}^b \mathbf{V}(\mathbf{R}) P_s^a + \mathbf{P}^a \mathbf{W}(\mathbf{R}) \mathbf{P}^{b\dagger} \tag{33}$$

5.2

The Lattice Sum

The sum of the interaction energies between all pairs of lattice sites is carried out for a random distribution of the different types of defects (HS, LS, and M) over the lattice sites of the metal atoms. The unit cell contains n equivalent sites which are related to each other by symmetry transformations as described by Eq. (23). The double sum between all pairs (indices a, b)

$$E_{direct} = \frac{1}{2} \sum_{a \neq b}^N E_{d,int}^\infty(\mathbf{R}_{ab}) \tag{34}$$

is split up to a sum over unit cells (indices μ, ν) and the equivalent sites inside the unit cells (indices i, j)

$$E_{direct} = \frac{1}{2} \sum_{\mu \neq \nu} \sum_{i,j}^n E_{d,int}^\infty(\mathbf{R}_{\mu\nu}^{ij}) + \frac{1}{2} \sum_{\mu} \sum_{i \neq j}^n E_{d,int}^\infty(\mathbf{R}_{\mu\mu}^{ij}) \tag{35}$$

The random distribution has the consequence that average tensors $\bar{\mathbf{P}}^i$ of all sites i in the unit cell, which are related by translational symmetry, enter the energy and that the sum over all pairs of sites can be reduced to the sum over the sites of one unit cell to all other unit cells. Index u is fixed to site number 1 of the unit cell:

$$E_{direct} = \frac{N}{n} \sum_{\nu \neq 1} \sum_{ij}^n E_{d,int}^\infty(\mathbf{R}_{1\nu}^{ij}) + \frac{N}{2n} \sum_{i \neq j}^n E_{d,int}^\infty(\mathbf{R}_{11}^{ij}) \tag{36}$$

where N/n is the number of unit cells and the average tensors $\bar{\mathbf{P}}^i$ have to be inserted. The lattice sums can be carried out giving tensors $\mathbf{V}_\Sigma$ and $\mathbf{W}_\Sigma$ deter-

mined by the crystallographic structure and the elastic constants of the compound:

$$\begin{aligned} \mathbf{V}_\Sigma &= \frac{1}{2n} \left[\sum_v \sum_{ij}^n \left[D^{2i} \mathbf{V}(\mathbf{R}_{lv}^{ij}) + D^{2j} \mathbf{V}(\mathbf{R}_{lv}^{ij}) \right] + \sum_{i \neq j}^n D^{2j} \mathbf{V}(\mathbf{R}_{11}^{ij}) \right] \\ \mathbf{W}_\Sigma &= \frac{1}{2n} \left[\sum_v \sum_{ij}^n D^{2i} \mathbf{W}(\mathbf{R}_{lv}^{ij}) D^{2j\dagger} + D^{2i} \mathbf{W}(\mathbf{R}_{11}^{ij}) D^{2j\dagger} \right] \end{aligned} \quad (37)$$

With these lattice sums the direct interaction energy is written concisely as

$$E_{direct} = N \left(\bar{\mathbf{P}}^1 \mathbf{V}_\Sigma \bar{\mathbf{P}}^1 + \bar{\mathbf{P}}^1 \mathbf{W}_\Sigma \bar{\mathbf{P}}^{1\dagger} \right) \quad (38)$$

Inserting the average tensor components $\bar{\mathbf{P}}_\xi = x\gamma_{HS} \mathbf{P}_\xi^{HL} - x\mathbf{P}_\xi^{ML} + \mathbf{P}_\xi^M$, $\xi = s, M$ and collecting all terms depending on γ_{HS} the direct interaction energy per molecule E_{direct}/Nx has a similar structure as Eq. (27) for the interaction energy caused by the image stress field:

$$\begin{aligned} \frac{1}{Nx} E_{direct} &= x \left(\mathbf{P}^{HL} \mathbf{V}_\Sigma \mathbf{P}_s^{HL} + \mathbf{P}^{HL} \mathbf{W}_\Sigma \mathbf{P}^{HL\dagger} \right) \gamma_{HS}^2 \\ &\quad - x \left(\mathbf{P}^{HL} \mathbf{V}_\Sigma \mathbf{P}_s^{ML} + \mathbf{P}^{ML} \mathbf{V}_\Sigma \mathbf{P}_s^{HL} + \mathbf{P}^{HL} \mathbf{W}_\Sigma \mathbf{P}^{ML\dagger} + \mathbf{P}^{ML} \mathbf{W}_\Sigma \mathbf{P}^{HL\dagger} \right) \gamma_{HS} \\ &\quad + \left(\mathbf{P}^{HL} \mathbf{V}_\Sigma \mathbf{P}_s^M + \mathbf{P}^M \mathbf{V}_\Sigma \mathbf{P}_s^{HL} + \mathbf{P}^{HL} \mathbf{W}_\Sigma \mathbf{P}^{M\dagger} + \mathbf{P}^M \mathbf{W}_\Sigma \mathbf{P}^{HL\dagger} \right) \gamma_{HS} \end{aligned} \quad (39)$$

From this a contribution to the interaction constant and the energy shift proportional to the concentration x immediately follows as

$$\begin{aligned} \Gamma_d &= -x \left(\mathbf{P}^{HL} \mathbf{V}_\Sigma \mathbf{P}_s^{HL} + \mathbf{P}^{HL} \mathbf{W}_\Sigma \mathbf{P}^{HL\dagger} \right) \\ \Delta_d &= -x \left(\mathbf{P}^{HL} \mathbf{V}_\Sigma \mathbf{P}_s^{ML} + \mathbf{P}^{ML} \mathbf{V}_\Sigma \mathbf{P}_s^{HL} + \mathbf{P}^{HL} \mathbf{W}_\Sigma \mathbf{P}^{ML\dagger} + \mathbf{P}^{ML} \mathbf{W}_\Sigma \mathbf{P}^{HL\dagger} \right) \end{aligned} \quad (40)$$

6

Interaction by the Anharmonicity of the Lattice

Lattice expansion leads to a decrease of vibrational frequencies which for a Debye lattice is expressed by

$$\frac{\Delta\omega_D}{\omega_D} = -\gamma_G \frac{\Delta V}{V} \quad (41)$$

where ω_D is the Debye frequency and γ_G the Grüneisen constant. As the bulk modulus K is proportional to the square of ω_D Eq. (41) becomes for the change of K

$$\frac{\Delta K}{K} = -2\gamma_G \frac{\Delta V}{V} \quad (42)$$

so that for small $\Delta V/V$ the dependence of K on V can be written with respect to the reference values K_0 and V_0 as

$$K(V) = K_0 \left(1 - 2\gamma_G \frac{V - V_0}{V_0} \right) \quad (43)$$

All elastic energy contributions are proportional to the bulk modulus K . As only the volume change of the crystal is considered in the following, the Eschelby constant γ_0 reflecting the structure properties of the isotropic medium is taken to be constant. The volume dependence of the reference volumes v_0 and the volume per molecule v_m lead to higher order contributions and therefore are neglected. The elastic self energy of one molecule, which is the first term in Eq. (12) (equal to the first term in Eq. 25) has to be integrated including the volume dependence of the bulk modulus. Taking V_0 equal to Nv_m the difference $V - V_0$ becomes $\gamma_0(v_\alpha - v_0)$. Integration yields a third order correction term of the misfit $v_\alpha - v_0$ which decreases the self energy when $v_\alpha - v_0 > 0$ as a result of the decreasing bulk modulus:

$$\begin{aligned} e^\alpha &= \int_{v_0}^{v_\alpha} \frac{(\gamma_0 - 1)}{v_0} K(v) (v - v_0) dv \\ &= \frac{1}{2} K_0 (\gamma_0 - 1) \frac{(v_\alpha - v_0)^2}{v_0} - \frac{1}{N^2} \frac{2}{3} K_0 (\gamma_0 - 1) \gamma_0 \gamma_G \frac{(v_\alpha - v_0)^3}{v_0 v_m} \end{aligned} \quad (44)$$

The change of the bulk modulus by a second defect will also change the self energy of the first one, which means that the volume dependence of K leads to an interaction between defects. The following expression for the self energy E_{self} of N defects can be proven by complete induction:

$$\begin{aligned} E_{self} &= \frac{1}{2} K_0 (\gamma_0 - 1) \sum_{\alpha}^n \frac{(v_\alpha - v_0)^2}{v_0} \\ &\quad - K_0 (\gamma_0 - 1) \gamma_0 \gamma_G \frac{1}{N} \left[\sum_{\alpha}^N \frac{(v_\alpha - v_0)}{v_m} \sum_{\alpha}^N \frac{(v_\alpha - v_0)^2}{v_0} - \frac{1}{3} \sum_{\alpha}^N \frac{(v_\alpha - v_0)^3}{v_m v_0} \right] \end{aligned} \quad (45)$$

For $N=1$ Eq. (45) is the same as Eq. (44). Introducing defect $N+1$, the volume $\Delta V = \gamma_0 \sum_{\alpha}^N (v_\alpha - v_0) + (v - v_0)$ is inserted into $K(v)$. The integral which is the self energy of defect $N+1$ is added to Eq. (45) together with the energy change δ of the N defects already present:

$$\delta = -\frac{1}{2} K_0 (\gamma_0 - 1) \sum_{\alpha}^N \frac{(v_\alpha - v_0)^2}{v_0} \cdot 2\gamma_G \frac{(v_{N+1} - v_0)}{Nv_m} \quad (46)$$

E_{self} for $N+1$ defects preserves the shape of Eq. (45).

The two correction terms in brackets are of different order of magnitude as the first one is the product of two sums with N^2 and the sum of a second one with N contributions. Therefore, neglecting the second term E_{self} can be written as

$$\begin{aligned} E_{self} &= \frac{1}{2} K_0 (\gamma_0 - 1) \sum_{\alpha} \frac{(\nu_{\alpha} - \nu_0)^2}{\nu_0} \left[1 - 2\gamma_G \frac{\gamma_0}{N} \sum_{\alpha} \frac{(\nu_{\alpha} - \nu_0)}{\nu_m} \right] \\ &= \sum_{\alpha} e_{self,s}^{\alpha} [1 - 2\gamma_{G,s} \varepsilon_s] \end{aligned} \quad (47)$$

The definition of $e_{self,s}^{\alpha}$ is obvious. The correction depends on the average, so that it can be expressed by the ε -tensor component. The Grüneisen constant has now an index s in order to extend Eq. (47) to anisotropic deformations with indices $M=0, 1c, 1s, 2c, 2s$. As a result of the same structure for all components the self energy for the anisotropic deformation of type M can be written as

$$\begin{aligned} e_{self,M}^{\alpha} &= \frac{1}{30} \frac{3\gamma_0^2 + 4\gamma_0^2 + 5(P_M^{\alpha})^2}{\gamma_0^2(\gamma_0 - 1)} \frac{K\nu_0}{K\nu_0} \\ E_{self,M} &= \sum_{\alpha} e_{self,M}^{\alpha} [1 - 2\gamma_{G,M} \varepsilon_M] \end{aligned} \quad (48)$$

The self energy now has an index M which extends also to $M=s$ representing the spherical part discussed above. If the averages and the sums are expressed as above by the fraction x of spin changing molecules and γ_{HS} , the correction to the self energy per molecule has a contribution proportional to γ_{HS} and γ_{HS}^2 . The coefficient of γ_{HS}^2 gives a contribution Γ_m to an ‘infinite’ range interaction constant and the coefficient Δ_M of γ_{HS} to the energy separation between the HS and LS states:

$$\begin{aligned} \Gamma_M(x) &= x 2\gamma_{G,M} \varepsilon_M^{HL} (e_{self,M}^{HS} - e_{self,M}^{LS}) \\ \Delta_M(x) &= x 2\gamma_{G,M} \left[\varepsilon_M^{HL} (e_{self,M}^M - e_{self,M}^{LS}) + \varepsilon_M^{ML} (e_{self,M}^{HS} - e_{self,M}^{LS}) \right] \end{aligned} \quad (49)$$

The correction for the spherical part of the deformation tensor was calculated by Meissner [16] and extended to the anisotropic contribution by Jung [6, 17]. Again the ratios $\Delta_M/\Gamma_M=2$ and 0 are obtained for metal ions of the size of HS and LS ions, respectively. The sums $\sum_M \Gamma_M(x), \sum_M \Delta_M(x)$ give the total correction to the interaction constant and the energy separation proportional to x , respectively. As only the sum of self energy differences $\sum_M e_{self,M}^{HS} - e_{self,M}^{LS}$ is accessible from experiments and not each contribution M , the correction cannot be calculated. Estimates are given below.

7 Short Range Interaction

Very large interaction constants have been observed, much larger than can be explained by the contributions discussed so far. Even the direct interaction at typical distances between molecules does not exceed $10\text{--}100\text{ cm}^{-1}$ [17], while in the chain compound $[\text{Fe}(\text{Htrz})(\text{trz})(\text{BF}_4)_2]$ ($\text{Htrz}=1,2,4\text{-}4H\text{-triazole}$ and $\text{trz}=1,2,4\text{-triazolato}$) [18] an interaction constant of more than 10^3 cm^{-1} was observed [19]. The basic structure of this material is a linear chain with octahedral $\text{Fe}(\text{Htrz})_6$ chromophores linked to each other through the 1,2 nitrogen atoms of three bridging triazole ligands [20].

The idea is that the presence of strong short range interactions are caused by steric hindrance of neighboring molecules. If two metal atoms share bridging ligand molecules, the spin state change of one iron ion displaces the ligand as a result of the change of bond length. This displacement directly influences the ligand field strength of the other iron ion and consequently its energy separation between HS and LS state. A decrease of the energy separation implies a ferro-elastic type (positive) of interaction and, vice versa, an increase implies negative contribution to the interaction constant.

Direct experimental evidence of large changes in energy separations between HS and LS states has not yet been achieved. Metal dilution studies of dimers (simplest case) or chain compounds with metal ions of different size like $\text{M}=\text{Mn}, \text{Zn}, \text{Co}, \text{Ni}$ are not available. Work along these lines are in progress.

8 Application

8.1 $[\text{Fe}(\text{propyltetrazole})_6](\text{BF}_4)_2$

The space group of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ ($\text{ptz}=\text{propyltetrazole}$) is $R\bar{3}$ with only one molecule per unit cell. This is the situation where all components of the elastic dipole tensor can be known. From temperature dependent X-ray measurements the axial strain tensor ε_{ik} was evaluated and from Brillouin scattering the 6 elastic constants describing the elasticity of an axial symmetric compound were obtained at room temperature [6]. Using the method of Voigt [21] the isotropic averages $K=4.81\times 10^9\text{ Jm}^{-2}$ and $\gamma_0=1.49$ of the 6 elastic constants were determined. The temperature dependence of K (down to 132 K) and γ_0 has been estimated from the temperature dependence of one of the 6 elastic constants c_{33} which was measured by backscattering in the direction of the threefold axis. The result is an interaction constant due to the image pressure of $\Gamma_{\text{image}}^i + \Gamma_{\text{image}}^a = 30\text{ cm}^{-1} + 55\text{ cm}^{-1}$ and a negative

contribution $\Gamma_d = -29 \text{ cm}^{-1}$ arising from the direct interaction. The sum of these values, 56 cm^{-1} , is about 1/3 of the experimental value of $\Gamma = 169 \text{ cm}^{-1}$.

Jung et al. [6] could evaluate the self energy from the transition curve of the highly diluted mixed crystal $[\text{Fe}_x\text{Zn}_{1-x}(\text{ptz})_6](\text{BF}_4)_2$ ($x=0.005$). The volume dependence of the bulk modulus K according to the Grüneisen approximation of Eq. (43) and the temperature dependence of the volume as obtained from X-ray studies was inserted for the self energy (see Eq. 25) such that $\Delta e_{\text{self}}(T) = e_{\text{self}}(0) \times K(V(T))/K(V(0))$. With reasonable assumptions derived from the temperature dependence of the Lamb-Mössbauer factor and the quadrupole splitting for the electronic HS state and the vibrational frequencies in the HS and LS states, a temperature independent electronic energy, $\Delta e_{\text{elect}} = -750 \text{ cm}^{-1}$, and elastic self energy at $T=0$, $\Delta e_{\text{self}}(0) = 1015 \text{ cm}^{-1}$, were evaluated. This result is remarkable since the HS state is to be expected the ground state of the 'free' complex $[\text{Fe}(\text{ptz})_6]^{2+}$ when $\Delta e_{\text{self}} = 0$. The large positive elastic self energy difference is responsible for the LS state becoming the ground state in the solid below ca. 220 K.

As $\Delta e_{\text{self}} = \sum M e_{\text{self},M}$ and the different contributions are not known, Jung et al. [6] calculated the contribution to the interaction constant and energy shift taking the full $\Delta e_{\text{self}}(0)$ energy for $M=s$, the trace of the ε -tensor. With the pre-factor $2\gamma_{G,s}\varepsilon_s^{\text{HL}}$ of Eq. (49) and $\Delta e_{\text{self}}(T=125 \text{ K}) = 780 \text{ cm}^{-1}$, $\gamma_{G,s} = 2.8$ [6], and the actual value of $\varepsilon_s^{\text{HL}} = 0.020$ [7] the contribution to the interaction constant of 87 cm^{-1} becomes even larger than that caused by the image pressure and direct interaction. All contributions together give a value of 143 cm^{-1} which is close to the experimental one. The measured value of $\Delta = 318 \text{ cm}^{-1}$ is almost twice ($\Delta/\Gamma = 1.88$) the value of Γ , which fits very well to the similarity of the ε -tensor of the Fe-molecule in the HS state and the Zn-molecule as defects.

8.2

Picolyl Amine Compounds

When the dependency of the interaction in spin crossover compounds on the deformation tensor and the elastic dipoles, respectively, was first derived, the expressions were applied to two compounds, $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ and $[\text{Fe}(\text{pic})_2]\text{Cl}_2 \cdot \text{MeOH}$ (pic=picolylamine) [15]. Contrary to $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, which has just one molecule per unit cell, the monoclinic ($P2_1/c$ [22]) EtOH compound has four and the orthorhombic (Pbca [23]) MeOH compound eight equivalent sites per unit cell. So in both cases the measured deformation tensor ε is the result of an additive cooperation of four and eight elastic defects of different orientations, respectively, a situation which has led to Eq. (24). The knowledge of the tensors ε does not help at all in the calculation of the anisotropic part of the direct interactions. Since the first calculation of the elastic interaction had already shown that the isotropic part ($M=s$) gave numbers which were by an order of magnitude

too small, there was a need to have some idea about the size of the anisotropic part in order to estimate whether the contribution of the elastic interaction is important enough to be studied.

The rigorous assumption of equally elastic media of both compounds the spin crossover molecules are embedded in different orientations enables one to determine all dipole tensor components [15]. The very similar volume v_m per molecule, $v_m(\text{EtOH}, 115 \text{ K})=590 \text{ \AA}^3$ and $v_m(\text{MeOH}, 115 \text{ K})=577 \text{ \AA}^3$ [24], and the same $M=s$ tensor components, $\epsilon_s(\text{EtOH})=2.43 \times 10^{-2}$ and $\epsilon_s(\text{MeOH})=2.44 \times 10^{-2}$ [11], are consistent with this assumption. For the monoclinic structure the two tensor components ϵ_{1s} , ϵ_{2s} vanish with the two-fold axis parallel to the y-axis of the coordinate system of the crystal. The orthorhombic structure with the three orthogonal twofold axes taken as the axes of the coordinate system has three tensor components (ϵ_{1c} , ϵ_{1s} , ϵ_{2s}) which vanish by symmetry.

In the case of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ the elastic dipole (mathematically treated as a point dipole) is by inversion symmetry located at the iron position fixed to the center of the $[\text{Fe}(\text{ptz})_6]^{2+}$ complex. Although in the case of the pic complex symmetry arguments do not determine the location of the elastic dipoles in the unit cell and the iron sites have no special symmetry, the point dipoles are again fixed to the iron ions. A coordinate system to the $[\text{Fe}(\text{pic})_3]^{2+}$ complex can be unequivocally oriented with respect to the three bidentate 2-aminomethylpyridine ligands [15]. Since the six nitrogen atoms bound to the iron do not form a regular octahedron the coordinate system is chosen such that the $\sum_j^6 \cos^2(\delta_j)$ becomes minimal, where δ_j is the angle between the direction from iron to nitrogen atom j and the corresponding coordinate axis. With respect to these local coordinate systems, the relative orientations of which are given by the symmetry of the crystal, there are five unknown components ($M=0, 1s, 1c, 2s, 2c$) of the elastic dipole tensor $P_M^{\text{HL},\text{local}}$. These are transformed to the crystal system by a transformation matrix $T_{M,M'}^i$ for each site $i=1,\dots,n$ (calculated by the relative orientation of the n local systems to the crystal system) such that

$$P_{M'}^{\text{HL},i} = \sum_M P_M^{\text{HL},\text{local}} T_{MM'}^i \quad (50)$$

The relation to the measured ϵ_M tensor components is given by Eq. (24). For each crystal there are five equations. If an ϵ_M tensor component is zero by symmetry, Eq. (24) is fulfilled by symmetry and represents no condition for the components $P_M^{\text{HL},\text{local}}$. In this way the ten equations for the two compounds give just five independent equations for the five components $P_M^{\text{HL},\text{local}}$ of the elastic dipole tensor of the $[\text{Fe}(\text{pic})_3]^{2+}$ complex when changing the spin state.

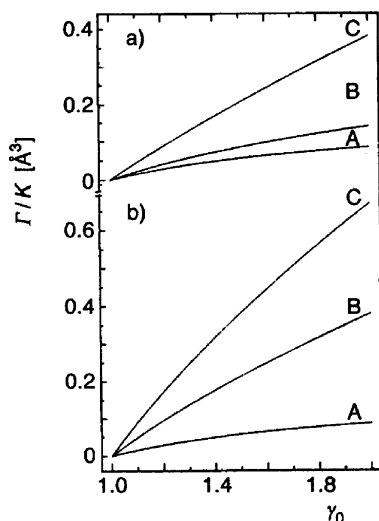


Fig. 1a,b The interaction constant Γ divided by the bulk modulus K is plotted vs the Eshelby constant γ_0 for two compounds $[Fe(pic)_3]Cl_2 \cdot sol$: **a** sol=MeOH; **b** sol=EtOH. Γ/K was calculated from the measured deformation tensor ϵ of the two compounds. The three curves for each compound show the different contributions included in the calculation. Curves A take into account only the isotropic part of the deformation tensor. Curves B include the interaction from the anisotropic image pressure. Curves C represent the elastic interaction including the direct interaction between the elastic dipoles

For $P_M^{HL,local}/K/(\gamma_0 - 1)$ the values $(-21.4, 1.7, -26.4, 7.1, 15.6)$ for the components ($M=0, 1s, 1c, 2s, 2c$) were derived following the described procedure [15]. As K and γ_0 are unknown for these compounds the ratio Γ/K of the interaction constant and the bulk modulus (Γ/K depends no longer any more on K) was plotted vs the Eshelby constant γ_0 for the different contributions, the isotropic part, the part caused by anisotropic image pressure, and the direct interactions. The direct interaction was calculated for a spherical crystal summing over a sphere of radius of about 30 times the largest lattice constant including more than 10^6 defects.

In Fig. 1 the different contributions to Γ/K are plotted vs γ_0 for both compounds. The dependency of Γ/K on γ_0 of the isotropic part, the image pressure, is the same for both compounds as the P_s^{HL} tensor components are the same. The anisotropic image strain produces a much larger contribution for the EtOH than for the MeOH solvate. For the MeOH solvate all the image contributions considered together are much too small to account for the measured interaction constant for a reasonable K -value. So far, only the ϵ -tensors are used for the calculation. The calculation of the direct interaction requires the P^{HL} tensor. This contribution turns out to be almost the

same for both compounds and is the dominant contribution to G/K for the MeOH solvate.

An interesting result is the fact that the ratio of the $(\Gamma/K)_{EtOH}$ and $(\Gamma/K)_{MeOH}$ for each value of γ_0 is close to the experimental value. At $\gamma_0=1.5$ the ratio is the same as the experimental one, $175 \text{ cm}^{-1}/98 \text{ cm}^{-1}=1.78$. At this point a value of the bulk modulus $K=175 \text{ cm}^{-1}/0.37 \text{ \AA}=9.1 \text{ GPa}$ is needed to obtain the interaction constant $\Gamma=175 \text{ cm}^{-1}$. In order to preserve this ratio any further contribution to the Γ/K values has to have the same ratio. This condition is very unlikely to be fulfilled. The interaction by the anharmonicity of the lattice should be of similar size for both compounds so that its value can only be very small. The estimation by taking the total self-energy as a pre-factor for the spherical deformation ε_s , as done for the ptz compound, does not work here. It is known that in liquid solution the transition takes place around room temperature, i.e., about 200 K higher than in the solid. This difference requires a negative energy shift of about -10^3 cm^{-1} when the complex $[Fe(pic)_2]^{2+}$ is embedded in the solid lattice [1]. This energy shift has to be interpreted as the difference in the elastic self energy for the HS and LS states and with $\gamma_G=3$ and $\varepsilon_s^{HL}=0.024$ a contribution of 144 cm^{-1} is obtained following the procedure for the ptz compound. Not more than 10% of this value can be accepted to leave the ratio close to the experimental one (see Fig. 1).

This example shows that the determination of the contribution to the interaction by the anharmonicity of the lattice is a very uncertain and it is not possible to estimate it even within an order of magnitude.

9 Conclusion

The elastic interaction between the spin crossover molecules in the HS and LS states and the molecules containing other metal ions in metal diluted mixed crystals is based on the different size and shape of these molecules. As a simple consequence, the different molecules do not fit equally well to the lattice. The dependence of the unit cell parameters on the fraction of molecules in the HS and LS states makes the misfit of molecules evident. The elastic energies involved changing in the size and shape of the molecules are built up by a strain field which depends on the distance as $1/r^3$ and therefore behaves as a long range interaction. Long range interactions are generally well approximated by a mean field approximation. The structure of elasticity theory even allows to separate estimations of the different contributions to the elastic energy. The image pressure (stress field) on the free surface of the crystal represents an infinite range interaction and is exact in the mean field treatment. It can be completely calculated from the measured deformation tensor difference ε^{HL} and the elastic constants of the com-

pound. Within the approximation of an isotropic elastic medium characterized by the bulk modulus K and the Eshelby constant γ_0 this contribution to the elastic energy has been calculated. It turns out to be of the right order of magnitude even though the full size is not obtained as compared to the interaction constants fitted to phenomenological free energy expressions. The fact that a deformation tensor of the lattice can be evaluated from X-ray structure measurements implies a homogeneous distribution of the different types of molecules, at least on the scale of scattering volumes large enough to produce the observed diffraction peaks.

The calculation of the interactions between individual molecules requires the concept of dipolar defects. The position of the defect in the unit cell and its dipolar tensor $\mathbf{P}^{HL}$ can only be fixed if there is one molecule in the unit cell with inversion symmetry. This situation has been met in the first example discussed, $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. The sum of the interaction energies over a random distribution of molecules in the HS and LS states yields a value of similar size as the contribution from the image pressure.

The more general case of equivalent molecules in the unit cell cannot be treated without further assumptions. Fixing the positions of the dipoles at the metal sites can be considered as a weak assumption. The hidden components of the dipolar tensor $\mathbf{P}^{HL}$, which cannot be determined from the ϵ^{HL} tensor as a consequence of the symmetry of the unit cell and the additivity of the strains caused by the tensor $\mathbf{P}^{HL}$, prevent an estimation of this energy contribution. That the calculation of this contribution could be achieved in the case of the two picolylamine compounds, $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ and $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{MeOH}$, required the more rigorous assumption of equal elastic properties of both compounds, such that the orientations of the molecules in the unit cell has been taken as the only difference between the crystals. Again the contribution of the direct interaction is of similar size as the image part.

The further contribution caused by the anharmonicity of the lattice needs to include not only the difference of the misfits of the molecules in the lattice but also the absolute values of the elastic dipole tensors $\mathbf{P}^\alpha$, $\alpha = \text{HS}, \text{LS}, \text{M}$. The $\mathbf{P}^\alpha$ can in no way be measured or estimated. This restriction makes precise predictions and therefore comparisons of interaction energies impossible.

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Density Functional Theory Calculations for Spin Crossover Complexes

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Abstract Density functional theory (DFT) provides a theoretical framework for efficient and fairly accurate calculations of the electronic structure of molecules and crystals. The main features of density functional theory are described and DFT methods are compared with wavefunction-based methods like the Hartree-Fock approach. Some recent applications of DFT to spin crossover complexes are reviewed, e.g., the calculation of Mössbauer parameters, of vibrational modes and of differences of entropy, vibrational energy, and total electronic energy between high-spin and low-spin isomers.

Keywords Density functional theory · Spin crossover · Vibrational modes · Transition temperature

1 Introduction

The spin crossover (SCO) phenomenon can be explained qualitatively by ligand-field theory [1]. Together with empirical parameters, the ligand-field model gives also quantitative explanations and even has some predictive power. The most important merit of ligand-field theory is probably, that it

provides an easy to understand model. Instead, *ab initio* or first principles¹ methods for calculating the electronic structure in a sense resemble a black box: all calculated quantities are automatically derived from the Schrödinger equation. Electronic structure calculations are, therefore, not meant to replace the ligand-field model but to complement it. These methods are most useful, if quantitative accuracy is needed or if quantities that have not been measured are to be predicted.

With respect to electronic structure calculations, transition-metal complexes are intricate objects. This is especially true for SCO complexes where the almost vanishing energy difference between different spin multiplicities results from a delicate balance of various factors. For exactly this reason these complexes are very interesting test objects for judging the quality of theoretical methods, in particular, if these methods can predict the true ground state multiplicity. Methods based on density functional theory (DFT) are currently the natural choice for calculating the electronic structure of transition-metal complexes. DFT methods are efficient enough to handle large molecules (e.g., containing 100 atoms as an order of magnitude) and they provide fairly accurate results for many quantities. Unlike DFT methods wavefunction-based methods can, in principle, produce any desired accuracy. However, SCO complexes are by far too large to be treated with sophisticated wavefunction-based methods. Those methods that can actually be applied to SCO complexes, like the Hartree-Fock approach, yield poor results in comparison to DFT methods.

This chapter is divided in two parts. In the first part density functional theory will be introduced and the most important DFT methods and some recent developments that are especially relevant to SCO complexes will be discussed. The second part reviews some applications related to SCO compounds, i.e., examples are described for the calculation of molecular geometry, Mössbauer parameters, normal modes of vibrations and IR, Raman, and nuclear inelastic scattering (NIS [2]) intensities. From the normal modes of vibrations, the vibrational energy and entropy differences can be derived with reasonable accuracy. One of the quantities of SCO complexes that is a challenge to calculate is the total electronic energy difference ΔE between the high-spin (HS) and the low-spin (LS) state; yet, this difference has been calculated for several complexes with at least reasonable accuracy. Finally, calculations for iron(II) SCO complexes with substituted tris(pyrazolyl) ligands are presented; they provide an example of how DFT calculations might be used to support the design of future SCO complexes with specified properties.

¹ Since there is no consensus in the literature on whether DFT methods should be called *ab initio* or first principles, these terms will be avoided in the following.

2 Density Functional Theory

The electronic ground state of a system containing N electrons is usually described by the many-electron wavefunction $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, which is a solution of the many-electron Schrödinger equation (the coordinates $\mathbf{x}_i$ comprise space coordinates $\mathbf{r}_i$ and spin coordinates $s_i = \pm 1/2$). The central point of density functional theory (see [3–9] for an overview) is the observation that the ground state can be equivalently described by the one-particle charge density $\rho(\mathbf{r})$, which is defined by

$$\rho(\mathbf{r}_1) = e \sum_{s_1} \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (1)$$

where the integration over $\mathbf{x}_i$ includes integration over $\mathbf{r}_i$ and summation over s_i . Modern DFT started with the theorems of Hohenberg and Kohn² in 1964. The first Hohenberg-Kohn theorem [10] states that there is a one-to-one mapping between the ground-state charge density $\rho_0(\mathbf{r})$, the external potential of the nuclei $v_{\text{ext}}(\mathbf{r})$ and the ground-state wavefunction Ψ_0 :

$$\rho_0(\mathbf{r}) \leftrightarrow v_{\text{ext}}(\mathbf{r}) \leftrightarrow \Psi_0. \quad (2)$$

While it is intuitively obvious that the external potential determines the wavefunction, which in turn determines the charge density, it was unknown before that for each (non-degenerate) ground-state density $\rho_0(\mathbf{r})$ there exists exactly one external potential $v_{\text{ext}}(\mathbf{r})$. The first Hohenberg-Kohn theorem is valid for any kind of local external potential. In the special but most important case, that $v_{\text{ext}}(\mathbf{r})$ describes the nuclear electrostatic potential of a molecule containing M nuclei with atomic numbers Z_n and positions $\mathbf{R}_n$,

$$v_{\text{ext}}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0} \sum_{n=1}^M \frac{eZ_n}{|\mathbf{R}_n - \mathbf{r}|}, \quad (3)$$

the theorem can be understood by very intuitive arguments that are attributed [11] to E. B. Wilson: if $\rho_0(\mathbf{r})$ is known, Z_n and $\mathbf{R}_n$ can be derived from the cusps of $\rho_0(\mathbf{r})$; thus $v_{\text{ext}}(\mathbf{r})$ is defined and the number of electrons N can be determined by integration of $\rho_0(\mathbf{r})$ over space. The second Hohenberg-Kohn theorem [10] states that for a given external potential v there exists a functional $E_v[\rho] \geq E_0$ that yields minimum energy for the ground state density $\rho_0(\mathbf{r})$. The functional for the total energy can be written as a sum of two functionals with quite different properties: $E_v[\rho] = E_{\text{ne}}[\rho] + E_{\text{HK}}[\rho]$. The first term, $E_{\text{ne}}[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$, describes the interaction of the electrons with the external potential and depends on the particular molecule, but it is

² Walter Kohn was awarded the Nobel Prize for chemistry in 1998 for his contributions to density functional theory.

straightforward to calculate. The second term, the Hohenberg-Kohn functional $E_{\text{HK}}[\rho]$, is a universal functional, i.e., it does not depend on the particular system. Unfortunately, only the existence of this functional can be proven, but an exact expression for $E_{\text{HK}}[\rho]$ is not known. First attempts to realize such a functional in an approximate way were made already in the early stage of quantum mechanics by Thomas and Fermi (see [4] for a review), long before density functional theory was founded. They derived an expression for the electronic energy $E_{\text{TF}}[\rho] = \int [t(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + j(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r}$ that uses local potentials: $t(\mathbf{r}) = (3\hbar^2/10me)(3\rho(\mathbf{r})/8\pi e)^{2/3}$ for the kinetic energy, $v_{\text{ext}}(\mathbf{r})$ for the external potential, and

$$j(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \quad (4)$$

for the classical Coulomb self-interaction of a given charge density. In quantum mechanics $j(\mathbf{r})$ describes which effective potential is seen by a reference electron, that moves in the average Coulomb field of all electrons (including the reference electron, thus including unwanted self-interaction of the reference electron). The Thomas-Fermi model is the first example of a density functional method, but due to the rather coarse approximation of the kinetic energy, this model never gained importance for applications to real systems. Surprisingly, the way to improve the kinetic-energy functionals leads back to wavefunctions. For this reason the Hartree-Fock method, the fundamental wavefunction-based procedure for electronic-structure calculations, will be reviewed in the next section.

2.1

Hartree-Fock Method

One of the earliest attempts in quantum chemistry has been made by Hartree [12] writing the many-electron wavefunction of an ion as the product of single-particle functions, called orbitals, $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N)$. If Ψ is written in this form, known as the Hartree product, the probability of finding a particular electron i at position $\mathbf{r}_i$ does not depend on the positions or the spins of the other electrons, in other words the electron positions and spins are not correlated. Using the effective potential $j(\mathbf{r})$ for the electron-electron interaction, a set of one-electron Schrödinger equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + ev(\mathbf{r}) + ej(\mathbf{r}) - \hat{k}(\mathbf{x}) \right] \psi_i(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}), \quad (5)$$

can be formulated, called canonical Hartree-Fock equations (see, e.g., [4, 13]), where the first operator in parentheses stands for the kinetic energy. The operator $\hat{k}(\mathbf{x})$, which is defined by

$$\hat{k}(\mathbf{x})\psi_i(\mathbf{x}') = \frac{e^2}{4\pi\epsilon_0} \sum_{k=1}^N \int \frac{\psi_k^*(\mathbf{x}')\psi_k(\mathbf{x})\psi_i(\mathbf{x}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{x}', \quad (6)$$

has to be included, if the antisymmetry of the wavefunction has to be considered, that means $\Psi(\dots, \mathbf{x}_i, \dots, \mathbf{x}_k, \dots) = -\Psi(\dots, \mathbf{x}_k, \dots, \mathbf{x}_i, \dots)$ for arbitrary electrons i and k . This can be reached by forming a suitable linear combination of the Hartree product and its permutations with respect to the electron coordinate, e.g., $\Psi(\mathbf{x}_1, \mathbf{x}_2) = [\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)]/\sqrt{2}$, with the generalization to the N -electron case, $\Psi = \det[\psi_i(\mathbf{x}_k)]/\sqrt{N!}$, known as the Slater determinant. Since $j(\mathbf{r})$ depends on the orbitals of all other electrons $k \neq i$, Eq. (5) has to be solved iteratively until a self-consistent set of orbitals ψ_i , $i=1\dots N$, has been reached. It can be shown that this procedure leads to the lowest total energy E that is possible for a trial function in the form of a Slater determinant or in the form of a Hartree product, depending on whether the operator $\hat{k}(\mathbf{x})$ is included in the one-electron Schrödinger equation or not. In the first case, the procedure is the well-known Hartree-Fock method; in the latter case it is the Hartree approximation. The total electronic energy E is not equal to the sum of the one-electron energies ϵ_i , since otherwise the electron-electron interaction between the electrons would be counted twice. The total energy can be written as a sum of one kinetic-energy term and of three potential-energy terms $E = E_{\text{kin}} + E_{\text{ne}} + E_{\text{Coul}} - E_{\text{x}}$, with

$$E_{\text{kin}} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r}, \quad (7)$$

$$E_{\text{ne}} = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \quad (8)$$

$$E_{\text{Coul}} = \frac{1}{4\pi\epsilon_0} \iint \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r}, \quad (9)$$

$$E_{\text{x}} = \frac{e^2}{4\pi\epsilon_0} \sum_{i,k}^N \iint \frac{\psi_i^*(\mathbf{r})\psi_k^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_k(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r}. \quad (10)$$

E_{ne} and E_{Coul} represent the classical potential energy of a charge distribution $\rho(\mathbf{r})$ in an external potential $v_{\text{ext}}(\mathbf{r})$. The third contribution to the potential energy, the exchange energy E_{x} , has no analogue in classical physics and is not present, if the wavefunction is written as a Hartree product. In the Hartree approximation the antisymmetry of the wavefunction is taken into account only by the Pauli principle, not allowing two electrons of the same spin to have the same orbital. That means a particular electron is assigned to a particular orbital, contrary to the fact that electrons are indistinguishable. As for the example of the He ^1S ground state and the corresponding ^3S

excited state it becomes clear that the total electronic energies calculated in the Hartree approximation³ (-5.105 and -3.057 MJ mol⁻¹, respectively) are only a first, qualitative approximation to the experimental values (-7.624 and -5.721 MJ mol⁻¹ [15]). One reason for the failure of quantitative agreement is the presence of self-interaction of each electron in the effective potential $j(\mathbf{r})$. The failure for the ^3S excited state is also due to the fact that the Hartree product is not antisymmetric.

In the Hartree-Fock method, the self-interaction of the individual electrons cancels, since it is included in the potential $j(\mathbf{r})$ and in the operator $\hat{k}(\mathbf{x})$. This cancellation of self-interaction is a very fortunate property of the Hartree-Fock method. For DFT methods, the incomplete cancellation of self-interaction is a problem, because the classical Coulomb interaction E_{Coul} is calculated exactly, whereas the exchange energy E_x is calculated only approximately. The inclusion of exchange leads to calculated energies for the He ^1S ground state and ^3S excited state (-7.513 and -5.229 MJ mol⁻¹, respectively) in reasonable agreement with the experimental values. The remaining difference between the calculated and the measured energies is mainly due to the electron correlation that is missing, because the wavefunction is written as a Hartree product or as a Slater determinant. Taking additionally into consideration the correlation of the positions of electrons leads to a reduction of the total electronic energy since the electrons can avoid each other. The correlation energy can be defined as difference between the true energy E and the Hartree-Fock energy E_{HF} :

$$E_c = E - E_{\text{HF}}. \quad (11)$$

Taking into account the Coulomb correlation, the monodeterminantal wavefunction must be replaced by a linear combination of Slater determinants. Using such an approach the energy of the He ^1S ground state can be lowered by 107 kJ mol⁻¹, reaching thus almost the experimental value. The remaining difference of 4 kJ mol⁻¹ is mostly due to relativistic effects and the finite mass of the He nucleus.

2.2

Local Density Approximation

The first density functional method that successfully describes real systems was introduced by Slater [16]. His idea was to replace the computational demanding Hartree-Fock exchange by the approximation $E_x[\rho] = \int v_x(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ with

³ This work, using the cc-VQZ basis set [14].

$$v_x(\mathbf{r}) = -\frac{9\alpha}{32\pi\epsilon_0} \left[\frac{3e^2}{\pi} \rho(\mathbf{r}) \right]^{1/3}. \quad (12)$$

This approach has been called $X\alpha$ method after the semiempirical parameter α , which has been introduced later by Schwartz [17]. Although, originally meant to approximate the Hartree-Fock approach, the $X\alpha$ method turned out to be superior in some areas like solid-state physics or transition-metal chemistry. Kohn and Sham established a sound theoretical basis for this method later: they proposed a system of non-interacting electrons in order to calculate accurately the kinetic energy in the DFT framework [18]. These non-interacting electrons move in the classical Coulomb potential of the nuclei and the electronic charge density, described by $v(\mathbf{r})$ and $j(\mathbf{r})$, respectively. The non-classical electron-electron interactions that give rise to E_x^{HF} and E_c in the Hartree-Fock approach are considered together in an effective potential $v_{xc}(\mathbf{r})$, the exchange-correlation potential. If the exchange operator $\hat{k}(\mathbf{x})$ in Eq. (5) is replaced by the term $ev_{xc}(\mathbf{r})$, one gets the so-called Kohn-Sham equations that can be solved iteratively, completely in analogy to the Hartree-Fock equations. In general, the resulting orbitals, the so-called Kohn-Sham orbitals, have a different meaning than the Hartree-Fock orbitals. Provided an exact expression is known for $v_{xc}(\mathbf{r})$, the squares of the Kohn-Sham orbitals add up precisely to the true ground-state density $\rho_0(\mathbf{r})$ and the energy of the highest occupied orbital equals the negative of the ionization energy (similar relations for the other orbital energies do not hold; there is no equivalent to Koopmans' theorem).

The total electronic energy in the Hartree-Fock scheme is given by $E^{\text{HF}} = E_{\text{kin}}^{\text{HF}} + E_{\text{ne}}^{\text{HF}} + E_{\text{Coul}}^{\text{HF}} - E_x^{\text{HF}} + E_c$, where the superscript denotes that Hartree-Fock orbitals are used for the evaluation of the individual contributions defined by Eqs. (7)–(11). In the Kohn-Sham scheme the total energy is given by $E^{\text{KS}} = E_{\text{kin}}^{\text{KS}} + E_{\text{ne}}^{\text{KS}} + E_{\text{Coul}}^{\text{KS}} - E_{xc}^{\text{KS}}$, where the exchange-correlation energy is defined by $E_{xc}^{\text{KS}} = \int v_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ and the superscript denotes that Kohn-Sham orbitals have been used in Eqs. (7)–(9). If the Hartree-Fock orbitals would be equal to the Kohn-Sham orbitals, the exchange-correlation energy E_{xc}^{KS} could be interpreted as the sum of the exchange energy E_x^{HF} and the correlation energy E_c in the Hartree-Fock scheme. However, in real systems E_{xc}^{KS} comprises also the differences $(E_{\text{kin}}^{\text{HF}} - E_{\text{kin}}^{\text{KS}})$, $(E_{\text{ne}}^{\text{HF}} - E_{\text{ne}}^{\text{KS}})$, and $(E_{\text{Coul}}^{\text{HF}} - E_{\text{Coul}}^{\text{KS}})$.

The Kohn-Sham scheme defines the functional E_{xc} that represents exchange and correlation. A separation of E_{xc} into exchange and correlation parts is not well defined. In practice, however, approximations to E_{xc} are given as a sum of separate exchange and correlation functionals. If the exchange-correlation potential $v_{xc}(\mathbf{r})$ at a given position $\mathbf{r}$ depends only on the charge density $\rho(\mathbf{r})$ at that position (as in Eq. 12), then $v_{xc}(\mathbf{r})$ is called *local*, and the functional $E_{xc}[\rho]$ belongs to the local density approximation (LDA).

In retrospect the $X\alpha$ method can be regarded as the first LDA method and the success of this method is due to the fact that the exchange potential $v_x(\mathbf{r})$ in Eq. (12) contains a certain extent of correlation energy.

2.3

Generalized Gradient Approximation

The exchange operator $\hat{k}(\mathbf{r})$ defined in Eq. (6) is a non-local operator, because it depends on the value of the orbitals ψ_i at all points in space. This fact has led to an improvement in the LDA by taking into account non-local effects. The first step in this direction is represented by exchange-correlation potentials of the form $v_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$, which include information about the gradient of the charge density. Surprisingly, first attempts to construct density functionals in this way did not lead to an improved accuracy. It turned out that additional restrictions (e.g., certain sum rules [3, 6, 7, 19]) had to be enforced. The class of density functionals that are constructed in this way are known as generalized gradient approximations (GGA). These functionals have led to major improvements and they are, together with the hybrid functionals (discussed in the next section), usually chosen if DFT methods are applied. Strictly speaking, these functionals are not non-local, because also $v_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$ depends on the properties of the charge density and its gradient at position $\mathbf{r}$ only. For this reason these functionals are sometimes called semilocal. A variety of different GGA functionals have been presented and applied in the last two decades (for an overview see [3]). Some popular GGA methods are Becke's exchange functional [20] together with the correlation functional of Lee, Yang, and Parr [21, 22] (known as BLYP method), Perdew and Wang's exchange functional and their gradient-corrected correlation functional [23] (PW91 method), or Becke's exchange functional [20] together with Perdew's gradient-corrected correlation functional [24] (BP86).

2.4

Hybrid Functionals

The Hartree-Fock exchange energy E_x^{HF} , Eq. (10), can be calculated exactly, while in DFT only approximate exchange functionals are available. E_x is usually about one order of magnitude larger than the correlation energy E_c , Eq. (11). Therefore, at first sight it seems to be promising to replace the approximate exchange functionals by E_x^{HF} combined with an approximate correlation functional. Such a hybrid method indeed performs significantly better than the Hartree-Fock method but delivers poor results in comparison to GGA methods [3]. Obviously, by combining approximations for E_x and E_c a cancellation of errors occurs, which is not the case if the exact expression E_x^{HF} is used. It should be noted also that for non-interacting Kohn-Sham or-

bitals the separation of exchange and correlation interaction is artificial. Despite this, combining the Hartree-Fock exchange with approximate density functionals has led to major improvements. Becke introduced a hybrid functional that includes 20% Hartree-Fock exchange [25]. From this functional the currently most popular hybrid functional, B3LYP, was later derived [26] where the exchange correlation energy is defined as follows:

$$E_{xc}^{B3LYP} = (1 - a)E_x^{LSD} + aE_x^{HF} + bE_x^{B88} + cE_c^{LYP} + (1 - c)E_c^{LSD} \quad (13)$$

with the semiempirical parameters $a=0.2$, $b=0.72$, and $c=0.81$. With the B3LYP method, an average error of the atomization energy of less than 10 kJ mol⁻¹ has been obtained for the G2 test set [3]. A similar accuracy can be reached only with high-level wavefunction-based methods, which are computationally much more demanding. In its ability to predict the ground-state multiplicity of iron(II) SCO complexes, B3LYP usually fails. Instead, pure DFT methods predict the correct ground state but they exceed in favoring the LS state [27, 28]. Reiher et al. ascribed this behavior to the admixture of Hartree-Fock exchange and proposed a reparameterization of the B3LYP method by setting $a=0.15$ in Eq. (13) [29]. First applications of this new method, called B3LYP*, suggest that the reduced admixture of Hartree-Fock exchange leads to more accurate results for the energy splitting between states with different spin multiplicity. At the same time the B3LYP* method exhibits an accuracy of atomization and ionization energies that is comparable to B3LYP [30].

3 Applications

The application of DFT to SCO complexes is a fairly recent development. Only in the past few years have GGA and hybrid functionals emerged and speed and memory of modern computers increased such that DFT calculations on SCO complexes could be performed. First calculations have focused on the frequency shift of the iron-ligand bond stretching vibrations [31–33]. The calculation of intensities for IR, Raman, and nuclear inelastic scattering (NIS [2]) spectra enabled the interpretation of spectroscopic data on the basis of the calculated normal modes [34–36]. The reasonable agreement that has been obtained for calculated and measured frequencies has encouraged the calculation of vibrational entropy and energy differences [27, 37, 38]. One of the most difficult problems, the calculation of the difference of total electronic energy between HS and LS isomers, has been approached only very recently [28, 38]. The reparameterization of the hybrid functional B3LYP brought the first methodological progress in this respect [29, 30]. Still, the accuracy of the electronic energy difference is not sufficient to cal-

culate transition temperatures exactly, but calculations for several iron(II) complexes with substituted pyrazolyl ligands have demonstrated that it is possible to predict qualitatively the effect of ligand substitution on the spin-transition temperature [27]. To do so, a simple model [39] has been used, that allows an explanation for gradual transitions, where the molar HS fraction $\gamma_{\text{HS}}(p, T)$ at given pressure p changes smoothly over a large interval of temperature T :

$$\gamma_{\text{HS}}(p, T) = 1/[1 + \exp(\Delta G/k_B T)]. \quad (14)$$

Here ΔG denotes the difference (HS-LS) of the Gibbs free energy,

$$G = E_{\text{el}} + E_{\text{vib}} + pV - TS, \quad (15)$$

depending on the total electronic energy E_{el} , the vibrational energy E_{vib} , pressure p , volume V , temperature T , entropy S , and, implicitly, on γ_{HS} . This means that Eq. (14) has to be solved iteratively. The molar HS fraction γ_{HS} is used for the determination of many properties of spin crossover materials, for instance the transition temperature $T_{1/2}$. It is defined by

$$\gamma_{\text{HS}}(p, T_{1/2}) = 1/2 \quad (16)$$

The term $p\Delta V$ cannot be calculated in the molecular approximation that is usually applied. A typical value of $\Delta V \approx 7 \text{ cm}^3 \text{ mol}^{-1}$ [40] leads to a contribution to the free energy of $p\Delta V \approx 0.7 \text{ J mol}^{-1}$ at ambient pressure and temperature. This is far less than the error margin of the other contributions to ΔG , and the neglect of $p\Delta V$ is therefore justified.

3.1

Molecular Geometry and Mössbauer Parameters

For many SCO complexes, X-ray structures in either the LS or HS state or in both states are not available. In these cases, an optimization of the molecular geometry has to be the first step of a computational study. This means that the derivatives of the total energy with respect to the nuclear coordinates have to be calculated, and the coordinates have to be varied until the energy reaches a local minimum. There are several reasons why this procedure is also applied when X-ray structures are actually available. If calculated quantities for different complexes and spin states are compared, the differences might sensitively depend on the method that was used to determine the molecular geometry. This is clearly the case for differences of the total electronic energy (see below). In addition, most algorithms for frequency calculations demand a preceding geometry optimization. The comparison of measured and calculated geometries of SCO complexes is hampered by the fact that X-ray measurements are performed for solid samples whereas, to our knowledge, all calculations have been performed for free molecules. Some

Table 1 Measured and calculated iron-ligand bond distances in Å

Complex	Method	Fe-N _{NCS}			Fe-N _{lig}		
		LS	HS	Δ	LS	HS	Δ
[Fe(phen) ₂ (NCS) ₂]	X-Ray [54]	1.96	2.06	0.10	2.00	2.20	0.2
	DFT	1.90	1.98	0.08	1.93	2.17	0.24
[Fe(tpa)(NCS) ₂] (β)	X-Ray [55]	1.95	2.08	0.13	1.96	2.21	0.25
	EXAFS [35]	1.95	2.05	0.10	1.95	2.19	0.24
	DFT	1.91	2.00	0.09	1.93	2.23	0.30
[Fe(bptn)(NCS) ₂] ^a	X-Ray [56]		2.10			2.20	
	DFT	1.91	2.03	0.12	1.94	2.18	0.24
[Fe(tptMetame)]	X-Ray [57]				2.04	2.24	0.20
	DFT				2.09	2.25	0.16

^a bptn=*N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine

typical examples for measured and calculated iron-ligand bond distances are given in Table 1. The iron-ligand bond has been chosen because it belongs to the structural parameters of SCO complexes that are most difficult to calculate and because, to a first approximation, it can be regarded as the reaction coordinate of the spin crossover. Most of the calculated iron-ligand bond distances given here are a few picometers smaller than the experimental values. Since this is true for both spin states, the deviations cancel out in part when the increase of the bond length (Δ) upon spin crossover is calculated (Table 1).

Another test for the reliability of a computational study, besides the comparison of X-ray structure and calculated molecular geometry, is the investigation of Mössbauer parameters. Mössbauer spectroscopy is one of the key techniques for the investigation of iron(II) SCO complexes. Two basic parameters that can be obtained from Mössbauer spectra are the quadrupole splitting ΔE_Q and the isomer shift δ . The latter reflects the total electronic charge density at the iron nucleus, while ΔE_Q provides information about the anisotropy of the electric field gradient at the iron center [41]. The quadrupole splitting can be qualitatively explained in the ligand-field model; it takes values of $\approx 1\text{--}4\text{ mm s}^{-1}$ for an iron(II) HS complex and of $\approx 0\text{ mm s}^{-1}$ for an LS complex. Electronic structure calculations are needed for a more accurate description. For iron(II) SCO complexes with substituted tris(pyrazolyl)methane ligands [42], measured and calculated data are compared in Table 2.

The parent complex of this series [27] consists of an iron(II) center and two tris(pyrazol-1-yl)methane ligands ([Fe(tpm)₂](PF₆)₂, compound **1a**, Fig. 1). Additional complexes are obtained, if hydrogens of the pyrazole rings are substituted. Compounds **2a**, **2b**, and **2c** consist of an iron(II) center and two tris(3-methyl-pyrazol-1-yl)methane ligands [the letters denote the counterions PF₆[−] (a), ClO₄[−] (b), and BF₄[−] (c)]. Compounds **3a**, **4b**, and **5b**

Table 2 Measured quadrupole splitting ΔE_Q and isomer shift δ in mm s^{-1} (values calculated with B3LYP/6-311G in parentheses)^a

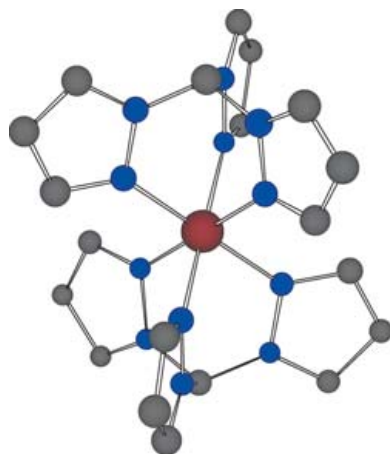
Complex	ΔE_Q		δ	
	LS	HS	LS	HS
1a	0.30 (0.10)	2.20 (3.81)	0.47	0.85
2a	0.39 (0.01)	3.96 (3.75)	0.53	1.13
2b	0.43 (0.01)	3.71 (3.75)	0.53	1.24
2c	0.36 (0.01)	3.99 (3.75)	0.53	1.13
3a	0.32 (0.09)	3.55 (-)	0.51	0.97
4b	0.35 (0.12)	3.12 (3.34)	0.48	1.41
5b	- (-)	3.99 (-)	-	1.15

^a All values taken from [28]

are derived from tris(4-methyl-pyrazol-1-yl)methane, tris(4-bromo-pyrazol-1-yl)methane, and tris(3,5-dimethyl-pyrazol-1-yl)methane, respectively.

The calculated quadrupole splittings for the LS isomers are all close to zero (Table 2) as expected from the ligand-field model, while the measured values are about 0.3–0.4 mm s^{-1} larger. One reason for this deviation is that the high symmetry of the free molecule (D_{3d} according to the calculation) is reduced in the solid-state environment. The measured quadrupole splittings for the HS isomer are in the range from 3 to 4 mm s^{-1} , except for complex 1a. For the latter complex, where the transition temperature is about 355 K, the quadrupole splitting of the HS state has been measured at room temperature only. The large deviation between the calculated and the measured ΔE_Q values for this complex is very likely due to a decrease of ΔE_Q with in-

F

**Fig. 1** Molecular structure of the HS isomer of complex 1 calculated with B3LYP/6-311G. Hydrogens have been omitted for clarity

creasing temperature which is ascribed to the small splitting of the t_{2g} orbital energies. The calculated quadrupole splittings of the SCO complexes 2–5 are in agreement with the experimental data. The small differences of ΔE_Q for complexes 2a, 2b, and 2c illustrate the small influence of the counterions, which is not included in the calculation for the free molecule.

In the case of temperature-dependent Mössbauer spectroscopy, the areas of the subspectra for the HS and LS isomers are used to determine the molar HS fraction γ_{HS} . For this purpose, the measured areas have to be corrected for the Lamb-Mössbauer factors f_{LM}^{HS} and f_{LM}^{LS} , which can be quite different for HS and LS isomers. These factors can be determined experimentally by nuclear resonant forward scattering [2, 35], or they can be calculated employing DFT methods. For molecular crystals the Lamb-Mössbauer factor can be approximated by a product of a lattice factor and a molecular factor [43]. For $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ a change of the molecular Lamb-Mössbauer factor from 0.92 (LS isomer at 34 K) to 0.75 (HS isomer at 107 K) has been calculated [35]. In order to calculate the complete Lamb-Mössbauer factor, calculations for a molecular crystal with periodic boundary conditions have to be performed.

3.2

Vibrational Modes and IR, Raman, and NIS Spectra

It is well known that the entropy change accompanying the crossover from the LS to the HS state is positive. This entropy difference is due to the different spin state degeneracies and the changes of vibrational frequencies. The vibrational contribution to the entropy difference can be explained qualitatively by a simple model based on ligand-field theory [1]. Accompanying the transition from the LS to the HS state, two Fe 3d electrons are transferred from the t_{2g} into the e_g orbitals. Actually, these molecular orbitals are antibonding linear combinations of Fe 3d atomic orbitals and ligand atomic orbitals. Therefore, emptying the π -antibonding t_{2g} molecular orbitals stabilizes the iron-ligand bonds, whereas filling the more covalent σ -antibonding e_g orbitals with electrons destabilizes these bonds. As a consequence, the frequency of the bond stretching vibrations is decreased. This frequency shift is generally difficult to observe by IR and Raman spectroscopy, since typical SCO complexes have a few hundred vibrational modes. It is very difficult to make a complete assignment of vibrational modes to the large number of observed lines. For the well-studied SCO complexes $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (phen=1,10-phenanthroline) Takemoto et al. [44] reported a decrease of the iron-ligand bond stretching frequency by a factor of two. Similar frequency shifts have been reported for several other SCO complexes [45]. This corresponds to a decrease of the force constant by the surprisingly large factor of four. With the development of nuclear inelastic scattering (NIS) [2] a spectroscopic technique became available that focused on the iron-ligand

bond-stretching vibrations. At first NIS spectra were recorded for powder samples of the SCO complexes $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ (tpa=tris(2-pyridylmethyl)amine) [2, 31, 32, 35] and $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$ [46] (bpp=bis(2,6-bis(pyrazol-3-yl)pyridine)), and later for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [36]. Angular resolved measurements have been performed for a single-crystalline sample of $[\text{Fe}(\text{tptMetame})]$ [2, 34] (tptMetame=1,1,1-tris((N-(2-pyridylmethyl)-N-methylamino)methyl)ethane). Comparison of the measured NIS spectra with simulated spectra based on DFT frequency calculations for free molecules allowed the assignment of the observed peaks to normal modes, which have predominant iron-ligand bond-stretching character [32, 34, 36]. A perfectly octahedral metal complex should exhibit six metal-ligand bond-stretching modes transforming according to the A_{1g} , E_g , and T_{1u} irreducible representations of the octahedron group O_h . Since the *gerade* modes A_{1g} and E_g do not contribute to the mean-square-displacement of the metal center, these modes are not seen in the NIS spectra. In the spectrum of an ideally octahedral complex only one threefold degenerate *ungerade* T_{1u} mode would be visible. Due to distortions of the molecular symmetry, the degeneracy of the T_{1u} modes is lifted. If the complex does not possess inversion symmetry, the metal-ligand bond-stretching modes that correspond to A_{1g} and E_g representations in octahedral symmetry can also become visible [2]. In Table 3 the frequencies of the bond-stretching modes that have been observed in the NIS spectra of $[\text{Fe}(\text{tptMetame})]$, $[\text{Fe}(\text{tpa})(\text{NCS})_2]$, and $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ are given. The averaged increase of the bond-stretching vibrations are 40%, 47%, and 31%, respectively. This corresponds to an increase of the force constant by a factor of two. Comparison of the assignment made by Takemoto et al. [44] with the calculated normal coordinates suggests that one Fe-N-CS bending mode has been assigned as Fe-N bond-stretching mode by Takemoto, leading thus to an increase of the Fe-N bond-stretching frequency shift.

Apart from the assignment of the iron-ligand bond-stretching vibrations the comparison of the measured and simulated NIS spectra is of importance also as a quality test of the calculated normal modes. The NIS intensity depends on the eigenvalues and on the eigenvectors of the normal modes of vibrations. A similar test is provided by the comparison of measured and calculated IR and Raman intensities. For the complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ the comparison of measured and calculated IR, Raman, and NIS intensities has

Table 3 Iron-ligand bond stretching frequencies in cm^{-1} observed by NIS

Complex	Ref	HS	LS
$[\text{Fe}(\text{tptMetame})]$	[34]	226, 266	323, 331, 355, 371
$[\text{Fe}(\text{tpa})(\text{NCS})_2]$	[32]	242, 282	347, 379, 427
$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$	[36]	229, 331	359, 366, 377

been used to obtain a complete assignment of the 147 normal modes of vibration [36].

Detailed comparison of measured IR and Raman frequencies and calculated frequencies using a large basis set and different DFT methods have been performed by Reiher and coworkers [37, 38]. They have demonstrated the importance of intermolecular interactions for an accurate calculation of the N-C stretching frequency of the isothiocyanates.

3.3

Entropy and Vibrational Energy Differences

In the previous section it has been shown that the molecular vibrations of spin crossover complexes can be calculated with reasonable accuracy. Therefore, it is worthwhile to use the calculated vibrational modes to compute thermodynamic quantities such as the vibrational entropy and the vibrational energy. The temperature-dependent vibrational energy $E_{\text{vib}}(T)$ and vibrational entropy contribution $S_{\text{vib}}(T)$ of a molecule containing M atoms can be calculated according to

$$E_{\text{vib}}(T) = k_{\text{B}} T \sum_{i=1}^{3M-6} x_i \coth(x_i) \quad (17)$$

and

$$TS_{\text{vib}}(T) = E_{\text{vib}}(T) - k_{\text{B}} T \sum_{i=1}^{3M-6} \ln[2 \sinh(x_i)], \quad (18)$$

where ω_i is the angular frequency of vibrational mode i and $x_i = \hbar\omega_i/2k_{\text{B}}T$. The vibrational energies have to be discussed on a purely theoretical basis, since there are no experimental data available for spin crossover complexes. The differences of vibrational energy influence the transition temperature according to Eq. (15), but the calculated results suggest that this influence is quite small. The situation is different for the entropy where experimental data are available for the difference between HS and LS isomers. Qualitative agreement can be obtained between the calculated entropy differences of free molecules and measured data for solid samples and for solutions (Table 4).

Table 4 Calculated and measured entropy differences in $\text{J mol}^{-1} \text{K}^{-1}$ and exp. transition temperatures in K

Complex	ΔS		$T_{1/2}$
	Exp	DFT	
$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$	49 [58]	60	176
$[\text{Fe}(\text{tacn})_2]^{2+}$ in $\text{D}_2\text{O}^{\text{a}}$	61(3) [59]	55	344
$[\text{Fe}(\text{tacn})_2]^{2+}$ in acetone ^a	73(37) [59]	55	328

^a tacn=1,4,7-Triazacyclononane

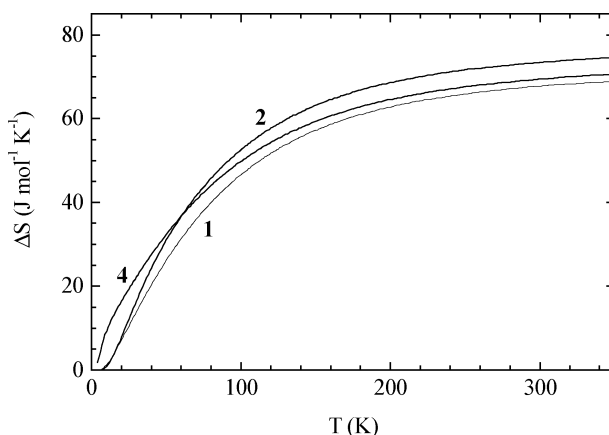


Fig. 2 Temperature dependent vibrational entropy difference for complexes 1, 2, and 4 calculated with BLYP//LANL2DZ (taken from [28])

Baranovic [47] has shown that the agreement can be significantly improved if solvation effects are taken into account in the calculation.

For the experimentally thoroughly investigated complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ detailed calculations by Brehm et al. [37] and by Reiher [38] suggest that pure DFT methods like BP86 give the best agreement with experimental entropy differences. For the example of iron(II) complexes with tris(pyrazolyl)methane ligands, the extent to which the entropy difference is influenced by different substituents at the ligands has been investigated [28]. The calculated differences are quite small (Fig. 2) and it can be concluded that the observed changes in $T_{1/2}$ are due mostly to changes of the total electronic energy differences ΔE_{el} .

3.4

Electronic Energy Differences

The total electronic energy difference between the HS and the LS isomer, $\Delta E_{\text{el}} = E_{\text{el}}^{(\text{HS})} - E_{\text{el}}^{(\text{LS})}$, is one of the most basic and yet most difficult to calculate quantities associated with SCO. Taking the entropy difference and transition temperature $T_{1/2}$ from experiment, the total energy difference can be roughly estimated by the relation

$$\Delta E_{\text{el}} \approx T_{1/2} \Delta S(T_{1/2}), \quad (19)$$

leading to values in the range of 1 to 30 kJ mol^{-1} . The calculated electronic energy of a typical SCO complex is of the order of some 10^6 kJ mol^{-1} . The energy difference is therefore, more than five orders of magnitude smaller than the absolute energy values. Since the total electronic energy of a transition metal complex cannot be calculated with an accuracy of some kJ mol^{-1}

(corresponding to a relative error of about 1 ppm), a successful calculation of ΔE_{el} depends on an extensive cancellation of errors. In other words, it is important that errors, which cannot be avoided, affect the calculated energy of both isomers in the same way. Due to the small energy difference between LS and HS isomers, calculations for SCO complexes are extremely sensitive to a bias towards a particular spin multiplicity. This makes SCO complexes ideal objects for testing electronic structure methods that should be able to predict the true ground state multiplicity of transition metal complexes. For transition metal complexes containing up to one hundred atoms, there are no high-level ab initio calculations available which serve as a benchmark, and therefore the results of any method can be judged only in the light of experimental results.

Concerning the spin multiplicity of iron(II) complexes, there are two classical examples, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, which exemplify the two extreme cases, namely the diamagnetic, LS $^1\text{A}_{1\text{g}}(\text{t}_{2\text{g}}^6)$ ground state and the paramagnetic, HS $^5\text{T}_{2\text{g}}(\text{t}_{2\text{g}}^4\text{e}_{\text{g}}^2)$ ground state [1]. For both complexes, the geometry of the free molecule has been optimized for the HS and for the LS state, using the Hartree-Fock method and various DFT methods. The calculated energy difference between the HS and the LS state (Table 5) shows that any of the applied methods yields the correct ground state for these two complexes. However, large differences are observed in the results of the individual methods. For the SCO complex $[\text{Fe}(\text{tpm})_2]^{2+}$ (complex 1), for example, the differences between the computational methods become even more obvious.

Unfortunately, most applicable methods have a bias towards either the LS or the HS state. This is most obvious in the case of the Hartree-Fock method, which systematically favors higher spin multiplicities. The reason is that in this method the correlation between electrons with the same spin projection (Fermi correlation) is taken into account by the exchange interaction.

Table 5 Energy difference ΔE (in kJ mol^{-1}) between HS and LS isomers

	$[\text{Fe}(\text{H}_2\text{O})_5]^{2+}$	$[\text{Fe}(\text{tpm})_2]^{2+}$	$[\text{Fe}(\text{CN})_6]^{4-}$
HF		−300.1 ^a	−1815.5
MP2		−137.1 ^b	
HFS			
BLYP		81.7 ^a	139.9
PW91		103.5 ^a	−1820.2
B3LYP	−562.4 ($\text{D}_{2\text{h}}$)	−7.3 ^a	0.6
	−238.2 ($\text{C}_{2\text{h}}$)		
B3LYP*		21.4	49.4
Experiment ^c	<<0	≈26	>>0

^a Taken from [28]

^b Using the geometry optimized with HF and employing the LANL2DZ basis set

^c Estimation based on experimental $T_{1/2}$ and calculated ΔS as explained in the text

Correlation between electrons with different spin projections (Coulomb correlation) is instead completely neglected in the Hartree-Fock scheme. For example, the four unpaired 3d electrons in an iron(II) HS complex avoid each other to a large extent due to the orthogonality of the 3d orbitals. In the LS complex, the three lowest 3d orbitals are doubly occupied and due to the monodeterminantal form of the wavefunction the spin-up and spin-down electrons occupying the same 3d orbital cannot avoid each other to the same extent. As a result, in the LS case the Coulomb repulsion between the electrons is too large.

The situation is better for DFT methods, which include some correlation effects, and in general, DFT methods predict the correct LS ground state for SCO complexes. However, pure DFT methods seem to favor the LS state leading to an energy difference ΔE_{el} which is too large [27, 29]. Currently, the most accurate functionals for the calculations are hybrid functionals, namely the B3LYP method. Although the B3LYP method often predicts the wrong ground state multiplicity [27–30], the deviation between the calculated ΔE_{el} and the true energy difference seems to be smaller than in the case of pure density functionals. The most accurate functional for this purpose is the reparameterized hybrid functional B3LYP* [29, 30] where the admixture of the Hartree-Fock exchange has been reduced in comparison to the B3LYP method.

For the calculation of vibrational frequencies, it has been found out that the accuracy of the calculated values can be improved if experimental geometries are used instead of optimized ones [48]. It is an appealing idea to use the same procedure for the calculation of electronic energy differences. The drawbacks of this procedure are illustrated with the SCO complex $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$. Chen et al. [49] obtained for the HS and the LS isomer of this complex total energies of -6789.985 and -6790.071 MJ mol $^{-1}$, respectively, using the B3LYP/3-21G method and an X-ray structure (site A) at 293 K [49]. The calculations were performed for free molecules. Calculations using the same DFT method and using the X-ray structure (site A) at 298 K given in [50], yielded total energies of -6790.013 and -6790.048 MJ mol $^{-1}$ [27]. Both calculations are in general agreement, but the resulting total energy differences (85 kJ mol $^{-1}$ [49] and 35 kJ mol $^{-1}$ [27]) deviate significantly. Since both calculations have been performed with identical methods implemented in the same program package, Gaussian98 [51], this deviation is probably due to very small differences in the X-ray structures given in [49, 50]. After optimization of the geometry of the free cation $[\text{Fe}(\text{tpen})]^{2+}$ using B3LYP/3-21G, total energies of -6790.168 MJ mol $^{-1}$ and -6790.158 MJ mol $^{-1}$ were obtained for the HS and the LS isomer, respectively [27]. The resulting energy difference $\Delta E_{\text{el}} = -10$ kJ mol $^{-1}$ suggests a HS ground state which is wrong. However, considering the error margin of these calculations (especially in view of the very small basis set) the results of all three calculations, using the X-ray structures in [49, 50] and the optimized geometries in [27],

are in agreement. The large deviations for ΔE_{el} that are traced back to the errors of the X-ray structures do not support the assumption that the accuracy of ΔE_{el} could be improved significantly by the use of X-ray structures.

The comparison of calculated electronic energy differences with experimental results is hampered by the fact that the large majority of experimental data has been gained for solid state samples. The electronic energy difference that has been derived from experimental data is therefore influenced by intermolecular interactions which are not present in calculations for free molecules. From the observed shifts of the transition temperatures when replacing counterions [28, 52, 53] it can be concluded that the influence of the intermolecular interactions is comparable in size with the error of the calculated ΔE_{el} when using for instance B3LYP*. The next step to increase the accuracy of ΔE_{el} should therefore be calculations with periodic boundary conditions.

3.5

Substituent Effects on the Transition Temperature

Due to the insufficient accuracy of the calculated total energy difference ΔE_{el} , it is not possible to predict the transition temperature of a SCO complex directly from theory. The situation can be different, if the shift of transition temperatures is of interest, e.g., when going from one complex to another very similar one. While the calculated absolute temperatures for these complexes are meaningless, the calculated temperature difference can be a reasonable value. This can happen when the errors of the calculated absolute temperature cancel to a large extent. Ideal objects for such a computational strategy are, for instance, iron(II) complexes with tris(pyrazolyl)methane ligands [42]. Some of these complexes have been studied by Mössbauer spectroscopy and magnetic susceptibility measurements, and from the observed spectra the molar high-spin fraction and the transition temperature have been extracted [28]. All substituents, except for bromine, lead to a decrease of the transition temperature. Density functional calculations have been carried out to compare the experimentally observed shifts of the transition temperature with those derived from theory. These calculations have been carried out for isolated complexes in vacuo. This approximation neglects interactions between neighboring complexes and interactions between the complexes and their counterions. Both interactions are known to considerably influence $T_{1/2}$. Calculations that do not regard these interactions can therefore at best be in qualitative agreement with the experiment. Nevertheless, such calculations for isolated complexes in vacuo may reveal information about the molecular contribution to substituent-induced shifts of $T_{1/2}$. This information can hardly be gained experimentally since any experiment with a solid sample will only reflect the combined influence of intra- and intermolecular interactions.

For the complexes **1a**, **2a**, **2b**, **2c**, **3a**, **4b**, and **5b**, which were introduced above, the transition temperatures have been determined by Mössbauer spectroscopy and magnetic susceptibility measurements [28]. For the compounds **2a** and **5b** the transition temperature determined by magnetic susceptibility measurements is close to 0 K and it might be that these complexes undergo only a partial or no spin transition. Except for compound **4b**, which has roughly the same transition temperature as the parent complex **1a** (≈ 355 K), all other compounds exhibit a lower transition temperature. Substituting a hydrogen atom of the pyrazol ring by a methyl group, as in compounds **2a**, **2b**, **2c**, and **3a**, decreases $T_{1/2}$ in comparison to the transition temperature of **1a**. The decrease is even greater if two hydrogens are substituted, as is the case for compound **5b**. Comparison of compounds **2a**, **2b**, and **2c** reveals an additional significant influence of the counteranion on $T_{1/2}$.

From the DFT calculations for complexes **1–5** the difference of electronic energy ΔE_{el} , of vibrational energy ΔE_{vib} , and of entropy ΔS was retrieved. It has been assumed, that the lowest electronic excitation energy is large compared to $k_{\text{B}}T$, and hence ΔE_{el} is regarded to be constant in the temperature range of interest. All calculated terms of the free energy depend significantly on the chosen method and basis set.

The temperature-dependent free energy difference $\Delta G(T)$ is calculated by summing up the terms given in Eq. (15) except for the volume change, which is neglected. Ideally, the points of intersection of the curves $\Delta G(T)$ with the abscissa should yield the transition temperatures $T_{1/2}$, according to its definition in Eq. (14). However, it is obvious that the calculated curves are shifted due to errors of ΔE_{el} , and this prevents the determination of absolute values for $T_{1/2}$. A rough estimate for the difference $\Delta T_{1/2}$ of transition temperatures when comparing two complexes **a** and **b** can be obtained by the expression

$$\Delta T_{1/2} \approx (\Delta E_{\text{el}}^{\text{b}} - \Delta E_{\text{el}}^{\text{a}}) / \Delta S(T_{1/2}^{\text{a}}) \quad (20)$$

where $T_{1/2}^{\text{a}}$ must be known from experiment and $\Delta S^{\text{a}}(T) \approx \Delta S^{\text{b}}(T)$ is assumed. Comparison of the shift of the transition temperature estimated in this way with experimental values yields agreement for the direction of the shift and for the order of magnitude of the shift.

It has been shown for the example of bis-tripodal chelates of iron(II) with tris(pyrazolyl)methane ligands that $T_{1/2}$ can be influenced significantly if methyl groups substitute hydrogen atoms of the pyrazole rings. The calculations presented here suggest that it should be possible with currently available density functional methods to predict the direction and the order of magnitude of a shift of the transition temperature.

It is interesting to note that the calculated shifts of ΔE_{el} , accompanying the change from the unsubstituted complex **1** to the substituted complexes, seem to be of similar order of magnitude for the HF methods and for the

Table 6 ΔE_{el} in kJ mol^{-1} calculated with the 6-311G basis set and with the Hartree-Fock and different DFT methods (values in brackets give the difference to complex 1)

Complex	HF	B3LYP	B3LYP*	BLYP	PW91
1	−300.1 ^a	−7.3 ^a	21.4	81.7 ^a	110.7 ^a
2		−39.5 ^a (32.2)	−12.7 (34.1)	39.1 ^a (42.6)	71.3 (39.4)
3		−6.1 (−1.1)	22.2 (−0.8)	83.4 (−1.6)	111.9 (−1.2)
4	−300.6 (0.5)	−7.7 (0.4)	19.8 (1.6)	79.1 (2.6)	107.6 (3.1)

^a Taken from [28]

DFT methods (Table 6, values in brackets). It seems that, when comparing similar complexes, a large part of the error of ΔE_{el} cancels out.

4 Summary

Density functional methods have been proven to provide fairly accurate results for many properties of SCO complexes. Even with modest basis sets, the geometrical structure can be described qualitatively. Using large basis sets, an accuracy of a few picometers can be obtained for bond lengths. Good agreement has been reached also for Mössbauer parameters, vibrational frequencies, and entropy differences. Due to the reparameterized hybrid functional B3LYP* an accuracy of about 10 kJ mol^{-1} can be reached for the total electronic energy difference. This is unfortunately still not sufficient for direct calculations of the transition temperature. However, DFT calculations can provide reasonable estimates for transition temperature differences, if complexes are investigated that differ only by small modifications of the ligands.

It is expected that calculations for solid samples using periodic boundary conditions will bring further progress in the field of electronic structure calculations for SCO complexes.

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Towards Spin Crossover Applications

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Abstract In this chapter we attempt to review the potential for the application of the spin crossover (SCO) phenomenon in various domains, such as molecular electronics, data storage, display devices. It is evident that SCO properties, such as room-temperature working range, chemical stability, low addressing power, short addressing time, full reversibility, are of promising value in the context of the stringent limits necessary in the future development of information technology, due to the unceasing miniaturization of the components. Of course, many requirements must be fulfilled before any use in a genuine device becomes feasible. Some of these are emphasized and discussed here. Additionally, this review reports recent progress in non-linear optics and photomagnetism of SCO materials.

Keywords Spin crossover · Molecular bistability · Molecular devices · Nanotechnology · Molecular electronics · Switchtronic

List of Abbreviations and Symbols

AFM	Atomic force microscope
β	First molecular hyperpolarizability tensor
bpp	2,6-Bis(pyrazol-3-yl)pyridine
btr	4,4'-Bitriazole
CD	Compact discs
CRT	Cathode-ray tube
Htrz	1,2,4-Triazole
Hyettrz	4-(2'-Hydroxyethyl)-1,2,4-triazole
ILCT	Intra-ligand charge transfer
LB	Langmuir-Blodgett
LCD	Liquid crystal display
MLCT	Metal-to-ligand charge transfer
MO	Magneto-optics
NH ₂ trz	4-Amino-1,2,4-triazole
NLO	Non-linear optics
PM-Bia	2'-Pyridylmethylene 4-aminobiphenyl
PM-PEA	N-2'-Pyridylmethylene-4-phenyl-ethynylaniline
PM-2PEA	N-2'-Pyridylmethylene-4-phenyl-ethynylphenylethynylaniline
SONLO	Second order non-linear optics
SPE	Super paramagnetic effect
trz	1,2,4-Triazolate(1-) ion
tvp	Bis-1,2-di(4-pyridyl)ethylene

1**Introduction**

In the last 30 years, the interest in “molecular materials”, possessing a property or a set of properties relevant for practical applications, has considerably increased. This growth mainly comes from the result of the development of communication devices and the necessity of component size reduction [1–4]. The molecular scale is increasingly being considered as the answer to the miniaturization of the components used in the construction of working devices [5–14]. The current large-downward (top-down) approach based on silicon technology forces solid-state physicists and electronic engineers to manipulate progressively smaller and smaller pieces of matter [15]. In regard to this, molecule-based devices offer prospects of sensitivity and selectivity levels that cannot be reached with conventional solid-state materials. It is necessary, however, to reproduce traditional electronic functions, as memories, modulators, rectifiers, transistors, switches and wires [5–14]. Today, many organic and coordination derivatives are being investigated. In this context, coordination complexes are especially promising since a judicious choice of metal ions and ligands allows one to modulate the final physical properties of the complexes, and even in some cases, to combine in a synergistic way different physical properties.

In the present review, we focus our attention on the spin crossover (SCO) property encountered in some coordination complexes having a d^n ($n=4-7$) electronic configuration. In some specific cases, iron(II) molecular materials may exhibit a change of the spin state under external perturbations (change of temperature, application of pressure, by light irradiation or by pulsed magnetic field [16, 17]) combined with (i) room-temperature working range, (ii) stability over successive cycles, (iii) low addressing power (about 5 mW/cm^2), (iv) short addressing time since the transition is purely electronic in nature (nanosecond scale), and (v) a hysteresis effect when the transition between the two states is accompanied by cooperative effects [18–20]. Many applications can then be envisaged. Here we attempt to illustrate the potential for application of the spin crossover (SCO) phenomenon in molecular electronics, data storage, display devices, non-linear optics, and photomagnetism. This treatment is certainly not exhaustive and the writers apologize for any omissions.

This work is organized in four sections. The first introduces the general context of molecular electronics and gives the main requirements that a molecular compound must fulfill to act as an active molecular switch. The SCO suitability is then analyzed. The second section reports some highlights concerning the current technology used to store data and the presence of a thermal hysteresis loop in SCO materials. The particular challenge in the design of cooperative clusters is emphasized. The third section deals with the fabrication of display devices. The state of the art is first recalled, then the various criteria that a molecular material has to fulfill before any use in genuine display devices is possible, are detailed. Finally, examples of data displays based on SCO materials are described. -The last section of this chapter focuses on the recent improvements in the design of switchable non-linear optical materials as well as the possibility to address spin states through light irradiation.

2

Towards the Design of Molecular Switches, a Switchtronic Challenge

2.1

The General Context of Molecular Electronics

For many years, the developments of telecommunication and internet networks have been concerned with the miniaturization of electronic devices. As an example, Intel co-founder Gordon Moore observed in 1965 that the number of transistors per cm^2 of silicon doubled every year and predicted that it would continue to do so for the next ten years [1]. In fact, this prediction has been remarkably realized and has gained the status of a “law”. It is now accepted that the number of transistors on a chip doubles approximate-

ly every 18 months [2]. However, there are some alarming signals starting to appear [15]. It seems that this size reduction, and thus this speed increase, can only continue for a finite time. The fabrication of small electronic devices becomes more and more difficult, and expensive, as the nanometer scale is approached. The current technology is based on the large-downward (top-down) approach, which means the fabrication and the manipulation of progressively smaller and smaller pieces of silicon matter.

Nowadays, the individual features found in commercially available personal computers are less than $1\text{ }\mu\text{m}$ across and compare with the size of a virus. There thus exist several significant challenges in the future miniaturization of such components. For instance, one important limitation in the fabrication process of a complete integrated circuit (including wires, resistors, capacitors and transistors) lies in the photolithographic steps [15, 21]. The wafer with a layer of photoresist is exposed through a patterned mask. The resolution obtained by using 248 nm irradiation is currently around 0.18 to $0.25\text{ }\mu\text{m}$. Future plans are in mind for using 193 nm (ArF Excimer Laser) and 157 nm (KrCl Excimer Laser) wavelengths in order to reach a size of 0.13 and $0.1\text{ }\mu\text{m}$ [15]. Even X-ray lithography ($\lambda < 1\text{ nm}$) or extreme UV lithography ($\lambda \approx 13\text{--}4.5\text{ nm}$) are being envisaged. The development of reliable techniques to produce conventional silicon-based devices with dimensions lower than 100 nm represents an exciting technological challenge [15].

In this particular context, the molecular or the atomic level is, more and more, considered as the size of the ultimate integrated circuit. This represents the small-upward (bottom-up) approach. Molecular-sized systems offer an exciting opportunity to use $\sim 10^{13}$ logic gates/ cm^2 in comparison with the 10^8 gates/ cm^2 of present microchips. In addition, the response times of molecular devices can be in the range of femtoseconds while the fastest present devices operate in the nanosecond regime. The goal is then to reproduce conventional microelectronic functions by using a single molecule, or a small group of molecules, carbon nanotubes, or nanoscale metallic or semiconductor wires. There are now some remarkable examples of molecular functions, as memories, modulators, rectifiers, transistors, switches, and wires [5, 9, 12, 14, 22–24]. In relatively few years, the “naive” expectation of the use of a molecule to perform electronic functions has become a widespread research field, named “Molecular Electronics”. Chemists, physicists, materials scientists, as well as electrical and chemical engineers, are working intensely on this bottom-up approach. Of course, numerous obstacles remain. We shall first examine the requirements that a molecular switch, which certainly represents the simplest device in the future of molecular-based electronics, must fulfill.

2.2

Molecular Switches

The characteristic that defines a molecular switch is the bistability domain with an “ON” and an “OFF” position. In its “ON” position, the molecular switch must either perform some function or allow another device to perform a function while in its “OFF” position, it must remain inactive. The two states can be isomers, an acid and its conjugate base, the oxidized and reduced forms of a redox active molecule, or even the complexed and uncomplexed forms of a receptor [10, 25–32]. Often, these transformations are reversible. The chemical system returns to the original state when the input signal is turned off. In some instances, the molecular switch produces a chemical, electrical, and/or optical output that varies in intensity with the switching process. For example, a change in pH, redox potential, absorbance, or emission intensity can accompany the interconversion between the two states of a molecular switch [10, 25–32].

In such a context, the molecular bistability associated with the SCO phenomenon is very relevant. The change of the spin state in a SCO material, as illustrated in Fig. 1, can be induced reversibly in a solid matrix under external inputs (temperature, pressure, light irradiation, pulsed magnetic field) [16, 17]. In response to these stimulations, the molecular SCO switches produce outputs that may be, for example, change in absorbance or in magnetic response. It then becomes possible to associate a piece of information with each of the LS and HS states. When the input is applied, the output changes from a low to a high value or from a high to a low value, depending on the logic convention positive or negative, respectively [12]. In others words, the color and/or the (dia)paramagnetic changes of SCO complexes can be regarded in the molecular electronics context as a binary coding (0-1). This is of particular importance since data processing and communication require the encoding of all the information in the form of binary digits. In fact, the SCO phenomenon allows the definition of a NOT gate, which is one of the three fundamental logic operations. Let us recall that a NOT operator only involves one input and one output while AND and OR operators combine two inputs and one output [12].

Of course the input and the output do not need to share the same transduction mechanisms. For instance, pyrazoline derivatives execute NOT operations by transducing a chemical input into an optical output [33, 34]. However, the increasing need for telecommunication and internet applications demands the continuous enhancement of the transmission capacity and speed of communication networks [35]. The present technology is principally based on optical signals. It becomes then crucial to identify molecular switches able to provide an optical input/output transduction mechanism. SCO materials, in this particular context, are promising since optical inputs

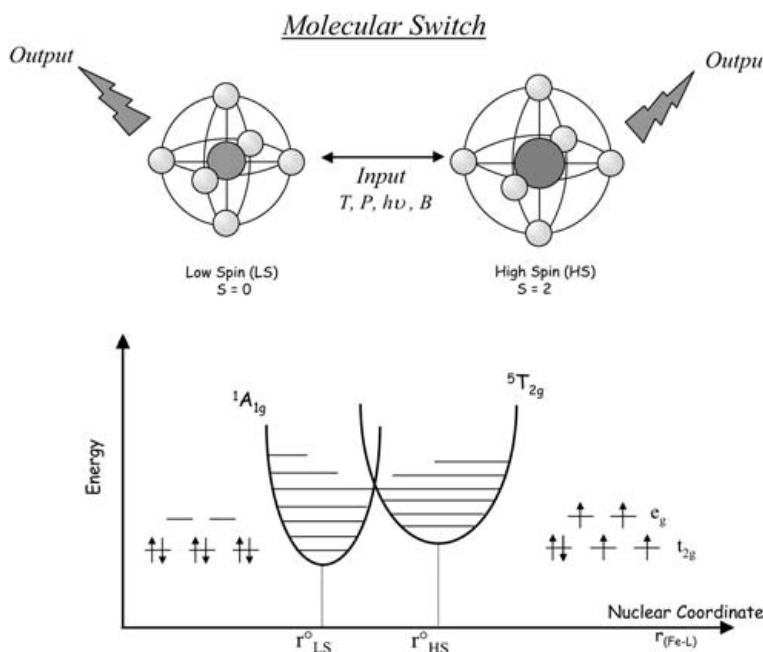


Fig. 1 Molecular switch based on the Iron(II) Spin Crossover (SCO) phenomenon. The Fe^{2+} ion has six valence electrons occupying the 3d orbitals. The input stimulation, i.e., temperature (T), light ($h\nu$), pressure (P) and magnetic field (B), induces the transformation of one state into the other and determines the intensity of the output signals, i.e., absorption, magnetic and volume changes

can be converted into optical outputs [16]. The last section of this review reports the recent progress in the domain of photomagnetism.

Let us mention, here, that in regard to traditional photochromic switches which also convert optical inputs into optical outputs, one of the main advantages of the SCO phenomenon is certainly the absence of any kind of fatigue. At the molecular scale, the ST in an iron(II) complex corresponds to an intra-ionic transfer of two electrons between the t_{2g} to the e_g orbitals, centered in the immediate environment of the iron metal center (Fig. 1). There is no through-space electron displacement. The transition can be reproduced as many times as needed without altering its characteristics, which is obviously crucial in a genuine device. It thus represents a major advantage but we are certainly only at the beginning of the adventure. That a SCO molecule makes logic operations is not sufficient to make a molecular electronic device. Today, hundreds, if not thousands, of chemical systems are already known to execute logic operations [12]. A molecular switch must fulfill many other requirements. For instance, it must be chemically stable once deposited on a surface or embedded into a matrix. Moreover, any

movement or reorganization of the active components must be impeded to ensure correct addressing and reading actions. The self-assembly of a molecular switch (on a surface or in a volume) certainly constitutes one of the more sensitive points. In a molecule-based device, each molecular switch must maintain a separate identity from the other switches around it. Finally, other problems may arise from processing complexity, power-supply requirements, rate of writing data, or cost.

Undoubtedly, the advances in SCO research are still far from meeting this list of requirements. The best example of molecular SCO switches organized on a surface is certainly given by the work of Mingotaud and Delhaès [36, 37]. These authors have succeeded in preparing Langmuir-Blodgett films with well ordered SCO complexes. The change of the spin state by light irradiation has been demonstrated [38]. This opens up exciting perspectives for the future.

3 Highlights of Data Storage

3.1 Current Technology

Today, magnetic and optical disk storage is taking over the primary role of providing storage, retrieval and world-wide distribution of information and knowledge. We report here a brief overview of the common media storage methods [39]. Hard drives store files as magnetically encoded areas on disks made of metal or spin glass material. The write heads align fields of magnetic particles on the surface and the read head registers a one or zero information depending on the polarity of the area. In Compact Discs (CD) the information is encoded by using optics. A typical optical disk is made of three layers: a polycarbonate base through which light can pass, a layer of aluminum, and a protective layer of acrylic on the top. The aluminum presents high area (pits) and flat section (land). The pits are typically 0.5 μm wide. The data read phase is performed using a laser beam. The latter passes through the polycarbonate layer, reflects off the aluminum layer and hits an opto-electronic device that detects changes in light intensity. The “pits” reflect light differently than the “lands”, and the opto-electronic sensor detects this change in reflectivity. In a traditional CD, the write phase can be done just once while a re-writable CD enables the storage and erasure of data. Instead of standard pits, the latter technology uses a phase change alloy whose reflectivity can be modified. Using a relatively high power laser, the phase change allows the alloy to have different refractivity indices, creating reflective and non-reflective “pits” and “lands”.

In parallel with these two common magnetic and optic technologies, the magneto-optical (MO) storage combines the two processes. MO drives write magnetically (with thermal assist) and read optically. To record data in a magneto-optical device, a laser heats up the medium, decreasing the medium coercivity to a level that allows its magnetism to be modified by a relatively weak magnetic field. Once the data are written, the area is then cooled, and the magnetic data are not subject to modification or erasure by magnetic forces encountered during the daily routine. To read the data from the MO medium, the drive does not use magnetic current induced in the heads by the changing magnetic flux on the disk, as a hard drive does, but instead takes advantage of the Kerr effect. Because of the Kerr effect, the polarization of light will change when it is shone upon an area of the disk that is magnetized. Shining a beam of polarized light on a magnetized surface causes the polarization of the light to shift slightly (usually less than 0.5°). If the magnetization is reversed, then the angle of change in polarization (the Kerr angle) is changed as well. The change in direction of magnetization can be detected as “1” and “0”, making MO convenient for data storage.

In the future, however, both the magnetic and conventional optical data storage technologies, where individual bits are stored as distinct magnetic or optical changes on the surface of a recording medium, will be approaching physical limits beyond which individual bits may be too small or too difficult to store. For instance, magnetically storing of data faces a limit imposed by the Super Paramagnetic Effect, or SPE [40]. SPE is a physical phenomenon that occurs in data storage when the energy that holds the magnetic spin of atoms making up a bit becomes comparable to the ambient thermal energy. When that happens, bits become subject to random “flipping” between 0s and 1s, destroying the information which they represent. Currently extensive efforts are being made to better understand this phenomenon. The energy barrier depends on the stored bit pattern and on magnetic interactions between adjacent particles. To now, the SPE is predicted to happen at about 6 Gbit/cm^2 but it is reasonable to expect that hard disk magnetic recording will push the limit into the $15\text{--}30 \text{ Gbit/cm}^2$ range [40]. Concerning the optical process, the limit is the track width and pit size linked to the diffraction-limited optics. If more tracks are to be added, they each must be smaller, so the ability of the recording head to accurately find the tracks, and increase the accuracy of the position sensor and stepper motor must be improved. Moreover, the pits have to be smaller. This imposes the use of a laser with higher frequency (shorter wavelength) to read and write on the CD. The nanophotonics is a new frontier that describes nanoscale optical science, much smaller than the wavelength of optical radiation and technology. Some examples have been already reported where nanoscale optical storage is carried out on magneto-optical and phase-change media with data densities up to 26 Gbit/cm^2 [41]. Consequently, it is impossible to predict the ultimate limits for magnetic and optical storage. In [42–43] are

examples of these, which predicted maximum densities of 0.3 Mbit/cm², 1 Mbit/cm², and 20 Mbit/cm². Today's best disk drives operate at nearly a hundred times the latter limit [40].

In fact, many other approaches, using alternative materials and techniques, are currently being explored by industrial and other research laboratories. Concerning magnetic storage, one solution is to make single grain magnetic bits [40]. This eliminates the statistical noise associated with granular media and increases the domain size by a factor of several hundred. This can be done by patterning a thin magnetic film into small sized islands, e.g., with stamping or ion beam patterning. Holographic storage is also extensively studied since it provides dramatic advances in both data storage density and transfer rates [44]. Unlike other storage methods, which record only on the surface of a disk, holographic digital data storage allows recording through the entire thickness of the material, which gives a huge increase in storage density. Scanning probe storage is also being extensively studied [45]. The principle is based on writing with an AFM tip on a plastic substrate. Marks smaller than 0.1 micrometer can be written in this manner. During the read process, the AFM tip scans the topography of the media upon contacting a data pit, a physical change or a deflection occurs in the tip and this change is sensed. The AFM process suffers, however, from the long time necessary to write the data. In this context, it was recently demonstrated that data-storage can be thermomechanically obtained in soft polymers [45]. This was accomplished by using a modified cantilever in which the tip was heated by applying a voltage across the legs of the cantilever. The contact of the heated cantilever with the polymer layer, constituted of 40 nm of polymethylmethacrylate, melts the surface and forms a pit. Each pit represents a bit of information. Multiple writing and erasing cycles have been carried out with no degradation of the substrate. Furthermore, the use of an array of 32×32 thermomechanical tips working in parallel fashion has allowed the writing of data in bit densities as high as 20–30 Gbit/cm². A prototype device called “Millipede” is now close to production [46].

In conclusion to this brief overview, the use of nanotechnology appears more and more relevant for the future development of memory devices. There exists today a large number of ways to realize data storage in a molecular system, as charge storage, conformational or positional shifting and physical transformation [14]. The molecular memory device can be a single molecule or even a limited number of molecules. In this latter case, we are faced with a cluster where each active center is chemically bound or organized in a strong interacting network. Each individual center acts in a synergistic way and confers on the cluster a memory property [20, 47–49]. In this sense, a significant breakthrough has been recently obtained by Hewlett Packard in collaboration with UCLA chemists [50, 51]. They report the achievement of the highest density electronically addressable memory reported to date. The bit density of the device is more than ten times greater

than today's silicon memory chips. The electronically switchable element seems to be an array of bistable molecules deposited on a single monolayer between metallic electrodes in a crossbar architecture. The switch belongs to the class of molecules called catenanes and rotaxanes [50, 51].

3.2

Memory Property of SCO Materials

In contrast to the dynamic nature of a molecular switch, a memory device represents a static component [14]. The ON state must be switched to the OFF state by applying an external stimulation, as a molecular switch, but the stored information must remain. If we consider the SCO phenomenon of an isolated complex involving only one metal center this condition is not reached. The course of the spin transition follows a Boltzmann approach with a temperature-dependent distribution over all HS vibronic states and the LS state. Consequently, the SCO phenomenon is gradual (Fig. 2). The input information is erased as soon as the external perturbation is stopped. Such a molecular system exhibits no static memory property.

To obtain a memory feature in a SCO material, it is now well established that the ST phenomenon must be accompanied by a hysteresis effect [47].

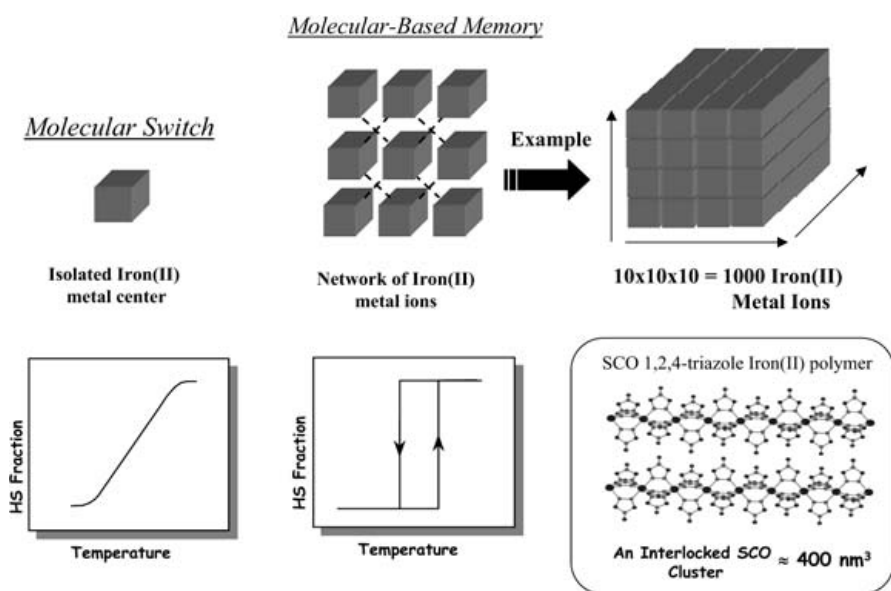


Fig. 2 Schematic drawing of a gradual spin conversion recorded for a molecular switch involving an isolated iron(II) metal center and of a thermal hysteresis loop obtained for a strongly interlocked polynuclear iron(II) cluster. The structure of the polymeric 1,2,4-triazole iron(II) compounds is deduced from the EXAFS investigation [92]

Many general articles have been devoted to this particular behavior [16, 52–54]. Thermal hysteresis in a SCO complex is the result of interactions between active sites within the lattice (Fig. 2) if there is no crystallographic phase change. In iron(II) SCO materials, the spin conversion is concomitant with a variation of the iron-to-ligand average bond distance, which is about 0.2 Å greater in the HS state [55]. When intermolecular interactions in the lattice are sufficiently strong, the change in molecular size can be transmitted from one site to another and this induces a cooperative effect. The extent of the propagation defines the size of the domain.

One of the first systems in which it was shown that a thermal hysteresis loop was associated with SCO was $[\text{Fe}(\text{4,7-(CH}_3)_2\text{phen})_2(\text{NCS})_2]$ complex, with $T_{1/2}\uparrow=121.7$ K and $T_{1/2}\downarrow=118.6$ K [56]. Since this report, many other SCO complexes have been described which display thermal hysteresis. Usually, in a mononuclear complex intermolecular interactions are weak and the width of the hysteresis loop remains below 20 K. Some rare examples, however, exhibit hysteresis widths in the 30–40 K range [57, 58]. All these examples have in common the presence of intermolecular π - π stacking of the aromatic ligands to generate a supramolecular organization in the crystal lattice. For instance, in the particular case of the $[\text{Fe}(\text{PM-PEA})_2(\text{NCS})_2]$ compound, the crystal packing shows very short contacts between phenyl rings belonging to adjacent molecules [57, 59]. A thermal hysteresis width of 37 K, with $T_{1/2}\uparrow=231$ K and $T_{1/2}\downarrow=194$ K, has been described. By replacing the two NCS groups bound to the iron(II) ion by the NCSe group, the thermal spin transition was shifted ($T_{1/2}\uparrow=256$ K and $T_{1/2}\downarrow=306$ K) and the compound is then bistable at 293 K [57].

Cooperativity may also be increased by covalent links between the active sites. The first experimental result supporting this idea was provided by the compound $[\text{Fe}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$ with $\text{btr}=4,4'$ -bis-1,2,4-triazole [60]. In this compound, each iron atom is surrounded by two NCS groups in *trans* position and four btr ligands coordinated through nitrogen at the 1- and 1'-positions. Non-coordinated water molecules are also hydrogen bonded to the peripheral nitrogen atoms of the triazole units. The iron(II) atoms are then involved in a two-dimensional network. The spin transition is extremely abrupt and the hysteresis width is 21 K ($T_{1/2}\uparrow=144.5$ K and $T_{1/2}\downarrow=123.5$ K). In addition, other two-dimensional (2D) and three-dimensional (3D) networks have been reported, such as $[\text{Fe}(\text{tvp})_2(\text{NCS})_2]$ ($\text{tvp}=\text{bis-1,2-di(4-pyridyl)ethylene}$) [61], $[\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4]$ [62], and $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ [63] systems. Typically these 3D compounds undergo strong cooperative spin transitions with 20–40 K width hysteresis loops. Another very interesting family of complexes are those involving the 1,2,4-triazole ligand. The general formula of this family is $[\text{Fe}(\text{Rtrz})_3]\text{A}_2\cdot n\text{H}_2\text{O}$ with A being the counter-anion and $n\text{H}_2\text{O}$ the number of non-coordinated water molecules. The structure is a linear chain of metal centers triply bridged by 1,2,4-triazole ligands (Rtrz) through the nitrogen atoms occupying the 1 and 2 positions

[64]. The first member of this family was reported by Haasnoot et al. in 1977 [65]. Larionov and Kahn have described other members of this family with wide thermal hysteresis (20–40 K) above room temperature [19, 20, 66, 67].

It is evident that there are numerous examples of SCO materials for which thermal hysteresis loops are observed. In addition to this, the overall number of iron(II) SCO systems is very large and will undoubtedly continue to grow. It is thus reasonable that new systems displaying a high degree of cooperativity will be found.

3.3

Design of SCO Cooperative Cluster—A Challenge

As already mentioned, the design of a system able to store information on the single molecule level or assemblies of molecules is particularly important in the development of information technology. The molecular bistability associated with the SCO phenomenon is of particular interest since logic operations can be executed. A piece of information can be associated with each of the LS and HS spin states. The hysteresis behavior linked to cooperativity confers a memory effect to the system. In the $T_{1/2}\uparrow$ – $T_{1/2}\downarrow$ temperature range, the nature of the observed state depends on the history of the molecular switch [68]. Moreover, as recently demonstrated, the input information in the center of a thermal hysteresis loop can be addressed by pulsed light irradiation [69], by pulsed magnetic field [17] or by pulsed pressure effect [70].

One of the main challenges for chemists in regard to the design of molecular-based memory devices is the control of the size of the SCO cluster which exhibits thermal hysteresis. The size available to date is far from the level of miniaturization required for the realization of nanoscale processors. Scanning electron microscopy, for instance, of the well-known SCO 1,2,4-triazole iron(II) complexes, reveals particles of around 5–10 μm (Fig. 3) [71]. However, by considering that a cluster consisting of 10^3 strongly interacting metal centers supposedly is able to exhibit cooperative behavior [72], this roughly corresponds, in the case of the 1,2,4-triazole iron(II) family, to a cube of around 7 nm per edge. Therefore, the design of nanoscale devices based on a SCO materials is then theoretically possible.

To reach this goal, the use of both the top-down and the bottom-up approaches can be envisaged. Concerning the former method, it is now well-known that the preparation of insoluble compounds by using conventional chemical reactions results in products which are heterogeneous with respect to particle mass and hence size due to random crystal growth. Production of fine or ultrafine particles then requires grinding and sieving steps which are not desirable for the SCO phenomenon. When a mechanical stress is exerted on coordination compounds in the solid state, a molecular distortion results and the SCO behavior, e.g., residual HS fraction at low temperature, irre-

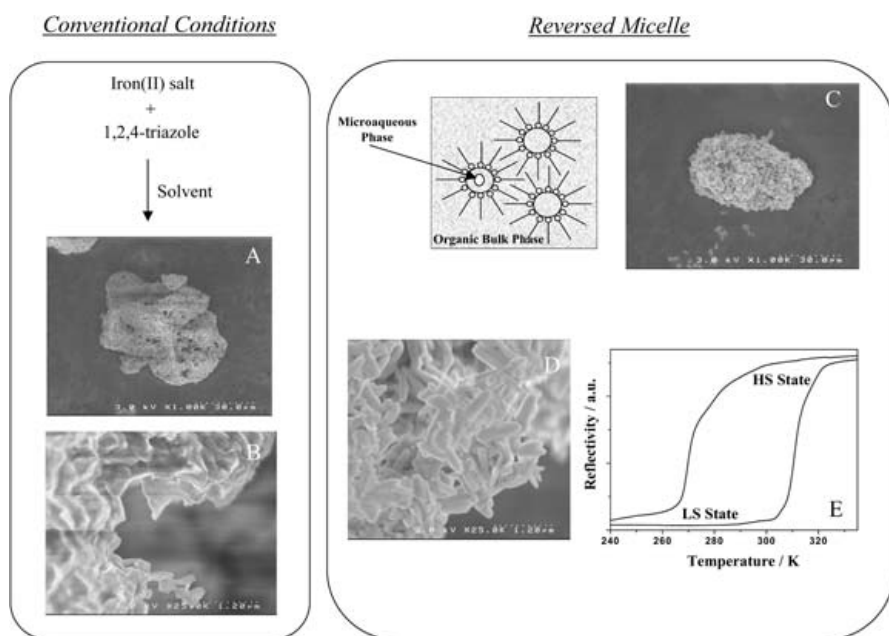


Fig. 3A–E $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ particles observed by using a scanning electron microscopy: **A,B** after conventional synthetic conditions; **C,D** prepared in $\text{H}_2\text{O}/\text{Lauropal}$ inverted water/oil microemulsions; **E** the thermal hysteresis loop of a collection of well-defined particles recorded by measurement of optical reflectivity

versibly changes [73, 74]. With regard to the bottom-up method, one of the approaches is based on the step-by-step synthesis. This method is particularly promising since each step of the synthesis can be precisely controlled. Examples of dinuclear [75], trinuclear [76] and tetranuclear [77] SCO systems, with cooperative interactions between the metal centers, have been described in the literature. The requirement to increase the number of metal centers involved in one molecule is not readily achieved. A considerable increase in theoretical and experimental knowledge will be a prerequisite to this being met. An alternative approach currently being developed to synthesize nanoscopic materials involves the use of water-in-oil (w/o) microemulsions [78–80]. Dispersed water pools act as microreactors where chemical reactions can be performed to generate the required product in the form of a colloidal (nano)dispersion. Along these lines, we have shown that by confining the synthesis to nanoscale water droplets formed in reverse microemulsions prepared from the Lauropal 205 surfactant, 1,2,4-triazole iron(II) particles with a uniform shape and size can be routinely prepared [71]. The current limit size of the cluster is about 60–200 nm. Figure 3 shows the thermal hysteresis loop recorded for a collection of individual clusters. The

loop remains in the vicinity of room temperature. AFM investigation, based on the volume change accompanying the spin transition, is in progress to record the hysteresis loop of just one individual cluster. One can expect an increase of the abruptness of the spin transition coupled to a sharp and well-defined hysteresis.

Of course, these investigations are in their early stages but the trend is clear. Today, the step-by-step approach may appear, at first sight, only interesting as basic research but the growth of nanoscience and the subsequent development of nanotechnology continuously opens news horizons. For instance, the design of a linear trinuclear compound exhibiting SCO properties can be regarded as an almost linear motor with, in fact, interesting function as an artificial muscle [81] able, in a microelectronic circuit, to pass the information from one individual element to another. Artificial molecular machines and motors appear as one of the emerging fields of chemistry [10, 13]. A molecular-level machine has been defined as an assembly of a distinct number of molecular components that are designed to perform machine-like movements (output) as a result of an appropriate external stimulation (input). Several systems are today known and many of them are based on chemical, photochemical and electrochemical processes. In such a context, the volume change associated with the SCO phenomenon and the absence of susceptibility to fatigue is of particular interest.

Another issue that may also have important consequences in the development of nanoscience is the design of materials able to amplify at the molecular scale an output signal. Any enhancement of the final output would reduce the difficulty for the reading operation. Along this line, in a cooperative SCO cluster the resulting output of an appropriate external stimulation is not only an individual response but a summation of individual contributions which lead to an amplification effect. This effect is not entirely clear and much effort is currently being expended to evaluate, for instance, the quantum efficiency of the photoconversion [82].

4

Devices for Data Displays

4.1

State of the Art

In the last 100 years, display technology has advanced impressively [83–85]. Information technology has moved from painstakingly slow generation and permanent storage on bulk materials, such as stone and paper, to the almost instantaneous production and transfer through the pervasive electronic and optical networks. Nevertheless, such evolution is far from complete. The recent progress of the mobile telecommunication networks opens new oppor-

tunities for terminal manufacturers [84]. Advances in new display technologies, such as reflective-color liquid-crystal displays, bistable displays, organic emissive displays, and microdisplays are beginning to be exploited [83].

The development of electronic displays began with the cathode-ray tube (CRT), which was first explored in the nineteenth century [86]. The first tube, invented by Braun, used a deflection and a fluorescent material for the display screen. Real progress began when large scale production of monochrome CRT-based television (TV) receivers commenced around 1945. The first successful shadow mask color picture tube was developed in the 1950s. The manufacturing expertise developed in this field was applied to the computer display industry. This kind of application/technology matching has been a hallmark of all successful display types: TV, digital watches, calculators, computer monitors, portable computers, etc.

Nevertheless, it rapidly became evident that the traditional bulky CRT was technically impossible to convert into a flat device. This achievement was fulfilled with the active-matrix-addressed Liquid Crystal Display (LCD) [87, 88]. Since the discovery of liquid crystallinity in 1888 by Reinitzer, one by one, every technical challenge posed by the CRT standard has been met and in many cases exceeded: operating lifetime, contrast ratio, response time, high power consumption, view-angle limitations. Today, LCD monitors are found in most electronics retail store. The writing and the addressing functions are accomplished by an electrooptical path. This starts with the electrical generation of an ultraviolet-emitting plasma followed by a conversion to red, green and blue wavelengths and a distribution of white light. This complexity coupled with production costs have stimulated the search for other technologies, such as plasma display, field emission display, organic light-emitting diode displays, or microdisplays [83–85]. These latter displays are defined as sub-1.5 in displays that are viewed indirectly either through magnifying optics near the eye or through a projection system that puts a large high pixel-count on a screen. The displays are built directly on a semiconductor substrate, which allows the integration of the electronics on to the same substrate for higher performance with lower manufacturing costs. Without doubt, much work remains to be done since those microdisplays will be based on a complex interaction of optics, electronics, packaging and chemistry.

Basically the writing and the addressing functions can be accomplished in a flat-panel display by several nonelectronic means: thermal, chemical, acoustic, mechanical, temporal, optical and various combinations thereof. Acoustically addressed displays have never become commercially widespread due to complexity and efficiency problems. Mechanical methods were employed early in the development of displays and went out of favor until the recent arrival of microelectromechanical modulators. Electronic addressing and writing is intuitively the best, but the present state of materials development demands some adaptation to the optical writing phenome-

non. Thermal and chemical addressing and writing have not been successful to date, typically due to reversibility and lifetime issues.

Concerning the SCO materials, in fact, it was only during the 1980s that researchers realized that thermal properties could be exploited in devices. Kahn et al. [18–20] listed a series of requirements that SCO materials must fulfill before any use in data display devices: (i) the transition must be abrupt, occurring within a few Kelvins, both in the warming mode at $T_{1/2}\uparrow$ and in the cooling mode at $T_{1/2}\downarrow$; (ii) the $\gamma_{\text{HS}}(T)$ curve must exhibit a hysteresis effect of at least 40 K. The ideal situation is when ambient temperature is centered in the middle of the thermal hysteresis loop; (iii) the transition between the low-spin (LS) and high-spin (HS) states must be accompanied by an easily detectable response, such as a change of color; (iv) the transition must be complete both at low temperature ($\gamma_{\text{HS}}=0$) and at high temperature ($\gamma_{\text{HS}}=1$); (v) finally, the system must be chemically stable, and must not be subject to fatigue over successive thermal cycles.

Not surprisingly, it quickly became evident that no pure SCO compound met all the criteria. For instance, in the series of mononuclear compounds, sufficiently broad hysteresis loops have been observed [57, 58] but the presence of aromatic rings connected to the FeN_6 core, indispensable to assure π - π stacking, also gives rise to intra-ligand or charge-transfer bands which mask the d-d bands in the visible region of the spectrum. Therefore, these materials do not exhibit a drastic visible color change with the ST and are thus inappropriate for display devices. To date, the best hope for successful application is provided by the iron(II)-1,2,4-triazole SCO materials. Almost all the criteria above have gradually been addressed and are now close to being realized. The developments in the modifications of these systems are considered below.

4.2

Towards the Design of Data Display

As already mentioned, many groups have investigated metal triazole complexes. The reasons for this interest are numerous, such as the modeling of enzymatic reactions, use as pharmaceutical or agricultural components, applications in materials science. One of the properties of triazole relevant to the last point is its ligand field strength which is in the vicinity of the SCO region for iron(II). Depending on the substituents within the triazole ring, the transition temperatures span the range 100 to 400 K [65–67, 89].

In fact, the features of the first thermal spin transitions recorded with iron(II)-1,2,4-triazole derivatives were not suitable for any of the applications mentioned above. Indeed, most of these complexes displayed SCO phenomena above room temperature, with relatively gradual ST and with hysteresis loops narrower than 50 K. However, their ease of synthesis, the chemical stability of the final iron(II) complexes, and the pronounced color change ac-

companying the ST strongly indicated that these materials may present some potential in the design of display devices. The absorption spectrum of the LS state corresponds to a broad band centered around 520 nm ($^1A_{1g} \rightarrow ^1T_{1g}$ transition) while the HS state does not show any band in the visible region, the $^5T_{2g} \rightarrow ^5E_g$ transition being located around 850 nm. In addition to this, it was found in some instances that very abrupt ST with well-shaped thermal hysteresis loops perfectly reproducible over successive thermal cycles, can be obtained. This was found for $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ with $T_{1/2\uparrow}=342$ K and $T_{1/2\downarrow}=310$ K [90], and for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ with $T_{1/2\uparrow}=383$ K and $T_{1/2\downarrow}=345$ K [19, 20, 91–93]. Several approaches have since been used to displace the thermal hysteresis loop so as to encompass room temperature.

One of the first approaches was to replace to some extent iron(II) ions by non-spin crossover atoms. This method was originally inspired by the work of Sorai and Gülich on the tris(2-picolyamine)iron chloride system [94]. These authors reported a linear change of the ST temperature with dilution by zinc. Similar effects were effectively observed in the 1,2,4-triazole series [95–97]. However, it soon became evident that this method resulted in a dramatic reduction of the color contrast between LS and HS states, relative to that of the pure compounds. Moreover, the abruptness of the thermal transition was found to decrease with the metal dilution.

A much more successful approach consisted of the design of “molecular alloys” by combining different ligands in the preparation of salts. The general formula of an alloy complex, combining $R^1\text{trz}$ and $R^2\text{trz}$ triazole ligands, was $[\text{Fe}(R^1\text{trz})_{3-3x}(R^2\text{trz})_{3x}]A_2 \cdot n\text{H}_2\text{O}$. The $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ of, for instance, $[\text{Fe}(\text{Htrz})_{3-3x}(\text{NH}_2\text{trz})_{3x}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, was found to vary linearly as a function of the concentration x [20]. The two ligands were chosen in such a way that the transition temperatures for one of the pure compounds are above room temperature, and for the other pure compound are below room temperature. For a given composition, room temperature has been found to fall in the middle of the hysteresis loop. Similar results were obtained by mixing counter-anions instead of mixing triazole ligands. The latter approach was based on the fact that the thermal spin transition for a given type of cationic chains, $[\text{Fe}(\text{Rtrz})_3]$, depends on the radius of the counter-anion, A [98]. The spin transition regime can then be fine-tuned through the composition of alloys, $[\text{Fe}(\text{Rtrz})_3]A^1A^2 \cdot n\text{H}_2\text{O}$. In the particular case of $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_{1.7}(\text{BF}_4)_{0.3}$, the $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ were found on either side of room temperature and the width of the thermal hysteresis was around 60 K [20].

4.3

Fabrication of Displays

The first principles of the application of iron-triazole systems in a display device were reported by Kahn et al. [20, 99]. The substrate consists of an aluminum plate, on which resistive dots and connecting electrodes were pre-

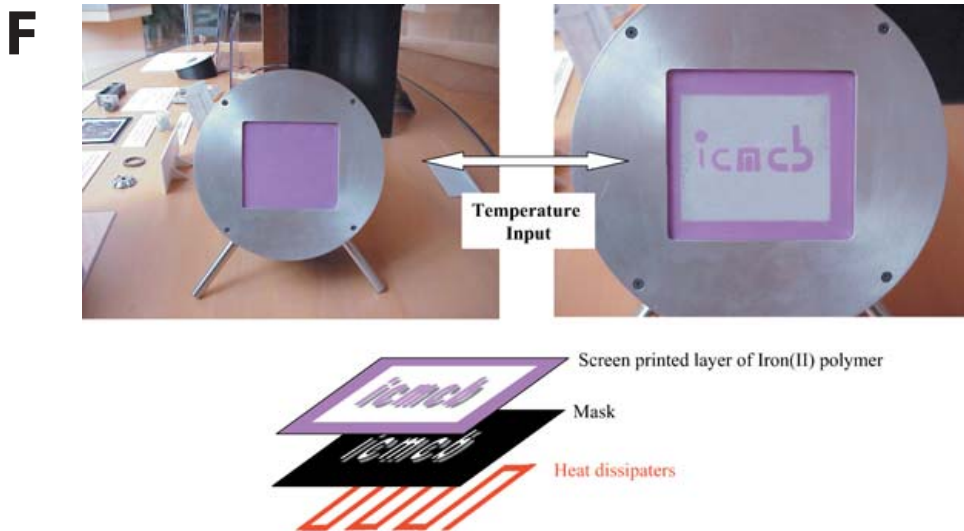


Fig. 4 Laboratory scale display. ST screens printed layer before writing (*left*) and after thermal writing (*right*). Schematic illustration of the display device involving the ST layer, the aluminum plate containing the ICMCB logo and the heat dissipater resistance (*bottom*). When the temperature exceeds the critical “up temperature” the material transits from purple to white and the ICMCB information is addressed

viously screen printed. The dots are addressed through columns and rows. A layer of the active SCO material is deposited as a printed ink on the substrate. The criteria required for the ink are (i) to adhere to the substrate, (ii) to be chemically inert to the spin transition materials, (iii) to protect the material from environmental influences, and (iv) to be mechanically compatible with a printing procedure involving heat. The dots, when electrically addressed, act as heat dissipaters. When the temperature is above $T_{1/2}\uparrow$, the material passes from violet to white. The information is stored as long as the system remains at a temperature within the hysteresis loop. To erase the information, the temperature has to be lowered below $T_{1/2}\downarrow$. This can be achieved with a Peltier element. Various related displays can be derived from this principle.

Figure 4 shows a display device based on the displacement of a heat aluminum plate [100]. When the heat plate is in contact with the polymer surface, the temperature increases above $T_{1/2}\uparrow$ and the thermochromic effect is observed. The ICMCB logo results from the design of the heat aluminum plate. The white color corresponds to the region where the polymer is in contact with the heat plate. In this latter system, the requirement of thermal hysteresis is not necessary. The presence of a well-defined abrupt thermal spin transition with a very low residual of HS and LS fractions is, however,

more crucial. In this context, triazole derivatives are obviously very good candidates.

4.4

Specific Aspects

In this particular section, our target is to present other perspectives which can be, in some aspects, related to the display arena. Let us first consider the very high sensitivity of the SCO materials to any temperature or pressure changes. This property may have some important applications in the sensor domain. For instance, in some cases the spin state is governed by the synergy between the spin transition and a dehydration-rehydration process. This happens, for example, for polymeric systems such as $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{tosylate})_2 \cdot 3\text{H}_2\text{O}$ [101] and $[\text{Fe}(\text{hyettrz})_3]\text{A}_2 \cdot 3\text{H}_2\text{O}$ (hyettrz=4-(2'-hydroxyethyl)-1,2,4-triazole and A=3-nitrophenyl-sulfonate) [102]. As the temperature increases, the non-coordinated water molecules are released, followed by an abrupt spin transition at 370 K from the metastable low spin state to the stable high-spin state. This phenomenon is accompanied by a pronounced thermochromism. The color changes from violet to white. The transition temperatures for the dehydrated material, $[\text{Fe}(\text{hyettrz})_3]\text{A}_2$, are $T_{1/2}\uparrow=110$ K and $T_{1/2}\downarrow=100$ K. In other words, once the starting violet material has turned white by heating, it remains white (in the HS state) when brought to room temperature. The materials cannot return to the hydrated LS state at room temperature without some decomposition involving, for example, oxidation of the iron(II) ions.

Such materials may be of use in applications in which detection of a specific temperature is required in a very simple, irreversible, and accurate way. The SCO material then acts as a thermal sensor giving an optical response only when $T_{1/2}\uparrow$ is reached, for instance as an alert mechanism when the temperature exceeds an upper limit. More interestingly, this thermal addressing accompanied by an abrupt and stable optical response may be used in a single-use display. Incorporation of SCO materials in a prepaid stored-value card has been envisaged [103]. Similar effects can be anticipated in many other SCO compounds showing dehydration-rehydration processes [104], e.g., $[\text{Fe}(\text{bpp})_2]\text{X}_2 \cdot 3\text{H}_2\text{O}$ (bpp=2,6-bis(pyrazol-3-yl)pyridine and X=BF₄ and I).

The above applications arise from the thermochromism associated with the spin transition. In some particular applications, it may be interesting to design temperature sensors which exploit a change of magnetic properties [68]. In this context, applications in magnetic resonance imaging are particularly promising. At the critical temperature, the spin transition causes a pronounced change of magnetic image, since the LS form is diamagnetic and the HS form is paramagnetic. Note that in this case the occurrence of a hysteresis loop is not important. More crucial is the presence of an abrupt spin transition at a desired temperature. For instance, human cancer cells

are more sensitive to heat than healthy cells. In the treatment, it is important to reach the temperature not higher than that at which damage of both healthy and diseased cells would take place. Work is underway to design materials with transition temperatures at this upper limit.

5

Recent Progress

5.1

Molecular Switches and Non-linear Optics

Second order non-linear optical (SONLO) materials have recently attracted much interest because of their potential applications in emerging optoelectronic technologies [105]. Investigations were focused initially on purely inorganic systems which were the first solids to demonstrate SONLO properties [106]. Attention was later directed towards organic materials. On the basis of a two-state model [107], donor-acceptor substituted π -systems have been synthesized and provided large SONLO responses. However, one major drawback of these push/pull substituted molecules is that strong non-linearities are often antagonized by a strong electronic absorption in the visible region. In an alternative way, octupolar molecules belonging to T_d , D_{3h} , or C_{2v} symmetry groups have attracted attention since significant SONLO molecular β values could be achieved with non-dipolar molecules [108]. Coordination compounds are extremely promising since NLO active ligands around the metal ion give highly symmetrical molecules and display metal-to-ligand (MLCT) or ligand-to-metal (LMCT) or metal centered (MCCT) charge transfer transitions in addition to the traditional π - π^* transitions of the conjugated system. Moreover, the symmetry properties of d-orbitals in coordination compounds are different from the s- and p-orbitals usually found in organic molecules [109].

In addition, coordination compounds are also of interest since they may be used to design switchable non-linear optical materials. The concept of such molecular switches has recently opened a large number of perspectives [110, 111]. Up to now, switchable SONLO responses of organic compounds have been obtained by photoisomerization [112], phototautomerization [113], or photocyclization [114]. The first example of a coordination compounds-based molecular switch was reported by Sakaguchi for a ruthenium(II) derivative in Langmuir-Blodgett (LB) films [115]. Coe et al. later used the redox-switching of the Ru-metal center to design various switchable SONLO compounds [116].

To achieve a pronounced SONLO switching effect, a molecule must be stable in two states that exhibit very different β responses. Complete reversibility and high switching speed are also highly desirable for practical

applications. Basically, such fundamental requirements are exhibited by the SCO phenomenon. An open question, however, is whether the spin transition between a paired and an unpaired electronic configuration is able to switch the SONLO response. The work previously reported by Di Bella et al. [116, 118] suggests that the NLO response is dependent on the electronic configuration of the metal center. The β responses of (*N,N'*-disalicylidene-1,2-phenylene-diaminato)M(II) compounds in planar geometry are found larger for paramagnetic Cu- and Co-derivatives than for the diamagnetic Ni-complex [117, 118]. In parallel with this work, we have recently examined the role of the metal electronic configuration in octahedral geometry by systematically varying the metal ions (M^{II} =Mn, Fe, Co, Ni, and Zn) in the two series of coordination compounds $[M(\text{PM-BiA})_2(\text{NCS})_2]$ and $[M(\text{PM-2PEA})_2(\text{NCS})_2]$ [119].

Direct hyper-Rayleigh scattering measurements have shown an enhancement of the molecular hyperpolarizabilities (β) from the d^8 to the d^5 metal electronic configuration. Highest SONLO responses were recorded for Mn compounds with full open-shell configuration (five unpaired electrons) and lowest values were obtained for Ni compounds with two unpaired electrons [119]. In fact, by taking into account the inverted vectorial direction of the metal-to-ligand charge transfer (MLCT) transition and the intra-ligand charge transfer (ILCT) transition (see Fig. 5), a direct enhancement of the β_{MLCT} along the d^8 - d^5 metal electronic configuration was observed. The ILCT transition is characterized by an intra-ligand charge transfer directed towards the pyridyl group, while in MLCT transition with the metal as donor the charge transfer occurs from the metal to the pyridyl group. The sum of the contributions of the MLCT and ILCT transitions leads to destructive interference. Assuming that the SONLO response of the Zn complexes directly reflects the ILCT contribution, the β values of the other compounds have been corrected to give the pure β_{MLCT} contributions (see Fig. 5). In both families of $[M(\text{PM-BiA})_2(\text{NCS})_2]$ and $[M(\text{PM-2PEA})_2(\text{NCS})_2]$, the highest β_{MLCT} values were found for the Mn compounds which possess five unpaired electrons. The β values of the Fe compounds in the paramagnetic HS state with four unpaired electrons ($t_{2g})^4(e_g)^2$ were found to be larger than those of the diamagnetic Zn compounds. This finding indirectly suggested that if the β value of the diamagnetic Fe compound (LS state) with six paired electrons is modeled by the response of the diamagnetic Zn ion, a drastic NLO change accompanying the SCO phenomenon can be expected [119].

Unfortunately, to the best of our knowledge, there exists no direct experimental proof of a spin crossover effect on the quadratic NLO response. The only evidence was obtained via a theoretical investigation performed by Lacroix [120] on the $[\text{Fe}(\text{5-NO}_2\text{-Sal-N}(1,4,7,10))]$ complex which undergoes a two step spin transition. An increase of about 25% of the NLO signal was found between the LS and the HS forms, mainly due to the structural changes occurring in the coordination sphere upon spin-state transition. Never-

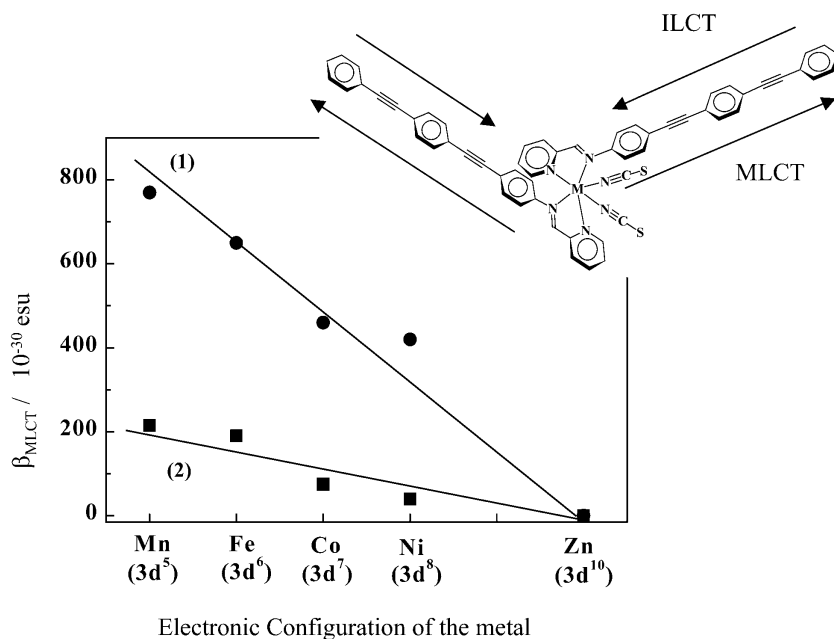


Fig. 5 *Left*: molecular hyperpolarizabilities associated to the metal-to-ligand charge transfer (MLCT) transition (β_{MLCT}) vs the d^{10} – d^5 metal electronic configuration of the metal complexes, $[\text{M}(\text{PM-BiA})_2(\text{NCS})_2]$ (1) and $[\text{M}(\text{PM-2PEA})_2(\text{NCS})_2]$ (2); *right* vectorial direction of the MLCT and the intra-ligand charge transfer (ILCT) transitions

theless, the recent application of Langmuir-Blodgett films [36, 37] may yield some new insights. The design of switchable SONLO materials based on the iron(II) SCO phenomenon may then become achievable.

5.2 Optical Addressing

Another interesting feature of the SCO phenomenon is that it offers the possibility to address spin states by light irradiation [16]. At the present time, as mentioned previously, numerous processes in communication networks involve optical connections. The information, for instance, is transferred over long distances in the form of optical signals propagating through interconnected optical fibers. The design of materials allowing optical manipulation is then of major importance. In the domain of transition metal complexes, there are several possibilities to induce light sensitive electronic changes accompanied by a drastic modification of magnetic and/or optical properties [121]. Among the best known and extensively studied systems, we cite metal-centered thermal spin transition (observed in iron(II) SCO materials), valence tautomerism (catecholate complexes of Co(II)), the met-

al-to-metal charge transfer (Prussian blue analogues), metal-to-ligand charge transfer (nitroprusside complexes), and finally, all ligand modifications which induce change of the spin state, such as isomerization (stilbenoid complexes) and open/close (diarylethene type ligands) processes.

The first photomagnetic effect on an iron(II) SC compound in solid state was reported by Decurtins et al. in 1984 [122]. The authors demonstrated the possibility of converting a LS state into a metastable HS state at low temperatures (≤ 50 K) by using green light irradiation. This phenomenon, called Light-Induced Excited Spin-State Trapping (LIESST), was extended, later by Hauser who showed that red light switches the system back to the LS state (reverse-LIESST) [123]. At present, most of the photomagnetic studies on iron(II) complexes involve the LIESST and reverse-LIESST processes with the ultimate goal of obtaining suitable materials for technical applications such as displays, information storage and sensors. In regard to these prospects, a deficiency of the LIESST effect is its temperature domain. The metastable HS state usually decays within minutes above 50 K. The photoinduced HS information is consequently quickly erased, except at very low temperatures.

The HS $\rightarrow$ LS relaxation process in iron(II) metal complexes has been investigated in considerable detail [124–128]. It is now established that the kinetics follow the non-adiabatic multi-phonon theory with a temperature independent relaxation below ~ 50 K and a thermally activated process above ~ 50 K which can be regarded as a tunneling from thermally populated vibrational levels of the HS state [129]. Nevertheless, in some unexplained cases, long-lived metastable HS states have been reported above 80–100 K [130–132]. It seems that some unknown secondary features in the nearby lattice surroundings of a light-generated HS complex molecule are able to stabilize the metastable HS state.

In the last four years, in collaboration with the Motorola company, we have introduced the notion of critical LIESST temperature, $T(\text{LIESST})$, defined as the temperature for which the light-induced HS information is erased [133]. Our idea was to constitute a database which collects the photomagnetic properties of a large number of iron(II) SCO compounds. It is evident that such $T(\text{LIESST})$ values are somewhat dependent on the detection method. This approach, however, is useful as it allows the rapid comparison of the photomagnetic properties of a series of SCO compounds, and the determination of the factors which play a role in the light-induced conversion effect.

The procedure adopted to record the $T(\text{LIESST})$ value of SCO compounds is the following (see Fig. 6): the sample is first slowly cooled to 10 K. The sample in the LS state is then irradiated into the metal-to-ligand charge-transfer band ($^1\text{MLCT}$) or into the $^1\text{A}_1 \rightarrow ^1\text{T}$ absorption band. The magnetic response of the compound is found to change rapidly, and usually after 1 h a photo-stationary limit is reached. The light irradiation is then switched

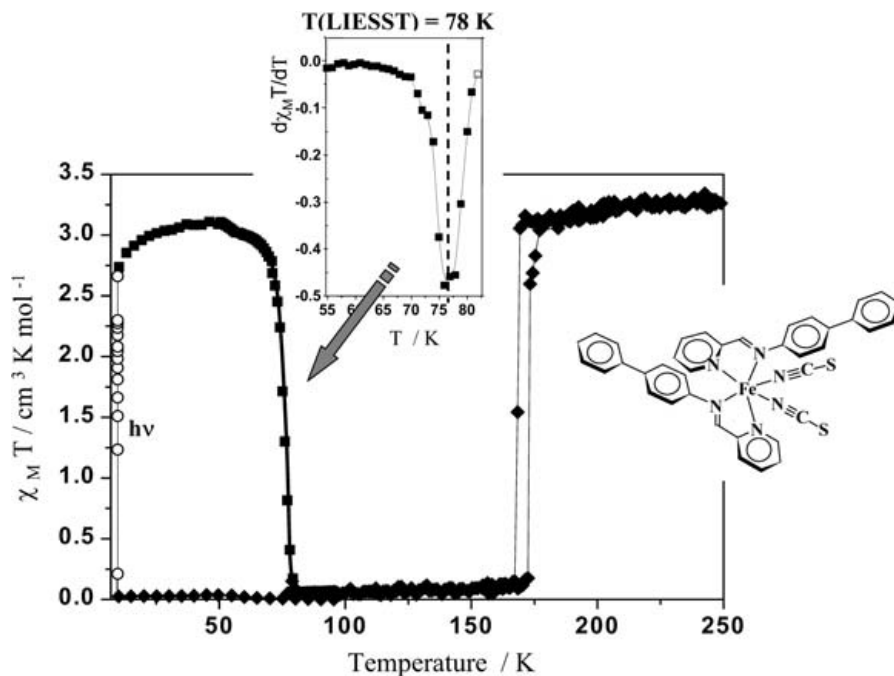


Fig. 6 T(LIESST) Procedure. Temperature dependence of $\chi_M T$ recorded in the cooling mode without irradiation (filled diamonds), during 1 h of irradiation at 10 K (empty circles) and in the warming mode after the light irradiation was applied for 1 h, then turned off (filled squares). The insert graph shows the derivative $d(\chi_M T)/dT$ plot as function of the temperature

off, and the temperature is increased at the rate of 0.3 K/min [133]. At low temperature, the HS→LS relaxation is controlled by the tunneling process up to ca. 40 K, and therefore the kinetics is very slow with respect to the time scale of the experiment. As a matter of fact, the time required to record the data up to 40 K is approximately three hours. Above ca. 40 K, the system reaches the thermally activated domain, and the HS→LS relaxation becomes increasingly more rapid. As a result of this behavior, $\chi_M T$ remains nearly constant as T increases from 10 K up to 40 K, then drops rapidly. In fact, a slight increase of $\chi_M T$ is usually observed between 10 to ca. 20 K, owing to the zero-field splitting within the spin quintet HS state. The $d(\chi_M T)/dT$ vs T plot shows a minimum at a temperature that we define as the T(LIESST) value; at this temperature, the light-induced information is erased in the SQUID setup. The behavior of $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ (PM-BiA=N-(2-pyridyl-methylene)aminobiphenyl) is typical and is illustrated in Fig. 6.

To date, more than 60 SCO compounds have been characterized by the same T(LIESST) procedure. It is becoming increasingly evident that a direct

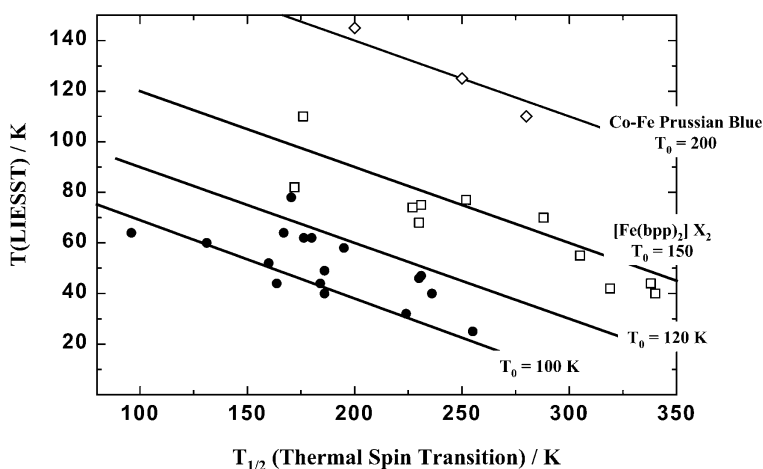


Fig. 7 Variation of $T(\text{LIESST})$ vs $T_{1/2}$ for spin crossover compounds. Data for the 120 and 100 T_0 lines are reported in [133]. The 150 T_0 line is the result of the linear regression obtained with the $[\text{Fe}(\text{bpp})_2]\text{X}_2 \cdot n\text{H}_2\text{O}$ family [134] and the 200 T_0 line is based on the work of Hashimoto [135]

relation exists between the $T(\text{LIESST})$ value and the thermal spin transition temperature, ($T_{1/2}$); i.e., $T(\text{LIESST}) = T_0 - 0.3 T_{1/2}$ with T_0 estimated at $T \rightarrow 0$ (Fig. 7) [133, 134]. The 150 T_0 line followed by the $[\text{Fe}(\text{bpp})_2]\text{X}_2 \cdot n\text{H}_2\text{O}$ complexes gives for the first time measurable $T(\text{LIESST})$ values with $T_{1/2}$ around room temperature [134]. The 200 T_0 line was recently reported by Hashimoto et al. [135] for the Co-Fe Prussian blue series where a charge-transfer-induced spin transition occurs between the $\text{Fe}^{\text{II}}(\text{LS}, S=0)\text{-CN-Co}^{\text{III}}(\text{LS}, S=0)$ site (LT phase) and the $\text{Fe}^{\text{III}}(\text{LS}, S=1/2)\text{-CN-Co}^{\text{II}}(\text{HS}, S=3/2)$ site (HT phase).

All these findings open up exciting prospects and extensive research efforts will be required to identify the key factors involved in the stabilization of the metastable HS state. We are currently pursuing this by investigating the influence of the coordination sphere (nature of the organic core, of the anion, of the hydration degree) and of the nature of the cooperativity on the magnitude the $T(\text{LIESST})$ [136].

6 Conclusions

Extensive progress has been made over the last 40 years in the spin crossover field and, nowadays, there are many reasons to believe in the use of such molecular materials in a genuine device in the not too distant future. The dimensions of synthetic molecular systems are now close to overlap with the levels of miniaturization required in microelectronics. At the same

time, the growing need for faster computers and internet applications is a stimulus to the exploration of innovative materials and operating principles for digital processing and communications. Within this context, the investigations of compounds exhibiting in a synergistic way multiple physical properties, as illustrated by the SCO phenomenon, are of particular interest. Of course, at the present early stages, only rudimentary examples of practical applications are known and, in certain cases, only a presentation of likely concepts has been given. Considerable fundamental studies are thus needed for a further understanding and to apply the many facets of this broad research field. It is for many of us an exciting and stimulating challenge.

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