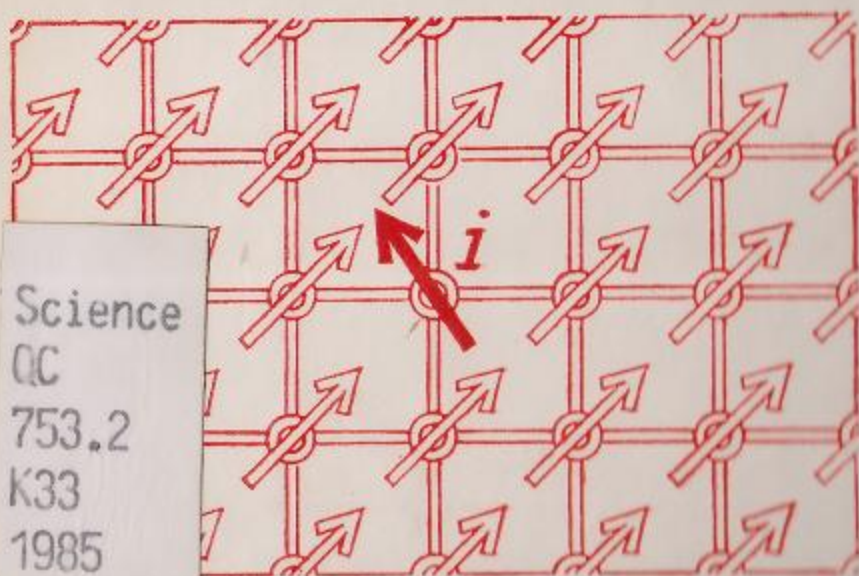


SCIENCE  
FOR EVERYONE

M.I. KAGANOV  
V.M. TSUKERNIK

# THE NATURE OF MAGNETISM



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# SCIENCE FOR EVERYONE

This popular-science physics book, dealing with precisely what its title suggests, exposes the reader to a fascinating interplay of classical, statistical, and quantum approaches to matter.

The book describes microscopic sources of magnetic field and explains why not all macroscopic bodies produce magnetic fields. The question why different bodies behave differently in response to an applied magnetic field is considered, and ferromagnetism and antiferromagnetism are explained in detail. The study of magnetic structures and other interesting problems are also discussed.



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М. И. Каганов  
В. М. Цукерник

## Природа магнетизма

Издательство «Наука», Москва

M. I. Kaganov  
V. M. Tsukernik

## The Nature of Magnetism

Translated from the Russian  
by V. I. Kisin



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## Introduction

### What is the Subject of This Book?

The title of the book represents fairly well the subject of this book. We shall attempt to explain the nature of magnetism.

One of the large branches of physics is the physics of electromagnetic phenomena. By the beginning of the 20th century it has seemed that the work of Faraday and Maxwell successfully completed this field of science: completed it in the sense that the main laws governing the behavior of electromagnetic fields were understood, that is, the necessary equations were written, and the task of subsequent generations of physicists was to search for more and more exotic solutions of these equations. But gradually it became clear that research in the field was far from complete. Owing to the injection of quantum ideas, the theory of electromagnetic phenomena has undergone essential changes, no less serious than those in mechanics. Nowadays we are much more careful in evaluating whether a part of physics has been completed or not. Any sufficiently developed science formulates not only its fundamental principles but also the boundaries beyond which these principles are not valid. Unless we go into subatomic structures, quantum mechanics and the theory of electromagnetism, that are basic for our understanding of the structure and prop-

erties of the surrounding world, can be successfully applied to study an enormously broad field of phenomena. There is no reason to doubt the validity of the laws at present: we are within the limits of their application.

The fundamental notion of the physics of electromagnetic phenomena is the electromagnetic field. A constant electromagnetic field, independent of time, separates into an electric and a magnetic fields. The two are very dissimilar. Nevertheless, the time-dependent electromagnetic field is a unified blend of the electric and magnetic fields. The energy of an electromagnetic wave concentrates alternately in the electric and magnetic fields, in similarity with the potential and kinetic energies of an oscillating pendulum.

Electromagnetic fields are detected by the senses of the human organism only if the electric and magnetic fields oscillate at extremely high frequencies. If this frequency is in the range from  $4 \cdot 10^{14}$  to  $7.5 \cdot 10^{14}$  Hz, the oscillations are perceived as visible light. The range of visible frequencies of an electromagnetic field occupies only a minor part of the frequency scale. But it would be frightening if this range did not exist because vision supplies us with most of the information about the surrounding world. "A picture is worth a thousand words": the truth of this maxim can be supported by quite modern calculations of information theory.

Static fields (both electric and magnetic) are not perceived by the human organism because it lacks appropriate receptors. Migratory birds seem to sense it, but even if it were so, we humans have no possibility to imagine what the birds feel.

It is obvious, however, that the lack of organs sensitive to electric and magnetic fields does not preclude us from finding out whether there is a field at a given point of space. The field can be not only detected but measured as well. The detection and measurement of electric and magnetic fields are implemented by means of instruments. There is a tremendous variety of such

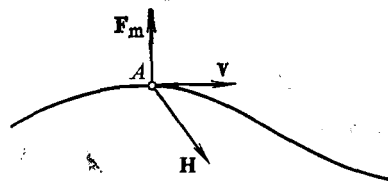


Fig. 1. Lorentz force  $F_m$  acting on a charge  $q < 0$  at a point A of the trajectory,  $v$  is the particle velocity,  $H$  is the magnetic field

instruments, but most of them\* are based on the following physical fact: if the electric field at a given point is nonzero and equals  $E$ , then an electric charge  $q$  placed at this point "feels" a force  $F_{el}$  equal to  $qE$ , and if there is a nonzero magnetic field  $H$ , a charge  $q$  moving at a velocity  $v$  "feels" a force  $F_m$  equal to  $\frac{q}{c} [v \times H]$ , where  $c$  is the speed of light in the vacuum, equal to  $3 \cdot 10^{10}$  cm/s (Fig. 1). And finally, if both the electric and magnetic fields are nonzero, the force

\* We write "most", but not "all", because some methods of measuring magnetic fields are known to be based on the interaction of a magnetic field with atomic and subatomic magnetic moments (see below), not with charges.

acting on an electric charge  $q$  is

$$\mathbf{F} = \mathbf{F}_{el} + \mathbf{F}_m = q \left( \mathbf{E} + \frac{1}{c} [\mathbf{v} \times \mathbf{H}] \right) \quad (4)$$

This force is called the *Lorentz force*.

The letters  $\mathbf{E}$ ,  $\mathbf{H}$ ,  $\mathbf{F}$ ,  $\mathbf{v}$  are set in boldface. This signifies that the quantities they denote are vectors.

It will be worth repeating: the electric and magnetic fields are vectors. This is inherent to

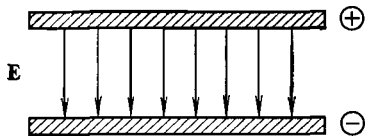


Fig. 2. Lines of force of the electric field between the plates of a plane capacitor

them. This fact was understood and used as a basis for the description of the electromagnetic field that finally reached the form of the famous Maxwell equations. These equations are so famous, or rather, so important, that their creation is justly regarded as one of the most important historic events.

There is no difficulty in producing an electric or magnetic field. The electric field fills the space between the plates of a charged capacitor (Fig. 2), and the magnetic field surrounds a wire through which electric current flows (Fig. 3).

Vector fields are shown in drawings by lines of force whose density is the greater, the higher is the field, and whose direction coincides with that of the vector (Fig. 4).

We have copied from a high-school physics textbook a drawing (see Fig. 4a) which shows that the charge (a small-radius ball in the figure) is a source of an electric field. If the charge is positive, the lines of force of the electric field

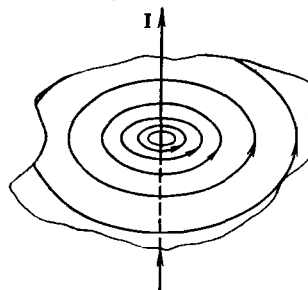


Fig. 3. Magnetic field around a straight conductor with current  $I$ . Magnetic lines of force are shown in a plane

leave the ball and go to infinity, becoming gradually less dense. If the charge is negative (see Fig. 4b), the lines of force go toward and enter the charge. These drawings are very important. By combining them we can understand the structure of the static electric field in all practically important cases.

The static electric field, its distribution in space, and its penetration into different kinds of matter is the subject of a special branch of the theory of electromagnetism, electrostatics. Electrostatics is based on the fact graphically expressed in Fig. 4a, b: the sources of an electric field are electric charges.

Usually the distribution of an electric field around a charge is demonstrated by using a tiny

but perfectly macroscopic (i.e. consisting of billions of atoms) sphere. Calculations and numerous experimental tests show that the strength of an electric field decreases with the distance

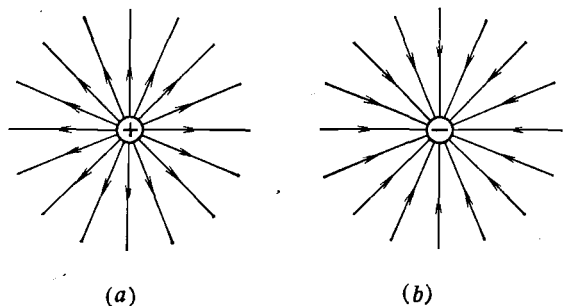


Fig. 4. Lines of force of the electric field of a fixed point charge  $q$ :

(a)  $q > 0$ ; (b)  $q < 0$

from the charge  $q$  in inverse proportion to the squared distance (Coulomb's law):

$$E = \frac{q}{r^2} \quad (2)$$

You are quite probably more familiar with a somewhat different formulation of Coulomb's law: the force acting on two charges  $q_1$  and  $q_2$ ,  $F_{\text{Coul}}$ , is inversely proportional to the squared distance between them:

$$F_{\text{Coul}} = \frac{q_1 q_2}{r^2}$$

The charges are repulsed if they are of like sign, and are attracted if they are of unlike signs.

The surprising fact is that this law holds both in the *macroscopic* and in the *microscopic* world. Sir Ernest Rutherford established by experiments with  $\alpha$  particles scattered by matter that an atomic nucleus (a single nucleus!) produces around itself an electric field governed by Coulomb's law (2). It is usual, in retelling Rutherford's experiments, to emphasize that these experiments proved the existence of the nucleus, that is, a positively charged blob of matter smaller than the atom by a factor of one hundred thousand. Of course, this was the main result. But the verification of Coulomb's law for distances to about  $10^{-13}$  cm is no less important. Just think: a simple law of inverse proportionality to squared distance holds both at distances commensurate to human scales (centimeters, meters) and at distances of the order of  $10^{-13}$  cm. And if we add that there are no reasons to doubt the validity of the law (2) at distances increased, say, to interstellar spacings, the universality of Coulomb's law becomes really staggering.

Coulomb's law can be recast in a slightly different form, by stating that the potential energy  $U$  of a charge  $q_2$  is distinct from zero and equals  $q_1 q_2 / r$  if a charge  $q_1$  is placed at the origin of coordinates. The energy can be determined to within a constant addend. Here we choose this addend so that  $U = 0$  at the infinite distance from  $q_1$  (for  $r \rightarrow \infty$ ). Then the sign of the potential energy  $U$  indicates whether we deal with attraction ( $U < 0$ ) or with repulsion ( $U > 0$ ).

The "energy" form of Coulomb's law is used in atomic physics more often than the "force" form.

The study of the atomic structure of matter reveals microscopic sources of electric fields in nature. These are electrons and protons. Their charges are equal in magnitude but opposite in sign. By convention, the charge of the proton,  $e_p$ , is assumed positive, and that of the electron,  $e$ , is assumed negative:

$$e_p = 4.8 \cdot 10^{-10} \text{ g}^{1/2} \cdot \text{cm}^{3/2} \cdot \text{s}^{-1} = -e \quad (3)$$

It should be emphasized that the electron and the proton have not merely microscopic (i.e. very small) charges but the smallest, or elementary, charges. No particles with fractional charges (in units of  $e$ ) have been found in nature.\*

Is the electron (or proton) charge large or small? Physics does not accept this abstract formulation of a question. We always have to add "in comparison with...". If the charge is regarded as a measure of interaction between particles, then it is tremendously large. Indeed, let us compare the repulsive force between two protons due to Coulomb's law,

$$F_{\text{Coul}} = -\frac{e_p^2}{r^2}$$

with the attractive force between them due to the law of gravitation,

$$F_{\text{gr}} = G \frac{m_p^2}{r^2}$$

\* In recent years much has been said and written about quarks of which nucleons—protons and neutrons—are composed. Several kinds (flavors) of quarks exist, with charges  $\pm(1/3)e$  and  $\pm(2/3)e$ . But it appears that somehow it is forbidden to quarks to exist in a free state (outside of nucleons).

The comparison is not difficult because both forces diminish in an identical manner, that is, in inverse proportion to the squared distance between the protons. The proton mass is  $m_p = 1.7 \times 10^{-24} \text{ g}$ , and the constant  $G$  in the law of gravitation is  $6.7 \cdot 10^{-8} \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{s}^{-2}$ . (See Problem 1\*.) The ratio of forces is  $F_{\text{Coul}}/F_{\text{gr}} \approx 4 \cdot 10^{42}$ . Electric forces exceed gravitational forces by a factor of more than  $10^{42}$ ! This is why gravitational forces are simply ignored when problems in atomic physics are considered.

And if electric forces are so strong, why are we able to disregard them in everyday situations and in technological processes?

The fact is that the ambient medium always contains numerous free charges (electrons and ions). Once a charge appears anywhere, free charges of the opposite sign are attracted and neutralize that charge. We mostly deal with neutral (noncharged) bodies. But gravitational forces cannot be neutralized. They increase with increasing mass, and are essential and predominant for macroscopic bodies, especially bodies in the outer space.

But the role played by an electric charge is not limited to the description of the interaction between charged particles. Presumably, everyone knows that under certain conditions a charged particle emits electromagnetic waves (neutral particles do not have this property). The measure of the ability of emitting radiation is the charge, or rather a dimensionless ratio  $e^2/\hbar c$  (you will

\* Problems are placed at the end of the book (see pp. 279-283).

have to take it for granted)\*. Here  $\hbar$  is the famous Planck's constant without which no formula of quantum physics is possible;  $\hbar \approx 10^{-27} \text{ g} \cdot \text{cm}^2 \cdot \text{s}^{-1}$ , so that  $e^2/\hbar c \approx 1/137$ . The fact that  $e^2/\hbar c \ll 1$  shows that in a certain sense the electron charge is small. It is thus large in one sense and small in another sense. This cannot be helped: the world is what it is.

Let us turn now to the magnetic field.

Magnetic charges are not found in nature. In 1931 one of the founders of quantum mechanics, Paul Dirac, suggested that magnetic charges must exist; he gave them the name *monopoles*. If monopoles existed, the world would be more symmetric and the theory of electromagnetism more beautiful. Much effort was spent in searching for the monopole. Several times sensational announcements claimed the discovery of the monopole, but later they were disproved. The monopole remains undiscovered.

But microscopic sources of a magnetic field do exist in nature. One of the first chapters describes them in detail.

Now it is time to outline briefly the subject of this book.

\* We will ask the reader to take what we say for granted as little as possible. But to be quite candid, this cannot be entirely avoided. Those who have read some physics-popularizing books on quantum mechanics may possibly be satisfied with the following "decoding" of this quotient. One over one hundred thirty-seven is the ratio of the electron "radius"  $e^2/m_e c^2$  to the Compton wavelength  $\hbar/m_e c$  ( $m_e$  is the electron mass,  $\approx 10^{-27} \text{ g}$ ). It is hard to say whether this is an explanation; at any rate, this helps to operate with quantities important in atomic physics, but primarily it shows how to compose dimensionless combinations of world constants.

First, as we have just mentioned, it deals with microscopic sources of a magnetic field.

Second, having explained that microscopic sources of a magnetic (and electric) field are electrons and protons, as well as neutrons (although, as follows from the name itself, they are not surrounded by an electric field), we explain why not each macroscopic body represents a macroscopic source of a magnetic field.

Third, we try to explain why different bodies behave differently when placed in a magnetic field.

Fourth, we speak in detail about bodies called *magnetic materials*. An important place among them is occupied by magnets, or *ferromagnetic materials*. They constitute macroscopic sources of a magnetic field.

This list does not exhaust the contents of the book. But we say nothing or nearly nothing about nuclear magnetism, do not cover the origin of the magnetic field of the Earth and other planets, and ignore exciting problems involved in the study of magnetic fields in outer space.

We feel certain compunctions in not speaking about the magnetic field of the Earth: indeed, the use of terrestrial magnetism for navigation (the compass) was the first application of magnetic properties in recorded history. Although, unfortunately, no rigorous criteria exist for evaluating the relative importance of inventions, everyone will probably agree that the compass, that is, a freely rotating magnetic needle, is one of the most important inventions of man.

We find consolation in the wise maxim of Kozma Prutkov (the collective pen name of



three Russian writers of 1850's, famous for their aphorisms) who wrote: "You cannot think of everything." And indeed you cannot. Magnetism is just as boundless as nature itself.

Readers are often scared away by mathematical complexities. We did take this factor into account but could not avoid using vectors and operations with them, the notions of function, and of its derivative and integral; however, we never go beyond this level. Some mathematical operations are intentionally shifted to Problems. A reader who solves the problems will understand the book much more profoundly than one who puts off solving them for some time in the future. But what worries us most about the reader's response does not concern mathematical difficulties. We expect that the main obstacle for the reader will be many new physical concepts.

We have tried to explain most of them in the text or in the footnotes; if some concepts still lack clarification, we ask forgiveness and request the reader to address comments or suggestions to us, c/o MIR Publishers. We shall be equally thankful for any other critical comments on the contents of the book.

We are deeply grateful to A. S. Borovik-Romanov and L. A. Prozorova, whose suggestions we followed where possible and whose kindness was a constant source of support during the difficult task of writing this book.

We also wish to thank Inna Kaganova for her help in preparing the manuscript for publication and Shevkhi Mevlyut for helping with the figures.

## Chapter 1

# Elementary Magnets

### 1.1. Electric and Magnetic Dipoles

The structure of the electric field produced by a point charge and that of the magnetic field around a thin wire through which electric current flows are so unlike that an idea of looking for an analogy between the two seems hardly justified. But let us avoid hasty conclusions.

Consider a system of two electric charges of identical magnitude and unlike signs, placed at a distance  $d$  from each other (Fig. 5). The strength of the electric field produced by this system at a point on the line drawn through the two charges is

$$E = \frac{q}{r^2} - \frac{q}{(r+d)^2} \quad (1.1)$$

We have simply added the strengths of fields produced by each charge because both vectors point along the same line. This is the advantage of symmetrically arranged points, that is, points on the line drawn through the charges. Let the point be far removed from the system of charges,  $r \gg d$ . Then

$$E = q \frac{2dr + d^2}{r^2 (r+d)^2} \approx \frac{2qd}{r^3} \quad (1.2)$$

At large distances from the charges  $q$  and  $-q$  the electric field strength decreases faster than the field strength due to a single charge. The

quantity  $p = qd$  is called the *electric dipole moment*, and a system of two charges of identical magnitude and unlike signs is called the *electric dipole*. The dipole moment is a vector, and by convention its direction is from the positive to the negative charge:

$$\mathbf{p} = q\mathbf{d} \quad (1.3)$$

The dipole moment determines the electric field of a neutral system of two charges (the

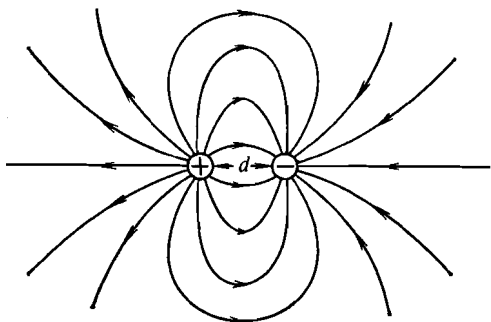


Fig. 5. Lines of force of the field of the electric dipole (dipole) at distances large in comparison with the spacing between the charges.

Adding the field strengths of two charges in accordance with the rules for addition of vectors at an arbitrary point again sufficiently far removed from the charges (i.e. in the case  $r \gg d$ ), we can obtain

$$\mathbf{E}(\mathbf{r}) = \frac{3(\mathbf{p} \cdot \mathbf{n})\mathbf{n} - \mathbf{p}}{r^3}, \quad \mathbf{n} = \frac{\mathbf{r}}{r} \quad (1.4)$$

(See Problem 2.)

Let us make use of formula (1.4) and trace the lines of force representing the field of a dipole (see Fig. 5). If we ignore the structure of the field at distances of the order of, or less than, the dipole size  $d$ , the dipole can be represented by a point (or rather, by a little arrow, because the dipole is a vector). From the viewpoint of an observer placed sufficiently far from the dipole, the origins and end points of the lines of force coincide.

Imagine now for a second that charges cannot be separated, that is, nature has only bound charges and no free charges. It is then natural to regard the dipoles, and not the charges, as elementary (simplest) sources of an electric field.

For dipoles to define *completely* the electric field under discussion, we should demand that the dipoles be microscopically small, say, as small as atoms, or even smaller. Then any macroscopic distance will be large (compared with the dipole size), and formulas (1.2)-(1.4) will be absolutely exact.

The neutrality of a system of charges, that is, the equality of the positive to the negative charge, can be established by the behavior of the electric field far from the system. The electric field around an electrically neutral system diminishes with distance  $r$  steeper than  $1/r^2$ . We can also speak of systems with dipolar neutrality, that is, systems whose dipole moment is zero. The decrease of the electric field with distance far from such systems is steeper than  $1/r^3$ . Figure 6 shows several systems of charges with zero dipole moment. (See Problem 3.)

Nonzero dipole moment of a system of charges

points to an asymmetry in the distribution of charges.

Obviously, it is not mandatory in this argument to assume that free charges cannot exist,

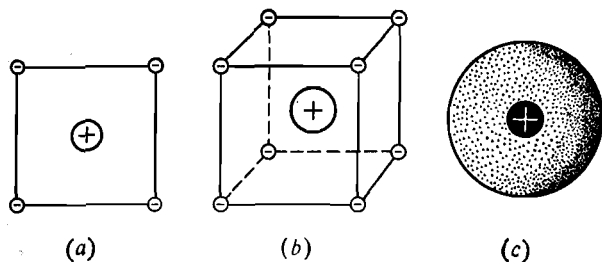


Fig. 6. Systems of charges with zero electric dipole moment:

(a) negative charges  $-q$  are at the vertices of the square, and a positive charge  $+4q$  is at its center; (b) similar arrangement for the cube, the central charge is  $+8q$ ; (c) a positive charge  $Q$  is at the center of the sphere, and a negative charge  $-Q$  is uniformly distributed over the sphere

but we know definitely that there are no *magnetic* charges in nature.

To look for elementary sources of a *magnetic* field, let us consider a circular current, that is, simply a ring made of wire, with area  $S$  and electric current flowing in it (we assume the current to be  $I$ ). To simplify the analysis by symmetry arguments, we calculate the magnetic field at a point on a straight line perpendicular to the plane of the contour (ring) and passing through its center (Fig. 7). We divide the contour into small segments with length  $\Delta l$  each. Accord-

ing to the Biot-Savart law, one such segment produces a magnetic field with strength

$$\Delta H = I \frac{\Delta l}{cr^2}$$

The definition of  $r$  is clear from Fig. 7.

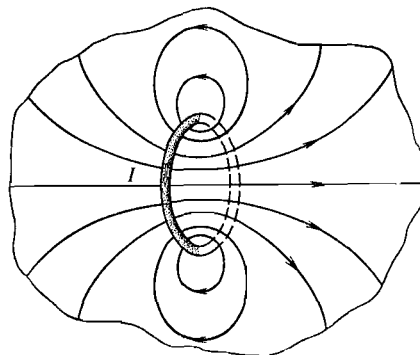


Fig. 7. Magnetic field of the closed current  $I$  flowing in a flat ring. Magnetic lines of force are shown in a plane perpendicular to the ring

Adding the fields produced by individual segments of the ring, we find

$$H = \frac{2IS}{cr^3} \quad (1.5)$$

This formula much resembles formula (1.2). On the basis of this analogy we can refer to the combination

$$\frac{IS}{c} = M_c \quad (1.6)$$

as to the *magnetic dipole moment* of a circular current. But if the magnetic dipole moment is

assigned a direction along the perpendicular to the plane of the circular current (with the sign dictated by the Ampère rule), the magnetic field of the circular current is expressed in terms of the vector  $\mathbf{M}_c$  (*magnetic dipole*) by a formula quite analogous to (1.4):

$$\mathbf{H}(\mathbf{r}) = \frac{3(\mathbf{M}_c \cdot \mathbf{n})\mathbf{n} - \mathbf{M}_c}{r^3} \quad (1.7)$$

To derive this formula, we must be able to add the magnetic fields  $\Delta H$  produced by individual segments  $\Delta l$  of the contour, taking into account that the added fields are vectors.

The fact that formulas (1.4) and (1.7) coincide (to within the selected notations) shows that the electric field produced by two charges of unlike signs and the magnetic field produced by a circular current have an absolutely identical structure, provided we ignore the field close to the charges or to the circular current. And in the limiting cases of infinitely proximate charges or of infinitesimal radius of the current ring the dependence of the fields on coordinates is perfectly identical.

The magnetic dipole can thus exist, and it is not necessary to "invent" any magnetic charges. A magnetic dipole is produced by the motion of ordinary electric charges.

In order not to be fascinated excessively by the similarity of the electric and magnetic dipoles, let us pay attention to a profound difference between these two vectors.

First, let us conduct an "imaginary experiment" shown in Fig. 8, namely, let us reflect both dipoles in a mirror. As a result, the direction of an electric

dipole will be reversed, while that of a magnetic dipole will be retained. Second, let us switch the flow of time ("time arrow") to reverse (this operation, possible only "on paper", is called

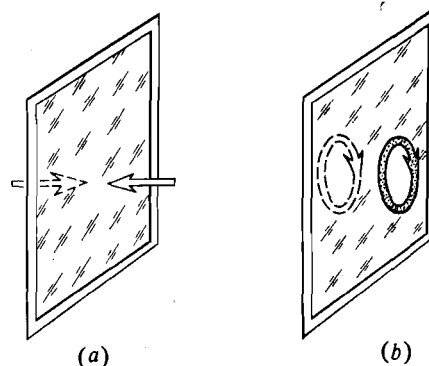


Fig. 8. Mirror reflection: (a) of an electric dipole; (b) of a magnetic dipole

"time reversal"). This operation does not affect the electric dipole but reverses the sign of the magnetic dipole: indeed, under time reversal all particles move in reverse directions and the current thus changes sign.

## 1.2. Gyromagnetic Ratio

There is a simple relation between the magnetic moment  $\mathbf{M}_c$  and the mechanical angular momentum  $\mathbf{L}$  of a system of charged particles. In order to find this relation, let us transform expression (1.6) for the magnetic moment  $\mathbf{M}_c$ . By the

definition of an electric current,  $I = (q/2\pi R) v$ . Indeed,  $q/2\pi R$  is the electric charge per unit length of the conductor, and the velocity  $v$  is the path covered by the charge per unit time. Since  $S = \pi R^2$ , we find

$$M_c = \frac{qvR}{2c} \quad (1.8)$$

On the other hand, the angular momentum  $L$  of the system in question is

$$L = m_q v R \quad (1.9)$$

where  $m_q$  is the mass of the moving charges.

Comparing (1.8) and (1.9), we find

$$\frac{M_c}{L} = \frac{q}{2m_q c} \quad (1.10)$$

Put in this form, the relation is not improved in comparison with formula (1.6) relating magnetic moment with the current  $I$ . However, if we recall that the current in a conductor is a flux of electrons, we immediately see that  $q = Ne$  and  $m_q = m_e N$ , where  $N$  is the number of moving electrons in the conductor (conduction electrons). Then (1.10) yields

$$\frac{M_c}{L} = \frac{e}{2m_e c} \quad (1.11)$$

The ratio of two macroscopic quantities (the magnetic moment of a circular current and the angular momentum of electrons making up this current) is found to be equal to a combination of the quantities characterizing microscopic charge carriers in the conductor. The ratio  $\gamma = M_c/L$  was given the name *gyromagnetic ratio*.

Expression (1.11) obtained for the circular motion of electrons remains valid regardless of the type of motion of the electrons. *If the mechanical angular momentum of this motion is  $L$ , then its magnetic moment is  $M = (e/2m_e c) L$ .*

Later we shall have to elaborate this statement. It was found that electrons *per se*, even when at rest, are sources of a magnetic field, being microscopic magnetic dipoles. But for some time we shall pretend that we are not aware of this fact.

The gyromagnetic ratio is often measured in units of  $e/2m_e c$ . In the case under consideration it must be assumed equal to unity. The gyromagnetic ratio would be thousands of times smaller if the current in the conductor were carried by ions instead of electrons. It is difficult to imagine that the gyromagnetic ratio can be greater than unity: indeed, electrons are the lightest of charged particles.

### 1.3. Elementary Sources of Magnetic Field: Do They Exist? Ampère's Hypothesis

The circular current, also called the current loop, is thus a magnetic dipole, the source of a magnetic field. But do such current loops exist in nature? And if they do, what are they?

At school we learn the molecular currents hypothesis advanced by Ampère. According to this hypothesis, a very daring one at the time (André Marie Ampère lived from 1775 to 1836), electric currents flow inside molecules and atoms, that is, atoms and molecules are current loops, and therefore magnetic dipoles. In fact, Ampère's

hypothesis was confirmed superbly when the electron structure of the atom had been understood. It was confirmed in the sense that, indeed, electrons moving around atomic nuclei produce electric currents, and current loops produce the magnetic field.\*

However, if these words are interpreted literally, in terms of classical (nonquantum) concepts (and only classical concepts were known in Ampère's time), the inescapable conclusion is: nature has no *elementary* magnets, that is, no *smallest* sources of a magnetic field. Consider the simplest atom: the hydrogen atom. In this atom a single electron revolves around a proton, moving, according to the classical laws of motion, in an elliptic orbit (its particular case is a circle; for the sake of simplicity, here we consider only this case).

The equality of the centrifugal to the Coulomb force gives the relation between the radius  $a$  of the electron orbit and its velocity  $v$ :

$$\frac{e^2}{a^2} = \frac{m_e v^2}{a}$$

\* Here is a short excerpt from A. Einstein's paper of 1915. This quotation will show how daring the hypothesis was in its time, and furthermore, it will help to understand that, as a rule, a hypothesis that seems to explain experimental facts poses, if it is sufficiently serious, new profound questions.

"Ampère's theory in its current (at the time of writing, of course—*M. K.* and *V. Ts.*) electron form faces a difficulty: according to Maxwell's equations, electrons moving in circular orbits must lose their kinetic energy through radiation, so that with time atoms and molecules must lose, or have already lost, their magnetic moments; *evidently, nothing of the sort occurs in reality*" (our italics—*M. K.* and *V. Ts.*).

or

$$\frac{e^2}{a} = m_e v^2 \quad (1.12)$$

The total energy  $\varepsilon$  of the electron is the sum of its potential and kinetic energies:

$$\varepsilon = -\frac{e^2}{a} + \frac{m_e v^2}{2} = -\frac{e^2}{2a}$$

or

$$a = -\frac{e^2}{2\varepsilon} \quad (1.13)$$

The energy  $\varepsilon$  of the electron thus determines unambiguously the radius of its orbit (do not be surprised with the minus sign: indeed, the electron energy in the atom is negative, and the arbitrary constant term in the potential energy is chosen so as to make energy vanish at the infinite distance from the nucleus, see p. 13). The angular momentum  $L$  of the electron equals  $m_e v a$ . From this and from (1.12) we find

$$L = m_e a \frac{e}{\sqrt{m_e a}} = e (m_e a)^{1/2}$$

and the magnetic moment of the hydrogen atom is

$$M_a = \frac{e^2}{2m_e c} (m_e a)^{1/2} \quad (1.14)$$

In classical mechanics an electron is allowed to have any energy, no matter how large its magni-



tude (it is a negative energy!), and hence the radius of its revolution around the nucleus can be arbitrarily small. Although the orbital velocity is large at small radii, the angular momentum diminishes with diminishing radius. When  $a \rightarrow 0$  (i.e. when  $|r| \rightarrow \infty$ ) the orbital angular momentum  $L$  and with it the magnetic moment  $M_a$  tend to zero. We have to conclude therefore that magnetic moments can be arbitrarily small and there are no fixed elementary magnets (in contrast to elementary charges).

But this conclusion is in contradiction with the reality. Our argument has a flaw. It is incorrect because it ignores the quantum nature of the motion of microscopic particles.

Frankly speaking, the laws of motion of atomic and subatomic particles were reconsidered not because of our microscopic magnets. Classical physics had to be revised under the pressure of the whole ensemble of facts discovered about the properties of atoms. The foremost of these was the fact of the very existence of stable identical atoms. Actually, formulas (1.12)-(1.14) constitute the classical theory of the hydrogen atom. But since classical physics imposes no constraints on the choice of the distance  $a$  at which the electron revolves around the nucleus, different hydrogen atoms could obviously be expected to differ from one another, that is, electrons could be closer to the nucleus in some atoms and farther away from it in other atoms. Besides, atomic size (orbit's radius) would be affected by collisions between atoms. Furthermore, when an electron, with its electric charge, moves with acceleration (note that in the motion along an elliptic orbit

the electron velocity changes both in magnitude and in direction, and in the motion along a circular orbit only in direction), electrodynamics requires it to emit electromagnetic waves, that is, to lose energy (see the quotation from Einstein's article on p. 28). As the electron energy decreases, the electron moves closer to the nucleus (see formula (1.13)) and finally has to fall on the nucleus. On the human time scale, the time during which it falls is negligibly small, about  $10^{-10}$  s.\* This is a conclusive evidence against the applicability of classical laws of motion to the motion of microscopic particles. It is impossible to save classical mechanics by assuming that the force acting between an electron and a proton is some unknown, non-Coulomb force: we have already mentioned that Rutherford's experiments on scattering of  $\alpha$  particles gave a direct demonstration of a Coulomb field produced by nuclei.

Below we shall give certain information on quantum mechanics, without which it will be virtually impossible to understand the nature of magnetic phenomena; but for the time being we pursue the following line.

Since the existence of elementary magnets requires that the radius of the electron trajectory in an atom have a definite value, let us borrow it from quantum mechanics. In particular, the

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\* See M. I. Kaganov, *Electrons, Phonons, Magnons*. Mir Publishers, Moscow, 1981, p. 34. The computation assumes that the "fall" begins at a distance of  $\approx 10^{-8}$  cm.

radius of the hydrogen atom is\*

$$a_1 = \frac{\hbar^2}{m_e e^2}$$

(See Problem 4.) Now we substitute  $a_1$  for  $a$  into formula (1.14). As a result, we obtain the following expression for the magnetic moment of the hydrogen atom:

$$M_a = \frac{e\hbar}{2m_e c} \quad (1.15)$$

As a rule, this ratio is denoted by the letter  $\mu_B$  and called the *Bohr magneton*.

The Bohr magneton is the elementary electron magnetic moment we are seeking. It is elementary in the sense that no electron can have a magnetic moment below  $\mu_B$ .

The quantities on the right-hand side of (1.15) are known (they were given above). Substituting the values of  $e$ ,  $\hbar$ ,  $m_e$ , and  $c$ , we find

$$\mu_B = 10^{-20} \text{ erg/gauss} \quad (1.16)$$

It must be clearly understood that we did not derive formula (1.15). Indeed, we took the size of the hydrogen atom "out of thin air". Moreover, we shall have a chance to see that the magnetic

\* As we said, the laws of classical physics do not make it possible to find the radius of the electron trajectory around the nucleus. The radius can be arbitrary. This is readily understood if you note that no expressions with the dimensionality of length can be constructed out of the two quantities,  $e$  and  $m_e$ , that enter into the equation of motion of the electron. Quantum mechanics introduces a supplementary quantity, Planck's constant  $\hbar$ . Out of the three quantities a combination with the dimensionality of length can be constructed.

moment due to the revolution of the electron around the proton in the ground state of the hydrogen atom (i.e. at the least possible energy) is zero.

We should like the reader to remember for the time being two facts:

- (i) elementary magnets exist, and
- (ii) by the order of magnitude the electron magnetic moments equal the Bohr magneton (1.15).

#### 1.4. A Brief Overview of Quantum Mechanics

Classical mechanics, often referred to as Newtonian mechanics to emphasize the role of its creator, provides a perfect description of the motion of macroscopic bodies, that is, bodies consisting of an enormous number of atoms and molecules.\* But the motion of electrons in atoms is governed by quantum, not classical, mechanics. This radically changes all properties of the atom, including its magnetic properties. Or, to put it more accurately, only quantum mechanics enables us to describe correctly (i.e. in agreement with experimental data) the properties of the atom, including the stability of atoms.

What are the distinctive features of the quantum laws of motion in comparison with the clas-

\* No attributes help to evaluate the tremendous number of atoms in a macroscopic body. We cannot comprehend such numbers. One cubic centimeter of a solid contains  $10^{22}$  atoms. If placed in a chain side by side (an atom's size is  $10^{-8}$  cm), they will cover more than a billion kilometers.

sical laws? The complete answer to this question comes only from studying quantum mechanics which is the part of modern physics studying the motion of microscopic objects, such as atoms, molecules, and particles of which they are composed. Any more or less serious acquaintance with quantum mechanics calls for a substantial mathematical foundation since the mathematics of quantum mechanics is sufficiently complicated. In addition, an understanding of the laws of quantum mechanics requires that certain habitual notion rooted in everyday experience be dropped. The overcoming of the inertia of personal experience may even prove a greater obstacle than mastering the mathematics of quantum mechanics. At any rate, the physicists who rejected or resisted quantum mechanics (and the great Einstein was one of them!) could not accept its fundamental physical postulates.

The presentation that follows is restricted to the corollaries of quantum mechanics, directly relevant to magnetic properties of electrons, atoms, molecules, and macroscopic bodies. A warning: the "corollaries" might appear strange. There is no use in doubting them. It is by resorting to these "corollaries" that we shall explain the nature of magnetism.

### *Uncertainty Relations. Particle-Waves*

One of the main features distinguishing quantum particles (i.e. particles whose motion is described by quantum mechanics) from classical particles (whose motion is described by Newtonian me-

chanics\*) is that they do not move along trajectories. As we are used in daily life to dealing with macroscopic bodies, our desire to transfer the easily visualizable notions of the motion of such bodies along a trajectory to microscopic objects whose motion cannot be directly observed is only natural. The properties of microscopic particles must be deduced from the results of experiments or observations, without forcing upon these particles the properties of macroscopic bodies. And the experimental data (e.g. spectral characteristics of atoms and molecules) are such that the notion of the electron trajectory in the atom has to be dropped. At any moment of time the trajectory is determined by the position of a particle and its velocity. The absence of a trajectory means that a quantum particle cannot have simultaneously definite coordinates (definite position) and definite velocity. The state of a quantum particle cannot be described in as much detail as that of a classical particle. The statement that *a particle cannot have simultaneously a definite coordinate and a definite velocity* is called the *uncertainty principle*.

The uncertainty principle signifies that a physical quantity which depends on the position (coordinate) and the velocity of a particle does not have, in the general case, a definite value. (It must be mentioned here that the angular momentum (1.9) is just such a quantity, because  $L$  is a function of coordinate  $R$  and velocity  $v$ .)

\* Quantum mechanics is capable of describing the motion of any body, but this is not necessary for the motion of macroscopic bodies: the error introduced by using equations of classical mechanics is negligible.

Quantitatively the uncertainty principle is written in the form of inequalities called the *uncertainty relations*, or *Heisenberg relations*:

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}, \quad \Delta p_y \Delta y \geq \frac{\hbar}{2}, \quad \Delta p_z \Delta z \geq \frac{\hbar}{2} \quad (1.17)$$

where  $\Delta x$ ,  $\Delta y$ ,  $\Delta z$  and  $\Delta p_x$ ,  $\Delta p_y$ ,  $\Delta p_z$  are uncertainties in coordinates  $x$ ,  $y$ ,  $z$  and in projections of momentum  $\mathbf{p} = m\mathbf{v}$  onto the axes  $x$ ,  $y$ ,  $z$ , respectively. A formal transition from quantum to classical mechanics occurs when Planck's constant  $\hbar$  tends to zero. Inequalities (1.17) mean the following: the smaller the error in one of the quantities, for instance,  $x$ , the greater the error in the other, namely,  $p_x$ . Note that the accuracy of defining  $x$  does not affect the accuracy of defining  $p_y$ . Physical quantities separate into peculiar pairs coupled by the uncertainty relation.

The main feature of quantum mechanics is obviously not the rejection of the classical description of motion but the formulation of methods with which to describe the behavior of microscopic particles. The nature of this description is essentially different from the one employed in classical physics. Since there are physical quantities which by virtue of the uncertainty relation do not have a definite value, quantum mechanics cannot do better than give the probabilities of specific values of the physical quantity in question. Note that the probabilistic nature of quantum mechanics is not caused by the incompleteness of our knowledge about a quantum system. This nature follows from the properties of

microscopic particles. This is how nature operates. To some extent, it is better to say that there is only a limited possibility of describing a quantum system in terms of classical quantities: coordinates and momenta. The measure of limitation is given by the uncertainty relations (1.17).

In optics there are relations similar to uncertainty relations. A plane electromagnetic wave with wave vector\*  $\mathbf{k}$  is known to fill up the whole space. However, an electromagnetic field can be concentrated within a finite, and even very small, element of space. This is achieved if a large number of waves is used. Such a combination of waves is called the *wave packet*. A wave packet is characterized by intervals  $\Delta k_x$ ,  $\Delta k_y$ ,  $\Delta k_z$  of the projections of wave vectors, required to concentrate the field in a region of space  $\Delta x$   $\Delta y$   $\Delta z$ . The set of wave vectors is the greater, the smaller is the region of space occupied by the wave packet:

$$\Delta x \Delta k_x \geq \frac{1}{2}, \quad \Delta y \Delta k_y \geq \frac{1}{2}, \quad \Delta z \Delta k_z \geq \frac{1}{2} \quad (1.18)$$

A comparison of inequalities (1.18) and (1.17) shows that they are equivalent if we assume

$$\mathbf{p} = \hbar \mathbf{k} \quad (1.19)$$

This spectacular equality, relating the momentum characterizing the motion of a particle to the wave vector characterizing the wave, was first written by the French physicist de Broglie in 1925. De Broglie also found the relationship

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\* The wave vector is a vector  $\mathbf{k}$  pointing along the wave propagation direction and equal in magnitude to  $k = 2\pi/\lambda$  ( $\lambda$  is the wavelength).

between the energy  $\varepsilon$  of the particle and the frequency  $\omega$  of the wave:

$$\varepsilon = \hbar\omega \quad (1.20)$$

Both equalities (1.19) and (1.20) are called the *de Broglie relations*. They signify recognition of wave properties of particles. For this reason quantum mechanics is often called *wave mechanics*.

The uncertainty relations and the de Broglie relations follow strictly from quantum mechanics. Quantum mechanics demonstrates just as rigorously that waves possess corpuscular properties (i.e. the properties of particles). Relations (1.19) and (1.20) can therefore be read from left to right (thereby putting the motion of a particle in correspondence with a wave process) as well as from right to left (thereby emphasizing the corpuscular properties of waves).

### Stationary States

Among the states of a physical system (such as a particle, atom, or molecule) there are such states in which one or several physical quantities simultaneously have strictly defined values. Such states are of fundamental importance in quantum mechanics, forming the basis for the description of any (arbitrary) state of physical systems. For instance, there exist states with definite values of the momentum of a particle. The uncertainty relations then dictate that the position of the particle is completely indeterminated in these states. The same follows from the de Broglie relations: the motion of a particle with momen-

tum  $\mathbf{p}$  is put in correspondence with a plane wave whose wave vector is  $\mathbf{k} = \mathbf{p}/\hbar$  and which fills the whole space.

A special role is played here by definite-energy states, called *stationary states*. A quantum system

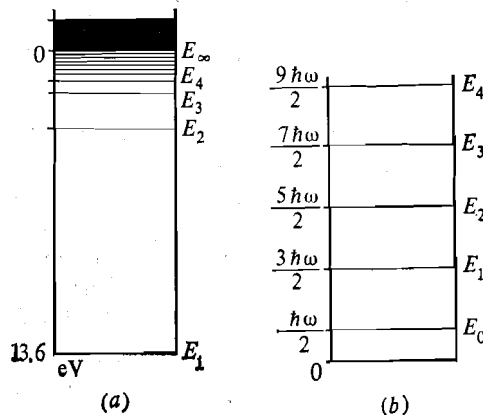


Fig. 9. Discrete energy levels:

(a) of an electron in a hydrogen atom  $E_n = -E_0/n^2$ ,  $n = 1, 2, \dots$ ;  $E_0 \approx 13.6$  eV; (b) of a harmonic oscillator at frequency  $\omega$  ( $E_n = (n + 1/2) \hbar\omega$ ,  $n = 0, 1, 2, \dots$ )

(e.g. an atom), when left alone, is in one of its stationary states.

The property that is probably the most characteristic for quantum systems is the discreteness of some physical quantities that can take on a continuous spectrum of values if treated in terms of classical physics. Thus, the energy of an electron in the atom can assume only certain discrete values (Fig. 9) that can be enumerated. They are called *energy levels*. Each value of

energy corresponds to one or several stationary states. If there are more than one such state, they differ in other physical quantities that are allowed to have definite values simultaneously with energy.

The oscillator is a very important, though simple, object in mechanics (both classical and quantum mechanics). Imagine a particle with mass  $m$  oscillating because a force  $F$  acts on it;  $F$  is proportional to the distance  $x$  between the particle and its equilibrium position ( $F = -kx$ ). This particle oscillates at a quite definite frequency  $\omega = \sqrt{k/m}$ . A classical particle can have an arbitrary vibrational energy  $\epsilon_{vib}$  (it is determined by the amplitude of vibrations), but a quantum particle can have only one vibrational energy from the set of discrete values (see Fig. 9b)

$$\epsilon_{vib} = (n + 1/2) \hbar\omega, \quad n = 0, 1, 2, \dots$$

It is natural to single out among the stationary states the one with the lowest energy. It is called the *ground state*. It is the truly stationary state because a physical system (say, an atom) can exist in the ground state indefinitely. Higher-energy states are excited states. They are only approximately stationary. An atom in an excited state can emit an electromagnetic wave and slide down to a lower-energy state. This "sliding down an energy-level staircase" finally brings the atom to its ground state. What is then a justification of regarding excited states of atoms as stationary? The justification is that the lifetime in the excited state is relatively long (on the atomic scale, of course). It is interesting to note that this fact is a corollary of the small charge of the electron.

Do you remember that  $e^2/\hbar c = 1/137$ ? Here is why: the lifetime of an atom in an excited state is approximately  $\tau_a (\hbar c/e^2)^3 \approx \tau_a (137)^3$ , where  $\tau_a$  is the time of revolution of the electron around its "orbit". The electron makes around the nucleus six million "revolutions" before coming down from the excited to the ground state! This is sufficient reason to regard the excited state as a stationary state.

It must certainly be clear to the reader that the words "orbit" and "revolutions" are in quotation marks because in fact an electron moving in an atom has no orbit. What then is meant by the time  $\tau_a$ ? Let us recall the de Broglie relation (1.20) and apply it to the difference between the energies of the excited and the ground state:

$$\hbar\omega = \epsilon_{exc} - \epsilon_{gr}, \quad \text{or} \quad \omega = \frac{\epsilon_{exc} - \epsilon_{gr}}{\hbar}$$

The frequency  $\omega$  and the oscillation period  $\tau$  are in inverse proportion to each other, that is,  $\tau = 2\pi/\omega$ . If instead of the frequency  $\omega$  we substitute the expression given above, the corresponding period will be that very "period of revolution"  $\tau_a$ :

$$\tau_a = \frac{2\pi\hbar}{\epsilon_{exc} - \epsilon_{gr}}$$

In some cases the motion of an electron in an atom can be described with high accuracy by classical mechanics. Then  $\tau_a$  calculated by the *quantum* formula indeed coincides with the classical period of revolution (with no quotation marks!).

We have formulated above some results ob-



tained in quantum mechanics, having said nothing about the mathematics by which they were derived. The description of the mathematical equipment is not one of our objectives. One remark is needed: there are several mathematical apparatuses of quantum mechanics, very different in form but essentially equivalent. One of them is based on an analysis of the solutions of the differential equation that the wave function of a quantum system must satisfy (E. Schrödinger's approach). Strictly prescribed operations with this function make it possible to extract all relevant physical consequences: the values of physical quantities that can be directly compared with experimental data.

The wave function is most often denoted by the letter  $\psi$ . Here we also use this notation. Take into account (it is important for what is to follow) that  $\psi$  is a complex function defined to within a complex factor. In other words, two wave functions  $\psi$  and  $\alpha\psi$  describe the same state if  $\alpha$  is a constant.

The physical meaning of the wave function is especially clear if  $\psi$  is a function of coordinate  $\mathbf{r}$  and time  $t$ . Then the quantity  $|\psi(\mathbf{r}, t)|^2$  is proportional to the probability of finding the particle at a point  $\mathbf{r}$  at a time moment  $t$  (M. Born).

### *More on Hydrogen Atom*

The simplest quantum system is the hydrogen atom: an electron revolving around a proton. The energy levels are given by a simple formula:

$$\epsilon_n = -\frac{me^4}{2\hbar^2} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots \quad (1.21)$$

What does this formula mean? It means that the hydrogen atom can be in different states, that is, in states with different energy. One state among them has the lowest energy; we have already mentioned that it is called the ground state. The electron energy in the ground state is

$$\epsilon_1 = -\frac{me^4}{2\hbar^2} \approx 13.6 \text{ eV} \approx 2.18 \cdot 10^{-11} \text{ erg}$$

This means that 13.6 eV of energy has to be expended in order to separate the electron from the proton. If the atom is in the excited, rather than the ground, state, it has already been said to be able to emit the extra energy in the form of light. The frequency of the emitted light is given by Bohr's formula which constitutes the law of conservation of energy in the creation of the photon by the hydrogen atom:

$$\epsilon_n - \epsilon_{n'} = \hbar\omega \quad (1.22)$$

All said above is strictly derivable in quantum mechanics. And now let us make an inconsistent step. Although we have assured the reader that quantum mechanics had done away with the concept of trajectory, we shall make use of the classical formula (1.13) together with the quantum formula (1.21). We shall see that the quantization of energy results in the quantization of the electron orbits.\* The electron can revolve

\* Such an eclectic mechanics that retained the features of classical mechanics but was supplemented with quantization conditions was constructed by Niels Bohr at the beginning of the 20th century to interpret atomic spectra. A successful explanation of hydrogen spectrum (formulas (1.21) and (1.22)) was a sign that physics is on the right track.

only along allowed orbits of radii  $a_n = (\hbar^2/m_e e^2) n^2$ . The ground state corresponds to the smallest radius of the orbit, equal to  $a_1 = \hbar^2/m_e e^2$ . We have already used this fact to calculate the value of the elementary magnet

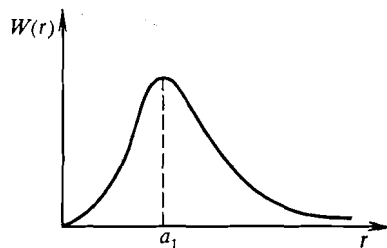


Fig. 10. Distribution of probability  $W(r)$  of finding an electron at a distance  $r$  from the nucleus of a hydrogen atom in the ground state. The area under the curve equals unity

(see p. 32). Unfortunately, a simple scheme that an attentive reader could devise

*quantization of orbits*  $\rightarrow$  *stable current loops*  
 $\rightarrow$  *elementary (atomic) magnets*

fails precisely because electrons do not move along trajectories. For instance, we cannot speak of any trajectory in the ground state. The quantity  $a_1$  fixes the radius of the sphere within which the electron can be found at the probability close to unity (Fig. 10). It would be absolutely impossible to try to define the position of the electron more accurately because it would contradict the uncertainty principle. And since there can be no current loop, we come to a strange result:

although the electron moves around the nucleus, its motion does not produce a magnetic moment.

But we know that elementary magnets are a reality. In order to sort out this confusion, it will be necessary to understand how the law of conservation of angular momentum is modified in quantum mechanics.

### 1.5. Angular Momentum. Space Quantization

The story of angular momentum logically belongs in the preceding section. We decided to make it a special section because it is especially important for understanding the nature of magnetism.

Conservation laws play an outstanding role in physics. In this respect atomic physics and the physics of magnetic phenomena are no exceptions. Electrons in the atom move in a force field with spherical symmetry; in other words, the force acting on the electron in the field around the nucleus depends on the distance separating the electron from the nucleus but is independent of the direction. Classical mechanics has "foreseen" for this case a special conservation law: the law of conservation of angular momentum:

$\mathbf{L} = [\mathbf{p} \times \mathbf{r}]$  is independent of time

(See Problem 5.) And what has quantum mechanics to say in this respect? Naturally, quantum mechanics also holds that angular momentum is conserved (this is a general rule: each "classical" conservation law has a quantum analogue; the converse is not correct: some quantum conserva-

tion laws have no analogues in classical physics).

The validity of the law of conservation of angular momentum signifies that an electron in a definite stationary state (i.e. in a state with a definite energy) can have a definite angular momentum. But ... is a particle allowed to have a definite angular momentum? Let us have a close look at the formula  $\mathbf{L} = [\mathbf{p} \times \mathbf{r}]$ . It contains simultaneously both  $\mathbf{p}$  and  $\mathbf{r}$ . But the uncertainty relations (1.17) forbid a particle to have a definite coordinate  $\mathbf{r}$  and a definite momentum  $\mathbf{p}$  at the same time. What does it lead to?

A rigorous quantum-mechanical analysis of the motion of a particle in a force field with a center of symmetry shows that the conserved angular momentum of the particle can be characterized by the length  $L$  and by its projection  $L_z$  onto some axis (here we denote it by  $z$ ).

A question that arises immediately is: "What axis?" The answer is: "Any axis!" This equivalence of axes emphasizes the isotropy of the force acting on the particle. Of course, if there is a reason that singles out a specific axis, the projection must be taken onto this very axis.

Quantum mechanics not only restricts the definition of angular momentum to two quantities ( $L$  and  $L_z$ ) instead of three (a classical vector is characterized by three projections) but in addition imposes strict constraints on the values of these quantities. The projection of angular momentum onto the  $z$ -axis can assume only the values

$$L_z = m\hbar, \quad m = 0, \pm 1, \pm 2, \dots, \pm l \quad (1.23)$$

and the length of the angular momentum vector can assume only the values

$$L = \hbar \sqrt{l(l+1)} > \hbar l, \quad l = 0, 1, 2, \dots \quad (1.24)$$

Angular momentum is thus one of the physical quantities which are *quantized*, that is, are allowed to take on only certain discrete values (see Problem 6) proportional to Planck's constant  $\hbar$ .

When it is necessary to specify the magnitude of angular momentum, it is normal to give just the value of  $l$ . Hereafter we shall invariably indicate the dimensionless quantity  $l$  instead of the magnitude of angular momentum and drop the factor  $\hbar$ .

Note that a particle may have zero angular momentum!

As a rule, when we say that a particle has a definite angular momentum, this means that the particle is in a state with a given value of  $l$ . The projection of  $L$  onto an axis can then take on one of  $2l + 1$  values. Let us clarify: angular momentum is allowed to have only discrete directions in space (actually, do not forget that the  $z$ -axis, the axis of quantization, has an arbitrary direction). This quantum property of angular momentum is called *space quantization* (Fig. 11).

With  $L$  and  $L_z$  fixed, the projections  $L_x$  and  $L_y$  do not have definite values; we can only determine the probabilities of specific values of these projections. Resorting to a classical image, we can represent the vector of angular momentum by a vector precessing around the  $z$ -axis. The angle between  $L$  and the  $z$ -axis is determined by

the value of  $L_z$ , that is, by  $m$  (see (1.23) and Fig. 11).

The easily visualized model of the "precessing" angular momentum explains why the maximum magnitude of the projection  $L_z$  is less than  $L$  (see (1.23) and (1.24)). If  $L$  were equal to  $\hbar l$ , the other two projections  $L_x$  and  $L_y$  would equal

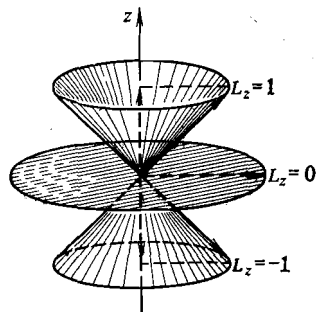


Fig. 11. Descriptive classical picture illustrating space quantization

zero in this state, that is, would have definite values simultaneously with  $L$  and  $L_z$ ; but this is forbidden.

The classical and quantum angular momenta are not separated by an insurmountable wall. When  $l \gg 1$ , space quantization is not very important, and the quantity  $L$ , equal to  $\hbar \sqrt{l(l+1)} \approx \hbar l [1 + 1/(2l)]$ , very nearly coincides with the classical value  $\hbar l$ .

To be more rigorous: the properties of classical angular momentum can be obtained by a limit transition to large values of  $l$ . This is an example of the general principle which states that quantum mechanics contains classical mechanics as a limiting case.

We are so interested here in angular momentum because it is related to magnetic moment. Quantum mechanics does not reject the relationship stated by (1.14), that is, it confirms that the gyromagnetic ratio for the electron is  $\gamma = e/2m_e c$ . Hence, if an electron is in a state with the projection of its angular momentum equal to  $m$  ( $m = 0, \pm 1, \pm 2, \dots, \pm l$ ), then the projection of its magnetic moment is

$$M_z = \frac{e\hbar}{2m_e c} m, \quad m = 0, \pm 1, \pm 2, \dots, \pm l \quad (1.25)$$

The conclusion that suggests itself is: a moving electron can "claim" to constitute an elementary magnet, provided it is in a state with nonzero angular momentum, that is, in a state with  $l \neq 0$ . On the other hand, it is important to emphasize that an electron revolving around the nucleus may be in the state with zero angular momentum. Obviously, this is a corollary of the absence of trajectory. Indeed, we have indicated that the electron in the hydrogen atom in the ground state has zero angular momentum. For this reason we shall not discuss here whether the quantum-mechanical results given above are a proof of the existence of elementary magnets. We shall recur to this aspect at the end of the chapter. Here we underline that by explaining the stability of atoms, quantum mechanics has at the same time demonstrated that the motion of electrons in atoms is such that the projections of their angular momenta are, in units of  $\hbar$ , integers; the fact that there is a relation between magnetic moment and angular momentum indi-

cates that an electron moving around the nucleus can be regarded as a stable magnetic moment, but with quantum properties. The most important of these properties is space quantization.

The stability of the magnetic moment of the electron revolving around the nucleus is of such a paramount importance for the understanding of the atomic nature of magnetism that we find it necessary to add a short summary to this section.

Electrons in atoms are in specific states. Each state is *stable*, in the sense that it can be changed only by imparting to electrons a finite amount of energy  $\Delta\epsilon$  (a portion which is large on atomic scale).

Each state is characterized by a definite angular momentum, and hence, a definite magnetic moment. The magnetic moment of an atom is therefore stable (in the same degree as the state of an electron in the atom).

### 1.6. Magnetic Moment in Magnetic Field

Until this section, magnetic moment has been treated only as a source of a magnetic field. This role of a magnetic moment will again be discussed later. But now that we established the existence of stable magnets in nature, we should discuss their behavior in an external magnetic field, that is, a field produced by other sources. In our treatment we consider the magnets to be so stable that their magnitudes are independent of the magnitude of the magnetic field. In the case of atomic magnets this is not a serious restriction. Quite the opposite is true: mostly it is

very difficult to create a magnetic field so strong as to change the values of atomic magnetic moments, provided these are distinct from zero (the appropriate estimate of the required magnetic field will be given in Ch. 2). Consequently, by the behavior of magnetic moments in magnetic fields, we always mean their rotation and translation as a whole.

We begin with a constant and uniform magnetic field.

You well know the property of a magnetic needle to assume a certain orientation in a magnetic field. It is known just as well that it is this very property that makes a magnetic needle so useful in orientation devices. There were times when the property of "spontaneous" orientation of the needle in space was interpreted as a miracle. But let us recall Einstein's words (written in connection with this very magnetic needle): "...the development of the thought world is in a certain sense a continuous flight from 'wonder'."\* The compass needle keeps to a certain orientation because this is energetically favored. The energy  $\epsilon_M$  of a magnetic moment  $M$  in a magnetic field  $H$  is

$$\epsilon_M = -M \cdot H = -MH \cos \theta \quad (1.26)$$

where  $\theta$  is the angle between the magnetic moment and the magnetic field. Clearly, the energy is minimum when  $\theta = 0$ .

If a magnetic moment deflects by an angle  $\theta$  from a magnetic field, the magnetic field applies

\* *The Library of Living Philosophers. Albert Einstein: Philosopher-Scientist.* Ed. by P. A. Schillp, Tudor Publishing Company, 1949.

to it a force moment perpendicular to the plane drawn through the magnetic field vector  $\mathbf{H}$  and the magnetic moment at the given moment of time. As a result, the magnetic moment rotates, tracing a cone around the magnetic field vector. Since magnetic moment differs from angular momentum by the factor  $e/2m_e c$ , the rotation frequency is

$$\omega_H = \frac{eH}{2m_e c} = \gamma H \quad (1.27)$$

We thus find that the gyromagnetic ratio (denoted here, as before, by  $\gamma$ ) plays a new role, relating the magnetic field  $H$  to the frequency of precession,  $\omega_H$ , of magnetic moment. (See Problem 7.) It will be encountered in this role considerably more often than in the role in which it first appeared on the scene (see (1.11)).

Formulas (1.26) and (1.27) hold for the classical magnetic moment. In the case of a quantum magnetic moment, space quantization must be taken into account. As we have mentioned earlier, magnetic moment can be in  $2l + 1$  states. Each state corresponds to the respective magnetic energy level equal to

$$\varepsilon_M^m = -\frac{e\hbar H}{2m_e c} m, \quad m = 0, \pm 1, \pm 2, \dots, \pm l \quad (1.28)$$

Such a system of levels is called equidistant (Fig. 12): the spacing between neighboring levels is independent of  $m$  and is equal to

$$\Delta\varepsilon = \varepsilon_M^m - \varepsilon_M^{m+1} = \frac{e\hbar H}{2m_e c} \quad (1.29)$$

If an electron "decides" to jump from one level to another, it has to absorb or emit a quantum of electromagnetic energy equal to  $\hbar\omega =$

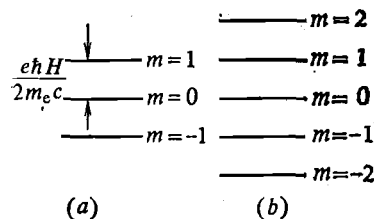


Fig. 12. Equidistant energy levels of magnetic moment in a permanent magnetic field:

(a)  $l = 1$ ; (b)  $l = 2$

$= e\hbar H / 2m_e c$ . The frequency of the electromagnetic field absorbed or emitted in a transition from

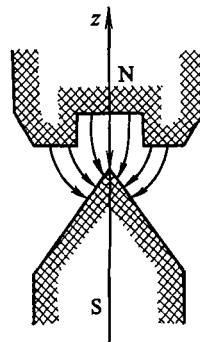


Fig. 13. In the vicinity of the axis of a magnet the magnetic field is directed along the  $z$ -axis and increases as we approach the tip, that is, the field is a function of  $z$

one magnetic level to another is  $\gamma H$ . It coincides with the frequency of the classical rotation of magnetic moment around magnetic field vector.



Now let the magnetic field  $H$ , aligned as before along the  $z$ -axis, be itself a function of the  $z$ -coordinate (Fig. 13). Consequently, the energy of a level is also a function of  $z$ :  $\varepsilon_M = \varepsilon_M(z)$ . Energy being a function of coordinate signifies that there is a force acting on the magnetic moment; it is equal to

$$F_H = M_z \frac{dH}{dz} \quad (1.30)$$

In the case of a classical magnetic moment,  $M_z$  must be replaced with  $M \cos \theta$ , and in the case of a quantum magnetic moment, with one of the  $2l + 1$  values of the projection of the magnetic moment onto the  $z$ -axis (see (1.25)).

### 1.7. Spin and Intrinsic Magnetic Moment of the Electron

The historical sequence of discoveries in physics, as well as in any other science, does not comply, unfortunately, with the logic of a story about science. It would be convenient to open this section as follows.

The force (1.30) acting on the magnetic moment makes it possible to measure the magnetic moment of atomic particles from their deflection in a nonuniform magnetic field through which they travel; furthermore, it is possible to confirm the validity of quantum-mechanical conclusions on space quantization. Indeed, after a beam of particles having a magnetic moment  $(e/2m_e c)L$  passes through a nonuniform magnetic field,  $2l + 1$  spatially separated beams must form (Fig. 14). This experiment was carried out by

the German physicists O. Stern and W. Gerlach in 1922. They were sending a beam of silver atoms through a nonuniform magnetic field. The result proved quite unexpected although it confirmed the reality of space quantization: the beam was split in two. It might seem that the beam need not split at all because the electrons

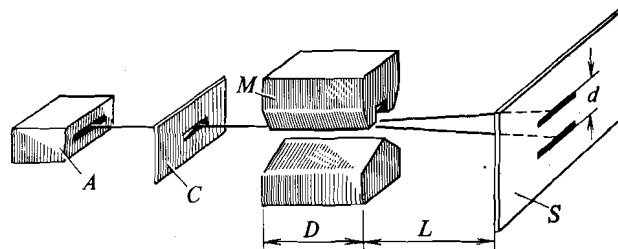


Fig. 14. Schematic diagram of the Stern-Gerlach experiment:

$A$ —source of silver atoms,  $C$ —collimator,  $M$ —magnet ( $D$ —distance travelled by a beam in a magnetic field with nonzero  $dH/dz$ ),  $S$ —screen ( $d$ —distance between the beam traces,  $L$ —distance from the magnet to the screen)

in a silver atom have zero angular momentum. Let us imagine that somehow an atom passing through the instrument is excited, that is, is lifted to a state with a higher energy and nonzero angular momentum. In this case the number of beams at the exit from the instrument must be odd:  $2l + 1$ . But the experiment demonstrated that the beam was definitely split in two! The beam was split as if  $l = 1/2$ , in blatant contradiction with the predictions of quantum mechanics.

This would be a convenient opening paragraph. It could be followed with a description of the Stern-Gerlach experiment the surprising result of which can be explained by the fact that the electron possesses a *spin*. (See Problem 8.)

Or we could begin the section in a different way. We could describe the experiment performed in 1915 by Einstein and de Haas\* who measured the gyromagnetic ratio directly and found that it was twice the value predicted theoretically. After this we could explain that the discrepancy between the theory and the experiment was caused by the *spin* of the electron.

Unfortunately, events did not follow a logically neat sequence. Because of a miscalculation, Einstein and de Haas obtained for the gyromagnetic ratio the value equal to  $e/2m_e c$ , that is, did not find a discrepancy with the theory at the time. Their article, moreover, was even entitled "Experimental Proof of Ampère's Molecular Currents". It should be emphasized that Einstein

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\* The articles by Einstein and Einstein-de Haas can be found in Einstein's *Collected Works*. Einstein and de Haas measured the amplitude of torsional vibrations of a rod caused by successive magnetizations. To increase the sensitivity of the technique, they used the resonance of the remagnetizing field and of the natural vibrations of the rod. Many readers may be surprised to learn that Einstein not only conducted theoretical research but also "worked with his hands". He actively participated in the experiment and even wrote a manual on the demonstration of the gyromagnetic effect. The interesting story of the discovery and subsequent application of the gyromagnetic effect can be found in an article by V. Ya. Frenkel (*Advances in Science and Technology in the USSR, Physics Series*, 1979, Vol. 128, Issue 2, p. 545 (in Russian)).

perfectly understood that Ampère's hypothesis contradicted classical physics (see the footnote to p. 28). It was for this reason that the experiment on determining the gyromagnetic effect was devised. It was meant to confirm (and its authors believed that it had confirmed) the existence of molecular currents. Quite a few experiments were carried out later to measure the gyromagnetic ratio. It proved to be twice the value given by formula (1.11).

Stern and Gerlach conducted their experiment in 1922 when it had already been suspected that the electron has a spin. The suspicion was borne from an analysis of atomic spectra (the main source of information about the structure of atoms at the time).

But what is the spin? And what is its relation-ship to the physics of magnetic phenomena?

In addition to the angular momentum caused by the motion of a particle in space (it is also called the *orbital* angular momentum, although the reader keeps in mind that quantum mechanics does not operate with orbits), a quantum particle\* may possess an angular momentum inherent to this particle. This momentum is called the inherent (intrinsic) momentum, or *spin*. Despite the obvious meaning of this English word, the notion of a particle with nonzero spin as a sphere or top of finite radius rotating around its axis does

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\* Of course, all particles are quantum particles. The combination "quantum particle" emphasizes that we deal with phenomena whose analysis must take into account quantum laws. Specifically, here a quantum particle means a particle whose orbital angular momentum is small compared with  $\hbar$ .

not represent the actual situation, not even as a rough approximation. The main reason for this is the impossibility to assign a finite radius to an elementary particle (e.g. the electron). Numerous such attempts failed because they were found to contradict the requirements of special relativity. The following argument clearly demonstrates that the spin is not a result of the spatial rotation of a particle: the projection of the intrinsic momentum of a particle can assume not only integral values (see (1.23) and (1.24)) but half-integral values as well.

We shall denote the value of spin by  $s$  (an analogue of  $l$ ), and its projection by  $s$  with subscript  $z$ , i.e.  $s_z$  (an analogue of  $m$ ).

For the electron:  $s = 1/2$ ;  
 $s_z = \pm 1/2$ ;  $2s + 1 = 2$

The proton, neutron, and neutrino also are spin- $1/2$  particles. The spin of the photon is 1, and that of all pions (there are three of them: one neutral pion,  $\pi^0$ , and two charged pions,  $\pi^+$  and  $\pi^-$ , with charges  $\pm e$ ) is zero.

The existence of the intrinsic momentum thus extends the set of possible values of angular momentum: the spin can be integral ( $s = 0, 1, 2$ , etc.) or half-integral ( $s = 1/2, 3/2, 5/2$ , etc.). The zero spin is considered integral.

Particles with zero and integral spin are called *bosons* (named after the Indian physicist Jagadis Bose), while particles with half-integral spin are called *fermions* (after Enrico Fermi). It will become clear later in the book why particles are divided into two classes.

The spin of an elementary particle is its in-

trinsic property in the same way as its charge and mass are. Neither the proton nor the electron can part with their spin, just as they cannot get rid of a part of their charge or mass. This is clear evidence of the elementariness of the electron, proton, neutron, and other particles that are regarded as elementary. Their elementariness does not preclude mutual transformations. But this is a quite different topic.

Dirac constructed the theory of the electron, that is, formulated an equation that the wave function of the electron must satisfy. This equation (called the Dirac equation) takes into account not only the wave properties of the electron but also the constraints imposed by relativity theory. Quantum mechanics satisfying these constraints is called *relativistic quantum mechanics*. When this theory appeared, particles with spin different from  $1/2$  had yet been unknown. Dirac presumed that the equality of spin to  $1/2$  was a logical corollary of relativistic quantum theory. Later, after a number of particles with non- $1/2$  spin had been discovered, it became clear that the Dirac equation was not the only allowed equation. The wave functions of particles with  $s \neq 1/2$  are governed by equations differing from the Dirac equation that gives an impeccably accurate description of the electron, that is, a spin- $1/2$  particle.

Relativistic quantum mechanics predicted that a charged particle with charge  $e$ , mass  $m_e$ , and spin  $1/2$  must have a magnetic moment with two projections equal to  $\pm e\hbar/2m_e c$ . Compare this expression with formula (1.25). You notice that the gyromagnetic ratio for the intrinsic

spin angular momentum is equal to  $e/m_e c$ , that is, to twice that for the orbital angular momentum. The classical (orbital) gyromagnetic ratio measured in units of  $e/2m_e c$  will be denoted by  $g_L$ , and the spin gyromagnetic ratio by  $g_s$ .

It must be emphasized that  $g_s = 2$  in units of  $e/2m_e c$  no matter what the value of  $s$  is (even if it is integral). The letter  $g$  will be used as a symbol of the total gyromagnetic ratio taking into account both the orbital and spin angular momenta. It is referred to as the *g factor*, or *Landé factor*.

Table 1

Particle	Sym- bol	Mass, g	Spin	Magnetic moment, erg/gauss
Electron	$e$	$m_e = 9.1 \cdot 10^{-28}$	$1/2$	$\frac{e\hbar}{2m_e c} = 0.9 \cdot 10^{-20}$
Proton	$p$	$m_p = 1.7 \cdot 10^{-24}$	$1/2$	$2.8 \frac{e\hbar}{2m_p c} = 1.3 \cdot 10^{-23}$
Neutron	$n$	$m_n = 1.01 \cdot m_p$	$1/2$	$1.9 \frac{e\hbar}{2m_n c} = 0.9 \cdot 10^{-23}$

We have already mentioned that the existence of the electron spin indeed explains the results of both the Stern-Gerlach and the Einstein-de Haas experiments. It was not the orbital but the intrinsic angular momentum of electrons that the two experiments revealed.

A short table (Table 1) lists the values of the spin and magnetic moments of the three most im-

portant particles of which all objects surrounding us, and we ourselves, are built.

The fact that the neutron, even though it is neutral, possesses a magnetic moment while the magnetic moment of the proton is greater by a factor of 2.8 than that predicted by the Dirac equation has been explained by the modern theory of elementary particles.

The number of electrons in a body is equal to that of protons, and the intrinsic magnetic moment of the electron is much greater than that of the proton. It is thus clear that the main role in magnetic properties of materials is played by electrons. True, it proved possible not only to detect and measure the magnetic moments of atomic nuclei (magnetic moments of practically all atomic nuclei have been determined) but also to study the magnetic properties of materials due to the magnetic moments of nuclei. The subdivision of the physics of magnetic phenomena dealing with the magnetic properties of nuclear particles is called the *nuclear magnetism*. Unfortunately, the nuclear magnetism has to be left out of this book.

### 1.8. *g* Factor

We have at last unraveled the elementary magnet. In most cases the intrinsic magnetic moment of the electron can be regarded as the elementary magnet. Its projection onto the axis is equal (to within the sign) to the Bohr magneton  $\mu_B = e\hbar/2m_e c$ . If the electron moves in such a manner that its orbital angular momentum is distinct from zero, the orbital and spin angular

momenta add. But how should we add "quantum" vectors, that is, vectors with discrete values of projection onto a selected axis? "Classical" vectors are added according to the parallelogram law. One thus has to know the length of each vector and the angle between them. When "quantum" vectors are added, the following procedure must be followed.

Let  $\mathbf{L}_1$  and  $\mathbf{L}_2$  be two vectors such that  $L_1^2 = (l_1 + 1)l_1$ ,  $L_2^2 = (l_2 + 1)l_2$ , and  $l_1, l_2$  are integral or half-integral numbers. Let us ask what can the vector  $\mathbf{J}$  be if it is equal to the sum of  $\mathbf{L}_1$  and  $\mathbf{L}_2$ ? In order to find the answer, let us project these vectors onto a common axis. Obviously, the maximum and minimum projections of the sum of two vectors are  $l_1 + l_2$  and  $|l_1 - l_2|$ . This means that the maximum projection of the vector  $\mathbf{J}$ , that is  $J$ , can assume the values from  $|l_1 - l_2|$  to  $l_1 + l_2$ . If we recall the expression for the square of a vector (see p. 47), we can operate with "quantum" vectors almost exactly as with classical vectors. For the sake of practice, let us calculate the possible discrete values of the scalar product  $\mathbf{L}_1 \cdot \mathbf{L}_2$  through  $l_1, l_2$ , and  $J$ . Finding the square of the equality

$$\mathbf{J} = \mathbf{L}_1 + \mathbf{L}_2$$

according to standard rules, we then use for  $L_1^2, L_2^2$ , and  $J^2$  the "quantum" expression (1.24):

$$J(J+1) = l_1(l_1+1) + l_2(l_2+1) + 2\mathbf{L}_1 \cdot \mathbf{L}_2$$

that is,

$$\mathbf{L}_1 \cdot \mathbf{L}_2 = \frac{1}{2} [J(J+1) - l_1(l_1+1) - l_2(l_2+1)] \quad (1.31)$$

Substituting for  $J$  its possible values from  $|l_1 - l_2|$  to  $l_1 + l_2$ , we find the set of possible discrete values of the scalar product  $\mathbf{L}_1 \cdot \mathbf{L}_2$ .

The vectors  $\mathbf{L}_1$  and  $\mathbf{L}_2$  may refer to the same particle (say, one vector is the orbital momentum, and the other is the spin momentum) or to different particles (e.g. we can ask what the angular momentum of two particles is if the momentum of one is  $\mathbf{L}_1$ , and that of the other is  $\mathbf{L}_2$ ).

The rule of addition of vectors will help us to find out what the spin of a system consisting of several electrons can be.

We begin with two electrons. Since each of the spins can align either along or against the axis, only the following situations are possible: (i) the spins are "antiparallel", with zero total spin ( $S = 0$ ), and (ii) the spins are "parallel", with unity total spin ( $S = 1$ ).

The words "parallel" and "antiparallel" are put in quotation marks because the two projections of the electron spin, ( $s_x, s_y$ ), as of any other angular momentum, do not have definite values.

There is an essential difference between the states with  $S = 0$  and  $S = 1$ . The state with zero spin, which is singular, is called a singlet. The state with unity spin can exist in three forms: with  $S_z = -1, 0$ , and  $1$ . This state is called a triplet.

To get a better feeling of the difference between classical and quantum momenta, let us calculate the value of  $\mathbf{s}_1 \cdot \mathbf{s}_2$  for  $S = 0$  and  $S = 1$  ( $\mathbf{s}_1$  and  $\mathbf{s}_2$  are the vectors of the spins of the first and second electrons,  $s_1 = s_2 = 1/2$ ). Note that the spin equal to  $1/2$  is the smallest momentum in nature, except, of course, zero momentum. This

is the case where the departure of quantum properties from classical properties reaches a maximum.\*

According to formula (1.31),

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \begin{cases} -3/4 & \text{for } S=0 \\ 1/4 & \text{for } S=1 \end{cases} \quad (1.32)$$

If the momenta were classical, the products  $\mathbf{s}_1 \cdot \mathbf{s}_2$  for "parallel" and "antiparallel" spins would differ only in sign and would equal  $\pm s^2 = \pm 1/4$ .

Table 2

$S=0$		$\uparrow\downarrow$
$S=1$	$S_z = -1$	$\downarrow\downarrow$
	$S_z = 0$	$\uparrow\downarrow + \downarrow\uparrow$
	$S_z = 1$	$\uparrow\uparrow$

Table 2 shows the projections of the spins of each electron in the singlet and triplet states (an arrow pointing down represents the state of an electron with  $s_z = -1/2$ , and an arrow pointing up represents  $s_z = 1/2$ ).

The reader should note specially that a spin configuration can be antisymmetric ( $S = 0$ ) or

\* When  $s = 1/2$ , the square of the length of the vector  $\mathbf{s}$  ( $s(s+1) = 3/4$ ) is three times the square of the projection  $s_z^2 = s^2 = 1/4$ .

symmetric ( $S = 1$ ). Look at the table and you will immediately realize that what is involved is an exchange of electrons. An understanding of the symmetry of spin configurations will be helpful in analyzing a concept, very important in the theory of magnetism, of the *exchange energy*.

Obviously, three electrons have a spin of  $1/2$  or  $3/2$ . In the general case, an even number of electrons produces integral spin configurations (including zero spin), and an odd number of electrons produces half-integral spin configurations.

Consider now a system of several electrons. Let the orbital angular momentum of the electrons be  $\mathbf{L}$ , and the spin momentum be  $\mathbf{S}$ . We remind the reader that specifying momenta means specifying their lengths  $L$  and  $S$  and their projections onto a chosen  $z$ -axis,  $L_z$  (one of the numbers  $-L, \dots, +L$ ) and  $S_z$  ( $-S, \dots, +S$ ). What will the magnetic moment of this electron system be?

If we go into finer detail of the question, the answer will appear almost automatically. The rotational properties of the system are characterized by the total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  whose maximum projection  $J$  can assume, according to the foregoing arguments, the values from  $|L - S|$  to  $L + S$ . The magnetic moment  $\mathbf{M}$  is proportional to  $\mathbf{J}$ , with the proportionality factor that we called the gyromagnetic ratio. Hence,

$$\mathbf{M} = g\mu_B \mathbf{J}, \quad \mu_B = \frac{e\hbar}{2m_0c} \quad (1.33)$$

and the problem reduces to finding the  $g$  factor as a function of  $L$ ,  $S$ , and  $J$ . Recall that the prob-

lem grew out of the differences between the gyromagnetic ratios for the orbital and intrinsic angular momenta ( $g_L = 1$  and  $g_s = 2$ ).

Taking into account the difference between  $g$  factors, we can write the following expression for the magnetic moment:

$$\mathbf{M} = \mu_B (\bar{\mathbf{L}} + 2\bar{\mathbf{S}}) = \mu_B (\mathbf{J} + \bar{\mathbf{S}}) \quad (1.33')$$

The bar over the vectors  $\mathbf{L}$  and  $\mathbf{S}$  indicates that their average (mean) values are taken. There is

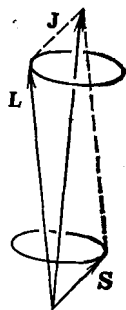


Fig. 15. Classical picture of the "precession" of the orbital  $\mathbf{L}$  and the spin  $\mathbf{S}$  angular momenta around the total angular momentum  $\mathbf{J}$

no bar over  $\mathbf{J}$  because only the total angular momentum  $\mathbf{J}$  is conserved (has a definite stationary value), while the vectors  $\mathbf{L}$  and  $\mathbf{S}$  precess around  $\mathbf{J}$  (Fig. 15). According to (1.33'), we are interested in the vector  $\bar{\mathbf{S}}$  which, quite naturally, is aligned along  $\mathbf{J}^*$  (this is clearly seen in Fig. 15), that is,  $\bar{\mathbf{S}} = a\mathbf{J}$ . The constant  $a$  is easily determined by using the following chain of equal-

\* Forget for a time that the vector  $\mathbf{S}$  is quantized and decompose it into two vectors: one pointing along the vector  $\mathbf{J}$ , and the other,  $\mathbf{S}_\perp$ , perpendicular to it, rotating around  $\mathbf{J}$ . Hence,  $\bar{\mathbf{S}}_\perp = 0$ .

ities:

$$\bar{\mathbf{J}} \cdot \bar{\mathbf{S}} = \mathbf{J} \cdot \bar{\mathbf{S}} = a\mathbf{J}^2 = aJ(J+1)$$

Note that we have resorted again to the quantum formula for  $\mathbf{J}^2$ . The value of  $\mathbf{J} \cdot \mathbf{S}$  is calculated in complete analogy to the derivation of formula (1.34):

$$\mathbf{J} \cdot \mathbf{S} = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)]$$

Hence,

$$a = \frac{1}{2} \left[ 1 - \frac{L(L+1) - S(S+1)}{J(J+1)} \right]$$

By comparing formulas (1.33) and (1.33'), we arrive at the sought formula for the  $g$  factor:

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (1.34)$$

If the spin is zero ( $S = 0$ ), then obviously  $J = L$  and  $g = 1$ ; but if  $L = 0$  and  $J = S$ , then  $g = 2$ . If  $J = 0$ , which is possible if  $L = S$ , then expression (1.33) is not defined, but, of course, there is no magnetic moment because all projections of the vector  $\mathbf{M}$  are zero.

The Landé  $g$  factor can also be zero if  $J \neq 0$ , for instance, when  $L = 2$ ,  $S = 3/2$ , and  $J = 1/2$ . This example shows that the  $g$  factor does not necessarily "lie" between 1 and 2.

To summarize: if a system of electrons has a specific total angular momentum  $\mathbf{J}$  formed by the sum of the orbital  $\mathbf{L}$  and spin  $\mathbf{S}$  momenta, the magnetic moment of this electron system is equal to the "quantum" vector  $\mathbf{M}$  (see (1.33)) whose projections onto a chosen axis are  $\mu_B g m_J$ ,

where  $m_J$  takes on one of the following values:  $-J$ ,  $-J + 1$ , . . . ,  $J - 1$ ,  $J$ , and the  $g$  factor is given by formula (1.34).

### 1.9. Structure of Atoms

All atoms, with the exception of the simplest of them, the hydrogen atom, contain more than one electron. The atoms of substances with well-pronounced magnetic properties (e.g. atoms of transition elements) are complex multiparticle systems. It is impossible to extract exact information on the motion of a system consisting of a large number of particles. Even in classical mechanics the exact solution is obtainable only for the problem of motion of two bodies. It is found, however, that a satisfactory explanation of atomic properties (at any rate, at a qualitative level) is obtained if certain very general features of motion of electrons in the atom are understood. We begin with describing these features.

The reader should keep in mind Mendeleev's periodic table in which the elements are arranged in the order of atomic number  $Z$ , that is, in the order of the number of electrons in the electron shell or the number of protons in the nucleus. Our nearest task is to understand why elements with different atomic numbers  $Z$  have different properties and, vice versa, why atoms located in similar squares of the periodic table (of course, they have different  $Z$ ) possess similar properties. Naturally, we shall pay special attention to magnetic properties of atoms.

Let us use a system of coordinates in which the nucleus is at rest. Now imagine an atom: its nu-

cleus is an immobile "cluster" of protons and neutrons, a source of a force field in which electrons move. Why does the addition of one electron to eighteen already present convert an atom of the inert gas argon into an atom of the metal potassium?

We begin with specifying the forces acting on electrons.

It might seem that this aspect is clear: electrostatic Coulomb forces of attraction to the nucleus and repulsive forces acting between electrons (these have already been mentioned). But now that we attempted to persuade the reader (and hope that the attempt was successful) that each electron not only carries electric charge but at the same time is a small magnet (magnetic dipole), the question about forces must be seen in a new light: Is it necessary, when analyzing the motion of electrons, to take into account their magnetic interaction with other electrons and with the nucleus?

And first of all: What is the "magnetic interaction"? Its result is familiar to everybody: like poles of magnets are repulsed, and unlike poles are attracted. To answer the question, we should derive the dependence of force on the distance between magnets (magnetic dipoles). In contrast to electrostatic forces which are functions only of the distance between charges, magnetic forces depend not only on the separation between dipoles but also on the orientation of "magnetic needles" with respect to each other and to the line connecting them (Fig. 16). We shall not derive the expression for the force of interaction between magnetic dipoles that is valid at distances



large in comparison with the size of a dipole. This formula is exact in the case of electrons because electrons must be regarded as pointlike particles. We shall give the expression not for the force but for the energy of interaction,  $U_M$ :

$$U_M = \frac{(\mathbf{M}_1 \cdot \mathbf{M}_2) - 3(\mathbf{M}_1 \cdot \mathbf{n}_{12})(\mathbf{M}_2 \cdot \mathbf{n}_{12})}{R_{12}^3}, \quad \mathbf{n}_{12} = \frac{\mathbf{R}_{12}}{R_{12}} \quad (1.35)$$

Here  $\mathbf{M}_1$  and  $\mathbf{M}_2$  are magnetic moments of two particles, and  $\mathbf{R}_{12}$  is the vector distance between

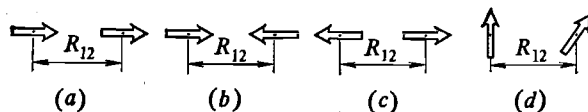


Fig. 16. The force of interaction between magnetic dipoles is a function not only of the distance between them but also of their mutual orientation:

(a) the magnetic dipoles are attracted ( $U_M < 0$ ); (b, c) the magnetic dipoles are repulsed ( $U_M > 0$ ); (d) the sign of  $U_M$  is given by (1.35)

them. The reference point for measuring energy is chosen in such a way that this energy is zero when magnetic dipoles are infinitely removed from each other (for  $R_{12} \rightarrow \infty$ ).

It is clear from (1.35) that the attraction between unlike poles (i.e. between magnetic dipoles parallel to each other and to the line connecting them) and the repulsion between like poles (i.e. between antiparallel magnets aligned along the line connecting them) are described correctly. (See Problem 9.)

When electrons in an atom are considered, by the order of magnitude, the energy of magnetic interaction between two particles is

$$U_M \approx \frac{\mu_B^2}{a^3}$$

where  $\mu_B$  is the Bohr magneton, and  $a$  is the mean distance between electrons, approximately equal to the diameter of the atom (this formula is identical to (1.35); we have replaced  $M_{1,2}$  with  $\mu_B$  and  $R_{12}$  with  $a$ , and neglected the angular dependence in the numerator).

It would be meaningless to evaluate the energy of magnetic interaction between an electron and the nucleus since it is definitely much smaller than  $U_M$ ; indeed, the magnetic moment of the nucleus is less than that of the electron by a factor of several thousand, being a superposition of the magnetic moments of the protons and neutrons which are thousands of times smaller than that of the electron (see Table 1).

The energy of electrostatic interaction between two electrons under the same conditions is

$$U_{\text{Coul}} = \frac{e^2}{a}$$

Dividing the expression for  $U_M$  by that for  $U_{\text{Coul}}$  and neglecting the factors of the order of unity, we find

$$\frac{U_M}{U_{\text{Coul}}} \approx \frac{(\hbar^2/a^2 m_e)}{m_e c^2}$$

This is a formula with far-reaching consequences. The denominator is the electron rest energy  $m_e c^2$ , and the numerator is an unusual combination

with the dimensionality of energy (verify this statement). Two approaches help to interpret this combination. First, let us turn to formula (1.21) for the energy of the electron in a hydrogen atom, expressing this energy in terms of the radius of the "orbit"  $a_n = (\hbar^2/m_e e^2) n^2$  (see p. 44). We notice that by the order of magnitude  $\hbar^2/a^2 m_e$  equals  $|\varepsilon_n|$ , that is, the electron energy in the atom. Second, let us use the uncertainty relation (see Sec. 1.4) stating that a particle cannot be restricted to a region of space of the order of  $a$  unless the particle is in motion. The minimum momentum of a particle within a region of the order of  $a$  is  $p \approx \hbar/a$ . Therefore,

$$\frac{\hbar^2}{a^2 m_e} \approx \frac{p^2}{m_e}$$

is the kinetic energy  $E_k$  of motion of the electron within the atom (of course, this is an order-of-magnitude estimate, since we omitted even the factor of 2). The second approach may seem less conclusive but it demonstrates that  $\hbar^2/a^2 m_e$  characterizes the energy of motion of any electron in any atom, not only in a hydrogen atom. In order to evaluate the size of an atom, we can use with satisfactory accuracy the quantity  $a \approx 3 \cdot 10^{-8}$  cm that will also be useful hereafter. In other words,

$$\frac{U_M}{U_{Coul}} \approx \frac{E_k}{m_e c^2} = \frac{v^2}{c^2}, \quad v = \frac{\hbar}{a m_e}$$

Electrons in atoms move at velocities small compared with the speed of light.\* Indeed, di-

\* Actually, heavy multielectron atoms contain electrons (the latter moving deep within the atom, close to the nucleus) whose velocity approaches the speed of light.

viding the mean momentum  $\hbar/a = 10^{-27}/3 \times 10^{-8}$  by the electron mass  $m_e \approx 10^{-27}$  g, we find  $v \approx 3 \cdot 10^7$  cm/s, which is much less than the speed of light.

The ratio  $U_M/U_{Coul}$  is thus much less than unity, that is, the energy of magnetic interaction  $U_M$  is much less than the energy of electrostatic interaction  $U_{Coul}$ :  $U_M \ll U_{Coul}$ . This conclusion is so important for the analysis that follows that we shall recast the ratio  $U_M/U_{Coul}$  in a more "impressive" form, by replacing  $a$  with the expression for the "radius" of the hydrogen atom in its ground state,  $a_1 = \hbar^2/m_e e^2$  (see p. 44). This yields

$$\frac{U_M}{U_{Coul}} \approx \left( \frac{e^2}{\hbar c} \right)^2 \approx \left( \frac{1}{137} \right)^2 \quad (1.36)$$

Unexpectedly, the inequality  $U_M \ll U_{Coul}$  is found to follow from the smallness (sic) of the electric charge (see p. 16).

It must be mentioned that the dimensionless combinations of world constants ( $e$ ,  $\hbar$ , and  $c$  in this particular case) are tremendously significant. It is even possible to suggest the following half-joking statement: our world is what it is precisely because several dimensionless combinations of world constants have the values they do:

$$\frac{e^2}{\hbar c} \approx \frac{1}{137}, \quad \frac{m_e}{m_p} \approx \frac{1}{1840}, \quad \frac{e^2}{G m_p^2} \approx 4 \cdot 10^{42}$$

and so forth. What is the meaning of these numbers? Why these values and not some others? So far scientists have been unable to answer these questions.

We have thus established that the decisive factor is the electrostatic interaction between electrons. In other words, in "constructing" an atom by adding electrons we can neglect the fact, important for the topic of this book, that electrons are tiny magnets. But this statement calls for a qualification: it is not possible to ignore the spin of the electron, as we shall have a chance to see quite soon.

In order to clarify the general picture of the motion of electrons in an atom, it can be assumed that the *mean* force applied to each electron by the nucleus and all other electrons (except the one under consideration) has a central symmetry (the center of symmetry coinciding with the nucleus). The stationary state of each electron in such a field can be characterized by a certain angular momentum specified by quantum numbers  $l$  ( $l = 0, 1, 2, \dots$ ) and  $m$  ( $m = -l, -l + 1, \dots, l - 1, l$ ; see above). But these two numbers prove insufficient for completely describing the state of the electron. One more number, called the principal quantum number and denoted by  $n$ , has to be introduced; the values it assumes are  $1, 2, 3, \dots$ . A triad ( $n, l$ , and  $m$ ) defines the state of the orbital motion of an electron in an atom. Recall that the free motion of an electron is also described by three numbers, namely, the three projections of its momentum. The numbers  $l$  and  $n$  are not completely independent: there is a constraint  $l \leq n - 1$ .

The spin state of an electron is determined by the projection of its spin onto some axis. We shall denote the value of the spin projection by the letter  $\sigma$ ;  $\sigma$  takes on two values:  $+1/2$  and

$-1/2$ . To recapitulate,

*the state of an electron in an atom is determined by four numbers  $n, l, m$ , and  $\sigma$ :*

$$n = 1, 2, \dots$$

$$l = 0, 1, 2, \dots, n - 1$$

$$m = -l, -l + 1, \dots, l - 1, l$$

$$\sigma = -1/2, 1/2$$

The energy of an electron is only weakly dependent on two of the four quantum numbers, namely,  $m$  and  $\sigma$ . This dependence can be neglected in the first approximation. This considerably facilitates the description of the structure of atoms. Neglecting the dependence of the electron energy on  $m$  and  $\sigma$  stems from neglecting the magnetic interaction (see (1.35)) and also (and primarily) from the isotropy of the space surrounding the electron shell of the atom. Indeed, what does it matter where the angular momentum is directed if all directions are equivalent? And it is the projection  $m$  of the momentum that is responsible for the direction of the momentum. This statement has a classical analogy: the energy of a particle moving in a field with central symmetry is independent of the orientation of its trajectory in space.

Small  $n$  and  $l$  correspond to low energy  $\epsilon(n, l)$ ; as a rule, energy increases as  $n$  and  $l$  increase. The dependence of  $\epsilon$  on  $n$ ,  $\epsilon = \epsilon(n)$ , for the hydrogen atom has already been given (see (1.21)). For reasons that are to some extent accidental the energy for the hydrogen atom is independent of  $l$ ,

Owing to a tradition, the states with different values of  $l$  are denoted, regardless of the value of  $n$ , by lower-case Roman letters, following the correspondence

$s\ p\ d\ f\ g\ \dots$  and so on in alphabetical order

$l = 0\ 1\ 2\ 3\ 4\ \dots$

The state of a single electron in an atom (without indicating the values of  $m$  and  $\sigma$ ) is denoted by a symbol consisting of a numeral giving the value of the principal quantum number  $n$  and a letter corresponding to the value of  $l$ . For instance, the symbol  $3p$  stands for the state of an electron with  $n = 3$  and  $l = 1$ . If several electrons are in a state with identical  $n$  and  $l$ , the number of electrons is indicated by the exponent (*no exponent in the case of a single electron*). Thus,  $3p^2$  stands for two electrons in the state  $3p$  ( $n = 3$  and  $l = 1$ ).

The distribution of electrons in an atom determines the *electron configuration* of the atom, that is, describes its electron shell. Are all configurations allowed? In particular, how many electrons can coexist in a state with the same  $n$  and  $l$ ? What is the maximum "exponent" in symbols such as  $3p$  or  $4d$ ?

In classical physics this question would reduce to asking how many identical particles are allowed to have identical energy and momentum. An immediate and natural answer would be: an infinite number. In quantum physics the situation is quite different. And here is why.

### *Pauli Exclusion Principle*

Identical particles manifest absolutely unlike behavior in classical and quantum physics. Classical particles, even absolutely identical, move each along its own trajectory. If the position of each of the particles is fixed at the initial instant of time, then by fixing the positions of the particles on their trajectories at a later instant, it is possible to point to the location of each particle, that is, possible to distinguish one particle from another. The situation in quantum mechanics is quite different because particles do not move along trajectories. Having fixed a particle at the initial instant of time, we cannot in principle pinpoint the same particle among its ilk at the later instants.

*In quantum mechanics identical particles are absolutely indistinguishable.*

This statement formulates the principle of indistinguishability of identical particles.\* As follows from this principle, a quantum state of a system remains unaltered if identical particles are interchanged.

Consider a wave function  $\Psi(1, 2)$  of two particles. The numerals 1 and 2 symbolically denote the coordinates of the first and second particles (and take into account the variable indicating the direction of the spins). Interchanging two particles (the first particle is placed where the second was, and the second takes the place of the first)

\* This greatly facilitates the construction of the picture of the world. By constructing the theory of *one* electron, we have constructed the theory of *any* electron.

is described by interchanging the arguments of the function  $\Psi(1, 2)$ :

$$\Psi(1, 2) \rightarrow \Psi(2, 1)$$

This operation must leave the state of the system unaltered. But this means that, as a result of interchanging, the wave function can only acquire a constant multiplier (see p. 42). Let us denote it by the letter  $\alpha$ . Then  $\Psi(2, 1) = \alpha\Psi(1, 2)$ . Having performed the interchanging twice, that is, having returned to the original situation, we find that  $\alpha^2 = 1$ , and hence, that either  $\alpha = 1$  or  $\alpha = -1$ . The value of the factor  $\alpha$  is determined not by the state of the system but by the sort of particles of which it is composed.

Since  $\alpha$  equals either  $+1$  or  $-1$ , there exist two types of particles:

for the first type, interchanging does not change the wave function:

$$(B) \quad \Psi(2, 1) = \Psi(1, 2) \quad (1.37)$$

for the second type, interchanging reverses the sign of the wave function:

$$(F) \quad \Psi(2, 1) = -\Psi(1, 2) \quad (1.38)$$

The property of particles we have just described has no classical analogue. Quantum mechanics led to the discovery of properties that are not associated with the force interaction between particles; even when particles do not interact with each other, the above-given permutation laws *must* be satisfied. Nature (quantum mechanics) imposes on a particle the rules of behavior in a collective of particles; indeed, by generalizing relations (1.37) and (1.38), we can deal with en-

sembles consisting of an arbitrary number of particles. The part of physics studying the behavior of large (macroscopic) ensembles of particles is called *statistical physics*. Particles for which (1.37) is valid are said to be governed by the *Bose-Einstein statistics*, and those for which (1.38) is valid are said to be governed by the *Fermi-Dirac statistics*. For this reason we put the letters (B) and (F) on the left of formulas (1.37) and (1.38).

Does a particle possess some "personal" property that determines to which of the two statistics the particle belongs? Yes, such a property exists. Pauli was able to show that

*particles with zero and integral spin are governed by the Bose-Einstein statistics, while particles with half-integral spin are governed by the Fermi-Dirac statistics.*

It is clear, therefore, why particles with zero or integral spin were called bosons, and those with half-integral spin were called fermions (see p. 58).

Let us return now to the question about the number of electrons that are allowed to coexist in one state. First, we should remind the reader that the electron spin is  $1/2$ , which makes *electrons* become *fermions*. Second, we formulate one of the fundamental principles of atomic physics, namely, the *Pauli exclusion principle*:

*a state can be occupied by no more than one electron.*

We shall prove the Pauli exclusion principle by using the property of antisymmetry of the

wave function of two electrons. We also have to supplement our knowledge of the wave function (see p. 42): the wave function of two noninteracting particles is constructed as a bilinear combination of the wave functions of the individual particles. Therefore, let one electron be in a state  $\{n, l, m, \sigma\} \equiv \{i\}$ , and the other in a state  $\{n', l', m', \sigma'\} \equiv \{i'\}$ . Then, according to rule (1.38),

$$\Psi(1, 2) = \Psi_{\{i\}}(1) \Psi_{\{i'\}}(2) - \Psi_{\{i'\}}(1) \Psi_{\{i\}}(2)$$

Hence, if the states  $\{i\}$  and  $\{i'\}$  are identical ( $\{i\} \equiv \{i'\}$ ), the wave function is identically zero; in other words, no such state exists.

We see that fermions are extremely individualistic and avoid like particles.

Each physical system tends to reach a state with minimum energy (we shall recur to this statement in the next chapter). This tendency plus the Pauli principle enable us to understand the structure of atoms and, as a result, the nature of Mendeleev's periodic law. The problem essentially reduces to distributing the  $Z$  electrons of an atom with the atomic number  $Z$  over energy states, taking into account that

(i) states with different  $m$  and  $\sigma$  but identical  $n$  and  $l$  correspond to the same energy, and

(ii) only one electron is allowed to have a given total set of quantum numbers  $\{n, l, m, \sigma\}$ .

The number of states with a specific value of  $l$  equals  $2(2l + 1)$ . Since  $l$  cannot exceed  $n - 1$ , each value of  $n$  corresponds to only a few values of  $l$ : only  $l = 0$  ( $s$  state) for  $n = 1$ ;  $l = 0$  and  $l = 1$  ( $s$  and  $p$  states) for  $n =$

$= 2$ , and so on. It is now easy to calculate how many electrons can have identical  $n$  and  $l$  in a general case (electrons with identical  $n$  and  $l$  form a "shell") and compile a table.

Table 3

State	Number of electrons
1s	2
2s, 2p	8
3s, 3p	8
4s, 3d, 4p	18
5s, 4d, 5p	18
6s, 4f, 5d, 6p	32

Table 3 shows the distribution of the number of states over groups with specified  $n$  and  $l$ . A comparison of this table with Mendeleev's periodic table shows that the periods of Mendeleev's table are the corollary of the consecutive filling of states with different  $n$  and  $l$ , arranged in groups, by electrons. The first group is filled in H and He atoms. In He the first shell is filled up. The filling of the second and third shells corresponds to the first two (short) periods of the periodic table comprising eight elements each (they end with Ne and Ar, respectively). Then follow two long periods with 18 elements each (ending with Kr and Xe, respectively) and a long period with 32 elements (ending with Rn); the filling of the last group of states only begins in the existing elements.

Chemical properties repeat themselves in going from one period to the next because the most important electrons for chemical properties are those in the outermost shells, beyond the completely filled shell (unfortunately, we cannot devote more space to this aspect here).

Obviously, the order in which the states are arranged in Table 3, corresponding to the order in which they are filled with electrons, stems from the dependence of the energy of electrons on  $n$  and  $l$ . By looking at the first rows of the table, we can formulate a simple rule: the first to be filled are the states with the lowest  $n$  and all admissible  $l$ , followed by the states with the next value of  $n$ . However, the situation is found to be not so simple in the fourth and all subsequent rows. For instance, according to the table, the filling of  $3d$  states must be preceded by the filling of  $4s$  states. But actually, if we look at the electron configurations of the group of iron (from Sc to Ni), we discover that there is competition between the  $4s$  and  $3d$  shells: for example, V has three electrons in the  $3d$  state and two in  $4s$ ; it is followed by Cr with five electrons in  $3d$  and one in  $4s$ , and Mn which has five electrons in  $3d$  and two in  $4s$ .

In order to come closer to our topic of magnetic properties, let us note that any set of electrons that completely fills a group of states with given  $n$  and  $l$  has zero total angular momentum, both orbital and spin ones. This occurs because filling requires that electrons with opposite projections of momenta be employed (see p. 49).

As examples, Table 4 shows the electron configurations of several elements.

Table 4

Element	Z	Configuration	Term
H	1	$1s$	$^2S_{1/2}$
He	2	$1s^2$	$^1S_0$
Li	3	$1s^2 2s$	$^2S_{1/2}$
Be	4	$1s^2 2s^2$	$^1S_0$
B	5	$1s^2 2s^2 2p$	$^2P_{1/2}$
...	...	...	...
Al	13	$1s^2 2s^2 2p^6 3s^2 3p$	$^2P_{1/2}$
...	...	...	...
Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$

The last column of the table gives the symbol (term) that summarizes the necessary information on the properties of the electron configuration of each atom in its ground state. The structure of the symbol is as follows: the capital Roman letter denotes the total orbital angular momentum of the electron configuration, the correspondence being (cf. p. 76):

$S P D F \dots$  and so on in alphabetical order

$L = 0 1 2 3 \dots$

The subscript denotes the total angular momentum  $J$ , and the superscript denotes the multiplicity, that is, the value of  $2S + 1$ , where  $S$  is the total spin of the electrons in the atom. For Be the term is  $^1S_0$ , that is,  $L=0$ ,  $J=0$ ,  $S=0$ ,

and for Al the term is  ${}^2P_{1/2}$ , that is,  $L = 1$ ,  $J = 1/2$ ,  $S = 1/2$ .

Looking at the atomic term written according to the rule formulated above, it is easy to calculate the  $g$  factor and find the magnetic moment of the atom.

Sufficiently accurate computational methods have been developed, and there exist relatively simple rules (the Hund rules) for determining the terms of any atom. Thereby *quantum mechanics solved the problem of the magnetic moments of the smallest structural units of matter, that is, atoms*. Although some atoms have terms with zero subscript on the right, that is, with  $J = 0$  (e.g. all inert gas atoms), most atoms have a nonzero total angular momentum, and hence, they represent microscopic magnets.

To conclude this section, we give the electron structure of the "most magnetic" of atoms, that of iron (Fe) (this atom gave the name to the "most magnetic" of properties: *ferromagnetism*):

Fe:  $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2}_{\text{argon shell}} \quad \text{term } {}^2D_4$

## 1.10. Exchange Energy

Let us consider atomic terms. For instance, the electron configuration of Mn ( $Z = 25$ ) is: Ar shell +  $3d^5 4s^2$ , and its term is  ${}^6S_{5/2}$ . Why is the spin of manganese electrons equal to  $5/2$ ? Obviously, the Pauli principle does not forbid the electrons to have other projections of spin as well. What makes all five electrons align parallel to one another?

Another example comes not from the theory of atoms but from the theory of molecules. The simplest molecule is the hydrogen molecule  $H_2$ . Two electrons move around two protons, forming a stable configuration. Two electrons can have a spin equal to 1 or to 0. Electrons in  $H_2$  have zero total spin. Why? These questions require an answer, and the answer is not trivial. The point is that the *reason for the realization of a specific spin configuration is not connected with the magnetic interaction between electrons*, although it is clear that the choice of a spin configuration is determined by energy efficiency: the configuration that is realized is that with the lowest energy.

We have shown at the beginning of the preceding section that the magnetic interaction is weak and can be neglected without significant error. But then we are left with only the electrostatic interaction which is insensitive to the spin state of electrons. Indeed, electrons with "parallel" spins and those with "antiparallel" spins are repulsed by one another with the identical force inversely proportional to the square of the distance separating them. Why then is the spin of electrons in manganese  $5/2$ , while in the hydrogen molecule it is zero? Seemingly, there cannot be any connection between the energy of an electron system and its spin, at any rate, as long as we neglect the magnetic interaction. But in reality the two are interrelated. The relation results from the antisymmetric properties of the wave function of electrons.

For the sake of simplification, we shall consider a system consisting of two electrons interacting only via electrostatic forces. Since we ne-



glect the magnetic interaction, we can completely ignore the spins of electrons while solving the problem of the energy of the system. Let  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  be the wave function describing the *orbital* motion of electrons. This fact is emphasized by the presence of only the coordinates of the electrons,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , as explicit arguments of the wave function; spin variables are omitted. We cannot completely forget about spin variables because the total wave function  $\Psi(1, 2)$  must be antisymmetric (see (1.38)). We cannot do better than to state that the total wave function  $\Psi(1, 2)$  is a product of the spin wave function  $S(\sigma_1, \sigma_2)$  describing the spin state of the electrons ( $\sigma_1$  and  $\sigma_2$  are spin variables) and the orbital wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  describing their orbital motion:

$$\Psi(1, 2) = S(\sigma_1, \sigma_2) \psi(\mathbf{r}_1, \mathbf{r}_2)$$

We have seen (see Table 2 on p. 64) that a spin configuration can be symmetric (if  $S = 1$ ) or antisymmetric (if  $S = 0$ ). But the function  $\Psi(1, 2)$  as a whole is antisymmetric. Hence, a symmetric spin function corresponds to an antisymmetric orbital function, and vice versa. This leads to the following conclusion:

when  $S = 0$ ,  $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_s$  is a *symmetric function*

when  $S = 1$ ,  $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a$  is an *antisymmetric function*

The symmetric and antisymmetric functions,  $\psi_s$  and  $\psi_a$ , describe *different* orbital motions of electrons and thus correspond to different energies. Specific circumstances determine which of

these energies is lower. In hydrogen molecules the minimum energy corresponds to the symmetric wave function describing the orbital motion. And this is the reason for the electron spin of  $\text{H}_2$  to be zero.

The result obtained above, namely, the dependence of the energy of a system of electrons on the symmetry of the wave function, and hence on spin, can be recast in a form that makes it possible to speak of the so-called *exchange interaction between electrons*.

Let us denote by  $E_s$  the energy of electrons corresponding to the wave function  $\psi_s$ , and by  $E_a$  the energy corresponding to  $\psi_a$ . From what we said above, there is a correspondence between the energy of a system and its spin:

$$E_s \leftrightarrow S = 0$$

$$E_a \leftrightarrow S = 1$$

We want to compose an expression of the spins of electrons (it is called the *spin Hamiltonian* and is denoted by  $\mathcal{H}_S$ \*) that assumes the value  $E_s$  for  $S = 0$  and  $E_a$  for  $S = 1$ .

To do this, we resort to formula (1.32):

$$\mathcal{H}_S = \frac{1}{4}(E_s + 3E_a) + (E_a - E_s) \mathbf{s}_1 \cdot \mathbf{s}_2$$

The values taken on by the spin Hamiltonian  $\mathcal{H}_S$  are the possible values of the energy of the

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\* The Hamiltonian is the quantum analogue of the Hamiltonian function. The Hamiltonian function is the energy expressed in terms of momenta and coordinates. The energy of motion of a free particle is  $(1/2)mv^2$ , and its Hamiltonian function is  $p^2/2m$  ( $\mathbf{p} = m\mathbf{v}$  is the momentum, and  $\mathbf{v}$  is the velocity).

system consisting of two electrons (the very  $E_s$  and  $E_a$  mentioned above). The first term,  $(1/4)(E_s + 3E_a) \equiv \bar{E}$ , is independent of the spin of the system and, as can readily be ascertained, represents the value of energy averaged over all possible spin states (three states with  $S = 1$  and one state with  $S = 0$ ); the second term is a function of the spin of the system. The difference  $E_a - E_s$  is usually written as a parameter  $A$  with minus sign. The spin Hamiltonian of two electrons then takes the form

$$\mathcal{H}_S = \bar{E} - A \mathbf{s}_1 \cdot \mathbf{s}_2 \quad (1.39)$$

This notation makes it possible to relate the energy efficiency of states with  $S = 0$  and  $S = 1$  to the sign of the parameter  $A$ . If  $A < 0$ , the "antiparallel" arrangement is preferable, and if  $A > 0$ , the "parallel" arrangement is preferable. The parameter  $A$  is called the *exchange integral*, and the second term in (1.39) is called the *exchange energy*, or the *exchange interaction*.

The origin of these terms must be explained. The attribute "exchange" appeared because the symmetric and antisymmetric wave functions describe the state of electrons that are interchanged. Furthermore, the parameter  $A$  is a measure of the frequency of this interchange. It is called the *exchange integral* because the calculation of  $A$  requires that certain expressions comprising wave functions be integrated. The term *exchange interaction* emphasizes that the structure of the spin Hamiltonian is such that the electrons are as if coupled through some specific interaction whose strength is a function of the relative orien-

tation of the spins of electrons. In this sense the exchange interaction reminds us of the magnetic interaction. The exchange integral  $A$  is a measure of interaction intensity.

Several features, very important for further discussion, must be underlined.

(i) The exchange interaction is isotropic. A rotation of all spins by the same angle does not change the value of the exchange energy. This is clear, for example, from the fact that expression (1.39) includes the scalar product of spins, and this product is not altered when both spins rotate by the same angle.

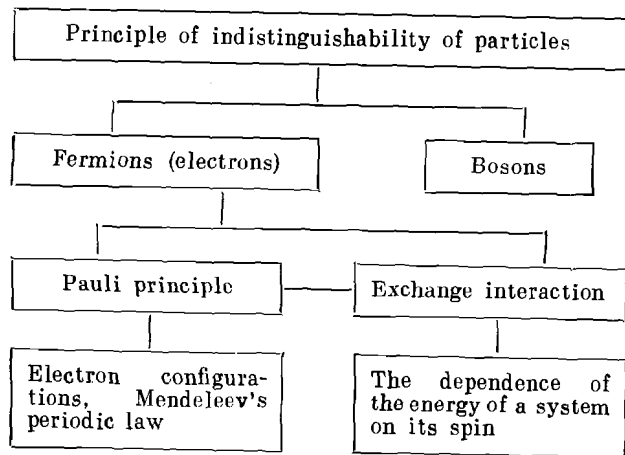
(ii) The intensity of the exchange interaction  $A$  is determined by the electrostatic energy of electrons and thus is not small, although  $|A|$  is, as a rule, somewhat less than the mean energy of electrostatic interaction (in our notation,  $|A| < \bar{E}$ ).

(iii) According to the arguments given above, the exchange integral can be either positive or negative. As far as the interaction within one atom is concerned,  $A$  is mostly positive (this constitutes one of the Hund rules); in the case of interatomic interaction  $A$  is predominantly negative, although cases of  $A > 0$  not merely happen but even explain the most spectacular magnetic property, namely, ferromagnetism.

In the case of interatomic exchange interaction (when the interacting electrons belong to different atoms) the exchange integral  $A$  essentially depends on the distance between atoms, sharply decreasing (exponentially) when atoms are removed at distances greater than the atomic size. Of

course, this can be proved only by substituting specific wave functions into a concrete exchange integral, although it should not be difficult to form a qualitative picture if the reader recalls that the exchange interaction is a result of interchanging of electrons.\*

In conclusion of the chapter we give a brief diagram outlining the logic of the last two sections:



\* Such statements tend to create an illusion of understanding. In fact, we wanted to stimulate the reader's interest. An aroused interest will encourage a more thorough analysis, which will lead to understanding.

## Chapter 2

### Paramagnetism and Diamagnetism

Now we move from the tiniest building blocks of matter to macroscopic bodies and will try to describe their magnetic properties. Even special monographs cannot enumerate the properties of *all* substances. This simply cannot be done: substances are too numerous. But even in antiquity scientists were aware that science begins with systematization. One has to remember that any systematization is approximate, calls for qualifications, supplements, explanations, and exclusions. The Soviet physicist Ya. G. Dorfman had a favored example of an illogical but *convenient* systematization: "A shoe store is divided into the sections of men's, women's, and seasonal footwear."

The magnetic properties of matter make it possible to suggest a simple and logical systematization. Substances are either diamagnetic or paramagnetic. The phrase "substances are either paramagnetic or diamagnetic" becomes impeccable if we qualify it with "at high temperatures".

Thus,

*at high temperatures a substance is either diamagnetic or paramagnetic.*

It remains for us to define paramagnetism and diamagnetism, as well as to describe the magnetic properties of materials at low temperatures.

## 2.1. Magnetic Susceptibility

If a piece of some material is placed between the poles of a magnet, or inside a solenoid through which electric current is run, the magnetic lines of force are somewhat redistributed as compared

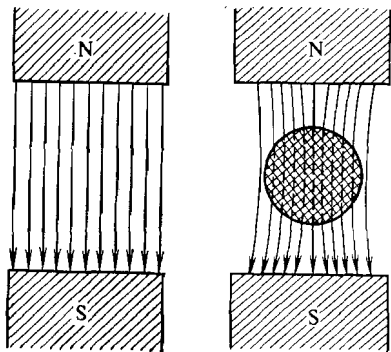


Fig. 17. Magnetic lines of force undergo redistribution if a body is introduced between the poles of a magnet

with their distribution when there is nothing between the poles or inside the solenoid (Fig. 17). When placed in a magnetic field, all substances are magnetized. This means that each element in the volume of a body behaves as a small magnet, and the magnetic moment of the body as a whole is a vector sum of the magnetic moments of all such elements. A measure of magnetiza-

## 2.1. Magnetic Susceptibility

tion of the body is the magnetic moment density  $\mathcal{M}$ . The dimensionality of  $\mathcal{M}$  follows from the fact that  $\mathcal{M}V$ , where  $V$  is the volume of the body, is the magnetic moment  $M$ . It is readily ascertained that the dimensionality of the magnetic moment density  $\mathcal{M}$  is identical to that of magnetic field:

$$[\mathcal{M}] = [H] = g^{1/2}/cm^{1/2} \cdot s$$

(See Problem 10.)

A nonzero magnetization  $\mathcal{M}$  appears only in response to a magnetic field and is a linear function of the field when the field is not too strong:

$$\mathcal{M} = \chi H \quad (2.1)$$

At any rate, this is the case at high temperatures.

The dimensionless factor  $\chi$  is called the *magnetic susceptibility*.

Paramagnetics are substances with  $\chi > 0$ , while diamagnetics have  $\chi < 0$ . The middle is excluded: there are no substances in nature with  $\chi = 0$ .\* As a rule, the paramagnetic susceptibility  $\chi_{para}$  is substantially greater than the diamagnetic susceptibility  $\chi_{dia}$ , that is,

$$\chi_{para} \gg |\chi_{dia}|$$

although there are some very important exceptions (see later, Sec. 2.6). The magnetic susceptibility of diamagnetics is practically independent of temperature, while that of paramagnetics depends on temperature very substantially.

\* The discovery of para- and diamagnetism was made by Michael Faraday.

Pierre Curie established in 1895 that

*the paramagnetic susceptibility decreases in inverse proportion to temperature  $T$ .*\*

This inverse proportionality holds quite well at sufficiently high temperatures in all paramagnetic materials. The statement given above is called *Curie's law*.\*\* As temperature is lowered, a systematic departure from this law is clearly observed, especially when solid and liquid paramagnetic substances are studied. The temperature dependence of the paramagnetic susceptibility is conveniently illustrated by  $1/\chi$  plotted as a function of  $T$ . Figure 18 shows that the experimental values of  $1/\chi$  linearly depend on temperature (at high  $T$ ) for all materials shown in the figure, but for some materials the extrapolated experimental line intersects the abscissa axis at a positive temperature  $\Theta_p$ , while for other materials the intercept is negative. The behavior  $\chi = \chi(T)$  can be described by a formula that generalizes Curie's law:

$$\chi = \frac{C}{T - \Theta_p}, \quad C \text{ and } \Theta_p \text{ are constants, } T \gg |\Theta_p| \quad (2.2)$$

\* We shall use the absolute temperature scale, called the Kelvin scale. The zero of this scale corresponds to the ground state of a body, when all thermal motion of its particles dies out. Although temperature is a habitual notion, the true physical meaning of temperature is not so easily comprehensible. Here we recommend a book in the same series, *Temperature* by Ya. A. Smorodinsky, published in English by Mir Publishers in 1984.

\*\* The independence of the diamagnetic susceptibility of temperature was also discovered by P. Curie. It was also Curie who discovered that ferromagnetism can be destroyed by increasing temperature (see below).

This formula is called the *Curie-Weiss law*. The quantity  $\Theta_p$  (even when  $\Theta_p < 0$ ) is called the *paramagnetic Curie point*. The attribute "paramagnetic" must not be left out. The concept of the "Curie point" as such has a different meaning that we shall discuss later. There is no contradiction between the impossibility of negative absolute temperatures and the cases in which  $\Theta_p$

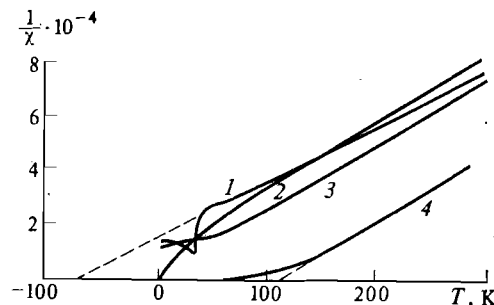


Fig. 18.  $1/\chi$  as a function of  $T$  in paramagnetics: curve 1— $\text{CuSO}_4$ ; curve 2— $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ; curve 3— $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ; curve 4—Ni

is below zero. If  $\Theta_p < 0$ , this merely indicates that  $\chi(T) < C/T$  at  $T \gg |\Theta_p|$ , while if  $\Theta_p > 0$ ,  $\chi(T) > C/T$ .

The constants  $C$  and  $\Theta_p$  in the Curie-Weiss law are different in different materials. Our problem is to establish how these constants are related to the characteristics of atoms and molecules of which substances are constructed.

The behavior of paramagnetic materials at temperatures close to the paramagnetic Curie

point,  $T \approx |\Theta_p|$ , is of substantial interest and will be discussed specially in this book after we explain why Curie's law holds at  $T \gg |\Theta_p|$  and why departures from this law are observed at  $T \approx |\Theta_p|$ .

The magnetic properties of materials are sometimes described by the magnetic susceptibility  $\chi$ , and sometimes in terms of the *magnetic permeability*

$$\kappa = 1 + 4\pi\chi \quad (2.3)$$

Clearly,

$\kappa > 1$  for paramagnetics

$\kappa < 1$  for diamagnetics

As follows from relations (2.1) and (2.3), the magnetic permeability is the proportionality factor between the vectors  $\mathbf{H}$  and  $\mathbf{B}$  introduced by the equality

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \quad (2.4)$$

This immediately gives  $\mathbf{B} = \kappa\mathbf{H}$  and  $\kappa = 1 + 4\pi\chi$ .

Although the vector  $\mathbf{B}$  is called the vector of magnetic induction, and  $\mathbf{H}$  the vector of magnetic field, the true meaning of  $\mathbf{B}$  is that  $\mathbf{B}$  (and not  $\mathbf{H}$ ) is the mean magnetic field in a medium. Each atom is a microscopic source of a magnetic field, and over interatomic spacings the field in a medium varies from point to point. Besides, atoms and electrons in the atoms always move. Consequently, the microscopic (true) field constantly varies. The value of the field measured by macroscopic instruments is the result of averaging over time and space of the microscopic field.

It is necessary to repeat:  $\mathbf{B}$  is the mean magnetic field.

When a magnetic field permeates a region occupied by matter, the absence of magnetic charges (see Sec. 1.1) is seen in that the magnetic lines of force never discontinue: the normal (perpendicular to the surface of a body) component

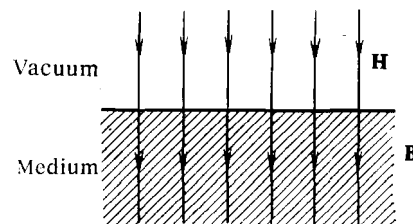


Fig. 19. Magnetic lines of force never discontinue when crossing a vacuum-medium boundary

of the vector  $\mathbf{B}$  is equal to the normal component of the vector  $\mathbf{H}$  outside the body (Fig. 19). Nevertheless, by convention it is the vector  $\mathbf{H}$ , and not  $\mathbf{B}$ , that we call the magnetic field. We hope that this discrepancy between the term and its meaning will not lead to confusion. As long as the magnetic permeability  $\kappa$  does not differ too much from unity, the difference between  $\mathbf{B}$  and  $\mathbf{H}$  is fairly insignificant.

We conclude this review section, that mostly offered statements about magnetism, with a definition of an ideal diamagnetic substance for which  $\chi = -1/4\pi$  and  $\kappa = 0$ . Since the magnetic permeability and, with it, the induction  $\mathbf{B}$  of this substance are zero, an ideal diamagnetic material has zero mean magnetic field. If such a materi-

al exists, it must repel magnetic lines of force. We shall see later (see Sec. 2.6) that

*superconductors are ideal diamagnetic materials.*

## 2.2. Magnetic Field Aligns Magnetic Moments

A comparison of diamagnetic and paramagnetic materials immediately reveals the difference between them: paramagnetic materials are composed of atoms or molecules possessing magnetic moments, while diamagnetic materials consist of atoms or molecules whose magnetic moments are zero. Now we can show that this observation formulates a significant feature: *bodies composed of atoms (molecules) having a magnetic moment must be paramagnetic, and those composed of atoms (molecules) with zero moment must be diamagnetic.*

In Ch. 1 we discussed the magnetic moments of individual atoms and found out that the number of atoms with nonzero magnetic moment is much greater than that of atoms with zero moment. But bodies mostly consist not of atoms but of molecules. The theory that describes in detail how atoms combine into molecules is quantum mechanics that makes it possible to calculate (at any rate, in principle) the forces acting between submolecular particles and to determine the electron structure of the resulting molecules. Here we cannot go into these aspects and only mention in passing that when two or more atoms with nonzero magnetic moments (we shall refer to such atoms as paramagnetic) combine to form a molecule, this molecule is often devoid of mag-

netic moment (it is diamagnetic) (we remind the reader that we only speak of the electron magnetic moment). In addition to the case of hydrogen molecule  $H_2$  already analyzed in Sec. 1.10 (a diamagnetic molecule formed of two paramagnetic atoms), we shall discuss the molecule of common salt, NaCl. The electron configurations and terms of sodium and chlorine atoms are:

Na:  $1s^2 2s^2 2p^6 3s, {}^2S_{1/2}$

Cl:  $1s^2 2s^2 2p^6 3s^2 3p^5, {}^2P_{3/2}$

Both the sodium and chlorine atoms are paramagnetic. This clearly follows from their terms.

The formation of a NaCl molecule goes through the formation of a  $Na^+$  ion whose electron shell is analogous to that of an atom of the inert gas Ne, and of a  $Cl^-$  ion whose electron shell is analogous to that of Ar. Therefore, both ions have zero magnetic moments. They form, by virtue of the electrostatic (Coulomb) attraction, a diamagnetic molecule. We wanted to emphasize that there exist more diamagnetic materials than one could guess by looking at the electron configurations of individual atoms. On the contrary, paramagnetic molecules are a rarity. The most familiar example is that of oxygen: the  $O_2$  molecule is paramagnetic.

Molecules in a gas constantly move, colliding with one another and the walls, and the free path length of a molecule is much greater than its size. An increase in temperature means that the mean velocity of the chaotic motion of molecules increases. In a solid, that is, in a crystal, molecules are arranged in a strictly defined order, and

the thermal motion manifests itself in an increased amplitude of vibrations around equilibrium positions. A liquid represents an intermediate phase. Molecules vibrate around random equilibrium positions which are not fixed but move, ensuring the fluidity of a liquid. An increase in a liquid's temperature means that the chaotic motion of molecules is intensified.

We ignored in this brief description of the states of aggregation whether molecules have magnetic moments or not. The reason for this was not only a desire to simplify a picture that is quite complex even without this complication but also that the presence or absence of magnetic moment in a molecule is not important as long as we are not interested in the magnetic properties of a material. The properties of liquid oxygen (paramagnetic molecules) do not differ qualitatively from the properties of liquid nitrogen (diamagnetic molecules). A different aspect is now important to us. In studying the macroscopic magnetic properties of paramagnetic materials, we can, at the first steps, ignore the positions and thermal motion of the centers of mass of the molecules and analyze only the position in space of the magnetic moments of these molecules. In order to clarify the magnetic properties of materials, we can visualize the paramagnetic molecules as microscopic needles, that is, tiny magnets that can be oriented in space in  $2J + 1$  ways.

An ensemble of particles whose behavior depends only on the directions of their magnetic moments is called the *gas of magnetic needles*.

A gas of magnetic needles is a convenient model for describing the properties of paramagnetic ma-

terials at high temperatures. The word "gas" only underlines the fact that the interaction between magnetic moments is neglected.

In order to go further, we shall have to resort to some results of statistical physics.\* But what is the thermal motion in a gas of magnetic needles placed in a magnetic field  $\mathbf{H}$ ? Statistical physics states:

*the number of particles  $N(m_J)$  with a definite projection of the magnetic moment  $\mathbf{M}$  onto the magnetic field  $\mathbf{H}$  is proportional to  $\exp(-\varepsilon_M/kT)$ ,*

where, according to (1.28) and (1.33),

$$\varepsilon_M = -\mathbf{M} \cdot \mathbf{H} = -g\mu_B H m_J$$

is the energy of the magnetic moment  $\mathbf{M}$  in the magnetic field  $\mathbf{H}$ , and  $k$  is the Boltzmann constant,  $k = 1.4 \cdot 10^{-16}$  erg/deg. The proportionality factor is chosen so as to satisfy a natural requirement: the sum of the number of particles (per unit volume) with different projections of a magnetic moment must be equal to the total number of particles  $N$  (per unit volume):

$$\sum_{m_J=-J}^J N(m_J) = N$$

---

\* *Statistical physics* is a special branch of physics that studies the laws governing the behavior and properties of macroscopic bodies, that is, bodies consisting of a colossal number of constituent particles: atoms, molecules, electrons, ions, etc.



Therefore,

$$\frac{N(m_J)}{N} = \frac{e^{\frac{\mu_B g H}{kT} m_J}}{\sum_{m_J=-J}^J e^{\frac{\mu_B g H}{kT} m_J}} \quad (2.5)$$

where  $J$  is the total momentum of an atom or a molecule. We remind the reader that the value of the  $g$  factor is determined by the values of  $L$ ,  $S$ , and  $J$  (see (1.34)).

This formula shows that the words "thermal motion" in the case of a gas of magnetic needles mean a certain, temperature-dependent distribution of particles over magnetic levels. This "definition" of thermal motion is very likely to surprise the reader. But this cannot be helped: in this particular case temperature means precisely what is stated by formula (2.5).

At absolute zero of temperature (as  $T \rightarrow 0$ ) all particles "assemble" at a magnetic level with  $m_J = J$ :

$$N_{m_J=J} = N, \quad N_{m_J \neq J} = 0$$

that is, the magnetic moments of all particles are "parallel" to the magnetic field. Of course, they are parallel only in the sense allowed by quantum mechanics. For this reason we retained the quotation marks (see p. 63).

When temperature tends formally to infinity (we shall discuss later what we understand by high and low temperatures), the quantity  $N(m_J)$  becomes independent of  $m_J$ :

$$\frac{N(m_J)}{N} = \frac{1}{2J+1}$$

that is, particles are distributed uniformly over all levels: the  $(2J+1)$ th part of the total number of particles is found at each level.

### Negative Absolute Temperatures

It is intuitively clear that temperature determines the energy of a gas (or is it determined by the energy of the gas?). Indeed, let us assume that we are able to produce a gas of magnetic needles with a specified energy, that is, we can fix the total energy of the magnetic-needles gas. We shall denote it by  $\mathcal{E}$ . Then, by virtue of (2.5)\*,

$$\mathcal{E} = -N\mu_B g H \frac{\sum_{m_J=-J}^J m_J e^{\frac{\mu_B g H}{kT} m_J}}{\sum_{m_J=-J}^J e^{\frac{\mu_B g H}{kT} m_J}}$$

and we can calculate the energy of the gas for each value of temperature. Let us analyze in detail the simplest case, namely,  $J = 1/2$  and  $g = 2$ . Energy as a function of temperature then takes the form

$$\mathcal{E} = -N\mu_B H \tanh \frac{\mu_B H}{kT} \quad (2.6)$$

When  $T$  tends (formally) to infinity, the energy  $\mathcal{E}$  tends to zero:  $\mathcal{E}_\infty = 0$ . The limit is zero as a

\* The formula for  $\mathcal{E}$  is derived on the basis of the following arguments: the energy of a gas is the sum of the energies of the particles occupying all the allowed levels. The energy of a particle at a given level (with a given  $m_J$ ) is the energy of the level multiplied by the number of particles occupying this level.

result of our choice of a reference point for magnetic levels. The energy of the lower level is  $-\mu_B H$ , and that of the upper level is  $+\mu_B H$ . At all finite temperatures energy is negative because there are more particles on the lower than on the upper level.

Now we want to pose an "improper" question. What will happen if we make the energy of a two-level gas greater than  $\mathcal{E}_\infty$ ? This requires that we

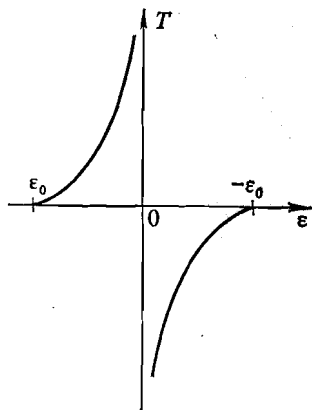


Fig. 20. Temperature as a function of the total energy of a system of magnets ( $J = 1/2$ ) in a magnetic field  $H$ ;  $\epsilon_0 = -N\mu_B H < 0$

"arrange" the distribution of particles in such a way that their number on the upper level exceeds that on the lower level (this distribution is said to be *inverse*). What temperature corresponds to such states? The answer is absolutely unexpected: "Negative temperature!" Figure 20 shows that the negative temperature is "found" to the right of the infinitely large positive temperature and corresponds to a higher energy.

Note that the possibility of introducing a

negative temperature follows from a finite number of levels in a system (in this particular case, in the gas of magnetic needles). Actual temperature is always positive. The concept of negative temperature is a convenient method of describing nonequilibrium states of systems possessing a finite number of levels; it is used in laser physics and its applications.

\* \* \*

Our treatment of temperature was rather careless: it tended either to zero or to infinity. To compensate for this, we emphasized the formality of these procedures. There are no abstract high or low quantities in physics (we had an opportunity to find that out). The value of a parameter of interest must always be compared with something else. What is the quantity with which the temperature  $T$  must be compared? In all the formulas of this subsection temperature appears in the ratio  $\mu_B H/kT$  (we have omitted the  $g$  factor because it is of the order of unity). Temperature must be regarded as low or high depending on whether  $\mu_B H/kT \gg 1$  or  $\mu_B H/kT \ll 1$ . Let us find the relation (in standard units) between  $T$  and  $H$  when  $\mu_B H = kT$ :

$$T \text{ K} = 0.5 \cdot 10^{-4} H \text{ Oe} \quad (2.7)$$

This relation is so important that it deserves a special analysis. In ordinary fields and at ordinary room temperatures ( $\approx 300 \text{ K}$ )  $kT > \mu_B H$ . Only at very low temperatures (in the vicinity of absolute zero) the inequality can be

reversed (the equality is reached at  $T = 0.5$  K in a magnetic field of  $H = 10^4$  Oe).

The physical meaning of the quantity  $\mu_B H$  is clear from formula (1.29);  $\mu_B H$  is the spacing between magnetic levels. And it was found that

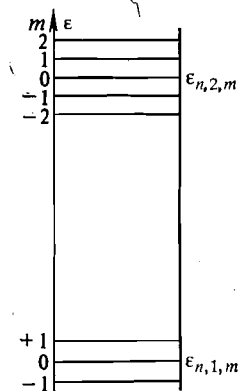


Fig. 21. Magnetic levels with different  $n$  and  $l$  are separated by a large "distance"

usually this spacing is small in comparison with  $kT$ , that is, with temperature expressed in energy units. Other (nonmagnetic) energy levels of atoms or molecules are separated from the lowest, ground level by distances of the order of several electron volts,  $1 \text{ eV} \approx 10^4$  K (Fig. 21). In normal conditions these levels are not excited\*, and we can safely forget about their existence and regard an atom (or a molecule) as a magnetic

\* The number of atoms in an excited state is proportional to  $\exp(-\Delta\epsilon_n/kT)$ , where  $\Delta\epsilon_n = \epsilon_n - \epsilon_0$ ,  $\epsilon_n$  is the energy of the excited state, and  $\epsilon_0$  is the energy of the ground state (at room temperature, i.e. at  $T = 300$  K), and if  $\Delta\epsilon_n \approx 1 \text{ eV} = 10^4$  K, we find  $\exp(-\Delta\epsilon_n/kT) \approx \exp(-300)$

needle and use the model of the magnetic-needles gas for calculations of magnetic properties.

Now we pass to the main statement of this section. We want to prove that the gas of magnetic needles is paramagnetic. To achieve this, we make use of distribution (2.5) and calculate the magnetic moment of the unit volume of this gas,  $\mathcal{M}$  (or rather, the projection of  $\mathcal{M}$  onto the magnetic field  $H$ )\*:

$$\mathcal{M} = N \mu_B g \frac{\sum_{m_J=-J}^J m_J e^{\frac{\mu_B g H}{kT} m_J}}{\sum_{m_J=-J}^J e^{\frac{\mu_B g H}{kT} m_J}} \quad (2.8)$$

Now we recall that  $\mu_B g H \ll kT$ . The exponentials in the denominator of (2.8) can be replaced with unities, and in the numerator we retain only the first (linear in  $H$ ) terms of the expansion of the exponential:

$$\mathcal{M} = \frac{N (\mu_B g)^2}{kT} \frac{1}{2J+1} \sum_{m_J=-J}^J m_J^2$$

But

$$\sum_{m_J=-J}^J m_J^2 = \frac{1}{3} J(J+1)(2J+1)$$

(the derivation of this formula is a useful exercise in algebra). Therefore,

$$\mathcal{M} = \frac{N (\mu_B g)^2}{3kT} J(J+1) H$$

\* See the footnote to p. 103.

and the magnetic susceptibility

$$\chi = \frac{N (\mu_{BG})^2}{kT} \frac{J(J+1)}{3} \quad (2.9)$$

is positive and governed by Curie's law, that is, indeed,

*the gas of magnetic needles is paramagnetic.*

Not only were we able to prove above this statement but we also succeeded in calculating as a "by-product" the constant in Curie's law. As we see from formula (2.7), it is possible to determine the value of the magnetic moment of the molecules in the gas, or rather, the quantity  $(\mu_{BG})^2/J(J+1)$ , by measuring the proportionality factor between  $1/T$  and  $\chi$ .

As we already know, departures from Curie's law become appreciable when temperature is lowered (especially in solid and liquid paramagnetic materials). This is only natural because in deriving formula (2.9) we neglected the interaction between atomic moments: the magnetic-dipole interaction and especially the exchange interaction. This is quite justified at high temperatures\*, so that we have met the goal of this

\* We can ignore the interaction of the particles of an ordinary classical gas at high temperatures because  $(3/2)kT$  is the mean kinetic energy of a molecule, so that the mean energy of interaction per one particle can of course be neglected if it is small compared with  $(3/2)kT$ . In a gas of magnetic needles temperature determines only the occupancy of magnetic levels. Has this anything in common with the interparticle interaction? Nevertheless we will be able to show (see Ch. 3) that the interaction can indeed be neglected at high temperatures, that is, the model of the gas is valid.

subsection. Later we shall describe the effects of this interaction.

### *Electron Paramagnetic Resonance*

We have found enough by now about atomic magnets and about the distribution of magnetic particles over energy levels, and are able now to discuss an interesting and important effect that is called the *electron paramagnetic resonance* (EPR).\*

When considering an individual magnetic moment in a constant uniform magnetic field (see Sec. 1.6), we were able to establish that a moment tilted with respect to the field direction precesses at a frequency  $\gamma H$ , where  $\gamma$  is the gyromagnetic ratio. When seen "sideways", the moment appears to be oscillating harmonically. But it is well known that if a body vibrating at its natural frequency is subjected to an alternating force at the same frequency, the resonance arises: the vibrating body removes energy from the source of the force.

Is it possible to create a periodic force acting on the magnetic moment? Yes, it is. All one has to do is to rotate the magnetic field, that is, to add to the constant component of the field another, alternating component acting on the magnetic moment and directed at right angles to the constant component; this alternating component must rotate around the former at

\* The electron paramagnetic resonance was discovered by E. K. Zavoisky in 1944 in experiments with iron-group salts. Arguments in favor of the possibility of EPR were suggested as early as 1922.

a frequency  $\omega$ .<sup>\*</sup> If  $\omega = \gamma H$ , the electron paramagnetic resonance sets in; it is manifested by an abrupt increase in the losses of the magnetic energy of the alternating magnetic field. This is the explanation of EPR in "classical" terms.

The quantum explanation is even simpler. Let us specify "the most quantum" of the gases: the gas of electron spins. Then,  $g = 2$ , and, as always,  $\mu_B$  is the Bohr magneton. In the electromagnetic wave field particles can jump from the lower to the upper level if the energy of the electromagnetic quantum, that is, one photon, equals the difference between the energies of the levels: when  $\hbar\omega = 2\mu_B H$ . Note that the classical and quantum conditions for EPR coincide because the spin gyromagnetic ratio is  $\gamma = e/m_e c$ .

Electromagnetic waves can interact not only with electron magnetic moments but also with nuclear magnetic moments. The energy of nuclear particles in a magnetic field depends on the value of the projection of its magnetic moment onto the magnetic field. As in the case of electron magnetic moments, a system of equidistant levels is produced so that transitions between these levels can be induced by electromagnetic radiation. This phenomenon is called the *nuclear magnetic resonance* (NMR).<sup>\*\*</sup> Qualitatively EPR

<sup>\*</sup> A longish sentence may have given the impression that implementation should be difficult. Usually a specimen is placed in a resonator in which a periodic high-frequency electromagnetic field is produced, and the resonator (with the specimen) is placed either between the poles of a magnet or inside a solenoid.

<sup>\*\*</sup> This nuclear magnetic resonance was discovered and explained by F. Bloch and E. Purcell in 1946 (Nobel Prize in physics, 1952).

and NMR are very similar, but quantitatively they differ very considerably because of the difference between the electron and nuclear magnetic moments. (See Problem 11.)

EPR and NMR have grown into important research tools, and their use is not restricted to physics; these techniques were employed in a number of instruments in chemistry, geology, biology, and other fields where one has to "peer into" a body without destroying it.

### 2.3. Diamagnetism

If we wanted the briefest possible definition of the nature of paramagnetism, it would be: a magnetic field *orients* the magnetic moments of atoms or molecules.

Diamagnetism arises because in any atom and in any molecule a magnetic field *produces* a magnetic moment proportional to this magnetic field. The magnetic moment appears because moving electrons are subjected to the Lorentz force  $\mathbf{F}$ :

$$\mathbf{F} = -\frac{e}{c} [\mathbf{v} \times \mathbf{H}] \quad (2.10)$$

The expression for the diamagnetic susceptibility can be rigorously derived only in terms of quantum mechanics. But we can choose an inconsistent approach: use classical mechanics to illustrate the cause leading to the diamagnetic effect, evaluate the value of the diamagnetic susceptibility, then give the exact formula, and only then indicate at what step the derivation was not rigorous. This is the approach we are to follow. This will teach us how to use the results

of quantum mechanics while operating in classical terms.

We shall see later that the diamagnetic susceptibility is quite small. If an atom already has a magnetic moment, its change due to diamagnetism is so small that can simply be neglected. Therefore diamagnetism is of interest only in such atoms (or molecules) that have no intrinsic (paramagnetic) moment.

We must start with constructing a "classical model" of a diamagnetic atom. Presumably, the simplest classical model without a magnetic moment is as follows\*: two electrons revolving around a nucleus in opposite directions along the same orbit (one clockwise and one counterclockwise). Obviously, each electron has an angular momentum (and hence, a magnetic moment), but the sum of the two momenta is zero.

Now let us place our "atom" in a magnetic field  $\mathbf{H}$  in such a manner that the orbits of electrons are in a plane perpendicular to the magnetic field. Before calculations, we shall make one more reservation: the magnetic field is so small that the Lorentz force (2.10) can be considered a small perturbation in comparison with the force acting on electrons in the field of the nucleus. Let  $\mathbf{v}_0$  be the velocity of the electron moving along a circle of radius  $R$  when the magnetic field  $\mathbf{H} = 0$ , and  $\mathbf{v}$  its velocity when  $\mathbf{H} \neq 0$ . Then, by equating the centripetal force to the radial projection of the force acting on the electron,

\* We remind the reader that one "quantum" electron can rotate and have zero magnetic moment, provided it is in the  $s$  state (see p. 47).

we can determine the change  $\Delta \mathbf{v}$  induced by the magnetic field in the velocity of the particle.

When  $\mathbf{H} = 0$ ,

$$\frac{m_e v_0^2}{R} = F_R$$

and when  $\mathbf{H} \neq 0$ ,

$$\frac{m_e v^2}{R} = F_R - \frac{eH}{c} v$$

Subtracting one equation from the other and retaining only the term linear in  $H$ , we obtain

$$\Delta v = -\frac{eH}{2m_e c} R \quad (2.14)$$

Note that the sign of  $\Delta v$  is independent of the direction of rotation while  $\mathbf{H} = 0$ . One electron in our two-electron atom rotates slightly faster, and the other slightly slower. The quantity  $\Delta v/R = -eH/2m_e c$  has the dimensionality of frequency. It is called the *Larmor frequency*  $\omega_L$  (named after the British physicist Joseph Larmor). We see that the Lorentz force (2.10) makes the electron revolve around the magnetic field. This motion is superposed on the motion of the electron at  $\mathbf{H} = 0$ .

We have analyzed above a very particular case, that of the magnetic field perpendicular to the plane of the orbit. A more general theorem can be proved (the *Larmor theorem*):

*Let the motion of electrons in the absence of magnetic field be known; the motion in a weak magnetic field  $\mathbf{H}$  will be the same as the motion without field with an additional rotation around  $\mathbf{H}$  at an angular velocity equal to the frequency  $\omega_L$ .*

The motion around  $\mathbf{H}$  is often called the *Larmor precession* (Fig. 22).

In fact, we have already met the Larmor precession in Sec. 1.6 when considering the rotation of magnetic moment in a magnetic field. This was essentially an example of application of the Larmor theorem: the motion of an electron

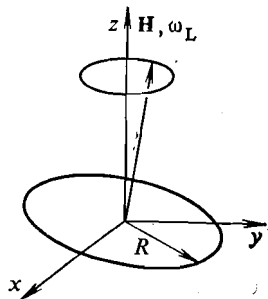


Fig. 22. The normal to the plane of trajectory precesses around the field  $\mathbf{H}$  at the Larmor frequency  $\omega_L$ ;  $R$ —radius of the trajectory

(at  $\mathbf{H} = 0$ ) produces a magnetic moment that precesses when placed in a magnetic field (naturally, at a Larmor frequency).

Let us go back to our “classical” atom. At  $\mathbf{H} \neq 0$  both electrons gain an additional angular momentum equal to  $m_e \Delta v R$  and aligned along the magnetic field. Consequently, the atom acquires a nonzero angular momentum equal to the sum of the momenta of the electrons. But with the angular momentum being distinct from zero, the atom must possess a magnetic moment  $M_a$ . Since the angular momentum is aligned along the field and the gyromagnetic ratio is negative (see (1.10),  $e < 0$ ), the magnetic

moment is aligned *against* the field\*:

$$M_a = 2 \frac{e}{2m_e c} m_e \Delta v R = -2 \frac{e^2 R^2}{4m_e c^2} H$$

Let us rewrite this expression in a form that will make it possible to get rid of the classical features of the model. A true “quantum” electron moves over a sphere of radius  $r$ , not along a circle  $x^2 + y^2 = R^2$ . Since  $r^2 = x^2 + y^2 + z^2$  and since all directions in a spherical atom are equivalent,  $R^2 = (2/3)r^2$ . We give  $r$  a subscript  $i$  indicating the number of the electron in the atom and write a correct quantum-mechanical expression for the diamagnetic moment of any atom containing  $Z$  electrons (in the atom discussed above,  $Z = 2$ ):

$$M_a = -\frac{e^2 H}{6m_e c^2} \sum_{i=1}^Z r_i^2 \quad (2.12)$$

If a unit volume of a body contains  $N$  atoms, its diamagnetic susceptibility is

$$\chi_{dia} = -\frac{e^2 N}{6m_e c^2} \sum_{i=1}^Z r_i^2 \quad (2.13)$$

This expression is strictly accurate if  $r_i^2$  is interpreted as the *quantum-mechanical mean*. The true meaning of these words can be grasped only after going into the details of the mathematical equipment of quantum mechanics (see p. 42). When evaluations are needed,  $r_i^2$  can be replaced with  $a^2$ , where  $a$  is the size of the atom.

\* If charges are positive, both the angular momentum and magnetic moment induced by the magnetic field  $\mathbf{H}$  are aligned against the field.

But what was the "trick" used in the derivation? The derivation is based on assuming the existence of stable atomic orbits (the radius  $R$  was assumed constant) and this can be justified only by quantum mechanics that states that there are discrete stable energy levels of atomic electrons.\*

All materials consist of atoms and molecules in which electrons move. Obviously, diamagnetism is a general property. Of course, diamagnetism exists also when atoms (or molecules) have magnetic moments (this has already been mentioned before). In the general case the magnetic susceptibility  $\chi$  must be written in the form

$$\chi = \chi_{\text{para}} + \chi_{\text{dia}}$$

The second term is negative, and it depends on the ratio between the diamagnetic and paramagnetic susceptibilities whether the substance is paramagnetic or diamagnetic. We shall presently demonstrate that  $|\chi_{\text{dia}}| \ll \chi_{\text{para}}$ , that is, if a substance is composed of atoms with magnetic moments, this substance is paramagnetic. Indeed,

$$\frac{\chi_{\text{dia}}}{\chi_{\text{para}}} = \frac{kTm_e a^2}{\hbar^2} \quad (2.14)$$

but  $\hbar^2/m_e a^2$  is, by an order of magnitude, the energy of an electron in the atom,  $\epsilon_a$  (see Sec. 1.4); it is approximately equal to one or several electron volts and  $1 \text{ eV} \approx 10^4 \text{ K}$ . Obviously, in normal conditions  $kT \ll \hbar^2/m_e a^2$ , and hence,  $|\chi_{\text{dia}}| \ll \chi_{\text{para}}$ .

By way of "justification", we can say that formula (2.13) was derived in 1905 by P. Langevin who did not go beyond classical physics.

The following arguments show with special clarity that the diamagnetic moment is small compared with the paramagnetic moment: the magnetic field that magnetizes the gas of magnetic needles must exceed  $kT/\mu_B$  (it was evaluated on p. 105), while the magnetic field necessary to induce the magnetic moment of an atom of the order of  $\mu_B = e\hbar/m_e c$  must be tremendously large: of the order of  $\epsilon_a/\mu_B \approx 10^8 \text{ Oe}$ . In this field the magnetic energy is of the order of the Coulomb energy; obviously this will result in a complete restructuring of the atom (in particular, formulas (2.12) and (2.13) cease to be valid). (See Problem 12.)

A magnetic field  $H \approx 10^8 \text{ Oe}$  could not be produced so far in terrestrial conditions, but fields on this scale or even stronger seem to be routine in space.

In contrast to the paramagnetic susceptibility, the diamagnetic susceptibility is independent of temperature. This is caused by the already discussed wide energy "gaps" between the ground state of the atom and its excited states (only the ground state contributes to the mean value, and the contribution of the excited states is exponentially small; see the footnote to p. 106).

The diamagnetic susceptibility is so much smaller than the paramagnetic susceptibility that even minute doping of a diamagnetic substance with paramagnetic atoms makes this substance paramagnetic.

There is another point: so far we have discussed only the electron magnetism (in fact, we listed on p. 60 the values of the magnetic moments of the proton and neutron). We are justified



by the smallness of nuclear magnetic moments (the proton magnetic moment is less by a factor of 700 than the Bohr magneton, that is, than the intrinsic magnetic moment of the electron). If, however, the object of study is diamagnetic and the nuclei of its atoms have magnetic moments, the nuclear paramagnetism may become appreciable. The expression for the nuclear paramagnetic susceptibility is readily written by analogy to the electron paramagnetic susceptibility (see formula (2.9)):

$$\chi_{\text{nuc}} = \frac{N_{\text{nuc}} \mu_{\text{nuc}}^2}{kT} \frac{I(I+1)}{3}$$

Here  $N_{\text{nuc}}$  is the number of paramagnetic nuclei per unit volume,  $\mu_{\text{nuc}}$  is the magnetic moment of the nucleus, and  $I$  is its spin.

Even if  $\chi_{\text{nuc}} \ll |\chi_{\text{dia}}|$ , it is possible to detect the nuclear paramagnetism by the temperature behavior of the magnetic susceptibility. It was in this way that B.G. Lazarev and L.V. Shubnikov discovered in 1936 the nuclear paramagnetism by measuring the magnetic susceptibility of crystalline hydrogen at temperatures very close to absolute zero and measured the magnetic moment of the proton.

### *Magnetism Is a Quantum Phenomenon*

We were emphasizing throughout the book that magnetic properties cannot be studied without using quantum mechanics. Nowadays any textbook on the physics of magnetic phenomena is totally based on quantum mechanics. Nevertheless, when we look at a huge electromagnet hoist-

ing up a car (such pictures are often shown in textbooks and science-popularizing books on magnetism), it is difficult to imagine that magnetism is a quantum phenomenon. Of course, any classification of macroscopic phenomena into quantum and classical phenomena is arbitrary, although we understand intuitively which of these phenomena must be regarded as classical. For example, the properties of gases are very well described by classical statistical physics. The characteristics of atoms or molecules of which gases are composed serve as the "initial conditions of the problem" and are taken as initial data, and calculations are carried out in accordance with the laws of classical physics. When we deal with a paramagnetic gas, we can assume that atoms possess microscopic magnetic moments  $M_a$ , neglect space quantization, and calculate the magnetic moment per unit volume by using the formulas of classical statistical physics. This gives us for the classical value of the paramagnetic susceptibility

$$\chi_{\text{cl}} = \frac{NM_a^2}{3kT} \quad (2.15)$$

(See Problem 13.)

One must keep in mind that the atomic magnetic moment has a quantum origin. This is seen, in particular, in the fact that  $M_a \approx e\hbar/m_e c$  is proportional to Planck's constant  $\hbar$ . The formal transition to classical physics occurs when  $\hbar$  tends to zero.\* As a result of this operation both

\* The diamagnetic moment also tends to zero as  $\hbar \rightarrow 0$  because the size of the atom vanishes together with  $\hbar$  ( $a \approx \hbar^2/m_e e^2$ ).

the paramagnetic moment and magnetic susceptibility  $\chi_{cl}$  also tend to zero.

A rigorous and consistent use of the formulas of classical statistical physics makes it possible to establish that whatever the interactions between particles, their total magnetic moment in the state of thermal equilibrium vanishes even if the particles are charged and placed in an external magnetic field.\* This astonishing fact occurs because the Lorentz force (2.10) produces no work (see Problem 14) and thus leaves the energy of a particle unaltered, while the equilibrium properties of particles are determined by their distribution over energy.

The general result of classical statistical physics, formulated above, emphasizes once again the limitations involved in deriving formula (2.13). If we acted consistently, the result would be zero.

To conclude this subsection, we want to write again the formula for the diamagnetic susceptibility (2.13), replacing  $\sum r_i^2$  with the square of the Bohr radius  $a^2 = (\hbar^2/m_e e^2)^2$ , and the number of atoms per unit volume,  $N$ , with the quantity  $1/a^3 = (m_e e^2/\hbar^2)^3$ . This last substitution signifies that we consider a body in a state of condensation, with the distance between atoms being of the order of the atomic size.

The result of the substitution is

$$|\chi_{dia}| \approx \frac{1}{6} \left( \frac{e^2}{\hbar c} \right)^2 \approx \frac{1}{6} \left( \frac{1}{137} \right)^2 \quad (2.16)$$

\* Of course, we cannot assume here that the particles have an intrinsic (spin) magnetic moment. We have already emphasized that the existence of spin and spin magnetic moment constitutes a purely quantum effect.

that is, the smallness of the diamagnetic susceptibility is a corollary of the smallness of the charge. We remind the reader that  $e^2/\hbar c$  is the dimensionless squared charge (see pp. 15-16).

## 2.4. Metals. Pauli Paramagnetism

Our starting point in studying paramagnetism and diamagnetism was that materials consist of atoms (or ions) and molecules. But there exist a very wide and very important class of substances, namely metals, consisting of ions and electrons. A metal is an ionic lattice embedded in a "sea" of electron gas. This notion, that at first glance seems extremely primitive, proves quite correct under a serious analysis. Furthermore, this notion can be simplified. We can forget the ions that don't let the electrons leave the metal\* and assume that electrons are in a metal sample as if in a box, one or several electrons per atom; the interaction between electrons can be neglected because on the average the repulsive forces are cancelled out by the forces of attraction to ions. The electrons that broke away from ions are called *free electrons*, or *conduction electrons*.

Of course, this is a simplified model. It is called the *Drude-Lorentz model*. Despite its ultimate simplicity, this model proved possible, after Sommerfeld had introduced the ideas of quantum statistics into it, to explain many properties of metals, and the results obtained in this frame-

\* To ask who restrains whom would, of course, be meaningless. Electrostatic repulsive forces would push ions away unless electrons compensated for these forces.

work are often in a good agreement with experimental data.

At the first glance, a metal must always be paramagnetic. Indeed, electrons represent a typical gas of magnetic needles. The number of electrons  $N_e$  per unit volume is tremendous:  $N_e \approx 10^{22}\text{--}10^{23} \text{ cm}^{-3}$ . On the atomic scale the magnetic moment of each electron is also very large, that is, equal to the Bohr magneton. True, the ions of the metal (they cannot be completely ignored) must be diamagnetic because after the separation of valence electrons their electron shells are much like the electron shells of the atoms of inert gases (the metals of transition elements, and the metals of the iron group among them, constitute an exception; we shall discuss them later). It seems that the diamagnetism of ions cannot overpower the paramagnetism of conduction electrons. Nevertheless, diamagnetic metals exist as well.

There is another fact that does not allow us to extend directly the conclusions obtained in analyzing the gas of magnetic needles to conduction electrons: the magnetic susceptibility of metals is practically independent of temperature.

What is the reason then? What causes the special properties of the electron gas in comparison with the classical gas of magnetic needles? The point is that the electron gas in a metal is a *quantum* gas. Quantum gases represent such an important object in the modern physics of liquid and solid states that they deserve a special subsection.

### *Fermi and Bose Gases*

We have mentioned earlier (see p. 58) that particles are divided into two classes: fermions and bosons. The difference between fermions and bosons lies in a specific quantum property due to a different behavior of the wave function under the interchange of particles. Let us try to find out when the "specific quantum properties" must manifest themselves in a gas of particles with mass  $m_a$  each. The value of the particle mass is quite important for the analysis to follow, so that we began our characterization of the gas by fixing the mass of its particles. Let the number of gas particles per unit volume be  $N$ , and the gas temperature be  $T$ . It should not be difficult to deduce that the mean distance between the particles in a gas,  $d$ , is  $N^{-1/3}$ ; it is obviously independent of temperature. According to classical physics, the mean energy of gas particles is  $\bar{\varepsilon} = (3/2)kT$ . Hence, the mean momentum is  $\bar{p} = \sqrt{3kTm_a}$ . Now let us recall the uncertainty relations (1.17). As long as the uncertainty in a physical quantity (coordinate and momentum in the present case) is small in comparison with its mean value, we can forget about the quantum properties of the system: it behaves as a classical system. But if this condition is not met, we have to analyze the system by using quantum laws.

The mean distance between particles indicates the accuracy with which the coordinate of an individual particle can be indicated, that is, it defines the uncertainty  $\Delta x$ :  $\Delta x \approx d = N^{-1/3}$ . Therefore, by virtue of the uncertainty relations (1.17) the momentum of each particle has an

uncertainty  $\Delta p$  no less than  $\hbar/d = \hbar N^{1/3}$ . As temperature decreases,  $\bar{p}$  also decreases and drops to about  $\Delta p$  at a temperature  $T_q$  such that  $kT_q = \hbar^2 N^{2/3}/m_a$ . Therefore,

at  $T \gg T_q$  a gas can be considered classical, and at  $T \lesssim T_q$  the laws of quantum mechanics must be taken into account;

$$T_q = \frac{\hbar^2 N^{2/3}}{m_a k} \quad (2.17)$$

At  $T \lesssim T_q$  the gas is said to be *degenerate* (degenerate Fermi gas if the particles of the gas are fermions, and degenerate Bose gas if they are bosons).

Let us calculate  $T_q$  for a gas of magnetic needles, for example, oxygen. Taking  $m_a = 0.5 \cdot 10^{-22}$  g (for the  $O_2$  molecule) and  $N = 2.7 \cdot 10^{19}$  cm $^{-3}$ , we obtain  $T_q \approx 10^{-3}$  K. Before its quantum properties manifest themselves, oxygen will turn into a liquid (at  $-183^\circ\text{C} \approx 90$  K) and then into a solid (at  $-219^\circ\text{C} \approx 54$  K). But in liquid and solid (nonmetallic) paramagnetic bodies the interaction between magnets becomes appreciable at low temperatures, and the model of the gas of noninteracting magnetic needles has to be dropped.

The picture is quite different if we turn to the electron gas in metals. At  $N_e \approx 10^{23}$  cm $^{-3}$  and  $m_e \approx 10^{-27}$  g,  $T_q \approx 10^5$  K (sic), that is, metals always (at any temperature) contain the quantum electron gas.

The properties of Bose gases at  $T \lesssim T_q$  will be discussed in Ch. 3. Here we are going to speak

only about the properties of Fermi gases; indeed, electrons are fermions.

Since in normal conditions the temperature  $T$  is much less than  $T_q$ , we first have to analyze the limiting case, namely, the behavior of the electron gas at  $T = 0$ .

The state of a free electron is characterized by its momentum  $\mathbf{p}$  and the projection of its spin  $s_z$

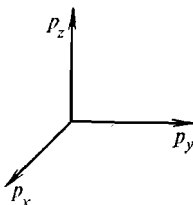


Fig. 23. Momentum space. Marked on the coordinate axes are the projections of a particle momentum

( $s_z = \pm 1/2$ ). In zero magnetic field the electron energy  $\varepsilon$  is independent of the spin direction and is determined only by momentum:

$$\varepsilon = \frac{p^2}{2m_e}, \quad \text{or} \quad p_x^2 + p_y^2 + p_z^2 = 2m_e \varepsilon \quad (2.18)$$

Let us take a Cartesian system of coordinates, with the projections of momentum marked on its axes (Fig. 23). We have "created" the *momentum space*. In this space, momentum as a function of energy (2.18) is represented by a sphere of radius  $\sqrt{2m_e \varepsilon}$ . Imagine now that the whole momentum space is divided into infinitely small cells. Each cell corresponds to a specific value of momentum  $\mathbf{p}$ . The number of states (cells)  $dN_e$  with electron momenta between  $p$  and  $p + dp$  is proportional to the volume of the spherical

layer of thickness  $dp^*$ :

$$4\pi p^2 dp \propto \sqrt{\epsilon} d\epsilon$$

(see (2.18)).

The function  $g(\epsilon) = dN_e/d\epsilon$  is called the *density of states*. A more consistent analysis makes

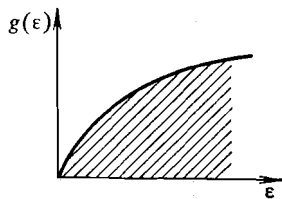


Fig. 24. Density of states of the system of free electrons

it possible to establish not only that  $g(\epsilon) \propto \sqrt{\epsilon}$  but also to calculate the proportionality factor:

$$g(\epsilon) = \frac{\sqrt{2}}{\pi^2 \hbar^3} V m_e^{3/2} \sqrt{\epsilon} \quad (2.19)$$

( $V$  is the volume of the metallic specimen). The area under the curve (2.19) (Fig. 24) determines the number of states with energy less than  $\epsilon$ . Since the Pauli exclusion principle requires that each state be occupied with only one electron, at  $T = 0$  the electrons fill up all states up to those with some maximum energy called the *Fermi energy*,  $\epsilon_F$ .

The Fermi energy is found from the condition that all  $N_e$  electrons of the metal be less than it. This means that in order to determine the Fermi

\* Because at this juncture we are interested in the number of states with a certain value of momentum, whatever its direction.

energy we have to integrate the density of states from 0 to  $\epsilon_F$  and equate it to  $N_e$ :

$$N_e = \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{2\sqrt{2}}{3\pi^2 \hbar^3} V m_e^{3/2} \epsilon_F^{3/2}$$

whence

$$\epsilon_F = \left( \frac{3\pi^2 N_e}{V} \right)^{2/3} \frac{\hbar^2}{2m_e} \quad (2.20)$$

Note that to within a numerical factor  $(3\pi^2)^{2/3}/2$  the Fermi energy  $\epsilon_F$  coincides with the quantity  $kT_F$ .

A graphic illustration of the filling of states with free electrons is obtained in the momentum

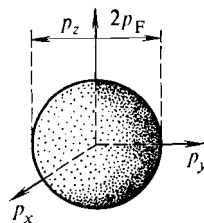


Fig. 25. At  $T = 0$  electrons fill up the states with energy less than  $\epsilon_F$ . In the momentum space these states lie within a sphere of radius  $p_F$

space: at  $T = 0$  the electrons fill in this space the sphere (the Fermi sphere) of radius

$$p_F = \sqrt{2m_e \epsilon_F} = \hbar \left( \frac{3\pi^2 N_e}{V} \right)^{1/3}$$

(Fig. 25). The radius of the Fermi sphere is  $p_F \approx \hbar/d$ , where  $d$  is the average distance between two electrons (by the order of magnitude, this distance equals the size of the crystal unit cell,  $a$ ).

We see that the motion of particles does not stop at absolute zero of temperature. The Pauli principle is "stronger" than the tendency of the

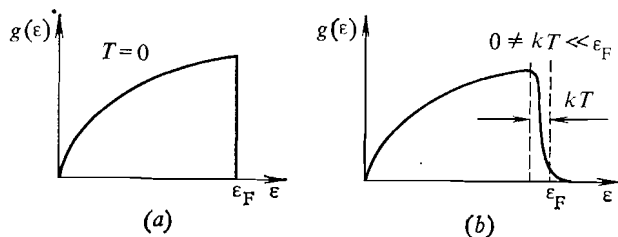


Fig. 26. Energy distribution of Fermi-gas particles at  $T = 0$  (a); the area under the curve  $g = g(\epsilon)$  ( $0 < \epsilon < \epsilon_F$ ) is equal to the number of electrons. At  $kT \ll \epsilon_F$  it departs only slightly from the distribution at  $T = 0$  (b).

system to drop to the least-energy state at  $T = 0$ . (See Problem 15.)

Figure 26a shows the distribution of gas particles over energies at  $T = 0$ . This distribution changes only slightly at a nonzero low temperature ( $T \ll T_q$ ) (Fig. 26b).

\* \* \*

Now we can return to describing the magnetic properties of conduction electrons. When the magnetic field  $\mathbf{H} \neq 0$ , the energy of electrons with spin oriented along the field is not equal to that of electrons with spin oriented against the field. By marking the direction of spin by an arrow (pointing up for the former and pointing

down for the latter), we find (see (1.28)):

$$\begin{aligned}\epsilon_{\uparrow} &= \frac{p^2}{2m_e} - \mu_B H \\ \epsilon_{\downarrow} &= \frac{p^2}{2m_e} + \mu_B H\end{aligned}\quad (2.21)$$

As before, here  $\mu_B = e\hbar/2m_e c$ .

How do the  $N_e$  electrons fill up their states (cells) in this case? Figure 27 shows the distribution of electrons over energy when the

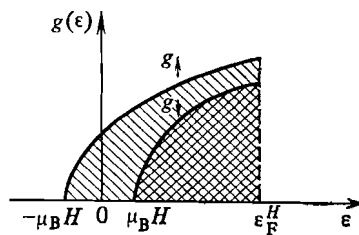


Fig. 27. Energy distribution of Fermi-gas particles in the presence of a magnetic field ( $T = 0$ ):  $g_{\uparrow}$  — density of states of electrons with magnetic moment oriented along the field;  $g_{\downarrow}$  — that of electrons with magnetic moment oriented against the field. The area under each of the curves equals the number of the respective electrons

magnetic field is switched on. Note that the levels of filling are identical for the electrons with spin along the field and for the electrons with spin against the field (both  $\epsilon_{\uparrow}$  and  $\epsilon_{\downarrow}$  are smaller than the Fermi energy in the field  $\mathbf{H}$ ,  $\epsilon_F^H$ ). If these levels were different, some electrons would "climb" to states with a different direction of spin, and the energy of the system would be lowered.

The number of electrons with spin along the magnetic field is somewhat greater than that of electrons with oppositely oriented spins,  $N_{\uparrow} > N_{\downarrow}$ , because  $\varepsilon_{\uparrow} < \varepsilon_{\downarrow}$ . As a result the electron gas is magnetized along the field, that is, it is *paramagnetic*. In order to calculate the magnetic moment of the electron gas, we have to find the difference between the numbers of oppositely oriented electrons:

$$M_e = \mu_B (N_{\uparrow} - N_{\downarrow})$$

We thus have to calculate  $N_{\uparrow}$  and  $N_{\downarrow}$ . This is not difficult if we note that the density of states with a spin in a given direction,  $g_{\uparrow}(\varepsilon)$  (or  $g_{\downarrow}(\varepsilon)$ ), differs from  $g(\varepsilon)$  only in a factor 1/2 and in the reference point for energy. A simple calculation based on that the energy  $\mu_B H$  is small in comparison with the Fermi energy  $\varepsilon_F$  at practically any achievable magnetic field  $H$  (see Problem 16) shows that

$$M_e = \mu_B^2 \left( \frac{dN_e}{d\varepsilon_F} \right)_{H=0} \cdot H$$

and the magnetic susceptibility is

$$\chi_P = \frac{3\mu_B^2}{2} \frac{N_e}{\varepsilon_F} \quad (2.22)$$

Here we have used expression (2.19).

The paramagnetism of the degenerate electron gas is called the *Pauli paramagnetism*, or *free-electron paramagnetism*.

In order to refer the magnetic susceptibility, as before, to unit volume, assume that  $N_e$  is the number of conduction electrons per  $1 \text{ cm}^3$ .

Comparing (2.22) with classical formula (2.15), we notice that the main difference lies in  $kT$  being replaced with  $\varepsilon_F$ . Since always  $\varepsilon_F \gg kT$ , it is clear that taking into account the quantum effects (the Pauli principle) has significantly diminished the value of the paramagnetic susceptibility as compared with its classical value. Owing to degeneracy of the properties of electron gas, temperature is not as important a factor as in classical gases. In particular, the Pauli paramagnetic susceptibility is practically independent of temperature. The paramagnetic susceptibility of the Fermi gas is of the same order of magnitude as the diamagnetic susceptibility of a liquid or a solid. (See Problem 17.)

## 2.5. Metals. Landau Diamagnetism

In describing diamagnetism, we attempted to persuade the reader that diamagnetism is a general phenomenon in nature. Is then the electron gas an exception? This suspicion is based on the following "arguments". We have emphasized that the derivation of the formula for the diamagnetic susceptibility (2.13) was based on two starting points: the Larmor theorem and the stability of orbits. Free electrons have no stable orbits and are not subject to the Larmor theorem. Nevertheless, the electron gas possesses both the paramagnetic and *diamagnetic* susceptibility, the so-called *Landau diamagnetism*. It is fairly difficult to derive the formula for the diamagnetic susceptibility of the electron gas, so that we

simply give it here:

$$\chi_L = -\frac{1}{3}\chi_P \quad (2.23)$$

How does it happen that the electron gas has diamagnetism? Free electrons have no discrete

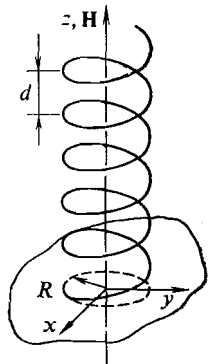


Fig. 28. An electron in the magnetic field  $\mathbf{H}$  moves along a helix of radius  $R = mc v_{\perp} / |e| H$ , the pitch of the helix (along the magnetic field) being equal to

$$d = v_z / \omega_c = mc v_z / |e| H$$

$$v_{\perp} = \sqrt{v_x^2 + v_y^2}$$

stationary states at  $\mathbf{H} = 0$ , but they appear at  $\mathbf{H} \neq 0$ . It is said that

*the motion of electrons in a magnetic field is quantized.*

The nature of the quantized motion of electrons in a magnetic field is simple. The Lorentz force (1.20) makes the electron revolve around  $\mathbf{H}$  at a vibration frequency  $\omega_c = eH/mc^*$  (Fig. 28).

\* This is the frequency at which electrons revolve in a cyclotron, hence, the name of the *cyclotron frequency*. Note that  $\omega_c = 2\omega_L$ , where  $\omega_L$  is the Larmor precession frequency. The Larmor theorem (see p. 113) does not hold for the motion of free electrons because in this case the Lorentz force cannot be treated as a small perturbation. There is no other (strong) force in comparison with which the Lorentz force is weak.

Moreover, the electron obviously has to move along the field. This last motion is not affected at all by the Lorentz force. The energy of the electron is the sum of the energies of motion along the field and in a plane perpendicular to the field. Let us look at the motion of the electron in a plane perpendicular to the magnetic field. The word "look" must be treated here literally rather than in its metaphorical meaning. Namely, if we look at the rotating electron sideways, we notice that it vibrates at the cyclotron frequency  $\omega_c$  (see Fig. 28). This is not merely a verbal analogy. The formulas describing the motion of the electron in a plane perpendicular to the magnetic field reduce to the formulas describing the vibrations of a particle. And you already know that a particle vibrating at a frequency  $\omega$  is allowed to have only discrete energy levels  $\varepsilon_n = \hbar\omega (n + 1/2)$  ( $n = 0, 1, 2, \dots$  are integers) (see p. 40).

Please reread the last paragraph. We think that now you are not going to be very surprised to find that

*the energy of motion of an electron in a magnetic field can assume only the following values:*

$$\varepsilon = \hbar\omega_c \left( n + \frac{1}{2} \right) + \frac{p_H^2}{2m_e}, \quad n = 0, 1, 2, \dots \quad (2.24)$$

where  $p_H$  is the projection of momentum  $\mathbf{p}$  onto  $\mathbf{H}$ .

If the intrinsic magnetic moment of the electron is taken into account, the levels (2.24) split into



two systems of levels:

$$\varepsilon_{\uparrow} = \left(n + \frac{1}{2}\right) \hbar \omega_c + \frac{p_H^2}{2m_e} - \mu_B H$$

$$\varepsilon_{\downarrow} = \left(n + \frac{1}{2}\right) \hbar \omega_c + \frac{p_H^2}{2m_e} + \mu_B H$$

We already know the result of this splitting, and this is the Pauli paramagnetism. Hence, for the time being, we are going to ignore it.

When the energy levels of electrons (2.24) are known, it is possible to calculate their magnetic moment and then the magnetic susceptibility of the electron gas. If the magnetic moments of electrons are not taken into account, the electron gas is diamagnetic, with

$$\chi_L = -\frac{1}{12} \frac{e^2 \hbar^2}{m_e^2 c^2} \frac{N_e}{\varepsilon_F} = -\frac{1}{3} \chi_P$$

But if we consider both the diamagnetism and the paramagnetism of the electron gas, we arrive at the formula for the net magnetic susceptibility (see formula (2.22)):

$$\chi_e = \chi_P - \frac{1}{3} \chi_P = \frac{2}{3} \chi_P = \mu_B^2 \frac{N_e}{\varepsilon_F} \quad (2.25)$$

It is positive, that is, the paramagnetism is predominant. How can we explain the fact that certain metals are diamagnetic? Of course, the ion skeleton of the metal is also there, and it is diamagnetic (see above); its susceptibility must be subtracted from  $\chi_e$ . And since  $\chi_e$  is numerically small, the sign of the magnetic susceptibility of a metal can be either positive or negative. However, this argument (though it is quite

correct) cannot explain why a number of metals (such as bismuth) are highly diamagnetic.

The magnetic properties of the electron gas find their complete explanation if we take into account another fact not included in the Drude-Lorentz-Sommerfeld model. Conduction electrons move not in "vacuum" but in a field of forces created by the ions of the crystal lattice. The study of the motion of electrons in a periodic field of the lattice is the subject of a special chapter of quantum physics of solid state: the *band theory*. One of the conclusions of this theory states: in certain cases the motion of an electron through a lattice can be considered quasifree\* and the ordinary electron mass  $m_e$  must be replaced in expression (2.18) with the effective mass  $m^*$ , that is, we assume that

$$e = \frac{p^2}{2m^*} \quad (2.26)$$

The difference between the effective and the ordinary mass takes into account the interaction between an electron and lattice ions.

What is the effect of the replacement  $m_e \rightarrow m^*$  on the formulas given above? The Bohr magneton  $\mu_B$  is not affected by this replacement (the intrinsic magnetic moment of the electron is a characteristic as "private" as the electron charge  $e$ , and neither of them is related to the motion of

\* Adding the prefix "quasi" (from the Latin *quasi* for as if, almost) sometimes is a method of "and none will be the wiser". The best interpretation of the prefix "quasi" would be: "All is not as simple as the authors make you believe in the text" (see M. I. Kaganov, *Electrons, Photons, Magnons*, Mir Publishers, Moscow, 1981; see also Sec. 3.8).

the electron through a lattice\*), so that we readily obtain from (2.22) and (2.25) that

$$\chi_e = \left[ 1 - \frac{1}{3} \left( \frac{m_e}{m^*} \right)^2 \right] \chi_P, \quad \chi_P = \frac{3}{2} \frac{\mu_B^2 N_e}{\varepsilon_F^*}, \quad (2.27)$$

$$\varepsilon_F^* = \left( \frac{3\pi^2 N_e}{V} \right)^{2/3} \frac{\hbar^2}{2m^*}$$

The effective electron mass can be less than the "true" electron mass and sometimes, however paradoxical it may sound, much less. Such metals can only be diamagnetic. This explains why bismuth is highly diamagnetic.

## 2.6. Superconductors: Ideal Diamagnetics

If we try to put the gist of our story of the Landau diamagnetism in a "nutshell" and formulate the causes of this phenomenon, then we obtain the following residue: diamagnetism arises because electrons rotate around magnetic lines of force. And it is obvious that calculations must be carried out in the framework of quantum mechanics: indeed, we deal with the motion of microscopic particles, namely, electrons.

Each conduction electron moves independently of others. In a certain sense, it is a spurious coin-

\* This statement is rather too strong: the interaction of the intrinsic magnetic moment of electrons with the orbital magnetic moment of electrons and ions (the so-called *spin-orbit interaction*, or *coupling*) is important in some conductors. The spin-orbit interaction changes the intrinsic magnetic moment of the electron. Moreover, the electron magnetic moment feels the interaction with other electrons. This can also change the value of  $\mu_B$ . The essential thing is that  $\mu_B \neq eh/2m^*c$ , so that in all cases  $\chi \neq (2/3)\chi_P$ .

cidence that the cyclotron frequency  $\omega_c = eH/m_e c$  is identical for all electrons. In a more rigorous theory that takes into account the field of ions this property is not preserved: the rate of rotation of an electron depends on its energy and on the projection of its momentum onto the magnetic field. This somewhat changes the quantization formulas, thereby changing the value of the diamagnetic susceptibility.

But is it possible for electrons to rotate around the magnetic field as a whole, say, to flow as water in a rotating vessel? Of course, it is impossible in normal conditions. A coherent rotation of electrons means that a macroscopic current flows through a conductor. However, the conductor must thereby get warmer, and the current must damp out. The magnetic field that induced this motion when it was switched on cannot sustain the current because it does no work. Therefore, the motion of electrons cannot be coherent.

But ... there always exist exceptions to rules. And these exceptions invariably only confirm the rules, provided we find out what made the exceptions possible. Most of the metals transform, at very low temperatures (in the vicinity of absolute zero), into a peculiar *superconducting state*\* characterized by zero resistance. Metals in superconducting state are called *superconductors*.

\* To date the material with the highest temperature of superconducting transition is the alloy  $Nb_3Ge$ . It equals 23 K. When preparing the book for publication, we left blank spaces for the name of the material and for the record-high transition temperature. The search for high-temperature superconductors never ends. The above-mentioned alloy was discovered in 1973.

They have already been mentioned in the first section of the present chapter.

The current that flows through a superconductor is indeed not damped out. Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes in the course of measuring the conductivity of mercury; and for many years the factors causing the creation of the superconducting state remained a puzzle. Only 46 years later (in 1957) John

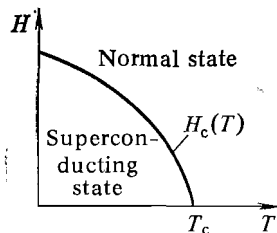


Fig. 29. Phase diagram of a superconductor. The curve  $H = H_c(T)$  separates the normal state from the superconducting state

Bardeen, Leon Cooper, and John Schrieffer were able to construct the microscopic theory of this unique phenomenon. Unfortunately, here it would be impossible to speak about superconductivity in detail. The reader will have to accept a statement: a current flowing through a superconducting circuit is not damped out. What then are the consequences for the magnetic properties of these materials?

Electrons become capable of completely pushing out the magnetic lines of force from the bulk of the metal. For this to happen, a current must flow on the surface of a superconductor, producing a magnetic moment  $\mathcal{M}$  directed oppositely to the magnetic field and equal to  $-(1/4)\pi\mathcal{H}V$ . Hence, in a superconductor  $\mathbf{B} = \mathbf{H} + 4\pi\mathcal{M} = 0$ ,

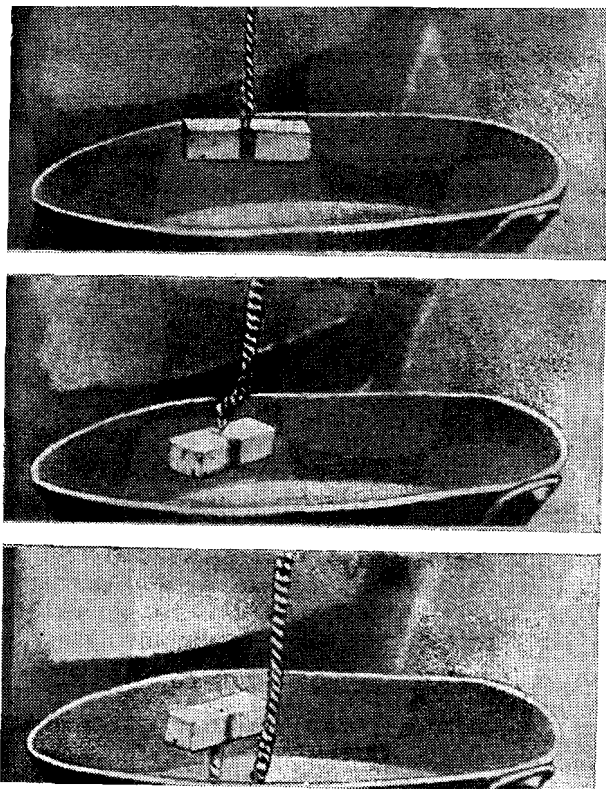


Fig. 30. Magnetic cushion. A magnet hovers over a superconducting plate

so that

*a superconductor is an ideal diamagnetic material.*

We chose to write "electrons are capable of", "current *must* flow along the surface". These are rhetorical expressions. But the situation in superconductors placed in a magnetic field is precisely this: a surface current appears, and the magnetic lines of force are thereby pushed out of the bulk of the superconductor. This is the so-called *Meissner effect*. The magnetic field is repelled because this is energetically favorable: the energy of a metal is lower at  $\mathbf{B} = 0$  than at  $\mathbf{B} \neq 0$ . (Strictly speaking, the current in a superconductor flows not along the surface but in the subsurface layer with thickness  $\delta \approx 10^{-5}$  cm.)

One more remark must be made: the behavior of superconductors described above is observed in relatively weak magnetic fields. A strong magnetic field destroys superconductivity: it causes the metal to switch to the normal (non-superconducting) state. Figure 29 shows the diagram of state of a superconductor. You see the boundary for the existence of the superconducting state.

The repulsion of the magnetic field from a superconductor is clearly demonstrated by hovering of a magnet over the superconductor (Fig. 30). (See Problem 18.)

## Chapter 3

### Ferromagnetism

Some of the solids are such that they are magnetized *spontaneously*, by virtue of internal forces, and thus can serve as macroscopic sources of a magnetic field. These are *ferromagnetic materials*, or simply *ferromagnetics*. Ferromagnetism exists not at all temperatures. As temperature increases, the intrinsic spontaneous magnetic moment of a body decreases and vanishes at a certain temperature  $T_c$ , called the *Curie temperature* (of course, if the external magnetic field is zero, that is,  $\mathbf{H} = 0$ ). Above the Curie temperature ferromagnetic materials<sup>u</sup> become paramagnetic.

*At high temperatures all ferromagnetic materials are paramagnetic, but not all paramagnetic materials are ferromagnetic at low temperatures.*

Different materials have different values of the Curie temperature  $T_c$  and of the spontaneous magnetic moment density  $\mathcal{M}_s$  (at  $T \rightarrow 0$ ) (see Table 5).

Table 5

Material	Fe	Co	Ni
$\mathcal{M}_s$ , erg/gauss	1735	1445	509
$T_c$ , K	1043	1403	631

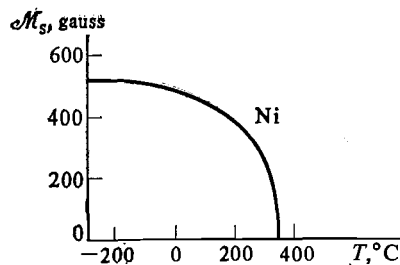


Fig. 31. Spontaneous magnetic moment density of Ni as a function of temperature

Figure 31 plots the temperature dependence of the spontaneous magnetic moment density  $\mathcal{M}_s(T)$  of nickel.

### 3.1. Self-Ordering of Atomic Magnets

The analysis of physical systems consisting of a macroscopic number of interacting particles is one of the most complicated problems in quantum physics. Although sufficiently general approaches to solving such problems are available, no single recipe is known. In each concrete case it is necessary to develop a more or less adequate model by simplifying the problem so that it allows for a consistent mathematical solution.

A comparison with experimental data and evaluation of neglected terms make it possible to establish the range of validity of the model. Quite often the model describes the situation "in general", while departing from the truth in finer details.

This brief introduction is meant as a warning

to the reader: what we present in this section is a simplified model of ferromagnetism, a model reflecting the behavior of the system but not aspiring to give a detailed description. It is called the *self-consistent field model*. This term took root after the model had been found fruitful in various domains of the physics of condensed

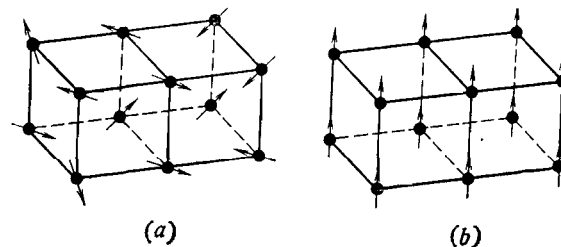


Fig. 32. A crystal composed of paramagnetic atoms: (a) temperature  $T$  above the Curie temperature  $T_C$ ; (b)  $T = 0$ , all moments point in the same direction

matter. When applied to ferromagnetism, it is called the *Curie-Weiss model* because it explained the origin of the Curie-Weiss law (see pp. 94-95, formula (2.2)).

Let us start with postulating the existence of a gas of magnetic needles; indeed, as we have said above, all ferromagnetic materials are paramagnetic at high temperatures. We suggest that the reader imagine a crystal in each of whose lattice sites there is an atom equipped with an arrow representing the magnetic moment (Fig. 32).

In order to avoid cumbersome calculations, we assume that  $J = 1/2$ ,  $g = 2$ , and  $m_J$  assumes

two values:  $+1/2$  and  $-1/2$ ; the magnetic moment of each individual atom equals the Bohr magneton  $\mu_B$ . This is not the simplification mentioned above. This simplification is easily replaced with the model of a magnetic-needles gas with an arbitrary angular momentum  $\mathbf{J}$  of each individual magnet.

In most cases it is assumed that the magnetic moments of the atoms that comprise a ferromagnetic body are of spin, not of orbital, origin. But why? What makes a theorist ignore the orbital magnetic moment?

Electrons in an atom move in a field with central symmetry; consequently, their angular momentum is conserved and can be used as a characteristic of the stationary state of the atom. The field of forces in a solid in which electrons move is not centrally symmetric, so that the angular momentum is not conserved, and other physical quantities have to be used to characterize this motion (we cannot go into details here). The spin of an atom is only weakly related to the orbital motion of electrons. Thus it can be regarded as a "good" quantum number. The spin-spin interaction as well as the interaction between spins and the orbital motion of electrons only orient the atomic spins in space, without changing the quantity of each atomic spin. The change would involve a large loss of energy and its probability is therefore very low (see p. 106). These are the arguments that make it possible to operate in terms of the gas of magnetic needles, *with the magnetic needle interpreted as the spin magnetic moment of an atom.*

The Curie-Weiss model consists in a *simplifying assumption* that magnetic moments are ordered

not only by an external magnetic field  $\mathbf{H}$  but also by the cumulative action of all magnetic moments; this assumption *reduces* to replacing the magnetic field  $\mathbf{H}$  with an effective self-consistent field\*:

$$\mathbf{H}_{\text{eff}} = \mathbf{H} + \alpha \mathcal{M} \quad (3.1)$$

We shall do our best to substantiate this expression in the next section, but for the Curie-Weiss model formula (3.1) is fundamental. The constant  $\alpha$  must be related to the observed quantities and thus must be found experimentally.

Using formulas (2.8) and (3.1), we find a transcendental equation for determining the magnetic moment density  $\mathcal{M}$  of the ferromagnetic (the Curie-Weiss equation):

$$\mathcal{M} = N\mu_B \tanh \frac{\mu_B (H + \alpha \mathcal{M})}{kT} \quad (3.2)$$

where  $N$  is the number of atoms per unit volume.

The rest of this section is devoted to analyzing this equation and its solutions.

We begin with the principal point: finding out whether the Curie-Weiss equation describes ferromagnetism, that is, the appearance of spontaneous (in zero external magnetic field) magnetization  $\mathcal{M}_s$ . To achieve this, let us analyze the solution of equation (3.2) at  $H = 0$ :

$$\mathcal{M}_s = N\mu_B \tanh \alpha \frac{\mu_B \mathcal{M}_s}{kT} \quad (3.3)$$

We denote

$$x = \alpha \frac{\mu_B \mathcal{M}_s}{kT}, \quad b = \frac{kT}{\alpha \mu_B^2 N}$$

\* This is indeed a fundamental simplification. We shall discuss it later.

It is readily seen that in these notations equation (3.3) can be rewritten in the form

$$bx = \tanh(x) \quad (3.3')$$

convenient for graphical analysis. Look at Fig. 33. You notice that in the case  $b > 1$  the equation has a single solution,  $x = 0$ , and in the case

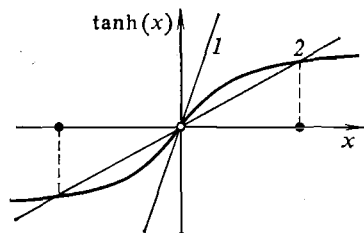


Fig. 33. Graphical solution of the Curie-Weiss equation (3.3):

1—straight line with slope  $b$  greater than unity; 2—straight line with slope  $b$  less than unity. The points on the abscissa axis are the roots of equation (3.3)

$b < 1$  there are three solutions. The inequality  $b > 1$  means that  $T > \alpha(\mu_B^2 N/k)$ . If  $\alpha > 0$ , then, by virtue of equation (3.3), the spontaneous magnetization is zero ( $\mathcal{M}_s = 0$ ) at high temperatures. It is natural to regard the quantity  $\alpha(\mu_B^2 N/k)$  as equal to the Curie temperature  $T_c$  because the spontaneous magnetization vanishes precisely at  $T = T_c$ . Thus

$$\alpha \frac{\mu_B^2 N}{k} = T_c$$

Actually, we have yet to check whether equation (3.2) describes the paramagnetism of the magnetic-

needles gas at  $T > T_c$ . So far we keep in mind that  $\alpha > 0$ .

But what does it mean that there are three solutions at  $T < T_c$ ? Obviously, we have to choose one of them. What should our criterion be? The answer is: the solution  $\mathcal{M}_s = 0$  is unstable and thus cannot be realized, while the

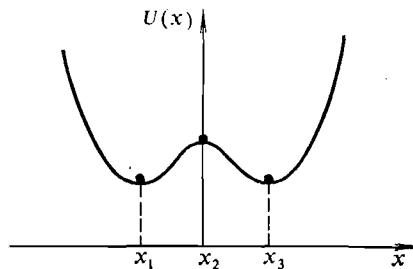


Fig. 34. Potential energy of a particle: the force acting on the particle becomes zero at points  $x_1$ ,  $x_2$ , and  $x_3$ ; at points  $x_1$  and  $x_3$  the particle is in a stable equilibrium, and at  $x_2$  it is in an unstable equilibrium

nonzero solutions ( $\mathcal{M}_s \neq 0$ ) are stable. Only one of them is realized. So far we need not worry which one of the two: they differ only in the direction of the vector  $\mathcal{M}_s$ , and we are interested in the magnitude of this vector.

If we dealt with a single particle, the stable and unstable states could be illustrated with the curve of potential energy  $U$  as a function of the  $x$ -coordinate. Let the potential energy have the form shown in Fig. 34. The force acting on the particle equals zero at three points, where  $U(x)$

reaches extrema:

$$x_1 = -x_3 \neq 0, \quad x_2 = 0$$

But the position of the particle is stable only at  $x_1$  and  $x_3$  (at which  $U(x)$  reaches minima). From the point  $x_2 = 0$  (where  $U(x)$  reaches the maximum) the particle slides down after any arbitrarily small perturbation.

Statistical physics formulates a strict rule that makes it possible to distinguish between the stable and unstable solutions of the Curie-Weiss equation. This rule is very similar to that given above. We have to find the value of  $\mathcal{M}_s$  at which a certain quantity called the *free energy* reaches a minimum. The free energy differs from the conventional energy in that it takes into account the number of ways in which a given macroscopic state with a given energy can be created. The state that can be realized in the maximum number of ways is stable. And the free energy is shown to reach the *maximum* at  $\mathcal{M}_s = 0$  if  $T < T_c$ .

Now let us clarify the dependence of  $\mathcal{M}_s$  on temperature at  $T < T_c$ . We begin with the range of temperatures in close vicinity of the Curie temperature ( $T \lesssim T_c$ ). At  $T = T_c$  the magnetic moment density  $\mathcal{M}_s = 0$ . Obviously, at  $T \approx T_c$  the magnetic moment is very small. We can therefore use an approximation for  $\tanh x$ :

$$\tanh x \approx x - \frac{1}{3}x^3, \quad x \ll 1$$

Substituting this expression for  $\tanh x$  into (3.3'), we find that  $x$  factors out and can be reduced (we are not interested in the zero solu-

tion), and the nonzero solution  $|x|$  is:

$$|x| = \sqrt{3(1-b)}$$

Now we have to restore the physical variables:

$$\mathcal{M}_s = N\mu_B \sqrt{3\left(1 - \frac{T}{T_c}\right)} \quad (3.4)$$

Note that when writing the factor in front of the radical we have replaced  $T$  with  $T_c$ . This replacement is dictated by the approximation for  $\tanh x$ .

At temperatures much lower than the Curie temperature ( $T \ll T_c$ ) we have to use an approximation for  $\tanh x$  at large values of  $x$ :

$$\tanh x \approx 1 - 2e^{-2x}, \quad x \gg 1$$

and obtain

$$\mathcal{M}_s = N\mu_B \left(1 - 2e^{-\frac{2T_c}{T}}\right), \quad T \ll T_c \quad (3.5)$$

The approximation used above required that we replaced the quantity  $\mathcal{M}_s$  in the exponential with its value at  $T = 0$  ( $\mathcal{M}_s|_{T=0} = N\mu_B$ ).

We find that the Curie-Weiss equation describes the total magnetization of a ferromagnetic material at  $T = 0$ : all magnetic moments align parallel to one another and  $\mathcal{M}_s = N\mu_B$ . As the temperature increases, the magnetic moment density diminishes, and at the moment when it vanishes, at  $T = T_c$ , the derivative  $d\mathcal{M}_s/dT$  tends to infinity.

A comparison of formulas (3.4) and (3.5) with Fig. 31 shows that in general features they give a faithful description of the temperature dependence  $\mathcal{M}_s(T)$ . The standard expression used in scientific publications for such situations is:



"The theory and experiment are in qualitative agreement." The word "qualitative" underlines that the author does not guarantee quantitative agreement. In our particular case the *quantitative* disagreement between experimental results and the theory is especially well pronounced at low temperatures: at  $T \ll T_c$  the spontaneous magnetic moment tends to saturation  $\mathcal{M}_s|_{T=0} = N\mu_B$  much slower than is predicted by formula (3.5).

We shall discuss a more careful comparison later, and now want to calculate the magnetic susceptibility of a ferromagnetic material above and below the Curie temperature. When calculating the magnetic susceptibility, we have to assume that the magnetic field  $H$  is infinitely small.\* At  $T > T_c$  the infinitely small magnetic field corresponds to infinitesimal magnetic moment density. Therefore,

$$\tanh \left[ \frac{\mu_B (H + \alpha \mathcal{M})}{kT} \right]$$

in equation (3.2) can be replaced with its argument, that is,

$$\mathcal{M} = \frac{N\mu_B^2 (H + \alpha \mathcal{M})}{kT}$$

or

$$\mathcal{M} = \frac{N\mu_B^2}{k(T - T_c)} H, \quad T > T_c, \quad H \rightarrow 0$$

\* The formal definition of the magnetic susceptibility  $\chi$  is the derivative  $d\mathcal{M}/dH$  at  $H \rightarrow 0$ . This definition of  $\chi$  coincides with the one used above when magnetization is a linear function of  $H$ .

whence

$$\chi = \frac{N\mu_B^2}{k(T - T_c)} \quad \text{at } T > T_c \quad (3.6)$$

and we find that the Curie-Weiss law indeed follows from the Curie-Weiss equation, that is, the self-consistent field model correctly describes the paramagnetic state of ferromagnetic materials at  $T > T_c$ .

The situation is somewhat more complicated at  $T < T_c$  because at temperatures below the Curie temperature we have both the spontaneous magnetic moment  $\mathcal{M}_s(T) = \mathcal{M}(T, H = 0)$  and the induced moment proportional to  $H$ :

$$\mathcal{M}(T, H) = \mathcal{M}_s(T) + \chi H, \quad \mu_B H \ll kT$$

Both terms are very small in the direct vicinity of the Curie temperature and when  $H$  tends to zero, so that we can use an approximate value of the hyperbolic tangent. Simple algebraic manipulations yield the following expression:

$$\chi = \frac{N\mu_B^2}{2k(T_c - T)} \quad \text{at } T \leq T_c \quad (3.7)$$

Figure 35 plots  $\chi$  as a function of temperature. Note that if temperature is counted off the Curie temperature, then  $\chi$  on the left (at  $T \leq T_c$ ) is twice as small as at the same distance from  $T_c$  on the right (at  $T \geq T_c$ ). (See Problem 19.)

Let us enumerate the conclusions that can be drawn (and that we have already drawn) from an analysis of the solution to the Curie-Weiss equation.

1. The assumption on the existence of an internal field proportional to magnetization ( $\alpha > 0$ ) enabled us to explain the appearance of intrinsic magnetization at  $T < T_c$ .

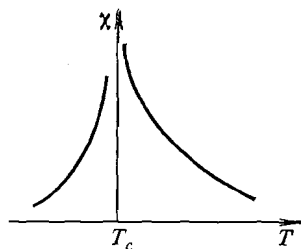


Fig. 35. Temperature dependence of the magnetic susceptibility of a ferromagnetic material,  $\chi$ , in the vicinity of the Curie temperature  $T_c$

2. The parameter  $\alpha$  introduced into the theory makes it possible to determine the Curie temperature:  $kT_c = \alpha\mu_B^2 N$ . Since

$$\mu_B N = \mathcal{M}_s|_{T=0} = \mathcal{M}_{s0}$$

we find  $\alpha = kT_c / \mu_B \mathcal{M}_{s0}$ . The parameter  $\alpha \gg 1$ . This can be verified by using Table 5 (see p. 141) and the value of the Bohr magneton  $\mu_B$ .

3. The magnetic moment diminishes as the temperature increases and

$$-\left. \frac{d\mathcal{M}_s}{dT} \right|_{T=T_c} = \infty$$

4. The magnetic susceptibility increases as the temperature approaches the Curie temperature and tends to infinity at  $T = T_c$ . At  $T \rightarrow 0$ , the magnetic susceptibility  $\chi$  becomes exponentially small (see Problem 20); at  $T > T_c$  the Curie-Weiss equation yields the Curie-Weiss law,

### 3.2. Ferromagnetism as a Result of Exchange Forces

Let us analyze again the Curie-Weiss model. Obviously, its quintessence lies in the relationship between the effective field  $H_{\text{eff}}$  and the magnetic moment density. By virtue of our assumption, this relationship covers the interaction between atomic magnetic moments. But where did we take expression (3.1)? Of course, we could avoid posing this question. We could take this formula "out of the head", analyze its corollaries (and this we have already done), show the constants ( $\alpha$ ,  $N\mu_B$ ) in the equation can be related to the quantities found experimentally ( $T_c$ ,  $\mathcal{M}_{s0}$ ), make sure that the predicted temperature dependence of  $\mathcal{M}_s$  agrees with experimental data, and leave it at that. But then we have to understand clearly that the theory thus constructed is not microscopic but *phenomenological*, that is, a descriptive theory: one describing a phenomenon but not explaining it. We have to realize that we are ignorant of the origin of the principal expression (in the present case (3.1)) and do not know the nature (the physical meaning) of the factor  $\alpha$  and how it is related to microscopic atomic magnets and to the interaction between them.

The purpose of the present section is to clarify the physical meaning of the Curie-Weiss model.

Let us go back to p. 143. The arrows representing atomic magnetic moments are aligned parallel to one another owing to the interaction between them, while the thermal motion tends to disrupt the ordering. What are the forces acting between

atomic magnets? Much was said about it in the first chapter (see Sec. 1.10), and we have established that

*at atomic distances the exchange forces are much stronger than the magnetic-dipole forces.*

For this reason the forces responsible for ferromagnetism are precisely the exchange forces. In order to demonstrate this, let us make use of the spin Hamiltonian (1.39) that we can generalize by assuming that the exchange interaction acts between any two atoms of a crystal:

$$\mathcal{H}_S = \bar{E} - \sum_{i,k} A_{ik} \mathbf{s}_i \cdot \mathbf{s}_k \quad (3.8)$$

Summation is carried out over all atoms of the crystal, with the subscripts  $i$  and  $k$  enumerating its atoms. Now let us recall what we have said about the dependence of  $A$  on interatomic distance: exchange integrals  $A_{ik}$  rapidly diminish with distance. Therefore, although formally each atom of the crystal is coupled by the exchange interaction to all atoms, only the coupling between neighboratoms is significant. This argument enables us to rewrite expression (3.8) as follows:

$$\mathcal{H}_S = \bar{E} - \frac{1}{2} A \sum_i \mathbf{s}_i \cdot \sum'_k \mathbf{s}_k \quad (3.8')$$

The second summation symbol is primed to indicate that the summation over  $k$  takes into account only the neighbors closest to the  $i$ th atom.

Figure 36 illustrates that the number of nearest neighbors is six in a primitive cubic lattice, and eight in a body-centered lattice (we shall discuss

only cubic lattices). The exchange integral is factored out of the sum because the sample is uniform, so that all exchange integrals are identical; the factor  $1/2$  appears because each atom is counted twice in this summation.

Of course, the vectors  $\mathbf{s}_i$  and  $\mathbf{s}_k$  are "quantum" vectors. Each of them can orient in space in

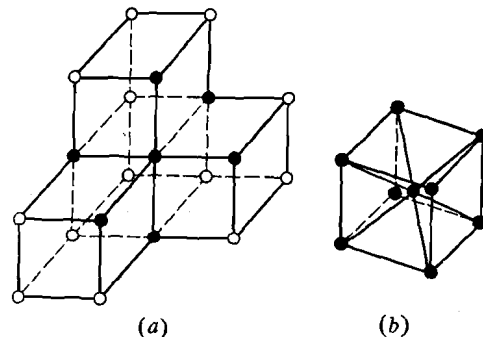


Fig. 36. Nearest neighbors of a lattice atom: (a) six neighbors in a primitive cubic lattice; (b) eight neighbors in a body-centered cubic lattice

$2s + 1$  ways. If  $s = 1/2$ , the vectors can orient either along or against... The choice of quantization axis, that is, the direction relative to which the spins are oriented, will be made later. At absolute zero of temperature all magnetic moments, and hence, all spins, are parallel to one another. At any rate, this was the corollary of the solution to the Curie-Weiss equation:  $\mathcal{M}_{s0} = N\mu_B$ . By virtue of (3.8'), when all spins are parallel to one another, the energy dependent on

the orientation of spins is

$$E_s = -\frac{zAN_s^2}{2} \quad (3.9)$$

where  $z$  is the number of nearest neighbors. At  $T = 0$  the energy of the crystal must take the lowest of all possible values. Of course, this is also true for its spin component. It is apparent that for the parallel arrangement of spins to correspond to the least energy, it is necessary for the exchange integral  $A$  to be positive:

*the condition of ferromagnetism:  $A > 0$*

When temperature is above absolute zero, magnetic moments are not so strictly disciplined: at very low temperatures only rare spins deviate from the common "correct" direction, but with increasing temperature the number of "unruly" spins increases and the net magnetic moment decreases. And finally, at a certain temperature, which is the Curie temperature  $T_c$ , all allowed directions become equally probable and the magnetic moment of a ferromagnetic material vanishes. At  $T > T_c$  this material behaves as paramagnetic material.

One should not think that the picture outlined above is static. Average numbers of "obedient" and "disobedient" spins are indeed time-independent, but if we could monitor the spin of an individual atom, we would observe that its direction constantly changes: it "points" now in one direction and then in another. This is the random (chaotic) thermal motion of spins.

At temperatures close to absolute zero the thermal motion of spins can be analyzed in

additional detail. We shall do that in Sec. 3.10.

The qualitative picture of breaking of the magnetic order, as outlined above under the assumption that the exchange interaction makes all spins align parallel to one another at absolute zero, does not enable us to derive from the spin Hamiltonian an expression for the effective field (3.1). Furthermore, this even cannot be done. In order to clarify this sad statement, we do as follows.

Let us find a relation between  $H_{\text{eff}} = \alpha \mathcal{M}_s$  (we set  $H = 0$ ) and the energy\* of the system. To achieve this, let us generalize formula (1.26) for the energy of a magnetic moment in an external field. According to this formula,  $H = -d\mathcal{E}_M/dM$  when the vectors  $\mathbf{H}$  and  $\mathbf{M}$  are parallel. In order for this formula to hold also for the effective field, we have to assume that

$$\mathcal{E}_M = -\frac{1}{2} \alpha \mathcal{M}_s^2 V \quad (3.10)$$

where  $V$  is the volume of a specimen. We remind the reader that the net moment of a ferromagnetic specimen is  $\mathbf{M} = \mathcal{M}V$ .

We see that in the Curie-Weiss model the free energy of a system is uniquely determined by magnetization. But formulas (3.8) and (3.8') show that in fact it essentially depends on the microscopic distribution of the spins of individual atoms. *It is the neglect of just this factor that constitutes the main simplification of the Curie-Weiss model, or rather, of the self-consistent field model.*

\* Specifically, the free energy if  $T \neq 0$  (see p. 148).

However, formula (3.10) is necessary to us not only for negative statements that point to our helplessness. It helps to "anchor" the Curie-Weiss model to real exchange forces that make ferromagnetism possible. For this "anchoring", let us compare formula (3.9) with (3.10) by substituting into it the value  $N\mu_B$  for the magnetic moment density  $\mathcal{M}_s$  at  $T = 0$ , and unity for  $V$  (then  $N$  denotes the number of atoms per unit volume). The two formulas coincide if we assume

$$\alpha = \frac{z}{4} \frac{A}{\mu_B^2 N} = \frac{z}{4} \frac{A}{\mu_B \mathcal{M}_{s0}} \quad \text{or} \quad kT_c = \frac{z}{4} A \quad (3.11)$$

Of course, it is this last formula that constitutes the main positive result of this section. The exchange integral  $A$  is a microscopic parameter whose value is determined by the structure of the atom and by interatomic spacings, that is, by the size of the unit cell of the crystal. Its calculation is the problem of *atomic* physics. And what we find out is that the exchange integral  $A$  determines one of the fundamental characteristics of ferromagnetic materials, their Curie temperature.

Furthermore, formula (3.11) makes possible a numerical evaluation of the parameter  $\alpha \approx A/\mu_B \mathcal{M}_{s0}$ . Recall what we said about the exchange integral in Sec. 1.10: its origin is electrostatic. Now let us evaluate the quantity  $\mu_B \mathcal{M}_{s0} = \mu_B^2 N$ . As  $A$ , it has the dimensionality of energy. And since  $N$  is the number of atoms per unit volume,  $N \approx 1/a^3$ , where, as always,  $a$  stands for interatomic distance. Consequently,  $\mu_B^2 N \approx \mu_B^2/a^3$  is the energy of the magnetic dipole-

dipole interaction. As we have shown on p. 73, this energy is much less than the energy of electrostatic interaction,  $U_{\text{Coul}}$ , and hence, than  $A$ . By virtue of these arguments (and on the basis of a comparison with experimental data), we find that  $\alpha \gg 1$ .

### *Ferromagnetic Metals*

The section above is central to this chapter because it explains the nature of ferromagnetism. But it may have baffled the reader. Indeed, the best-known ferromagnetic materials (iron, cobalt, nickel) are metals. Why then was nothing said about free electrons, which we treated as dielectrics? One possible justification is that there exist numerous ferromagnetic dielectrics, and our analysis is directly applicable to them. But actually, it also works with ferromagnetic metals. In fact, either  $d$  or  $f$  shells of the atoms of all ferromagnetic metals are only partly filled (see Sec. 1.9). The electrons on these shells are close to the nucleus (they lie in the atom) and are practically insensitive to the fact that atoms assemble to form a crystal. The main role in the formation of the ferromagnetic moment is played precisely by  $d$  and  $f$  electrons of magnetic metals. The following picture will be helpful: the electron magnetic moments, interacting via the exchange interaction, are localized in the sites of crystal lattice. But in contrast to dielectrics, they are immersed in a gas of free electrons, with electrons also participating in the formation of a magnetic moment. However, the Pauli principle does not

allow the spins of all conduction electrons to completely align parallel to one another: they are only slightly magnetized by  $d$  or  $f$  electrons. The magnetization is realized through the exchange interaction.

This simplified picture of the "organization" of ferromagnetic metals is called the  $s$ - $d(f)$  exchange model because conduction electrons are the  $s$  electrons of the atoms making up the metal.

The main simplification of the  $s$ - $d(f)$  exchange model is that it neglects the role of conduction electrons in the exchange interaction between  $d$  or  $f$  electrons.

Although the utilization of ferromagnetic metals had begun long before the nature of magnetism was understood, it was the magnetism of metals that proved especially difficult for complete clarification. This field of the physics of magnetic phenomena is being actively developed at the present moment.

### 3.3. The "Para-Ferro" Transition:

#### One of the Second-Order Phase Transitions

A change in external conditions changes the properties of bodies. By heating up a semiconductor we increase its conductivity, and by heating up a ferromagnetic material we decrease its magnetization. By compressing a solid we diminish its volume, and so forth. The list of such examples can be indefinitely long.

As a rule, a small change in external conditions (temperature or pressure) results in a small change of properties. Therefore the "properties-external

### 3.3. The "Para-Ferro" Transition

conditions" dependence can be plotted by a continuous curve. We have already seen an example of such curves: magnetization or magnetic susceptibility as a function of temperature. But sometimes a slight change in external conditions results in "catastrophic" consequences: either one of the characteristics of a body changes jumpwise or a property appears that was absent before. Figure 37 shows the specific volume of gas as a function of pressure. You see that at a certain pressure the specific volume changed jumpwise. The gas turned into a liquid. An example of the

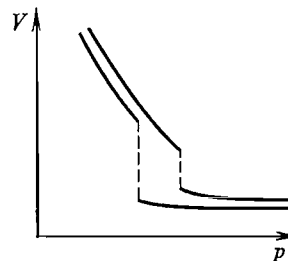


Fig. 37. Specific volume  $V$  as a function of the pressure  $p$  in the gas-liquid phase transition (two isotherms are shown)

appearance (disappearance) of a property has been described above: the magnetization of a body appears (disappears) at the Curie temperature  $T_c$ . At  $T > T_c$  magnetization is absent, as it is absent at exactly the Curie temperature (of course, in zero magnetic field). The jumpwise change in volume is an example of a first-order phase transition, and the appearance (disappearance) of magnetization, or the "para-ferro" transition, is an example of a second-order phase transition. Obviously, examples do not constitute a rigorous definition. It would be difficult to

define the first- and second-order phase transitions strictly without deviating from the gist of our story. And we decline to digress. Note only that the presence of a jump is a sign of a first-order phase transition, while the absence of a jump is a sign of a second-order phase transition.

Naturally, similar characteristics must be used to establish the presence or absence of a jump. For instance, in some substances magnetization changes jumpwise under certain conditions: a magnetic first-order phase transition takes place. We shall encounter this situation later (see Ch. 4). On the other hand, specific heat undergoes a jumpwise change in the "para-ferro" transition. But in a first-order transition heat is released or absorbed both in melting and in boiling (recall the Clapeyron-Clausius equation). Unfortunately, space does not allow us to go into the details of all these extremely interesting aspects.

We already know that the equilibrium value of magnetic moment minimizes the energy (or rather, free energy  $F$ ) of a body. Quite a few characteristics of physical systems possess this property of minimizing the free energy. In order not to limit the discussion to only magnetic properties, we denote by the letter  $\eta$  a parameter characterizing some property of a body. The free energy  $F$  is a function of this parameter:  $F = F(\eta)$ . In a first-order phase transition  $\eta(T) \equiv 0$  at  $T \geq T_{cr}$  and  $\eta(T) \neq 0$  at  $T < T_{cr}$ ;  $T_{cr}$  is the temperature of a second-order phase transition if  $\eta(T_{cr}) = 0$ . The equilibrium value  $\eta = \eta(T)$  is found from the condition of a

minimum:

$$\frac{dF}{d\eta} = 0, \quad \frac{d^2F}{d\eta^2} > 0 \quad (3.12)$$

We want to show how the function  $F(\eta)$  is deformed when temperature changes (this is in fact the cause of the phase transition). Figure 38 shows a case of a first-order phase transition, and Fig. 39 shows a case of a second-order phase transition. You notice that in the former case a new minimum is formed on the curve  $F = F(\eta)$ , and that at  $T > T_{cr}$  this minimum becomes deeper than the first minimum. However,

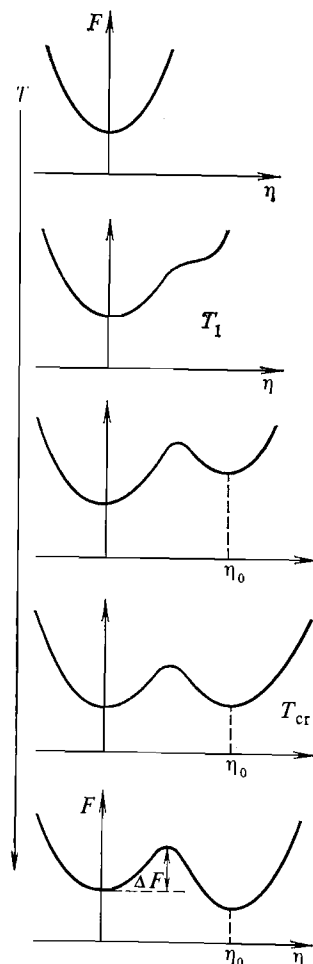


Fig. 38. Temperature-induced transformation of the dependence of the free energy  $F$  on the parameter  $\eta$  in a first-order phase transition. A new minimum appears at  $T = T_1$  (when  $\eta \neq 0$ ). At  $T_1 < T < T_{cr}$ , the state with  $\eta = \eta_0 \neq 0$  is metastable, and at  $T > T_{cr}$ , it becomes stable

to get into the "new" minimum from the "original" minimum, the system has to overcome a certain potential barrier, that is, climb over the "hump" of height  $\Delta F$  separating the minima. At low temperatures such a process is, as a rule, quite difficult (its probability is proportional to  $\exp(-\Delta F/kT)$ ), and the system may stay in a supercooled or a superheated state. Such states are said to be metastable. Sometimes geological eons are not enough for a transition from a metastable to a stable state, and a body stably exists in a metastable state (a good example of an extremely stable metastable state is diamond whose spontaneous transition into graphite has never been observed).

The appearance of a new minimum (below  $T_{cr}$ ) in a second-order phase transition transforms the original minimum into a maximum (see Fig. 39). Obviously, neither supercooling nor superheating is then possible. (See Problem 21.)

Of course, this picture is extremely schematic and approximate, but it gives a correct qualitative characterization of the difference between the phase transitions of the second and first orders. The discrepancy between a true and a simplified picture is especially significant in the case of second-order phase transitions (it will be clear somewhat later what causes the extreme complexity of the problem in analyzing second-order phase transitions). We have already had a chance to point out that Figs. 38 and 39 plotting  $F(\eta)$  much resemble the dependence of the potential energy  $U$  on the  $x$ -coordinate that makes it possible to study the conditions of stability of a body moving along the  $x$ -axis. For the sake of

retaining this analogy, we refer to the parameter  $\eta$  as a "generalized coordinate" and to the state of the system described by the parameter  $\eta$  as to a "body". Thus, a "body" is in a stable or in

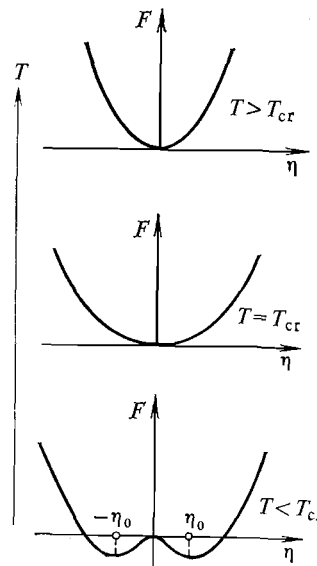


Fig. 39. Same as in Fig. 38, but for a second-order phase transition. A stable state with  $\eta=0$  transforms (at  $T > T_{cr}$ ) into an unstable state, and stable states with  $\eta = \pm\eta_0 \neq 0$  appear (at  $T < T_{cr}$ ).

a metastable state at a point with a "generalized coordinate" at which  $F(\eta)$  has a minimum.

What do we mean when we say that a body is in a particular state? This means that thermal motion makes the "body" vibrate at low amplitude around just this point. (To make it perfectly clear, imagine a pendulum at rest; it only oscillates because of molecular impacts from the sur-



rounding air. Even if the pendulum is enclosed in a housing and the air is evacuated, the pendulum will slightly oscillate because the chaotic thermal motion of the atoms composing the pendulum will shift its center of gravity.) The amplitude of vibrations of the "body" depends on the steepness of the curve  $F(\eta)$  at the point of equilibrium.\* And now look at Fig. 39. The curve  $F = F(\eta)$  in this figure (at  $T = T_{cr}$ ) is very flattened because it must turn into a curve with a maximum and two minima in response to a small change in temperature.\*\* Clearly, the amplitude of vibrations at  $T = T_{cr}$  is large.

Taking these vibrations into account proved to be a very complicated problem. Only in recent years physicists gained assurance that they are able to describe the properties of physical systems in close vicinity of the point of a second-order phase transition with a high degree of accuracy. However strange it may seem, this required that the properties of physical systems be considered in spaces (that exist on paper only) with fractional dimensions (our world is three-dimensional, a plane is a two-dimensional space, a line is one-dimensional...).

When a change in the parameter  $\eta$  describes a second-order phase transition, it is also called the order parameter. In the case of the "para-ferro" transition the reason for this term is obvious: the magnetic moment density  $M_s$  is a measure of ordering of atomic spins.

\* The height to which the "body" is lifted above the equilibrium point is determined by temperature  $T$ .

\*\* Trace this transformation using Problem 21.

Let us give another example of a second-order phase transition: the ordering of an alloy CuZn. Figure 40 shows the crystal lattice of this alloy. At high temperatures the atoms of copper and zinc are randomly distributed: they occupy arbitrary sites of the lattice with equal probability (which is, naturally, equal to  $1/2$ ). Beginning with a certain temperature (also called the Curie

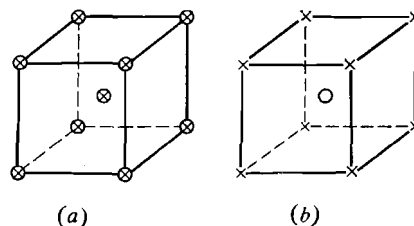


Fig. 40. Arrangement of zinc atoms (crosses) and copper atoms (circles) in an ordered alloy:

(a) at  $T > T_{cr}$ ; (b) at  $T = 0$

temperature) the probabilities start to deviate from  $1/2$ , first slightly, but as temperature tends to zero the probabilities tend to zero and unity, respectively, that is, a complete ordering sets in.

One last remark to conclude this section. As a rule, a second-order phase transition changes the symmetry of a body.\* (The first to notice this fact was L. D. Landau who used it to construct a phenomenological theory of such transitions.) Indeed, the appearance of ferromagnetism singles out a certain direction in the system of

\* As additional reading on symmetry, we recommend H. Weyl, *Symmetry*, 1952.

atomic magnetic moments, and the ordering of an alloy changes the period of crystal lattice. Another interesting feature is that in immediate vicinity of  $T_{cr}$  the order parameter is still infinitely small, while the symmetry has already changed: symmetry changes jumpwise because a body can have either one or some other symmetry. A continuous transition from one symmetry to another is impossible.

### 3.4. What Is the Direction of the Magnetic Moment of Ferromagnetics? Energy of Magnetic Anisotropy

As a result of the isotropy of the exchange interaction discussed in Sec. 1.10 the direction of the magnetic moment of a ferromagnetic material is not specified. Of course, if a ferromagnetic material is placed in a magnetic field  $\mathbf{H}$ , it is energetically favorable for the magnetic moment to align along  $\mathbf{H}$ . But do there exist some internal causes, inherent in the body itself, that force the magnetic moment density  $\mathcal{M}_s$  orient in a crystal in a definite way? Of course, they exist.

First, these are dipole-dipole forces acting between atomic magnetic moments. Since the energy of the dipole-dipole interaction (1.35) is a function of orientation of magnetic moments relative to the straight line joining them, the energy of this interaction in a ferromagnetic crystal in which such lines are fixed to the crystal lattice must be a function of orientation of the vector  $\mathcal{M}_s$ .

Second, the spin magnetic moments of atoms creating the total magnetic moment of a ferro-

magnetic material interact with electron currents. These last are caused by the orbital motion and are oriented in space in a definite manner. As a result, some spin orientations are more energetically favorable than others.

Each of the two above-described interactions can be put in correspondence with the energy dependent on the spatial orientation of the magnetic moment density  $\mathcal{M}_s$ . It is called the *anisotropy energy*.

*The anisotropy energy is determined by the magnetic dipole-dipole and spin-orbit interactions.*

The anisotropy energy is often divided into the intraionic and interionic energies. The intraionic energy results from the anisotropic distribution of electrons within an ion owing to the effect of the electric field produced by surrounding ions. And it can be said that in general the anisotropy energy is ultimately a consequence of nonisotropic distribution of electrons in the crystal lattice.

But why could we neglect the anisotropy energy when discussing the formation of spontaneous magnetic moment in ferromagnetic materials? Because this energy is much smaller than the exchange energy. In order to emphasize this fact, the exchange energy is said to be of *electrostatic* origin, while the anisotropy energy to be of *relativistic* origin. If the speed of light  $c$  were infinite, the anisotropy energy would be zero. This is easily found by considering the magnetic dipole-dipole energy. It has already been evaluated earlier (see p. 72), and we found that it is

less than the electrostatic energy by a factor of  $c^2/v^2$ , while the exchange energy differs from the electrostatic energy only slightly, if at all. Since the anisotropy energy is much less than the exchange energy, it leaves the formation of the magnetization  $\mathcal{M}_s$  practically unaffected and is responsible only for the orientation of the vector  $\mathcal{M}_s$ .

The expression for the anisotropy energy  $\mathcal{E}_{an}$  cannot be derived here. This is a difficult problem, not yet completely solved. We shall make use of a phenomenological description (the definition of the concept "phenomenological theory" was given on p. 153) based on an analogy between the anisotropy energy and the energy of a magnetic moment in a uniform external magnetic field. Indeed, it is the magnetic field that orients the magnetic moment. Let a crystal contain a certain direction defined by a unit vector  $\mathbf{n}$  along which it is advantageous for the magnetic moment to be oriented. This direction is called the singled-out axis, or the *anisotropy axis*.

Then it would be desirable to follow this analogy and write

$$\mathcal{E}_{an} = -\beta \mathcal{M} \cdot \mathbf{n} V, \quad \beta > 0$$

We have dropped the subscript  $s$  from  $\mathcal{M}$ .

We would like to do it, but ... cannot. And here is why. Magnetization  $\mathcal{M}$  is a vector sum of atomic magnetic dipoles. And magnetic dipoles reverse their directions under time reversal, that is, under the operation  $t \rightarrow -t$  (this was mentioned on p. 25). Hence, the direction of  $\mathcal{M}$  is also reversed. The energy cannot change sign under time reversal (in these cases energy is

said to be invariant under time reversal\*)... . Hence, the expression written above cannot be correct. The expression for energy must include the vector  $\mathcal{M}$  to an even power. Only then the replacement of  $t$  with  $-t$  leaves energy invariant. The simplest expression satisfying this condition is

$$\mathcal{E}_{an} = -\frac{1}{2} \beta (\mathcal{M} \cdot \mathbf{n})^2 V, \quad \beta > 0 \quad (3.13)$$

This is the expression we are to use. The problem of a microscopic theory is to calculate the factor  $\beta$ , called the *anisotropy constant*. Note (this will prove useful later) that the anisotropy constant is dimensionless. The value of  $\beta$  is different in different ferromagnetic materials, but it is practically always much less than the exchange parameter  $\alpha$  (see formulas (3.10) and (3.14)). The reason for this has already been mentioned: the smallness of the relativistic interaction in comparison with the electrostatic interaction. Expression (3.13) is valid for some but not for any crystals. It is valid for uniaxial crystals (e.g. for crystals with hexagonal unit cell, Fig. 41), but for cubic ferromagnetic materials a more complicated dependence of  $\mathcal{E}_{an}$  on the direction of the vector  $\mathcal{M}$  must be used.

Formula (3.13) shows that there are two most advantageous directions for the vector  $\mathcal{M}$ : parallel and antiparallel to  $\mathbf{n}$ . This uncertainty cannot be eliminated by the internal forces in a ferro-

\* This is especially clear from the expression for the energy of a free particle,  $\mathcal{E} = mv^2/2$ . Under the reversal  $t \rightarrow -t$  the sign of the velocity  $v$  is reversed, while that of  $v^2$  is not.

magnetic material and leads to important consequences (see Sec. 3.5). At the moment let us place a ferromagnetic material in an external

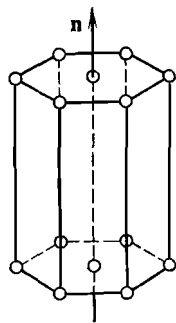


Fig. 41. Unit cell of a hexagonal crystal

magnetic field  $\mathbf{H}$  and try to determine the direction of  $\mathbf{M}$  in this case.

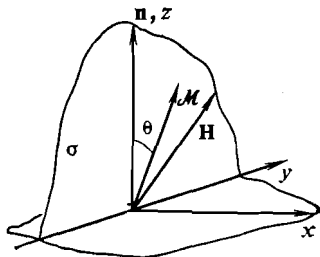


Fig. 42. At  $\mathbf{H} \neq 0$  the magnetic moment is in the plane  $\sigma$  stretched on the vectors  $\mathbf{n}$  and  $\mathbf{H}$ . At  $\mathbf{H} = 0$  the magnetic moment aligns parallel or antiparallel to  $\mathbf{n}$

As always, we must start with minimizing the energy  $\mathcal{E}_{\text{an}}$ . In the case under consideration,

$$\mathcal{E}_{\text{an}} = \left[ -\frac{1}{2} \beta (\mathbf{M} \cdot \mathbf{n})^2 - \mathbf{M} \cdot \mathbf{H} \right] V \quad (3.14)$$

The vectors  $\mathbf{n}$  and  $\mathbf{H}$  define a plane  $\sigma$  (Fig. 42). It is not advantageous for  $\mathbf{M}$  to tilt out of this

plane because energy would then be increased. Therefore we have to find a single angle  $\theta$  between  $\mathbf{M}$  and  $\mathbf{n}$ . Expression (3.14) gives the following detailed dependence of  $\mathcal{E}_{\text{an}}$  on  $\theta$ :

$$\begin{aligned} \mathcal{E}_{\text{an}} = & -V \left( \frac{1}{2} \beta \mathcal{M}^2 \cos^2 \theta + H_x \mathcal{M} \sin \theta \right. \\ & \left. + H_z \mathcal{M} \cos \theta \right) \end{aligned} \quad (3.14')$$

We have directed the  $z$ -axis along  $\mathbf{n}$ , and the  $x$ -axis perpendicularly to  $\mathbf{n}$  in the plane  $\sigma$ .

The condition of the minimum of  $\mathcal{E}_{\text{an}}$  is written as follows:

$$\begin{aligned} \frac{\partial \mathcal{E}_{\text{an}}}{\partial \theta} & \equiv V \mathcal{M} \left( \frac{1}{2} \beta \mathcal{M} \sin 2\theta - H_x \cos \theta \right. \\ & \left. + H_z \sin \theta \right) = 0 \\ \frac{\partial^2 \mathcal{E}_{\text{an}}}{\partial \theta^2} & \equiv V \mathcal{M} (\beta \mathcal{M} \cos 2\theta + H_x \sin \theta \\ & + H_z \cos \theta) > 0 \end{aligned} \quad (3.15)$$

The condition of positiveness of the second derivative singles out among the solutions of equations (3.15) those that correspond to a minimum, not to a maximum. A replacement  $\sin \theta = \xi$  transforms equation (3.15) into an algebraic equation of the fourth degree in  $\xi$ :

$$(\beta \mathcal{M} \xi - H_x)^2 (1 - \xi^2) = H_z^2 \xi^2 \quad (3.16)$$

As we know from algebra, an equation with real coefficients may have both real and complex

pairwise-conjugate roots.\* The total number of roots is equal to the degree of the equation, i.e. to four in this case. It is then clear that equation (3.16) has either two real roots or four. We are obviously interested only in real roots. Since the right-hand side of the equation is positive, the absolute value of the real roots does not exceed unity. Hence, each of them defines an angle  $\theta$ .

The sign of the second derivative determines whether an extremal point is a maximum or a minimum. However, direct testing is quite difficult. Indeed, each root has to be substituted into the expression of the second derivative, but it is practically impossible to find a manageable explicit expression of the roots of equation (3.16) (look at it carefully: it is a general, not biquadratic, equation of the fourth degree). We shall resort to qualitative arguments. They make it possible to outline the situation.

When equation (3.16) has four real roots, two of them correspond to a minimum of the function  $\mathcal{E}_{\text{an}} = \mathcal{E}_{\text{an}}(\theta)$  (see (3.14')) and two to a maximum. Clearly minima and maxima alternate. The deepest minimum corresponds to the stable state, and the shallower minimum to a metastable state (similar arguments were given in Sec. 3.3). When equation (3.16) has two real roots, the function  $\mathcal{E}_{\text{an}} = \mathcal{E}_{\text{an}}(\theta)$  has one minimum and one maximum. The transition from one case to another is caused by changing the magnitude and direction of a magnetic field  $\mathbf{H}$

\* This means that if  $\xi = \xi_1 + i\xi_2$  is a root of the equation, then  $\bar{\xi} = \xi_1 - i\xi_2$  is also a root of the same equation ( $\xi_1$  and  $\xi_2$  are real numbers).

(i.e. the values of the projections  $H_x$  and  $H_z$ ) and is realized by a merging of one maximum with the neighbor minimum. Obviously, the ferromagnetic material then loses the possibility of being in a metastable state.

Let us find the range of projections  $H_x$  and  $H_z$  of a magnetic field, in which a ferromagnetic material has a metastable state. We shall be able to show now that this region is bounded by a curve in the plane  $H_x, H_z$  whose equation is easily obtained by resorting to the following arguments: since the points of this curve are those at which a minimum and a maximum of the function  $\mathcal{E}_{\text{an}} = \mathcal{E}_{\text{an}}(\theta)$  merge, the second derivative  $\partial^2 \mathcal{E}_{\text{an}} / \partial \theta^2$  on this curve must vanish. In other words, the inequality sign in (3.15) must be replaced with the equality sign.

We thus have two equations conveniently written in the form

$$\frac{H_x}{\sin \theta} - \frac{H_z}{\cos \theta} = \beta \mathcal{H}$$

$$\frac{H_x}{\sin^3 \theta} + \frac{H_z}{\cos^3 \theta} = 0 \quad \text{or} \quad \frac{H_x^{1/3}}{\sin \theta} + \frac{H_z^{1/3}}{\cos \theta} = 0$$

Eliminating  $\theta$  from these equations\*, we arrive at the equation of the sought curve:

$$H_x^{2/3} + H_z^{2/3} = (\beta \mathcal{H})^{2/3} \quad (3.17)$$

This curve is the so-called astroid because its shape resembles that of a four-ray star (from the Greek *astron* for star). The astroid (Fig. 43)

\* For elimination, we have to find  $\sin \theta$  and  $\cos \theta$  from the above equations and to substitute them into the identity  $\sin^2 \theta + \cos^2 \theta = 1$ .

divides the plane  $H_x, H_z$  into two parts. Which of these parts contains metastable states, and which does not? This question is easily answered after considering very strong magnetic fields (formally, at  $H \rightarrow \infty$ ) when the anisotropy

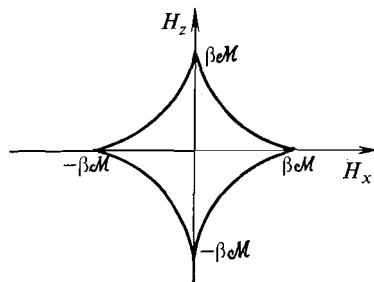


Fig. 43. The region of metastable states of a ferromagnetic material. If the tip of the vector  $\mathbf{H}$  falls inside the astroid, the material has a stable and also a metastable state

energy can simply be neglected. In this case  $\mathcal{E}_{an} = \mathcal{E}_{an}(\theta)$  has a single minimum at which the vector  $\mathbf{M}$  is parallel to  $\mathbf{H}$ , that is, at  $\tan \theta = H_x/H_z$ ; hence, no metastable states are possible. Therefore,

*if  $H_x$  and  $H_z$  "lie" outside the astroid, then there are no metastable states, and if they "lie" inside, then there are metastable states.*

It is clear from symmetry-based arguments that at  $\mathbf{H} = 0$ , as well as at  $H_z = 0$  and  $H_x < \beta M$ , the curve  $\mathcal{E}_{an} = \mathcal{E}_{an}(\theta)$  has two equally deep minima. (See Problem 22.) A ferromagnetic material selects one of the two states, being "guided" by arguments that will be explained in the next section.

### 3.5. Domains

Let us repeat the conclusion arrived at in the preceding section: in a "symmetrically" applied weak magnetic field (i.e. in a field perpendicular to the anisotropy axis and not exceeding  $\beta M$ ) the stable and metastable states become indistinguishable, and the corresponding to them directions of the magnetization vector become equally advantageous. Thus, if  $\mathbf{H} = 0$ , the magnetic moment can be directed with equal "gain" in any direction along the anisotropy axis as long as it does not deviate from this axis. But which of these two directions will be actually selected? Clearly, the selection involves something that we did not take into account.

Let a magnetic field, no matter how weak, be applied along the anisotropy axis. Of course, the direction along the field is more advantageous than the opposite direction, and this is the direction chosen by the magnetic moment. And now let us remove the field gradually (infinitely slowly in order not to "shake up" the magnetic specimen, or it might demagnetize (see below)). The states with oppositely oriented magnetic moments do have identical energy but are separated with an energy barrier whose height is determined by the anisotropy energy. When the field vanishes, magnetization may not overcome this barrier. Then the magnetic moment of the specimen retains the direction imposed by the magnetic field. This produces a state in which a ferromagnetic material possesses spontaneous magnetization (of course, at a temperature below the Curie temperature).

Nevertheless, this "frozen-in" state of magnetization is metastable, and not stable, despite its obvious advantage in energy. There is another state with a lower energy. Indeed, any specimen is bound. When magnetized, it acts as a source of a magnetic field in the surrounding space. But the magnetic field has a positive energy whose density (i.e. energy per unit volume) is

$$\mathcal{E}_H = \frac{H^2}{8\pi} \quad (3.18)$$

This expression was not taken "out of thin air". It follows from Maxwell's equations. The energy of the magnetic field was totally neglected in our calculations of the energy of a ferromagnetic material, although the total energy of the magnetic field can be very high. For instance, it is infinite in the case of an infinite magnetized plate (Fig. 44a) because its magnetic field fills all space, with the strength of the field not diminishing with distance and equal to  $4\pi M$  (see p. 96).<sup>\*</sup> We have to conclude that the state of magnetization analyzed above (we regarded it as the most energetically favorable) in fact has a very high energy. How can we help matters and diminish the total energy? At the first glance, it is necessary to reject the orientation of the magnetic moment along the anisotropy axis and arrange the moment perpendicularly to the axis. Then we would "lose" in anisotropy energy but

<sup>\*</sup> In fact, when saying that the plate is "infinite", we only mean that two of its dimensions are much greater than the third. When the plate dimensions are finite, its magnetic field in fact diminishes at distances large in comparison with the plate size.

would seemingly diminish the magnetic field energy. This is a poor solution. Each plate is bounded on all sides. Magnetic lines of force always "stream" out of it to fill the space around the plate. The magnetic field energy will be, as before, very high, and the "loss" in anisotropy

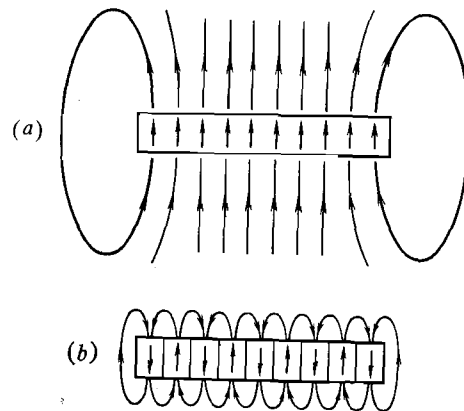


Fig. 44. Magnetic field around a ferromagnetic plate: (a) the plate is uniformly magnetized; (b) the plate separates into domains

energy cannot be compensated for. An analysis shows that the advantages related to the minimum in anisotropy energy should not be discarded (at any rate, discarded completely). But we can make use of the equivalence of the two directions of magnetization along the anisotropy axis. Let us divide the plate into alternating identical segments. Let the vector of magnetization have the same direction relative to the axis within each segment, and alternate in neighbor seg-

ments, making the plate effectively demagnetized. These segments are called the regions of spontaneous magnetization, or *domains* (Fig. 44b). The figure shows that having left one domain, the lines of force enter the neighbor domain. Therefore, the "spreading" of the lines of force is relatively insignificant, that is, the magnetic field diminishes sufficiently rapidly as we move away from the surface (the field is significant at distances of the order of domain size).

Of course, the energy of the magnetic field,  $\mathcal{E}_H$ , around a plate divided into domains is much less than the energy of a magnetized plate. By the order of magnitude,

$$\mathcal{E}_H^d \approx M^2 S d \quad (3.19)$$

where  $d$  is the thickness of a domain, and  $S$  is the area of the plate equal to  $L^2$ . Of course, this is not an exact expression because we have omitted all numerical factors, although they may considerably depart from unity (thus, the numerical factor in (3.18) equals  $(8\pi)^{-1} \approx 1/25$ ). All formulas of this section are thus of qualitative nature.

A demagnetized plate has the same energy of magnetic anisotropy as a magnetized plate. Indeed, it seems that the formation of domains is favorable for a ferromagnetic specimen. But a question immediately arises: how many domains should form in a ferromagnetic plate? From the standpoint of magnetic field energy, the greater the number of domains, the better. This is true because as the number of domains increases, their size diminishes, and magnetic lines of force "crowd" closer to the plate, the field falls

off more steeply with distance from the plate, and the energy of magnetic field decreases (see (3.19)). But what stands in the way of "fragmentation" of domains? It would seem that the magnetic anisotropy energy should remain the same at any fractionation into domains. On the other hand, experiments unequivocally demonstrate that domains have quite definite macroscopic sizes determined by the shape and size of the specimen.

In order to make ends meet, we must pay attention to the boundary between adjacent domains. We did not hesitate to arrange the magnetic moments in adjacent domains so that they pointed in opposite directions, having forgotten that from the standpoint of exchange interaction (3.8') this is a "crime", because the exchange energy is at minimum when neighbor spins are parallel, and at maximum (sic) when they are antiparallel. And the exchange interaction is the most important interaction of all... .

It is thus clear that antiparallel spins must not be placed alongside. An analysis shows that the transition from one direction of a magnetic moment to the opposite direction is gradual\*: it occurs over a distance of the order of

$$\delta = a \left( \frac{A}{\mu_B \beta \mathcal{M}} \right)^{1/2} \quad (3.20)$$

where  $a$  is the interatomic spacing, so that the vector of magnetization rotates by  $180^\circ$  in a plane

\* The analysis is based on calculating such a distribution of magnetization that has the least energy, provided the magnetic moments far from the boundary point in opposite directions.



parallel to the boundary between domains (Fig. 45). This results in a finite-thickness transition layer, resembling a wall, instead of an abrupt (geometric) boundary between the domains. It is indeed said to be a *domain wall*. Its structure is such that the transition from one domain to another consumes the least energy (the thicker the domain wall, the higher the exchange energy, and the thinner the wall, the higher the

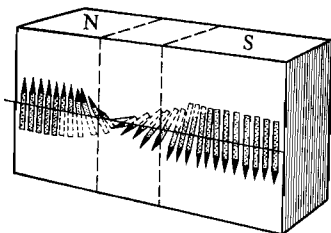


Fig. 45. Domain wall. The magnetic moment  $\mathcal{M}$  rotates, remaining always parallel to the plane separating two domains. Far from the domain wall the magnetic moments align along the anisotropy axis, in opposite directions on the two sides

anisotropy energy). With the distribution of the magnetic moment known, it is possible to calculate the energy related to the formation of one domain wall. It is roughly equal to  $\Delta = \mathcal{M}^2 \delta$  per 1 cm<sup>2</sup> of the wall (here again the numerical factor was omitted). Having calculated this energy, we can forget about the structure of domain walls and again consider them to be abrupt boundaries but such that they carry additional energy  $\Delta$ . We shall discuss later the conditions of validity of this approach.

Now we see what prevents the fractionation of a ferromagnetic specimen into excessively small domains: the formation of new domains increases the energy of domain walls and limits fractionation. In order to calculate the size  $d$  of an individual domain, let us write an expression for the energy of a demagnetized ferromagnetic plate. Since the number of domain walls is  $L/d$ , the surface area of a boundary between domains is  $lL$ ,  $l$  being the plate thickness (see Fig. 44b), the energy (obviously with the exchange energy as a reference point) is

$$\mathcal{E} = S \left( d + \delta \frac{l}{d} \right) \mathcal{M}^2 \quad (3.24)$$

As always, the domain size is found from the condition of a minimum, in this particular case the minimum of expression (3.24). The energy  $\mathcal{E}$  is minimum if  $d = \sqrt{\delta l}$ .

This important result was obtained by Ya. I. Frenkel, L. D. Landau, and E. M. Lifshitz. The notion of domains is essential for understanding the nature of ferromagnetism: in accord with experimental data,

*in its ground state a ferromagnetic material of finite size is demagnetized because it separates into domains.*

The domain size depends on the characteristics of the ferromagnetic material (they enter into the parameter  $\delta$ ). The size grows with the increasing size of the specimen, proportionally to the square root of the smallest size of the plate.

An attentive reader should regard our line of reasoning as totally illogical. At the begin-

ning of the section we tried to determine the direction of a magnetic moment and thus assumed that a ferromagnetic specimen is uniform, that is, its magnetization is independent of coordinates; then we found that the magnetic moment is nonuniform around the boundary between domains. Several lines later we again "forgot" about it, having correspondingly written formula (3.20). Furthermore, in deriving the Curie-Weiss equation (see Sec. 3.2), we deliberately neglected the possibility of nonuniform magnetization. Have we any right to take and then not to take into account this inhomogeneity? Is not it an arbitrariness that seems to be unacceptable in science? Of course not! Let us start with proving that a domain wall can be replaced with a geometric boundary. In all likelihood everyone will agree that this can be done if the domain wall thickness  $\delta$  is much less than the domain size  $d$ , that is, when  $d \gg \delta$ , so that our discussion holds for sufficiently thick plates ( $l \gg \delta$ ). Indeed, the formation of domains is not advantageous at all for ferromagnetic specimens of sufficiently small size (if all dimensions of the specimen are of the order of  $\delta$ ). Such ferromagnetic particles do exist and are not demagnetized, constituting a single domain.

Now let us find out what gives us the right to operate with the results obtained by solving the Curie-Weiss equation. The most nonuniform regions in a demagnetized ferromagnetic specimen are domain walls. The degree of nonuniformity is characterized by the thickness  $\delta$  of domain walls. But  $\delta \gg a$ , that is, on the atomic scale ferromagnetic samples are uniform even in the

vicinity of domain walls.\* The approach used above is thus justified. It has a right to exist, provided the following strong inequalities hold:

$$l \gg \delta \gg a \quad (3.22)$$

It must be emphasized that the second inequality holds because the exchange energy is much greater than the anisotropy energy; this fact has already been discussed above.

The formation of a periodic domain structure can be regarded as an example of a fairly general phenomenon, namely, *spontaneous breaking of symmetry*: it is energetically favorable for a homogeneous highly symmetric ferromagnetic material to lower its symmetry and transform into a periodic structure.

We have already seen examples of spontaneous symmetry breaking: a transition from the paramagnetic to the ferromagnetic state violates the isotropy inherent in each point of a paramagnetic material, owing to the formation of a macroscopic magnetic moment (indeed, it has to point in some direction).

The above-discussed example of a domain structure (in a plate cut perpendicularly to the anisotropy axis) is certainly a particular case. Sometimes domain walls are arranged in a different way. It happens (as a rule) that domain shapes are not as simple as we have described (e.g. Fig. 46a shows a domain structure in an iron

\* We remind the reader that the exchange interaction decreases very quickly with distance; in fact, it binds only neighbor atoms, thus linking all the atoms of a ferromagnetic specimen in a "relay" manner (see formula (3.8')).

film; you see that it is far from simple). Cylindrical domains, called magnetic bubbles (Fig. 46b), are formed in some ferromagnetic films; these were found useful in computer technology, as computer memory elements.

But whatever the domain structure, the main conclusion always holds: it is energetically ad-

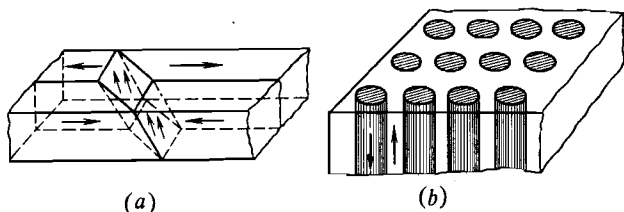


Fig. 46. "Complex" domain structures: (a) the domain structure in an iron film; (b) magnetic bubbles. Arrows indicate the direction of magnetization far from domain walls

vantageous for the total magnetic moment of a finite sufficiently large ferromagnetic specimen to be zero.

Why then permanent magnets exist? In order to answer this question, it is necessary to understand the processes of magnetization and demagnetization of ferromagnetic materials.

### 3.6. Technical Magnetization Curve

By definition, the *magnetization curve* is the dependence of the magnetic moment of a body on the applied (external) magnetic field. As for the attribute "technical", it will be explained later.

The dependence of the magnetic moment of a paramagnetic material (or of a ferromagnetic material at a temperature above the Curie temperature) on the magnetic field is linear up to very high fields. Saturation, that is, approach to a maximum possible magnetization, occurs

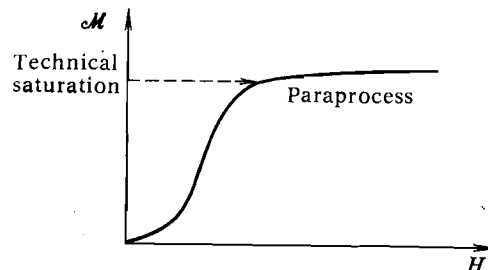


Fig. 47. Virgin curve of magnetization

either at very low temperatures or at very high magnetic fields, in accord with the condition  $\mu_B H \gg kT$  (see Sec. 2.2).

The magnetization curve of a ferromagnetic material looks absolutely different. It is illustrated in Fig. 47. You notice from this figure that at  $H = 0$  the magnetization  $M$  is also zero. This is in agreement with what we said in the preceding section: a ferromagnetic is demagnetized when in zero external magnetic field. The magnetization curve starting at the origin of coordinates is called the *virgin curve*. As the magnetic field increases, magnetization grows first slowly but then much more steeply: magnetization increases several tenfold over a relatively narrow interval of the field. Then the rate of

growth of magnetization slows down again, and the so-called *technical saturation* sets in. Magnetization up to technical saturation is called *technical magnetization*, and the corresponding segment of the curve is called the *technical magnetization curve*.\*

If we continue increasing the magnetic field after technical saturation has been reached, magnetization changes slowly, increasing almost as a linear function of the field. This linear increase in magnetization with the field is called the *paraprocess*, which underlines the similarity with the linear dependence of the magnetization field of paramagnetic materials.

The difference between the technical magnetization curve of ferromagnetic materials and the corresponding curve of paramagnetic materials obviously stems from the presence of magnetized macroscopic regions (domains) in ferromagnetic specimens even at  $H = 0$ , and the role of the external magnetic field reduces to aligning their magnetic moments.\*\* As we have mentioned, in paramagnetic materials the magnetic field aligns *microscopic* atomic magnetic moments.

In order to find a qualitative explanation of technical magnetization, let us again consider a plate of a uniaxial ferromagnetic material (see Fig. 44). However, now we apply the external

\* Note that numerical characteristics of the virgin curve not only vary among different ferromagnetics but also somewhat vary among specimens of the same material. As a rule, the behavior of the curve is preserved.

\*\* Of course, the alignment of the magnetic moments of the domains means the destruction (elimination) of the domain structure because the domains differ only in the direction of the magnetic moments.

magnetic field to this plate at a certain angle to the anisotropy axis. The field disturbs the equivalence of the two directions along the axis and makes that direction which is at an acute angle to the field more favorable. In other words, it is advantageous for the domains with the magnetic moment along the field to grow, and for those with the moments against the field to shrink. But how do some domains grow and others shrink?

Since the direction of magnetization in a domain wall changes continuously from point to point (see Fig. 45), the magnetic moment within the wall can rotate even at an arbitrarily weak magnetic field, the rotation being at a small angle in a weak field. As a result, magnetization distribution changes and thereby the domain wall shifts (Fig. 48), and the body will manifest nonzero magnetization.

Further growth of a magnetic field results in an additional displacement of domain boundaries and in a continuous growth of magnetization. Let us emphasize that the linear segment on the virgin curve (at  $H \rightarrow 0$ ) follows from the existence of finite-thickness domain walls. If the boundary between domains were infinitely thin, a finite magnetization could be produced only by reversing the direction of the magnetic moments simultaneously in all "unfavorable" domains, and this would call for a considerably strong field.

At a certain strength of the magnetic field, "unfavorable" domains almost disappear, and the rate of increase of magnetization diminishes. Therefore, the range of the magnetic field in

which magnetization grows at the maximum rate corresponds to the motion of domain walls. Further increase in magnetization is caused by the rotation of the total magnetic moment toward

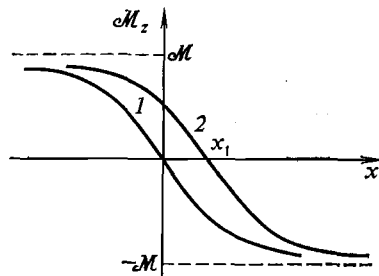


Fig. 48. Shift in the position of a domain wall in the magnetic field: curve 1—projection of the magnetic moment onto the anisotropy axis as a function of coordinate;  $x = 0$  is the domain wall at  $H = 0$ ; curve 2—same at  $H \neq 0$ ; the domain wall is shifted by  $x_1$

the direction of the magnetic field. This rotation is frustrated (as compared with the rotation of the magnetic moments within the domain walls), and consequently in this range of field the curve  $M = M(H)$  is less steep. When finally all magnetic moments align along the field, the ferromagnetic specimen is macroscopically homogeneous and its spontaneous magnetic moment is in the most favorable position: technical saturation has set in. Further increase in magnetization as the field grows (the paraprocess) is a result of the struggle of the magnetic field with the thermal motion of individual atomic spins, in

which the magnetic field is an ally of the exchange interaction, and their common opponent is the tendency to chaos, present at any finite temperature.

Now consider a process inverted with respect to magnetization: demagnetization. Let the magnetic field that has magnetized a ferromagnetic specimen to technical saturation gradually diminish. Obviously, magnetization will also diminish with the field. But must the decrease in magnetization trace the same curve as that representing magnetization (see Fig. 47)? Not necessarily. In an ideal ferromagnetic specimen (containing no impurities, lattice defects, dislocations, etc.; here we deal only with such objects) everything depends on whether the point representing the magnetic field falls inside or outside the astroid in Fig. 43. If the point is outside the astroid (where no metastable states exist), the point in the plane  $H, M$  will move (at least at the beginning) along the virgin magnetization curve. And if the point representing the saturation magnetic field falls inside the astroid (where there are metastable states), then magnetization will diminish together with the field along the curve of metastable states. Each point on this curve corresponds to a magnetization greater than that on the virgin curve. When the magnetic field vanishes, magnetization does not become zero because an energy barrier must be overcome for demagnetization, that is, for dividing a specimen into domains (see Secs. 3.4 and 3.5). We have already explained that a state of magnetization of a ferromagnetic material in the absence of an external field is metastable but frequently

it may be sustained indefinitely long. This fact is familiar from childhood to anybody who played with a permanent magnet.

The magnetization of a ferromagnetic material in the absence of an external magnetic field is called the *residual magnetization*. In order to "remove" the residual magnetization, that is, forcefully demagnetize the specimen, it is necessary to apply a sufficiently strong magnetic field directed against the field of magnetization. The strength of this demagnetizing field is called the *coercive force*. Ferromagnetic materials greatly differ in coercive force: from tenth of one oersted to thousands of oersteds. Materials with a high coercive force are said to be *magnetically hard*, and those with a low coercive force are said to be *magnetically soft*. Both hard and soft materials find applications in modern technology.

By continuing the increase in the field in the direction opposite to the initial magnetizing field, we can again magnetize the specimen to its technical saturation. The decrease in the oppositely directed field will lead, in the case of metastable states, to magnetization varying along a curve below the virgin curve. The residual magnetization will be formed again, and again a field equal to the coercive force will have to be applied to remove this magnetization, but now this field will be along the initial field... The words "and so on" would be in place here because further intensification of the field will bring magnetization to technical saturation.

The above-described processes of magnetization and remagnetization are shown in Fig. 49. The salient feature of this curve is the irrever-

sible variation of magnetization with field: the magnetization and demagnetization of a ferromagnetic material follow different curves. This irreversibility is called the *magnetic hysteresis*, and the closed curve shown in the figure is called the *hysteresis loop*. Let us emphasize that

*the hysteresis is one of the manifestations of metastable states.*

The attribute "technical" (technical saturation, technical magnetization curve) marks not only

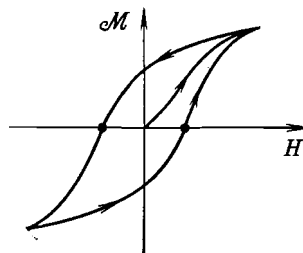


Fig. 49. Hysteresis loop

the fact of technical importance of the magnetization curves of real magnetic materials but also the dependence of the magnetization process on the technology of manufacturing a specimen. The point is that numerical characteristics of a technical magnetization curve, hysteresis loop, and coercive force essentially depend on the state of the specimen and the technological procedures involved. This is employed in industry to produce magnets with desired properties. The physical reason for the sensitivity of the technical magnetization curve to the state of a sample

lies in the dependence of the anisotropy constant  $\beta$  on the structure of crystal lattice. As a result of an increase in  $\beta$  within regions with defects, the magnetic moment "clings" to them, and a relatively strong field is required to "force" its reorientation. The study of the technical magnetization curve and the development of magnetic materials with required magnetic properties form an important chapter in the application-oriented physics of magnetic phenomena.

### 3.7. Spin Waves

Strictly speaking, the two preceding sections are a digression from our main topic because they describe not the *nature* of ferromagnetism but the properties of real finite-size specimens. In this section we return to the description of the nature of the ferromagnetic state. We shall find out how the spontaneous magnetic moment of a ferromagnetic specimen depends on temperature at low temperatures, that is, close to absolute zero. As we have mentioned, formula (3.5) contradicts the experimentally measured temperature dependence of a magnetic moment.

In order to find out the temperature dependence of a physical quantity, we have to know the motion of atomic particles of which a body is composed. We already had an opportunity to see the truth of this statement when the magnetic properties of metals were discussed (see Secs. 2.4 and 2.5). Statistical physics relates the motion of individual atomic particles to macroscopic properties of bodies. As long as a gas is concerned,

the meaning of the words "individual atomic particle" is clear. But are they meaningful in a solid which differs from a gas precisely in that it has no *individual* atomic particles because all particles interact with one another? We shall see that the role of individual atomic particles is played in crystals by *quasiparticles* that we shall discuss later.

Too many incomprehensible terms have been used above: spin waves in the title of the section, and quasiparticles in its text; now let us add another hardly comprehensible word combination: the energy spectrum of a physical system. In this section we describe the energy spectrum of ferromagnetic materials. Hopefully, the meaning of these words will be clear to the reader a little later.

Let us recall the remark made about the Curie-Weiss model (see p. 143): in the general case the energy of a ferromagnetic specimen is not determined unambiguously by its magnetization. The energy is expressed via the total magnetic moment of a body only when all atomic magnetic moments are parallel to one another. This is why we were able to relate the constant  $\alpha$  of the phenomenological theory to the exchange integral  $A$  (see formula (3.11)). This unambiguous relationship is possible because the complete ordering can be produced in only one manner.

In what follows it will be more convenient to operate not with the magnetic moment but with the spin of a ferromagnetic material.

In the ground state of a ferromagnetic material the spins of all atoms are thus "parallel"

to one another. Their common "direction"\* is fixed, for instance, by the anisotropy axis along which the magnetic field is applied. Any deviation of the spin from this direction involves

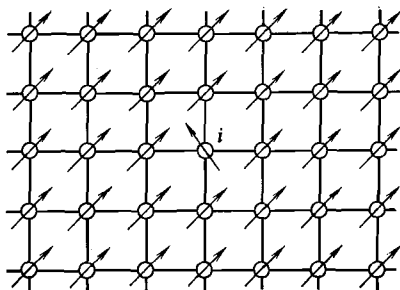


Fig. 50. Spin of the  $i$ th atom is deflected from the "direction" common for other spins

an increase in energy. Assume that the atom with the deviating spin is in the  $i$ th lattice site (Fig. 50). It would seem then that the energy of the ferromagnetic material must differ from the ground state energy (3.9) because of the change in the energy of interaction of the  $i$ th atom and its nearest neighbors. But this intuitive interpretation proves incorrect: it ignores the quantum nature of the spin. Of course, the state in which the spin of the  $i$ th atom deviates from the others is allowed to exist. But we cannot be satisfied with this: we want this state to be *sta-*

\* We want to emphasize again that the "direction" of spin (and generally, of any quantum-mechanical moment) is a convenient way to describe states with a given value of spin projection.

*tionary, to have a definite energy.* But this is an excessive demand. We have already mentioned (see Sec. 1.4) that not any two physical quantities are allowed by quantum mechanics to have simultaneously definite values. Thus, for a ferromagnetic material, that is, for a system of the spins whose behavior is described by the Hamiltonian (3.8'), the energy of the system and the projection of the spin of the  $i$ th atom (if it differs from the projections of the spins of the other atoms) cannot have definite values simultaneously. This statement is so important for understanding further explanations that we shall illustrate it with an example of the simplest spin system composed of two electrons (spin-1/2 particles) coupled by the exchange interaction (see formula (1.39)).

It is clear from Table 2 on p. 64 that the value of the scalar product  $\mathbf{s}_1 \cdot \mathbf{s}_2$  (and hence, of energy) is determined by the total spin of the system of two electrons, and only in two of the four stationary states the projection of each spin is defined. These are the states with  $S = 1$  but  $S_z = +1$  and  $S_z = -1$ . In these states each of the electrons has a definite spin projection: if  $S_z = 1$ , both electrons have  $s_z = +1/2$ , and if  $S_z = -1$ , both have  $s_z = -1/2$ . In the other two states ( $S = 0$ , and  $S = 1$  with  $S_z = 0$ ) the projections  $s_z = 1/2$  and  $s_z = -1/2$  for each electron are "mixed", that is, in these states none of the electrons has a definite spin projection.

Analogues of the states with  $S = 1$  and  $S_z = \pm 1$  for a ferromagnetic material are the states with  $S = Ns$  and  $S_z = \pm Ns$ , that is, the states



with the lowest exchange energy (of course, for  $A > 0$ ), and, at the same time, the states with definite values of spin projections for each atom (for any  $i$ ,  $s_{iz} = +s$  if  $S_z = Ns$ , and  $s_{iz} = -s$  if  $S_z = -Ns$ ). In other stationary states (as in the case of two electrons) the projections of the spins of individual atoms do not have definite values. Table 2 also hints how to characterize the stationary states of a system of the spins related by the exchange interaction (note that the Hamiltonian (3.8'), whose properties we are now studying, is a generalization of the Hamiltonian (1.39)). According to the table, the projection of the total spin has a definite value in all four stationary states. This property of stationary states is also preserved in the case of interest to us now: that of a system of the atomic spins described by the Hamiltonian (3.8'). Consequently, although there are no stationary states with a "deflected" spin in a given lattice site,

*there exist stationary states with a definite value of the  $S_z$  projection of the total spin of the whole ferromagnetic specimen onto the anisotropy axis.*

It is intuitively clear that at low temperatures that are of interest to us now, the important states are those close to the ground state. Let us consider a stationary state with  $S_z = Ns - 1$ , that is, with a minimum decrease in the projection of the total spin. One would like to realize this state by changing the spin projection of one atom by unity:  $s \rightarrow s - 1$ . But we have seen that this is forbidden by quantum mechanics. Hence, the deflected spin (the spin with the projection  $s - 1$ ) must belong to the whole

crystal. It is often said to be "spread" over the whole crystal lattice. By way of illustration, this situation can be pictured as the hopping of the deflected spin from one atom to another owing to exchange interaction. In quantum terms this means that the  $\Psi$  function of the stationary state with  $S_z = Ns - 1$  has a periodic wave-form and describes a consecutive deflection of the atomic spins in crystal lattice sites. It very much reminds us of the de Broglie wave mentioned in relation to the properties of free particles (see Sec. 1.4). It is referred to as the *spin wave* (hence the title of the section).

As the de Broglie wave, the spin wave is characterized by a wave vector  $\mathbf{k}$  to which, by analogy to free particles, we can relate the momentum:

$$\mathbf{p} = \hbar \mathbf{k} \quad (3.23)$$

As any stationary state, the spin wave is characterized by its energy. Traditionally, it is measured off the ground state energy. The energy of a free particle is

$$\varepsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

where  $m$  is the particle mass. The spin wave energy  $\varepsilon$  is also a function of wave vector. If a ferromagnetic material has a primitive cubic lattice, then

$$\varepsilon(\mathbf{k}) = 2A(3 - \cos k_x a - \cos k_y a - \cos k_z a) \quad (3.24)$$

where  $a$  (the lattice parameter) is the distance between the nearest neighbor atoms, and  $k_x$ ,

$k_y$ ,  $k_z$  are the projections of the wave vector  $\mathbf{k}$  onto the edges of the cubic unit cell of the lattice.

This comparison of a spin wave with a particle was dictated not only by pedagogical arguments. The resemblance is indeed striking: both the particle and the spin wave have identical dynamic characteristics; namely, momentum  $\mathbf{p}$  and energy  $\epsilon$  as a function of momentum. It should be emphasized that the latter feature is a corollary of quantum mechanics.\* The energy of a classical wave is a function of amplitude and thus can assume no matter how small values. The resemblance between a quantum spin wave and a particle is so strong that a special particle with momentum  $\mathbf{p} = \hbar\mathbf{k}$  and energy  $\epsilon = \epsilon(\mathbf{p})$  is "introduced"; this particle is governed by formula (3.24). This particle is called the *magnon*. We request that the reader reread all that was said about the de Broglie relations (see pp. 37-38). The "introduction" of the magnon signifies that formulas (1.19) and (1.20) are read from right to left, thereby recognizing the corpuscular properties of the spin wave.

The magnon is not quite an ordinary particle. Do not forget that it is nothing less than an elementary excitation of ordered magnetic moments of a ferromagnetic material, or the wave of spin deflections. Once a ferromagnetic drops to its ground state, the magnon disappears. Contrary to this behavior, ordinary particles (elec-

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\* In fact, this is a result of the spatial quantization of the spin whose projection can only change in a discrete manner (see Sec. 1.5, formula (1.23)).

trons, protons, atoms, etc.) neither vanish nor are born from nothing.

In order to emphasize the specificity of particles introduced for the description of elementary excitations in macroscopic bodies, they are referred to as *quasiparticles*.

It has been underlined several times in this section that a spin wave is an elementary excitation. But in what sense is the wave of deflections of spins elementary if it "involves" all the atoms of a ferromagnetic specimen? In the sense, and only in this sense, that this excitation cannot be decomposed into more elementary ones: there cannot exist simpler stationary states of a ferromagnetic with the spin projection equal to  $Ns - 1$ .

We have thus explained two of the three unfamiliar terms introduced at the beginning of this section (the spin wave and the quasiparticle). The third was the energy spectrum. Now we shall discuss the energy spectrum of ferromagnetics.

We have thus found that a minimum possible change in the spin of a ferromagnetic, and hence, of its magnetic moment, results in an increment of the energy of the ferromagnetic by  $\epsilon(\mathbf{k})$  which is a function of the wave vector  $\mathbf{k}$ . It has been already mentioned that with the magnetic moment of a crystal fixed, its energy is not determined unambiguously. There is a whole band of possible (allowed) values of energy corresponding to the magnetic moment equal to  $(Ns - 1)2\mu_B$  ( $g = 2$  for  $J = s$ , and  $g\mu_B$  is the smallest possible change in the projection of the magnetic moment of an individual atom). According to (3.24), the width of this band is  $12A$  because

$\varepsilon(\mathbf{k}) = 0$  at  $ak_x = ak_y = ak_z = 0$  and  $\varepsilon(\mathbf{k}) = 12A$  at  $ak_x = ak_y = ak_z = \pm\pi$  (Fig. 51). Note that the band of allowed values of energy is not separated by a gap from the ground state energy  $E_S$  given by (3.9). The band appears as a result of exchange energy. This is clear because the width of the gap vanishes when  $A \rightarrow 0$  (see formula (3.24)).

Forget for a moment the exchange interaction. Let the crystal consist of  $N$  identical noninteract-

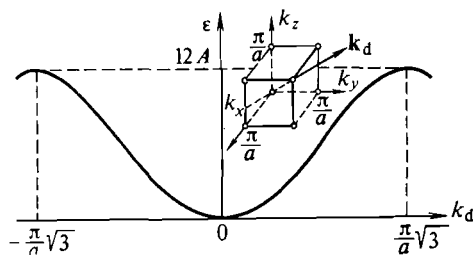


Fig. 51. Magnon energy  $\varepsilon$  as a function of the projection  $k_d$  of the wave vector  $\mathbf{k}$  onto the body diagonal of the cube

ing atoms, all of which occupy the ground state. Each of the atoms has its own system of energy levels, and these systems are identical. Consider the lowest excited state of our "crystal". Clearly, it corresponds to raising one of the atoms to its lowest excited state. It is unimportant which of the atoms is excited since all are identical. The same excitation energy corresponds to  $N$  different states (equal to the number of atoms) because the state is defined not only by its energy but also, in this particular case, by specifying

which of the atoms is excited. A level corresponding to more than one state is said to be *degenerate*.\* In this particular case the energy level is  $N$ -fold degenerate, with  $N$  being a fantastically large number ( $\sim 10^{23}$  per  $1 \text{ cm}^3$ ). The exchange interaction "cancels" degeneracy, that is, one degenerate level is replaced with  $N$  levels located within a  $12A$ -wide band. If  $N$  formally tends to infinity, the distances between levels tend to zero, and the allowed energy levels fill the whole band. This creates an *energy band*, that is, the band of allowed values of energy. Let us repeat and remember:

*the exchange interaction cancels degeneracy and turns a level into an energy band.*

The absence of a gap between the ground state of a ferromagnetic and the states with one magnon, or, which is the same, the equality of the energy of a spin wave with  $\mathbf{k} = 0$  to zero, has a profound physical meaning. The excitation with zero momentum (or with infinite wavelength) corresponds to a rotation of the magnetic moment of the ferromagnetic specimen as a whole (this changes the projection of the total spin onto an axis by unity). *Energy cannot be changed by this rotation because the exchange interaction is isotropic.* A spin wave with a nonzero wave vector describes the nonuniform excitation of the ferromagnetic. It is not surprising that the energy of such a wave is not zero. The following picture is convenient when the concept of the magnon

\* Unfortunately, the term "degeneracy" has several meanings in physics (cf. the term "degenerate gas" (see p. 124)).

is used: the energy  $\varepsilon(\mathbf{p})$  is the energy of the motion of the magnon, or its kinetic energy. It is then natural that  $\varepsilon(\mathbf{p}) = 0$  at  $\mathbf{p} = 0$ .

The magnon-particle resemblance becomes especially clear for magnons with very small momenta. Since at  $ak_j \ll 1$  ( $j = x, y, z$ )

$$\cos ak_j \approx 1 - \frac{1}{2}(ak_j)^2$$

formulas (3.24) and (3.23) yield

$$\varepsilon(\mathbf{p}) = A \frac{a^2 p^2}{\hbar^2} \text{ at } ap \ll \hbar \quad (3.25)$$

$$p^2 = \hbar^2 (k_x^2 + k_y^2 + k_z^2)$$

In this form the magnon energy depends on momentum in the same way as the energy of a free particle with the mass  $m^* = \hbar^2/2Aa^2$ . The quantity  $m^*$  is called the *effective magnon mass*. The inverse proportionality of the effective mass to the exchange integral is natural: lighter particles move easier, and the motion of a magnon is caused by the exchange interaction.

If a ferromagnetic specimen is placed in an external magnetic field along which the magnetic moments of atoms align, then the change in the spin projection of a single atom by unity is accompanied by an increase in energy by  $2\mu_B H$ . As a result, the energy of the spin wave (3.24) is augmented by the same amount:

$$\varepsilon(\mathbf{k}) = 2A(3 - \cos ak_x - \cos ak_y - \cos ak_z) + 2\mu_B H \quad (3.26)$$

This formula resembles expression (2.20) for the electron energy in a magnetic field. The

exchange-interaction component of the energy, depending on momentum  $\mathbf{p} = \hbar\mathbf{k}$ , is an analogue of the electron kinetic energy, while the term  $2\mu_B H$  is an analogue of the energy of the electron spin in a magnetic field. Therefore it can be interpreted as the energy of the *magnon spin* in the magnetic field  $H$ . The factor 2 signifies that the magnon must be assigned a spin twice that of the electron, that is, magnons are spin-1 quasiparticles. On the other hand, the increment to energy due to the electron spin is seen to assume two values:  $+\mu_B H$  and  $-\mu_B H$ , in correspondence with the spin orientation along the field or against it (since  $e < 0$ , the directions of the spin and magnetic moment of the electron are opposite). A unity spin has three projections:  $+1$ ,  $0$ ,  $-1$ . Seemingly, the increment to the magnon energy must also assume three values:  $-2\mu_B H$ ,  $0$ , and  $+2\mu_B H$ . The fact that formula (3.26) contains a single value of the spin term signifies that only one of the three possible states with different spin projections is realized: that with the projection equal to  $-1$ . The physical cause of this result is clear: a magnon (spin wave) is born in order to diminish the spin projection of a ferromagnetic specimen; this is only possible if the magnon has a negative spin projection. This last remark on the implementation of only one of the three spin states of a magnon does not cancel the statement that

*a magnon is a spin-1 quasiparticle.*

The expression (3.24) for the magnon energy  $\varepsilon(\mathbf{k})$  is periodic in each of three variables: in  $k_x$ , in  $k_y$ , and in  $k_z$  (the cosine is a periodic

function). All three periods are identical and equal to  $2\pi/a$ . Periodicity in energy is a direct consequence of periodicity of the crystal. Not only the energy of a magnon but its wave function as well has this property. This means that two states with wave vectors  $\mathbf{k}$  and  $\mathbf{k}'$  are *physically indistinguishable* if

$$k'_x - k_x = \frac{2\pi}{a} n_1, \quad k'_y - k_y = \frac{2\pi}{a} n_2, \quad k'_z - k_z = \frac{2\pi}{a} n_3$$

and  $n_1, n_2, n_3$  are integers. These last equalities can be recast in a compact form by introducing a vector  $\mathbf{K}$  with "integer" components:

$$K_x = \frac{2\pi}{a} n_1, \quad K_y = \frac{2\pi}{a} n_2, \quad K_z = \frac{2\pi}{a} n_3$$

Two states are thus physically indistinguishable if the wave vectors  $\mathbf{k}$  and  $\mathbf{k}'$  differ by a vector  $\mathbf{K}$ :

$$\mathbf{k}' = \mathbf{k} + \mathbf{K}$$

Consequently, all *distinct* states of a magnon are determined by the wave vectors in a cubic cell with edges equal to  $2\pi/a$ . A crystal lattice can be constructed of the vectors  $\mathbf{K}$  (constructed on paper, that is). It is called the *reciprocal lattice*. All distinct states of a magnon have wave vectors belonging to one unit cell of the reciprocal lattice. If we multiply the length of the edges of the unit cell of the reciprocal lattice by  $\hbar$ , we obtain a unit cell containing those values of momentum that correspond to distinct states of the magnon.

The situation with ordinary particles is quite different. The states with different "true" momenta always differ from one another, and mo-

mentum can take on arbitrary, even no matter how large, values.\* This distinguishes the free-particle momentum from the momentum we assigned to a quasiparticle (magnon in this particular case). This difference is emphasized by calling the momentum of quasiparticles the *quasimomentum*. Note that the prefix "quasi" in the word quasimomentum is used not because we are concerned with a quasiparticle. Examples can be given when the state of a true particle in a stationary state is characterized by a quasimomentum, and conversely, when a quasiparticle is characterized by a momentum. An example of the former is an electron (a particle) in a crystal lattice\*\*, and an example of the latter is a photon (a quasiparticle, a quantum of an electromagnetic field) in vacuum.

The replacement of momentum with quasimomentum is a consequence of the geometric properties of the world "inhabited" by magnons. It is quasimomentum and not momentum that describes the states of any quasiparticles that are quantum analogues of elementary excitations in crystals. This aspect will reappear later in the book.

By way of digression, let us clarify the meaning of the phrase "geometric properties of the world". If a crystal lattice is translated by a vector con-

\* But in this case energy must be expressed not by the habitual formula  $\varepsilon = p^2/2m$  but by the relativistic formula  $\varepsilon = \sqrt{m^2c^4 + c^2p^2}$ .

\*\* When analyzing the properties of conduction electrons in metals, we simplified the situation by "throwing out" of the metal its lattice constructed of positive ions (see Sec. 2.4).

necting two equivalent lattice sites, the lattice coincides with itself. The smallest displacement superposing a cubic lattice on itself equals  $a$  and must be carried out along one of its axes:  $x$ ,  $y$ , or  $z$  (see Fig. 50). On the contrary, an empty space is uniform and thus coincides with itself for any displacement, even an infinitesimal displacement. The length of the edge of a reciprocal lattice unit cell, inversely proportional to  $a$ , defines the range of quasimomenta. In the case of an empty space the lattice parameter can be assumed equal to zero. Consequently, the unit cell of the reciprocal lattice is infinitely large. In this sense the momentum is a quasimomentum with infinitely large unit cell of the reciprocal lattice.

### Spin Complexes

An elementary (minimum) excitation of the magnetic system of ferromagnetics thus can (and must) be pictured as the creation of a quasiparticle, that is, of a magnon, characterized by its quasimomentum  $\mathbf{p} = \hbar\mathbf{k}$  and energy  $\varepsilon = \varepsilon(\mathbf{p})$  given by formula (3.24) or (3.26). It is then natural to ask whether an arbitrary excited state of a ferromagnetic specimen can be described as a state with a specific number of magnons. The affirmative answer to this question would mean that formulas (3.24) and (3.26) completely define the energy spectrum of the ferromagnetic. Unfortunately, the answer is negative. Or rather, negative in the general case. In other words, sometimes it is possible and sometimes it is not.

In order to clarify this behavior, let us ana-

lyze the simplest case in which the excitation of a magnetic system is the minimum deflection of two spins or a double deflection of one spin.\* It would be very tempting to associate one magnon to each deflection. Then the excitation energy would be the sum of the energies of these two magnons. However, the actual situation is

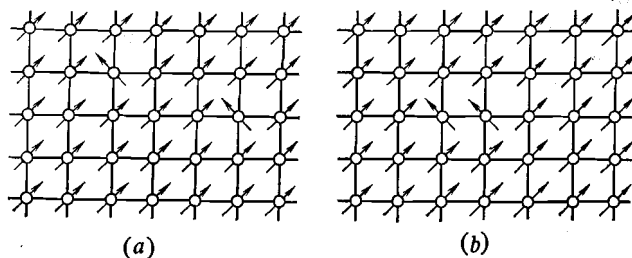


Fig. 52. Among nonstationary states of a crystal some states are such that the spins of two atoms are "deflected" from the common direction. These two atoms can be located far from each other (a) or be adjacent (b)

more intricate. The thing is that some of nonstationary (sic) states with two deflected spins are such that the deflected spins happen to be adjacent (Fig. 52). But then formula (3.8') dictates that the exchange interaction between them should be appreciable. Consequently, two magnons *interact* with each other.

An interaction between any particles either

\* We mean here the states with spin projection  $S_z = Ns - 2$ . If the spin of an individual atom is  $s = 1/2$ , a double deflection of the spin of this atom is impossible: once the spin projection of the atom diminished from  $s_z = 1/2$  to  $s_z = -1/2$ , it cannot diminish any more.

leads to the scattering of these particles on each other or to the formation of a bound system of these two particles (obviously, only if the particles are attracted to each other). In the first of these cases, that of scattering, the particles approach and then part, so that most of the time they are so far from each other that the interaction between them can be simply ignored, and the energy and momentum of the two particles equal, to a high accuracy, to the sum of their energies and momenta, respectively.

In the second case the formation of a bound state signifies that the particles do not "part" (there is a maximum distance by which the particles can be separated). A good example of such a "two-particle system" is the Earth and the Moon moving around the Earth along a nearly circular orbit. The energy of the Moon, equal to the sum of its kinetic and potential energies, is negative (the negative component is the potential energy in the case of attraction if we assume that the interaction energy tends to zero when the bodies recede to infinity). If the energy of a moving "particle" is positive (as it is for comets), then no bound state can be formed despite the attraction: a comet leaves the Earth and sometimes the solar system as well.

A quantum analogue of the Earth-Moon system is the hydrogen atom. The states with negative energy are bound states (with energy given by formula (1.21)). Zero energy separates the bound states of the electron in an atom from the free states in which the electron is scattered by the nucleus. The two examples (one cosmic and one

atomic) are illustrations of the following statement:

*depending on the value of energy in a system of two attracting particles, the particles may be either bound or free.*

Let us return to the system of two magnons. Let us single out the motion of the two magnons as an entity (with a quasimomentum equal to the sum of their individual quasimomenta) and their relative motion. It is found that the magnons are *attracted* to each other, with the magnitude of attraction depending on the total quasimomentum. This situation would be impossible for particles in vacuum. There it is always possible to change for an inertial frame of reference in which the center of mass of the particles is at rest, that is, their total momentum is zero. Note that nothing depends, and cannot depend, on the velocity with which the chosen inertial reference frame moves (this is the essence of the Galileo relativity principle). No such transition is possible in a crystal: quasiparticles move relative to the lattice which constitutes a unique frame of reference. The dependence of the interaction between magnons on their total quasimomentum is another manifestation of the fundamental difference between quasimomentum and momentum.

If the total quasimomentum exceeds a certain threshold value, then attraction is sufficiently strong and there exists in addition to states in which magnons are scattered, a certain state (with the same total quasimomentum) in which the magnons form a bound system. The energy of such

a state is less than the sum of the energies of free magnons. This situation is descriptively illustrated by the motion of two adjacent deflected spins through the crystal lattice (see Fig. 52b).

A bound state of two magnons is called the *spin complex*.

Consequently, under certain conditions there exists, in addition to states composed of two free magnons, a state with lower energy in which two magnons form a spin complex. In the case of three spin deflections there exist three types of state: three free magnons, a spin complex consisting of two magnons and one free magnon, and finally, a complex consisting of three magnons. The generalization to a larger number of spin deflections is obvious...

Clearly the energy spectrum of ferromagnetics is quite complex. In principle, with the energy spectrum of a body known we can calculate all its thermodynamic characteristics: specific heat, magnetic moment, and so on. However, if the spectrum is too complicated, the corresponding formulas become unwieldy and, therefore, useless. The calculation of the thermodynamic characteristics of ferromagnetics is considerably simplified if the temperature is much lower than the Curie temperature  $T_c$ . We shall see that in this case the main contribution to thermodynamic characteristics is made by states with a small number of magnons when the interaction between the magnons is a negligible factor. We are justified then in completely neglecting the interactions between the magnons. Consequently,

*at low temperatures a system of magnons can be treated as an ideal gas.*

We shall have an opportunity to recur to this fantastically fruitful model, but now want to take up a tempting possibility of treating spin waves in terms of a classical, and therefore very illustrative, description.

### 3.8. Spin Waves as Waves of Nonuniform Precession

Let us forget for a while the quantum nature of spins and consider them as magnetic needles (small magnets) which, as we well know, strongly interact among themselves in ferromagnetics. The forces responsible for the interaction are exchange forces that try to align all magnets parallel to one another. They are indeed so aligned in the ground state, and the magnetic moment per unit volume of a ferromagnetic material,  $\mathcal{M}$  (or magnetic moment density, or magnetization; these are different names for the same quantity), is simply the arithmetic sum of the magnetic moments of individual atoms located within this volume.

Now let us fix our attention on one of these magnetic needles and write an expression for its energy of interaction with all other magnets. This is achieved simply by dropping the summation over one of the subscripts in (3.8'). Also, we multiply and divide the whole expression by  $\mu_B^2$  in order to switch from the spins of atoms to their magnetic moments. Hence, the interaction energy between the  $i$ th magnetic moment and all other magnetic needles has the following



form:

$$E_i = -\mu_B \cdot i \left( \frac{A}{2\mu_B^2} \sum_h' \mu_{B,h} \right), \quad i = 1, \dots, N \quad (3.28)$$

Compare this expression with formula (1.26) describing the interaction between a magnetic moment and a magnetic field  $\mathbf{H}$ . You observe that the vector

$$\frac{A}{2\mu_B^2} \sum_h' \mu_{B,h}$$

plays the role of the magnetic field. And it is indeed called the *effective magnetic field* and is denoted by

$$\mathbf{H}_{\text{eff}} = \frac{A}{2\mu_B^2} \sum_h' \mu_{B,h} \quad (3.29)$$

A magnetic moment deflected from the magnetic field  $\mathbf{H}$  rotates around the field at a frequency  $\gamma H$  (see Sec. 1.6). One could think that a magnetic moment deflected from the equilibrium position rotates at a frequency easily calculable from formula (3.29), recalling that at equilibrium all magnetic moments are parallel. However, the reality is again more complicated. Expression (3.28) describes the interaction of any of  $N$  magnetic moments ( $N$  is the number of magnetic atoms in a crystal) with its surrounding. This means that there are  $N$  expressions such as (3.28). The motions (rotations) of all magnetic moments are interrelated. It is not possible to find the motion of one magnetic moment without analyzing the motion of all magnets. We have indicated

that already when describing the quantum states of a system of spins.

An analysis of rotation of the system of magnets shows that the simplest form of their motion is the propagation of waves of nonuniform precession. A look at Fig. 53 is sufficient to understand what nonuniform precession is. Each wave is characterized by its wave vector  $\mathbf{k}$ . We can

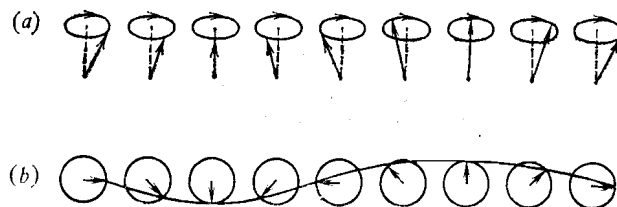


Fig. 53. Nonuniform precession of atomic spins: (a) the lateral view of a string of spins; (b) the top view, giving a wave plotted by a curve connecting the tips of spin vectors

calculate the wave frequency  $\omega$ . It proves to be a function of the wave vector, and this function can be found only by analyzing the equations of motion of all atomic magnetic moments. The equations are derived by means of (3.28). Unfortunately, here we are unable to carry out this analysis and have to give only the conclusions. The quantum and classical approaches yield identical results; the dependence of the frequency of a nonuniform precession wave,  $\omega$ , on the wave vector  $\mathbf{k}$  coincides with that of magnon energy (3.24) if it is divided by Planck's constant  $\hbar$  (recall the de Broglie relation).

In other words,

*a magnon is a wave of the nonuniform precession of atomic magnetic moments.*

We have often stressed that the exchange interaction is isotropic. It aligns magnetic moments but does not single out the direction along which the magnetic moment  $\mathcal{M}$  must be directed. This direction is fixed either by a magnetic field or by anisotropic forces described in Sec. 3.4.

As a result of the isotropy of exchange interaction the frequency of precession waves (or magnon energy) tends to zero as the wave vector  $\mathbf{k}$  tends to zero. If  $\mathbf{k} = 0$ , this is the wave of uniform precession ( $\lambda = 2\pi/k = \infty$ ), that is, merely a rotation of all magnetic moments by the same angle, and we already know that the exchange interaction does not "notice" this operation. But if nonexchange interactions are "switched on" (anisotropy energy, magnetic field), then the uniform precession of all magnetic moments will proceed at a quite definite frequency. We denote it by  $\omega_0$ . In the simplest cases it is added to the frequency of nonuniform precession.

The wave of precession of atomic magnetic moments takes into account the discrete structure of the crystal: the rotating magnets are precisely *atomic* magnets. Limiting the picture to waves with small wave vectors ( $ak \ll 1$ ) (and it will be shown in Sec. 3.10 that this range is the most interesting to us), we can be satisfied with a *macroscopic* description of the motion of magnetic moments, by introducing the mean density of the magnetic moment in a ferromagnetic material,  $\mathcal{M} = \mathcal{M}(\mathbf{r}, t)$ , that is, the vector

sum of the atomic magnetic moments in unit volume.

The oscillating quantity in a nonuniform precession wave with a small wave vector is the magnetic moment density of the ferromagnetic.\* In particular, uniform precession is the rotation of the magnetic moment of the specimen as a whole, and a small-momentum magnon (we remind the reader that momentum  $\mathbf{p} = \hbar\mathbf{k}$ ) is a wave of the nonuniform precession of magnetization (magnetic moment density).

The advantage of the classical approach lies in its simplicity and descriptiveness. But it must be borne in mind that it is not as exact as the quantum approach. Consequently, it is necessary to know the limits of applicability of the classical description in order to avoid errors.

### 3.9. Gas of Magnons

Now let us consider the case of a ferromagnetic material at a temperature low in comparison with the Curie temperature  $T_c$  when the material is in a state of maximum ordering, i.e. in the ground state.

At low temperatures magnons in ferromagnetics are few, and therefore their "collisions" are infrequent and the interaction between them can be ignored. We have already mentioned that this interaction can be neglected completely and the

\* The word "oscillates" must not be interpreted literally. It means precisely the *nonuniform precession*. Although a wave propagates through the ferromagnetic,  $\mathcal{M}^2(\mathbf{r}, t) \equiv \mathcal{M}_0^2$  ( $\mathcal{M}_0$  is the magnetic moment density at saturation), and the magnetic moment only rotates.

system of magnons can be treated as an ideal gas.

Of course, spin complexes are allowed to form, but at low temperatures their number is extremely small\* and we can neglect them as well.

At low temperatures magnons thus form an ideal gas of quasiparticles. But in the range of low temperatures not only quasiparticles but ordinary "true" particles as well manifest the quantum properties of systems especially well (see Sec. 2.4). The question that naturally arises then is: Do magnons become bosons or fermions? Are their collective properties described by the Bose-Einstein or Fermi-Dirac statistics?

You remember that particles with zero and integral spins are bosons, while particles with half-integral spin are fermions. This theorem can be generalized to quasiparticles as well. The spin of a magnon is unity, so that magnons are bosons, and the magnon gas is a Bose gas.

### *Bose Gas*

It is high time we recall our promise and describe the properties of a degenerate Bose gas, that is, a Bose gas at temperatures much lower than

$$T_q = \frac{\hbar^2}{km} \left( \frac{N}{V} \right)^{2/3}$$

\* We shall see (although we expect it to be intuitively clear) that at  $T \ll T_c$  magnons predominantly have energy  $\varepsilon \ll kT$ , that is, energy much less than the magnon band width  $12A$  (according to (3.11),  $\nabla k T_c = zA/4$ ). Such magnons have a low quasimomentum and they cannot form a spin complex, while the number of magnons with high momenta is very small.

(see formula (2.17)). No degenerate Bose gases of "true" particles exist at such temperatures: all of them turn into liquids at  $T \gg T_q$  and solidify (helium is the only exception). We shall describe the properties of a Bose gas, dictated by the laws of quantum statistics, if such gas existed (attempts are being made nowadays to produce a degenerate Bose gas artificially).

Let a volume  $V$  be filled with  $N$  Bose particles at  $T \ll T_q$ . Each particle moves according to the laws of quantum mechanics, and its energy is determined by its momentum:  $\varepsilon = p^2/2m$ . We remind the reader that inevitably the coordinate of the particle has no definite value. As in the case of a Fermi gas (see p. 125), we begin at absolute zero of temperature when the system must be in its ground state, that is, the state with the lowest energy. Bosons are not governed by the Pauli principle, and so nothing precludes them from transferring to the state with zero momentum. This macroscopic accumulation of particles in a state with  $p = 0$  is called the *condensate*. Hence,

*the ground state of a boson gas is the condensate.*

An elementary excitation of the gas of bosons is equivalent to one particle leaving the condensate, that is, to the creation of a moving particle with  $p \neq 0$ . Since most methods of detecting a particle are based on detecting its motion, the particles of the condensate "do not exist" but are "born" when motion starts. Quantum statistics makes it possible to determine the mean number of particles with momentum  $p \neq 0$ , that is, the equilibrium distribution function

at  $T < T_0$ :

$$\bar{n}_p = \frac{1}{\frac{\varepsilon(p)}{e^{kT}} - 1} \quad (3.30)$$

If we are interested in the mean density  $\bar{n}(\varepsilon)$  of particles in an infinitesimal interval of energy from  $\varepsilon$  to  $\varepsilon + d\varepsilon$ , this last expression must be multiplied by the density of states\*  $g(\varepsilon)$  equal to

$$\frac{(2s+1)V}{\sqrt{2}\pi^2\hbar^3} m^{3/2} \sqrt{\varepsilon}$$

where  $s$  is the particle spin ( $s = 0, 1, 2, \dots$ ):

$$\bar{n}(\varepsilon) = \frac{(2s+1)Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon}{kT}} - 1} \quad (3.31)$$

The total number of moving Bose particles at a temperature  $T$  is found by integrating over energy:

$$N_p = \frac{(2s+1)m^{3/2}}{\sqrt{2}\pi^2\hbar^3} V \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} \quad (3.32)$$

Although at  $\varepsilon = 0$  the integrand tends to infinity, the integral has a quite definite value and is proportional to  $T^{3/2}$ . The number of particles in the condensate,  $N_0$ , equals the total number of particles  $N$  minus  $N_p$ . At a temperature

\* We described the density of states and explained why it is proportional to  $\sqrt{\varepsilon}$  on p. 126. The formula given here differs from (2.19) in that it is written for an arbitrary spin. In the case of the electron we have to substitute  $s = 1/2$ , arriving, of course, at formula (2.19).

$T = T_0$  where

$$kT_0 \approx \frac{3.31}{2s+1} \frac{\hbar^2}{m} \left( \frac{N}{V} \right)^{2/3} \quad (3.33)$$

the condensate disappears; at  $T > T_0$  all the particles move. The behavior of Bose gases is usually studied by gradually lowering the temperature, so that the point  $T_0$  is called the temperature of the *Bose-Einstein condensation*. At

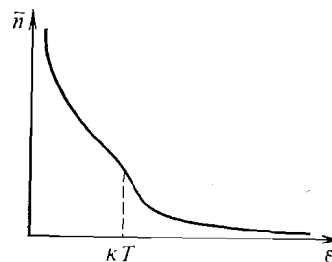


Fig. 54. Energy distribution of Bose-gas particles with  $p \neq 0$ , in arbitrary units. The area under the curve  $\bar{n} = \bar{n}(\varepsilon)$  equals the total number  $N_p$  of gas particles moving in a container

$T < T_0$  a finite number of particles is at rest, being a part of the condensate. The specific behavior of Bose gases must be revealed in all its thermodynamic properties. Thus, at  $T < T_0$  the heat capacity of a Bose gas is proportional to  $T^{3/2}$  (the heat capacity of a classical gas is independent of temperature, while that of a Fermi gas linearly tends to zero).

To conclude this subsection, let us have a look at the energy distribution of particles at  $T < T_0$ . And we literally mean "look". Figure 54 plots

the mean particle density  $\bar{n}(\epsilon)$ . You observe that practically all the particles concentrate on the interval from 0 to  $kT$ , and as energy increases, the density exponentially tends to zero.

\* \* \*

Let us return to the gas of magnons. We shall use the approach developed in the preceding section and described in italics on p. 216. We shall begin with a wave of nonuniform precession. It is characterized by a wave vector  $\mathbf{k}$  and frequency  $\omega$ . If we can speak about frequency (in this particular case  $\omega(\mathbf{k})$ ), we can speak of an "oscillator" whose frequency is  $\omega(\mathbf{k})$ . It is not so important what oscillates as long as it *oscillates*. According to quantum mechanics, the oscillator energy is known to assume the values equal to

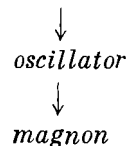
$$\epsilon_{n\mathbf{k}} = \frac{1}{2} \hbar \omega(\mathbf{k}) + n_{\mathbf{k}} \hbar \omega(\mathbf{k}) \quad (3.34)$$

We intentionally chose this form instead of a more familiar formula  $(n + 1/2) \hbar \omega$  in order to emphasize that the energy  $n_{\mathbf{k}} \hbar \omega(\mathbf{k})$  is the energy of the excited state. The state of a ferromagnetic is fixed by prescribing the numbers  $n_{\mathbf{k}}$ , that is, the degrees of excitation of each oscillator. Since a wave of nonuniform precession can be put in correspondence with a magnon with qu momentum  $\mathbf{p} = \hbar \mathbf{k}$  and energy  $\hbar \omega(\mathbf{k})$ , the degree of excitation of an oscillator (the number  $n_{\mathbf{k}}$ ) can be regarded as the number of magnons\* with

\* The introduction of magnons is justified precisely by the fact that in units of  $\hbar \omega(\mathbf{k})$  the excitation energy can assume only integral values. Evidently, the deriva-

wave vector  $\mathbf{k}$  or momentum  $\mathbf{p} = \hbar \mathbf{k}$ . This can be illustrated by the following diagram:

*spin wave as a wave of nonuniform precession*



When defining the state of a ferromagnetic, we need not know the exact (corresponding to each instant) values of the numbers  $n_{\mathbf{p}}$  of magnons (we have switched completely to corpuscular terms, having replaced  $\mathbf{k}$  with  $\mathbf{p}$ ). In order to derive the temperature dependence of the quantities characterizing the gas of magnons, it is sufficient to know the *mean* number of magnons with momentum  $\mathbf{p}$ , that is, the distribution function of the magnons,  $\bar{n}_{\mathbf{p}}$ . Our nearest problem is to find this function.

But first another digression.

### Quantum Oscillator

Let us turn to formula (2.5) on p. 102. On the left-hand side of the equality we see the ratio of the number of particles with energy  $\epsilon_M$  to the total number of particles. This ratio can be regarded as the probability  $W_M$  for a particle

tion given here is far from being rigorous. The formulas given above are strictly proved in ferromagnetism theory. Among other things, it is proved that formula (3.34) holds, and this formula is of paramount importance of this part of our story about the magnon gas.

to have a given energy  $\varepsilon_M$ . On the right-hand side we find

$$\frac{e^{-\frac{\varepsilon_M}{kT}}}{\sum_M e^{-\frac{\varepsilon_M}{kT}}}$$

that is,

$$W_M = \frac{e^{-\frac{\varepsilon_M}{kT}}}{\sum_M e^{-\frac{\varepsilon_M}{kT}}}$$

with summation in the denominator carried out over all possible quantum states. This simple relation (simple until we try to specify  $\varepsilon_M$ ) is the basis of physical statistics. We want to apply it to an oscillator with frequency  $\omega$ . Then

$$W_n = \frac{e^{-n \frac{\hbar\omega}{kT}}}{\sum_{n=0}^{\infty} e^{-n \frac{\hbar\omega}{kT}}} \quad (3.35)$$

is the probability that the oscillator is in the  $n$ th quantum state. The mean value (often called the *expectation value* in probability theory) of any physical quantity which depends on the degree of excitation of the oscillator, that is, is dependent on  $n$ , is found by multiplying this quantity by  $W_n$  and summing over all  $n$ . First

we find the mean value of the degree of excitation:

$$\bar{n} = \sum_{n=0}^{\infty} n W_n = \frac{\sum_{n=0}^{\infty} n e^{-n \frac{\hbar\omega}{kT}}}{\sum_{n=0}^{\infty} e^{-n \frac{\hbar\omega}{kT}}}$$

The infinite sum in the denominator is the sum of terms of a geometric progression with the first term equal to unity and the common ratio  $\exp(-\hbar\omega/kT)$ . Consequently,

$$\sum_{n=0}^{\infty} e^{-n \frac{\hbar\omega}{kT}} = \sum_{n=0}^{\infty} \left( e^{-\frac{\hbar\omega}{kT}} \right)^n = \frac{1}{1 - e^{-\frac{\hbar\omega}{kT}}}$$

The sum in the numerator is obtained from the sum in the denominator if the latter is differentiated with respect to  $x = \hbar\omega/kT$  and taken with reverse sign:

$$\sum_{n=0}^{\infty} n e^{-n \frac{\hbar\omega}{kT}} = -\frac{d}{dx} \left( \sum_{n=0}^{\infty} e^{-nx} \right) \Big|_{x=\frac{\hbar\omega}{kT}}$$

Finally we obtain

$$\bar{n} = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} \quad (3.36)$$

Before discussing this important formula, let us find the mean value of the oscillation energy:

$$\bar{\varepsilon} = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \quad (3.37)$$

This expression immediately shows how to transform to classical statistics: if  $\hbar\omega \ll kT$ ,

$$e^{\frac{\hbar\omega}{kT}} \approx 1 + \frac{\hbar\omega}{kT}$$

and we have to conclude that

*in conditions where the classical description is valid the mean oscillation energy is equal to temperature in energy units:  $\bar{\epsilon} = kT$ .*

The mean degree of excitation of an oscillator under the same conditions is  $\bar{n} \sim kT/\omega$ . Formally, the proportionality factor includes Planck's constant but this is unimportant because it cancels out in the calculation of mean values.

The derivation of formulas (3.36) and (3.37) reproduced above was first carried out by Max Planck in 1900 when he studied the radiation emitted by a blackbody, that is, a body that emits but does not reflect electromagnetic waves (a small hole in the wall of a large cavity is a good model of a blackbody). In order to explain experimental facts, Planck had to make an assumption that signified the rejection of classical physics: he had to recognize that an oscillator can occupy only those states in which its energy is a multiple of  $\hbar\omega$  (see (3.34)). Planck chose the value of the constant (Planck's constant) that provided the best fit of the experimental and theoretical curves.\*

\* Even today, after more than 80 years elapsed since Planck's constant has been introduced, we see no possibility of calculating it. It is not calculated, just as other fundamental constants in physics are not: the

\* \* \*

It is clear from the diagram given on p. 223 that the equilibrium distribution function for magnons

$$\bar{n}_p = \frac{1}{e^{\frac{\epsilon(p)}{kT}} - 1} \quad (3.38)$$

is identical to the distribution function in a Bose gas at a temperature below that of the Bose-Einstein condensation. An ensemble of magnons is indeed a Bose gas.

Formulas (3.38) and (3.30) differ in that formula (3.38) describes the distribution of all magnons. There is no magnon condensate.

If the temperature of a ferromagnetic material is much less than its Curie temperature, the main role in its properties is played, as we know from the analysis of a degenerate Bose gas, by particles (by quasiparticles, namely, magnons, in this particular case) with energy less than  $kT$ . We can thus make use of approximate formula (3.25) and also of formulas (3.34) and (3.32) in which, however,  $2s + 1$  must be replaced with 1 because (as you remember) only one spin state of the three possible spin states of the magnon is realized, namely, that with  $s_z = -1$ . The particle mass  $m$  must be replaced with the effective magnon mass  $m^* = \hbar^2/2Aa^2$  (see p. 204).

speed of light  $c$  and electron charge  $e$ . They must be measured. It is interesting to note that the most accurate values of Planck's constant  $\hbar$  were obtained by means of a superconducting device, that is, by the methods of solid-state quantum physics.

When the equilibrium distribution function  $\bar{n}_p$  is known, it is possible to calculate a number of macroscopic quantities that characterize the magnon gas, and hence, the ferromagnetic material. The quantity that is of maximum interest for us is the magnetic moment of the gas of magnons in unit volume, that is, its magnetization. This important aspect calls for a separate section.

### 3.10. Magnetization and Heat Capacity of Ferromagnetics at Low Temperatures

When considering the behavior of magnons in a ferromagnetic specimen placed in a magnetic field, we observed that each magnon "carries" a magnetic moment equal to twice the Bohr magneton and pointing against the magnetization of the ferromagnetic. Consequently, the magnetization of unit volume of the material,  $\mathcal{M}(T)$ , is the difference between the magnetic moment at absolute zero,  $\mathcal{M}_0 = N\mu_{BS}$ , and the magnetic moment of the magnon gas. This last is simply equal to the number of magnons  $N_{\text{magn}}$  times  $2\mu_B$ . Therefore,

$$\mathcal{M}(T) = N\mu_{BS} - 2\mu_B N_{\text{magn}} \quad (3.39)$$

If the magnetic field  $H$  is low ( $\mu_B H \ll kT$ ) (see p. 105), we can set it to zero and resort to formula (3.32), without forgetting to replace  $m$  with the magnon effective mass and  $2s + 1$  with 1. As a result, we obtain

$$\mathcal{M}(T) = N\mu_{BS} \left[ 1 - 0.1 \left( \frac{kT}{A} \right)^{3/2} \right] \quad (3.40)$$

(that the integration in formula (3.32) is carried out to infinity need not bother us: the contribution of states with energy higher than  $kT$  is absolutely negligible). We have taken into account that each unit cell of the crystal contains one atom with the magnetic moment  $\mu_{BS}$ , that is,  $1/a^3 = N$ .

This relation first derived by Felix Bloch in 1930 is often called *Bloch's law*, or *the law of 3/2*, thus indicating the exponent with temperature.

We now see how wrong the result obtained in the Curie-Weiss model was. Both formulas (3.5) and (3.40) were derived under the assumption that only exchange forces act among atomic magnetic moments. However, the Curie-Weiss model assumes that the energy of a spin system is unambiguously determined by the total magnetization, while the correct quantum-mechanical theory reveals the existence of magnons whose excitation leads to demagnetization of a ferromagnetic specimen with increasing temperature. Obviously, the power and not the exponential character of magnetization dependence occurs because the number of magnons  $N_{\text{magn}}$  increases according to a power law. But *why* does  $N_{\text{magn}}$  increase by a power law and not otherwise? In order to explain this (this follows formally from (3.32)), let us consider a more complicated case of a strong magnetic field or of a very low temperature ( $\mu_B H \gg kT$ ). To make the analysis more general, we denote the quantity  $2\mu_B H$  in formula (3.26) by  $\epsilon_0$ , thereby emphasizing that this is the energy of a magnon "at rest", the magnon with  $\mathbf{p} = 0$ , and realizing that it is



determined by all nonexchange interactions.

In this case the number of magnons is given by a formula very similar to (3.32), but with integration carried out not from zero but from  $\varepsilon_0$ :

$$N_{\text{magn}} = \frac{1}{4\pi^2 a^3} \frac{1}{A^{3/2}} \int_{\varepsilon_0}^{\infty} \frac{\sqrt{\varepsilon - \varepsilon_0} d\varepsilon}{\frac{\varepsilon}{e^{kT}} - 1} \quad (3.41)$$

(See Problem 23.)

If  $kT \ll \varepsilon_0$ , the unity in the denominator can be dropped and the number of magnons proves to be exponentially small:

$$N_{\text{magn}} \approx \frac{1}{8\pi^{3/2} a^3} e^{-\frac{\varepsilon_0}{kT}} \left( \frac{kT}{A} \right)^{3/2} \quad (3.42)$$

Now compare the energy distributions of magnons when  $\varepsilon_0 = 0$  and when  $\varepsilon_0 \neq 0$ . If  $\varepsilon_0 \neq 0$ , the distribution has a maximum at  $\varepsilon \approx kT$ , that is, most of the magnons have an energy roughly equal to temperature (in energy units), but if  $\varepsilon_0 \gg kT$ , the total number of particles is exponentially small. If  $\varepsilon_0 = 0$ , most of the magnons have energies less than  $kT$  but the total number of magnons is proportional to  $(kT)^{3/2}$ . The root of the matter is thus whether the band of allowed energy values is separated from the ground state by a gap or not. The existence of a gap leads to the exponential dependence of the number of magnons, and hence, of magnetization, on temperature. Note that in ferromagnetics the gap is not of exchange-interaction origin, and for this reason the correct result is so drastically different from that obtained in the Curie-Weiss model. (See Problem 24.)

A gap in the energy spectrum of excited states

of a macroscopic body is a very frequent phenomenon. Naturally, it always entails the exponential temperature dependence of those macroscopic characteristics of a body that are determined by the excited states. This demonstrates the applicability of the formula that we called the basis of physical statistics (see the formula on p. 224).

When the energy distribution function of magnons is known, we can find the internal energy of the magnon gas, that is, the sum of the energies of individual magnons:

$$E_{\text{magn}} = \int_0^{\infty} \varepsilon \bar{n}(\varepsilon) d\varepsilon \quad (3.43)$$

where  $\bar{n}(\varepsilon) = g(\varepsilon)/e^{\varepsilon/kT} - 1$ .

Acting by analogy to our earlier calculations and assuming that  $\varepsilon_0 = 0$ , we readily establish that  $E_{\text{magn}} \propto T^{5/2}$ . Obviously, the magnon energy tends to zero as temperature tends to zero, but at a rate that will be shown presently to be relatively low. (See Problem 25.) In fact, our interest in the temperature dependence of magnon energy stems from just this feature.

By definition, the heat capacity of a body is the amount of heat consumed by the body upon its heating by one degree. If the volume of the body remains unchanged, the supplied heat goes to increase its internal energy, that is, the obtained heat equals the increment in the internal energy of the body,  $E_{\text{th}}$ . Consequently, if the volume is fixed (and the volume of a solid can be regarded as fixed practically always), the heat capacity  $C$  equals  $dE_{\text{th}}/dT$ . Beyond any doubt,

magnons contribute to the internal energy of ferromagnetics. Consequently, we can speak of the magnon part of ferromagnetics' heat capacity:

$$C_{\text{magn}} = \frac{dE_{\text{magn}}}{dT} \quad (3.44)$$

By now it is clear that the magnon heat capacity of ferromagnetics, just like their magnetization, is a linear function of  $T^{3/2}$ . The exact formula for  $C_{\text{magn}}$  (per  $1 \text{ cm}^3$ ) will not be out of place:

$$C_{\text{magn}} \approx 0.1kN \left( \frac{kT}{A} \right)^{3/2} \quad (3.45)$$

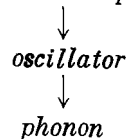
(we have again replaced  $1/a^3$  with  $N$ ). Here is why the exact formula is needed. When we deal with magnetization, only magnons are responsible for its temperature dependence at  $T \ll T_c$ . This is not so when we deal with heat capacity. We have hinted already at the explanation when introducing a distinction between the internal energy and the magnon energy of a body. The motion of atomic particles in a solid is not limited to the excitation of its spin system. There are excited states in which the positions of atomic spins are not altered at all. The most important among such motions are vibrations of atoms (or ions) around their equilibrium positions. This is described in the next subsection.

### Phonons

Atoms vibrate in all solids, not only in ferromagnetics. For this reason the contents of this subsection refer to arbitrary solids.

The atoms of solids, of course, interact: by attractive forces at large distances and by repulsive forces at short distances. Otherwise nothing could hold the atoms in the elegant structure that is a crystal with the periodically repeated arrangement of atoms in space. Should an atom be displaced from its equilibrium position, the forces mentioned above force it to return to that position; however, its neighbor atoms cannot remain "indifferent", and a wave of atomic displacements from the equilibrium positions will travel through the crystal. The simplest (elementary) form of such waves is a wave with a certain wave vector  $k$  and frequency  $\omega$  dependent on  $k$ . And now we follow the familiar path outlined by the diagram on p. 223:

*wave of atomic displacements*



The last line gives the name of the quasiparticle put in correspondence (by the de Broglie relations) with the wave of displacements. It was called the *phonon* because the waves of displacements are the familiar sound waves (acoustic waves) propagating through crystals (from the Greek *phōnē* for sound), at least when the wavelength  $\lambda = 2\pi/k$  is of macroscopic dimensions, much greater than the lattice parameter  $a$ , that is, when  $ak \ll 1$ . To recapitulate,

*the phonon momentum (quasimomentum) is  $\hbar k$ ,  
the phonon energy is  $\varepsilon = \hbar \omega(k)$ .*

As with any other quasiparticle existing in a periodic crystal lattice, the phonon energy is a periodic function of quasimomentum (Fig. 55a). However, since we are mostly inter-

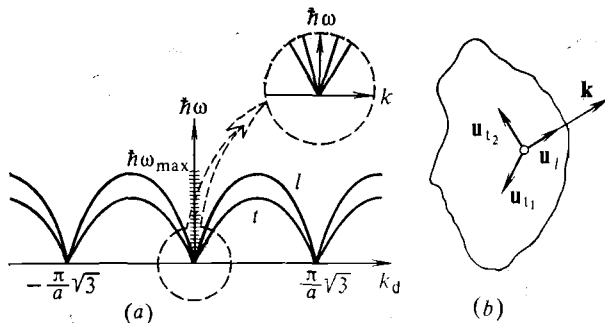


Fig. 55. (a) Phonon energy as a function of projection  $k_d$  of the wave vector onto the body diagonal of the cube (cf. Fig. 51) for longitudinal ( $l$ ) and transverse ( $t$ ) waves. When  $k \rightarrow 0$ ,  $\hbar\omega$  is a linear function of  $k$  (see inset). The range of allowed values of the phonon energy is shaded. (b) The displacement of atoms in the longitudinal ( $l$ ) wave is parallel to  $k$ , and in transverse waves ( $t$ ; two waves) it is perpendicular to  $k$ ;  $u$ —vector of atomic displacement

ested in the lowest excited states of bodies, we can limit the analysis to the relation between the frequency  $\omega$  and the wave vector  $k$  that holds for long-wavelength sound, with  $\lambda$  much greater than the lattice parameter  $a$ :

$$\omega = c_{\text{sound}}k, \quad \text{or} \quad \hbar\omega = c_{\text{sound}}p \quad (3.46)$$

where  $c_{\text{sound}}$  is the sound velocity independent (to a high accuracy) of sound frequency.\* Sound velocity differs for different types of solids. "On the average" it is between  $10^4$  and  $10^5$  cm/s.

Three types of acoustic waves propagate in solids: two of them are transverse waves and one is longitudinal (Fig. 55b clearly shows the directions of atomic vibrations in each of these waves). The velocities of the transverse and longitudinal waves somewhat differ, but we shall neglect this, keeping in mind that there exist three species of phonons.

The same Fig. 55 shows the region of allowed values of phonon energies. Note that it starts from zero: no gap separates it from the ground state of the crystal!

A perusal of the subsection "Quantum Oscillator" immediately shows: the number of phonons with momentum  $p$  is given by (3.36) or (3.38), only the phonon energy (3.46) must be substituted for  $\hbar\omega$  or  $\varepsilon(p)$ . Unfortunately, we cannot make use of formula (3.31) (as we did in the case of magnons) because the density of states  $g_{\text{ph}}(\varepsilon)$  of phonons does not coincide with the density of states of ordinary particles and magnons. Taking up again the derivation of the formula for the density of states (2.19) of electrons (see p. 126), we readily find that  $g_{\text{ph}}(\varepsilon) \sim \sim \varepsilon^2$  when  $\varepsilon \rightarrow 0$ . The exact formula for three

\* A more conventional form of relation (3.46) is  $v = c_{\text{sound}}/\lambda$ , where  $v$  is the cyclic frequency, and  $\lambda$  is the wavelength; since  $\omega = 2\pi\nu$  and  $k = 2\pi/\lambda$ , we obtain the relations given in the text.

species of phonons is

$$g_{\text{ph}}(\varepsilon) = \frac{3V\varepsilon^2}{2\pi^2\hbar^3 c_{\text{sound}}^3}$$

and hence,

$$\bar{n}_{\text{ph}}(\varepsilon) = \frac{3V}{2\pi^2\hbar^3 c_{\text{sound}}^3} \frac{\varepsilon^2}{e^{\frac{\varepsilon}{kT}} - 1}, \quad \varepsilon \ll \varepsilon_{\text{max}} \quad (3.47)$$

We have also indicated the conditions under which the formulas are valid. Indeed, we used the relation (3.46) valid only for low-energy phonons;  $\varepsilon_{\text{max}}$  is the maximum energy allowed to a phonon. The quantity  $\varepsilon_{\text{max}}/k = \Theta$  is called the *Debye temperature*. As a rule, it does not exceed several hundred Kelvins. Thus, it equals 90 K for Pb, 210 K for Ag, 180 K for KBr, and 280 K for NaCl. Diamond has an exceptionally high Debye temperature: about 2000 K.

The Debye temperature is an important characteristic of crystals. If the temperature of a body is much greater than the Debye temperature, there is no need to turn to quantum mechanics in treating atomic vibrations (see the statement in italics on p. 226). But if  $T \ll \Theta$ , the quantum treatment is mandatory. As you remember, we are interested in the low-temperature behavior. To be precise: we limit the analysis to the temperature range  $T \ll \Theta$ . In this case we can forget about the limitation in formula (3.47) and can show, in complete analogy to the earlier analysis, that the phonon energy is proportional to the fourth power of temperature ( $E_{\text{ph}} \propto T^4$ ), and the phonon heat capacity to the third power of  $T$  ( $C_{\text{ph}} \propto T^3$ ).

Figure 56 shows the phonon distribution function at low temperatures. You notice that the energy of most phonons is of the order of  $kT$ .

We shall give the exact expression for the phonon heat capacity of unit volume of the

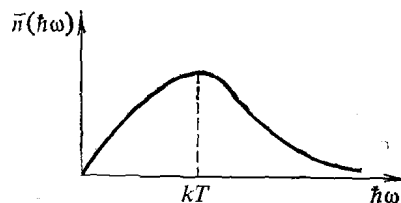


Fig. 56. Energy distribution of phonons. The area under the curve  $\bar{n} = \bar{n}(\hbar\omega)$  equals the total number of phonons at a temperature  $kT \ll \hbar\omega_{\text{max}}$

crystal containing a single atom per unit cell:

$$C_{\text{ph}} \approx \frac{2\pi^2 k}{5} \left( \frac{T}{\hbar c_{\text{sound}}} \right)^3 \quad (3.48)$$

(See Problem 26.) We remind the reader that we chose not to distinguish between the velocities of transverse and longitudinal acoustic waves.

Phonons constitute one of the basic heat reservoirs of solids. The decrease in heat capacity with decreasing temperature is probably the first macroscopic phenomenon that was explained in terms of quantum mechanics (A. Einstein and P. Debye), or in modern terms, by introducing phonons.

Now look carefully at formulas (3.45) and (3.48). They are very similar. Both state that the heat capacities—that of magnons and that

of phonons—tend to zero as temperature tends to zero. But the magnon component tends to zero slower than the phonon component:

$$\frac{C_{\text{ph}}}{C_{\text{magn}}} \propto T^{3/2} \rightarrow 0 \quad \text{as } T \rightarrow 0$$

At sufficiently low temperatures the heat capacity of a body is determined by magnons if the Curie temperature  $T_c$  is greater than the Debye temperature  $\Theta$ . Phonons “have the upper hand” at very low temperatures ( $kT \ll \varepsilon_0$ ): the heat capacity of ferromagnetics is determined by phonons as  $T \rightarrow 0$  because the number of magnons is exponentially small (see (3.42)) (a little earlier it was possible to ignore  $\varepsilon_0$  completely). What was described in this subsection holds for non-metallic ferromagnetics. In metals conduction electrons play an important role at low temperatures, and their heat capacity is proportional to temperature (this is also a quantum property; it follows from the degeneracy of the electron gas, see Sec. 2.4). Since the electron heat capacity diminishes with temperature slower than both the phonon and magnon components, it is the electron component that determines the behavior of heat capacity in metals when temperature tends to zero.

## Chapter 4

### Antiferromagnetism

We have mentioned, when describing the properties of paramagnetics (see Sec. 2.1), that the paramagnetic Curie temperature  $\Theta_p$  in the Curie-Weiss law is negative in a number of materials, and in the third chapter, when deriving the Curie-Weiss law for ferromagnetics at temperatures above the Curie temperature  $T_c$ , we found that  $\Theta_p$  (coinciding with  $T_c$  in the Curie-Weiss model) is determined by the exchange integral (see formula (3.11)). It is natural to assume that the negative sign of  $\Theta_p$  in these materials stems from the negative sign of the exchange integral. It would be natural to pose a general question: What should be the behavior, at decreasing temperatures, of paramagnetics if the exchange interaction between their atoms is high but the exchange integral is negative? L. D. Landau was probably the first to formulate this question (in 1933); he was able to show that such materials must undergo a peculiar magnetic phase transition of the second order, not accompanied by the creation of a macroscopic spontaneous magnetic moment. Later such materials were called *antiferromagnetics*. Soon after Landau's work the antiferromagnetic state was discovered experimentally by L. V. Shubnikov and his co-workers (in 1935). Table 6 lists some antiferromagnetics and gives their phase

Table 6

Antiferromagnetic	$T_N$ , K
$\text{NiSO}_4$	37
$\text{FeSO}_4$	21
$\text{NiO}$	520
$\text{FeO}$	188
$\text{NiF}_2$	73.2
$\text{FeF}_2$	78.3

transition temperatures  $T_N$ . The temperature of the phase transition into the antiferromagnetic state is called the Néel temperature in honor of the French physicist Louis Néel who was awarded in 1970 the Nobel Prize in physics for his work on antiferromagnetism.

#### 4.1. Antiferromagnetic Ordering

It has already been mentioned that both in antiferromagnetics and in ferromagnetics the main role is played by the exchange interaction. It is then natural to turn to the Hamiltonian (3.8'), in which we set  $A < 0$ . Let us forget for a time about the quantum nature of exchange interaction and even about spins and assume that  $\mathbf{s}_i$ ,  $\mathbf{s}_k$  are ordinary classical vectors of a prescribed length, and formula (3.8') determines how the energy of a body depends on their mutual arrangement (it will be demonstrated later, in Sec. 4.3, that the classical model is a necessity because there is no rigorous quantum theory of antiferromagnetism). The word "mu-

tual" is essential here because the exchange interaction is isotropic with respect to the joint rotation of all spins. We find that the minimum value of energy in the case of negative  $A$  is reached for the spin configuration in which the spins pointing along some direction and against

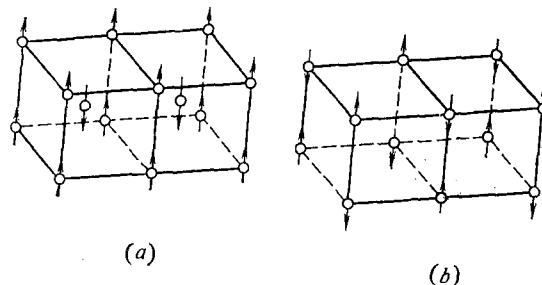


Fig. 57. Antiferromagnetic ordering of magnetic moments: (a) in a body-centered cubic lattice; (b) in a primitive cubic lattice

it alternate (Fig. 57). Indeed, with this configuration each of the scalar products for the nearest neighbor spins will be maximum in magnitude and negative in sign. Energy will thereby be minimized.

A configuration with alternating spins can be regarded as two ferromagnetic lattices embedded in each other (usually called *magnetic sublattices*), interacting via the negative exchange interaction. Figure 57 shows the simplest antiferromagnetic structure. More complicated structures are possible. One of them is the structure of  $\text{UO}_2$  as shown in Fig. 58. If it is described in terms of sublattices, four sublattices must be introduced. Although in what follows we do not

go beyond antiferromagnetics with two sublattices, it should be mentioned that various and sometimes very sophisticated magnetic structures have been discovered and are studied nowadays. For instance, in rare-earth metals the spins in

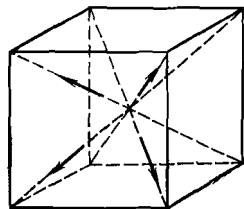


Fig. 58. Magnetic structure of the compound  $\text{UO}_2$  described by four magnetic sublattices. The spins of magnetic atoms align along the cube diagonals

adjacent atomic planes are rotated relative to each other by a certain angle. The magnetic structure is then a helix (Fig. 59a).

Furthermore, there exists a large class of materials which as if combine the properties of ferromagnetics and antiferromagnetics. They are called *ferrimagnetics*, or *ferrites*. These are materials whose magnetic system can be pictured as a system of several sublattices which do not add up to zero magnetic moment (e.g. because the magnetization of one sublattice is several times greater than that of the other; Fig. 59b). One important particular case of ferrites is that of weak ferromagnetics: antiferromagnetics in which the angle between the magnetic moments of sublattices slightly deviates from  $180^\circ$  (Fig. 59c).

It is clear from Fig. 57 that the macroscopic magnetic moment of antiferromagnetics is zero. But this means that the antiferromagnetic state

cannot manifest itself by a magnetic field surrounding this specimen, as the ferromagnetic state can. But is it then possible to "recognize"

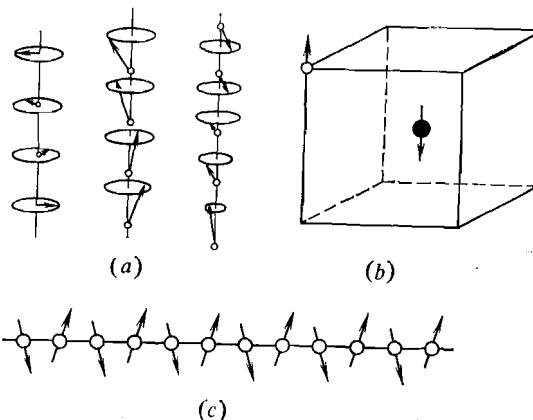


Fig. 59. Complex magnetic structures: (a) helical structures; (b) the magnetic structure of a ferrite: the magnetic moment at the vertex of the cubic unit cell is less than the atomic magnetic moment at the center of the cell; (c) the magnetic structure of a weak ferromagnetic material

an antiferromagnetic structure? To answer this question, we need to recall how crystal structures are "recognized" in the general case.

Not only can a regular arrangement of atoms be detected but the distances between the atoms can also be measured by using x-rays. The x-ray structure analysis is based on the interference which in this case makes the amplitude of the electromagnetic waves reflected by identical atom-

ic planes large when the difference between the optical path of the corresponding rays is equal to, or is a multiple of, the wavelength of the x-ray radiation. If a crystal is modelled by stacked parallel planes (Fig. 60), we can readily derive the condition that shows in what

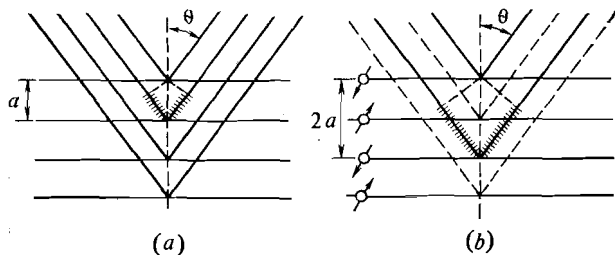


Fig. 60. The Bragg-Wulff condition of interference. The difference between the optical path length of the rays reflected by two adjacent equivalent atomic planes (hatched on the drawing) must equal an integral number of light wavelengths:

(a) an ordinary crystal; (b) an antiferromagnetic crystal (the distance between the equivalent atomic planes is  $2a$ )

directions the interference conditions are met. This is the so-called Bragg-Wulff condition:

$$n \frac{\lambda}{2a} = \cos \theta \quad (4.1)$$

where  $n$  are integers,  $\lambda$  is the x-ray wavelength,  $a$  is the separation between atomic planes, and  $\theta$  is the incidence angle of the rays, equal to the reflection angle. If the wavelength  $\lambda$  is longer than twice the interatomic distance  $a$ , interference is impossible (and this is why we have to use x-rays with wavelength of several ang-

stroms). If  $\lambda < 2a$ , several maxima can be observed, their number being found from the condition  $\cos \theta < 1$ . Figure 60b in which the alternating planes are marked with arrows pointing to opposite directions shows the same "crystal" as in Fig. 60a but in its antiferromagnetic state. It might seem that in this case the interference pattern should be that of a crystal with doubled interatomic spacing: additional maxima should appear for the same wavelength. Yes, we might expect them but we would be wrong. X-rays "feel" only the distribution of electric charge. They cannot distinguish between atoms with different orientation of a magnetic moment. Hence,

*the x-ray structure analysis does not reveal the magnetic structure of crystals.*

Should we use electrons? Owing to their quantum wave properties, they also interfere and can be used to find crystal structures (according to the de Broglie relation, their wavelength is  $2\pi\hbar/p$ , where  $p$  stands for momentum). Moreover, electrons have a magnetic moment and thus interact differently with atoms whose magnetic moments are different. Nonetheless, if we carried out an experiment with an antiferromagnetic material scattering electrons, we would in all likelihood miss the desired effect. The thing is that electric interaction forces are greater by a factor of  $137^2$  than the forces of interaction between magnetic moments. This has already been mentioned in Ch. 1 when the atomic structure was described (see Sec. 1.9). Therefore, identical atoms with oppositely orient-



ed magnetic moments will scatter almost identically, and the slight difference is practically immeasurable. We wish there were microscopic particles having a magnetic moment but no charge.

But such particles exist. These are neutrons. True, their magnetic moment is small (see Table 1 on p. 60), but they are not charged. Since the interaction of neutrons with atomic magnetic moments leads to their scattering, we can indeed find out by using neutron beams how magnetic moments are arranged in antiferromagnetic crystals. (See Problem 27.) Therefore,

*the elastic scattering of neutrons is a method for analyzing magnetic structures.*

We have emphasized that we mean elastic scattering, that is, such scattering in which a neutron is scattered but its energy remains unaltered (see below).

Although the magnetic moment of a body is zero both in the paramagnetic and in antiferromagnetic states, their magnetic characteristics are obviously quite different. At high temperatures the magnetic susceptibility is governed by the Curie-Weiss law, and at the Néel point it reaches a maximum; as temperature is lowered further, the magnetic susceptibility diminishes. If measurements are carried out with single crystals, it is possible to reveal the difference in the behavior of the longitudinal  $\chi_{\parallel}$  and transverse  $\chi_{\perp}$  susceptibilities (Fig. 61). In measuring the longitudinal susceptibility the magnetic field is applied along the aligned magnetic moments, and in measuring the transverse sus-

ceptibility it is applied perpendicularly to them. When temperature passes through the Néel point, the heat capacity of an antiferromagnetic

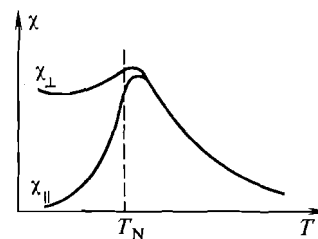


Fig. 61. Transverse  $\chi_{\perp}$  and longitudinal  $\chi_{\parallel}$  susceptibilities of antiferromagnetics as functions of temperature ( $T_N$  is the Néel point)

undergoes a jumpwise change (Fig. 62); this effect is typical of the phase transitions of the second order.

As always (see Sec. 3.3), a second-order phase transition is a “disorder-to-order” transition.

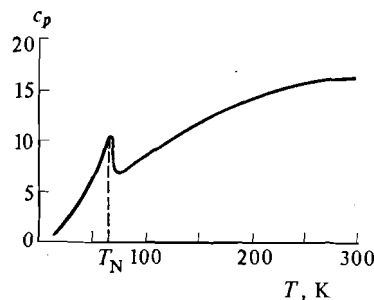


Fig. 62. Temperature dependence of the heat capacity of the antiferromagnetic  $\text{MnF}_2$

In this particular case the “disorder” is found in the absolute identity of all lattice sites (of course, those sites in which magnetic atoms are

located), so that the mean magnetic moment is zero at each site. Beginning with the Néel point (at  $T \leq T_N$ ), an "order" appears and lattice sites grow to be different: in some of them the mean magnetic moment "points" in one direction, and in the others it points in the opposite direction. The transition is smooth (and it must be for any phase transition of the second order) because at the Néel point the mean magnetic moment in a lattice site is zero, then increases with decreasing temperature, and reaches its maximum possible value at  $T = 0$ . This behavior imparts more physical meaning to the statement made on p. 241 that an antiferromagnetic is composed of two ferromagnetic sublattices inserted into each other.\*

#### 4.2. Magnetic Field Changes the Structure of Antiferromagnetics

For a ferromagnetic material at a temperature low compared with the Curie temperature the role of a permanent uniform magnetic field is rather minor: it deflects the magnetic moment and partially suppresses magnetic disorder, realizing what we termed the paraprocess (see p. 188). For antiferromagnetics the magnetic field plays a more interesting role. A stronger magnetic field may change the magnetic structure of an antiferromagnetic: it may induce *magnetic phase*

\* We described in Sec. 3.3 how ordering sets in in the CuZn alloy. The antiferromagnetic ordering thus strongly resembles the ordering of alloys. The role of "alloy components" is played by atoms with differently oriented magnetic moments.

*transitions*. This is the subject of the present section.

Let us assume that the magnetic field changes the orientation of the magnetic moments of the sublattices, but leaves their length unaltered. This assumption which is observed to hold well in wide ranges of parameters (temperature, anisotropy and exchange constants, etc.) is the theoretical foundation for studying the *orientational transitions* in magnetic materials. On the other hand, this assumption simplifies the problem to such an extent that it can be solved almost completely even on the pages of this booklet.

We have thus to find out how a magnetic field  $H$  affects the magnetic structure of an antiferromagnetic in which the magnetic moments of sublattices,  $M_1$  and  $M_2$ , are antiparallel in the absence of an external magnetic field:

$$M_1 = -M_2 = M \quad (4.2)$$

and align along the anisotropy axis  $n$ . Such antiferromagnetics are called the "easy-axis"-type antiferromagnetics (Fig. 63a). For the sake of further simplification, we assume that the magnetic field is also applied along the anisotropy axis, that is, along the "easy axis" (the case of a longitudinal field).

To identify a structure means to determine the directions of magnetic moments at which their energy is minimum. When writing expressions for the energy of an antiferromagnetic, we start with arguments similar to those that we used in analyzing the Curie-Weiss model (see formulas (3.10) and (3.14)), assuming energy to be

completely defined by the magnitude and direction of the magnetic moments of sublattices (calculated per unit volume). Omitting the terms independent of the direction of the vectors  $\mathcal{M}_1$  and  $\mathcal{M}_2$ , we obtain

$$\mathcal{E} = \delta \mathcal{M}_1 \cdot \mathcal{M}_2 - \frac{1}{2} \beta [(\mathcal{M}_1 \cdot \mathbf{n})^2 + (\mathcal{M}_2 \cdot \mathbf{n})^2] - (\mathcal{M}_1 + \mathcal{M}_2) \cdot \mathbf{H} \quad (4.3)$$

The three terms describe "different" energies: the first represents the exchange energy (the

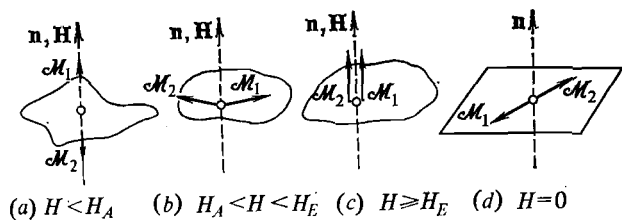


Fig. 63. Equilibrium orientation of the magnetic moments in antiferromagnetics:

(a-c) an "easy-axis"-type antiferromagnetic; (d) an "easy-plane"-type antiferromagnetic

constant of exchange interaction, proportional to the exchange integral, is denoted by the letter  $\delta$ ; obviously, it is advantageous for the magnetic moments to be antiparallel if  $\delta > 0$ ); the second term represents the anisotropy energy ( $\beta$  is the anisotropy constant;  $\beta > 0$  for "easy-axis"-type antiferromagnetics, and the magnetic

moments align along the anisotropy axis  $\mathbf{n}^*$ ); the third term represents the magnetic energy, that is, the energy of interaction between the magnetic moments and the magnetic field  $\mathbf{H}$  (the magnetic energy equals zero when the magnetic moments  $\mathcal{M}_1$  and  $\mathcal{M}_2$  are antiparallel).

The isotropic exchange interaction has a priority over the anisotropic interaction because  $\delta \gg \beta$ . The two constants have zero dimensionality because  $\mathcal{E}$  is the energy density. By the order of magnitude,  $\delta \approx |A|/\mu_B \mathcal{M}_0$ ;  $\beta \approx 1$ ;  $\mu_B$  is, as always, the Bohr magneton; and  $\mathcal{M}_0$  here stands for the magnetization of the sublattice far from the Néel point  $T_N$  which, as in ferromagnetic materials, is determined by the exchange integral ( $kT_N \approx |A|$ ). The estimates of the parameters  $\delta$  and  $\beta$  coincide with the estimates of the parameters  $\alpha$  and  $\beta$  for ferromagnetics (see pp. 158 and 171). We want to emphasize that the direction of the magnetic moments in antiferromagnetics is determined not only by the relativistic anisotropic interaction but also by the isotropic exchange interaction that "strives" for an antiparallel alignment of the magnetic moments of the sublattices.

It can be shown that an asymmetric arrangement of magnetic moments relative to the anisotropy axis  $\mathbf{n}$  is energetically disadvantageous.

\* Antiferromagnetics with  $\beta < 0$  are said to be "easy-plane"-type antiferromagnetics because at  $\mathbf{H} = 0$  the moments  $\mathcal{M}_1$  and  $\mathcal{M}_2$  lie in a plane perpendicular to the vector  $\mathbf{n}$  (Fig. 63d). We have slightly simplified the expression for the anisotropy energy by omitting the term  $\beta' (\mathcal{M}_1 \cdot \mathbf{n})(\mathcal{M}_2 \cdot \mathbf{n})$ . This term makes the results less descriptive, while changing them rather insignificantly.

(See Problem 28.) For this reason we consider here only the three configurations shown in Fig. 63a, b, c and compare them. First we write the expressions for the energies of these configurations:

$$\mathcal{E}_{\uparrow\downarrow} = -(\delta + \beta) \mathcal{M}^2 \quad (4.4)$$

$$\mathcal{E}_{\nearrow\swarrow} = \delta \mathcal{M}^2 \cos 2\theta - \beta \mathcal{M}^2 \cos^2 \theta - 2\mathcal{M}H \cos \theta \quad (4.5)$$

$$\mathcal{E}_{\uparrow\uparrow} = \delta \mathcal{M}^2 - \beta \mathcal{M}^2 - 2\mathcal{M}H \quad (4.6)$$

The correspondence between these formulas and the configurations in Fig. 63 is clear from the introduced notations. Formulas (4.4) and (4.6) are "final", and formula (4.5) must be used to find the angle  $\theta$  minimizing the energy  $\mathcal{E}_{\nearrow\swarrow}$ .

This is a problem for finding a minimum:

$$\frac{d\mathcal{E}_{\nearrow\swarrow}}{d\theta} \equiv 2\mathcal{M}^2 \sin \theta \left[ -(2\delta - \beta) \cos \theta + \frac{H}{\mathcal{M}} \right] = 0 \quad (4.7)$$

$$\begin{aligned} \frac{d^2\mathcal{E}_{\nearrow\swarrow}}{d\theta^2} &\equiv -4\delta\mathcal{M}^2 \cos 2\theta + 2\beta\mathcal{M}^2 \cos 2\theta \\ &+ 2\mathcal{M}H \cos \theta > 0 \end{aligned}$$

According to expressions (4.7), the energy reaches an extremum either at

$$\cos \theta = \frac{H}{H_E}, \quad H_E = (2\delta - \beta) \mathcal{M} \quad (4.8)$$

or at

$$\sin \theta = 0 \quad (4.9)$$

Since  $\cos \theta < 1$ , the first solution is meaningful if  $H < H_E$ . In strong fields only solution (4.9)

works, when both magnetic moments are *parallel* to each other. We see from the expression for the second derivative that the structure  $\uparrow\uparrow$  corresponds to a minimum in energy when  $H > H_E$ : the magnetic field has "defeated" the exchange interaction and forced both magnetic moments to "lie" along the field. Solution (4.8) minimizes energy (4.5) if the magnetic field is weaker than  $H_E$ . The energy  $\mathcal{E}_{\nearrow\swarrow}$  then takes on the following value:

$$\mathcal{E}_{\nearrow\swarrow} = -\mathcal{M}^2 \delta - \frac{H^2}{2\delta - \beta} \quad (4.5')$$

By comparing the energy  $\mathcal{E}_{\nearrow\swarrow}$  with the energy of the antiparallel configuration  $\mathcal{E}_{\uparrow\downarrow}$ , we find that at

$$H = H_A = \mathcal{M} \sqrt{\beta(2\delta - \beta)}$$

they become equal, at  $H < H_A$  the configuration  $\uparrow\downarrow$  has a lower energy, and at  $H > H_A$  the configuration  $\nearrow\swarrow$  is energetically more advantageous, with magnetic moments nearly perpendicular to the anisotropy axis\*, that is,  $\mathcal{E}_{\nearrow\swarrow} < \mathcal{E}_{\uparrow\downarrow}$ .

Knowing the dependence of energy on the magnetic field, we can calculate the magnetic moment of the antiferromagnetic material that, in this particular case, we denote by  $\mathfrak{M}$ . As the magnetic field, it is also directed along the anisotropy axis. In the  $\nearrow\swarrow$ -phase  $\mathfrak{M}_{\nearrow\swarrow} =$

\* Since  $\beta \ll \delta$ , we notice that  $\theta \approx \pi/2$  at  $H = H_A$ . Indeed,

$$\cos \theta = \sqrt{\frac{\beta}{2\delta - \beta}} \ll 1$$

$= -d\mathcal{E}_{\nearrow}/dH$ , and therefore,

$$\begin{aligned} \mathcal{M}_{\uparrow\downarrow} &= 0 & \text{at } H \leq H_A \\ \mathcal{M}_{\nearrow} &= \frac{H}{\delta - \frac{\beta}{2}} & \text{at } H_A \leq H \leq H_E \\ \mathcal{M}_{\uparrow\uparrow} &= 2\mathcal{M} & \text{at } H > H_E \end{aligned} \quad (4.10)$$

Figure 64 shows how the magnetic moment depends on the magnetic field. You notice that

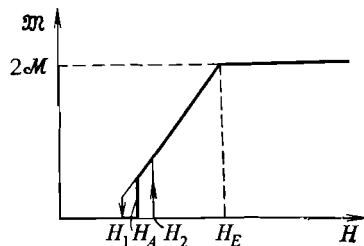


Fig. 64. Magnetic moment of an "easy-axis"-type antiferromagnetic specimen as a function of the magnetic field applied along the chosen axis. The hysteresis loop (thin lines with arrows) manifest the presence of metastable states in the range  $H_1 < H < H_2$

antiferromagnetics undergo transitions twice: at  $H = H_A$  a jumpwise reorientation of magnetic moments occurs via a first-order phase transition (the field  $H_A$  is therefore called the *reorientation field*). The reorientation is completed at  $H = H_E$  because then the angle between the magnetic moments of sublattices dwindles to zero, and these magnetic moments "flop together". This is a second-order phase transition: the magnetic

moment is continuous but the magnetic susceptibility changes jumpwise. If  $H < H_A$ , the  $\nearrow$ -phase is metastable, and at  $H > H_A$  the metastable phase is  $\downarrow$ . The existence of metastable states results in a hysteresis. The width of the hysteresis loop (shown by thin lines with arrows in Fig. 64) is determined by the values of the fields at which the phases become unstable (instability fields): the  $\downarrow$ -phase is stable until the field reaches the value

$$H_2 = \sqrt{\beta(2\delta + \beta)} \mathcal{M}$$

and the  $\nearrow$ -phase is stable until

$$H > H_1 = H_2 \frac{2\delta - \beta}{2\delta + \beta}$$

It can be readily ascertained that

$$H_1 < H_A < H_2$$

Since  $\beta \ll \delta$ , the hysteresis loop is very narrow compared with the reorientation field:

$$H_2 - H_1 = H_A \frac{2\beta}{\sqrt{(2\delta)^2 - \beta^2}} \approx H_A \frac{\beta}{\delta} \ll H_A$$

Unfortunately, the instability fields  $H_1$  and  $H_2$  cannot be calculated if only symmetric configurations are considered. We would have to find the dependence of energy on the directions of magnetic moments  $\mathcal{M}_1$  and  $\mathcal{M}_2$  when these are arranged asymmetrically.

The "flop-together" field  $H_E$  is very high for most antiferromagnetic materials (it is proportional to the exchange-interaction constant  $\delta$ , see (4.8)). However, some materials have an anomalously weak exchange interaction (e.g.

$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ). These materials become antiferromagnetic at temperatures of about 2 K. In these materials it was possible to observe not only the reorientation of magnetic moments (a first-order phase transition at  $H = H_A$ ) but also the "flopping-together" (a second-order phase transition at  $H = H_E$ ) at which an antiferromagnetic material "converts" into a ferromagnetic material.

Of course, Fig. 64 is merely schematic because it does not reflect the "struggle" between the magnetic field and the thermal disorder (the effect of the magnetic field that we call the paraprocess). This "struggle" is especially well pronounced at high magnetic fields ( $H \gtrsim H_E$ ). If the paraprocess is taken into account, at  $H > H_E$  the magnetic moment slightly increases with increasing magnetic field, and at  $H < H_A$  the magnetic moment is small but still does not vanish (at any rate, at  $T \neq 0$ ).

#### 4.3. Spin Waves: Magnons in Antiferromagnetics

The temperature dependence of the magnetic moments of the sublattices in the neighborhood of the Néel point  $T_N$  can be found by means of the self-consistent field model (see p. 145) which generalizes the Curie-Weiss model to the case of two sublattices. However, we already know that this model "does not work" at low temperatures (at  $T \ll T_N$ ), leading to substantial errors. The correct result can be obtained only if we know how atomic magnetic moments move,

that is, if the energy spectrum of the antiferromagnetic material is known.

The excited states of an antiferromagnetic can be treated similarly to what we did in the case of a ferromagnetic: begin with a state in which the spin of an individual atom is deflected from its "correct" orientation, conclude that this state is nonstationary, "construct" a spin wave, and so forth (see Sec. 3.7). But on the other hand, we know that excitations of maximum interest at low temperatures are spin waves with wavelengths large compared with the interatomic distance. And we saw that such waves can be treated as the nonuniform precession of magnetization (see Sec. 3.8). In two-sublattice antiferromagnetics we have to deal with two magnetizations:  $\mathcal{M}_1$  and  $\mathcal{M}_2$ . Each magnetic moment precesses around its equilibrium position but these precessions are not independent because of the exchange interaction.

As in the case of ferromagnetics, we begin with discussing the uniform precession and describe it for three configurations given above:  $\uparrow\downarrow$ ,  $\nearrow\searrow$ , and  $\uparrow\uparrow$ . Unfortunately, all we can give is just a description. The derivation of relevant formulas requires a slightly higher level of knowledge in mathematics than the one we take for granted. But the physics is simple: each magnetic moment is subjected to an effective field that depends on the "other" moment. This is why the precessions are not independent.

*Configuration  $\uparrow\downarrow$  ( $H < H_A$ ).* The motion of two magnetic moments is decomposed into the sum of two independent periodic motions. Both moments participate in each of them. The fre-

quencies of these motions (precessions) will be denoted by  $\omega_+$  and  $\omega_-$ . An analysis shows that

$$\omega_{\pm} = \gamma(H_2 \pm H) \quad (4.11)$$

$$H_2 = \sqrt{\beta(2\delta + \beta)} \mathcal{H}$$

where  $\gamma$  is the gyromagnetic ratio (see p. 52).

Figure 65a shows how the magnetic moments of each sublattice precess in each of the two

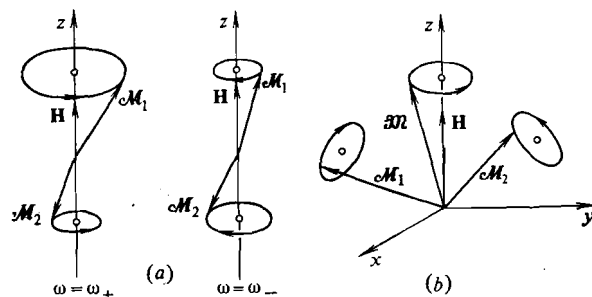


Fig. 65. Precession of the magnetic moments of the sublattices in an "easy-axis"-type antiferromagnetic material (the magnetic field points along the anisotropy axis): (a)  $H < H_A$ ; (b)  $H_A < H < H_E$

motions. In the [motion at frequency  $\omega_+$  the moment along the field ( $\mathcal{M}_1$  in the figure) is deflected from the axis slightly more than the other ( $\mathcal{M}_2$  in the figure) pointing against the field; the situation is reversed in the motion at frequency  $\omega_-$ . Note that at  $H = H_2$  the precession frequency drops to zero; this is a *sign of instability*.

*Configuration  $\nearrow \nwarrow$  ( $H_A < H < H_E$ ).* A rotation of the magnetic moments, preserving the angle between them, around the magnetic field parallel to the chosen axis does not affect the state of the antiferromagnetic material: it is degenerate relative to the position of the plane in which the magnetic moments lie. Consequently, the frequency related to this motion is zero. This may baffle the reader. Indeed, such a system of magnetic moments could be expected to rotate at any frequency, but somehow this frequency occurs to be zero.

This statement becomes more comprehensible when quantum-mechanical concepts are applied. Assume that the frequency of oscillations of a system of the magnetic moments that preserve the angle between them is  $\Omega \neq 0$ . Then this motion is related to energy levels  $\hbar\Omega (n + 1/2)$ . But the rotation of the plane in which the magnetic moments lie does not change the energy of the system. Hence,  $\Omega = 0$ . We hope that now the reader is pacified.

The precession of magnetic moments in the motion with nonzero frequency is shown in Fig. 65b. The figure also shows the precession of the total magnetic moment  $\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2$ . The frequency of this motion increases with increasing magnetic field  $H$ . It equals zero at  $H = H_1$ , indicating that the  $\nwarrow \nearrow$ -configuration is unstable, and at  $H = H_E$  it coincides with the precession frequency of a ferromagnetic material with the magnetic moment equal to  $2\mathcal{M}$ , the situation indeed expected for the ferromagnetic configuration  $\uparrow\uparrow$ .

Figure 66 plots the frequencies of uniform

precession as functions of the magnetic field  $H$ .

Obviously, the ensuing arguments coincide with those that were "rehearsed" in Sec. 3.8. The transition from uniform precession to non-uniform precession makes the precession frequency

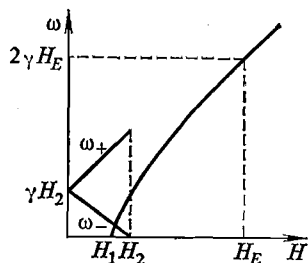


Fig. 66. Precession frequencies in an "easy-plane"-type antiferromagnetic material as a function of the magnetic field parallel to the anisotropy axis

depend on the wave vector  $k$ . Then follows the familiar scheme:

*wave*  $\rightarrow$  *oscillator*  $\rightarrow$  *quasiparticle*

As in ferromagnetics, the quasiparticles are called magnons (or, infrequently, antiferromagnons). Of course, the wave-quasiparticle transition involves the use of the de Broglie relations: the magnon momentum is  $\hbar k$ , and its energy is  $\hbar\omega$ . When  $H < H_A$  (here we consider only this case), there are two types of magnons in antiferromagnetics with two sublattices. Their energy depends on momentum in a slightly more complicated manner than for ferromagnetics' magnons. When the momentum is small, then

$$\varepsilon^{\pm}(\mathbf{p}) = 2\mu_B [H_2^2 + (H'_E a k)^2]^{1/2} \pm 2\mu_B H \quad (4.12)$$

where  $2\mu_B = \hbar\gamma$ , and  $a$  is the crystal lattice parameter. The coefficient in front of  $k^2$  is writ-

ten in the form demonstrating its order of magnitude ( $H'_E \approx H_E \gg H_2$ ) and showing that it originates in the exchange interaction. Note that the presence of the terms  $\pm 2\mu_B H$  in expressions (4.12) is not the basis for interpreting  $\varepsilon^+$  and  $\varepsilon^-$  as the energies of two out of the three states of one spin-1 particle (cf. p. 205). These terms refer to distinct magnons. *Each of the magnons of an antiferromagnetic material is a spin-1 quasiparticle*, but for each magnon only one of the three possible spin states is realized ( $s_z = -1$  for one and  $s_z = +1$  for the other). Just as in ferromagnetic materials,

*magnons in antiferromagnetics are bosons.*

Formula (4.12) shows the structure of the energy spectrum in antiferromagnetics. The first excited states are separated by a gap from the ground state. When  $H = 0$ , the gap is wide (at any rate, as compared with ferromagnetic materials) because it depends not only on the anisotropy constant  $\beta$  but also on a large exchange-interaction constant  $\delta$  (see (4.11)). True, the gap vanishes at  $H = H_2$ , but an "easy-axis"-type antiferromagnetic specimen will be restructured "in advance" (at  $H < H_2$ ; see the preceding section).

Knowing the dependence of the magnon energy on the momenta and statistical properties of magnons (knowing them to be bosons), one can calculate the temperature dependence of the total magnetic moment and heat capacity. Clearly, as temperature tends to absolute zero, the numbers of magnons will tend to zero exponentially (the gap) and this will affect the tem-



perature dependence of characteristics of antiferromagnetic materials. We cannot go into the details of this because, among other reasons, the theoretical predictions made on the basis of magnon concepts are not confirmed experimentally for antiferromagnetics as successfully as they are for ferromagnetics. The cause is the wide energy gap: the contribution of magnons is too small to be reliably detected.

A comparison of magnons in ferro- and antiferromagnetics reveals one peculiar feature. If we neglect anisotropic forces and the magnon-magnetic field interaction, magnons in ferromagnetic materials become very similar to ordinary particles with the mass  $m^* = \hbar^2/2Aa^2$  (see formula (3.25)). Let us apply the same operation to magnons in antiferromagnetics. We set  $H = 0$  in (4.12) and "switch off" the anisotropic forces (i.e.  $H_2$  tends to zero). This greatly simplifies the dependence of the magnon energy on momentum:

$$\epsilon^\pm(\mathbf{p}) = c^* p, \quad c^* = \frac{2\mu_B H'_E a}{\hbar} \quad (4.13)$$

The result is very similar to the dependence of the phonon energy on momentum. The velocity of a magnon  $c^*$  is determined by the exchange interaction. Formula (4.13) holds not for all values of momentum: it is valid if

$$\frac{H_2}{H'_E} \ll \frac{ap}{\hbar} \ll 1 \quad (4.13')$$

However, if  $H_2 \ll H_E$ , there is a temperature range ( $2\mu_B H_2 \ll kT \ll 2\mu_B H'_E$ ) in which the "quasiphonon" formula (4.13) is acceptable. At

these temperatures the contribution of magnons to thermodynamic characteristics of antiferromagnetics much resembles the contribution of phonons. For instance, under these conditions the magnon heat capacity is proportional, as the phonon heat capacity, to  $T^3$  (see p. 236).

We tried to describe antiferromagnetics and their properties with only a minimum help from quantum mechanics. And on p. 240 we clearly stated that a rigorous quantum-mechanical theory does not exist.

The thing is that in reality the state with antiparallel spins in distinct sublattices does not constitute a stationary state of an antiferromagnetic material described by the Heisenberg Hamiltonian (3.8) or (3.8'). This is best understood by considering a system of spins with  $s = 1/2$ . Let the spin at an arbitrary lattice site be directed upward. Then the spins in the neighbor sites belonging to the other sublattice are directed downward, that is, are in the state we are now discussing. The very meaning of exchange interaction is such that in the case  $s = 1/2$  it reduces to interchanging the electrons occupying neighbor lattice sites. This interchanging disturbs the alternation of upward- and downward-pointing spins: the state will change because the pairs of neighbor atoms will appear with identically directed spins, but the wave function of the stationary state cannot be altered by this interchanging and can only be multiplied by a certain quantity, namely, the value of energy in the stationary state. Hence, if the state we consider is not stationary, the true ground state must be something different. This is an absolute-

ly correct statement (it is as correct as it is trivial). But the basic questions are: What is the basic state? What is its wave function? What is its energy? So far we do not know the answers. Nobody succeeded in finding the ground state of *three-dimensional* antiferromagnetics. Hans Bethe calculated the ground-state energy of a one-dimensional antiferromagnetic with interactions only along the line as early as 1931 (at the present time one- and two-dimensional systems again attract the attention of physicists). Of course, his result differs from the "classical" energy of two sublattices with oppositely directed spins. Nevertheless, attempts to generalize this result to the two- and three-dimensional cases have so far failed.

Bethe's result was obtained for a system of atoms with spins  $s = 1/2$ . The greater  $s$  is, the smaller must the difference be between the results of classical calculation (or rather, semiclassical because the interaction itself is a quantum effect) and the exact quantum-mechanical calculation. When  $s \gg 1$ , the space quantization of spins becomes unimportant, the spin becomes a classical moment that varies only in direction. Strictly speaking, the results outlined above hold precisely for systems consisting of "classical" spins. But in order not to conclude at this gloomy note, we should indicate that the eclecticism of the theory of antiferromagnetics at low temperatures (viz. the semiclassical nature of the ground state and the quantum-mechanical approach to analyzing the energy spectrum) does not stand in the way of attempts (which are often quite successful) to explain and interpret

a wide scope of experimental facts: thermodynamic, kinetic, and high-frequency, including optical, data. The true "internal structure" of antiferromagnetic materials is probably not very different from that described above. This remark in no way diminishes the importance of constructing a rigorous theory.

#### 4.4. How to "See" an Individual Magnon?

We hope that, having read our exposition of magnons in ferro- and antiferromagnetics, you feel respect to these quasiparticles. The knowledge of their properties (e.g. the magnon energy as a function of quasimomentum) will make it possible to calculate the properties of magnetic materials and to compare our theoretical constructions with experimental data. But a different approach is possible: to use the experimental data and certain general notions of energy spectrum and try to find out the properties of magnons. Let us compose the following logical sequence. Experiments show that the deviation  $\Delta\mathcal{M}$  of the spontaneous magnetic moment of ferromagnetic materials from its value at  $T = 0$  is proportional to  $T^{3/2}$  (cf. with (3.40)). The deviation  $\Delta\mathcal{M}$  of the magnetic moment  $\mathcal{M}$  from saturation is caused by magnons. Magnons are bosons. Consequently, the laws of statistics dictate that the magnon energy be proportional to the square of momentum. Moreover, the proportionality factor between  $\Delta\mathcal{M}$  and  $T^{3/2}$  enables us to calculate the effective magnon mass. (See Problem 29.)

The method of studying quasiparticles (not

only magnons) by analyzing the temperature dependence of thermodynamic quantities is very frequently used. Even a mathematical technique was developed to reconstruct, from the temperature dependence of the heat capacity of a body, the density of the number of quasiparticles, namely, bosons, in a wide range of energy. But a physicist invariably dreams of isolating the object he studies. When studying electrons, it is preferable to deal with a single electron, and while studying magnons, to deal with a single magnon.

Let us estimate to within an order of magnitude how many magnons are "required" for the magnetic moment to depart by 1% from its saturation value. According to formula (3.39),

$$\frac{\Delta \mathcal{M}}{\mathcal{M}} = \frac{N_{\text{magn}}}{N}$$

that is,  $N_{\text{magn}}/N = 10^{-2}$ . Hence,  $N_{\text{magn}} = 10^{-2}$ . That is,  $N \approx 10^{20}$  (sic) in each cubic centimeter. In a certain sense this is not much, in comparison with the number of magnetic atoms, but in the absolute sense (as compared with unity) their number is macroscopically enormous. Of course, we can lower temperature (we remind the reader that  $N_{\text{magn}} \propto T^{3/2}$ ). The number of magnons will decrease but still remain large, macroscopically large. This is a good thing, otherwise we could not make use of the formulas derived for Bose gases, that is, for systems consisting of a macroscopic number of Bose particles. Although this is a good thing in this sense, it leaves us no hope of isolating a single magnon by decreasing temperature. Quite different techniques based

on the resonant interaction of penetrating radiation with magnons are used to study the behavior of individual magnons.

The term "penetrating radiation" is not an exact one: it is "something" that can penetrate the analyzed object to a sufficient depth (e.g. electromagnetic or acoustic waves or neutrons). The principal features will be better understood after we give several examples.

### *Ferromagnetic Resonance*

When describing the electron paramagnetic resonance (EPR, see p. 109), we discussed the possibility of resonant interaction between electromagnetic waves and a precessing magnetic moment. But if the magnetic moment of an atom can precess, so can the mean magnetic moment of a body, provided it is not zero. A ferromagnetic sample has the magnetic moment, and so it can precess (see Sec. 3.8). Hence, if the frequency of electromagnetic waves coincides with that of precession, resonance must set in, which can be detected by a sharply enhanced absorption of the electromagnetic energy in a ferromagnetic specimen (Fig. 67). As a rule, the experiment is performed in such a way that the frequency of electromagnetic radiation (we mean the radio-frequency band of radiation) is not varied in measurements but the magnetic field applied to the specimen is changed. We know that the precession frequency  $\omega_0$  is a function of the magnetic field  $H$ . If the electromagnetic radiation frequency  $\omega$  is chosen correctly, then the frequencies coincide at a certain strength of the

magnetic field and resonance occurs:  $\omega = \omega_0(H)$ .

But, on the other hand, the frequency of the uniform precession of a magnetic moment,  $\omega_0$ , equals, to within Planck's constant, the energy of a magnon at rest,  $\varepsilon_0$ . We can therefore "regard" the ferromagnetic resonance from the quantum

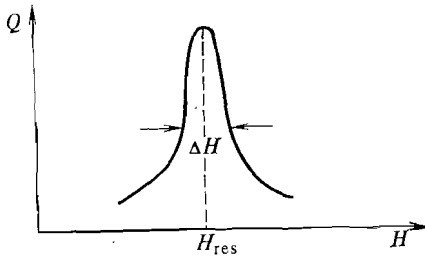


Fig. 67. Energy absorbed by a ferromagnetic specimen as a function of the permanent magnetic field has a resonance nature;  $\Delta H$  is the width of the resonance curve

standpoint. After multiplying by Planck's constant, the resonance condition takes the form of equality of the photon energy  $\hbar\omega$  to the energy of a magnon at rest:

$$\hbar\omega = \varepsilon_0 \quad (4.14)$$

and indicates that in resonance conditions a photon is transformed into a magnon:

*photon*  $\rightarrow$  *magnon*

Obviously, this transformation must obey the energy and momentum conservation laws. The law of energy conservation has already been written (see (4.14)). And how about momentum

conservation? Indeed, a photon has a momentum equal to  $\hbar\omega/c$ .<sup>\*</sup> Do we have to take it into account? Since the resonance corresponds to a photon transformed into a magnon, that is, to the disappearance of one quasiparticle and the creation of another, the two conservation laws reduce to the equality of the energies of a magnon and a photon with equal momenta:  $\varepsilon_0 + p^2/2m^* = cp$ , where  $m^*$  is the effective magnon mass. Since  $cp = \hbar\omega$ , we find

$$\varepsilon_0 + \frac{(\hbar\omega)^2}{2m^*c^2} = \hbar\omega \quad (4.15)$$

What we obtain here is more complicated than (4.14). But before drawing conclusions, it is necessary to evaluate the newly appeared additional term  $(\hbar\omega)^2/2m^*c^2$  as compared with  $\varepsilon_0$ . Let us assume it to be very small (this assumption will be immediately verified). Then  $\hbar\omega \approx \varepsilon_0$ . Let us estimate the second term on the left-hand side of equation (4.15):  $(\hbar\omega)^2/2m^*c^2 \approx \varepsilon_0^2/2m^*c^2$ . We notice that the value of the ratio of interest depends on the parameter  $v_0 = (\varepsilon_0/2m^*)^{1/2}$  with the dimensionality of velocity (we know the value of the speed of light). In order to evaluate  $v_0$ , we have to evaluate the effective magnon mass  $m^*$  (see p. 204). Assuming  $a \approx 3 \cdot 10^{-8}$  cm, and  $A = kT_c$  ( $k \approx 1.4 \cdot 10^{-16}$  erg/deg), we find

$$m^* \approx \frac{\hbar}{Aa^2} \approx m_e \frac{10^2}{T_c, \text{ K}} \quad (4.16)$$

<sup>\*</sup> The dependence of the photon energy  $\varepsilon = \hbar\omega$  on momentum is  $\varepsilon = cp$ , where  $c$  is the speed of light. Indeed,  $\omega = 2\pi c/\lambda$  ( $\lambda$  is the wavelength). Multiplying by  $\hbar$  we obtain the formula given above because  $2\pi\hbar/\lambda = p$  according to the de Broglie relations.

The electron mass  $m_e \approx 10^{-27}$  has been introduced into this formula to facilitate evaluations. You find that if  $T_c \approx 10^2$  K, the effective magnon mass is close to the electron mass.

The velocity  $v_0$  essentially depends on  $\varepsilon_0$ . Let a ferromagnetic specimen be placed in a strong field  $H = 10^4$  Oe; then  $\varepsilon_0 = 2\mu_B H$  (as a rule, in this strong field the anisotropy energy plays only a minor role). But according to estimate (2.7), this field corresponds to an energy  $kT$  at  $T = 1$  K. Therefore, at  $T_c \approx 10^2$  K we have  $\varepsilon_0 \approx 10^{-16}$  erg and  $v_0 \approx 3 \cdot 10^5$  cm/s. A seemingly high velocity, but still negligible in comparison with that of light:  $v_0^2/c^2 \approx 10^{-10}$ . Clearly, the second term in (4.15) can be omitted: the photon momentum need not be taken into account. But we hear the attentive reader to ask: "What about the second root of equation (4.15)?" It can be ignored because the expression for the magnon energy, used above, holds only at small momenta (the situation is clarified in Fig. 68).

We devote so much space to the magnon-photon interaction in order to make several general remarks:

—as a rule, quasiparticles in crystals move relatively slowly, at velocities much less than the speed of light;

—the ferromagnetic resonance is not a unique case when a photon transforms into a quasiparticle; in antiferromagnetic materials the antiferromagnetic resonance is possible, with a photon transforming into an antiferromagnon (see Problem 30); in many crystals a photon may

transform into an optical phonon\*, and so on; —the velocity of quasiparticles,  $v$ , being small compared with the speed of light ( $v \ll c$ ), a photon always transforms into a quasiparticle

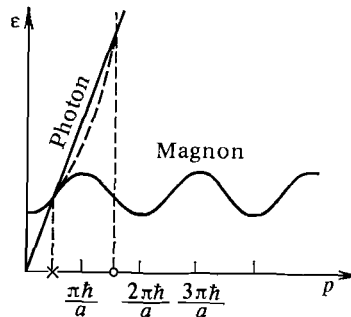


Fig. 68. Graphical solution of the equation  $\varepsilon(p) = cp$ . The root is marked with a cross. There is no second root in the true dependence of the magnon energy  $\varepsilon$  on the momentum  $p$ . This root appears if the true dependence of the magnon energy on momentum is replaced with a quadratic equation

"at rest" (furthermore, this transformation is possible if the energy of the quasiparticle is nonzero).

The ferromagnetic (or antiferromagnetic) resonance thus makes it possible to observe an individual magnon but unfortunately a magnon at rest (with  $\mathbf{p} = 0$ ). In fact, the information obtained by resonance techniques is not limited

\* Optical phonons are quasiparticles that correspond to such waves in nonprimitive crystals in which the atoms belonging to one unit cell vibrate relative to one another.

to fixing the magnon, that is, to measuring the energy of a zero-momentum magnon. The observation of resonance signifies the measurement of that value of the magnetic field at which the resonance sets in; hence, we can establish how the frequency of uniform precession depends on magnetic field (determine  $\gamma$ , find out the role of anisotropy energy, etc.). Furthermore, and this is possibly the most important result, an analysis of the resonance curve (see Fig. 67) enables us to evaluate the *magnon lifetime*  $\tau$ . Figure 67 shows that the absorption of energy (the photon  $\rightarrow$  magnon transformation) is possible not only if the frequencies are exactly equal but in a certain interval  $\Delta\omega_0 = \gamma \Delta H$ , as if the energy of a magnon is not prescribed very accurately; there is a spread in magnon energies (for the sake of simplicity we assume the photon energy to be exactly known). The same can be said in quantum terms (see pp. 34-38): *the magnon energy has no definite value*. Quantum mechanics states that the energy of a state has a definite value only if the state is *stationary*, that is, if its lifetime is infinite. But if a state is nonstationary, it is subject to a relation quite similar to the uncertainty relation:

$$\Delta\varepsilon \cdot \tau \gtrsim \hbar \quad \text{or} \quad \tau \Delta\omega \gtrsim 1 \quad (4.17)$$

where  $\Delta\varepsilon$  is the uncertainty in the energy of the state, and  $\tau$  is its *mean lifetime*.

But why is a magnon not an everlasting entity? What imposes limits on its lifetime? Some hints were given in Sec. 3.7: magnons collide with other magnons. Besides, they may collide with phonons that are always present in crystals.

By regarding a magnon as a particle (omitting the prefix "quasi"), we can readily imagine that it is scattered in collisions with defects that are inevitably encountered in crystals: impurity atoms, grain boundaries, dislocations (this term denotes the edges of truncated atomic planes), and simply with specimen boundaries. We thus find that the factors shortening the magnon lifetime are numerous. In their totality they are called the *dissipative processes*. To summarize,

*the ferromagnetic resonance is a method of studying dissipative processes involving magnons.*

### Ferroacoustic Resonance

The desire to "observe" individual magnons by resonance methods leads to the idea of employing waves that "move" slower than electromagnetic waves. Such waves are available: these are sound waves whose velocity is hundreds of thousands of times less than the speed of light. If we cannot "see", let us try to "listen" to magnons.

The resonant interaction is capable of converting a phonon into a magnon. In this transformation the equation describing the conservation laws for energy and momentum will differ from equation (4.15) only in the replacement of the speed of light  $c$  with that of sound  $c_{\text{sound}}$ . Since  $c_{\text{sound}} \approx 10^5$  cm/s, the situation is radically changed. For simplicity let us assume that  $\varepsilon_0 = 2\mu_B H$  (e.g. the anisotropy energy is enormously low) and let us find the value of the magnetic field at which the resonant interaction

is possible (find the resonant field):

$$2\mu_B H = \hbar\omega - \frac{(\hbar\omega)^2}{2m^*c_{\text{sound}}^2} \quad (4.18)$$

The right-hand side, being a function of  $\hbar\omega$ , has a maximum at  $\hbar\omega = m^*c_{\text{sound}}^2$  and vanishes

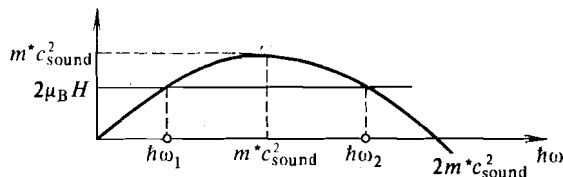


Fig. 69. Graphical solution of equation (4.18);  $\omega_1$  and  $\omega_2$  are resonance frequencies at  $2\mu_B H < m^*c_{\text{sound}}^2/2$

at  $\hbar\omega = 2m^*c_{\text{sound}}^2$  (Fig. 69). It is clear (the figure shows it with extreme lucidity) that the resonance is possible if

$$2\mu_B H < 1/2 m^*c_{\text{sound}}^2$$

( $m^*c_{\text{sound}}^2/2$  is the value taken on by the right-hand side of (4.18) at the maximum) when  $\hbar\omega < 2m^*c_{\text{sound}}^2$ . If the acoustic frequency and magnetic field are such that the resonant field essentially depends on the second term in (4.18), then we can find from the resonance condition the effective magnon mass  $m^*$  (can "listen" to a moving magnon).

### Inelastic Scattering

In both methods described above the "research agent" (a photon or a phonon) perishes, its dying being the evidence of resonance. Aren't

there more "peaceful" methods of extracting information on a quasiparticle? There are. These methods are based on the inelastic scattering of neutrons or photons. The scattering is said to be *inelastic* if the interaction with the scatterer changes the energy of a particle.

Let us consider again the scattering of neutrons in ferro- or antiferromagnetics (see Sec. 4.1). There are many ways for a neutron to change its energy. Each such channel is characterized by its probability. There is also a nonzero probability that the neutron energy will not be altered.

We know that under proper conditions the energy-conserving scattering (inelastic scattering) gives information on the magnetic structure of crystals.

There is also a finite probability for a neutron, traversing a ferro- or antiferromagnetic specimen, to emit (or absorb) a spin wave or, in corpuscular terms, to create (or absorb) a magnon. Calculation of the probabilities of various scattering processes is not an elementary problem of quantum mechanics (we shall not give the corresponding formulas, even without deriving them). But we can clarify the *principal* possibility of creation or absorption of a magnon by a neutron, correctly assuming that if the conservation laws allow a process, the process takes place. The conservation laws for energy and momentum must thus be obeyed in the creation or absorption of a magnon by a neutron. Let us denote the neutron momentum prior to and after the scattering by  $\mathbf{p}_n$  and  $\mathbf{p}'_n$ . The neutron energy is  $\varepsilon_n = p_n^2/2m_n$ . The momentum and energy of the magnon are  $\mathbf{p}$

and  $\varepsilon(\mathbf{p})$ . Then

$$\frac{p_n^2}{2m_n} \pm \varepsilon(\mathbf{p}) = \frac{p_n'^2}{2m_n}, \quad \mathbf{p}_n' = \mathbf{p}_n \pm \mathbf{p}$$

The two conservation laws can be written as a single equation but one that contains vectors (to be specific, we chose the absorption of a magnon):

$$\frac{p_n^2}{2m_n} + \varepsilon(\mathbf{p}) = \frac{(\mathbf{p}_n + \mathbf{p})^2}{2m_n} \quad (4.19)$$

Now we want to find out whether this equation has a solution. If it has, the process is al-

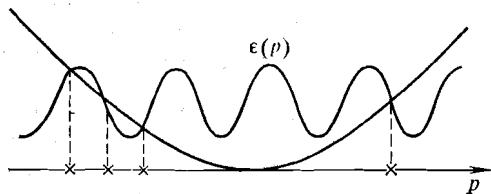


Fig. 70. Graphical solution of equation (4.19). The abscissa axis gives the magnon momentum pointing along a "good" direction. The roots of the equation are marked with crosses

lowed. The simplest way to establish the existence of a solution (as a rule, several solutions exist) is to analyze Fig. 70. But if solutions exist, the method gives a direct possibility of measuring the magnon energy as a function of the magnon quasimomentum. It is then necessary to measure independently the change in the neutron momentum (it is equal to the magnon quasimomentum  $\mathbf{p}$ ) and the change in the neutron energy (it is

equal to the magnon energy  $\varepsilon(\mathbf{p})$ ). Many elegant methods of realizing this idea were suggested. It was by analyzing the inelastic scattering of neutrons in ferro-, ferri-, and antiferromagnetics that the main properties of magnons in these materials were obtained.

Optics joined the magnon research in recent years. Transparent magnetic materials have been synthesized. The application of lasers, that is, of sources of coherent light, to physical experiments made it possible to study the inelastic scattering of photons by such magnetic materials. The creation or absorption of a magnon leads to a change in a photon frequency (because the photon energy is proportional to its frequency). This effect can be detected by a change in the color of a light beam.

The information on magnetic materials that can be extracted from inelastic scattering experiments is not exhausted by the dependence of the energy of magnons on their quasimomentum. As in resonance investigations, it proves possible to clarify numerous interesting details of dissipative processes involving magnons.

\* \* \*

Concluding a discussion about an actively developing field of science is a bit like cutting a dialogue short in midsentence. What reassures us is that at the outset we formulated a well-defined task: to describe the *nature of magnetic phenomena*; we hope this goal was achieved. There is almost no end to what can be said about magnetic phenomena. The reader now possibly



realizes that the magnetic properties of materials are inseparably linked to their microscopic structure and can be understood only if the structure and composition of materials, the interatomic, intermolecular, and interionic forces are clearly understood. Sometimes (but certainly not always) magnetic properties can be "isolated": can be treated without resorting to the structure of microscopic particles. This is how the model of magnetic-needles gas and all its consequences can appear. With microscopic particles and their properties known, it is far from simple to "compose" the macroscopic picture. On many occasions we had to turn to statistical physics. The pages where we had to operate in terms of statistical physics were probably the most difficult for understanding and the least descriptive.

Clearly realizing this, we attempted to help the reader with explanations. We do not know whether the attempt really succeeded.

A last remark: our discussion here has been somewhat confined by our limited tools. This approach was not always emphasized. We have attempted to stimulate the reader to look for explanations of the facts and properties that require greater knowledge, that is, to stimulate the yearning for just this knowledge.

## Problems

**Problem 1.** Calculate  $G$  by taking the value of acceleration due to gravity  $\approx 9.8 \text{ m/s}^2$  and finding the remaining necessary information about the Earth in a handbook or an encyclopaedia.

**Problem 2.** Derive formula (1.4).

**Problem 3.** Calculate the field far from two identical antiparallel dipoles spaced by a distance  $l$  from each other, on the perpendicular to the line connecting them.

**Problem 4.** Show that  $\hbar^2/m_e c^2$  is the only possible combination with the dimensionality of length, constructed of  $e$ ,  $m_e$ , and  $\hbar$ . Explain why the speed of light  $c$  is omitted from the set of quantities from which the size of the atom is constructed.

**Problem 5.** Those who are familiar with differentiation and know the meaning of vector product will easily derive from Newton's equation  $d\mathbf{p}/dt = \mathbf{F}$  (the increment of momentum  $\mathbf{p}$  per unit time equals the force  $\mathbf{F}$ ) that  $\mathbf{L} = [\mathbf{p} \times \mathbf{r}] = \text{const}$ , that is,  $\mathbf{L}$  is independent of time (obviously, we assume that  $\mathbf{F}$  is a central force:  $\mathbf{F} \parallel \mathbf{r}$ ).

**Problem 6.** Using the formulas of classical mechanics, calculate the change in the velocity

of a particle with mass 1 g moving in a circular orbit of radius 1 cm when the orbital angular momentum changes because  $L$  is incremented by unity. Try to explain why quantization can be neglected in the motion of macroscopic bodies.

**Problem 7.** Find a numerical relationship between the wavelength of an electromagnetic wave with frequency  $\omega_H$  and magnetic field  $H$ .

**Problem 8.** Find the magnet-screen distance  $L$  in the Stern-Gerlach experiment necessary for the separation of 0.0044 mm between the traces of the beams. In the Stern-Gerlach experiment  $dH/dz = 2.2 \cdot 10^5$  Oe/cm. The width of the non-uniform field region,  $D = 10$  cm (see Fig. 14), the velocity of the atomic beam was  $10^6$  cm/s.

**Problem 9.** Derive formula (1.35). This can be done by using formula (1.26) for the energy of a magnetic dipole in a magnetic field, assuming that the field  $H$  is produced by another dipole (see formula (1.7)).

**Problem 10.** Find the dimensionality of  $H$  and  $\mathcal{M}$ .

**Problem 11.** Rewrite the EPR and NMR conditions as relations between electromagnetic wavelength and magnetic field. Find the numerical value of the proportionality factor for the electron and the proton (see Table 1 on p. 60).

**Problem 12.** Using formula (2.12), show that the magnetic moment of a diamagnetic atom  $\sim \mu_B$  if  $eH \approx e^3/a^2$ .

**Problem 13.** Derive the formula

$$\mathcal{M} = NM_a L \left( \frac{M_a H}{kT} \right), \quad L(x) = \coth x - \frac{1}{x} \quad (2.15')$$

by taking into account that the number of particles whose magnetic moment makes an angle  $\theta$  with the magnetic field  $H$  is proportional to  $\exp(M_a H \cos \theta / kT)$  (see p. 107).

Derive from (2.15') an expression for  $\chi_{cl}$  (formula (2.15'), as (2.13), was derived by Langevin).

**Problem 14.** Prove that the work of the Lorentz force is zero.

**Problem 15.** Calculate the mean energy of a particle in a Fermi gas at  $T = 0$  and express this energy via the Fermi energy  $\varepsilon_F$ .

**Problem 16.** Show that the equality  $\mu_B H = \varepsilon_F$  is reached at  $H \approx 10^8$  Oe. The most colossal magnets produce magnetic fields not exceeding  $5 \cdot 10^6$  Oe.

**Problem 17.** Show that  $\chi_P \approx (1/137)^2$  to within a factor of the order of unity (cf. the derivation of formula (2.16)).

**Problem 18.** Explain why the magnet shown in Fig. 30 does not fall onto the plate. The hovering-magnet experiment was first performed by V. K. Arkadyev in 1945. Nowadays this phenomenon has found technical applications.

**Problem 19.** Derive all the formulas of this section for  $J = 1$ ; it would be even better if you derived them for arbitrary  $J$ . Possibly, this is the most complicated of the suggested problems.

**Problem 20.** Show that by virtue of the Curie-Weiss equation

$$\chi = \left( \frac{d\mathcal{M}}{dH} \right)_{H \rightarrow 0} \propto e^{-\frac{2T_c}{T}} \quad \text{at } T \rightarrow 0$$

(see the footnote to p. 150).

**Problem 21.** Using the expression

$$F = \frac{1}{2} a (T - T_{cr}) \eta^2 + \frac{1}{4} b \eta^4$$

( $a$ ,  $b$  are constants), calculate  $\bar{\eta}$  and show that for  $b > 0$  this function describes a second-order phase transition (L. D. Landau, 1937). Find a relation between the parameters  $a$ ,  $T_{cr}$ ,  $b$  and the quantities characterizing the “para-ferro” transition.

**Problem 22.** Verify this statement.

**Problem 23.** Use the arguments employed in deriving an expression for the density of states  $g(\epsilon)$  (see p. 126) and the dependence of the magnon energy on momentum at  $\mathbf{p} \ll \hbar/a$  to derive formula (3.41).

**Problem 24.** Use (3.42) and calculate  $\mathcal{M}(T)$  at  $\epsilon_0 = 2\mu_B H \gg kT$ ; compare the result with (3.5). For a numerical evaluation take  $H = 1000$  Oe and  $T_c = 10^3$  K.

**Problem 25.** Find the function  $E_{\text{magn}}(T)$  at  $kT \ll \epsilon_0$ .

**Problem 26.** Calculate the phonon component of heat capacity by using formula (3.47).

**Problem 27.** Roughly estimate the energy that neutrons must have in order to be used for analyzing crystal structures.

**Problem 28.** Prove (preferably without calculations) that an asymmetric arrangement of the magnetic moments  $\mathcal{M}_1$  and  $\mathcal{M}_2$  at  $\mathbf{H} = H\mathbf{n}$  is energetically unfavorable.

**Problem 29.** Verify that formula (3.40) does not contradict the definition of the effective magnon mass given on p. 204.

**Problem 30.** Find the condition of the antiferromagnetic resonance for a two-sublattice “easy-axis”-type antiferromagnetic material in its three configurations. Can the resonance occur in the antiparallel configuration?