

## 1.5. Magnetic properties

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### 1.5.1. Introduction

In the present chapter, we shall give a short review of the structure and some properties of magnetic substances that depend mainly on the symmetry of these substances. Aspects related to the magnetic symmetry receive the most emphasis. The magnetic symmetry takes into account the fact that it is necessary to consider time inversion in addition to the usual spatial transformations in order to describe the invariance of the thermodynamic equilibrium states of a body.

The symmetry of magnetic materials depends not only on the mean charge density function  $\rho(\mathbf{r})$ , but also on the mean current density  $\mathbf{j}(\mathbf{r})$  and the mean spin density  $\mathbf{S}(\mathbf{r})$ . The symmetry of the function  $\rho(\mathbf{r})$  is called the crystallographic or crystallochemical symmetry of a body. If the current density  $\mathbf{j}(\mathbf{r})$  in the crystal is not zero, an orbital magnetic moment is produced. It is obvious that there can be no macroscopic current in a substance which is in thermodynamic equilibrium and in which the integral  $\int \mathbf{j} \, d\tau$  over the magnetic elementary cell is always equal to zero. The current  $\mathbf{j}$ , however, may produce a macroscopic nonzero magnetic moment  $\mathbf{m}(\mathbf{r})$ . We shall consider below the function  $\mathbf{m}(\mathbf{r})$ , which determines the space distribution of the total (spin plus orbital) magnetic moment density. The symmetry of the distribution of the magnetic moment density  $\mathbf{m}(\mathbf{r})$  may be considered as the symmetry of the arrangement and orientation of the mean atomic (or ionic) magnetic moments in the crystal (we shall not consider the magnetism of the conduction electrons in this chapter).

The first part of the chapter is devoted to a brief classification of materials according to their magnetic properties. If  $\mathbf{m}(\mathbf{r}) \equiv 0$  at every point, the substance is magnetically disordered. There are two types of such substances: diamagnets and paramagnets. Their most important features are briefly outlined in Section 1.5.1.1.

If  $\mathbf{m}(\mathbf{r}) \neq 0$ , the substance possesses a magnetic structure. There are two cases to be considered: (1) The integral of  $\mathbf{m}(\mathbf{r})$  over the primitive cell is not zero ( $\int \mathbf{m} \, d\tau \neq 0$ ); such a substance is called ferromagnetic. (2)  $\int \mathbf{m} \, d\tau = 0$ ; such a substance is called antiferromagnetic. The integration is performed over the magnetic elementary cell, which may differ from the crystallographic one. This crude classification is detailed in Section 1.5.1.2.

The classification of ferromagnets according to the type of the magnetic structure is given in Section 1.5.1.2.1. The concept of the magnetic sublattice is introduced and the ferromagnets are divided into two groups: one-sublattice ferromagnets and multi-sublattice ferro- and ferrimagnets. Collinear and non-collinear ferromagnets are described.

In Section 1.5.1.2.2, the antiferromagnets are classified by the types of their magnetic structures: collinear, weakly non-collinear and strongly non-collinear antiferromagnets.

Incommensurate structures are briefly mentioned in Section 1.5.1.2.3.

The study of magnetically ordered crystals has led to a generalization of the theory of crystallographic symmetry. This generalization is based on the fact that  $\mathbf{m}(\mathbf{r})$  changes sign under a specific transformation  $R$ , which is equivalent to time inversion. The invariance of the equation of motion is preserved under  $R$ . The symmetry that admits the operation  $R$  along with ordinary crystallographic transformations (translations, rotations and reflections) is called the magnetic symmetry. Section 1.5.2 is devoted to magnetic symmetry. Different types of magnetic point

(Section 1.5.2.1) and magnetic space (Section 1.5.2.3) groups are defined. The 22 magnetic Bravais lattices are displayed in Section 1.5.2.2. All magnetic groups (both point and space) are categorized into three types: (1) The groups that possess  $R$  as an additional element. The crystals which belong to such space groups satisfy  $\mathbf{m}(\mathbf{r}) = -\mathbf{m}(\mathbf{r})$  at every point, hence  $\mathbf{m}(\mathbf{r}) = 0$ . Such crystals are found to be paramagnetic or diamagnetic. Crystals with a point group that possesses  $R$  as an additional element may also be antiferromagnetic. This is the case if  $R$  appears in the space group multiplied by some translations but not as a separate element. (2) The groups that do not possess  $R$  at all. (3) The groups that contain the element  $R$  only in combination with some other elements (translations, rotations, reflections). The latter two types of space groups describe magnetically ordered crystals.

The transition from the paramagnetic state to the magnetically ordered state entails a transition from one magnetic group to another. These transitions are considered in Section 1.5.3. Section 1.5.3.1 gives an example of the analysis of such transitions in terms of magnetic symmetry and introduces the concept of ferromagnetic and antiferromagnetic vectors, which characterize the magnetic structures. The phenomenological theory of magnetic transitions is based on the Landau theory of second-order phase transitions. Section 1.5.3.3 is dedicated to this theory (see also Section 3.1.2). The Landau theory is based on the expansion of the thermodynamic potential into a series of the basic functions of irreducible representations of the space group of the crystal under consideration. It is essential to distinguish the exchange and the relativistic terms in the expansion of the thermodynamic potential (see Section 1.5.3.2).

The domain structure of ferromagnets and antiferromagnets is considered in Section 1.5.4, where  $180^\circ$  and T-domains are described. The change from a multidomain structure to a single-domain structure under the action of an applied magnetic field explains the magnetization process in ferro- and ferrimagnets. The existence of  $180^\circ$  domains in antiferromagnets was shown in experiments on piezomagnetism and the linear magnetoelectric effect.

Non-collinear antiferromagnetic structures (weakly ferromagnetic, non-collinear and non-coplanar antiferromagnetic structures) are described in Section 1.5.5. The existence of these structures is directly connected with the magnetic symmetry. Such a structure arises if the irreducible representation responsible for the phase transition into the ordered state is two- or three-dimensional. Correspondingly, the magnetic group allows the coexistence of two or three different ferro- or antiferromagnetic vectors.

Besides the magnetic phase transition from the disordered into the ordered state, there exist transitions from one magnetic structure into another. Amongst them, there are reorientation transitions, which are obtained by a rotation of the ferromagnetic or antiferromagnetic vector relative to the crystallographic axis. They are analysed in Section 1.5.6.

Sections 1.5.7 and 1.5.8 are devoted to phenomena that can be (and were) predicted only on the basis of magnetic symmetry. These are piezomagnetism (Section 1.5.7) and the magnetoelectric effect (Section 1.5.8). The reciprocal of the piezomagnetic effect (Section 1.5.7.1) is linear magnetostriction (Section 1.5.7.2). The magnetoelectric effect has been investigated far more than piezomagnetism. In addition to the linear magnetoelectric effect (Section 1.5.8.1), effects of higher order (Section 1.5.8.2) have also been observed. In connection with the

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magnetolectric effect, ferromagnetic and antiferromagnetic ferroelectrics are also considered (Section 1.5.8.3). Such ‘multi-ferroic’ crystals have received much attention in recent years. For this reason, Section 1.5.8.3 has been updated by M. Kenzelmann.

In Section 1.5.9, the magnetostriction in ferromagnets is discussed. Only fundamental points of this problem are considered.

As noted above, only those problems of magnetism that are closely connected with magnetic symmetry are considered in this chapter. However, these problems are only outlined briefly here because of the restricted size of this volume. For the same reason, it is impossible to give an exhaustive list of references. The references given here include selected publications on magnetic symmetry and those describing the first experimental work devoted to the properties connected with magnetic symmetry. Because the magnetolectric effect has recently attracted considerable attention, some references have been added in Section 1.5.8 of this second edition.

The Gaussian system of units was used in this chapter in the first edition of this book, as was usual for the early work on the topics of this chapter. At present, the majority of publications on magnetism use the legal SI units. Therefore, all equations are now given in both systems in this chapter. Fortunately, many relations do not depend on the choice of units, in most other cases only a small modification is sufficient to make the equations valid in both systems; only a few equations have to be written in two forms. In the figures and tables showing the results of early measurements, the Gaussian units have been kept and the conversion factors are indicated.

### 1.5.1.1. Magnetically disordered materials

A crystal placed in a magnetic field  $\mathbf{H}$  is magnetized. The magnetized state is characterized by two vectors, the magnetization  $\mathbf{M}$  (the magnetic moment per unit volume) and the magnetic induction  $\mathbf{B}$ . In Gaussian units the magnetic induction is given by

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}. \quad \text{G}(1.5.1.1)$$

This equation shows how the units of  $\mathbf{B}$ ,  $\mathbf{H}$  and  $\mathbf{M}$  are related in the Gaussian system. The unit for  $\mathbf{B}$ , the gauss (G), and for  $\mathbf{H}$ , the oersted (Oe), also coincide in magnitude, whereas the unit for  $\mathbf{M}$ , usually called emu  $\text{cm}^{-3}$ , is  $4\pi$  times larger than the gauss and the oersted. In SI units the magnetic induction is given by

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}), \quad \text{SI}(1.5.1.1)$$

where  $\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2}$  is the magnetic constant. It is also known as the vacuum permeability; its dimension can also be written as  $\text{V s A}^{-1} \text{ m}^{-1}$  or  $\text{H m}^{-1}$ . The Gaussian units are related to the corresponding SI units as follows:  $1 \text{ G} = 10^{-4} \text{ tesla (T)}$ ,  $1 \text{ Oe} = 10^3/(4\pi) \text{ A m}^{-1}$ ,  $1 \text{ emu cm}^{-3} = 10^3 \text{ A m}^{-1}$ . Introducing  $\mu_0^*$ , where  $\mu_0^* = \mu_0$  in SI units and  $\mu_0^* = 1$  in Gaussian units, most equations in this chapter can be written in a form that is valid in both systems.

Historically, the two fields  $\mathbf{H}$  and  $\mathbf{B}$  have been called the magnetic field  $\mathbf{H}$  and the magnetic induction  $\mathbf{B}$ . The International Organization for Standards (ISO) recommends ‘magnetic field  $\mathbf{H}$ ’ and ‘magnetic flux density  $\mathbf{B}$ ’. We are aware that it would be more appropriate to call  $\mathbf{B}$  the magnetic field strength and  $\mathbf{H}$  the magnetic excitation (see *e.g.* Hehl *et al.*, 2009) and to consider the properties that we shall describe as functions of  $\mathbf{B}$  rather than of  $\mathbf{H}$ . For easy comparison with published work, we shall stick to the historic approach. Note that except for ferromagnetic crystals,  $|\mathbf{M}|$  is negligible compared to  $|\mathbf{H}|$ , so that, instead of an applied field  $\mathbf{H}$ , we have  $\mathbf{B} = \mu_0^*\mathbf{H}$ , and *vice versa*.

In magnetically disordered materials, the vectors  $\mathbf{B}$  and  $\mathbf{M}$  are linear in the magnetic field. Using a Cartesian coordinate system, this can be expressed as

$$M_i = \chi_{ij}H_j \quad \text{and} \quad B_i = \mu_{ij}H_j, \quad (1.5.1.2)$$

where  $\chi_{ij}$  is the dimensionless magnetic susceptibility per unit volume and  $\mu_{ij}$  is the permeability; summations over the repeated indices  $j$  are assumed. The susceptibility is frequently referred to one mass unit or to one mole of substance. The mass susceptibility is written as  $\chi_g$ , the molar susceptibility as  $\chi_{\text{mol}}$ . The Gaussian units for  $\chi$ ,  $\chi_g$ ,  $\chi_{\text{mol}}$  and their SI equivalents are given in Table 1.5.10.1. The Gaussian unit for  $\chi$  is  $4\pi$  times larger than the SI unit. Thus, we obtain  $\chi^{\text{SI}} = 4\pi\chi^{\text{G}}$ .

All three vectors  $\mathbf{H}$ ,  $\mathbf{M}$  and  $\mathbf{B}$  are axial vectors (see Section 1.1.4.5.3), the symmetry of which is  $\infty/m$ . Accordingly, the components of these vectors perpendicular to a mirror plane do not change sign on being reflected by this plane, whereas the components parallel to the plane do change sign. Consequently, these three vectors are invariant with respect to inversion. The quantities  $\chi_{ij}$  and  $\mu_{ij}$  are components of second-rank polar tensors. With respect to the principal axes, the tensors become diagonal and both, the magnetic susceptibility and the permeability of a crystal, are characterized by the three values of the principal susceptibilities and principal permeabilities, respectively.

The magnetically disordered materials are divided into two types: diamagnets ( $\chi < 0$ ) and paramagnets ( $\chi > 0$ ).

Diamagnetism is a universal property of all materials. It is associated with the tendency of all the electrons to screen the applied external field according to the Lenz rule. For materials in which the electron orbits are spherically symmetric, the relation for the diamagnetic susceptibility was calculated by Langevin. For monoatomic substances he obtained, in Gaussian units,

$$\chi^{\text{G}} = -N \frac{e^2}{6mc^2} \left( \sum_{i=1}^{i=Z} \overline{r_i^2} \right) \quad \text{G}(1.5.1.3)$$

and, in SI units,

$$\chi^{\text{SI}} = -N \frac{e^2\mu_0}{6m} \left( \sum_{i=1}^{i=Z} \overline{r_i^2} \right), \quad \text{SI}(1.5.1.3)$$

where  $N$  is the number of atoms per unit volume,  $Z$  is the number of electrons per atom,  $e$  and  $m$  are the charge and the mass of the electron, respectively, and  $\overline{r_i^2}$  are the mean squares of the radii of the electron orbits. In polyatomic substances, the summation must be done over all types of atoms. In most chemical compounds, the orbits are not spherical and the calculation of the diamagnetic susceptibility becomes more complicated. In metals, the conduction electrons contribute significantly to the diamagnetic susceptibility. The diamagnetic susceptibility of most substances is very small ( $\chi^{\text{G}} \simeq 10^{-6}$ ,  $\chi^{\text{SI}} \simeq 10^{-5}$ ) and isotropic. Rare exceptions are bismuth and some organic compounds, in which the diamagnetism is strongly anisotropic.

Most paramagnetic materials contain ions (or free atoms) with a partly filled inner electronic shell. Examples are the transition metals and the rare-earth and actinide elements. Atoms, molecules and point defects possessing an odd number of electrons are also paramagnetic. Ions with a partly filled inner electronic shell possess orbital  $\mathbf{L}$  and spin  $\mathbf{S}$  angular momenta, which determine the total angular momentum  $\mathbf{J}$  provided the spin–orbit interaction is strong compared with the crystal field.

The magnetic susceptibility of paramagnets follows the Curie–Weiss law in low magnetic fields ( $\mu_B B \ll k_B T$ ):

$$\chi = \frac{N\mu_0^* p^2 \mu_B^2}{3k_B(T - \Delta)}, \quad (1.5.1.4)$$

where  $N$  is the number of magnetic ions (or atoms) per volume unit,  $\mu_B$  is the Bohr magneton,  $p$  is the effective number of Bohr magnetons,  $k_B$  is the Boltzmann factor and  $\Delta$  is the Weiss constant. The Weiss constant is related to the interaction between

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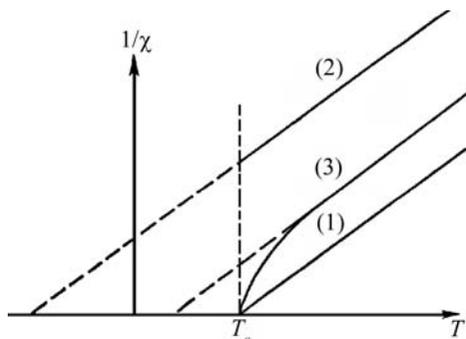


Fig. 1.5.1.1. Temperature dependence of  $1/\chi$  at high temperatures for different types of materials: (1) ferromagnet; (2) antiferromagnet; (3) ferrimagnet.

the magnetic moments (mostly exchange interaction) and to the effect of the splitting of electron levels of the paramagnetic ion in the crystalline electric field. Many paramagnets that obey the Curie–Weiss law transform into magnetically ordered materials at a temperature  $T_c$ , which is of the order of  $|\Delta|$ . The sign of  $\Delta$  depends on the sign of the exchange constant  $J^{\text{ex}}$  [see relation (1.5.1.7)]. For the substances that at low temperatures become ferromagnets, we have  $\Delta > 0$ , for antiferromagnets  $\Delta < 0$ , and for ferrimagnets the temperature dependence of  $\chi$  is more complicated (see Fig. 1.5.1.1). For those paramagnets that do not go over into an ordered state,  $\Delta$  is close to zero and equation (1.5.1.4) changes to the Curie law.

The value of the effective number of Bohr magnetons  $p$  depends strongly on the type of the magnetic ions and their environment. For most rare-earth compounds at room temperature, the number  $p$  has the same value as for free ions:

$$p = g[J(J+1)]^{1/2}, \quad (1.5.1.5)$$

where  $g$  is the Landé  $g$ -factor or the spectroscopic splitting factor ( $1 \leq g \leq 2$ ) and  $J$  is the quantum number of the total angular momentum. In this case, the paramagnetic susceptibility is practically isotropic. Some anisotropy can arise from the anisotropy of the Weiss constant  $\Delta$ .

The behaviour of the transition-metal ions is very different. In contrast to the rare-earth ions, the electrons of the partly filled shell in transition metals interact strongly with the electric field of the crystal. As a result, their energy levels are split and the orbital moments can be ‘quenched’. This means that relation (1.5.1.5) transforms to

$$p_{ij} = (g_{\text{eff}})_{ij}[S(S+1)]^{1/2}. \quad (1.5.1.6)$$

Here the value of the effective spin  $S$  represents the degeneration of the lowest electronic energy level produced by the splitting in the crystalline field;  $(g_{\text{eff}})_{ij}$  differs from the usual Landé  $g$ -factor. The values of its components lie between 0 and 10–20. The tensor  $(g_{\text{eff}})_{ij}$  becomes diagonal with respect to the principal axes. According to relation (1.5.1.6), the magnetic susceptibility also becomes a tensor. The anisotropy of  $(g_{\text{eff}})_{ij}$  can be studied using electron paramagnetic resonance (EPR) techniques.

The Curie–Weiss law describes the behaviour of those paramagnets in which the magnetization results from the competition of two forces. One is connected with the reduction of the magnetic energy by orientation of the magnetic moments of ions in the applied magnetic field; the other arises from thermal fluctuations, which resist the tendency of the field to orient these moments. At low temperatures and in strong magnetic fields, the linear dependence of the magnetization *versus* magnetic field breaks down and the magnetization can be saturated in a sufficiently strong magnetic field. Most of the paramagnetic substances that obey the Curie–Weiss law ultimately develop magnetic order as the temperature is decreased.

The conduction electrons in metals possess paramagnetism in addition to diamagnetism. The paramagnetic susceptibility of the conduction electrons is small (of the same order of magnitude as the diamagnetic susceptibility) and does not depend on temperature. This is due to the fact that the conduction electrons are governed by Fermi–Dirac statistics.

### 1.5.1.2. Magnetically ordered materials

#### 1.5.1.2.1. Ferromagnets (including ferrimagnets)

As stated above, all magnetically ordered materials that possess a spontaneous magnetization  $\mathbf{M}_s$  different from zero (a magnetization even in zero magnetic field) are called ferromagnets. The simplest type of ferromagnet is shown in Fig. 1.5.1.2(a). This type possesses only one kind of magnetic ion or atom. All their magnetic moments are aligned parallel to each other in the same direction. This magnetic structure is characterized by one vector  $\mathbf{M}$ . It turns out that there are very few ferromagnets of this type in which only atoms or ions are responsible for the ferromagnetic magnetization (CrBr<sub>3</sub>, EuO *etc.*). The overwhelming majority of ferromagnets of this simplest type are metals, in which the magnetization is the sum of the magnetic moments of the localized ions and of the conduction electrons, which are partly polarized.

More complicated is the type of ferromagnet which is called a ferrimagnet. This name is derived from the name of the oxides of the elements of the iron group. As an example, Fig. 1.5.1.2(b) schematically represents the magnetic structure of magnetite (Fe<sub>3</sub>O<sub>4</sub>). It contains two types of magnetic ions and the number of Fe<sup>3+</sup> ions ( $\mu_1$  and  $\mu_2$ ) is twice the number of Fe<sup>2+</sup> ions ( $\mu_3$ ). The values of the magnetic moments of these two types of ions differ. The magnetic moments of all Fe<sup>2+</sup> ions are aligned in one direction. The Fe<sup>3+</sup> ions are divided into two parts: the magnetic moments of one half of these ions are aligned parallel to the magnetic moments of Fe<sup>2+</sup> and the magnetic moments of the other half are aligned antiparallel. The array of all magnetic moments of identical ions oriented in one direction is called a magnetic sublattice. The magnetization vector of a given sublattice will be denoted by  $\mathbf{M}_i$ . Hence the magnetic structure of Fe<sub>3</sub>O<sub>4</sub> consists of three magnetic sublattices. The magnetizations of two of them are aligned in one direction, the magnetization of the third one is oriented in the opposite direction. The net ferromagnetic magnetization is  $M_s = M_1 - M_2 + M_3 = M_3$ .

The special feature of ferrimagnets, as well as of many antiferromagnets, is that they consist of sublattices aligned antiparallel to each other. Such a structure is governed by the nature of the main interaction responsible for the formation of the ordered magnetic structures, the exchange interaction. The energy of the exchange interaction does not depend on the direction of the interacting magnetic moments (or spins  $\mathbf{S}$ ) relative to the crystallographic axes and is represented by the following relation:

$$U_{\text{ex}} = - \sum_{m,n} J_{mn}^{\text{ex}} \mathbf{S}_m \mathbf{S}_n. \quad (1.5.1.7)$$

Here  $\mathbf{S}_m, \mathbf{S}_n$  are the spins of magnetic atoms (ions) and  $J_{mn}^{\text{ex}}$  is the exchange constant, which usually decreases fast when the distance between the atoms rises. Therefore, usually only the nearest-neighbour interaction needs to be taken into account. Hence, according to (1.5.1.7), the exchange energy is a minimum for the state in which neighbouring spins are parallel (if  $J^{\text{ex}} > 0$ ) or antiparallel (if  $J^{\text{ex}} < 0$ ). If the nearest-neighbour exchange interaction were the only interaction responsible for the magnetic ordering, only collinear magnetic structures would exist (except in triangle lattices). Together with the exchange interaction, there is also a magnetic dipole interaction between the magnetic moments of the atoms as well as an interaction of the atomic magnetic electrons with the crystalline electric field. These interactions are much smaller than the exchange interaction.

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They are often called relativistic interactions. The relativistic interactions and the exchange interaction between next-nearest atoms bring about the formation of non-collinear magnetic structures.

A simple non-collinear structure is the magnetic structure of a weak ferromagnet. It contains identical magnetic ions divided in equal amounts between an even number of sublattices. In the first approximation, the magnetizations of these sublattices are antiparallel, as in usual antiferromagnets. In fact, the magnetizations are not strictly antiparallel but are slightly canted, *i.e.* non-collinear, as shown in Fig. 1.5.1.2(c). There results a ferromagnetic moment  $M_D$ , which is small compared with the

sublattice magnetization  $M_i$ . The magnetic properties of weak ferromagnets combine the properties of both ferromagnets and antiferromagnets. They will be discussed in detail in Section 1.5.5.1.

### 1.5.1.2.2. Antiferromagnets

As discussed above, the exchange interaction, which is of prime importance in the formation of magnetic order, can lead to a parallel alignment of the neighbouring magnetic moments as well as to an antiparallel one. In the latter case, the simplest magnetic structure is the collinear antiferromagnet, schematically shown in Fig. 1.5.1.3(a). Such an antiferromagnet consists of one or several pairs of magnetic sublattices of identical magnetic ions located in equivalent crystallographic positions. The magnetizations of the sublattices are oriented opposite to each other.

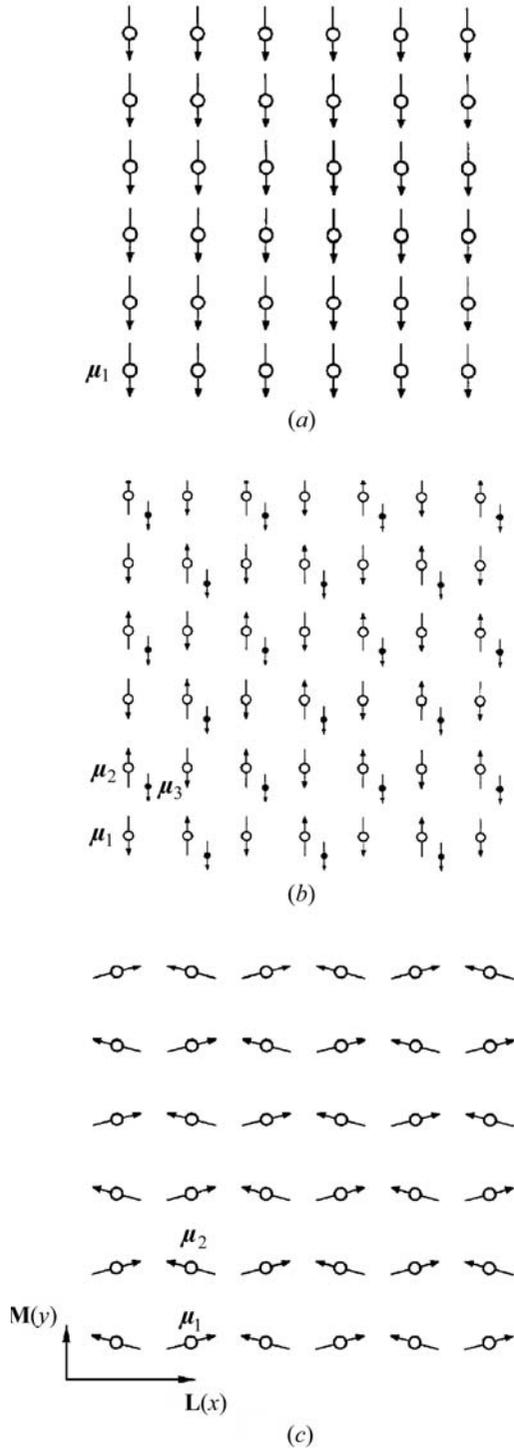


Fig. 1.5.1.2. Ordered arrangements of magnetic moments  $\mu_i$  in: (a) an ordinary ferromagnet  $\mathbf{M}_s = N\mu_1$ ; (b) a ferrimagnet  $\mathbf{M}_s = (N/3)(\mu_1 + \mu_2 + \mu_3)$ ; (c) a weak ferromagnet  $\mathbf{M} = \mathbf{M}_D = (N/2)(\mu_1 + \mu_2)$ ,  $\mathbf{L} = (N/2)(\mu_1 - \mu_2)$ ,  $L_x \gg M_y$ ;  $M_x = M_z = L_y = L_z = 0$ .  $N$  is the number of magnetic ions per volume unit.

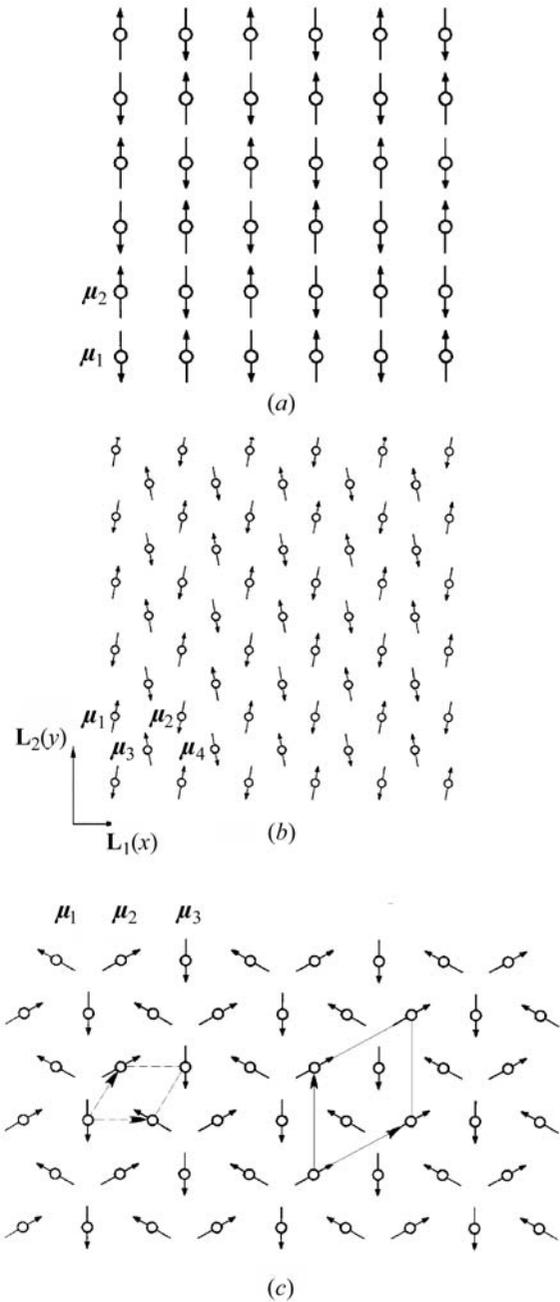


Fig. 1.5.1.3. Ordered arrangements of magnetic moments  $\mu_i$  in: (a) an ordinary two-sublattice antiferromagnet  $\mathbf{L} = (N/2)(\mu_1 - \mu_2)$ ; (b) a weakly non-collinear four-sublattice antiferromagnet  $\mathbf{L}_1(x) = (N/4)(\mu_1 - \mu_2 - \mu_3 + \mu_4)$ ,  $\mathbf{L}_2(y) = (N/4)(\mu_1 - \mu_2 + \mu_3 - \mu_4)$ ; (c) a strongly non-collinear three-sublattice antiferromagnet  $\mathbf{L}_1 = (N/3)3^{1/2}(\mu_2 - \mu_1)$ ,  $\mathbf{L}_2 = (N/3)(\mu_1 + \mu_2 - \mu_3)$ . The broken lines show the crystallographic primitive cell and the solid lines the magnetic primitive cell.

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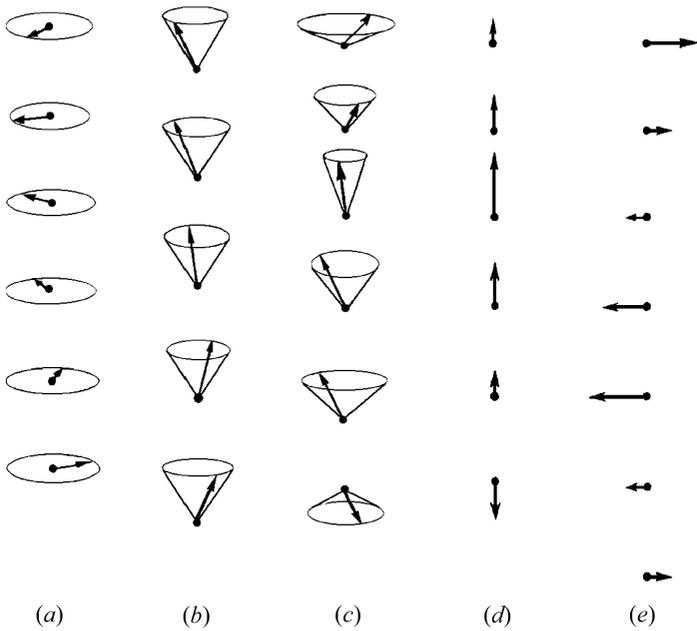


Fig. 1.5.1.4. Helical and sinusoidal magnetic structures. (a) An antiferromagnetic helix; (b) a cone spiral; (c) a cycloidal spiral; (d) a longitudinal spin-density wave; (e) a transverse spin-density wave.

Fig. 1.5.1.3(b) shows a weakly non-collinear antiferromagnet, in which the vectors of magnetization of four equivalent sublattices form a cross with a small tilting angle  $2\alpha$ . Such a structure can be considered as an admixture of ‘weak antiferromagnetism’  $\mathbf{L}_1$  with easy axis  $Ox$  to an ordinary antiferromagnet  $\mathbf{L}_2$  with easy axis  $Oy$ . This weak antiferromagnetism is of the same origin as weak ferromagnetism. Its nature will be discussed in detail in Section 1.5.5.2.

The minimum of the exchange interaction energy of three spins located at the corners of a triangle corresponds to a structure in which the angles between two adjacent spins are  $120^\circ$ . Correspondingly, many hexagonal crystals possess a triangular antiferromagnetic structure like the one shown in Fig. 1.5.1.3(c). The sum of the magnetizations of the three sublattices in this structure equals zero. In tetragonal crystals, a  $90^\circ$  antiferromagnetic structure can exist, which consists of four equivalent sublattices with magnetizations oriented along the positive and negative directions of the  $x$  and  $y$  axes.

Finally, in addition to the electronic magnetically ordered substances, there exist nuclear ferro- and antiferromagnets (below 1 mK for some insulators and below 1  $\mu$ K for metals).

### 1.5.1.2.3. Helical and sinusoidal magnetic order

There are many more complicated non-collinear magnetic structures. Fig. 1.5.1.4(a) shows an antiferromagnetic helical structure. It consists of planes perpendicular to the  $z$  axis in which all the magnetic moments are parallel to each other and are perpendicular to  $\mathbf{z}$ . The polar angle of the direction of the moments changes from plane to plane by some constant  $\delta$ . Thus, the magnetization vectors describe a spiral along the axis of the crystal. Such structures were observed in hexagonal rare-earth metals. A specific feature is that they often are incommensurate structures. This means that  $2\pi/\delta$  is not a rational number and that the period of the magnetic spiral is not a multiple of the period of the lattice.

Similar to the antiferromagnetic helix, ferromagnetic helical or spiral structures exist [see Fig. 1.5.1.4(b)] in which the magnetizations of the layers are tilted to the axis at an angle  $\theta$ . As a result, the vectors of the magnetization of the layers are arranged on the surface of a cone. The ferromagnetic magnetization is aligned along the  $z$  axis. This structure is called a ferromagnetic helix. It usually belongs to the incommensurate magnetic structures.

More complicated antiferromagnetic structures also exist: sinusoidal structures, which also consist of layers in which all the magnetic moments are parallel to each other. Fig. 1.5.1.4(c) displays the cycloidal spiral and Figs. 1.5.1.4(d) and (e) display longitudinal and transverse spin density waves, respectively.

## 1.5.2. Magnetic symmetry

As discussed in Section 1.5.1, in studies of the symmetry of magnetically ordered crystals one should take into account not only the crystallographic elements of symmetry (rotations, reflections and translations) but also the time-inversion element, which causes the reversal of the magnetic moment density vector  $\mathbf{m}(\mathbf{r})$ . Following Landau & Lifshitz (1957), we shall denote this element by  $R$ . If combined with any crystallographic symmetry element  $G$  we get a product  $RG$ , which some authors call the space-time symmetry operator. We shall not use this terminology in the following.

To describe the symmetry properties of magnetically ordered crystals, one should use magnetic point and space groups instead of crystallographic ones, see also Section 1.2.5.

By investigating the ‘four-dimensional groups of three-dimensional space’, Heesch (1930) found not only the 122 groups that now are known as magnetic point groups but also the seven triclinic and 91 monoclinic magnetic space groups. He also recognized that these groups can be used to describe the symmetry of spin arrangements. The present interest in magnetic symmetry was much stimulated by Shubnikov (1951), who considered the symmetry groups of figures with black and white faces, which he called antisymmetry groups. The change of colour of the faces in antisymmetry (black–white symmetry, see also Section 3.3.5) corresponds to the element  $R$ . These antisymmetry classes were derived as magnetic symmetry point groups by Tavger & Zaitsev (1956). Beside antisymmetry, the concept of colour (or generalized) symmetry also was developed, in which the number of colours is not 2 but 3, 4 or 6 (see Belov *et al.*, 1964; Koptsik & Kuzhukeev, 1972). A different generalization to more than two colours was proposed by van der Waerden & Burckhardt (1961). The various approaches have been compared by Schwarzenberger (1984).

As the theories of antisymmetry and of magnetic symmetry evolved often independently, different authors denote the operation of time inversion (black–white exchange) by different symbols. Of the four frequently used symbols ( $R = E' = \underline{1} = 1'$ ) we shall use in this article only two:  $R$  and  $1'$ .

### 1.5.2.1. Magnetic point groups

Magnetic point groups may contain rotations, reflections, the element  $R$  and their combinations. A set of such elements that satisfies the group properties is called a magnetic point group. It is obvious that there are 32 trivial magnetic point groups; these are the ordinary crystallographic point groups supplemented by the element  $R$ . Each of these point groups contains all the elements of the ordinary point group  $\mathcal{P}$  and also all the elements of this group  $\mathcal{P}$  multiplied by  $R$ . This type of magnetic point group  $\mathcal{M}_{P1}$  can be represented by

$$\mathcal{M}_{P1} = \mathcal{P} + R\mathcal{P}. \quad (1.5.2.1)$$

Table 1.5.2.1. Comparison of different symbols for magnetic point groups

Schoenflies	Hermann–Mauguin	Shubnikov	
$D_{4R}$	4221'	4:21'	4:21
$D_4$	422	4:2	4:2
$D_4(C_4)$	42'2'	4:2'	4:2
$D_4(D_2)$	4'22'	4':2	4:2