

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

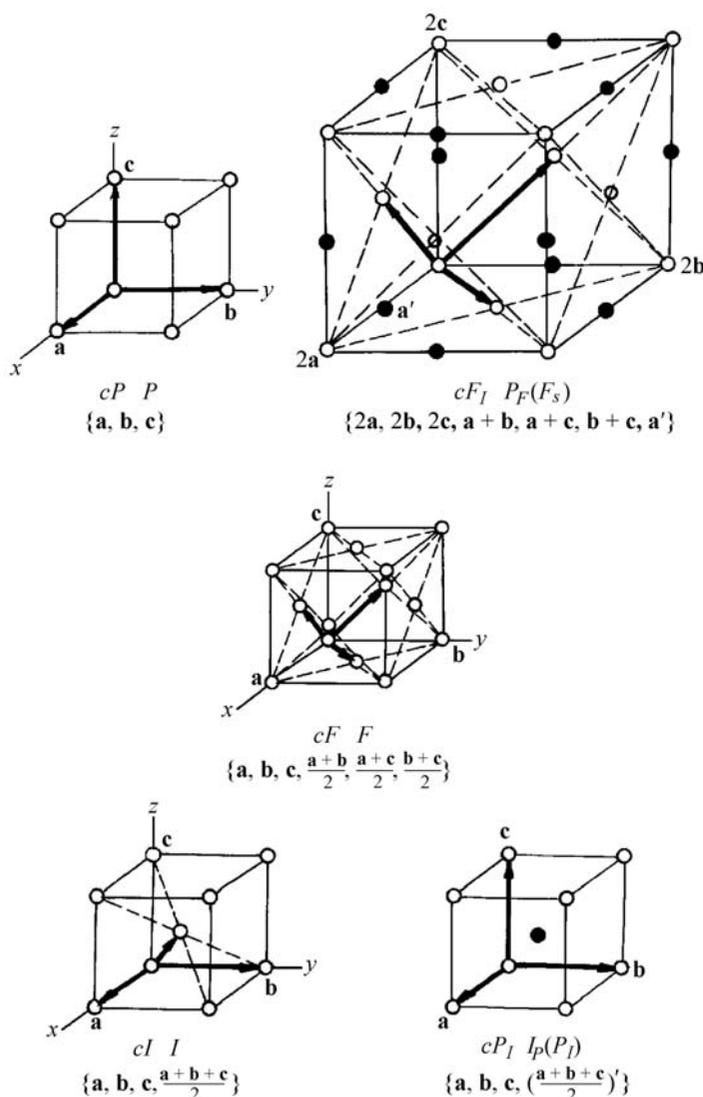


Fig. 1.5.2.7. Magnetic lattices of the cubic system.

magnetic unit cell coincides with the classical one. Forty-four groups of type II describe different ferromagnetic crystals; the remaining antiferromagnets.

The nontrivial magnetic space groups belong to type III, \mathcal{M}_{G_3} . This consists of 1191 groups, in which R enters only in combination with rotations, reflections or translations. These groups have the structure described by relation (1.5.2.2). The magnetic space groups of this type are divided into two subtypes.

Subtype III^a contains those magnetic space groups \mathcal{M}_{G_3} in which R is not combined with translations. In these groups, the magnetic translation group is trivial. To these space groups correspond magnetic point groups of type \mathcal{M}_{P_3} . There are 674 magnetic space groups of subtype III^a; 231 of them admit ferromagnetism, the remaining 443 describe antiferromagnets.

In the magnetic space groups of the subtype III^b, R is combined with translations and the corresponding point groups are of type \mathcal{M}_{P_1} . They have a nontrivial magnetic Bravais lattice. There are 517 magnetic space groups of this subtype; they describe antiferromagnets.

In summary, the 230 magnetic space groups that describe dia- and paramagnets are of type I, the 275 that admit spontaneous magnetization are of types II and III^a; the remaining 1146 magnetic space groups (types II, III^a and III^b) describe antiferromagnets.

1.5.2.4. Exchange symmetry

The classification of magnetic structures on the basis of the magnetic (point and space) groups is an exact classification.

However, it neglects the fundamental role of the exchange energy, which is responsible for the magnetic order (see Sections 1.5.1.2 and 1.5.3.2). To describe the symmetry of the magnetically ordered crystals only by the magnetic space groups means the loss of significant information concerning those properties of these materials that are connected with the higher symmetry of the exchange forces. Andreev & Marchenko (1976, 1980) have introduced the concept of exchange symmetry.

The exchange forces do not depend on the directions of the spins (magnetic moments) of the ions relative to the crystallographic axes and planes. They depend only on the relative directions of the spins. Thus the exchange group \mathcal{G}_{ex} contains an infinite number of rotations U of spin space, *i.e.* rotations of all the spins (magnetic moments) through the same angle about the same axis. The components of the magnetic moment density $\mathbf{m}(\mathbf{r})$ transform like scalars under all rotations of spin space. The exchange symmetry group \mathcal{G}_{ex} contains those combinations of the space transformation elements, the rotations U of spin space and the element R with respect to which the values $m(\mathbf{r})$ are invariant. Setting all the elements U and R equal to the identity transformation, we obtain one of the ordinary crystallographic space groups \mathcal{G} . This space group defines the symmetry of the charge density $\rho(\mathbf{r})$ and of all the magnetic scalars in the crystal. However, the vectors $\mathbf{m}(\mathbf{r})$ may not be invariant with respect to \mathcal{G} .

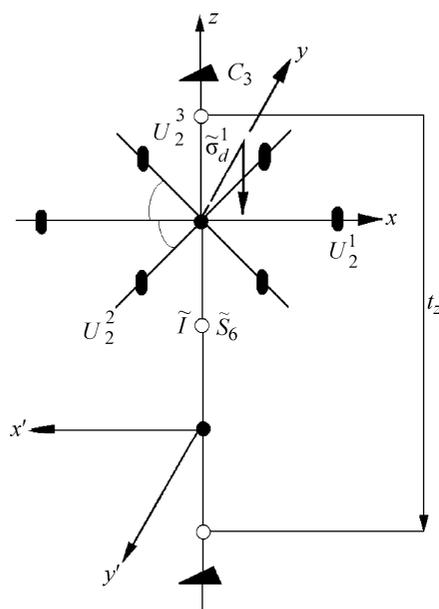
The concept of exchange symmetry makes it possible to classify all the magnetic structures (including the incommensurate ones) with the help of not more than three orthogonal magnetic vectors. We shall discuss this in more detail in Section 1.5.3.3.

More information about magnetic symmetry can be found in Birss (1964), Cracknell (1975), Joshua (1991), Koptsik (1966), Landau & Lifshitz (1957), Opechowski & Guccione (1965), and in Sirotnin & Shaskol'skaya (1979).

1.5.3. Phase transitions into a magnetically ordered state

Most transitions from a paramagnetic into an ordered magnetic state are second-order phase transitions. A crystal with a given crystallographic symmetry can undergo transitions to different ordered states with different magnetic symmetry. In Section 1.5.3.3, we shall give a short review of the theory of magnetic second-order phase transitions. As was shown by Landau (1937), such a transition causes a change in the magnetic symmetry. The magnetic symmetry group of the ordered state is a subgroup of the magnetic group of the material in the paramagnetic state. But first we shall give a simple qualitative analysis of such transitions.

To find out what ordered magnetic structures may be obtained in a given material and to which magnetic group they belong, one has to start by considering the crystallographic space group \mathcal{G} of the crystal under consideration. It is obvious that a crystal in which the unit cell contains only one magnetic ion can change only into a ferromagnetic state if the magnetic unit cell of the ordered state coincides with the crystallographic one. If a transition into an antiferromagnetic state occurs, then the magnetic cell in the ordered state will be larger than the crystallographic one if the latter contains only one magnetic ion. Such antiferromagnets usually belong to the subtype III^b described in Section 1.5.2.3. In Section 1.5.3.1, we shall consider crystals that transform into an antiferromagnetic state without change of the unit cell. This is possible only if the unit cell possesses two or more magnetic ions. To find the possible magnetic structures in this case, one has to consider those elements of symmetry which interchange the positions of the ions inside the unit cell (especially glide planes and rotation axes). Some of these elements displace the magnetic ion without changing its magnetic moment, and others change the moment of the ion. It is also essential to know the positions of all these elements in the unit cell. All this information is contained in the space group \mathcal{G} . If the magnetic ordering occurs without change of the unit cell, the translation

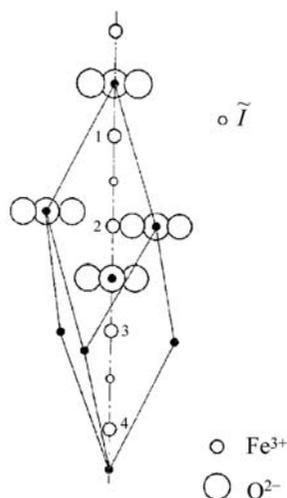
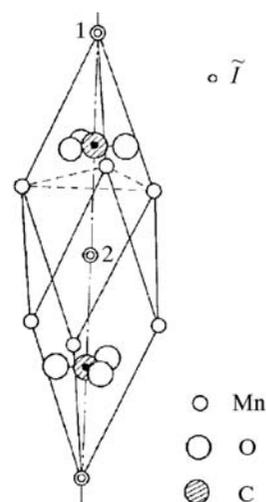

 Fig. 1.5.3.1. Arrangement of the symmetry elements of the group \tilde{D}_{3d}^6 .

group \mathcal{T} in the ordered state does not contain primed elements. Therefore, there is no need to consider the whole crystal space group \mathcal{G} . It will suffice to consider the cosets of \mathcal{T} in \mathcal{G} . Such a coset consists of all elements of \mathcal{G} that differ only by a translation. From each coset, a representative with minimum translative component is chosen. We denote a set of such representatives by $\tilde{\mathcal{G}}$; it can be made into a group by defining AB ($A, B \in \tilde{\mathcal{G}}$) as the representative of the coset that contains AB . Obviously, $\tilde{\mathcal{G}}$ is then isomorphic to the factor group \mathcal{G}/\mathcal{T} and therefore to the point group \mathcal{P} of \mathcal{G} .

Once more, we should like to stress that to construct the magnetic structures and the magnetic groups of a given crystal it is not enough to consider only the point group of the crystal, but it is necessary to perform the analysis with the help of its space group in the paramagnetic state or the corresponding group of coset representatives. An example of such an analysis will be given in the following section.

1.5.3.1. Magnetic structures in rhombohedral crystals

Following Dzyaloshinskii (1957a), we consider crystals belonging to the crystallographic space group $D_{3d}^6 = R\bar{3}c$. To this group belong α - Fe_2O_3 and the carbonates of Mn^{2+} , Co^{2+} and Ni^{2+} . Weak ferromagnetism was first observed in these materials.


 Fig. 1.5.3.2. Crystallographic structure of transition-metal oxides of the type α - Fe_2O_3 .

 Fig. 1.5.3.3. Crystallographic structure of transition-metal carbonates of the type MnCO_3 .

Cr_2O_3 , in which the magnetoelectric effect was discovered, also belongs to this group. The magnetic ordering in these materials occurs without change of the unit cell.

The representatives of the cosets D_{3d}^6/\mathcal{T} form the group \tilde{D}_{3d}^6 . Its symmetry operations are shown in Fig. 1.5.3.1. Directed along the z axis is the threefold axis C_3 and the sixfold roto-inversion axis \tilde{S}_6 . Three twofold axes U_2 run through the points \bullet at right angles to the z axis. One of these axes is directed along the x axis. Arranged normal to each of the U_2 axes are three glide planes $\tilde{\sigma}_d$. The y axis is directed along one of these planes. The centre of inversion \tilde{I} is located at the point \circ , lying on the z axis halfway between two points \bullet . The sign $\tilde{}$ means that the corresponding operation is accompanied by a translation along the z axis through half the period of the crystal (\tilde{I} means that the inversion centre is shifted from the point \bullet to the point \circ). In Fig. 1.5.3.1, the elementary period of translation along the z axis is marked by t_z . Thus the crystallographic group \tilde{D}_{3d}^6 has the following elements:

$$E, 2C_3, 3U_2, \tilde{I}, 3\tilde{\sigma}_d, 2\tilde{S}_6 \quad \{1, \pm 3_z, 3(2_\perp), \tilde{I}, 3(c = \tilde{m}), \pm \tilde{3}_z\}. \quad (1.5.3.1)$$

In two types of crystals, considered below, the magnetic ions are arranged on the z axis. If we place the magnetic ion at point 1 located between points \circ and \bullet (see Fig. 1.5.3.2), then using symmetry operations (1.5.3.1) we obtain three additional positions for other magnetic ions (points 2, 3, 4). Thus, the elementary cell will contain four magnetic ions. This is the structure of oxides of trivalent ions of iron and chromium (Fe_2O_3 , Cr_2O_3). The structure of these oxides is shown in Fig. 1.5.3.2. If the positions of the magnetic ions coincide with the positions of the inversion centre \circ , we obtain the structure of the carbonates of the transition metals (MnCO_3 , CoCO_3 , NiCO_3 , FeCO_3), which is shown in Fig. 1.5.3.3.

Evidently, the formation of a magnetic structure in the crystal does not result in the appearance of new elements of symmetry. The magnetic groups of magnetically ordered crystals may lack some elements contained in the crystallographic group and some of the remaining elements may happen to be multiplied by R (primed). Let us find the groups of symmetry that correspond to all possible collinear magnetic structures in rhombohedral crystals with four magnetic ions in the elementary cell. We shall assume that the magnetic moments are located at the points of the ion positions 1–4; they will be marked μ_a . The symmetry transformations cannot change the length of the vectors of the magnetic moments but they can change the direction of these vectors and interchange the positions of the sites $1 \leftrightarrow 2, 3 \leftrightarrow 4$

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

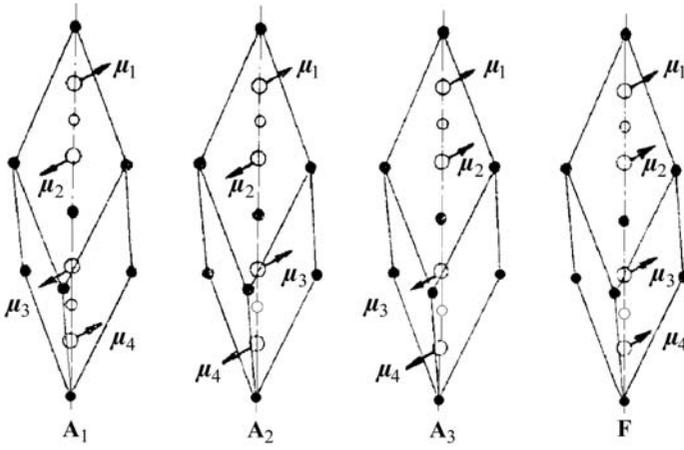


Fig. 1.5.3.4. Four types of magnetic structures of rhombohedral oxides of transition metals. The direction of μ_α is shown conventionally.

and $1 \leftrightarrow 3, 2 \leftrightarrow 4$. This interchange of the vectors $\mu_1, \mu_2, \mu_3, \mu_4$ means that these vectors form a basis of a reducible representation of the group \tilde{D}_{3d}^6 . The following linear combinations of μ_α form irreducible representations¹ of \tilde{D}_{3d}^6 :

$$\begin{aligned} \mathbf{l}_1 &= \mu_1 - \mu_2 - \mu_3 + \mu_4 \\ \mathbf{l}_2 &= \mu_1 - \mu_2 + \mu_3 - \mu_4 \\ \mathbf{l}_3 &= \mu_1 + \mu_2 - \mu_3 - \mu_4 \\ \mathbf{m} &= \mu_1 + \mu_2 + \mu_3 + \mu_4. \end{aligned} \quad (1.5.3.2)$$

Vectors \mathbf{l}_α characterize the antiferromagnetic states and are called antiferromagnetic vectors. The ferromagnetic vector \mathbf{m} gives the total magnetic moment of the elementary cell. These vectors describe the four possible collinear magnetic structures. Three are antiferromagnetic structures: A_1 ($\mathbf{l}_1 \neq 0, \mathbf{l}_2 = \mathbf{l}_3 = \mathbf{m} = 0$), A_2 ($\mathbf{l}_2 \neq 0, \mathbf{l}_3 = \mathbf{l}_1 = \mathbf{m} = 0$), A_3 ($\mathbf{l}_3 \neq 0, \mathbf{l}_1 = \mathbf{l}_2 = \mathbf{m} = 0$) and one is a ferromagnetic structure, F ($\mathbf{l}_1 = \mathbf{l}_2 = \mathbf{l}_3 = 0$). All these types are presented schematically in Fig. 1.5.3.4.

In the description of the structures of orthoferrites, other symbols were introduced to define the linear combinations of μ_α and to denote the antiferromagnetic structures under consideration (see Bertaut, 1963). The two types of symbols are compared in Table 1.5.3.1.

It should be borne in mind that in each of these types of magnetic ordering the respective vectors \mathbf{l}_α and \mathbf{m} may be directed along any direction. There are 12 types of such structures in which \mathbf{l}_α or \mathbf{m} are directed along one of the axes or planes of symmetry. To find out to which group of magnetic symmetry each of these structures belongs, one needs to investigate how each element of the crystallographic symmetry transforms the Cartesian components of the four vectors. This is shown in Table 1.5.3.2 for the group \tilde{D}_{3d}^6 . If the component keeps its direction, it is marked by the + sign; the - sign corresponds to reversal of the component direction. In some cases, the transformation results in a change of the direction of the components $l_{\alpha i}$ or m_i through an angle other than 0 or π . This is marked by 0. With the help of Table 1.5.3.2, we can easily describe all the elements of symmetry of the magnetic group that corresponds to each structure ($A_{\alpha i}$ or F_i) with the aid of the following rule. All the elements that yield the + sign are included in the magnetic group as they stand, while

¹ By omitting its translative part, each element of \tilde{D}_{3d}^6 is mapped on the corresponding element of the point group $D_{3d} = \tilde{3}m$. This mapping also establishes a one-to-one correspondence between the representations of \tilde{D}_{3d}^6 and those of $D_{3d} = \tilde{3}m$.

² In Section 1.5.3.3, we shall show that this rule corresponds in the Landau theory of phase transitions to the general law that the magnetically ordered state is described by $L_{\alpha i}$ or M_i , which form the basis of one of the irreducible representations of the paramagnetic space group of the crystal.

Table 1.5.3.1. Two types of symbols for collinear antiferromagnetic and ferromagnetic structures

Symbol	Alternative symbol
A_1	A
A_2	G
A_3	C
F	F

the elements yielding the - sign must be multiplied by R ; the elements which are marked by the sign 0 are not included in the magnetic group.² With the aid of this rule, Table 1.5.3.3 of the elements of the magnetic groups for the structures under consideration was compiled. In Table 1.5.3.4, the symbols of the magnetic point groups of all the 12 magnetic structures considered are listed. The crystals with two ions in the elementary cell have only two sublattices and their antiferromagnetic structures belong to the same groups as the structures $A_{3i} = C_i$.

One can see from Tables 1.5.3.3 and 1.5.3.4 that, in accordance with general theory, the magnetic point groups of the crystals under consideration are subgroups of the trivial magnetic point group $D_{3dR} = \tilde{3}m1'$ to which they belong in the paramagnetic state. In the example considered, the translation group does not change in going from the paramagnetic to the ordered state. Thus the same statement made for the point groups is also true for the space groups. Putting $R = E$ gives a subgroup of the crystallographic group of the crystal. For the magnetic structures with the ferromagnetic or antiferromagnetic vector directed along the z axis, it turns out that the magnetic group is isomorphic to the crystallographic group. This rule is obeyed by all (optically) uniaxial crystals if the transition occurs without change of the elementary cell. (Optically uniaxial are the non-cubic crystals with a point group possessing a threefold, fourfold or sixfold axis.)

Tables 1.5.3.3 and 1.5.3.4 show that different types of collinear structures may belong to the same point group (and also to the same space group). For the antiferromagnetic structure A_{3y} and the ferromagnetic F_x the group is $2/m$, and for the structures A_{3x} and F_y it is $2'/m'$. Thus the symmetry allows a phase to be simultaneously ferromagnetic and antiferromagnetic. That is not ferrimagnetic order because all the ions in the four sublattices are identical and their numbers are equal. The ferromagnetic vector \mathbf{m} and the antiferromagnetic one \mathbf{l}_3 are perpendicular and $|\mathbf{m}| \ll |\mathbf{l}_3|$. This phenomenon is called weak ferromagnetism and will be discussed in detail in Section 1.5.5.1. Like weak ferromagnetism, the symmetry also allows the coexistence of two orthogonal antiferromagnetic structures A_1 and A_2 . This gives rise to weakly non-collinear antiferromagnetic structures.

The strongly non-collinear structures are described by another set of basis vectors for the irreducible representations of the group \tilde{G} . If the magnetic ions μ_α in the crystal form triangular planes one gets instead of (1.5.3.2) the relations for the basis vectors:

$$\begin{aligned} \mathbf{l}_1 &= \sqrt{3}(\mu_1 - \mu_2) \\ \mathbf{l}_2 &= \mu_1 + \mu_2 - \mu_3 \\ \mathbf{m} &= \mu_1 + \mu_2 + \mu_3. \end{aligned} \quad (1.5.3.3)$$

1.5.3.2. Exchange and magnetic anisotropy energies

It is pertinent to compare the different kinds of interactions that are responsible for magnetic ordering. In general, all these interactions are much smaller than the electrostatic interactions between the atoms that determine the chemical bonds in the material. Therefore, if a crystal undergoes a transition into a magnetically ordered state, the deformations of the crystal that

1.5. MAGNETIC PROPERTIES

Table 1.5.3.2. Sign variation of the components of antiferromagnetic and ferromagnetic vectors during transformations of the group \tilde{D}_{3d}^6 in rhombohedral crystals with four magnetic ions

Vector components	Elements of symmetry									
	E	$2C_3$	U_2^1	U_2^2	U_2^3	\tilde{I}	$\tilde{\sigma}_d^1$	$\tilde{\sigma}_d^2$	$\tilde{\sigma}_d^3$	$2\tilde{S}_6$
	1	$\pm 3z$	$2x$	$2_{\perp}^{(2)}$	$2_{\perp}^{(3)}$	$\tilde{\mathbf{i}}$	c_x	$c_{\perp}^{(2)}$	$c_{\perp}^{(3)}$	$\pm \tilde{\mathbf{3}}$
l_{1x}	+	0	+	0	0	−	−	0	0	0
l_{1y}	+	0	−	0	0	−	+	0	0	0
l_{1z}	+	+	−	−	−	−	+	+	+	−
l_{2x}	+	0	−	0	0	−	+	0	0	0
l_{2y}	+	0	+	0	0	−	−	0	0	0
l_{2z}	+	+	+	+	+	−	−	−	−	−
l_{3x}	+	0	−	0	0	+	−	0	0	0
l_{3y}	+	0	+	0	0	+	+	0	0	0
l_{3z}	+	+	+	+	+	+	+	+	+	+
m_x	+	0	+	0	0	+	+	0	0	0
m_y	+	0	−	0	0	+	−	0	0	0
m_z	+	+	−	−	−	+	−	−	−	+

give rise to the change of its crystallographic symmetry are comparatively small. It means that most of the non-magnetic properties do not change drastically. As an example, the anisotropic deformation of the crystal that accompanies the transition into the ordered state (see Section 1.5.9.1) is mostly not larger than 10^{-4} .

The formation of the ordered magnetic structures is due mainly to the exchange interaction between the spins \mathbf{S}_α (and corresponding magnetic moments $\boldsymbol{\mu}$ of the atoms or ions). The expression for the exchange energy can contain the following terms [see formula (1.5.1.7)]:

$$\mathbf{S}_\alpha \mathbf{S}_\beta, \quad \mathbf{S}_\alpha [\mathbf{S}_\beta \mathbf{S}_\gamma]. \quad (1.5.3.4)$$

The exchange interaction decreases rapidly as the distance between the atoms rises. Thus, it is usually sufficient to consider the interaction only between nearest neighbours. The exchange interaction depends only on the relative alignment of the spin moments and does not depend on their alignment relative to the crystal lattice. Therefore, being responsible for the magnetic ordering in the crystal, it cannot define the direction of the spontaneous magnetization in ferromagnets or of the antiferromagnetic vector. This direction is determined by the spin-orbit and magnetic spin-spin interactions, which are often called relativistic interactions as they are small, of the order of v^2/c^2 , where v is the velocity of atomic electrons and c is the speed of light. The relativistic interactions are responsible for the magnetic anisotropy energy, which depends on the direction of the magnetic moments of the ions with regard to the crystal lattice. The value of the exchange energy can be represented by the effective exchange field H_e . For an ordered magnetic with a transition temperature of 100 K, $H_e \simeq 1000$ kOe. Thus the external magnetic field hardly changes the value of the magnetization \mathbf{M} or of the antiferromagnetic vector \mathbf{L} ; they are conserved quantities to a good approximation. The effective anisotropy field H_a in cubic crystals is very small: 1–10 Oe. In most non-cubic materials, H_a is not larger than 1–10 kOe. This means that by applying an external magnetic field we can change only the direction of \mathbf{M} , or sometimes of \mathbf{L} , but not their magnitudes.

Table 1.5.3.3. Magnetic groups of symmetry in rhombohedral oxides of trivalent transition-metal ions

Type of magnetic structure	Magnetic moments are directed along the axis		
	x	y	z
$A_1 = A$	$E; U_2; \tilde{I}R; \tilde{\sigma}_dR$	$E; U_2R; \tilde{I}R; \tilde{\sigma}_d$	$E; 2C_3; 3U_2R; \tilde{I}R; 3\tilde{\sigma}_d; 2\tilde{S}_6R$
$A_2 = G$	$E; U_2R; \tilde{I}R; \tilde{\sigma}_d$	$E; U_2; \tilde{I}R; \tilde{\sigma}_dR$	$E; 2C_3; 3U_2; \tilde{I}R; 3\tilde{\sigma}_dR; 2\tilde{S}_6R$
$A_3 = C$	$E; U_2R; \tilde{I}; \tilde{\sigma}_dR$	$E; U_2; \tilde{I}; \tilde{\sigma}_d$	$E; 2C_3; 3U_2; \tilde{I}; 3\tilde{\sigma}_d; 2\tilde{S}_6$
$F = F$	$E; U_2; \tilde{I}; \tilde{\sigma}_d$	$E; U_2R; \tilde{I}; \tilde{\sigma}_dR$	$E; 2C_3; 3U_2R; \tilde{I}; 3\tilde{\sigma}_dR; 2\tilde{S}_6$

The magnetic anisotropy energy U_a can be represented as an expansion in the powers of the components of the vectors \mathbf{M} or \mathbf{L} . The dependence of U_a on the direction of the magnetization is essential. Therefore, one usually considers the expansion of the spontaneous magnetization or antiferromagnetic vector in powers of the unit vector \mathbf{n} . The anisotropy energy is invariant under time reversal. Therefore, the general expression for this energy has the form

$$U_a = K_{ij}n_i n_j + K_{ijk\ell}n_i n_j n_k n_\ell + K_{ijklmn}n_i n_j n_k n_\ell n_m n_n, \quad (1.5.3.5)$$

where $K_{ij}, K_{ijk\ell}, K_{ijklmn}$ are tensors, the components of which have the dimension of an energy density. The forms of the tensors depend on the symmetry of the crystal. There are at most two independent components in K_{ij} . For a uniaxial crystal, the second-order term in the anisotropy energy expansion is determined by one anisotropy constant, K . Instead of using the components of the unit vector \mathbf{n} , its direction can be described by two angles: polar θ and azimuthal φ . Correspondingly, the anisotropy energy for a uniaxial crystal can be written as

$$U_a = K(n_x^2 + n_y^2) = K \sin^2 \theta. \quad (1.5.3.6)$$

This relation is equivalent to

$$U_a = K(1 - n_z^2) = K - K \cos^2 \theta. \quad (1.5.3.7)$$

The direction of the magnetization vector \mathbf{M} in a ferromagnet or of the antiferromagnetic vector \mathbf{L} in an antiferromagnet is called the direction or the axis of easy magnetization. The crystals in which this axis is aligned with a threefold, fourfold or sixfold axis of the magnetic point group are called easy-axis magnetics. The magnetic crystals with the main axis higher than twofold in the paramagnetic state in which, in the ordered state, \mathbf{L} (or \mathbf{M}) is perpendicular to this axis are often called easy-plane magnetics. The anisotropy in this plane is usually extremely small. In this case, the crystal possesses more than one axis of easy magnetization and the crystal is usually in a multidomain state (see Section 1.5.4).

If the anisotropy constant K is positive, then the vector \mathbf{n} is aligned along the z axis, and such a magnetic is an easy-axis one.

Table 1.5.3.4. Magnetic point groups in rhombohedral oxides of transition metals

Type of magnetic structure	Magnetic moments are directed along the axis		
	x	y	z
$A_1 = A$	$C_{2h}(C_2) = 2/m'$	$C_{2h}(C_s) = 2'/m$	$D_{3d}(C_{3v}) = \tilde{3}m$
$A_2 = G$	$C_{2h}(C_2) = 2'/m$	$C_{2h}(C_2) = 2'/m'$	$D_{3d}(D_3) = \tilde{3}m'$
$A_3 = C$	$C_{2h}(C_i) = 2'/m'$	$C_{2h} = 2/m$	$D_{3d} = \tilde{3}m$
$F = F$	$C_{2h} = 2/m$	$C_{2h}(C_i) = 2'/m'$	$D_{3d}(S_6) = \tilde{3}m'$

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

For an easy-plane magnetic, K is negative. It is convenient to use equation (1.5.3.6) for easy-axis magnetics and equation (1.5.3.7) for easy-plane magnetics. In the latter case, the quantity K is included in the isotropic part of the thermodynamic potential Φ , and (1.5.3.7) becomes $U_a = -K \cos^2 \theta$. Instead we shall write $U_a = K \cos^2 \theta$ in the following, so that K becomes positive for easy-plane ferromagnetics as well.

Apart from the second-order term, terms of higher order must be taken into account. For tetragonal crystals, the symmetry allows the following invariant terms in the anisotropy energy:

$$\begin{aligned} U_a(4) &= K_1(n_x^2 + n_y^2) + K_2(n_x^2 + n_y^2)^2 + K_{xxyy}n_x^2n_y^2 \\ &= K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_{\perp} \sin^4 \theta \sin^2 2\varphi; \end{aligned} \quad (1.5.3.8)$$

the azimuthal angle φ is measured from the twofold axis x in the basal plane and the constant K_{\perp} determines the anisotropy in the basal plane.

Trigonal symmetry also allows second- and fourth-order invariants:

$$\begin{aligned} U_a(3) &= K_1(n_x^2 + n_y^2) + K_2(n_x^2 + n_y^2)^2 \\ &\quad + K'_{\perp} \frac{1}{2} n_z [(n_x + in_y)^3 + (n_x - in_y)^3] \\ &= K_1 \sin^2 \theta + K_2 \sin^4 \theta + K'_{\perp} \cos \theta \sin^3 \theta \cos 3\varphi, \end{aligned} \quad (1.5.3.9)$$

where φ is measured from the x axis, which is chosen parallel to one of the twofold axes. For easy-plane magnetics and $K'_{\perp} > 0$, the vector \mathbf{n} is directed along one of the twofold axes in the basal plane. If K'_{\perp} is negative, then \mathbf{n} lies in a vertical mirror plane directed at a small angle to the basal plane. For the complete solution of this problem, the sixth-order term must be taken into account. This term is similar to the one that characterizes the anisotropy of hexagonal crystals. The expression for the latter is of the following form:

$$\begin{aligned} U_a(6) &= K_1(n_x^2 + n_y^2) + K_2(n_x^2 + n_y^2)^2 \\ &\quad + K''_{\perp} \frac{1}{2} [(n_x + in_y)^6 + (n_x - in_y)^6] \\ &= K_1 \sin^2 \theta + K_2 \sin^4 \theta + K''_{\perp} \sin^6 \theta \cos 6\varphi, \end{aligned} \quad (1.5.3.10)$$

where x and φ have the same meaning as in (1.5.3.9).

The symmetry of cubic crystals does not allow any second-order terms in the expansion of the anisotropy energy. The expression for the anisotropy energy of cubic crystals contains the following invariants:

$$U_a(\text{cub}) = K_1(n_x^2n_y^2 + n_x^2n_z^2 + n_y^2n_z^2) + K_2n_x^2n_y^2n_z^2. \quad (1.5.3.11)$$

In considering the anisotropy energy, one has to take into account spontaneous magnetostriction and magnetoelastic energy (see Section 1.5.9). This is especially important in cubic crystals. Any collinear cubic magnetic (being brought into a single domain state) ceases to possess cubic crystallochemical symmetry as a result of spontaneous magnetostriction. If K_1 is positive, the easy axis is aligned along one of the edges of the cube and the crystal becomes tetragonal (like Fe). If K_1 is negative, the crystal becomes rhombohedral and can be an easy-axis magnetic with vector \mathbf{n} parallel to one of the spatial diagonals (like Ni) or an easy-plane magnetic with \mathbf{n} perpendicular to a spatial diagonal. We shall discuss this topic in more detail in Section 1.5.9.3.

The considerations presented above can be applied to all crystals belonging in the paramagnetic state to the tetragonal, trigonal or hexagonal system that become easy-plane magnetics in the ordered state. All of them, including the cubic crystals, may possess more than one allowed direction of easy magnetization.

In the example considered in the previous section, these directions can be aligned along the three twofold axes for the structures A_1^x, A_2^x, A_3^x, F^x and can be parallel to the three mirror planes for A_1^y, A_2^y, A_3^y, F^y .

It is worth noting that in some applications it is more convenient to use an expansion of the anisotropy energy in terms of surface spherical harmonics. This problem has been considered in detail by Birss (1964).

1.5.3.3. The thermodynamic theory of transitions into a magnetically ordered state

According to Landau (1937) (see also Landau & Lifshitz, 1951), a phase transition of the second kind can be described by an order parameter η , which varies smoothly in the neighbourhood of the transition temperature T_c . The order parameter $\eta = 0$ when $T \geq T_c$ and rises continuously as the temperature is decreased below T_c but the symmetry of the crystal changes suddenly. The order parameter can be a scalar, a vector or a tensor.

Consider a crystal with known space group in the paramagnetic state. In this section, we show how the Landau theory allows us to determine the magnetic space groups that are possible after a second-kind phase transition into an ordered state. The application of the Landau theory to the magnetic transitions into different types of antiferromagnets was made by Dzyaloshinskii (1957a,c; 1964). In these cases, the order parameter is the magnetic moment density $\mathbf{m}(\mathbf{r})$. To determine the equilibrium form of this function, it is necessary to find the minimum of the thermodynamic potential Φ , which is a functional of $\mathbf{m}(\mathbf{r})$. Since the transition is continuous and $\mathbf{m}(\mathbf{r}) = 0$ for $T \geq T_c$, the value of $\mathbf{m}(\mathbf{r})$ must be very small in the neighbourhood below the transition point. In this region, the thermodynamic potential Φ will be expanded into a power series of $\mathbf{m}(\mathbf{r})$. To find the proper form of this expansion, it is convenient to represent $\mathbf{m}(\mathbf{r})$ as a linear combination of functions that form bases of the irreducible representations of the space group of the paramagnetic phase \mathcal{M}_G :

$$m^i(\mathbf{r}) = \sum_{n,\alpha} M_{n,\alpha}^i \varphi_{n,\alpha}(\mathbf{r}), \quad (1.5.3.12)$$

where $\varphi_{n,\alpha}(\mathbf{r})$ are functions that transform under the representation n (α is the number of the function in the representation) and $i = x, y, z$. In this expansion, the quantities $M_{n,\alpha}^i$ are independent of \mathbf{r} and transform with respect to i as the components of an axial vector. The functions $\varphi_{n,\alpha}(\mathbf{r})$ are transformed into combinations of one another by the elements of the group \mathcal{M}_G . Instead, these elements can be regarded as transforming the coefficients $M_{n,\alpha}^i$ and leaving the functions $\varphi_{n,\alpha}$ invariant. In this case, the quantities $M_{n,\alpha}^i$ transform according to the direct product of the representation n of \mathcal{M}_G and the representation formed by the components of the pseudovector. This representation is reducible in the general case. Irreducible representations p, q, \dots can be obtained by forming linear combinations of the $M_{n,\alpha}^i$. Let us denote these combinations by $c_{p,\alpha}, c_{q,\alpha}, \dots$. These variables can be considered as components of the order parameter, and the thermodynamic potential can be expanded into a power series of $c_{p,\alpha}$. The terms of this expansion must be invariant under the transformations of the magnetic space group of the crystal in the paramagnetic state \mathcal{M}_G . This group possesses R as a separate element. Therefore the expansion can contain only even terms. For each irreducible representation, there is only one invariant of second order – the sum of the squares. Consequently, retaining only the square terms, the expansion of the thermodynamic potential Φ has the form:

$$\Phi(T) = \Phi_0(T) + \sum_p A_p(T) \sum_{\alpha} c_{p,\alpha}^2 \quad (1.5.3.13)$$

1.5. MAGNETIC PROPERTIES

To minimize Φ , it is necessary to add the terms of the fourth power. All the coefficients $A_p(T)$ in the relation (1.5.3.13) depend on the temperature. At $T \geq T_c$ all $c_{p,\alpha} = 0$. This solution corresponds to the minimum of Φ if all $A_p(T)$ are positive. The transition into the ordered state occurs if one of the quantities $A_p(T)$ changes its sign. This means that the transition temperature T_c is the temperature at which one of the coefficients $A_p(T_c) = 0$. This coefficient has the form:

$$A_p(T) = \lambda(T - T_c). \quad (1.5.3.14)$$

Accordingly, the corresponding magnetic structure is defined by the order parameters $c_{p,\alpha}$ and belongs to the representation p .

The representation of the space group is realized by a set of functions of the following type:

$$\varphi_{\mathbf{k}_\beta}(\mathbf{r}) = u_{\mathbf{k}_\beta}(\mathbf{r}) \exp(i\mathbf{k}_\beta \mathbf{r}), \quad (1.5.3.15)$$

where the values of the vectors \mathbf{k} are confined to the Brillouin zone in the reciprocal lattice and the function $u_{\mathbf{k}_\beta}(\mathbf{r})$ is periodic in the real lattice. The irreducible representation defined by the vector \mathbf{k}_β contains the functions with all the vectors \mathbf{k}_β that belong to the same star. The star is the set of the vectors \mathbf{k}_β obtained by applying all the transformations g_i of the corresponding point group to any vector of the star (see also Section 1.2.3.3). If we denote it as \mathbf{k}_1 , then the set of the vectors of the star consists of all inequivalent vectors of the form $g_i \mathbf{k}_1$.

There are three types of transition we have to consider: (1) the magnetic lattice is commensurate with the crystallographic one and $\mathbf{k} \neq 0$; (2) the magnetic lattice is incommensurate with the crystallographic one; (3) $\mathbf{k} = 0$ and the magnetic lattice coincides with the crystallographic lattice. Below we shall discuss in detail only the first and the third type of transition.

(a) $\mathbf{k} \neq 0$.

It is found that the first type of transition occurs if the arms of the star \mathbf{k}_β are aligned along specific isolated crystallographic directions and its vectors are equal to 1/2, 1/3 or 1/4 of some translation in the reciprocal lattice (Lifshitz, 1942). Then the magnetic structure is described by one of the 22 nontrivial Bravais types of magnetic lattices shown in Figs. 1.5.2.1–1.5.2.7.

As an example, let us consider a magnetic transition in UO_2 . In the paramagnetic state, it is a crystal with a face-centred cubic structure (space group $\mathcal{O}_h^5 = Fm\bar{3}m$) (for details see Dzyaloshinskii & Man'ko, 1964; Izyumov & Naish, 1979; Izyumov, Naish & Petrov, 1979; Izyumov, Naish & Syromiatnikov, 1979; Barbara *et al.*, 1988). Primitive translations of the crystallographic lattice are (see Fig. 1.5.3.5):

$$\mathbf{a}_1 = (a/2)(0, 1, 1), \quad \mathbf{a}_2 = (a/2)(1, 0, 1), \quad \mathbf{a}_3 = (a/2)(1, 1, 0). \quad (1.5.3.16)$$

Primitive translations of the reciprocal lattice are:

$$\mathbf{b}_1 = (2\pi/a)(-1, 1, 1), \quad \mathbf{b}_2 = (2\pi/a)(1, -1, 1), \\ \mathbf{b}_3 = (2\pi/a)(1, 1, -1). \quad (1.5.3.17)$$

Let us assume that there is one magnetic ion in the primitive cell in the position $(0, 0, 0)$ and that the transition takes place over a three-armed star $\{\mathbf{K}_{10}\}$ (for the definition of the symbols of the stars see Kovalev, 1987):

$$\mathbf{k}_1 = (\mathbf{b}_1 + \mathbf{b}_2)/2 = (2\pi/a)(0, 0, 1) \\ \mathbf{k}_2 = (\mathbf{b}_1 + \mathbf{b}_3)/2 = (2\pi/a)(0, 1, 0) \\ \mathbf{k}_3 = (\mathbf{b}_2 + \mathbf{b}_3)/2 = (2\pi/a)(1, 0, 0). \quad (1.5.3.18)$$

If μ_1 is the magnetic moment at the site $(0, 0, 0)$, the value of $\mu_i(\mathbf{k}_j)$ at $\mathbf{t}_i = (a/2)(h_i, k_i, l_i)$ may be obtained for each \mathbf{k}_j with the help of the following relation:

$$\mu_i(\mathbf{k}_j) = \mu_1 \exp[i(\mathbf{k}_j \mathbf{t}_i)]. \quad (1.5.3.19)$$

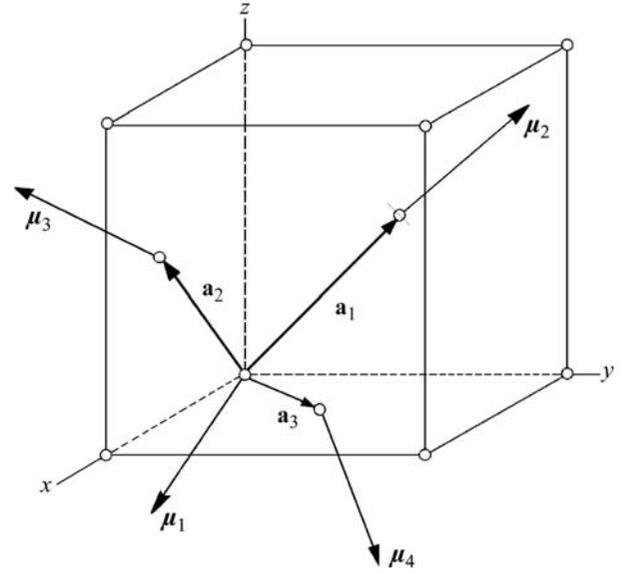


Fig. 1.5.3.5. The conventional unit cell of UO_2 . Only the positions of the magnetic U^{4+} ions are shown. The vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ form a basis of a primitive cell of the crystallographic lattice; $\mu_1, \mu_2, \mu_3, \mu_4$ are the magnetic moments of the ions belonging to the four magnetic lattices.

From this relation, it follows that $\mu_i(\mathbf{k}_j) = \pm \mu_1$ for different combinations of \mathbf{t}_i and \mathbf{k}_j . The signs of the magnetic moments μ_i at the four sites at the corner and the face centres of the conventional unit cell are displayed in Table 1.5.3.5.

Table 1.5.3.5 shows that for each arm of the vector star \mathbf{k}_j , there exists a linear combination of the four vectors μ_i ($i = \text{lattice site}$) which is a basis of the representation of one of the arms. According to Table 1.5.3.5, these linear combinations have the following forms:

$$\mathbf{l}_1 = \mu_1 - \mu_2 - \mu_3 + \mu_4 \\ \mathbf{l}_2 = \mu_1 - \mu_2 + \mu_3 - \mu_4 \\ \mathbf{l}_3 = \mu_1 + \mu_2 - \mu_3 - \mu_4. \quad (1.5.3.20)$$

None of the vectors \mathbf{l}_α is a basis of an irreducible representation of the whole space group $\mathcal{O}_h^5 = Fm\bar{3}m$ in the case under consideration. The basis functions of the irreducible representation are formed by linear superposition of the basis functions of each arm. One of these representations, τ_3 , is a superposition of the following components of \mathbf{l}_α : l_{1z}, l_{2y} and l_{3x} . This corresponds to the following orientations of the magnetic moments located in different corners of the primitive unit cell:

$$\mu_1 \sim [\bar{1}, \bar{1}, \bar{1}], \quad \mu_2 \sim [\bar{1}, 1, 1], \quad \mu_3 \sim [1, \bar{1}, 1], \quad \mu_4 \sim [1, 1, \bar{1}]. \quad (1.5.3.21)$$

Thus the magnetic structure of UO_2 consists of four primitive cubic magnetic sublattices \mathbf{M}_i inserted into each other. According to (1.5.3.21), the magnetization vectors of these sublattices \mathbf{M}_i are aligned along the space diagonals of the cubic lattice. This magnetic structure for UO_2 was predicted theoretically by Dzyaloshinskii & Man'ko (1964) (using the representation approach in the way discussed above) and established by neutron scattering by Faber *et al.* (1975).

Table 1.5.3.5. The signs of $\mu_i(\mathbf{k}_j)$ for four sites \mathbf{t}_i of the conventional unit cell (the corners of a primitive cell)

	\mathbf{t}_1 $a(0, 0, 0)$	\mathbf{t}_2 $(a/2)(0, 1, 1)$	\mathbf{t}_3 $(a/2)(1, 0, 1)$	\mathbf{t}_4 $(a/2)(1, 1, 0)$
\mathbf{k}_1	+	−	−	+
\mathbf{k}_2	+	−	+	−
\mathbf{k}_3	+	+	−	−

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

This example shows that the Landau theory can solve complicated problems of phase transitions where the magnetic lattice does not coincide with the crystallographic one and the magnetic structure is strongly non-collinear. Here only a qualitative analysis has been given; Section 1.5.3.3.1 and Section 1.5.3.3.2 will be devoted to quantitative solutions connected with phase transitions into an ordered state.

As was discussed in Section 1.5.2, Andreev & Marchenko (1976, 1980) introduced the concept of exchange magnetic symmetry. This concept is based on neglecting the relativistic interactions in comparison with the exchange interaction. In such an approach, the orientation of the magnetic moments relative to the crystallographic axis is arbitrary and the crystallographic transformations act on the magnetic moments not as on vectors but as on scalars. In the exchange approximation, three magnetic vectors can be introduced that describe any magnetic structure. These vectors are mutually orthogonal. All magnetic structures can be classified into four types. (1) Collinear ferromagnets or ferrimagnets are described by one ferromagnetic vector \mathbf{M} . (2) Collinear antiferromagnets are described by one antiferromagnetic vector \mathbf{L} . (3) Non-collinear ferromagnets are described by one ferromagnetic vector \mathbf{M} and one or two antiferromagnetic vectors \mathbf{L}_α . (4) Non-collinear antiferromagnets are described by two or three antiferromagnetic vectors \mathbf{L}_α . The Andreev and Marchenko approach describes the magnetic structure of UO_2 considered above by three antiferromagnetic vectors which are aligned along $[1, 0, 0]$, $[0, 1, 0]$ and $[0, 0, 1]$, respectively.

(b) *Incommensurate structures* (see also Section 1.10.1).

In the second type of transition, \mathbf{k}_β differs slightly from one of the rational values ($1/2, 1/3, 1/4$). Then the magnetic structure is incommensurate with the crystallographic lattice. Such non-collinear structures are shown in Fig. 1.5.1.4 (antiferromagnetic and ferromagnetic helices). A detailed analysis of this problem is given by Andreev & Marchenko (1976, 1980).

(c) $\mathbf{k}_\beta = 0$.

To the third type belong transitions for which $\mathbf{k}_\beta = 0$. In this case, the magnetic primitive cell coincides with the crystallographic one and antiferromagnetic ordering is allowed only if there is more than one magnetic ion in the primitive cell. As stated above, only this type of ordering allows collinear ferromagnetism. Therefore, we shall discuss this type of transition later in more detail.

Let us consider the phase transition in a uniaxial crystal with four magnetic ions in the primitive cell, as was done by Dzyaloshinskii (1957a). Now the average density of the magnetic moment $m^i(\mathbf{r})$ in (1.5.3.12) is determined by the average values of the magnetic moments of each ion, $\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \boldsymbol{\mu}_3, \boldsymbol{\mu}_4$. In (1.5.3.12), there is no longer any need to distinguish the coefficients $M_{n\alpha}^i$ and the functions $\varphi_{n,\alpha}(\mathbf{r})$. Their product $M_{n,\alpha}^i \varphi_{n,\alpha}(\mathbf{r})$ is now replaced by the linear combinations of the components of $\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \boldsymbol{\mu}_3, \boldsymbol{\mu}_4$ transforming according to the corresponding irreducible representation of the point group \mathcal{P} of the crystal (the space group of which is \mathcal{G}). To illustrate this, we shall take for \mathcal{G} the group $D_{3d}^6 = R\bar{3}c$, which was discussed in Section 1.5.3.1. There we introduced the linear combinations (1.5.3.2) $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3, \mathbf{m}$ of the

vectors $\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \boldsymbol{\mu}_3, \boldsymbol{\mu}_4$. The components of these linear combinations are basis functions of the irreducible representations of the corresponding point group $D_{3d} = \bar{3}m$. The characters of the representations of this group are given in Table 1.5.3.6. It follows from this table that all z components of the vectors \mathbf{l}_α and \mathbf{m} are transformed according to different one-dimensional representations of D_{3d} (i.e. $\Gamma_1, \dots, \Gamma_4$). Following the rule introduced in Section 1.5.2.1 [see relation (1.5.2.2)], we established the magnetic point groups displayed in the last column of Table 1.5.3.6. The symbols for the magnetic structures are given in the corresponding column. The x, y components are transformed by two-dimensional representations: m_x, m_y and l_{3x}, l_{3y} are transformed according to the same representation Γ_5 ; a similar situation holds for the pairs l_{1x}, l_{1y} and l_{2x}, l_{2y} , which are transformed according to Γ_6 . It is obvious that if the magnetic structure possesses x, y components of the magnetic vectors, the magnetic point group (which must be a subgroup of D_{3d}) will contain only four elements of the group D_{3d} : E, C_2, I, σ_\perp . These elements form the point group $C_{2h} = 2/m$. The point group C_{2h} has four one-dimensional representations, which according to relation (1.5.2.2) generate the four magnetic point groups listed in the last column of Table 1.5.3.6. To each of these magnetic point groups corresponds a definite magnetic structure, which is a mixture of x and y components of \mathbf{l}_3 and \mathbf{m} or \mathbf{l}_1 and \mathbf{l}_2 . The symbols of these structures are also listed in the table (by definition, the twofold axis is aligned along the x axis).

According to the relation (1.5.3.13), the thermodynamic potential Φ contains a sum of quadratic terms of basis functions for each irreducible representation. Thus it contains the following invariants, which correspond to the one-dimensional representations:

$$A_1' l_{1z}^2 + A_2' l_{2z}^2 + A_3' l_{3z}^2 + B' m_z^2. \quad (1.5.3.22)$$

The invariants formed with the x, y components of the vectors $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3, \mathbf{m}$, which are basis functions of two-dimensional representations, have the following form:

$$A_1''(l_{1x}^2 + l_{1y}^2) + A_2''(l_{2x}^2 + l_{2y}^2) + A_3''(l_{3x}^2 + l_{3y}^2) + B''(m_x^2 + m_y^2). \quad (1.5.3.23)$$

The thermodynamic potential for any uniaxial crystal possesses such invariants of second order. For crystals belonging to the space group D_{3d}^6 it is possible to construct additional invariants, which are linear combinations of the mixed products of the x and y components of the pairs of vectors $\mathbf{l}_1, \mathbf{l}_2$ and \mathbf{l}_3, \mathbf{m} and are transformed according to the same two-dimensional representations. These invariants have the following form:

$$l_{1x} l_{2y} - l_{1y} l_{2x}, \quad l_{3x} m_y - l_{3y} m_x. \quad (1.5.3.24)$$

These terms are responsible for 'weakly non-collinear' structures; we discuss their properties in the Section 1.5.5 and shall not take them into account now.

Before writing the whole expression of the thermodynamic potential, let us combine expressions (1.5.3.22) and (1.5.3.23) to

Table 1.5.3.6. *Characters of the irreducible representations of the group $D_{3d} = \bar{3}m$ and corresponding magnetic structures*

Representation	Magnetic vector components	Elements of symmetry						Magnetic structure	Magnetic point group
		E	$2C_3$	$3C_2$	I	$2S_6$	$3\sigma_d$		
Γ_1	l_{3z}	1	1	1	1	1	1	C_z	$D_{3d} = \bar{3}m$
Γ_2	m_z	1	1	-1	1	1	-1	F_z	$D_{3d}(S_6) = \bar{3}m'$
Γ_3	l_{1z}	1	1	-1	-1	-1	1	A_z	$D_{3d}(C_{3v}) = \bar{3}'m$
Γ_4	l_{2z}	1	1	1	-1	-1	-1	G_z	$D_{3d}(D_3) = \bar{3}'m'$
Γ_5	l_{3x}, m_y	2	-1	0	2	-1	0	C_x, F_y	$C_{2h}(C_i) = 2'/m'$
	m_x, l_{3y}							C_y, F_x	$C_{2h} = 2/m$
Γ_6	l_{1x}, l_{2y}	2	-1	0	-2	1	0	A_x, G_y	$C_{2h}(C_2) = 2'/m'$
	l_{2x}, l_{1y}							A_y, G_x	$C_{2h}(C_x) = 2'/m$

1.5. MAGNETIC PROPERTIES

separate the exchange terms from the relativistic ones. This can be performed in two ways:

$$\begin{aligned} A_1' l_{1z}^2 + A_1''(l_{1x}^2 + l_{1y}^2) &= (A_1/2) \mathbf{l}_1^2 + (a_1/2) l_{1z}^2 \quad \text{or} \\ A_1' l_{1z}^2 + A_1''(l_{1x}^2 + l_{1y}^2) &= (A_1/2) \mathbf{l}_1^2 + (a_1/2)(l_{1x}^2 + l_{1y}^2). \end{aligned} \quad (1.5.3.25)$$

Similar rearrangements are performed for \mathbf{l}_2 , \mathbf{l}_3 and \mathbf{m} . Summing expressions (1.5.3.22) and (1.5.3.23) and taking into account expression (1.5.3.25), we obtain the final expression for the thermodynamic potential Φ limited to the terms of second order:

$$\begin{aligned} \Phi_1 &= \Phi_0 + (A_1/2) \mathbf{l}_1^2 + (A_2/2) \mathbf{l}_2^2 + (A_3/2) \mathbf{l}_3^2 + (B/2) \mathbf{m}^2 \\ &\quad + (a_1/2) l_{1z}^2 + (a_2/2) l_{2z}^2 + (a_3/2) l_{3z}^2 + (b/2) m_z^2. \end{aligned} \quad (1.5.3.26)$$

In this expression, the coefficients of the terms representing the exchange interaction are denoted by capital letters. It is mainly these terms that are responsible for the transition to the ordered state. The much smaller relativistic terms are responsible for the orientation of the vectors \mathbf{l}_α or \mathbf{m} . Their coefficients are denoted by small letters.

To minimize the potential (1.5.3.26), it is necessary to add terms of the fourth order, which are restricted to the exchange terms. The total expression for the thermodynamic potential Φ will then be

$$\Phi = \Phi_1 + \frac{1}{4} \sum_{\alpha} C_{\alpha} \mathbf{l}_{\alpha}^4 + \frac{1}{4} C' \mathbf{m}^4 + \frac{1}{2} \sum_{\alpha} D_{\alpha} (\mathbf{l}_{\alpha} \mathbf{m})^2 + \frac{1}{2} \sum_{\alpha} D'_{\alpha} \mathbf{l}_{\alpha}^2 \mathbf{m}^2. \quad (1.5.3.27)$$

As pointed out above, one of the coefficients A_{α} or B vanishes at the transition temperature T_0 . This coefficient may be expanded in a series of $(T - T_0)$ [see (1.5.3.14)]. At $T < T_0$, a ferro- or antiferromagnetic structure will be realized, the type of which is determined by minimization of the thermodynamic potential (1.5.3.27).

As an example, we shall consider in the next two sections the simplest cases, the uniaxial ferromagnet and the uniaxial antiferromagnet. When doing this, we shall not restrict ourselves to a certain crystallographic structure as in the case above. For the sake of simplicity, it will be assumed that the primitive cell contains only two magnetic ions and therefore there is only one antiferromagnetic vector \mathbf{l} . Further, we shall introduce new variables:

$$\mathbf{M} = (N/2) \mathbf{m}, \quad \mathbf{L} = (N/2) \mathbf{l}, \quad (1.5.3.28)$$

where N is the number of magnetic ions per cm^3 .

1.5.3.3.1. Uniaxial ferromagnet

The temperature of transition from the paramagnetic to the ferromagnetic state is called the Curie temperature. The thermodynamic treatment of the behaviour of uniaxial ferromagnets in the neighbourhood of the Curie temperature T_c is given below.

In the case of a ferromagnet ($\mathbf{L} = 0$), the thermodynamic potential (1.5.3.27) near T_c including the magnetic energy $-\mathbf{M}\mathbf{H}$ is given by (see 1.5.3.25)

$$\tilde{\Phi} = \Phi_0 + (B/2) \mathbf{M}^2 + (b/2)(M_x^2 + M_y^2) + (C/4) \mathbf{M}^4 - \mathbf{M}\mathbf{H}, \quad (1.5.3.29)$$

where $\tilde{\Phi}$ is used to designate the thermodynamic potential in variables p, T, \mathbf{H} [instead of $\Phi(p, T, \mathbf{M})$]; at the given field, $\tilde{\Phi}$ should be a minimum. The equilibrium value of the magnetization \mathbf{M} is found by minimizing the thermodynamic potential.

First consider the ferromagnet in the absence of the external field ($\mathbf{H} = 0$). The system of equations $\partial \tilde{\Phi} / \partial \mathbf{M} = 0$ has three solutions:

$$(I) \quad M_x = M_y = M_z = 0 \quad (1.5.3.30)$$

$$(II) \quad M_z = 0; \quad M_x^2 + M_y^2 = M_{\perp}^2 = -\frac{B+b}{C} \quad (1.5.3.31)$$

$$(III) \quad M_x = M_y = 0; \quad M_z^2 = -\frac{B}{C}. \quad (1.5.3.32)$$

In the whole range of temperatures $T > T_c$ when $B > 0$, the minimum of the potential is determined by solution (I) (*i.e.* absence of a spontaneous magnetization). The realization of the second or third state depends on the sign of the coefficient b . If $b > 0$, then the third state is realized, the magnetization \mathbf{M} being directed along the axis. In this case, the transition from the paramagnetic into the ferromagnetic state will take place at $T_c = T_0$ (when $B = 0$). If $b < 0$, the magnetization is directed perpendicular to the axis. In this case, the Curie temperature is $T_c = T_0 - b/\lambda$ (when $B + b = 0$). In the absence of a magnetic field, the difference between the two values of T_c has no physical meaning, since it only means another value of the coefficient B [see (1.5.3.25)]. In a magnetic field, both temperatures may be determined experimentally, *i.e.* when B becomes zero and when $B + b$ becomes zero.

If a magnetic field \mathbf{H} is applied parallel to the z axis and $b > 0$, the minimization of the thermodynamic potential Φ leads to

$$H/M = CM^2 + B. \quad (1.5.3.33)$$

This relation has been verified in many experiments and the corresponding graphical representations are known in the literature as Arrott-Belov-Kouvel plots (see Kouvel & Fisher, 1964). Putting $B = \lambda(T - T_c)$ according to (1.5.3.14), equations (1.5.3.32) and (1.5.3.33) may be used to derive expressions for the initial magnetic susceptibilities (for $H \rightarrow 0$):

$$\chi_0 = \frac{1}{2\lambda(T_c - T)^{\gamma}}, \quad T < T_c, \quad (1.5.3.34)$$

$$\chi_0 = \frac{1}{\lambda(T - T_c)^{\gamma}}, \quad T > T_c, \quad (1.5.3.35)$$

where $\gamma = 1$.

The Landau theory of phase transitions does not take account of fluctuations of the order parameter. It gives qualitative predictions of all the possible magnetic structures that are allowed for a given crystal if it undergoes a second-order transition. The theory also explains which of the coefficients in the expression for the thermodynamic potential is responsible for the corresponding magnetic structure. It describes also quantitative relations for the magnetic properties of the material if

$$1 \gg (T - T_c)/T_c \gg T_c B^2 / b\alpha^3, \quad (1.5.3.36)$$

where α is the coefficient in the term which describes the gradient energy. In this chapter, we shall not discuss the behaviour of the material in the fluctuation region. It should be pointed out that, in this region, γ in relations (1.5.3.34) and (1.5.3.35) depends on the dimensionality of the structure n and equals 1.24 for $n = 1$, 1.31 for $n = 2$ and 1.39 for $n = 3$. Similar considerations are relevant to the relations (1.5.3.31) and (1.5.3.32), which describe the temperature dependence of spontaneous magnetization.

The relations (1.5.3.31) and (1.5.3.32) describe the behaviour of the ferromagnet in the 'saturated' state when the applied magnetic field is strong enough to destroy the domain structure. The problem of the domains will be discussed later (see Section 1.5.4).

The transition from the paramagnetic to the ferromagnetic state is a second-order transition, provided that there is no magnetic field. In the presence of a magnetic field that is parallel to the easy axis of magnetization, the magnetic symmetry of the crystal is the same ($M_z \neq 0$) both above and below T_c . From the point of view of symmetry, no transition occurs in this case.

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

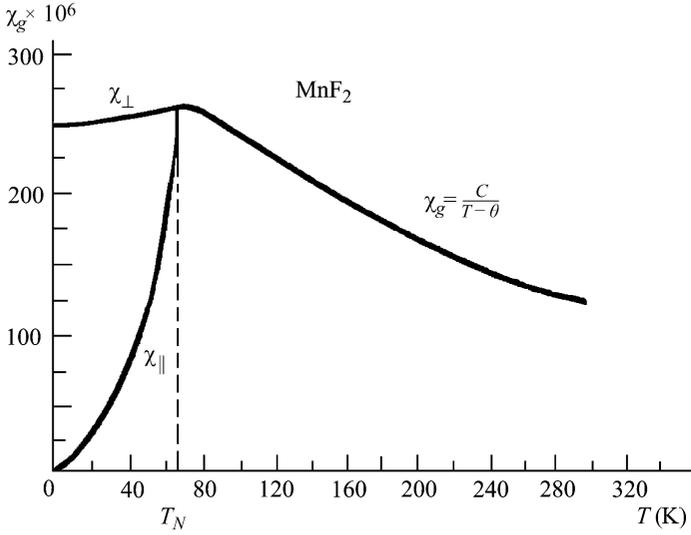


Fig. 1.5.3.6. Temperature dependence of the mass susceptibility χ_g for a uniaxial antiferromagnet along (χ_{\parallel}) and perpendicular (χ_{\perp}) to the axis of antiferromagnetism (see Foner, 1963).

1.5.3.3.2. Uniaxial antiferromagnet

Now let us proceed to the uniaxial antiferromagnet with two ions in the primitive cell. The thermodynamic potential $\tilde{\Phi}$ for such an antiferromagnet is given in accordance with (1.5.3.26) and (1.5.3.27) by (Landau, 1933)

$$\begin{aligned} \tilde{\Phi} = & \Phi_0 + (A/2)\mathbf{L}^2 + (B/2)\mathbf{M}^2 + (a/2)(L_x^2 + L_y^2) \\ & + (b/2)(M_x^2 + M_y^2) + (C/4)\mathbf{L}^4 + (D/2)(\mathbf{LM})^2 \\ & + (D'/2)\mathbf{L}^2\mathbf{M}^2 - \mathbf{MH}. \end{aligned} \quad (1.5.3.37)$$

If the magnetic field is absent ($\mathbf{H} = 0$), then $\mathbf{M} = 0$ because B , D and $D' > 0$. Then three possible magnetic states are obtained by minimizing the potential with respect to \mathbf{L} only:

$$(I) \quad L_x = L_y = L_z = 0 \quad (1.5.3.38)$$

$$(II) \quad L_z = 0; \quad L_x^2 + L_y^2 = L_{\perp}^2 = -\frac{A+a}{C} \quad (1.5.3.39)$$

$$(III) \quad L_x = L_y = 0; \quad L_z^2 = -\frac{A}{C}. \quad (1.5.3.40)$$

When $a < 0$, state (II) with $L_z = 0$ is thermodynamically stable. When $a > 0$, state (III) is stable and the antiferromagnetic vector is directed along the axis. This means that the term with the coefficient a is responsible for the anisotropy of the uniaxial antiferromagnet. We introduce the effective anisotropy field:

$$H_a = aL = 2aM_0, \quad (1.5.3.41)$$

where M_0 is the sublattice magnetization.

Formulas (1.5.3.39) and (1.5.3.14) in the form $A = \lambda(T - T_c)$ yield the expression for the temperature dependence of the sublattice magnetization:

$$L^2 = (\lambda/C)(T_N - T), \quad (1.5.3.42)$$

where T_N is the Néel temperature. The assertions relating to formulas (1.5.3.34) and (1.5.3.35) concerning the fluctuation region are also valid for the temperature dependence of the sublattice magnetization.

The minimization of the potential $\tilde{\Phi}$ with respect to \mathbf{M} for given $\mathbf{L} \neq 0$ when $\mathbf{H} \neq 0$ yields the following relation for the magnetization:

$$\mathbf{M} = \chi_{\perp}\mathbf{H} - (\chi_{\perp} - \chi_{\parallel})(\mathbf{qH})\mathbf{q}, \quad (1.5.3.43)$$

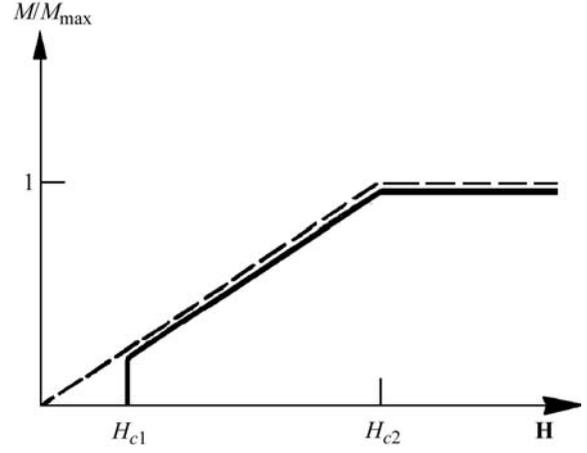


Fig. 1.5.3.7. Dependence of the relative magnetization M/M_{\max} on the magnetic field at $T = 0$. The dashed line corresponds to $\mathbf{H} \perp O_z$, the full line to $\mathbf{H} \parallel O_z$. H_{c1} is the field of spin-flop, H_{c2} is the field of spin-flip.

where $\mathbf{q} = \mathbf{L}/|L|$. Thus the magnetization of an antiferromagnet is linear with the magnetic field, as for a paramagnet, if the magnetic field is not too strong. The main difference is in the anisotropy and temperature dependence of the susceptibility. The parallel susceptibility χ_{\parallel} decreases when the temperature is lowered, and χ_{\perp} does not depend on temperature ($\chi_{\perp} = 1/B$) (see Fig. 1.5.3.6). The coefficient B belongs to the exchange term and defines the effective exchange field

$$H_e = \frac{1}{2}BL = BM_0. \quad (1.5.3.44)$$

As seen from Fig. 1.5.3.6, $\chi_{\perp} > \chi_{\parallel}$. Therefore, when the magnetic field applied parallel to the axis of a uniaxial antiferromagnet reaches the critical value

$$H_{c1}^2 = aL^2/(\chi_{\perp} - \chi_{\parallel}) \simeq aBL_0^2 = 2H_aH_e \quad (1.5.3.45)$$

(L_0 is the value of L at $T = 0$), a flopping of the sublattices from the direction along the axis to some direction in the plane perpendicular to the axis occurs. In this spin-flop transition (which is a first-order transition into a new magnetic structure), the magnetization jumps as shown in Fig. 1.5.3.7.

A second-order transition into a saturated paramagnetic state takes place in a much stronger magnetic field $H_{c2} = 2H_e$. This transition is called a spin-flip transition. Fig. 1.5.3.7 shows the magnetic field dependence of the magnetization of a uniaxial antiferromagnet. Fig. 1.5.3.8 shows the temperature dependence of both critical fields.

The quantitative behaviour of the critical magnetic fields in the neighbourhood of T_N for both directions of the magnetic field ($\mathbf{H} \parallel O_z$ and $\mathbf{H} \perp O_z$) can be determined from the theory of second-order phase transitions starting from the thermodynamic potential $\tilde{\Phi}$ and taking into account that L is small and $DL^2 \ll B$ close to T_N .

In the presence of the magnetic field $\mathbf{H} \perp O_z$, \mathbf{L} is parallel to O_z , $\mathbf{LM} = 0$, the coefficient A at L^2 is replaced by $A + 2D'H^2/B^2$ and the latter is zero at the new transition point. The critical field is given by the relation

$$H_{c2}^2 = (\lambda B^2/2D')(T_N - T), \quad \mathbf{H} \perp O_z. \quad (1.5.3.46)$$

If the field is applied parallel to the z axis, then \mathbf{L} remains parallel to O_z if $H < H_{c1}$ ($H_{c1} \simeq aB^2/D$ in the neighbourhood of T_N). Therefore,

$$H_{c2}^2 = \frac{\lambda B^2}{2(D+D')}(T_N - T), \quad \mathbf{H} \parallel O_z, \quad H < H_{c1}. \quad (1.5.3.47)$$

If $H > H_{c1}$, \mathbf{L} becomes perpendicular to the z axis and the anisotropy term has to be taken into account:

1.5. MAGNETIC PROPERTIES

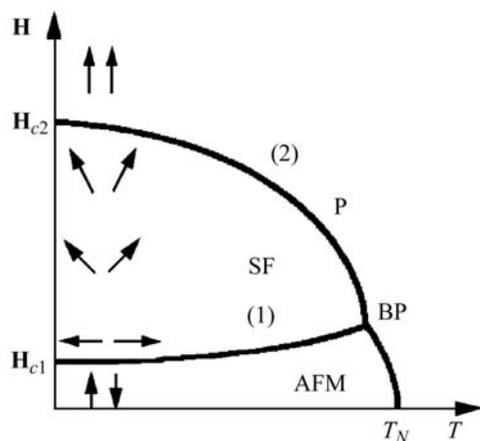


Fig. 1.5.3.8. Magnetic phase diagram for a uniaxial antiferromagnet in a magnetic field applied parallel to the axis. (1) The line of spin-flop transition (H_{c1}); (2) the line of spin-flip transition (H_{c2}); P, paramagnetic phase; AFM, easy-axis antiferromagnetic phase; SF, spin-flop phase; BP, bicritical point.

$$H_{c2}^2 = \frac{\lambda B^2}{2D'}(T_N - T - a/\lambda), \quad \mathbf{H} \parallel Oz, \quad H > H_{c1}. \quad (1.5.3.48)$$

Formulas (1.5.3.46)–(1.5.3.48) show that the transition temperature is reduced by applying the magnetic field. The displacement of the transition point is directly proportional to the square of the applied field. Fig. 1.5.3.9 shows the phase diagram of an antiferromagnet in the neighbourhood of T_N . Unlike ferromagnets, antiferromagnets maintain the second-order phase transition when a magnetic field is applied because the symmetry of the crystal in the antiferromagnetic state differs essentially from that in the paramagnetic state also if the crystal is placed into a magnetic field.

Formula (1.5.3.43) describes the magnetization process only in easy-axis antiferromagnets. For easy-plane antiferromagnets, the anisotropy in the plane is usually extremely small and the antiferromagnetic vector rotates freely in the basic plane. Therefore, for any direction of the magnetic field, the vector \mathbf{L} becomes

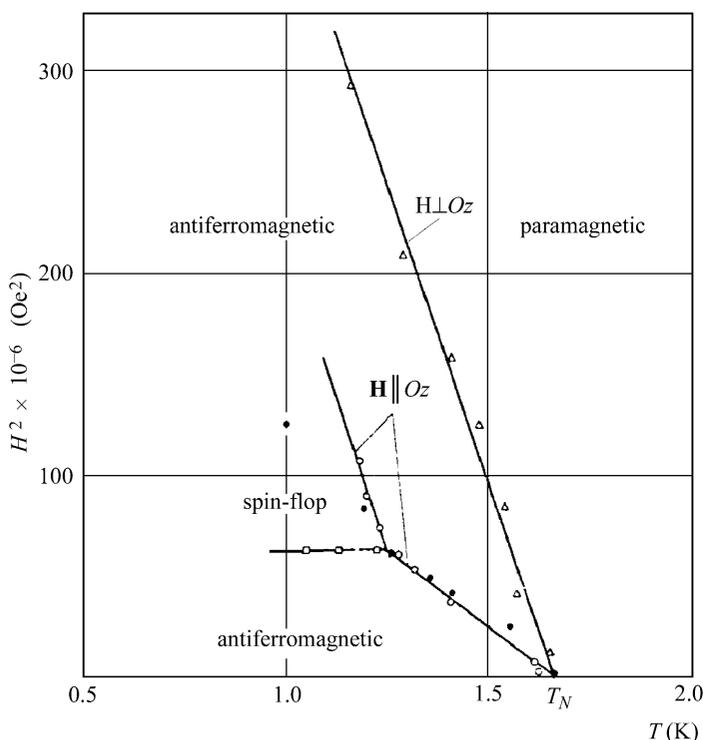


Fig. 1.5.3.9. Phase diagram for a uniaxial antiferromagnet in the proximity of T_N , calculated for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Experimental data are taken from Gijssman *et al.* (1959).

aligned perpendicular to the applied magnetic field. Correspondingly the magnetization becomes

$$\mathbf{M} = \chi_z H_z \hat{\mathbf{z}} + \chi_\perp H_\perp \hat{\mathbf{x}}, \quad (1.5.3.49)$$

where $\hat{\mathbf{z}}$ and $\hat{\mathbf{x}}$ are unit vectors parallel and perpendicular to the axis.

1.5.4. Domain structure

1.5.4.1. 180° domains

Neither symmetry nor energy considerations can determine the alignment of the magnetization vector \mathbf{n} in a non-chiral easy-axis magnetic (of ferro- or antiferromagnetic type). The vector \mathbf{n} may be aligned parallel or antiparallel to the positive direction of the z axis. Therefore, specimens of any magnetic are usually split into separate regions called domains. In each domain of an easy-axis magnetic, the vector \mathbf{n} has one of its two possible directions. Such domains are called 180° domains. Adjacent domains are separated by a domain wall, in which the magnetic moments are no longer strictly parallel (or antiparallel). As a result of this, both the exchange and the anisotropy energy rise inside the volume of the domain wall.

In ferromagnets (and ferrimagnets), the loss in the exchange and anisotropy energy in a multidomain sample is compensated by the gain in the magnetostatic energy. The existence of the domain structure is responsible for the behaviour of a ferromagnet in an applied magnetic field. There are two kinds of magnetization processes that one has to distinguish: the displacement of the domain walls and the rotation of the spontaneous magnetization vector from the easy direction to the direction of the applied magnetic field. The magnetization process will first be considered without taking the demagnetizing field into account. If the magnetic field is applied parallel to the axis of an easy-axis ferromagnet, the displacement of the domain wall will completely determine the magnetization process. If the sample contains no impurities and crystal defects, such a displacement must take place in an infinitely small magnetic field [see curve (1) in Fig. 1.5.4.1 and Fig. 1.5.4.3a]. If the magnetic field is applied perpendicular to the easy axis, the size of the domains does not change but their magnetization vectors rotate. Let us denote the spontaneous magnetization by M_s . Then the sample magnetization M rises linearly with respect to the applied magnetic field:

$$M = HM_s^2/2K_1, \quad (1.5.4.1)$$

where K_1 is defined by relations (1.5.3.8)–(1.5.3.10). Some nonlinearity in H can arise from the fourth-order term with K_2 [see curve (2) in Fig. 1.5.4.1 and Fig. 1.5.4.3c]. When $H = 2K_1/M_s = H_s$, the magnetizations of all the domains are rotated by 90° and the magnetization of the sample becomes oriented along the magnetic field; its value is saturated and is equal to the spontaneous magnetization M_s . If $T \neq 0$ K, there is an additional rise in magnetization with the magnetic field. This rise, which is called true magnetization, is relatively very small at all temperatures except for the temperature region close to the transition temperature. If the magnetic field is applied at an arbitrary angle θ to the easy axis, the magnetization process occurs in two steps [see curves (2) in Fig. 1.5.4.2 and Fig. 1.5.4.3b]. First, as a result of the wall displacement, the magnetization jumps to the value M_1 in a small magnetic field. Next, the rotation process follows and at H_s the sample becomes saturated [see curves (2) in Fig. 1.5.4.2]. It is essential to take the shape of the sample into account in considering the problem of the magnetization processes in ferromagnets, as the demagnetizing field can be up to $4\pi M$. In real materials, the displacement process is partly (at low fields) reversible and partly (at higher fields) irreversible. Therefore, complicated hysteresis processes arise in magnetizing ferromagnets.