

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

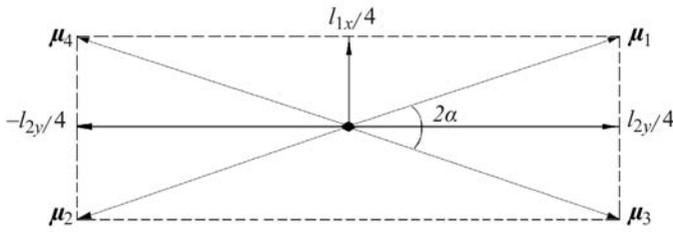


Fig. 1.5.5.6. A weakly non-collinear magnetic structure corresponding to (1.5.5.12).

the temperature dependence of the magnetic susceptibility in the neighbourhood of T_N for weak ferromagnets.

Similar anomalies in the neighbourhood of T_N are observed in materials with a symmetry allowing a transition into a weakly ferromagnetic state for which the sign of the anisotropy constant causes their transition into purely antiferromagnetic states.

1.5.5.2. Other weakly non-collinear magnetic structures

A thermodynamic potential $\tilde{\Phi}$ of the form (1.5.5.1) may give rise not only to the weak ferromagnetism considered above but also to the reverse phenomenon. If the coefficient B (instead of A) changes its sign and $b > 0$, the material will undergo a transition into a slightly canted ferromagnetic structure, in which $M_s \gg L_D$ and the expression for L_D is

$$L_D = (d/B)M_{s\perp}. \quad (1.5.5.11)$$

Experimental detection of such structures is a difficult problem and to date no-one has observed such a phenomenon.

The thermodynamic potential $\tilde{\Phi}$ of a four-sublattice antiferromagnet may contain the mixed invariant [see (1.5.3.24)]

$$d_1(L_{1x}L_{2y} - L_{1y}L_{2x}). \quad (1.5.5.12)$$

Such a term gives rise to a structure in which all four vectors of sublattice magnetization \mathbf{M}_α form a star, as shown in Fig. 1.5.5.6 (see also Fig. 1.5.1.3b). The angle 2α between the vectors μ_1 and μ_3 (or μ_2 and μ_4) is equal to d_1/A_2 if the main antiferromagnetic structure is defined by the vector \mathbf{L}_2 [see the caption for Fig. 1.5.1.3(b)]. Such a structure may occur in Cr_2O_3 . In most orthoferrites discussed above, such non-collinear structures are observed for all three cases: purely antiferromagnetic (\mathbf{G}_y) and weakly ferromagnetic ($\mathbf{G}_x\mathbf{F}_z$ and $\mathbf{G}_z\mathbf{F}_x$). The structure \mathbf{G}_y is not coplanar. Apart from the main antiferromagnetic vector \mathbf{G} aligned along the y axis, it possesses two other antiferromagnetic vectors: \mathbf{A} (aligned along the x axis) and \mathbf{C} (aligned along the z axis). The weakly ferromagnetic structure $\mathbf{G}_x\mathbf{F}_z$ has an admixture of the \mathbf{A}_y antiferromagnetic structure.

The helical (or spiral) structure described in Section 1.5.1.2.3 and depicted in Fig. 1.5.1.4 is also a weakly non-collinear antiferromagnetic structure. As mentioned above, this structure consists of atomic layers in which all the magnetic moments are parallel to each other and parallel to the layer. The magnetizations of neighbouring layers are antiparallel to a first approximation; but, more specifically, there is a small deviation from a strictly antiparallel alignment. The layers are perpendicular to a vector \mathbf{k} , which is parallel to the axis of the helix. The two mutually perpendicular antiferromagnetic vectors \mathbf{L}_α are both perpendicular to \mathbf{k} . These vectors define the helical structure by the following relation for the density of the magnetization $\mathbf{M}(\mathbf{r})$ in the layer with the coordinate \mathbf{r} (Dzyaloshinskii, 1964; Andreev & Marchenko, 1980):

$$\mathbf{M}(\mathbf{r}) = \mathbf{L}_1 \sin \mathbf{k}\mathbf{r} - \mathbf{L}_2 \cos \mathbf{k}\mathbf{r}. \quad (1.5.5.13)$$

Most helical structures are incommensurate, which means that the representation defined by the vector \mathbf{k} does not satisfy the Lifshitz condition (see Section 1.5.3.3).

1.5.6. Reorientation transitions

In many materials, the anisotropy constants change sign at some temperature below the critical temperature. As a result, the direction of the vector \mathbf{L} (or \mathbf{M}_s) changes relative to the crystallographic axes. Correspondingly, the magnetic symmetry of the material also changes. Such phase transitions are called reorientation transitions.

Cobalt is a typical ferromagnet and experiences two such reorientation transitions. It is a hexagonal crystal, which at low temperatures behaves as an easy-axis ferromagnet; its magnetic point group is $\mathbf{D}_{6h}(\mathbf{C}_{6h}) = 6/mmm'$. If the anisotropy energy were described by the relations (1.5.3.6) and (1.5.3.7) with only one anisotropy constant K_1 , the change of the sign of this constant would give rise to a first-order transition from an easy-axis to an easy-plane ferromagnet. This transition would occur at the temperature T_c at which $K_1(T) = 0$. In fact, the polar angle θ that determines the direction of the spontaneous magnetization increases progressively over a finite temperature interval. The behaviour of θ during the process of this reorientation may be obtained by minimizing the expression of the anisotropy energy (1.5.3.10), which contains two anisotropy coefficients K_1 and K_2 . If $K_2 > 0$, the minimum of U_a corresponds to three magnetic phases, which belong to the following magnetic point groups:

(1) $\mathbf{D}_{6h}(\mathbf{C}_{6h}) = 6/mmm'$; for this phase $\theta = 0, \pi$. It is realized at temperatures $T < T_1 = 520$ K, where $K_1 > 0$.

(2) $\mathbf{C}_{2h}(\mathbf{C}_i) = 2'/m'$; for this phase $\sin \theta = \pm(-K_1/2K_2)^{1/2}$. It is realized at temperatures $T_1 = 520 < T < T_2 = 580$ K, where $-2K_2 < K_1 < 0$.

(3) $\mathbf{D}_{2h}(\mathbf{C}_{2h}) = mm'm'$; for this phase $\theta = \pi/2$. It is realized at temperatures $T_2 = 580 < T < T_c = 690$ K, where $K_1 < -2K_2$.

The low-temperature phase is of the easy-axis type and the high-temperature phase is of the easy-plane type. The intermediate phase is called the angular phase. The two second-order phase transitions occur at temperatures which are the roots of the two equations

$$K_1(T_1) = 0; \quad K_1(T_2) + 2K_2(T_2) = 0. \quad (1.5.6.1)$$

The chain of these transitions (including the transition to the paramagnetic state at $T = T_c$) may be represented by the following chain of the corresponding magnetic point groups:

$$\begin{aligned} \mathbf{D}_{6h}(\mathbf{C}_{6h}) = 6/mmm' &\longleftrightarrow \mathbf{C}_{2h}(\mathbf{C}_i) = 2'/m' \\ &\longleftrightarrow \mathbf{D}_{2h}(\mathbf{C}_{2h}) = mm'm' \\ &\longleftrightarrow (\mathbf{D}_{6h} + \mathbf{RD}_{6h}) = 6/mmm1'. \end{aligned}$$

In Co and most of the other ferromagnets, the rotation of the spontaneous magnetization described above can be obtained by applying an external magnetic field in an appropriate direction. In many antiferromagnets, there occur similar reorientation transitions, which cannot be achieved by means of a magnetic field.

The first reorientation transition in antiferromagnets was observed in haematite ($\alpha\text{-Fe}_2\text{O}_3$), which at room temperature is a weak ferromagnet with magnetic structure \mathbf{A}_{3x} or \mathbf{A}_{3y} (see Tables 1.5.3.3 and 1.5.3.4 in Section 1.5.3.1). Morin (1950) found that the weak ferromagnetism in haematite disappears below $T_M \simeq 260$ K. At low temperature, haematite becomes an easy-axis antiferromagnet with the structure \mathbf{A}_{3z} . Unlike in cobalt, the transition at T_M is a first-order transition in haematite. This is so because the anisotropy constant K_2 is negative in haematite. As a result, there are only two solutions for the angle θ that lead to a minimum of the anisotropy energy $U_a(3)$ [(1.5.3.9)], $\theta = 0$ if $K_1 > -K_2$ and $\theta = \pi/2$ if $K_1 < -K_2$. The transition temperature T_M is defined by

$$K_1(T_M) + K_2(T_M) = 0. \quad (1.5.6.2)$$

1.5. MAGNETIC PROPERTIES

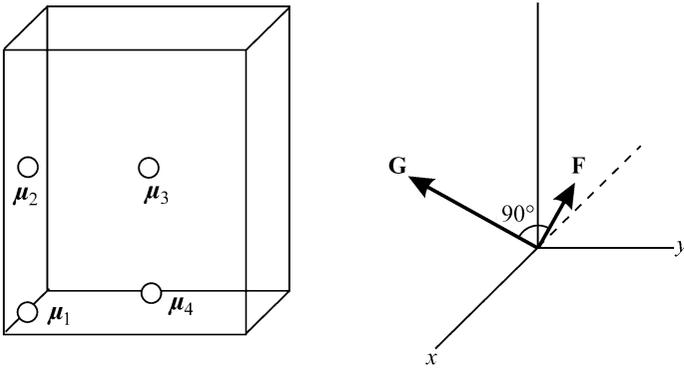


Fig. 1.5.6.1. Schematic representation of the rotation of the vectors \mathbf{G} and \mathbf{F} (in the xz plane) at a reorientation transition in orthoferrites.

There is the following change in the magnetic space groups at this transition:

$$R\bar{3}c' \xleftrightarrow{T_M} \begin{cases} P2/c \\ P2'/c' \end{cases} \quad (1.5.6.3)$$

$$(1.5.6.4)$$

Which of the two groups is realized at high temperatures depends on the sign of the anisotropy constant K'_\perp in equation (1.5.3.9). Neither of the high-temperature magnetic space groups is a subgroup of the low-temperature group. Therefore the transition under consideration cannot be a second-order transition.

Reorientation transitions have been observed in many orthoferrites and orthochromites. Orthoferrites of Ho, Er, Tm, Nd, Sm and Dy possess the structure $\mathbf{G}_x\mathbf{F}_z$ [see (1.5.5.8)] at room temperature. The first five of them undergo reorientation transitions to the structure $\mathbf{G}_z\mathbf{F}_x$ at lower temperatures. This reorientation occurs gradually, as in Co. Both vectors \mathbf{L} and \mathbf{M}_D rotate simultaneously, as shown in Fig. 1.5.6.1. These vectors remain perpendicular to each other, but the value of \mathbf{M}_D varies from $(d_1/B)L$ for M_{Dz} to $(d_2/B)L$ for M_{Dx} . The coefficients d_1 and d_2 belong to the terms L_xM_z and L_zM_x , respectively. The following magnetic point groups are observed when these transitions occur:

$$\frac{2'_x}{m'_x} \frac{2'_y}{m'_y} \frac{2_z}{m_z} \xleftrightarrow{T_1} \frac{2'_y}{m'_y} \xleftrightarrow{T_2} \frac{2_x}{m_x} \frac{2'_y}{m'_y} \frac{2'_z}{m'_z}. \quad (1.5.6.5)$$

Anomalies typical for second-order transitions were observed at the temperatures T_1 and T_2 . The interval $T_2 - T_1$ varies from 10 to 100 K.

At low temperatures, DyFeO_3 is an easy-axis antiferromagnet without weak ferromagnetism – \mathbf{G}_y . It belongs to the trivial magnetic point group $\mathbf{D}_{2h} = mmm$. At $T_M = 40$ K, DyFeO_3 transforms into a weak ferromagnet $\mathbf{G}_x\mathbf{F}_z$. This is a first-order reorientation transition of the type

$$\mathbf{D}_{2h} = mmm \xleftrightarrow{T_M} \mathbf{D}_{2h}(\mathbf{C}_{2h}) = m'm'm. \quad (1.5.6.6)$$

Reorientation transitions in antiferromagnets occur not only as a result of a sign change of the anisotropy constant. They can be governed by the applied magnetic field. In Section 1.5.3.3.2, we described the spin-flop first-order reorientation transition in an easy-axis antiferromagnet. This transition splits into two second-order transitions if the magnetic field is not strictly parallel to the axis of the crystal. There is a specific type of reorientation transition, which occurs in antiferromagnets that do not exhibit weak ferromagnetism, but would become weak ferromagnets if the antiferromagnetic vector was directed along another crystallographic direction. As an example, let us consider such a transition in CoF_2 . It is a tetragonal crystal with crystallographic space group $\mathbf{D}_{4h}^{14} = P4_2/mnm$. Below T_N , CoF_2 becomes an easy-axis antiferromagnet. The magnetic structure of this crystal is

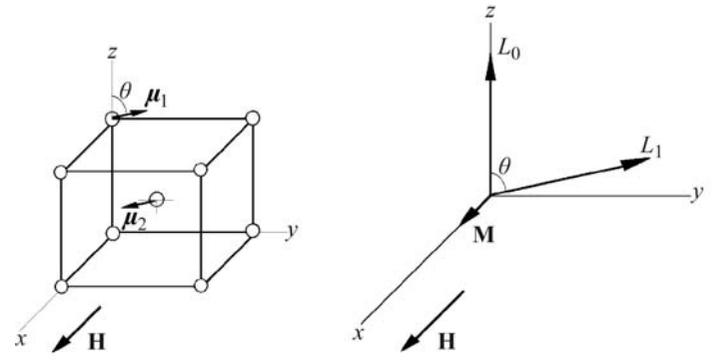


Fig. 1.5.6.2. Schematic representation of the rotation of the vector \mathbf{L} under the action of a magnetic field applied to CoF_2 perpendicular to the fourfold axis z (reorientation transition) (see Figs. 1.5.5.3a and b).

shown in Fig. 1.5.5.3. Its magnetic point group is $\mathbf{D}_{4h}(\mathbf{D}_{2h}) = 4'/mmm'$. Let us apply the magnetic field H parallel to the twofold axis x (see Fig. 1.5.6.2). In a typical antiferromagnet, the field stimulates a magnetization $M = \chi_\perp H$. The structure $\mathbf{D}_{4h}^{14} = P4_2/mnm$ allows weak ferromagnetism if \mathbf{L} is perpendicular to the z axis. As a result, if the vector \mathbf{L} is deflected from the z axis by an angle θ in the plane yz perpendicular to the x axis, the magnetization will rise according to the relation

$$M = \chi_\perp (H + H_D \sin \theta), \quad (1.5.6.7)$$

where $H_D = M_D/\chi_\perp$ [see (1.5.5.3) and (1.5.5.4)]. As a result, there is a gain in the magnetic energy, which compensates the loss in the anisotropy energy. The beginning of the deflection is a second-order transition. The balance of both energies determines the value of θ :

$$\sin \theta = (H_e/H_a H_D) H. \quad (1.5.6.8)$$

The second second-order transition occurs when θ becomes equal to $\pi/2$ at the critical field H_c :

$$H_c = H_D H_a / H_e. \quad (1.5.6.9)$$

After the reorientation transition, CoF_2 has the same magnetic point group as the weak ferromagnet NiF_2 , i.e. $\mathbf{D}_{2h}(\mathbf{C}_{2h}) = mm'm'$.

1.5.7. Piezomagnetism

As we have seen, the appearance of weak ferromagnetism in antiferromagnets is closely connected with their magnetic symmetry. If the magnetic point group of the antiferromagnetic crystal contains an axis of higher than twofold symmetry, the magnetic structure is purely antiferromagnetic. By applying an external force that disturbs the symmetry of the crystal and destroys the axis of high symmetry, one may create a structure possessing weak ferromagnetism. In the previous section, we considered such reduction of the symmetry with the aid of a magnetic field applied perpendicular to the main axis of the crystal. Another possibility for symmetry reduction is to apply an external pressure and to deform the crystal. Thus, in some antiferromagnetic crystals, a ferromagnetic moment may be produced on application of external stress. This phenomenon is called piezomagnetism.

To investigate the piezomagnetic effect from the phenomenological point of view, we have to add the terms of the magnetoelastic energy in the expansion of the thermodynamic potential. The magnetoelastic terms of the least degree in the expansion of the thermodynamic potential $\tilde{\Phi}$ for a given stable magnetic structure will be of the type $T_{ij} M_k L_l$ (T_{ij} are the components of the elastic stress tensor \mathbf{T}). These terms must be invariant relative