

## 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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

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  $\text{CoF}_2$ . It is a tetragonal crystal with crystallographic space group  $\mathbf{D}_{4h}^{14} = P4_2/mnm$ . Below  $T_N$ ,  $\text{CoF}_2$  becomes an easy-axis antiferromagnet. The magnetic structure of this crystal is 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  $\theta$  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  $\theta$ :

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

The second second-order transition occurs when  $\theta$  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,  $\text{CoF}_2$  has the same magnetic point group as the weak ferromagnet  $\text{NiF}_2$ , *i.e.*  $\mathbf{D}_{2h}(C_{2h}) = mm'm'$ .

### 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 to the crystallographic group of the material under examination.

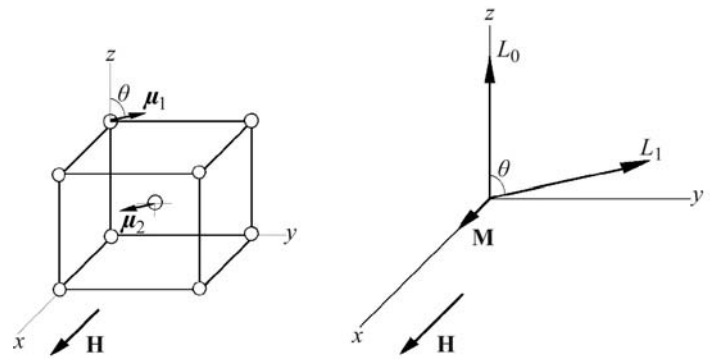


Fig. 1.5.6.2. Schematic representation of the rotation of the vector  $\mathbf{L}$  under the action of a magnetic field applied to  $\text{CoF}_2$  perpendicular to the fourfold axis  $z$  (reorientation transition) (see Figs. 1.5.5.3a and b).

If we consider the potential  $\Phi$ , which is a function of  $T$ ,  $\mathbf{T}$ ,  $\mathbf{H}$ , the terms of the magnetoelastic energy that are responsible for piezomagnetism are of the form  $H_i T_{jk}$ . Thus, for the piezomagnetic crystals the expansion of the thermodynamic potential should be expressed by

$$\Phi(T, \mathbf{T}, \mathbf{H}) = \Phi_0(T, \mathbf{H}) - \sum_{i,j,k} \Lambda_{ijk} H_i T_{jk}. \quad (1.5.7.1)$$

If at least one term of this expansion remains invariant under the magnetic symmetry of the given crystal, then the corresponding component  $\Lambda_{ijk}$  will not be zero and hence

$$M_i = -\partial\Phi/\partial H_i = -\partial\Phi_0/\partial H_i + \Lambda_{ijk} T_{jk}. \quad (1.5.7.2)$$

Thus, when a stress  $T_{jk}$  is applied, a magnetic moment is produced which is linear with the stress.

It follows from expression (1.5.7.1) that the converse of the piezomagnetic effect also exists, *i.e.* linear magnetostriction:

$$S_{jk} = -\partial\Phi/\partial T_{jk} = \Lambda_{ijk} H_i, \quad (1.5.7.3)$$

where  $S_{jk}$  are the components of the deformation tensor.

#### 1.5.7.1. Piezomagnetic effect

The possibility of the existence of a piezomagnetic effect was first foreseen by Voigt (1928). However, he assumed that it is sufficient to consider only the crystallographic symmetry in order to predict this effect. In reality, the crystals that do not possess a magnetic structure are characterized by the transformation  $R$  being contained in the magnetic group as an independent element. The transformation  $R$  changes the sign of the magnetic vectors  $\mathbf{H}$ ,  $\mathbf{L}$ ,  $\mathbf{M}$ . Hence, for such crystals all values of  $\Lambda_{ijk}$  vanish and piezomagnetism is forbidden. The magnetic groups of magnetically ordered crystals (ferromagnets and antiferromagnets) contain  $R$  only in combination with other elements of symmetry, or do not contain this transformation at all. Hence the piezomagnetic effect may occur in such crystals. This statement was first made by Tavger & Zaitsev (1956). The most interesting manifestation of the piezomagnetic effect is observed in antiferromagnets, as there is no spontaneous magnetization in these materials.

From equation (1.5.7.1) it follows that  $\Lambda_{ijk}$  is an axial tensor of third rank. Hence, apart from the restriction that piezomagnetism is forbidden for all para- and diamagnetic materials, it must be absent from the 21 magnetic point groups that contain the element  $C_i R = \bar{1}$  (see Table 1.5.7.1). The stress tensor  $T_{jk}$  is symmetrical ( $T_{jk} = T_{kj}$ ); see Section 1.3.2.4. Thus the tensor  $\Lambda_{ijk}$  is symmetrical in its last two indices. This is the reason why piezomagnetism is prohibited for three more magnetic point groups:  $\mathbf{O} = 432$ ,  $\mathbf{T}_d = \bar{4}3m$  and  $\mathbf{O}_h = m\bar{3}m$ . The remaining 66 magnetic point groups were found by Tavger (1958), who also

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Table 1.5.7.1. *The forms of the matrix characterizing the piezomagnetic effect*

Magnetic crystal class		Matrix representation $\Lambda_{i\alpha}$ of the piezomagnetic tensor
Schoenflies	Hermann–Mauguin	
$C_1$ $C_i$	1 $\bar{1}$	$\begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} & \Lambda_{14} & \Lambda_{15} & \Lambda_{16} \\ \Lambda_{21} & \Lambda_{22} & \Lambda_{23} & \Lambda_{24} & \Lambda_{25} & \Lambda_{26} \\ \Lambda_{31} & \Lambda_{32} & \Lambda_{33} & \Lambda_{34} & \Lambda_{35} & \Lambda_{36} \end{bmatrix}$
$C_2$ $C_s$ $C_{2h}$	2 (= 121) $m$ (= 1 <i>m</i> 1) $2/m$ (= 12/ <i>m</i> 1) (unique axis <i>y</i> )	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & \Lambda_{16} \\ \Lambda_{21} & \Lambda_{22} & \Lambda_{23} & 0 & \Lambda_{25} & 0 \\ 0 & 0 & 0 & \Lambda_{34} & 0 & \Lambda_{36} \end{bmatrix}$
$C_2(C_1)$ $C_3(C_1)$ $C_{2h}(C_i)$	$2'$ (= 12'1) $m'$ (= 1 <i>m'</i> 1) $2'/m'$ (= 12'/ <i>m'</i> 1) (unique axis <i>y</i> )	$\begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} & 0 & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{24} & 0 & \Lambda_{26} \\ \Lambda_{31} & \Lambda_{32} & \Lambda_{33} & 0 & \Lambda_{35} & 0 \end{bmatrix}$
$D_2$ $C_{2v}$ $D_{2h}$	222 $mm2$ [ $2mm$ , $m2m$ ] $mmm$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Lambda_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Lambda_{36} \end{bmatrix}$
$D_2(C_2)$ $C_{2v}(C_2)$ $C_{2v}(C_i)$ $D_{2h}(C_{2h})$	$2'2'$ $m'm'2$ $m'2'm$ [ $2'm'm'$ ] $m'm'm$	$\begin{bmatrix} 0 & 0 & 0 & 0 & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{24} & 0 & 0 \\ \Lambda_{31} & \Lambda_{32} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}$
$C_4, C_6$ $S_4, C_{3h}$ $C_{4h}, C_{6h}$	4, 6 4, 6 $4/m, 6/m$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{15} & -\Lambda_{14} & 0 \\ \Lambda_{31} & \Lambda_{31} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}$
$C_4(C_2)$ $S_4(C_2)$ $C_{4h}(C_{2h})$	$4'$ $4'$ $4'/m$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & \Lambda_{15} & 0 \\ 0 & 0 & 0 & -\Lambda_{15} & \Lambda_{14} & 0 \\ \Lambda_{31} & -\Lambda_{31} & 0 & 0 & 0 & \Lambda_{36} \end{bmatrix}$
$D_4, D_6$ $C_{4v}, C_{6v}$ $D_{2d}, D_{3h}$ $D_{4h}, D_{6h}$	422, 622 $4mm, 6mm$ $42m$ [ $4m2$ ], $\bar{6}m2$ [ $\bar{6}2m$ ] $4/mmm, 6/mmm$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\Lambda_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
$D_4(C_4), D_6(C_6)$ $C_{4v}(C_4), C_{6v}(C_6)$ $D_{2d}(S_4), D_{3h}(C_{3h})$ $D_{4h}(C_{4h}), D_{6h}(C_{6h})$	$42'2'$ , $62'2'$ $4m'm', 6m'm'$ $\bar{4}2'm'$ [ $\bar{4}m'2'$ ], $\bar{6}m'2'$ [ $\bar{6}2'm'$ ] $4/mm'm', 6/mm'm'$	$\begin{bmatrix} 0 & 0 & 0 & 0 & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{15} & 0 & 0 \\ \Lambda_{31} & \Lambda_{31} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}$
$D_4(D_2)$ $C_{4v}(C_{2v})$ $D_{2d}(D_2), D_{2d}(C_{2v})$ $D_{4h}(D_{2h})$	$4'22'$ $4'mm'$ $4'2m', \bar{4}'m2'$ $4'/mmm'$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Lambda_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Lambda_{36} \end{bmatrix}$
$C_3$ $S_6$	3 $\bar{3}$	$\begin{bmatrix} \Lambda_{11} & -\Lambda_{11} & 0 & \Lambda_{14} & \Lambda_{15} & -2\Lambda_{22} \\ -\Lambda_{22} & \Lambda_{22} & 0 & \Lambda_{15} & -\Lambda_{14} & -2\Lambda_{11} \\ \Lambda_{31} & \Lambda_{31} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}$
$D_3$ $C_{3v}$ $D_{3d}$	$32$ (= 321) $3m$ (= 3 <i>m</i> 1) $\bar{3}m$ (= $\bar{3}$ <i>m</i> 1)	$\begin{bmatrix} \Lambda_{11} & -\Lambda_{11} & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\Lambda_{14} & -2\Lambda_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
$D_3(C_3)$ $C_{3v}(C_3)$ $D_{3d}(S_6)$	$32'$ (= 32'1) $3m'$ (= 3 <i>m'</i> 1) $\bar{3}m'$ (= $\bar{3}$ <i>m'</i> 1)	$\begin{bmatrix} 0 & 0 & 0 & 0 & \Lambda_{15} & -2\Lambda_{22} \\ -\Lambda_{22} & \Lambda_{22} & 0 & \Lambda_{15} & 0 & 0 \\ \Lambda_{31} & \Lambda_{31} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}$
$C_6(C_3)$ $C_{3h}(C_3)$ $C_{6h}(S_6)$	$6'$ $\bar{6}'$ $6'/m'$	$\begin{bmatrix} \Lambda_{11} & -\Lambda_{11} & 0 & 0 & 0 & -2\Lambda_{22} \\ -\Lambda_{22} & \Lambda_{22} & 0 & 0 & 0 & -2\Lambda_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
$D_6(D_3)$ $C_{6v}(C_{3v})$ $D_{3h}(D_3), D_{3h}(C_{3v})$ $D_{6h}(D_{3d})$	$6'22'$ $6'mm'$ $\bar{6}'2m', \bar{6}'m2'$ $6'/m'mm'$	$\begin{bmatrix} \Lambda_{11} & -\Lambda_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2\Lambda_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
$T, T_h$ $O(T)$ $T_d(T)$ $O_h(T_h)$	23, $m\bar{3}$ $4'32'$ $\bar{4}'3m'$ $m\bar{3}m'$	$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Lambda_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Lambda_{14} \end{bmatrix}$

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constructed the 16 corresponding forms of the piezomagnetic tensors appropriate to each point group. They are represented in Table 1.5.7.1. (See also Birss & Anderson, 1963; Birss, 1964.)

Since the stress tensor  $T_{jk}$  is symmetrical, it has only six independent components. Therefore the notation of its components can be replaced by a matrix notation (Voigt's notation, see Section 1.3.2.5) in the following manner:

Tensor notation	Matrix notation
$T_{11}$	$T_1$
$T_{22}$	$T_2$
$T_{33}$	$T_3$
$T_{23}, T_{32}$	$T_4$
$T_{31}, T_{13}$	$T_5$
$T_{12}, T_{21}$	$T_6$

In matrix notation, equation (1.5.7.2) may be written in the form

$$M_i = \Lambda_{i\alpha} T_\alpha, \quad (1.5.7.4)$$

where  $i = 1, 2, 3$  and  $\alpha = 1, 2, 3, 4, 5, 6$ . These notations are used in Table 1.5.7.1. Notice that  $\Lambda_{ij} = \Lambda_{ji}$  for  $j = 1, 2, 3$ ,  $\Lambda_{i4} = 2\Lambda_{i23}$ ,  $\Lambda_{i5} = 2\Lambda_{i31}$ , and  $\Lambda_{i6} = 2\Lambda_{i12}$ .

The form of the matrix  $\Lambda_{i\alpha}$  depends on the orientation of the axes of the Cartesian coordinate system (CCS) with respect to the symmetry axes of the point group of the crystal under consideration. These symmetry axes may be rotation axes, rotoinversion axes or mirror-plane normals, all possibly combined with time reversal. The usual orientations of the CCS with respect to the symmetry axes can be expressed by the order of the entries in the Hermann–Mauguin symbol. An entry consists (apart from possible primes and bars) of a number  $N = 1, 2, 3, 4$  or  $6$  or the letter  $m$  or  $N/m (= \frac{N}{m})$ . The conventional rules will be followed: in the monoclinic and orthorhombic crystal systems the  $x, y$  and  $z$  axes of the CCS are parallel to the symmetry axes given in the first, second and third entries, respectively. In the monoclinic system, there is only one symmetry axis, which is usually chosen parallel to the  $y$  axis, and a short Hermann–Mauguin symbol with only one entry is usually used, e.g.  $2/m$  instead of  $12/m1$ . In the trigonal and hexagonal systems, the  $z, x$  and  $y$  axes are parallel to the symmetry axes given in the first, second and third entries, respectively. In the tetragonal system, the  $z$  axis is parallel to the symmetry axis given in the first entry, and the  $x$  and  $y$  axes are parallel to the symmetry axes given in the second entry, which appear in two mutually perpendicular directions. In the cubic system, the symmetry axes given in the first entry appear in three mutually perpendicular directions; the  $x, y$  and  $z$  axes of the CCS are chosen parallel to these directions. Alternative orientations of the same point group that give rise to the same form of  $\Lambda_{i\alpha}$  have been added between square brackets  $[\ ]$  in Table 1.5.7.1. Notice that the Schoenflies notation does not allow us to distinguish different orientations of the CCS with respect to the symmetry axes.

The forms of  $\Lambda_{i\alpha}$  for frequently encountered orientations of the CCS other than those given in Table 1.5.7.1 are

(1)  $112, 11m, 112/m$  (unique axis  $z$ ):

$$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{24} & \Lambda_{25} & 0 \\ \Lambda_{31} & \Lambda_{32} & \Lambda_{33} & 0 & 0 & \Lambda_{36} \end{bmatrix};$$

(2)  $112', 11m', 112'/m'$  (unique axis  $z$ ):

$$\begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} & 0 & 0 & \Lambda_{16} \\ \Lambda_{21} & \Lambda_{22} & \Lambda_{23} & 0 & 0 & \Lambda_{26} \\ 0 & 0 & 0 & \Lambda_{34} & \Lambda_{35} & 0 \end{bmatrix};$$

(3)  $22'2', 2m'm', mm'2' [m'2'm'], mm'm'$ :

$$\begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \Lambda_{26} \\ 0 & 0 & 0 & 0 & \Lambda_{35} & 0 \end{bmatrix};$$

(4)  $2'22', m'2m', 2'mm' [m'm2'], m'mm'$ :

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \Lambda_{16} \\ \Lambda_{21} & \Lambda_{22} & \Lambda_{23} & 0 & 0 & 0 \\ 0 & 0 & 0 & \Lambda_{34} & 0 & 0 \end{bmatrix};$$

(5)  $4'2'2, 4'm'm, \bar{4}'m'2, \bar{4}'2'm, 4'/mm'm$ :

$$\begin{bmatrix} 0 & 0 & 0 & 0 & \Lambda_{15} & 0 \\ 0 & 0 & 0 & -\Lambda_{15} & 0 & 0 \\ \Lambda_{31} & -\Lambda_{31} & 0 & 0 & 0 & 0 \end{bmatrix};$$

(6)  $6'2'2, 6'm'm, \bar{6}'m'2, \bar{6}'2'm, 6'/m'm'm$ :

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -2\Lambda_{22} \\ -\Lambda_{22} & \Lambda_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix};$$

(7)  $312, 31m, \bar{3}1m$ :

$$\begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & -2\Lambda_{22} \\ -\Lambda_{22} & \Lambda_{22} & 0 & 0 & -\Lambda_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix};$$

(8)  $312', 31m', \bar{3}1m'$ :

$$\begin{bmatrix} \Lambda_{11} & -\Lambda_{11} & 0 & 0 & \Lambda_{15} & 0 \\ 0 & 0 & 0 & \Lambda_{15} & 0 & -2\Lambda_{11} \\ \Lambda_{31} & \Lambda_{31} & \Lambda_{33} & 0 & 0 & 0 \end{bmatrix}.$$

Many connections between the different forms of  $\Lambda_{i\alpha}$  given above and in Table 1.5.7.1 have been derived by Kopský (1979a,b) and Grimmer (1991). These connections between the forms that the matrix can assume for the various magnetic or crystallographic point groups hold for all matrices and tensors that describe properties of materials, not just for the special case of piezomagnetism.

Dzyaloshinskii (1957b) pointed out a number of antiferromagnets that may display the piezomagnetic effect. These include the fluorides of the transition metals, in which the piezomagnetic effect was first observed experimentally (see Fig. 1.5.7.1) (Borovik-Romanov, 1959b). Below we shall discuss the origin of the piezomagnetic effect in fluorides in more detail.

The fluorides of transition metals  $MnF_2$ ,  $CoF_2$  and  $FeF_2$  are tetragonal easy-axis antiferromagnets (see Fig. 1.5.5.3). It is easy to check that the expansion of the thermodynamic potential  $\Phi$  up to terms that are linear in stress  $T_{ij}$  and invariant relative to the transformations of the crystallographic space group  $D_{4h}^{14} = P4_2/mnm$  is represented by

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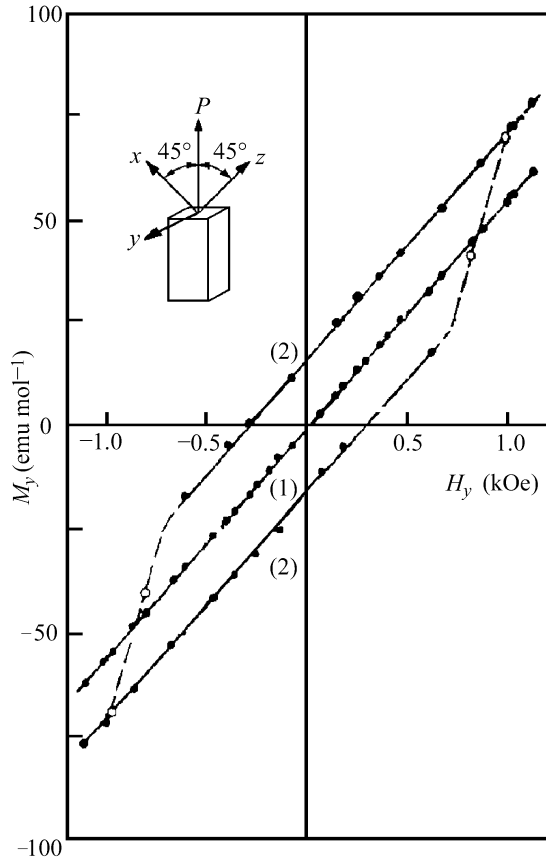


Fig. 1.5.7.1. The dependence of the magnetic moment of CoF<sub>2</sub> on the magnetic field. (1) Without stress; (2) under the stress  $T_{xz} = 33.3$  MPa (Borovik-Romanov, 1960).

$$\begin{aligned} \tilde{\Phi} = & \tilde{\Phi}_0 + (A/2)\mathbf{L}^2 + (a/2)(L_x^2 + L_y^2) \\ & + (B/2)\mathbf{M}^2 + (b/2)(M_x^2 + M_y^2) \\ & + d(L_x M_y + L_y M_x) \\ & + 2\lambda_1(M_x T_{yz} + M_y T_{xz})L_z \\ & + 2\eta_1(L_y T_{yz} + L_x T_{xz})L_z \\ & + 2\lambda_2 M_z L_z T_{xy} + 2\eta_2 L_x L_y T_{xy} - \mathbf{M}\mathbf{H}. \end{aligned} \quad (1.5.7.5)$$

In this expression, the sums  $(T_{ij} + T_{ji})$  that appear in the magnetoelastic terms have been replaced by  $2T_{ij}$ , as  $T_{ij} \equiv T_{ji}$ .

The analysis of expression (1.5.7.5) in the absence of stresses proves that fluorides may possess weak ferromagnetism provided that  $a < 0$  ( $L_z = 0$ ) (see Section 1.5.5.1). Here we shall discuss the easy-axis structure of the fluorides MnF<sub>2</sub>, CoF<sub>2</sub>, FeF<sub>2</sub> (see Fig. 1.5.5.3b). In the absence of magnetic fields and stresses only  $L_z \neq 0$  for this structure. All other components of the vector  $\mathbf{L}$  and the magnetization vector  $\mathbf{M}$  are equal to zero. The magnetic point group is  $\mathbf{D}_{4h}(\mathbf{D}_{2h}) = 4'/mmm'$ .

To transform the potential  $\tilde{\Phi}(L_i, M_j, T_{kl})$  [(1.5.7.5)] into the form  $\Phi(T, \mathbf{T}, \mathbf{H})$  [(1.5.7.1)], one has to insert into the magnetoelastic terms the dependence of the components of  $\mathbf{L}$  and  $\mathbf{M}$  on the magnetic field. The corresponding relations, obtained by minimization of (1.5.7.5) without the magnetoelastic terms, are

$$\begin{aligned} M_x = \frac{a}{a(B+b) - d^2} H_x; \quad L_x = -\frac{d}{a(B+b) - d^2} H_y; \\ M_y = \frac{a}{a(B+b) - d^2} H_y; \quad L_y = -\frac{d}{a(B+b) - d^2} H_x; \quad (1.5.7.6) \\ M_z = \frac{1}{B} H_z; \quad L_z \simeq \text{constant}. \end{aligned}$$

To a first approximation, the component  $L_z$  does not depend on the magnetic field.

Inserting the relations (1.5.7.6) for  $M_i$  and  $L_i$  into the magnetoelastic terms of (1.5.7.5), one gets the following expression for the corresponding terms in  $\Phi(T, H_i, T_{jk})$ :

$$\begin{aligned} \Phi(T, H_i, T_{jk}) = & \Phi_0(T, H_i) + 2L_z \frac{a\lambda_1 - d\eta_1}{a(B+b) - d^2} T_{yz} H_x \\ & + 2L_z \frac{a\lambda_1 - d\eta_1}{a(B+b) - d^2} T_{xz} H_y + 2L_z \frac{\lambda_2}{B} T_{xy} H_z. \end{aligned} \quad (1.5.7.7)$$

In this case, the expression for the magnetoelastic energy contains only three components of the stress tensor:  $T_{yz}$ ,  $T_{xz}$  and  $T_{xy}$ . Using (1.5.7.2), we get formulas for the three main components of the piezomagnetic effect:

$$M_x = 2L_z \frac{d\eta_1 - a\lambda_1}{a(B+b) - d^2} T_{yz} = 2\Lambda_{xyz} T_{yz} = \Lambda_{14} T_4, \quad (1.5.7.8)$$

$$M_y = 2L_z \frac{d\eta_1 - a\lambda_1}{a(B+b) - d^2} T_{xz} = 2\Lambda_{yxz} T_{xz} = \Lambda_{25} T_5, \quad (1.5.7.9)$$

$$M_z = -2L_z \frac{\lambda_2}{B} T_{xy} = 2\Lambda_{zxy} T_{xy} = \Lambda_{36} T_6. \quad (1.5.7.10)$$

In all three cases, the piezomagnetic moment is produced in the direction perpendicular to the shear plane. Comparing (1.5.7.8) and (1.5.7.9), we see that  $\Lambda_{25} = \Lambda_{14}$ . This is in agreement with the equivalence of the axes  $x$  and  $y$  in the tetragonal crystals. If the stress is applied in the plane  $xz$  (or  $yz$ ), the vector  $\mathbf{L}$  turns in the shear plane and a component  $L_x$  (or  $L_y$ ) is produced:

$$L_x = 2L_z \frac{\eta_1(B+b) - d\lambda_1}{a(B+b) - d^2} T_{xz}. \quad (1.5.7.11)$$

For  $T_{xy}$  stress, no rotation of the vector  $\mathbf{L}$  occurs.

Formulas (1.5.7.8)–(1.5.7.10) show that in accordance with Table 1.5.7.1 the form of the matrix  $\Lambda_{i\alpha}$  for the magnetic point group  $\mathbf{D}_{4h}(\mathbf{D}_{2h}) = 4'/mmm'$  is

$$\Lambda_{i\alpha} = \begin{bmatrix} 0 & 0 & 0 & \Lambda_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Lambda_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Lambda_{36} \end{bmatrix}. \quad (1.5.7.12)$$

The relations (1.5.7.8)–(1.5.7.10) show that the components of the piezomagnetic tensor  $\Lambda_{ijk}$  are proportional to the components of the antiferromagnetic vector  $\mathbf{L}$ . Thus the sign of the piezomagnetic moment depends on the sign of the vector  $\mathbf{L}$  and the value of the piezomagnetic effect depends on the domain structure of the sample (we are referring to S-domains). The piezomagnetic moment may become equal to zero in a polydomain sample. On the other hand, piezomagnetism may be used to obtain single-domain antiferromagnetic samples by cooling them from the paramagnetic state in a magnetic field under suitably oriented external pressure.

There are relatively few publications devoted to experimental investigations of the piezomagnetic effect. As mentioned above, the first measurements of the values of the components of the tensor  $\Lambda_{ijk}$  were performed on crystals of MnF<sub>2</sub> and CoF<sub>2</sub> (Borovik-Romanov, 1960). In agreement with theoretical prediction, three components were observed:  $\Lambda_{xyz} = \Lambda_{yxz}$  and  $\Lambda_{zxy}$ . The largest value obtained for these components was  $\Lambda_{14} = 21 \times 10^{-10}$  Oe<sup>-1</sup>. The piezomagnetic effect was also observed for two modifications of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Andratskii & Borovik-Romanov, 1966). The magnetic point group of the low-temperature modification of this compound is  $\mathbf{D}_{3d} = \bar{3}m$ . In accordance with form (7) given above, the following nonzero components  $\Lambda_{ijk}$  were found for the low-temperature state:

$$\Lambda_{xyz} = -\Lambda_{yxz}, \quad (1.5.7.13)$$

$$\Lambda_{yyy} = -\Lambda_{yxx} = -\Lambda_{xxy}. \quad (1.5.7.14)$$

## 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

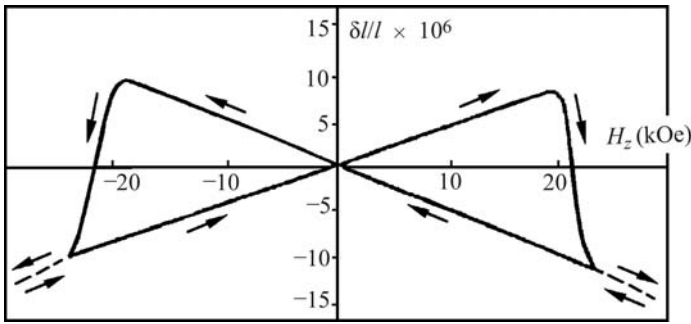


Fig. 1.5.7.2. Linear magnetostriction of  $\text{CoF}_2$  (Prokhorov & Rudashevskii, 1975).

The values of these components are one order of magnitude smaller than for  $\text{CoF}_2$ .

The temperature dependence of the components is similar for the piezomagnetic tensor and the sublattice magnetization. This means that the magnetoelastic constants  $\lambda_1$  and  $\lambda_2$  (as well as the constants  $B$  and  $d$ ) in the relations (1.5.7.7) and (1.5.7.8) depend only slightly on temperature.

### 1.5.7.2. Linear magnetostriction

From expression (1.5.7.3), it follows that a deformation of the sample may occur in a magnetic field. This deformation is linear with respect to the field. By its linear dependence, this effect differs essentially from ordinary magnetostriction, which is quadratic in the magnetic field. Most substances display such quadratic magnetostriction. The linear magnetostriction may be observed only in those ordered magnetics that belong to one of the 66 magnetic point groups that allow piezomagnetism and are listed in Table 1.5.7.1. The distinctive feature of linear magnetostriction is the dependence of its sign on the sign of the magnetic field and on the sign of the antiferromagnetic vector  $\mathbf{L}$ . The sign of  $\mathbf{L}$  characterizes the domain state of the specimen. Thus, observation of linear magnetostriction gives information about the domain state. In some materials, it has been observed that a sudden transition from one domain state to the opposite may occur in strong magnetic fields.

Linear magnetostriction (LM) was observed in  $\text{CoF}_2$  by Borovik-Romanov & Yavelov (1963) in a magnetic field applied parallel to the fourfold axis. The relations for the LM in  $\text{CoF}_2$  can be obtained by differentiating the expression of the thermodynamic potential  $\Phi$  [(1.5.7.7)]. If the magnetic field is applied along the  $y$  axis, a deformation  $S_{xz}$  appears:

$$S_{xz} = -\partial\Phi/\partial T_{xz} = 2L_z \frac{d\eta_1 - a\lambda_1}{a(B+b) - d^2} H_y = 2\Lambda_{yz} H_y = \Lambda_{25} H_z. \quad (1.5.7.15)$$

A similar formula holds for  $S_{yz}$  if the magnetic field is applied parallel to the  $x$  axis (with  $\Lambda_{14}$ , which is equal to  $\Lambda_{25}$ ).

If the magnetic field is applied parallel to the fourfold axis, the  $S_{xy}$  component of the deformation appears:

$$S_{xy} = -\partial\Phi/\partial T_{xy} = -2L_z(\lambda_2/B)H_z = -2L_z\lambda_2\chi_{\parallel}H_z = 2\Lambda_{zy}H_z = \Lambda_{36}H_3. \quad (1.5.7.16)$$

If the relations (1.5.7.15) and (1.5.7.16) are compared with (1.5.7.8)–(1.5.7.10), it is apparent that in accordance with theory the components of the tensors of the piezomagnetic effect (PM) and LM are identical.

Prokhorov & Rudashevskii (1969, 1975) extended the investigation of LM in  $\text{CoF}_2$ . They discovered that if the applied field becomes larger than 20 kOe, a jump in the magnetostriction occurs and it changes its sign (see Fig. 1.5.7.2). This jump is the result of a transition of the magnetic structure from one domain

state ( $\mathbf{L}_+$ ) into the opposite state ( $\mathbf{L}_-$ ). To explain such a transition, one has to take into account the term of third power in the expansion of the magnetic energy (Scott & Anderson, 1966),

$$U_m = A_i H_i + \frac{1}{2} \chi_{ij} H_i H_j + C_{ijk} H_i H_j H_k. \quad (1.5.7.17)$$

$C_{ijk}$  is an axial time-antisymmetric tensor, the sign of which depends on the sign of the domain. This term defines the dependence of the magnetic energy on the sign of the antiferromagnetic domain.

To date,  $\text{CoF}_2$  and  $\text{MnF}_2$  are unique in that LM and PM occur without rotating the antiferromagnetic vector  $\mathbf{L}$  if the magnetic field is applied along the fourfold axis (or pressure along a  $\langle 110 \rangle$  axis). In all other cases, these effects are accompanied by a rotation of  $\mathbf{L}$  and, as a result, the creation of new components  $L_i$ . To the latter belongs the LM in the low-temperature modification of  $\alpha\text{-Fe}_2\text{O}_3$ , which was observed by Anderson *et al.* (1964) (see also Scott & Anderson, 1966; Levitin & Shchurov, 1973). This compound displays PM, therefore it is obvious that LM will also occur (see Table 1.5.7.1).

LM has been observed in some orthoferrites. One of the orthoferrites,  $\text{DyFeO}_3$  at low temperatures, is a pure antiferromagnet, the vector  $\mathbf{L}$  of which is aligned along the  $y$  axis. Its magnetic point group ( $\mathbf{D}_{2h} = mmm$ ) allows PM and LM. The latter was observed when a magnetic field was applied parallel to the  $z$  axis by Zvezdin *et al.* (1985). There it was shown that  $\Lambda_{zxy} \neq 0$  if  $0 < H < H_c$ . At  $H_c \simeq 4$  kOe, a first-order phase transition into a weakly ferromagnetic state with magnetic point group  $\mathbf{D}_{2h}(\mathbf{C}_{2h}) = m'm'm$  ( $\mathbf{L} \parallel Ox, \mathbf{M}_D \parallel Oz$ ) occurs.

Many orthoferrites and orthochromites that possess weak ferromagnetism belong to the same point group, which possesses an ordinary centre of symmetry. Thus PM and LM are allowed for these phases of orthoferrites. If the magnetic field is applied parallel to  $Ox$ , they undergo a reorientation transition at which both vectors,  $\mathbf{L}$  and  $\mathbf{M}_D$ , being orthogonal, rotate in the  $xz$  plane. These intermediate angular phases belong to the magnetic point group  $\mathbf{C}_{2h}(\mathbf{C}_i) = 2'/m'$ .

LM was observed by Kadomtseva and coworkers (Kadomtseva, Agafonov, Lukina *et al.*, 1981; Kadomtseva, Agafonov, Milov *et al.*, 1981) in two such compounds,  $\text{YFeO}_3$  and  $\text{YCrO}_3$ . The  $\Lambda_{xz}$  components of the LM tensor were measured, which are allowed for the  $\mathbf{D}_{2h}(\mathbf{C}_{2h}) = m'm'm$  state.

The experimental data obtained to date for PM and LM are summarized in Table 1.5.7.2. The values of the components  $\Lambda_{iq}$  can be converted to SI units using  $1 \text{ Oe}^{-1} = 4\pi \times 10^{-3} \text{ m A}^{-1} = 4\pi \times 10^{-3} \text{ T Pa}^{-1}$ .

Table 1.5.7.2. Experimental data for the piezomagnetic effect (PM) and for linear magnetostriction (LM)

$a$ : antiferromagnetic phase;  $w$ : weak ferromagnetic phase.

Compound	$\Lambda_{iq} \times 10^{10} (\text{Oe}^{-1})$	$T$ (K)	PM or LM	Reference†
$\text{MnF}_2$	$\Lambda_{14} \simeq 0.2$	20	PM	(1)
$\text{CoF}_2$	$\Lambda_{14} = 21$	20	PM	(1)
	$\Lambda_{36} = 8.2$	20	PM	(1)
	$\Lambda_{36} = 9.8$	4	LM	(3)
$\text{DyFeO}_3$	$\Lambda_{36} = 6.0$	6	LM	(8)
	$\Lambda_{15} = 1.7$	6	LM	(6)
$\text{YFeO}_3$	$\Lambda_{15} \simeq 1$	6	LM	(7)
$\text{YCrO}_3$	$\Lambda_{22} = 1.9$	78	LM	(4)
	$\Lambda_{22} = 3.2$	77	PM	(2)
	$\Lambda_{22} = 1.3$	100	LM	(5)
	$\Lambda_{14} = 0.3$	78	LM	(4)
	$\Lambda_{14} = 1.7$	77	PM	(2)
$\alpha\text{-Fe}_2\text{O}_3$ ( $a$ )	$\Lambda_{14} = 0.9$	100	LM	(5)
	$\Lambda_{23} = 2.5$	292	PM	(2)
$\alpha\text{-Fe}_2\text{O}_3$ ( $w$ )				

† References: (1) Borovik-Romanov (1959b, 1960); (2) Andratskii & Borovik-Romanov (1966); (3) Prokhorov & Rudashevskii (1969, 1975); (4) Anderson *et al.* (1964); (5) Levitin & Shchurov (1973); (6) Kadomtseva, Agafonov, Milov *et al.* (1981); (7) Kadomtseva, Agafonov, Lukina *et al.* (1981); (8) Zvezdin *et al.* (1985).