

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

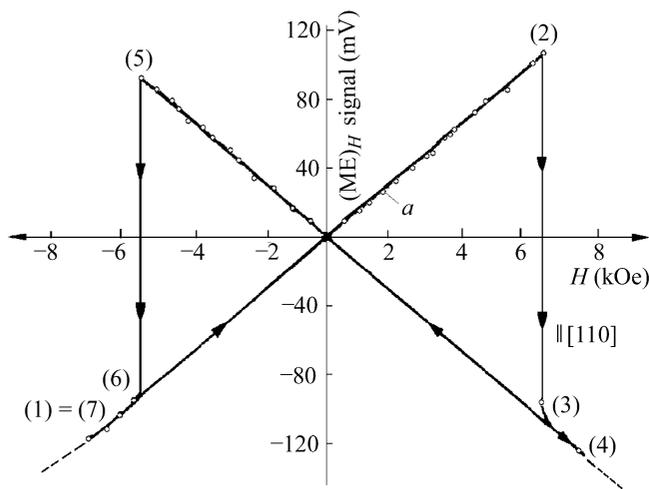


Fig. 1.5.8.2. The hysteresis loop in the linear magnetoelectric effect in ferromagnetoelectric $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ at 46 K (Ascher *et al.*, 1966).

Weiss constant. Later, Astrov *et al.* (1968) proved that these compounds undergo a transition into a weakly ferromagnetic state at temperatures $T_N = 11$ and 9 K, respectively.

BiFeO_3 is an antiferromagnet below $T_N = 643$ K. This was proved by neutron scattering (Kiselev *et al.*, 1962; Michel *et al.*, 1969) and magnetic measurements (Smolenskii *et al.*, 1962; see also Venetsev *et al.*, 1987). BiFeO_3 also possesses a spontaneous electric polarization. The magnetic point group above T_N is $3m1'$ and below it should have been $3m$ (Kiselev *et al.*, 1962), but in reality it possesses an antiferromagnetic spatially modulated spin structure (Sosnovska *et al.*, 1982). Another ferroelectric antiferromagnet, YMnO_3 , was found by Bertaut *et al.* (1964). It becomes ferroelectric at $T_c = 913$ K (with paramagnetic point group $6mm1'$) and antiferromagnetic at $T_N = 77$ K. Below this temperature, its magnetic point group is $6'mm'$. The antiferromagnetic ordering was also proved by investigating the Mössbauer effect (Chappert, 1965). The symmetries of both antiferromagnetic ferroelectrics described above do not allow weak ferromagnetism according to Table 1.5.5.2, and, experimentally, a spontaneous ferromagnetic moment has not been observed so far.

Since Schmid (1965) developed a technique for growing single crystals of boracites, these compounds have become the most interesting ferromagnetoelectrics. The boracites have the chemical formula $M_3\text{B}_7\text{O}_{13}\text{X}$ (where $M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Cr}^{2+}$ and $X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-, \text{NO}_3^-$). Many of them are ferroelectrics and weak ferromagnets at low temperatures. This was first shown for $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ (see Ascher *et al.*, 1966). The symmetries of all the boracites are cubic at high temperatures and their magnetic point group is $43m1'$. As the temperature is lowered, most become ferroelectrics with the magnetic point group $mm21'$. At still lower temperatures, the spins of the magnetic ions in the boracites go into an antiferromagnetic state with weak ferromagnetism. For some the ferromagnetoelectric phase belongs to the group $m'm2'$ and for others to $m'm'2, m', m$ or 1. In accordance with Table 1.5.8.4, the spontaneous polarization \mathbf{P} is oriented perpendicular to the weak ferromagnetic moment \mathbf{M}_D for the groups $m'm2'$ and m . There results a complicated behaviour of boracites in external magnetic and electric fields. It depends strongly on the history of the samples. Changing the direction of the electric polarization by an electric field also changes the direction of the ferromagnetic vector (as well as the direction of the antiferromagnetic vector) and *vice versa*.

As an example, Fig. 1.5.8.2 shows the results of measurements on Ni–I boracite with spontaneous polarization along [001] and spontaneous magnetization initially along [110]. A magnetic field was applied along [110] and the polarization induced along [001]

was measured. If the applied field was increased beyond 6 kOe, the induced polarization changed sign because the spontaneous magnetization had been reversed. On reversing the applied magnetic field, the rest of the hysteresis loop describing the ME_{\parallel} response was obtained.

If the spontaneous polarization is reversed, *e.g.* by applying an electric field, the spontaneous magnetization will rotate simultaneously by 90° around the polarization axis. Applying magnetic fields as described above will no longer produce a measurable polarization. If, however, the crystal is rotated by 90° around the polarization axis before repeating the experiment, a hysteresis loop similar to Fig. 1.5.8.2 but turned upside down will be obtained (*cf.* Schmid, 1967).

The similarity of the jumps in the curves of linear magnetostriction (see Fig. 1.5.7.2) and magnetoelectric effect in Ni–I boracite is noteworthy. More details about the present state of investigation of the ferromagnetoelectrics are presented in the review article of Schmid (1994b).

The ferromagnetoelectrics appear as type 4 and the ferroelectric antiferromagnets of type III^a as types 2 and 3 in Table 1.5.8.3. The table shows that the linear magnetoelectric effect is admitted by all ferromagnetoelectrics and all ferroelectric antiferromagnets of type III^a, except those that belong to the two point groups $C_6(C_3) = 6'$ and $C_{6v}(C_{3v}) = 6'mm'$.

Concluding Section 1.5.8, it is worth noting that the magnetoelectric effect is still actively investigated. Recent results in this field can be found in papers presented at the 1993 and 1996 conferences devoted to this subject (see Schmid *et al.*, 1994; Bichurin, 1997, 2002).

1.5.9. Magnetostriction

The transition to an ordered magnetic state is accompanied by a spontaneous distortion of the lattice, which is denoted spontaneous magnetostriction. The lattice distortion may be specified by the deformation (strain) components S_{ij} . The undeformed state is defined as the crystal structure that would be realized if the crystal remained in the paramagnetic state at the given temperature. This means that it is necessary to separate the magnetostrictive deformation from the ordinary thermal expansion of the crystal. This can be done by measurements of the magnetostriction in external magnetic fields applied in different directions (see Section 1.5.9.2). The magnetostriction arises because the first derivatives of the exchange and relativistic energies responsible for the magnetic order do not vanish at $S_{ij} = 0$. Thus these energies depend linearly on the deformations around $S_{ij} = 0$. That part of the magnetic energy which depends on the deformations (and consequently on the stresses) is called the magnetoelastic energy, U_{me} . To find the equilibrium values of the spontaneous magnetostriction, one also has to take the elastic energy into account.

The magnetoelastic energy includes both an exchange and a relativistic part. In some ferromagnets that are cubic in the paramagnetic phase, the exchange interaction does not lower the cubic symmetry. Thus the exchange part of U_{me} satisfies the relations

$$\partial U_{me}/\partial S_{ii} = B'_0 \quad \text{and} \quad \partial U_{me}/\partial S_{ij} = 0 \quad (i \neq j). \quad (1.5.9.1)$$

Such a form of the magnetoelastic energy gives rise to an isotropic spontaneous magnetostriction or volume change (volume striction) which does not depend on the direction of magnetization. In what follows, we shall analyse mainly the anisotropic magnetostriction.

The spontaneous magnetostriction deformations are so small (about 10^{-5}) for some ferro- and antiferromagnets that they cannot be observed by the usual X-ray techniques. However, in materials with ions possessing strong spin–orbit interactions (like Co^{2+}), it may be as large as 10^{-4} . The magnetostriction in rare-

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earth metals and their compounds with iron and cobalt are especially large (up to 10^{-3}).

Magnetostriction is observed experimentally as a change δl of the linear dimension along a direction specified by a unit vector $\boldsymbol{\beta} = (\beta_1, \beta_2, \beta_3)$:

$$\lambda_\beta = \delta l/l = \sum_{ij} S_{ij} \beta_i \beta_j, \quad (1.5.9.2)$$

where S_{ij} are the deformation components, which are functions of the components of the unit vector \mathbf{n} aligned in the direction of the magnetization. Only the symmetric part of the deformation tensor S_{ij} has been taken into account, because the antisymmetric part represents a rotation of the crystal as a whole.

The magnetostriction that arises in an applied magnetic field will be discussed in Section 1.5.9.2; Section 1.5.9.1 is devoted to the spontaneous magnetostriction.

1.5.9.1. Spontaneous magnetostriction

In this section, we shall assume that the crystal under consideration undergoes a phase transition from the paramagnetic state into a magnetically ordered state. The latter is a single-domain state with the magnetization (or the antiferromagnetic vector) aligned along the vector \mathbf{n} . As was mentioned above, to solve the problem of the spontaneous magnetostriction we have to minimize the sum of magnetoelastic and elastic energy.

Like the anisotropy energy, the anisotropic part of the magnetoelastic energy can be represented as a series in the components of the unit vector \mathbf{n} :

$$U_{me} = Q_{klmn} S_{kl} n_m n_n + Q_{klmnop} S_{kl} n_m n_n n_o n_p + \dots = V_{kl}^0 S_{kl}. \quad (1.5.9.3)$$

As for every ordered magnetic, this relation contains only even powers of the magnetization unit vector. The components of the tensors \mathbf{Q} are called magnetostrictive or magnetoelastic coefficients. They are proportional to even powers of the magnetization M ($Q_{klmn} \propto M^2$ and $Q_{klmnop} \propto M^4$). The symmetry of the tensors \mathbf{Q}_{klmn} and \mathbf{Q}_{klmnop} is defined by the crystallographic point group of the initial paramagnetic phase of the crystal.

It is convenient to consider the magnetoelastic energy as part of a general expansion of the free energy of a magnetic into a series with respect to the deformation (as the magnetostrictive deformations are small):

$$V = V^0 + V_{kl}^0 S_{kl} + \frac{1}{2} V_{klmn}^0 S_{kl} S_{mn} + \dots, \quad (1.5.9.4)$$

where all the expansion coefficients V^0 are functions of the components of the magnetization unit vector \mathbf{n} . The superscripts zero indicate that the expansion coefficients have been calculated relative to the undistorted lattice. Such a state in which, at a given temperature, there is no magnetic interaction to distort the crystal is not realizable practically. It will be shown below that the values of the coefficients V_{kl}^0 may be obtained experimentally by observing the magnetostriction in a magnetic field (see Section 1.5.9.2).

The first term in (1.5.9.4) is the anisotropy energy at zero deformation U_a^0 :

$$V^0 = U_a^0 = K_{ij}^0 n_i n_j + K_{ijkl}^0 n_i n_j n_k n_l + K_{ijklmn}^0 n_i n_j n_k n_l n_m n_n. \quad (1.5.9.5)$$

This expression has to be compared with the expression for the anisotropy at zero stress introduced in Section 1.5.3.2 [see (1.5.3.5)]. It is obvious that symmetry imposes the same restrictions on the tensors \mathbf{K} in both expressions for the anisotropy. Later, we shall discuss these two relations for the anisotropy in more detail.

The second term in (1.5.9.4) is the magnetoelastic energy density, which is displayed in equation (1.5.9.3) and represents the energy of anisotropic deformation.

The third term in (1.5.9.4) is quadratic in S_{kl} and can be considered as an additional contribution to the elastic energy arising from the distortion of the lattice by spontaneous magnetostriction. This term is small compared with the main part of the elastic energy, and the effect it produces is called a morphic effect and is usually neglected.

The equilibrium deformation components S_{ij}^* may be found by minimization of the sum of the magnetoelastic and elastic energies. The latter, U_{el} , is given by

$$U_{el} = \frac{1}{2} c_{ijkl} S_{ij} S_{kl}, \quad (1.5.9.6)$$

where c_{ijkl} are the elastic stiffnesses. The minimization leads to

$$\partial(U_{el} + U_{me})/\partial S_{ij} = c_{ijkl} S_{kl}^* + V_{ij}^0 = 0. \quad (1.5.9.7)$$

We shall replace the elastic stiffnesses c_{ijkl} in this equation by the elastic compliances s_{ijkl} , taking into account that Hooke's law may be written in two forms (see Section 1.3.3):

$$T_{ij} = c_{ijkl} S_{kl} \quad \text{or} \quad S_{ij} = s_{ijkl} T_{kl}. \quad (1.5.9.8)$$

Thus the relation for the equilibrium components of the strain S_{ij}^* becomes

$$S_{ij}^* = -s_{ijkl} V_{kl}^0. \quad (1.5.9.9)$$

Combining the relations (1.5.9.9) and (1.5.9.3), we get the following equation for the magnetostrictive strain components S_{ij} as a function of the magnitude M_s and direction $\mathbf{n} = \mathbf{M}_s/M_s$ of the magnetization \mathbf{M}_s :

$$\begin{aligned} S_{ij}^* &= -s_{ijkl} (Q_{klmn} n_m n_n + Q_{klmnop} n_m n_n n_o n_p + \dots) \\ &= M_s^2 N_{ijkl} n_k n_l + M_s^4 N_{ijklmn} n_k n_l n_m n_n + \dots \end{aligned} \quad (1.5.9.10)$$

Let us denote the spontaneous magnetostriction by λ_β^0 ($\boldsymbol{\beta}$ defines the direction of the magnetostriction relative to the crystallographic axes). According to (1.5.9.2), we obtain

$$\lambda_\beta^0 = M_s^2 N_{ijkl} \beta_i \beta_j n_k n_l + M_s^4 N_{ijklmn} \beta_i \beta_j n_k n_l n_m n_n. \quad (1.5.9.11)$$

Relation (1.5.9.11) shows that N_{ijklmn} can be chosen as symmetric in its first two indices and symmetric in its last four indices. It can therefore be represented by a 6×15 matrix $N_{\alpha A}$, where $\alpha = 1, \dots, 6$ and $A = 01, \dots, 15$. Table 1.5.9.1 lists the pairs ij that correspond to α and the quadruples $k\ell mn$ that correspond to A .

Similarly, N_{ijkl} can be chosen as symmetric in its first two and in its last two indices. It can therefore be represented by a 6×6 matrix $N_{\alpha\beta}$, where $\alpha, \beta = 1, \dots, 6$. The correspondence between the numbers 1 to 6 and pairs ij or $k\ell$ is given in Table 1.5.9.1.

The tensors N_{ijkl} and N_{ijklmn} must satisfy the symmetry of the paramagnetic state of the crystal under consideration. In the case of cubic crystals with fourfold axes (paramagnetic point groups $4321'$, $43m1'$ or $m\bar{3}m1'$), the two matrices $N_{\alpha\beta}$ and $N_{\alpha A}$ possess instead of the 36 and 90 independent components only 3 and 6, i.e. N_{11}, N_{12}, N_{44} and $N_{101}, N_{102}, N_{104}, N_{105}, N_{407}, N_{410}$, respectively. The exact form of the two matrices will be given in the following.

(a) Cubic crystals.

If the point group of the paramagnetic crystal is $4321'$, $\bar{4}3m1'$ or $m\bar{3}m1'$, it follows from the Neumann principle that the only nonvanishing components of $N_{\alpha\beta}$ are $N_{11} = N_{22} = N_{33}$, $N_{12} = N_{23} = N_{31} = N_{21} = N_{32} = N_{13}$ and $N_{44} = N_{55} = N_{66}$. Similarly, the only nonvanishing components of $N_{\alpha A}$ are $N_{101} = N_{202} = N_{303}$, $N_{102} = N_{203} = N_{301} = N_{103} = N_{201} = N_{302}$, $N_{104} = N_{205} = N_{306}$, $N_{105} = N_{206} = N_{304} = N_{106} = N_{204} = N_{305}$, $N_{407} = N_{508} = N_{609}$,

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$N_{410} = N_{511} = N_{612} = N_{413} = N_{514} = N_{615}$. The spontaneous magnetostriction (1.5.9.11) can then be written as

$$\lambda_{\beta}^0 = h_0 + h_1 S(n_1^2 \beta_1^2) + 2h_2 S(n_1 n_2 \beta_1 \beta_2) + h_3 S(n_1^2 n_2^2) + h_4 S(n_1^4 \beta_1^2 + \frac{2}{3} n_1^2 n_2^2) + 2h_5 S(n_1 n_2 n_3^2 \beta_1 \beta_2). \quad (1.5.9.12)$$

Here an operator $S()$ has been introduced, which denotes the sum of the three quantities obtained by cyclic permutation of the suffixes in the expression within the brackets. For example, $S(n_1^2 n_2 n_3 \beta_2 \beta_3) = n_1^2 n_2 n_3 \beta_2 \beta_3 + n_2^2 n_3 n_1 \beta_3 \beta_1 + n_3^2 n_1 n_2 \beta_1 \beta_2$.

The coefficients h_i are related in the following way to the components of the matrices $N_{\alpha\beta}$ and $N_{\alpha A}$ and the spontaneous magnetization M_s :

$$\begin{aligned} h_0 &= N_{12} M_s^2 + N_{102} M_s^4, \\ h_1 &= (N_{11} - N_{12}) M_s^2 - 6(N_{104} - N_{105}) M_s^4, \\ h_2 &= 2N_{44} M_s^2 + 4N_{410} M_s^4, \\ h_3 &= [-\frac{2}{3}(N_{101} + 2N_{102}) + 2(N_{104} + 2N_{105})] M_s^4, \\ h_4 &= [N_{101} - N_{102} + 6(N_{104} - N_{105})] M_s^4, \\ h_5 &= 4(3N_{407} - N_{410}) M_s^4. \end{aligned} \quad (1.5.9.13)$$

(b) Hexagonal crystals.

The equation for the spontaneous magnetostriction of a crystal that, in its paramagnetic state, has a point group $6221'$, $6mm1'$, $\bar{6}m21'$ or $6/mmm1'$, is of the following form [if we restrict ourselves to the quadratic terms in (1.5.9.11)]:

$$\lambda_{\beta}^0 = h_0 + h_1 n_3^2 \beta_3^2 + h_2 (n_1^2 \beta_1^2 + n_2^2 \beta_2^2) + h_3 (n_1^2 \beta_2^2 + n_2^2 \beta_1^2) + 2h_4 n_1 n_2 \beta_1 \beta_2 + 2h_5 n_3 \beta_3 (n_1 \beta_1 + n_2 \beta_2) + h_6 \beta_3^2. \quad (1.5.9.14)$$

The coefficients h_i are related to the components $N_{\alpha\beta}$ and the spontaneous magnetization as follows:

$$\begin{aligned} h_0 &= N_{13} M_s^2 \\ h_1 &= (N_{33} - N_{31}) M_s^2 \\ h_2 &= (N_{11} - N_{13}) M_s^2 \\ h_3 &= (N_{12} - N_{13}) M_s^2 \\ h_4 &= (N_{11} - N_{12}) M_s^2 \\ h_5 &= 2N_{44} M_s^2 \\ h_6 &= (N_{31} - N_{13}) M_s^2 \end{aligned} \quad (1.5.9.15)$$

Table 1.5.9.1. Correspondence between matrix indices α , A and tensor indices of the tensors describing spontaneous magnetostriction

α	ij	A	$k\ell mn$
1	11	01	1111
2	22	02	2222
3	33	03	3333
4	23, 32	04	2233, 2323, 2332, 3223, 3232, 3322
5	31, 13	05	3311, 3131, 3113, 1331, 1313, 1133
6	12, 21	06	1122, 1212, 1221, 2112, 2121, 2211
		07	1123, 1132, 1213, 1231, 1312, 1321, 2113, 2131, 2311, 3112, 3121, 3211
		08	2231, 2213, 2321, 2312, 2123, 2132, 3221, 3212, 3122, 1223, 1232, 1322
		09	3312, 3321, 3132, 3123, 3231, 3213, 1332, 1323, 1233, 2331, 2313, 2133
		10	2223, 2232, 2322, 3222
		11	3331, 3313, 3133, 1333
		12	1112, 1121, 1211, 2111
		13	3332, 3323, 3233, 2333
		14	1113, 1131, 1311, 3111
		15	2221, 2212, 2122, 1222

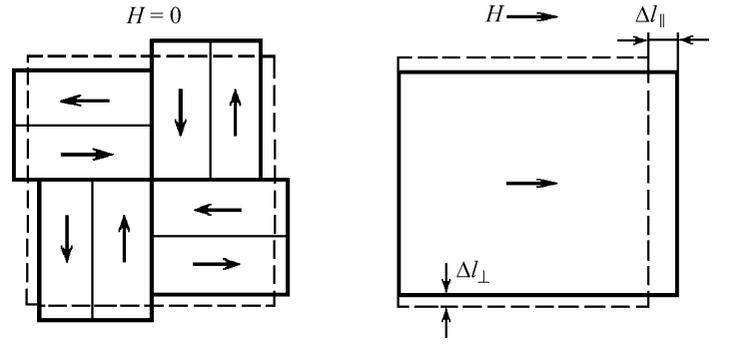


Fig. 1.5.9.1. Diagram explaining the occurrence of magnetostrictive strains in the demagnetized and saturated states of a cube-shaped crystal with a cubic prototype.

As mentioned above, the values of the magnetostrictive coefficients h_i and the spontaneous magnetostriction λ_{β}^0 may be obtained from measurements of magnetostriction in a magnetic field. The latter will be discussed in the next section.

Notice that there is some disagreement between our results (1.5.9.12)–(1.5.9.13) and the corresponding results of Mason (1951), and similarly between (1.5.9.14)–(1.5.9.15) and the results of Mason (1954).

1.5.9.2. Magnetostriction in an external magnetic field

There are three reasons for the magnetostriction arising in a magnetic field: (a) the transfer of the crystal into a single-domain state if the magnetic field is directed along one of the easy axes; (b) the deflection of the magnetization (or antiferromagnetic vector) by the magnetic field from the easy axis in a single-domain crystal; (c) the change of the magnetization in a sufficiently strong magnetic field.

Let us begin with case (a) and consider a crystal with cubic symmetry in the paramagnetic state (*i.e.* with a cubic prototype). We calculate the magnetostriction that occurs when the applied magnetic field transforms the crystal from the demagnetized multidomain state into the saturated single-domain state. This transformation is shown schematically in Fig. 1.5.9.1.

Each domain in the demagnetized state is distorted by spontaneous magnetostriction. The number of domains in the sample is usually much larger than shown in the figure. Thus a sample of a crystal with a cubic prototype which in the paramagnetic state has the form of a cube will retain this form in the ordered state. Its linear dimension will be changed as a result of magnetostriction. Averaging these strains over all the domains, one gets the spontaneous magnetostrictive change of the linear dimension of the sample, which is equal for any direction x , y or z :

$$(\delta l)_{\text{dem}}/l_0 = \lambda^{\text{dem}} = \overline{\lambda_{\beta}^0(n_k)}, \quad (1.5.9.16)$$

where n_k defines the directions parallel to all the easy axes of the crystal. For crystals with a cubic prototype, there are two principal ordered states: with the easy axis along the $\langle 111 \rangle$ directions as in nickel or along the $\langle 100 \rangle$ directions as in iron. Averaging the strains of all eight possible easy-axis directions of the domains in the $\langle 111 \rangle$ -type ferromagnet we obtain from (1.5.9.12) the following expression for the spontaneous magnetostriction of the demagnetized crystal:

$$\lambda^{\text{dem}} = h_0 + \frac{1}{3}(h_1 + h_3 + h_4). \quad (1.5.9.17)$$

In the case of the $\langle 100 \rangle$ -type ferromagnet, the averaging over the six groups of domains leads to

$$\lambda^{\text{dem}} = h_0 + \frac{1}{3}(h_1 + h_4). \quad (1.5.9.18)$$

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In the saturated state, the sample loses its cubic form. It becomes longer parallel to the magnetic field and thinner perpendicular to it. By definition, the demagnetized state is taken as a reference state for the magnetostriction in the magnetic field. Subtracting from the general relation for spontaneous magnetostriction (1.5.9.12) the expressions (1.5.9.17) and (1.5.9.18) for the demagnetized sample, Becker & Döring (1939) obtained the equations that describe the anisotropy of the magnetostriction caused by saturation magnetization of the $\langle 111 \rangle$ and $\langle 100 \rangle$ types of magnetic crystals:

$\langle 111 \rangle$ type:

$$\lambda_{\beta}^{\text{sat}} = h_1[S(n_1^2\beta_1^2) - \frac{1}{3}] + 2h_2S(n_1n_2\beta_1\beta_2) + h_3[S(n_1^2n_2^2) - \frac{1}{3}] + h_4[S(n_1^4\beta_1^2 + \frac{2}{3}n_1^2n_2^2) - \frac{1}{3}] + 2h_5S(n_1^2n_2n_3\beta_2\beta_3); \quad (1.5.9.19)$$

$\langle 100 \rangle$ type:

$$\lambda_{\beta}^{\text{sat}} = h_1[S(n_1^2\beta_1^2) - \frac{1}{3}] + 2h_2S(n_1n_2\beta_1\beta_2) + h_3S(n_1^2n_2^2) + h_4[S(n_1^4\beta_1^2 + \frac{2}{3}n_1^2n_2^2) - \frac{1}{3}] + 2h_5S(n_1^2n_2n_3\beta_2\beta_3). \quad (1.5.9.20)$$

Both types of magnetics with a cubic prototype are described by a two-constant equation if the terms of fourth power are neglected. This equation was obtained by Akulov (1928) in the form

$$\lambda_{\beta}^{\text{sat}} = \frac{3}{2}\lambda_{100}(n_1^2\beta_1^2 + n_2^2\beta_2^2 + n_3^2\beta_3^2 - \frac{1}{3}) + 3\lambda_{111}(n_1n_2\beta_1\beta_2 + n_2n_3\beta_2\beta_3 + n_3n_1\beta_3\beta_1), \quad (1.5.9.21)$$

where the constants λ_{100} and λ_{111} correspond to the magnetostrictive deformation of a 'cubic' ferromagnet along the direction of the magnetic field that is applied along the directions $\langle 100 \rangle$ and $\langle 111 \rangle$, respectively. Let us denote by Q_1 and Q_2 the following equal coefficients in the equation for the magnetoelastic energy (1.5.9.3):

$$Q_1 = Q_{xxxx} = Q_{yyyy} = Q_{zzzz}; \quad Q_2 = Q_{xyxy} = Q_{yzyz} = Q_{zxxz}. \quad (1.5.9.22)$$

According to (1.5.9.9), the coefficients λ_{100} and λ_{111} may be written as the following fractions of Q_i and the elastic stiffnesses $c_{\alpha\beta}$:

$$\lambda_{100} = \frac{Q_1}{c_{12} - c_{11}}, \quad \lambda_{111} = -\frac{1}{3} \frac{Q_2}{c_{44}}. \quad (1.5.9.23)$$

If the magnetic field transforms the crystal from the demagnetized to the saturated state and if the linear dimension of the sample along the magnetic field increases, then its dimension perpendicular to the field will decrease (see Fig. 1.5.9.1). It follows from relation (1.5.9.21) that the magnetostriction perpendicular to the magnetic field is

$$\lambda_{100}^{\perp} = -\frac{1}{2}\lambda_{100} \quad \text{and} \quad \lambda_{111}^{\perp} = -\frac{1}{2}\lambda_{111}. \quad (1.5.9.24)$$

Some data for magnetostriction of ferromagnets with prototype symmetry $m\bar{3}m1'$ are presented in Table 1.5.9.2.

In a uniaxial crystal, the magnetostriction in the magnetic field arises mainly as a result of the rotation of the magnetization vector from the direction of the easy axis to the direction of the applied field. The magnetostriction in the magnetic field of an easy-axis hexagonal ferromagnet can be obtained from the relation for the spontaneous magnetostriction (1.5.9.14). In the demagnetized state, such a ferromagnet possesses only two types of antiparallel domains, in which the magnetization is aligned

Table 1.5.9.2. Magnetostriction data for ferromagnets with prototype symmetry $m\bar{3}m1'$

Compound	$\lambda_{100} \times 10^6$	$\lambda_{111} \times 10^6$	References†
Fe	20.7	-21.2	(1)
Ni	-45.9	-24.3	(1)
Fe ₃ O ₄	-20	78	(2)
YIG ($T = 300$ K)	-1.4	-2.4	(3)
DyIG ($T = 300$ K)	-12.5	-5.9	(3)
DyIG ($T = 4.2$ K)	-1400	-550	(4)

† References: (1) Lee (1955); (2) Bickford *et al.* (1955); (3) Iida (1967); (4) Clark *et al.* (1966).

parallel or antiparallel to the hexagonal axis ($n_z = \pm 1$, $n_x = n_y = 0$).

Thus the magnetostriction of the demagnetized state is described by

$$\lambda_{\beta}^{\text{dem}} = h_0 + (h_1 + h_6)\beta_3^2. \quad (1.5.9.25)$$

The saturation magnetostriction can be calculated for different directions of the applied magnetic field using the equations (1.5.9.14), (1.5.9.15) and (1.5.9.25). If the magnetic field is applied along the x axis ($n_x = 1$, $n_y = n_z = 0$), the saturation magnetostrictions for three directions of the vector β : $\lambda_{\beta}^{\text{sat}} = \lambda_A, \lambda_B, \lambda_C$ are

$$\begin{aligned} \beta \parallel Ox \quad \lambda_A &= h_2, \\ \beta \parallel Oy \quad \lambda_B &= h_3, \\ \beta \parallel Oz \quad \lambda_C &= -h_1. \end{aligned} \quad (1.5.9.26)$$

If the magnetic field is applied at an angle of 45° to the hexagonal axis along the $[101]$ direction, the saturation magnetostriction along the magnetic field is described by

$$\lambda_D = \lambda_{101}^{\text{sat}} = \frac{1}{4}(h_2 - h_1 + 2h_5). \quad (1.5.9.27)$$

Using the constants $\lambda_A, \lambda_B, \lambda_C$ and λ_D introduced above, the general relation for the magnetostriction caused by magnetization to saturation can be presented in the form

$$\begin{aligned} \lambda_{\beta}^{\text{sat}} &= \lambda_A[(n_1\beta_1 + n_2\beta_2)^2 - (n_1\beta_1 + n_2\beta_2)n_3\beta_3] \\ &+ \lambda_B[(1 - n_3^2)(1 - \beta_3^2) - (n_1\beta_1 + n_2\beta_2)^2] \\ &+ \lambda_C[(1 - n_3^2)\beta_3^2 - (n_1\beta_1 + n_2\beta_2)n_3\beta_3] \\ &+ 4\lambda_D(n_1\beta_1 + n_2\beta_2)n_3\beta_3. \end{aligned} \quad (1.5.9.28)$$

A typical hexagonal ferromagnet is cobalt. The magnetostriction constants introduced above have the following values for Co at room temperature:

$$\begin{aligned} \lambda_A &= -45 \times 10^{-6} & \lambda_C &= +110 \times 10^{-6} \\ \lambda_B &= -95 \times 10^{-6} & \lambda_D &= -100 \times 10^{-6} \end{aligned}$$

A more sophisticated treatment of the symmetry of the magnetostriction constants is given in the monograph of Birss (1964) and in Zalesky (1981).

1.5.9.3. The difference between the magnetic anisotropies at zero strain and zero stress

The spontaneous magnetostriction makes a contribution to the magnetic anisotropy (especially in magnetics with a cubic prototype). Therefore, to find the full expression for the anisotropy energy one has to sum up the magnetic U_a^0 [see (1.5.9.5)], the magnetoelastic U_{me} [see (1.5.9.3)] and the elastic U_{el} [see (1.5.9.6)] energies. At zero strain ($S_{ij}^* = 0$), only $U_a^0 \neq 0$. At zero stress

$$\begin{aligned} U_a^0 + U_{\text{me}} + U_{\text{el}} &= U_a^0 + V_{ij}^0 S_{ij}^* + \frac{1}{2} c_{ijk\ell} S_{ij}^* S_{k\ell}^* \\ &= U_a^0 + \frac{1}{2} V_{ij}^0 S_{ij}^*. \end{aligned} \quad (1.5.9.29)$$

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

Table 1.5.10.1. Conversion of Gaussian to SI units

Symbol	Quantity	Gaussian unit and its SI equivalent
B	Magnetic induction	1 gauss (G) = 10 ⁻⁴ tesla (T)
H	Magnetic field	1 oersted (Oe) = 10 ³ /(4π) A m ⁻¹
M	Magnetization (= magnetic moment per unit volume)	1 emu cm ⁻³ = 10 ³ A m ⁻¹
α	Linear magnetoelectric tensor (rationalized units)	1 (dimensionless units) = 4π × 10 ⁻⁸ /3 s m ⁻¹
Λ	Piezomagnetic tensor	1 Oe ⁻¹ = 4π × 10 ⁻³ m A ⁻¹ = 4π × 10 ⁻³ T Pa ⁻¹
χ	Magnetic volume susceptibility	1 (dimensionless units) = 4π (dimensionless units)
χ_g	Magnetic mass susceptibility	1 cm ³ g ⁻¹ = 4π × 10 ⁻⁶ m ³ g ⁻¹
χ_{mol}	Magnetic molar susceptibility	1 cm ³ mol ⁻¹ = 4π × 10 ⁻⁶ m ³ mol ⁻¹

We used here the modified equation (1.5.9.7):

$$\frac{1}{2}c_{ijkl}S_{ij}^*S_{kl}^* = -\frac{1}{2}V_{ij}^0S_{ij}^* \quad (1.5.9.30)$$

Substituting the values for the spontaneous magnetostriction, the final equation for the anisotropy energy measured at atmospheric pressure may be written as

$$\begin{aligned} U_a &= U_a^0 + \frac{1}{2}V_{ij}^0S_{ij}^* \\ &= (K_{ij}^0 + K_{ij}')n_i n_j + (K_{ijkl}^0 + K_{ijkl}')n_i n_j n_k n_l \\ &\quad + (K_{ijklmn}^0 + K_{ijklmn}')n_i n_j n_k n_l n_m n_n + \dots \end{aligned} \quad (1.5.9.31)$$

As an example, for the ferromagnets with a cubic prototype this equation may be written as

$$U_a = (K_1^0 + K_1')S(n_1^2 n_2^2) + (K_2^0 + K_2')n_1^2 n_2^2 n_3^2. \quad (1.5.9.32)$$

The coefficients K_1' and K_2' may be expressed in terms of the saturation magnetostriction constants h_0, \dots, h_5 [see (1.5.9.12)] and the elastic stiffnesses $c_{\alpha\beta}$:

$$\begin{aligned} K_1' &= c_{11}[h_0(2h_4 - 3h_3) + h_1(h_1 - h_3 + 3h_4) - h_4(h_3 - 2h_4)] \\ &\quad + c_{12}[2h_0(2h_4 - 3h_3) - (h_1 + h_4)(h_1 + 2h_3)] - \frac{1}{2}c_{44}h_2^2, \end{aligned} \quad (1.5.9.33)$$

$$\begin{aligned} K_2' &= -c_{11}[3h_4(h_1 + h_3) + (h_4 - h_3)(4h_4 - 3h_3)] \\ &\quad + c_{12}[3h_4(h_1 + h_3) + h_3(5h_4 - 6h_3)] \\ &\quad - \frac{1}{2}c_{44}(6h_2 + h_5)h_5. \end{aligned} \quad (1.5.9.34)$$

For cubic crystals, K_1^0 and K_1' are of the same magnitude. As an example, for Ni one has $K_1^0 = 80\,000 \text{ erg cm}^{-3} = 8000 \text{ J m}^{-3}$ and $K_1' = -139\,000 \text{ erg cm}^{-3} = -13\,900 \text{ J m}^{-3}$.

1.5.10. Transformation from Gaussian to SI units

Numerical values of magnetic quantities are given in Gaussian units in this chapter. For each quantity that appears in a table or figure, Table 1.5.10.1 gives the corresponding Gaussian unit and its value expressed in SI units. More details on the transformation between Gaussian and SI units are given *e.g.* in the Appendix of Jackson (1999).

1.5.11. Glossary

α_{ij}	(linear) magnetoelectric tensor
β_{ijk}	nonlinear magnetoelectric tensor <i>EHH</i>
γ_{ijk}	nonlinear magnetoelectric tensor <i>HEE</i>
Δ	Weiss constant
Δn	magnetic birefringence
ε_{ij}	dielectric permittivity
λ	constant describing magnetostriction
Λ_{ijk}	tensor describing the piezomagnetic effect
$\Lambda_{i\alpha}$	matrix describing the piezomagnetic effect
μ_{ij}	magnetic permeability

μ	magnetic moment
μ_B	Bohr magneton
π_{ijkl}	piezomagnetoelectric tensor
$\rho(\mathbf{r})$	charge density
Φ	thermodynamic potential
χ_{ij}^e	dielectric susceptibility
χ_{ij}, χ_{ij}^m	magnetic susceptibility
B	magnetic induction
c	speed of light
c_{ijkl}	elastic stiffness
$d\tau$	volume element
e	charge of the electron
E	electric field
g	Landé g -factor
H	magnetic field
$\mathbf{j}(\mathbf{r})$	current density
J	total angular momentum
k	position vector in reciprocal space
k_B	Boltzmann factor
\mathbf{l}_i	sum of the magnetic moments in a unit cell, in which some of the moments are taken with opposite sign
\mathbf{L}_i	antiferromagnetic vector
L	orbital angular momentum (Section 1.5.1.1), antiferromagnetic vector (remainder of this chapter)
$\mathbf{m}(\mathbf{r})$	magnetic moment density
m	sum of the magnetic moments in a unit cell
M	magnetization (= magnetic moment per unit volume = ferromagnetic vector)
N	No. of atoms per unit volume
P	effective number of Bohr magnetons (Section 1.5.1), pressure (remainder of this chapter)
P	electric polarization
r	position vector in space
S(r)	spin density
S	spin angular momentum (of an atom or ion)
s_{ijkl}	elastic compliance
S_{ij}	strain tensor
T_{ij}	stress tensor
T	temperature
T_c	transition temperature, in particular Curie temperature
T_N	Néel temperature
U	energy
U_a	anisotropy energy
U_{el}	elastic energy
U_{me}	magnetoelastic energy
v	velocity
Z	atomic number (= number of electrons per atom)

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