1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES
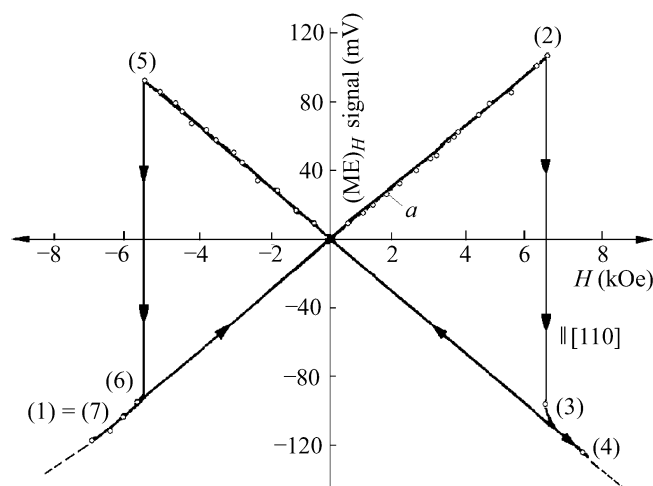

Fig. 1.5.8.2. The hysteresis loop in the linear magnetoelectric effect in ferromagnetoelectric $Ni_3B_7O_{13}I$ at 46 K (Ascher *et al.*, 1966).

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 Venevtsev *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 $M_3B_7O_{13}X$ (where $M = Cu^{2+}$, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cr^{2+} and $X = F^-$, Cl^-, Br^-, I^-, OH^-, NO_3^-). Many of them are ferroelectrics and weak ferromagnets at low temperatures. This was first shown for $Ni_3B_7O_{13}I$ (see Ascher *et al.*, 1966). The symmetries of all the boracites are cubic at high temperatures and their magnetic point group is $\bar{4}3m1'$. 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 **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 [$\bar{1}$10]. 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 (1994*b*).

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 $\mathbf{C}_6(\mathbf{C}_3) = 6'$ and $\mathbf{C}_{6v}(\mathbf{C}_{3v}) = 6'mm'$.

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

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

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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