

# Ferroelectromagnets

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The results are presented of the theoretical and experimental studies of ferroelectromagnets—crystals with magnetic and ferroelectric ordering. Considerable attention is paid to reviewing the results of the phenomenological analysis of the influence of the magnetoelectric interaction on the thermodynamic properties of ferroelectromagnets, their reaction to constant and variable electric and magnetic fields, the spectrum of spin waves and ferroelectric oscillations and the methods of exciting them. A table is presented of the expected magnetoelectric effects. The existing experimental studies of magnetoelectric interactions are described and the possible applications of ferroelectromagnets are discussed. A table is given of the known ferroelectromagnetic compounds.

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## 1. INTRODUCTION

Contemporary solid-state physics intensively studies the interactions of various subsystems of a crystal with one another. The study of electron-phonon, magnon-phonon, magnon-electron, and other interactions and their influence on static and dynamic phenomena in a crystal has led to the discovery of a number of new effects. The relatively recently discovered new class of materials called ferroelectromagnets is of undoubted scientific interest. The ferroelectromagnets are compounds in which magnetic and ferroelectric (or antiferroelectric<sup>1)</sup>) ordering exist simultaneously. The interaction of these ordered subsystems, which we herein after call the magnetoelectric interaction, introduces a number of features into the pattern of ferroelectric and magnetic phase transitions, into the spectrum of elementary excitations, and into the reaction of the system to electric and magnetic fields. Moreover, the magnetoelectric interaction induces a number of new, interesting effects.

<sup>1)</sup>Structural phase transitions accompanied by appreciable dielectric anomalies but not leading to spontaneous polarization are generally called antiferroelectric transitions.

The discovery of ferroelectromagnetic compounds was preceded by a period of intensive, fruitful development of the physics of magnetic phenomena and of ferroelectricity taken separately. The search for new ferroelectric compounds led a group of Leningrad physicists in 1958 to discover ferroelectrics having the perovskite structure with a considerable content of ions of iron.<sup>1,2</sup> The latter situation offered grounds for hoping that compounds with the perovskite structure could be simultaneously ferroelectrics and ferro(antiferro) magnetics.<sup>3</sup>

The possible coexistence of spontaneous magnetic moments and polarization does not contradict the general criteria for appearance of ferromagnetism and ferroelectricity taken separately. Magnetic ordering is governed by the exchange interaction of the electron spins, while ferroelectric ordering is governed by the redistribution of charge density in the lattice. In compounds of the perovskite type  $ABO_3$  (Fig. 1), the angles in the chains cation B–oxygen–cation B are close to  $180^\circ$ . Hence, when transition-element ions lie in the octahedral B positions, they can become ordered via an indirect exchange interaction through the oxide ions. Within the framework of the model theories being developed in those years, ferroelectric (FE) ordering in

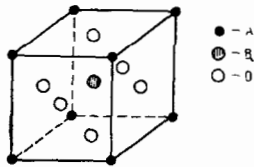


FIG. 1. Ideal unit cell of perovskite  $ABO_3$ . The B ion lies at the center of the cube and the oxide ions at the centers of the faces.

the perovskite lattice arises mainly from displacements of the A and B ions. Here the ordering is favored by the existence in the A sublattice of ions having a stereochemically active unshared pair of 6s-electrons ( $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Tl^+$ ), with ions of the transition elements in the B sublattice ( $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Nb^{5+}$ ,  $W^{6+}$ ,  $Mo^{6+}$ ) that have a noble-gas shell after the s- and d-electrons have been removed.<sup>4</sup> However, these ions do not possess a magnetic moment. In order to satisfy the conditions necessary for the appearance of ferroelectricity and magnetism, ions were introduced into the octahedral positions, some of which were ferroelectrically active, and the others magnetic. Thus in 1961 both the first ferroelectromagnet  $Pb(Fe_{2/3}W_{1/3})O_3$  which combined FE properties with antiferromagnetic properties, and the first ferroelectromagnetic solid solutions  $(1-x)Pb(Fe_{2/3}W_{1/3})O_3 + xPb(Mg_{1/2}W_{1/2})O_3$  (the ions in the octahedral positions are indicated in parentheses)<sup>5</sup> were prepared. Initially the measurements of the ferroelectromagnetic properties were performed on polycrystalline specimens, and then on single crystals of  $Pb(Fe_{2/3}W_{1/3})O_3$  and  $Pb(Fe_{1/2}Nb_{1/2})O_3$ .<sup>6</sup> One of the first ferroelectromagnets is also  $BiFeO_3$ , in which FE<sup>7,8</sup> and antiferromagnetic ordering<sup>9,10</sup> were found. At present about 50 ferroelectromagnetic compounds and some tens of solid solutions that combine ferro- and antiferroelectric properties with ferro-, ferri, and antiferromagnetic properties are known. A considerable number of the ferroelectromagnets, especially solid solutions, has been synthesized by the Moscow physicists.<sup>11</sup> Not only were the first ferroelectromagnetic crystals prepared in the USSR, but also the largest number of publications on these compounds has been noted here. Swiss, French, and Japanese scientists have also made a considerable contribution to the synthesis and study of ferroelectromagnets.

Practically all ferroelectromagnets are synthetic compounds, while only two natural crystals are known: congolite  $Fe_3B_7O_{13}Cl$  and chambersite  $Mn_3B_7O_{13}Cl$ .<sup>12,13</sup> One can classify the ferroelectromagnets into several fundamental classes according to structural features.

1. Compounds having the perovskite-type structure  $A(B_1, B_2, \dots)O_3$  (see Fig. 1) containing magnetic ions fully (e.g.,  $BiFeO_3$ ) or partially occupying the octahedral B positions. They include the first ferroelectromagnetic compounds  $Pb(Fe_{2/3}W_{1/3})O_3$ ,  $Pb(Fe_{1/2}Nb_{1/2})O_3$ ,  $Pb(Co_{1/2}W_{1/2})O_3$ ,  $BiFeO_3$ , the rhenium-containing perovskites  $Pb(B_{1/2}Re_{1/2})O_3$  ( $B = Fe, Mn, Ni, Co$ )<sup>14,15</sup>, and others (Nos. 1-16 in Table I). The compounds  $Bi_{m+1}B_mO_{3m+3}$  ( $B = Fe^{3+}, Ti^{4+}$ ) have also been synthesized, and have a layered perovskite-like structure<sup>16</sup> that amounts to

TABLE I. Ferroelectromagnets.

| Compound                       | Type of electric order | Type of magnetic order | $\Theta_E, K$                          | $\Theta_M, K$          | Magnetolectric measurements                                      |
|--------------------------------|------------------------|------------------------|--|------------------------|--|
| 1. $Pb(Fe_{2/3}W_{1/3})O_3$    | FE                     | AFM                    | 178                                    | 363                    | Measurement of internal magnetic field at the FE transition      |
| 2. $Pb(Fe_{1/2}Nb_{1/2})O_3$   | FE                     | AFM                    | 387                                    | 143                    | $M_c(\vec{E})$   |
| 3. $BiFeO_3$                   | AFE?<br>FE             | AFM                    | 1123<br>?                              | $\approx 650$          | $\epsilon(\Theta_M)$ , induction of P in spin-flop               |
| 4. $Eu_{1/2}Ba_{1/2}TiO_3$     | FE                     | FM                     | 165 <sup>186</sup>                     | 4, 21 <sup>56</sup>    |  |
| 5. $Pb(Mn_{2/3}W_{1/3})O_3$    | AFE?                   | AFM                    | 473 <sup>144</sup>                     | 203 <sup>144</sup>     | $\epsilon(\Theta_M)$   |
| 6. $Pb(Mn_{1/2}Re_{1/2})O_3$   | AFE?                   | FIM                    | 393                                    | 103                    |  |
| 7. $Pb(Mn_{1/2}W_{1/2})O_3$    | AFE?                   | AFM                    | 423                                    | 100                    |  |
| 8. $Pb(Fe_{1/2}Ta_{1/2})O_3$   | FE                     | AFM                    | 233                                    | 180 <sup>147</sup>     |  |
| 9. $Pb(Fe_{1/2}Re_{1/2})O_3$   | AFE?                   | FIM                    | 433                                    | > 283                  |  |
| 10. $Pb(Co_{1/2}Re_{1/2})O_3$  | AFE?                   | AFM                    | 403                                    | < 77                   |  |
| 11. $Pb(Ni_{1/2}Re_{1/2})O_3$  | AFE?                   | FIM                    | 343                                    | < 77                   |  |
| 12. $Pb(Co_{1/2}W_{1/2})O_3$   | AFE                    | WFM                    | 305                                    | 9                      |  |
| 13. $BiMnO_3$                  | FE                     | FM                     | 88                                     | 103, 110               |  |
| 14. $Cd(Fe_{1/2}Nb_{1/2})O_3$  | AFE                    | AFM                    | 773                                    | 48                     |  |
| 15. $Bi_2Bi_1Fe_2Ti_2O_{18}$   | AFE?<br>FE             | AFM<br>FM?             | 753<br>$\Theta_{EI}=1174$              | 723? <sup>159</sup>    | $\chi^{ME}$ ? <sup>158</sup>                                     |
| 16. $Bi_3Ti_3Fe_3O_{27}$       | FE                     | WFM                    | $\Theta_{EI}=1025^{158}$<br>1103, 1073 | 363, 403               | Induction of an electric signal by a magnetic field              |
| 17. $YMnO_3$                   | FE                     | AFM                    | 913, 933                               | $\approx 80$           |  |
| 18. $YBmO_3$                   | FE                     | AFM<br>WFM             | 983, 993                               | 87, 3<br>3, 8          |  |
| 19. $HoMnO_3$                  | FE                     | AFM<br>WFM             | 873                                    | 76<br>5                |  |
| 20. $ErMnO_3$                  | FE                     | AFM                    | 833                                    | 79                     |  |
| 21. $TmMnO_3$                  | FE                     | AFM                    | > 573                                  | 86                     |  |
| 22. $LuMnO_3$                  | FE                     | AFM                    |  | 91                     |  |
| 23. $ScMnO_3$                  | FE                     | AFM                    |  | 120                    |  |
| 24. $Cr_2B_7O_{13}Cl$          | FE                     | AFM                    | $\approx 260$                          | 25                     |  |
| 25. $Cr_3B_7O_{13}Br$          | FE                     | AFM                    | 4                                      | 50                     |  |
| 26. $Cr_3B_7O_{13}I$           | FE                     | AFM                    | 4                                      | 95                     |  |
| 27. $Mn_3B_7O_{13}Cl$          | FE                     | AFM                    | 680                                    | $\approx 65^1$         |  |
| 28. $Mn_3B_7O_{13}Br$          | FE                     | AFM                    | 566                                    | $\approx 6^{21}$       |  |
| 29. $Mn_3B_7O_{13}I$           | FE                     | WFM                    | 412                                    | 26 <sup>112</sup>      | $m(\vec{E})$   |
| 30. $Fe_3B_7O_{13}Cl$          | FE                     | WFM                    | $\approx 609$                          | $\approx 11$           | $m(\vec{E})$   |
| 31. $Fe_3B_7O_{13}Br$          | FE                     | WFM                    | $\approx 495$                          | $\approx 17$           | $m(\vec{E})$   |
| 32. $Fe_3B_7O_{13}I$           | FE                     | WFM                    | $\approx 349$                          | $\approx 30$           |  |
| 33. $Co_3B_7O_{13}Cl$          | FE                     | WFM                    | 623                                    | 11, 5, 15              | $\chi^{ME}$ , $m(\vec{E})$                                       |
| 34. $Co_3B_7O_{13}Br$          | FE                     | WFM                    | 458                                    | 20                     |  |
| 35. $Co_3B_7O_{13}I$           | FE                     | WFM                    | $\approx 197$                          | 38                     | $m(\vec{E})$ , $\epsilon(\Theta_M)$                              |
| 36. $Cu_3B_7O_{13}Cl$          | FE                     | AFM<br>WFM             | 365                                    | 20                     | $\chi^{ME}$  |
| 37. $Cu_3B_7O_{13}Br$          | FE                     | WFM                    | 226                                    | 8, 4 <sup>121</sup>    |  |
| 38. $Ni_3B_7O_{13}Cl$          | FE                     | AFM<br>WFM             | 610                                    | 24                     | $\epsilon(\Theta_M)$   |
| 39. $Ni_3B_7O_{13}Br$          | FE                     | WFM                    | 398                                    | 25<br>9 <sup>113</sup> | $\chi^{ME}$  |
| 40. $Ni_3B_7O_{13}I$           | FE                     | WFM                    | 64                                     | 30, 40                 | $m(\vec{E})$   |
| 41. $BaNiF_4$                  | FE                     | AFM                    | 1593                                   | 64                     | $\chi^{ME}$ , $\epsilon(H)$ , P(H),<br>$m(\vec{E})$              |
| 42. $BaMnF_4$                  | PE                     | WFM                    |  | 70 <sup>122</sup>      | Anomaly in the pyroelectric signal at $T \approx \Theta_M^{100}$ |
| 43. $BaCoF_4$                  | FE                     | AFM                    | 1153                                   | 25                     | $\epsilon(\Theta_M)$   |
| 44. $BaFeF_4$                  | PE                     | AFM                    |  | 69, 6                  |  |
| 45. $Li(Fe_{1/2}Ta_{1/2})O_3F$ | FE                     | AFM                    | 853                                    | 54, 2 <sup>182</sup>   | Induction of an electric current by a magnetic field             |
| 46. $Cr_2BeO_4$                | FE                     | AFM                    | 28 <sup>52</sup>                       | 28 <sup>52</sup>       |  |
| 47. $PbMn_2O_4$                | FE?                    | WFM                    | 250 <sup>129</sup>                     | 63 <sup>129</sup>      | $m(\vec{E})$   |
| 48. $Co_{1-2x}Mn_{1+2x}O_4$    | FE                     | FIM                    | 170 <sup>130</sup>                     | 170 <sup>130</sup>     | $\chi^{ME}$  |
| 49. $Cu(HCOO)_2 \cdot 4H_2O$   | AFE                    | WFM                    | $\approx 235$                          | 17                     |  |
| 50. $\beta-Th_2(MoO_4)_3$      | FE                     | AFM                    |  | 2 <sup>181</sup>       |  |
| 51. $\beta-NaFeO_2$            | FE                     | WFM                    | 723 <sup>162</sup>                     | 723 <sup>162</sup>     |  |
| 52. $FeS$                      | FE                     | AFM                    | 411?                                   | $\approx 593$          |  |

Notes: The data marked with a question mark require more precise determination. Notation: Fe—ferroelectric, AFE—antiferroelectric, PE—pyroelectric, FM—ferromagnet, AFM—antiferromagnet, WFM—antiferromagnet with weak ferromagnetism, FIM—ferrimagnet,  $\chi^{ME}$ —static ME susceptibility,  $M_c$ —spontaneous magnetization,  $\vec{E}$ —amplitude of the alternating electric field,  $\epsilon$ —dielectric permittivity.

alternating bismuth-oxygen and perovskite-like packets with different numbers of octahedra in the packets (Fig. 2). The octahedral positions contain the ions  $Fe^{3+}$  and  $Ti^{4+}$ . The exchange interaction between the  $Fe^{3+}$  ions within a packet occurs along the chain of atoms  $Fe-O-Fe$  forming an angle  $\approx 180^\circ$ . The  $Fe^{3+}$  ions of adjacent pack-

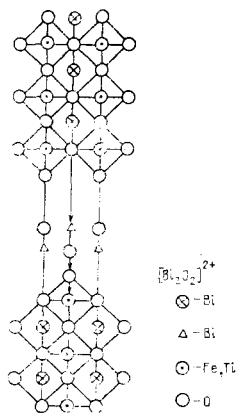


FIG. 2. Structure of the perovskite-like layered ferroelectromagnet having the general formula  $\text{Bi}_{m+1}\text{B}_m\text{O}_{3m+3}$ .<sup>16</sup>

ets are separated by a layer made of the diamagnetic ions  $\text{Bi}^{3+}$  and  $\text{O}^{2-}$ .

2. The hexagonal rare-earth manganites having the overall formula  $\text{RMnO}_3$ , where  $\text{R} = \text{Y}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu},$  or  $\text{Sc}$ , which were discovered by Bertaut and his associates,<sup>17</sup> are ferroelectromagnets with antiferromagnetic or weak ferromagnetic properties.<sup>18-20</sup> Their crystal structure is shown in Fig. 3. The trigonal bipyramids are connected by their vertices to form layers perpendicular to the sixfold axis. The Mn atoms lie inside the bipyramids, while the rare-earth atoms lie between the layers of bipyramids. The hexagonal structure in these compounds arises from the smallness of the ionic radii of the rare-earth ions and the presence of covalent Mn-O bonds.

3. The boracites—compounds with the general formula  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$ , where  $\text{M}$  is a bivalent metal ion,  $\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Cu},$  or  $\text{Ni}$ , and  $\text{X} = \text{Cl}, \text{Br},$  or  $\text{I}$ —are ferroelectric-antiferromagnets (some having weak ferromagnetism). The first ferroelectromagnetic boracites were synthesized and subsequently extensively studied by the Swiss physicists. In the high-temperature phase all the boracites have the cubic symmetry  $\bar{4}3m$ . Phase transitions arise with decreasing temperature in the sequence  $\bar{4}3m \rightarrow mm2 \rightarrow m \rightarrow 3m$ . In some compounds the

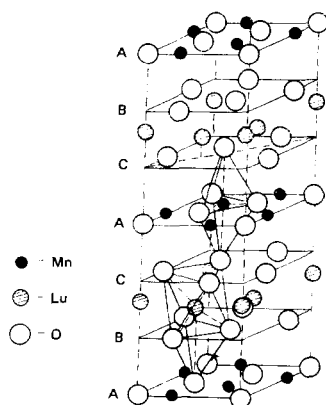


FIG. 3. Structure of the hexagonal manganite  $\text{LuMnO}_3$ .

$3m$  and/or the  $m$  phases do not appear. The transition to the orthorhombic phase  $mm2$  is accompanied in all the boracites by the onset of FE properties. In some cases this is an improper FE transition.<sup>21</sup> The magnetic ordering in the boracites arises at temperatures considerably below room temperature. In the Ni-I boracite the temperatures of the FE and the magnetic transitions apparently coincide,<sup>22-24</sup> and an improper FE transition takes place.<sup>25</sup>

4. The compounds  $\text{BaMF}_4$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) have an orthorhombic crystal structure in the high-temperature phase. The lattice of the isomorphous  $\text{BaMnF}_4$  and  $\text{BaCoF}_4$  consists of distorted  $\text{MF}_4$  octahedra connected by their vertices to form layers separated by the non-magnetic Ba ions. The  $\text{M}-\text{F}-\text{M}$  configuration in the layer is close to linear.<sup>26</sup> The  $\text{BaMF}_4$  compounds are pyro- or ferroelectrics. The temperatures of the FE transitions obtained by extrapolation lie above the corresponding melting points.<sup>27</sup> At high enough temperatures, antiferromagnetic or weak ferromagnetic ordering arises,<sup>28,29</sup> while antiferroelectric and ferroelectroelastic<sup>28,30</sup> properties can also arise.

In addition to the compounds listed above, there are ferroelectromagnetic compounds of other structural types. For example, the oxide ferroelectric-antiferromagnetic  $\text{Li}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_2\text{F}$  has a structure of the pseudolimonite type.<sup>31</sup> Antiferromagnetic ordering of helical type arises in the triclinic compound  $\text{Cr}_2\text{BeO}_4$  below 28 K, and apparently, simultaneously FE properties with a value of the spontaneous polarization 4-6 orders of magnitude smaller than in ordinary ferroelectrics.<sup>32</sup>

Table I gives the currently known ferroelectromagnetic compounds and indicates the type of electric<sup>2)</sup> and magnetic ordering and the corresponding temperatures of the electric ( $\Theta_E$ ) and magnetic ( $\Theta_M$ ) transitions. One can find a detailed bibliography on the crystal structure, the history of discovery of the ferroelectromagnetic properties, and other physical characteristics of the listed compounds in the earlier reviews.<sup>11,33-41</sup> Table I gives the literature reference only in the cases that contain new data. The classification presented in Table I characterizes the electric and magnetic properties of the materials. However, we must bear in mind the fact that the transition to the FE state is only a special case of transitions that occur with lowering of the crystal-lattice symmetry. The latter can, e.g., be accompanied by a transition to the ferroelectroelastic state: the appearance of a spontaneous deformation that can be switched by the action of mechanical stresses. Aizu<sup>42</sup> has classified the FE, ferromagnetic, and ferroelectroelastic properties in terms of the crystal-symmetry groups, and has indicated the groups that allow the coexistence of different types of ordering, in particular FE, magnetic, and ferroelectroelastic ordering simultaneously [the latter can exist, e.g., in the boracites and in terbium molybdate  $\beta\text{-Tb}_2(\text{MoO}_4)_3$ ].

<sup>2)</sup>Henceforth the expressions "electric order," "electric transition," etc., will be used instead of the more unwieldy "ferroelectric or antiferroelectric order," "ferroelectric or antiferroelectric transition," etc.

We shall restrict the treatment in this review to casting light on only the magnetic and electric properties of spontaneously polarized dielectric crystals, paying major attention to the magnetoelectric interaction. Thus far a considerable, weakly-interrelated theoretical and experimental material has been accumulated. A systematization of it can facilitate the elucidation and unification of the experimental and theoretical problems in the studies in this new field of solid-state physics.

## 2. THE NATURE OF MAGNETOELECTRIC (ME) INTERACTIONS

Landau and Lifshits have pointed out the possible existence in magnetically ordered crystals of an equilibrium electric polarization proportional to the magnetic-field intensity and of an equilibrium magnetization proportional to the electric-field intensity (linear magnetoelectric effect).<sup>43</sup> The linear magnetoelectric (ME) effect has been treated by Dzyaloshinskii<sup>44</sup> from the standpoint of magnetic symmetry. Magnetically ordered crystals showing a linear ME effect are commonly called magnetoelectrics. A considerable number of studies has been devoted to linear (and in recent years also nonlinear) ME effects in magnetoelectrics. Nonlinear ME effects can occur in any materials, not necessarily magnetically ordered. A ferroelectromagnet differs from the other materials in that it shows spontaneous ME effects in addition to the ME effects induced by external fields. They are caused by the existence in the crystal of spontaneous FE and magnetic moments. The existence of these gives rise to certain differences in the ME interactions in ferroelectromagnetics as compared with magnetoelectrics. Primarily this difference involves the magnitude of the ME interaction energy (ME energy).

In magnetically ordered crystals, the ME energy is induced by external fields, which weakly perturb the spin system. Yet if a spontaneous polarization arises in a magnetic crystal, then the spin subsystem will be strongly acted on by the internal electric field of the order of  $10^8$  V/cm that arises. The estimates show that the ME energy corresponding to such field values can be of the order of the exchange energy. Experimental evidence also exists that the ME energy in a ferroelectromagnet can be comparable with the magnitudes of the intrinsic spin and FE energies<sup>22, 45</sup> (see Sec. 5).

In order to characterize the ME interactions, we can conveniently classify them into two components: the magnetically isotropic exchange interaction and the anisotropic interaction.

### a. The exchange, magnetoisotropic ME energy

This energy describes the change in the isotropic exchange interaction when an electric polarization arises and the effect of the spin exchange field on the magnitude of the polarization of the crystal.

As a rule, the unit cell of a ferroelectromagnet is complicated. The magnetic cations are separated by nonmagnetic ions, and the exchange interaction is indirect. The ions of the lattice are displaced in FE

ordering. Generally this alters the equilibrium distances between the magnetic ions, i.e., alters the exchange integral. Moreover, owing to the Stark effect, the change in the electric field in the crystal in the FE transition perturbs the wave functions of both the magnetic electrons themselves, and of the electrons of the intermediate atoms participating in the indirect exchange. Consequently it alters the overlap of the electron wave functions, as well as the value of the transport integral of the magnetic electrons and the magnitude of the indirect exchange interaction. The existing theoretical studies of the mechanisms of ME interactions in ferroelectromagnetics are of a qualitative nature. In estimates it is convenient to assume, first, that the magnetic ions participate in the FE ordering as all the atoms of the lattice do, and second, that they are displaced by electrostriction. In the former case the change in exchange energy results from the direct interaction of the spin subsystem with the ferroelectric subsystem. In the latter case the interaction of the FE with the spin subsystem is mediated through the elastic subsystem. The latter mechanism will be discussed at the end of this section.

The stated mechanisms of the exchange ME interaction of a ferroelectromagnet correspond to the Helmholtz free energy density, which we shall represent as a power series in the projections of the electric moment  $\mathbf{P}(\mathbf{r})$  and magnetic moment  $\mathbf{M}_s(\mathbf{r})$  ( $s$  is the number of the magnetic sublattice):

$$F_{\text{ME}}^{\text{exch}} = - \left( \Gamma_{ss}^i P^i + \frac{1}{2} \gamma_{ss}^{ij} P^i P^j \right) \mathbf{M}_s \cdot \mathbf{M}_s + \dots \quad (2.1)$$

The first term in (2.1), which is linear in the polarization, can exist only in ferroelectromagnets with a noncentrosymmetric paraphase (we shall denote as a paraphase a phase in which  $\mathbf{P}=0$ ,  $\mathbf{M}_s=0$ ).

A numerical estimate of the phenomenological constants  $\gamma$  and  $\Gamma$  of the exchange ME interaction from dimensionality considerations yields ambiguous results owing to the considerable variation in the structural, magnetic, and FE characteristics of ferroelectromagnets: the magnitudes of the lattice constants, of the exchange integral, and of the electric polarization. The results of calculations<sup>46</sup> of the contribution of the indirect exchange interaction to the magnitude of the polarization of a ferroelectric-antiferromagnet lacking an inversion center yield the following order of magnitude for the constant  $\Gamma_{ss}^{ij}$ :  $\Gamma$ :

$$\Gamma \sim \frac{a_c d_0 N}{\mu^3 X_E} \left( \frac{\epsilon_{\text{exch}}}{\epsilon_{\text{coul}}} \right)^2.$$

Here  $a_c$  is the lattice constant,  $d_0$  is the atomic dipole moment,  $N$  is the density of magnetic ions,  $X_E$  is the dielectric susceptibility,  $\mu$  is the Bohr magneton,  $\epsilon_{\text{exch}}$  is the indirect exchange energy, and  $\epsilon_{\text{coul}}$  is the Coulomb energy.

We can write the Hamiltonian of the exchange ME interaction caused by the change in the distances between the magnetic ions in the FE transition in the form

$$\hat{H}_{\text{ME}}^{\text{exch}} = \sum_{i, k} \left[ V_{ik}^i (u_i^i - u_k^i) + \frac{1}{2} V_{ik}^{ij} (u_i^i - u_k^i) (u_i^j - u_k^j) \right] \hat{S}_i \hat{S}_k. \quad (2.2)$$

Here  $u_i^j$  is the  $j$ th projection of the displacement of the

$i$ th ion from the equilibrium position in the paraphase;  $V_{ik}^I$  and  $V_{ik}^{II}$  are the values of the first and second derivatives of the exchange integral with respect to the distance between the ions (in the equilibrium position). Our calculation using the Hamiltonian of (2.2) in the approximation of a molecular field and of nearest neighbors for a ferroelectromagnet with a displacement-type FE subsystem and a polarization along the  $j$  axis leads to the following relationship of the exchange parameter  $\gamma^{jj} = \gamma^j$  to the microscopic constants:

$$\gamma^j = -\frac{6V^j V_0^2(\Theta) \epsilon_b a_c^2}{z^2 \mu^2 a^3} \quad (2.3)$$

Here we have  $V^j = \sum_k V_{ik}^{jj}$  (summation over nearest neighbors),  $z$  is the charge of the ion,  $\Theta_E$  is the Curie temperature,  $b$  is the anharmonicity constant, and  $V_0$  and  $a$  are respectively the constants of the attraction and repulsion forces of the ions in the lattice (we follow the notation of Ref. 47). If we assume that  $z = 3 \times 10^{-10}$  CGSE units,  $a_c = 5 \times 10^{-9}$  cm,  $V_0 \approx a \sim \epsilon_{at} \cdot a_c^{-2}$  ( $\epsilon_{at}$  is the atomic energy),  $b \sim \epsilon_{at} \cdot a_c^{-4}$ ,  $\Theta_E \cdot \epsilon_{at}^{-1} \sim 10^{-2}$ ,  $V^j \sim a_c^{-2} \cdot I$  ( $I$  is the exchange integral between nearest neighbors) and  $I \sim 10^{-14}$  erg, we get the value  $\gamma^j \sim 10^{-7}$  dyne $^{-1}$  cm $^2$ .

The reverse effect—change in the polarization upon onset of magnetic order—can be treated as resulting from the Zeeman splitting of the levels by the exchange field. In turn, owing to the electron-phonon interaction, this is accompanied by displacement of the ions. Estimates of the exchange ME interaction parameter arising from this mechanism<sup>48</sup> yield a value  $\gamma \sim 10^{-7}$  dyne $^{-1}$  cm $^2$ .

### b. The anisotropic ME energy

This energy describes the change in the magnetic-anisotropy energy when an electric polarization arises, together with the action of the anisotropic magnetic field of the spins on the magnitude of the polarization.

The free energy of the anisotropic ME interactions can be represented as a series, each term of which is invariant with respect to the symmetry group of the paraphase of the crystal:

$$F_{ME}^{aniso} = -\left( \Lambda_{ss'}^{jll'} P^j + \frac{1}{2} \lambda_{ss'}^{jjl'l'} P^j P^{j'} \right) M_s^l M_{s'}^{l'} + \dots \quad (2.4)$$

One expects the largest value of the anisotropic ME energy in ferroelectromagnets having  $\Lambda \neq 0$ . In particular, for ferroelectric-ferromagnets this implies the necessary absence of a symmetry center in the paraphase.

The terms having  $s = s'$  in (2.4) describe the change in the energy of single-ion magnetic anisotropy under the action of the FE subsystem. One of the mechanisms of this change is the following: in FE ordering the varying internal electric field gives rise to a Stark splitting of the electron levels of the magnetic ions by altering the spin-orbital and spin-spin interactions, and hence also altering the energy of the single-ion magnetic anisotropy.<sup>49</sup> The ME energy corresponding to the second term in (2.4) arises in the fourth approximation of perturbation theory: the second approximation in the spin-orbital interaction and the second in the Stark effect<sup>49,50</sup>:

$$E_{ME} \sim \frac{(zEx)^2 \xi^2 S^2 L^2}{\Delta_1 A_2^2}$$

Here  $(zEx)$  is the FE energy,  $\xi$  is the spin-orbital interaction constant,  $S$  is the spin,  $L$  is the orbital angular momentum,  $\Delta_1$  is the exchange energy, and  $\Delta_2$  is the Coulomb coupling energy. For values of  $zEx \sim 10^{-13}$  erg,  $\xi \sim 10^{-14}$  erg,  $\Delta_1 \sim 10^{-14}$  erg, and  $\Delta_2 \sim 10^{-11}$  erg, we obtain  $E_{ME} \sim 10^{-18}$  erg, or  $10^4$ – $10^5$  erg·cm $^{-3}$  (for  $a_c^3 \sim 10^{-22}$ – $10^{-23}$  cm $^3$ ). If we assume that  $P^2 \sim 10^9$  CGSE units, and  $M^2 \sim 10^5$  G $^2$ , then the value of the anisotropic ME interaction constant  $\lambda_{ss}$  will be of the order of  $10^{-9}$ – $10^{-10}$  dyne $^{-1}$  cm $^2$ .

If the crystal contains several magnetic sublattices, then, as we know, they have an anisotropic interaction energy, which is a combination of the spin-orbit energy with the indirect-exchange and crystal-field energies. The change in this energy in the presence of a FE subsystem is described in (2.4) by the terms with  $s \neq s'$ .

In addition to the mechanisms mentioned above, a source of the isotropic and anisotropic ME energies can be the electromagnetoelastic interaction.<sup>49</sup> The existence in the crystal of the elastic subsystem causes the FE ordering to be accompanied by electrostriction, which changes the dimensions of the crystal. In turn, owing to the magnetostrictive interaction, this alters the magnetic state and vice versa. The state of the elastic subsystem is characterized by the strain tensor  $u_{ik}$ , and the free energy that depends on  $u_{ik}$  is equal to

$$F = F_1(u_{ik}) + F_2(P, u_{ik}) + F_3(M, u_{ik}) + F_4(u_{ik}, \sigma_{im}) + \dots$$

Here  $F_1$ ,  $F_2$ , and  $F_3$  are respectively the elastic, electroelastic, and magnetoelastic free energies.  $F_4$  is the energy of the external stresses  $\sigma_{im}$ . Minimization of the free energy with respect to  $u_{ik}$  followed by substitution of their equilibrium values into  $F$  yields an expression for the ME energy that is quadratic in the moments, and which consists of an isotropic exchange component of the type of (2.1) and of anisotropic terms of the form of (2.4). In order of magnitude we have  $F_{ME} \sim c u_M \mu_E$ , where  $c$  is the elastic constant,  $u_E$  is the electrostriction, and  $u_M$  is the magnetostriction. If we assume that  $c \sim 10^{12}$  erg·cm $^{-3}$ ,  $u_E \sim 10^{-3}$ – $10^{-2}$ , and  $u_M \sim 10^{-5}$ – $10^{-4}$ , then we obtain  $F_{ME} \sim 10^4$ – $10^6$  erg·cm $^{-3}$ . In compounds containing rare-earth ions, where the magnetostriction can reach values  $u_M \sim 10^{-3}$ , the magnitude of  $F_{ME}$  can be of the order of  $10^7$  erg·cm $^{-3}$ . That is, the electromagnetoelastic energy can play a substantial role in materials having a large electrostriction and magnetostriction.

The specific ME interaction is electrostatic in nature, while an anisotropic ME energy arises only when we take spin-orbital coupling into account. Therefore, in crystals in which the exchange energy predominates over the magnetic-anisotropy energy, we can expect that  $F_{ME}^{exch} \gg F_{ME}^{aniso}$  (this relationship holds, e.g., in Cr $_2$ O $_3$ <sup>51</sup>).

### 3. THERMODYNAMIC THEORY

One can describe the equilibrium properties of a crystal in the ferroelectromagnetic phase within the framework of the Landau theory by using an expansion of the free energy in powers of the electric and magnetic moments that is invariant with respect to the sym-

metry group of the paraphase. Strictly speaking, such an expansion can be applied when the temperature of the FE ( $\Theta_E$ ) and magnetic ( $\Theta_M$ ) transitions lie close together. In the general case the values of  $\Theta_E$  and  $\Theta_M$  differ, and the ferroelectromagnetic phase can be separated from the paraphase by a considerable temperature interval. However, if there are no structural transitions in this temperature interval, then as before, we can expand the free energy in powers of the moments to describe the thermodynamic properties of the ferroelectromagnet.

The presence of any type of invariants in the free energy is determined by the symmetry group of the paraphase. If the symmetry of any subgroup of this group allows the simultaneous existence of  $\mathbf{P} \neq 0$  and  $\mathbf{M}_s \neq 0$ , then a transition to the ferroelectromagnetic state can occur. One can find in the literature an enumeration of the classes among which one can expect in a transition the joint realization of FE and of ferromagnetic ordering,<sup>52</sup> an indication of the classes<sup>53-56</sup> and space groups<sup>57-59</sup> that allow ferroelectromagnetic structures that combine various magnetic and FE properties, and an analysis of the directions of  $\mathbf{P}$  and  $\mathbf{M}$  in the domain and the types of domain walls.<sup>60</sup> Cases have been studied in which the symmetry of the crystal allows exchange ME invariants that are linear in the polarization.<sup>61</sup>

### a. Thermodynamic relationships

The group-theoretical approach enables one to find the form of the free energy and the equilibrium orientations of the moments. However, the question remains open of the phase transitions between the different equilibrium states, of the temperature-dependence of the thermodynamic characteristics of the crystal, and of its behavior in external fields. In ferroelectromagnets, along with the magnetic and dielectric susceptibilities one employs the concept of the magnetoelectric susceptibility, which characterizes the change in the magnetization under the action of an electric field, and in the polarization under the action of a magnetic field. The responses of the system to the action of an external field  $\mathbf{E}$  and magnetic field  $\mathbf{H}$  is described by the generalized susceptibility tensor

$$\hat{X} = \begin{pmatrix} \hat{X}^E & \hat{X}^{EM} \\ \hat{X}^{ME} & \hat{X}^M \end{pmatrix}.$$

Here  $(X^E)_{ik} = X^E_{ik}$ ,  $X^M_{ik}$ , and  $X^{EM} = X^{ME}$  are respectively the second-order tensors of the dielectric, magnetic, and magnetoelectric susceptibilities:

$$\begin{aligned} X^E_{ik} &= \frac{\partial P_i}{\partial E_k}, & X^{EM}_{ik} &= \frac{\partial P_i}{\partial H_k}, \\ X^{ME}_{ik} &= \frac{\partial M_i}{\partial E_k}, & X^M_{ik} &= \frac{\partial M_i}{\partial H_k} \quad (i, k = 1, 2, 3). \end{aligned} \quad (3.1)$$

The components of the generalized susceptibility tensor can be expressed in terms of the derivatives of the thermodynamic potential  $\Phi = \Phi(\mathbf{P}, \mathbf{M}_s)$  with respect to the components of the FE and magnetic moments. A ferroelectric-ferromagnet obeys the relationships<sup>62</sup>

$$\begin{aligned} \hat{X}^M &= [\hat{A} - \hat{C}\hat{B}^{-1}\hat{C}]^{-1}, & \hat{X}^E &= [\hat{B} - \hat{C}\hat{A}^{-1}\hat{C}]^{-1}, \\ \hat{X}^{EM} &= \hat{X}^{ME} = [\hat{C} - \hat{A}\hat{C}^{-1}\hat{B}]^{-1}. \end{aligned} \quad (3.2)$$

Here we have

$$A_{ik} = \frac{\partial^2 \Phi}{\partial M_i \partial M_k}, \quad B_{ik} = \frac{\partial^2 \Phi}{\partial P_i \partial P_k}, \quad C_{ik} = \frac{\partial^2 \Phi}{\partial M_i \partial P_k}$$

In the simplest case in which the directions of the external fields and of the FE and magnetic moments coincide, we can easily convince ourselves that the conditions that  $\Phi(P, M)$  and the expressions (3.2) should be a minimum imply that the electric and magnetic susceptibilities are positive and also yield the inequality

$$(X^{ME})^2 < X^E X^M. \quad (3.3)$$

The condition (3.3) defines the upper bound of the absolute magnitude of the ME susceptibility ( $X^{ME}$  can have either sign). This implies that we should expect the largest value of  $X^{ME}$  in crystals having large values of  $X^E$  and  $X^M$ , i.e., in ferroelectric-ferromagnets.<sup>63</sup>

### b. Phase transitions in the absence of external fields

Generally a ferroelectromagnet possesses two temperature transitions: a ferroelectric transition  $\Theta_E$  and a magnetic transition  $\Theta_M$ . These temperatures can coincide if the FE transition is improper and is induced by the magnetic transition. In this case the ME interaction energy contains terms that are even in the magnetic moments and odd in the components of the polarization vector. This can imply the appearance of a  $P \sim M^2$  at a temperature below  $\Theta_M$  (an improper FE transition<sup>64</sup>). Such a transition occurs in nickel-iodine boracite. In particular, an improper FE transition can arise with magnetic ordering of helical type if the ME energy contains terms of the form  $P_i M'_s (\partial M'_s / \partial x_k)$ . It is likely that such a transition occurs in the ferroelectric-antiferromagnet  $\text{Cr}_2\text{BeO}_4$ , which has a helical magnetic structure and a centrosymmetric  $D_{2h}^{16}$  paraphase<sup>3,32</sup>.

The temperatures of the FE and magnetic transitions can also coincide when there are no invariants linear in  $P$  in the ME energy for a sufficiently large value of the ME interaction. Here the phase transition is first-order.<sup>65</sup>

The following results have been obtained in studying the second-order temperature phase transitions in a ferroelectromagnet<sup>49,62,66</sup>: 1) fulfillment of the "twinning law" for  $T = \Theta_E < \Theta_M$ , just as for an ordinary FE transition; 2) appearance of a break in the temperature-dependence of the magnet (FE) susceptibility at the temperature of the FE (magnetic) transition; 3) a jump in the magnetic (FE) susceptibility at the temperature of the FE (magnetic) transition. The latter effect is analogous, e.g., to the jumps in the heat capacity and in the elastic moduli in second-order phase transitions.

The break in the temperature-dependence of the susceptibility is a first-order effect with respect to the ME interaction, while the jump is a second-order effect. Owing to the break in the temperature-dependence  $X^M(T)$  at  $T = \Theta_E$ , the values of the magnetic susceptibility below  $\Theta_E$  will differ from the values obtained by extrapolation into the region  $T < \Theta_E$  of the temperature-dependence.

<sup>3)</sup>We view as erroneous the opinion<sup>32</sup> that the observed improper FE transition results from the loss by the crystal of a center of symmetry in the magnetic transition.



dence  $X^M(T)$  from the paraelectric phase. We shall denote this difference below as  $\Delta X^M$ . Whenever  $\Theta_E$  and  $\Theta_M$  are separated widely enough (so that we can neglect the dependence of the magnetic parameters on the temperature near  $\Theta_E$ ), this difference will increase in absolute magnitude as a function of the temperature proportionally to the square of the spontaneous polarization:

$$\Delta X^M \sim P^2(T) \quad (T \ll \Theta_E).$$

Analogously the change in the dielectric permittivity  $\Delta\epsilon = 4\pi\Delta X^E$  for  $T < \Theta_M < \Theta_E$  will be proportional to the square of the magnetic-order parameter:

$$\Delta\epsilon \sim M^2(T) \quad (T \ll \Theta_M).$$

The sign of  $\Delta X^M$  ( $\Delta\epsilon$ ) depends on the sign of the constant ME interaction, and can have either value.

As we have pointed out above, the appearance of  $\Delta X^M$  ( $\Delta\epsilon$ ) below  $\Theta_E$  (or  $\Theta_M$ ) is a first-order effect with respect to the ME interaction. Therefore we should expect first of all an experimental confirmation of this effect, rather than of the weaker jump in the susceptibility, which is second-order in the interaction. Actually, the ferroelectromagnets manifest precisely a break, rather than a jump, in the dielectric permittivity at the temperature of the magnetic transition (see Sec. 5). Study of the temperature-dependence of  $\Delta X^M$  ( $\Delta\epsilon$ ) at  $T \leq \Theta_E$  ( $\Theta_M$ ) can yield information on the critical index of the order parameter that arises.

An analysis of the temperature-dependence of the ME susceptibility near the temperatures of second-order phase transitions within the framework of the Landau theory shows that, if  $\Theta_E < \Theta_M$ , then near  $\Theta_E$  we find  $X^{EM} \sim (\Theta_E - T)^{-1/2}$ .<sup>62,66</sup> When  $\Theta_M < \Theta_E$ ,<sup>67</sup> we have

$$X^{ME} \sim (\Theta_M - T)^{k-1}.$$

Here  $k \geq \frac{1}{2}$  is the exponent in the temperature-dependence of the magnetization  $\mathbf{m} = \sum_s \mathbf{M}_s$  ( $s$  is the number of the magnetic sublattice), and  $m \sim (\Theta_M - T)^k$ . The exponent is  $k = \frac{1}{2}$  for a ferromagnetic transition or a transition to a weakly ferromagnetic phase whose magnetization arises from invariants of second order in the thermodynamic potential. Here the ME susceptibility is anomalously high near the second phase-transition temperature  $\Theta_M$ :  $X^{ME} \sim (\Theta_M - T)^{-1/2}$ . Yet if the weak ferromagnetic moment arises from fourth-order invariants, then we have  $k = \frac{3}{2}$  and  $X^{ME} \sim (\Theta_M - T)^{1/2}$ .

The results presented above pertain to the case of second-order phase transitions. However, most of the known FE transitions are first-order transitions, or else first-order close to second. As we know, in order to describe them, we must take into account the thermodynamic potential of sixth-order terms in the order parameter. In particular, in treating temperature transitions described by two order parameters, it is essential to take into account sixth-order anharmonicity in analyzing the singular points in the phase diagram.<sup>68</sup>

### c. Ferroelectromagnets in external fields

The static ME susceptibility of (3.1) describes the response of the ferroelectromagnet to constant external

electric and magnetic fields. These fields can also shift the phase-transition temperature. The change in the temperature  $\Theta_M$  of the magnetic transition under the action of an external electric field  $\mathbf{E}$  for a ferroelectromagnet having  $\Theta_M < \Theta_E$  is<sup>49</sup>

$$\frac{\partial \Theta_M}{\partial E_i} = - \frac{\partial \alpha}{\partial P^2} \left( \frac{\partial \alpha}{\partial T} \right)^{-1} \sum_{h=1}^3 2P_{0h} X_{hi}^E. \quad (3.4)$$

Here  $P_0$  is the spontaneous polarization, and  $\alpha = \alpha(P^2, T)$  is the coefficient of the  $\mathbf{M}^2$  term in the thermodynamic potential. Equation (3.4) implies that the magnitude of the shift in  $\Theta_M$  is linear in the field  $E$  and is proportional to the first power of the constant exchange ME interaction.

Just like certain magnetic crystals, ferroelectromagnets can exhibit a piezomagnetoelectric effect,<sup>49,69</sup> which consists of the appearance of a deformation  $u_{ih}$  under the simultaneous action of electric and magnetic fields:

$$u_{ih}^{EM} = \pi_{ihjl} E_j H_l. \quad (3.5)$$

The piezomagnetoelectric coefficients  $\pi_{ihjl}$  are related to the tensors of the piezomoduli  $d_{ihj}$  and to the tensor of the coefficient  $D_{ihl}$  of the magnetostrictive para-phase by

$$\pi_{ihjl} = \frac{\partial d_{ihj}}{\partial H_l} = \frac{\partial D_{ihl}}{\partial E_j}. \quad (3.6)$$

These relationships can be verified experimentally by measuring in the same single crystal the dependences of the electroelastic deformations (piezomoduli) on the magnetic field  $\mathbf{H}$  and of the magnetostriction on  $\mathbf{E}$ .

The ME interaction can alter the type of phase transition, and can also induce additional transitions in the magnetic and FE subsystems.<sup>70,71</sup>

Let us write the thermodynamic potential of a uniaxial ferroelectromagnet having  $\Theta_E < \Theta_M$  far from the magnetic-transition temperature in the form

$$\Phi = - \frac{1}{2} \beta M_z^2 - \mathbf{M}\mathbf{H} - \frac{1}{2} \kappa P^2 + \frac{1}{4} \delta P^4 - \frac{1}{2} \lambda P^2 M_z^2. \quad (3.7)$$

Here we have  $P = P_z$  ( $z$  is the easy ferroelectric and magnetic axis),  $\beta$  is the magnetic anisotropy constant,  $\kappa$  is the FE constant, and  $\lambda$  is the anisotropic ME interaction constant. Since we can consider  $\mathbf{M}^2$  to be a constant when far from the magnetic-transition temperature, the exchange ME interaction having the energy  $(-\frac{1}{2})\gamma M^2 P^2$  only renormalizes the FE constant:  $\kappa = \kappa_0 + \gamma M^2$  ( $\kappa_0$  is the value of  $\kappa$  in the paraphase).

If the constant  $\lambda$  of the anisotropic ME interaction in Eq. (3.7) is positive, then a second-order transition from the FE to the paraelectric state can occur near the temperature of the FE transition as a magnetic field is applied (Fig. 4). When  $\lambda < 0$  the reverse effect takes place: induction of polarization by a magnetic field  $H > H_c$  at a temperature  $T \approx \Theta_E$ .<sup>4)</sup> These effects imply a shift in the Curie temperature  $\Theta_E$  in a magnetic field by the amount

<sup>4)</sup> Analogous effects also arise upon rotating the magnetic field by 90°. <sup>72</sup>

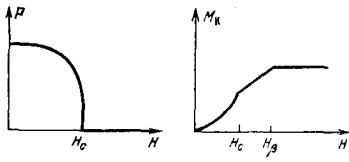


FIG. 4. A possible dependence of the electric polarization and the magnetization on the value of the magnetic field.<sup>70</sup>  $M_{||}$  is the projection of the magnetization on the direction of a magnetic field perpendicular to the spontaneous magnetic moment.

$$\Delta\Theta_E = \Theta_E(H) - \Theta_E(0) = -\lambda H^2 C (2\pi\beta^2)^{-1}. \quad (3.8)$$

Here  $C$  is the Curie-Weiss constant.

In turn, the FE transition in the field  $H_c$  induces an additional second-order transition in the magnetic subsystem (see Fig. 4). The magnitude of the transition field  $H_c$  is smaller than the magnetic anisotropy field  $H_\beta$ .

When a magnetic field is applied far from  $\Theta_E$  ( $T < \Theta_E$ ), the magnetic phase transition in the field  $H_\beta$  can also be altered by the influence of the ME interaction. If the constants  $\lambda$  and  $\beta$  in (3.7) have opposite signs, then the FE transition can be accompanied by a reorientation of the spontaneous magnetic moment from the easy axis to the basal plane or vice versa ("easy magnetic axis" -- "easy magnetic plane" transition), owing to the re-normalization of the magnetic anisotropy constant due to the ME interaction ( $\beta - \beta + \lambda P_0^2$ ).

#### d. Phase transitions in a Ferroelectric-antiferromagnet in a magnetic field

The phase diagram of a ferroelectric-antiferromagnet in a magnetic field differs appreciably from the phase diagrams of noninteracting FE and magnetic subsystems.<sup>73,74</sup> Let us write the thermodynamic potential of a uniaxial ferroelectric-antiferromagnet having two magnetic sublattices and temperature of the magnetic and FE transitions that do not lie close together ( $\Theta_M > \Theta_E$ ) in the form

$$\Phi = \Delta (M_1 M_2) - H (M_1 + M_2) - \frac{1}{2} \beta (M_1^2 + M_2^2) - \beta_1 M_{1z} M_{2z} - \frac{1}{2} \kappa_0 P^2 + \frac{1}{4} \delta P^4 - \frac{1}{2} \gamma P^2 (M_1 M_2). \quad (3.9)$$

The last term in (3.9) describes the exchange interaction of the FE and antiferromagnetic subsystems. It is contained in the thermodynamic potential of any ferroelectric-antiferromagnet, independently of its symmetry. In (3.9) we have omitted the weaker relativistic terms, which can lead to a linear ME effect in crystals having a certain symmetry.

Figure 5 shows the equilibrium states of a ferroelectric-antiferromagnet of the "easy magnetic axis" type in a magnetic field parallel to the easy axis  $z$  as a function of the magnitude of the field and of the FE parameter  $\kappa$ . The value of  $\kappa$  increases with decreasing temperature, and here we assume that the  $\kappa(T)$  relationship is linear:

$$\kappa = \kappa_0 - \gamma M_0^2 = 2\pi C^{-1} (\Theta_E^0 - T). \quad (3.10)$$

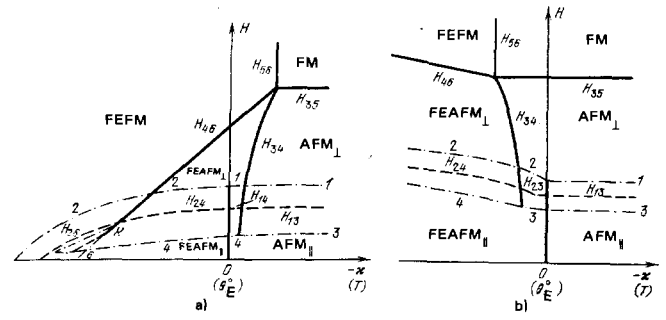


FIG. 5. Equilibrium states of a uniaxial ferroelectric-antiferromagnet in the case  $\gamma > 0$ ,  $\delta > 0$ ,  $\beta + \beta_1 > 0$ ,  $3\gamma^2 M_0^2 \delta^{-1} < \beta - \beta_1$  (a), and in the case  $\gamma > 0$ ,  $\delta > 0$ ,  $\beta + \beta_1 > 0$  (b).<sup>75</sup> The dot-dash lines and the numbers indicate the boundaries of the phases with the given number,  $H_{ik}$  is the field for the phase transition between the  $i$ th and  $k$ th phases. The curves for the second-order phase transitions are denoted by heavy lines, and those of first-order by dotted lines. For perspicuity the spin-reversal region is drawn on an enlarged scale.

Here  $M_0$  is the magnetization of the sublattice, and  $\Theta_E^0$  is the temperature of the FE transition at  $H=0$ . In the symbols for the phases in the diagrams, FE denotes ferroelectric, FM ferromagnetic, and AFM antiferromagnetic order. The subscript indicates the orientation of the antiferromagnetism vector with respect to the  $z$  axis. The purely magnetic states have odd numbers, and the ferroelectromagnetic states even numbers, namely: 1) AFM<sub>||</sub>; 2) FEA FM<sub>||</sub>; 3) AFM<sub>⊥</sub>; 4) FEA FM<sub>⊥</sub>; 5) FM; 6) FEFM.

In the absence of a ME interaction, the phase diagram far from  $\Theta_M$  would consist of the vertical line of the second-order FE transition  $T = \Theta_E^0$ , and the two horizontal lines of the magnetic transitions:  $H = H_{13}$  (spin reversal, spin-flop) and  $H = H_{35}$  (transition to the ferromagnetic phase). As we see from the diagrams, the ME interaction complicates the diagram and enriches it with new phase transitions. Extra lines have appeared for the FE ( $H_{46}$ ) and magnetic ( $H_{34}$ ) second-order phase transitions, which occur both with varying magnetic field and varying temperature. The possibility has arisen of a phase transition from the antiferromagnetic to the ferroelectric-ferromagnetic state with decreasing temperature. When  $\gamma > 0$  the transition from the ferroelectric-antiferromagnetic state to the ferroelectric-ferromagnetic state at low temperatures becomes a first-order transition, and the critical point  $K$  of the second-order transitions arises on the phase diagram. With decreasing temperature the spin reversal is replaced by a transition of the metamagnetic type ( $H_{24} - H_{26}$ ).

Both the spin-flop and the metamagnetic transition are accompanied by a jump in the electric polarization. That is, they induce a first-order transition between two FE phases. Replacement of the FE transition by a first-order transition occurs near the reversal field and the temperature  $\Theta_E^0$ .

If we neglect the paraprocesses, the temperature of the second-order FE transition varies in magnetic fields larger than the reversal field in proportion to the square of the magnetic field intensity:

$$\Theta_E - \Theta_E^0 = \gamma H^2 \pi^{-1} (2\Delta)^{-2} C. \quad (3.11)$$



The shift in  $\Theta_F$  quadratic in the field arises from the exchange ME interaction. The relativistic ME energy omitted in (3.9) can give rise to a linear shift in  $\Theta_F$  in a magnetic field,  $\Delta\Theta_F \sim H$ . This can happen in ferroelectric-antiferromagnets whose symmetry allows a ME interaction energy linear in the magnetization, i.e., in particular, in crystals having a linear ME effect.

The results given above do not exhaust all the variety of the phase transitions inducible by the ME interaction. In particular, an "easy magnetic axis"—"easy magnetic plane" transition can occur upon onset of FE ordering in an antiferromagnet owing to the renormalization of the magnetic-anisotropy constant by the ME interaction energy.<sup>75</sup>

#### 4. THEORY OF THE HIGH-FREQUENCY PROPERTIES OF FERROELECTROMAGNETS

##### a) Spectrum of elementary excitations

At low temperatures ( $T \ll \Theta_F, \Theta_M$ ), small oscillations of the electric and magnetic moments with respect to the equilibrium positions propagate as spin waves and polarization waves, which prove to be coupled via the ME interaction. The quanta of these coupled oscillations are called ferroelectromagnons.<sup>76</sup>

The ferroelectromagnon spectrum has been studied theoretically to a greater degree than other properties of ferroelectromagnets. Without presenting the explicit expressions for the spectrum, we shall merely formulate the fundamental results and make preliminary numerical estimates employing the values of the parameters of the ME interaction  $\gamma$  and  $\lambda$  that were introduced in the last section. Here the possibility is not ruled out of overestimating or underestimating the magnitude of the effect, since the values of these parameters can apparently vary over a considerable range.

The spin waves are coupled very weakly with the polarization waves in ferroelectric-ferromagnets.<sup>76-78</sup> Here the ME coupling arises via the relativistic interactions, while the value of the homogeneous ferromagnetic resonance is considerably smaller than the optical frequency, so that the noninteracting branches can cross only near the boundary of the Brillouin zone. The ME interaction shifts the frequency of the polarization waves to a considerably smaller extent than it does the spin frequency, the greatest relative change in which is of the order of  $(\Delta\omega_c/\omega_c) \sim \lambda^2 M_0^2 (\delta\beta)^{-1}$ . For the values  $\lambda \sim 10^{-9}$  dyne<sup>-1</sup> cm<sup>2</sup>,  $M_0^2 \sim 10^5$  G<sup>2</sup>,  $\delta \sim 10^{-11}$  dyne<sup>-1</sup> cm<sup>2</sup>, and  $\beta \sim 1$ , we have  $\Delta\omega_c \sim 10^{-2} \omega_c$ . Along with this, the ME interaction causes the low-frequency branch of the ferroelectromagnon spectrum to cease to be a pure spin spectrum, as an admixture of FE oscillations arises in it. The ratio of the amplitudes of the polarization and magnetization in this wave is<sup>79</sup>:

$$\frac{p}{m} \sim \frac{\lambda}{\delta} \frac{M_0}{P_0} \sin 2\theta. \quad (4.1)$$

Here  $\theta$  is the angle between the equilibrium moments  $\mathbf{M}_0$  and  $\mathbf{P}_0$ . Using the values of the parameters given above and assuming that  $M_0 P_0^{-1} \sim 10^{-2}$ , we obtain  $p/m \sim \sin 2\theta$ . In a field of the order of the magnetic-anisotropy field, the amplitude of the polarization in the low-

frequency branch  $\omega_1$  is of the order of the amplitude of the magnetization. Here one can expect an effect of enhancement of the intensity of Raman scattering of light at the frequencies  $\omega \pm \omega_1$ .

In ferroelectromagnets having two (or more) magnetic sublattices the coupling of the spin waves and the polarization waves can be greater than in a ferroelectric-ferromagnet, since it arises not only from the relativistic, but also from the exchange ME interaction<sup>80,84</sup>:

$$F_{ME} = -\frac{1}{2} \gamma P^2 (\mathbf{M}_1 \mathbf{M}_2) + \frac{1}{2} P^2 (\lambda_1 M_{1z} + \lambda_2 M_{2z} + \lambda_3 M_{3z}). \quad (4.2)$$

The free energy in (4.2) describes the ME interaction in a uniaxial crystal having no weak ferromagnetism. It leads to a coupling of the FE and spin oscillations only in the case of a noncollinear orientation of the spins in the ground state. This noncollinearity can be created, e.g., by an external magnetic field.

In a ferroelectric-antiferromagnet with an orientation of the magnetic field along the easy axis or in the base plane, an ME interaction of the form of (4.2) couples the polarization waves only with the lower spin branch  $\omega_{1c}$ . The magnitude of this coupling depends on the magnetic field. The variation of the FE frequency is small even in strong magnetic fields, while the relative variation in the frequency of the lower spin branch is  $(\Delta\omega_{1c}/\omega_{1c}) \sim (H/H_c)^2$ , where  $H_c$  is the exchange field. In contrast to a ferromagnet, where we always have  $\Delta\omega_c \ll \omega_c$ , in an antiferromagnet  $\Delta\omega_c$  can be of the order of  $\omega_c$ , but only in very strong fields of the order of the exchange fields. The "admixture" of FE oscillations in the lower branch of the spectrum is the following:

$$\frac{p}{m} \sim \frac{H}{H_m}, \quad \frac{p}{l} \sim \sqrt{\frac{\beta}{\Delta}} \frac{H}{H_m}. \quad (4.3)$$

Here  $l$  is the amplitude of the oscillations of the antiferromagnetism vector,  $\Delta$  is the exchange constant, and  $H_m = (\delta P_0 / \gamma M_0) H_c$ . Estimates of the field  $H_m$  with the values of the parameters given above show that the field  $H_m \sim 10^{-2} H_c$ , i.e., considerably smaller than the exchange field.

If a ferroelectric-antiferromagnet can possess a weak ferromagnetism, then we should add to the ME interaction energy of (4.2) the corresponding anisotropic terms, e.g.,  $\Delta \mathbf{P} \cdot (\mathbf{M}_1 \times \mathbf{M}_2)$ .<sup>81</sup> It turns out,<sup>82</sup> in contrast to (4.2), that this interaction couples the FE oscillations with the upper spin branch  $\omega_{2c}$ , rather than coupling with  $\omega_{1c}$ . Since the spins are noncollinear in the weakly ferromagnetic state, the coupling arises even in the absence of a magnetic field. The fact that ME interactions of the form of (4.2) and ME interactions of the Dzyaloshinskii type couple the FE oscillations with different branches of the spin spectrum, one of these showing coupling even in the absence of an external magnetic field, can be employed for studying separately the magnitudes of these interactions.

We note that the ME energy of (4.2) does not give rise to a gap in the activationless antiferromagnetic branch (e.g., in  $\omega_{1c}$  in the case of "easy magnetic plane" (EMP) anisotropy). However, a gap can appear in ferroelectric-antiferromagnets owing to the ME interaction.<sup>83,84</sup> This effect is analogous to the appear-

ance of an activation frequency in the magnetic spectrum of antiferromagnets owing to the magnetoelastic<sup>85</sup> or ME interaction.<sup>86</sup> In contrast to antiferromagnets, where the magnitude of the ME gap is proportional to the external electric field, in ferroelectric-antiferromagnets an ME gap exists even in the absence of an electric field. According to the estimates of Ref. 83 the contribution of the ME interaction to the magnitude of the gap can exceed that from the magnetoelastic interaction by an order of magnitude or more.

The presence of the ME gap in the spin-wave spectrum gives rise to the effect of exchange amplification of the dynamic relativistic ME coupling in ferroelectric-antiferromagnets,<sup>84</sup> which is analogous to the phenomenon of exchange amplification of the magnetoelastic coupling in antiferromagnets.<sup>85</sup>

We should expect the greatest coupling of the spin waves with the polarization waves in ferroelectric-ferrimagnets.<sup>87</sup> Here the polarization oscillations at the frequency  $\omega_E$  are coupled not only with the lower but also with the upper branch  $\omega_{2c}$  of the spin waves. This coupling is greater by a factor of  $\Delta/\beta \sim 10^2$  than in a ferroelectric-antiferromagnet. The increase in the coupling arises from the approach of the interacting branches: just like  $\omega_E$ , the frequency  $\omega_{2c}$  lies in the infrared range. This implies the possibility of a resonance interaction of the FE and the upper spin waves, e.g., whenever their frequencies approach one another as  $\omega_E$  declines near the temperature of a FE transition. In ferroelectric-ferro(antiferro) magnets, owing to the considerable remoteness of the frequencies  $\omega_E$  and  $\omega_c$  from one another, a resonance interaction between them seems unlikely.

The spin and polarization waves in a ferroelectromagnet interact not only among themselves, but also with other elementary excitations of the crystal. Owing to the electro- and magnetoelastic interactions, a coupling arises of the ferroelectromagnons with acoustic phonons,<sup>88,89</sup> and owing to the electric and magnetic dipole interactions—with electromagnetic waves.<sup>88,90</sup> Study of these interactions can yield information on the ferroelectromagnon spectrum and on the role of the ME energy therein. In particular, the ME interaction must alter the scattering cross-sections for light and neutrons by polarization and spin waves.<sup>91</sup> This alteration is maximal under resonance conditions, when the FE and spin frequencies coincide.

The concept of the role of ME interactions in relaxation processes is essential for the experimental study of the spectrum and other high-frequency properties of ferroelectromagnets. The problem of the effect of the ME energy on the lifetime of a FE phonon and of a magnon has been little studied. The existing calculations of the probabilities of absorption of a FE phonon by a spin wave, of scattering of a spin wave by a FE phonon in a ferroelectric-ferromagnet,<sup>92</sup> and of decay of a FE phonon into two spin waves in a ferroelectric-antiferromagnet<sup>93</sup> allow us to assume that the ME interaction can contribute appreciable to relaxation processes.

## b) Behavior in variable external fields

By affecting the spectrum and character of the spin and FE oscillations, the ME interaction introduces features into the behavior of a ferroelectromagnet in variable external fields. Possibilities arise of resonance absorption of the energy of an alternating magnetic field at the FE frequency and of resonance absorption of electric energy at the spin-wave frequency.<sup>76-78,87,94</sup> The magnitude of this absorption is determined by the anti-Hermitian component of the tensor of the high-frequency ME susceptibility [in the absence of dissipation we have  $X_{im}^{EM}(\mathbf{k}, \omega) = X_{mi}^{ME}(\mathbf{k}, \omega)$ ].

The greatest amount of absorption of the energy of an electric (or magnetic) field at the spin (or FE) frequency can occur when the resonance frequencies  $\omega_E$  and  $\omega_c$  lie close. In a ferroelectric-ferrimagnet having  $\Theta_M > \Theta_E$  and  $\omega_E > \omega_{2c}$ , the FE and upper-spin-branch frequencies can approach one another near the Curie temperature  $\Theta_E$ , where the frequency of the soft FE mode falls appreciably. In order to decrease the activation polarization frequency  $\omega_{E0} \sim P_0$ , one can also employ a second-order FE transition in a magnetic field (see Sec. 3). Near resonance, the ratio of the amount of absorption of the energy of the electric field at the spin frequency to the amount of absorption at the FE frequency ( $K_E$ ) can be of the order of unity.<sup>94</sup>

In a ferroelectric-antiferromagnet in which  $\omega_c \ll \omega_E$ , the value of  $K_E$  is smaller by a factor of  $\Delta$  than in a ferroelectric-ferrimagnet. We expect the smallest value of  $K_E$  to occur in a ferroelectric-ferromagnet crystal, where only the relativistic interaction participates in the dynamical ME coupling far from phase-transition temperatures ( $T \ll \Theta_E, \Theta_M$ ).

The spin subsystem can participate in detection of an alternating electric field applied to a ferroelectromagnet.<sup>94</sup> For example, let a crystal having an "easy magnetic axis" (EMA) anisotropy be situated in the alternating electric field  $e_x = e_0 \cos \omega t$  ( $\mathbf{e} \parallel \mathbf{P} \parallel z$ ) and in a constant magnetic field  $\mathbf{H} \parallel x$ . A term arises in the constant component of the magnetization proportional to the square of the amplitude of the electric field:  $\Delta M_x \sim e_0^2 M_0^{-1} (X^{ME})^2$ . This effect is possible not only in ferroelectromagnets, but since its magnitude is proportional to the square of the ME susceptibility, it can be more noticeable in ferroelectromagnetic crystals, especially near phase-transition temperatures. In particular, a change in the magnetization along the  $x$  axis must be accompanied by a magnetostrictive change in the dimensions of the crystal.

The effect of magnetoelectric frequency doubling can arise in a ferroelectromagnet in alternating external fields. Since the ME energy is quadratic in the spin operators, then, e.g., in the resonance excitation of the spins by an alternating magnetic field  $\mathbf{h} = \mathbf{h}_0 \cos \omega t$ , terms  $\Delta p$  arise in the electric polarization that are proportional to the square of the magnetic field intensity and which oscillate at the doubled frequency  $2\omega$ . An estimate of the effect in a ferroelectric-antiferromagnet lacking a center of symmetry yields the value<sup>48</sup>

$$\Delta P = g^2 h_0^2 \omega_0^{-2} P_0 \left( \frac{e_{\text{exch}}}{e_{\text{coul}}} \right)^2. \quad (4.4)$$

Here  $g$  is the gyromagnetic ratio, and  $\omega_0 \sim \Delta g M_0$  is the exchange frequency.

### c) Excitation of ferroelectromagnetic oscillations

One of the methods of studying the system of elementary oscillations of a crystal is to create an instability in it by using external fields. Calculations exist for ferroelectromagnets of parametric excitation,<sup>95-97</sup> and of the onset of instability under the action of an electric field<sup>98,99</sup> that oscillates rapidly while slowly varying in space, and of a flux of electrons.<sup>81,79</sup>

The ME interaction makes possible the parametric excitation of spin waves by a homogeneous electric field. In a ferroelectric-antiferromagnet a ME interaction of the form  $F_{\text{ME}} = -\tilde{\Lambda} \mathbf{e} \cdot (\mathbf{M}_1 \times \mathbf{M}_2)$ , where  $\mathbf{e}$  is the alternating electric field, gives rise to the following magnitude of the threshold excitation field<sup>95</sup>:

$$e_{\text{thr}} = \begin{cases} e_{\text{thr}}^0 = 2\eta_c (\tilde{\Lambda})^{-1} \frac{\omega_{\text{co}}}{gM_0} & \text{(EMP),} \\ e_{\text{thr}}^0 \sqrt{1 - \frac{H^2}{H_0^2}} & \text{(EMA).} \end{cases} \quad (4.5)$$

In (4.5)  $H$  is the intensity of the constant magnetic field,  $H_0$  is the spin-reversal field,  $\omega_{\text{co}} = \omega_c(0)$  is the spin frequency for  $\mathbf{k}=0$  ( $\mathbf{k}$  is the wave vector), and  $\eta_c$  is the relative damping decrement of the spin waves. For a crystal of the EMP type excitation is possible at a frequency of the external field  $\omega = 2\omega_{1c}(0)$ ,  $2\omega_{2c}(0)$ , or  $\omega_{1c}(0) \pm \omega_{2c}(0)$ , while for a crystal of the EMA type if the electric or magnetic dipole interactions are not taken into account excitation is possible at the overall frequency of  $\omega = \omega_{1c}(0) + \omega_{2c}(0)$ . For the values  $\omega_c/gM_0 \sim 10$ ,  $\tilde{\Lambda} \sim 10^{-3} \text{ G}^{-1}$ ,<sup>95</sup> and  $\eta_c \sim 10^{-2}$ , we obtain a value of the excitation field  $e_{\text{thr}}^0 \sim 10^4 \text{ V/cm}$ . This value declines near the spin-reversal field. When  $H - H_0 \sim 10^{-2} H_0$ , we find  $e_{\text{thr}} \sim 10^3 \text{ V/cm}$ .

The magnitude of  $e_{\text{thr}}$  in (4.5) arises from the relativistic ME interaction. Allowance for the stronger exchange ME interaction leads to correspondingly smaller values (by two or three orders of magnitude) of the excitation fields.<sup>97</sup> That is, we can suppose that instability of spin waves in an electric field will arise owing to the exchange ME interaction. Thus, for an ME energy of the form  $F_{\text{ME}} = -(\frac{1}{2}) \gamma P^2 (\mathbf{M}_1 \cdot \mathbf{M}_2)$ , the value of the threshold field is

$$e_{\text{thr}} = \frac{4\eta_c}{\gamma} \frac{\delta P_0}{\Delta} \left( \frac{\omega}{gM_0} \right)^2. \quad (4.6)$$

If as above we assume that  $\omega/gM_0 \sim 10$ ,  $\eta_c \sim 10^{-2}$ ,  $\gamma \sim 10^{-7} \text{ dyne}^{-1} \text{ cm}^2$ ,  $\delta \sim 10^{-11} \text{ dyne}^{-1} \text{ cm}^2$ ,  $\Delta \sim 10^2$ , and  $P_0 \sim 10^4 - 10^5 \text{ CGSE units} \approx 10^7 \text{ V/cm}$ , we obtain  $e_{\text{thr}} \sim 10 \text{ V/cm}$ .

In a ferroelectric-ferromagnet a homogeneous alternating electric field directed along the easy axis and along the equilibrium magnetization will parametrically excite magnons owing to the ME and electric and magnetic dipole interactions.<sup>96</sup> The magnitude of the threshold field is:

$$e_{\text{thr}} = \frac{\eta_c}{\lambda} \delta P_0 (\pi \sin^2 \theta)^{-1} \left( \frac{\omega_c}{gM_0} \right)^2. \quad (4.7)$$

Here  $\theta$  is the angle between the direction of propagation of the wave and the easy axis, and  $\lambda \sim 10^{-9} \text{ dyne}^{-1} \text{ cm}^2$  is the relativistic ME interaction constant. Waves propagating in the basal plane are excited most easily. For these, employing the values given above for  $\eta_c$ ,  $\lambda$ ,  $\delta$ , and  $P_0$ , and also assuming that  $\pi^{-1} \omega_c^2 (gM_0)^{-2} \sim 10$ , we have  $e_{\text{thr}} \sim 10^4 \text{ V/cm}$ .

In the formulas (4.5)–(4.7) for the excitation fields we have assumed that the condition of parametric resonance is fulfilled, in which the frequency of the electric field is of the same order of magnitude as the spin frequencies. In this case the threshold instability fields are not so large, and are experimentally attainable. Under certain conditions an electric field having a frequency much larger than the spin frequency also can excite spin waves, but this requires higher values of the excitation field. A rapidly oscillating electric field that varies slowly in space excites spin waves in a ferroelectric-antiferromagnet at values of the fields exceeding the threshold values of (4.5) and (4.6) by one or two orders of magnitude.<sup>98,99</sup>

Ferroelectromagnetic oscillations can also be excited by an electric current in semiconductors<sup>81</sup> or by an electron beam moving in a narrow cylindrical channel through a dielectric.<sup>79</sup> Electrons moving through a crystal produce Cherenkov excitation of oscillations. In magnetic materials the excitation of spin waves arises from the interaction of the electron beam with the electromagnetic field of the magnetic material and is dynamical and relativistic in character. The rate of growth of the spin waves is proportional to  $(v/c)^{2/3}$  ( $v$  and  $c$  are the velocities of the electrons and of light), and excitation is efficient at high enough beam velocities.<sup>100</sup> A different situation occurs in ferroelectromagnets, where an electrostatic interaction exists between the electrons of the beam and the electric dipole moment of the crystal. This interaction can lead to the onset of instability of the FE oscillations, and owing to ME coupling—to instability of the spin waves. This excitation method is electrostatic, and the rate of growth of the waves does not contain the small factor  $(v/c)^{2/3}$ . Both spin and FE oscillations are excited. However one cannot excite in this way the soft FE mode, which lacks an electrostatic field ( $\mathbf{k} \cdot \mathbf{p} = 0$ ).

## 5. EXPERIMENTAL STUDIES OF ME INTERACTIONS IN FERROELECTROMAGNETS

In spite of the considerable number of effects predicted by the theoreticians, the experimental study of ferroelectromagnetic crystals is still in its initial stage. The greatest number of experimental studies has been devoted to synthesis of ferroelectromagnets and establishment of the types of electric and magnetic order. Study of the nature and magnitude of the ME interactions presupposes the existence of sufficiently perfect single crystals having a low electric conductivity. There are still only a few such ferroelectromagnets. In addition to requiring single crystal, the study of the linear ME effect requires a preferential single domain character,<sup>101,102</sup> since the ME susceptibility of the linear effect in  $180^\circ$  domains has opposite signs.

A preferential orientation of the moments in polycrystals and in single crystals is created by applying electric and magnetic fields near the phase-transition temperatures.<sup>103</sup>

### a) ME measurements in single crystals

1) *Boracites*. The first measurements of the ME effect in ferroelectromagnets that clearly demonstrated a coupling between electric and magnetic ordering were performed in Ni-I boracite.<sup>22</sup> Measurements of the magnetic susceptibility established the presence of a broad maximum at a temperature of 120 K,<sup>104</sup> which has been explained in the literature in various ways (temperature-excited paramagnetism,<sup>105</sup> low-dimensional magnetic order<sup>23</sup>), and a sharp maximum at 64 K, which corresponds to the transition to the antiferromagnetic state with weak ferromagnetism.<sup>22</sup> Dielectric measurements show the presence below 64 K of FE properties. Apparently the latter arise simultaneously with the weakly ferromagnetic properties as the result of an improper FE transition. Below  $\Theta = \Theta_E = \Theta_M = 64$  K the electric-polarization vector lies along the [001] axis, while the spontaneous magnetic moment  $\mathbf{M}_c$ , whose direction was determined by the Faraday effect, lies in a plane perpendicular to  $\mathbf{P}$ .<sup>22</sup> If we take the direction of  $\mathbf{M}_c$  as the y axis, then the magnetic point group of this state is  $m'm2'$ . The study of Ascher *et al.*<sup>22</sup> found a clearly marked interrelation of the orientations of  $\mathbf{P}$  and  $\mathbf{M}_c$ : electric switching of  $\mathbf{P}$  by  $180^\circ$  from the direction [001] to [00 $\bar{1}$ ] rotates  $\mathbf{M}_c$  by  $90^\circ$ . And vice versa: rotation of a sufficiently strong magnetic field by  $90^\circ$  reorients  $\mathbf{P}$ . This phenomenon can be treated from the group-theoretical standpoint.<sup>106</sup> The number of domains, i.e., different orientations of the moments that possess the same energy in the absence of external fields, is the ratio of the orders of the groups of the paraphase ( $\bar{4}3m$ ) and of the ordered phase ( $m'm2'$ ). For Ni-I boracite this ratio is 12, and one can obtain all 12 types of domains from the initial state (Fig. 6a) by applying the operations of the group  $\bar{4}3m$ . The action of the operation  $\bar{4}$  on the state shown in Fig. 6(a) yields a state with inverted polarization and magnetization rotated by  $90^\circ$  [Fig. 6(b)].

The ferroelectromagnetic phase of Ni-I boracite allows a linear ME effect, i.e., a linear coupling between the variables  $\mathbf{P}$  and  $\mathbf{H}$ ,  $\mathbf{M}$  and  $\mathbf{E}$ . In the magnetic  $m'm2'$  state the non-zero components of  $\mathbf{X}_{ME}$  of the linear ME effect are  $\alpha_{yx}^{EM} = \alpha_{xy}^{EM}$  and  $\alpha_{zy}^{EM} = \alpha_{yz}^{EM}$ . That is, the following relationships hold:

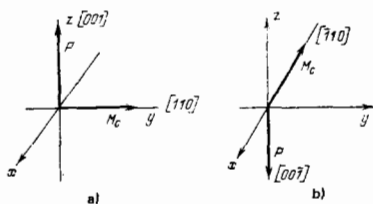


FIG. 6. Possible directions of the equilibrium moments in Ni-I boracite.<sup>106</sup>

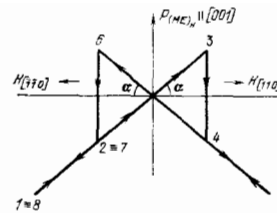


FIG. 7. ME hysteresis loop in Ni-I boracite at 46 K.<sup>22</sup> The magnetic field lies along  $\pm[110]$  (in pseudocubic indexing).

$$\begin{aligned} P_x &= \alpha_{xy}^{EM} H_y, & P_y &= \alpha_{yz}^{EM} H_z, \\ m_z &= \alpha_{zy}^{ME} E_y, & m_y &= \alpha_{yx}^{ME} E_x. \end{aligned} \quad (5.1)$$

In the formulas of (5.1)  $\mathbf{P}$  (or  $\mathbf{m}$ ) is the change in the electric (or magnetic) moment that arises in a magnetic (or electric) field. The  $P(H)$  relationship obtained experimentally<sup>22</sup> is shown by the magnetoelectric hysteresis loop ("bowtie") of Fig. 7. The value of the ME susceptibility at 15 K is  $\alpha_{xy}^{EM} = 3.8 \times 10^{-4}$ . Figure 8 shows the temperature-dependence of  $\alpha_{xy}$ . The reversal of sign of  $\alpha_{xy}$  at 60 K and the existence of a small peak near  $\Theta$  has been attributed<sup>107</sup> to the existence of domains in the specimen, and it was suggested that this peak should disappear in measurements in strong magnetic fields. Induction of a magnetic moment in Ni-I boracite by an alternating electric field has also been observed.<sup>45</sup> The obtained temperature-dependence of the ME susceptibility resembles that shown in Fig. 8. The authors of Ref. 45 consider that the linear ME effect corresponds to temperatures  $T < 60$  K, while a nonlinear ME effect is observed in the temperature interval 60–64 K, associated with the rearrangement of the domain structure in the electric field.

A ME frequency-doubling effect has been observed in Ni-I boracite: the appearance of a  $m(\bar{E})$  signal at a frequency twice the frequency of the electric field.<sup>45</sup> The magnitude of this effect is maximal near  $\Theta$ . The measurements of the dielectric permittivity that were performed showed its strong dependence on the magnitude and direction of the magnetic field. The greatest  $\epsilon_{xx}(H)$  variation was observed near  $\Theta$ , where a rotation of the magnetic field  $H = 12.5$  kOe by  $90^\circ$  led to a 30% change in the value of the dielectric permittivity as compared with its value at  $H = 0$  (Fig. 9). This phenomenon indicates the strong interaction of the electric

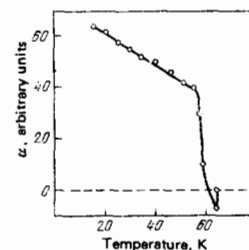


FIG. 8. ME susceptibility of Ni-I boracite as a function of the temperature.<sup>22</sup> The measurements were taken after cooling from a temperature above 65 K in fields  $H = 7.6$  kOe  $\parallel [110]$  (cubic) and  $E = 10$  kV/cm  $\parallel [001]$  (cubic).

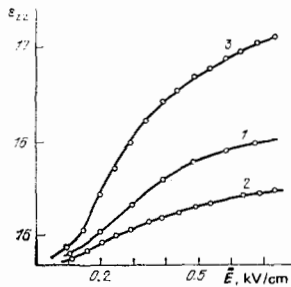


FIG. 9. Dependence of the dielectric permittivity of Ni-I boracite on the amplitude of the alternating electric field  $\bar{E}$  at 62 K in a magnetic field  $H = 12.5$  kOe.<sup>45</sup> 1— $H \parallel M_c$ , 2— $H \parallel M_a$ , 3— $H \perp M_c$ .

and magnetic subsystems near the phase-transition temperature.

An unusual type of temperature-dependence of the spontaneous magnetization has been found in Ni-I boracite, with a maximum in the region of 50 K,<sup>23</sup> and also an asymmetry of the dielectric and magnetic hysteresis loops,<sup>22,24</sup> and an unusual course of the magnetization curve.<sup>108</sup> In order to explain these and similar phenomena, one must know the magnetic structure of the crystal below the transition temperature. However, we cannot view the magnetic structure of Ni-I boracite as having been finally established. The neutron-diffraction studies<sup>109</sup> indicate the weak ferromagnetic ordering found earlier.<sup>22</sup> These results are contradicted by the data of Ref. 110, where a weak ferromagnetism was not established. The error of both of the cited studies<sup>109,110</sup> has been shown by Plakhtii *et al.*<sup>111</sup> They note the ambiguity of establishment of the type of magnetic order from neutron-diffraction data on polycrystalline powders: completely different models can yield equally good agreement with experiment. To elucidate the magnetic structure one needs magnetic and ME measurements, which allow one to establish the direction of magnetization. Such information is given, e.g., by determining the nonzero components of the linear ME effect.<sup>22</sup> Subsequent measurements of  $\alpha_{ik}^{ME}$  show<sup>112</sup> the presence in addition to  $\alpha_{xy}$  and  $\alpha_{yz}$  of other nonzero components of the ME susceptibility:  $\alpha_{xx}$ ,  $\alpha_{yy}$ ,  $\alpha_{xz}$ ,  $\alpha_{zz}$ , and  $\alpha_{zx}$ , with  $\alpha_{yz} \approx \alpha_{xy} \approx \alpha_{xx} \approx \alpha_{yy} \approx \alpha_{xz} \gg \alpha_{zz}$ ,  $\alpha_{zx}$ . The different components of  $\alpha_{ik}$  prove to be associated with different groups of magnetic ions in the unit cell (the cell of Ni-I boracite contains 12 magnetic ions). The existence of a larger number of nonzero components of  $\alpha_{ik}$  than had been assumed previously indicates a magnetic class lower than  $m'm2'$ .

The linear ME effect has been studied also in other orthorhombic boracites: in monocrystalline Ni-Cl<sup>113</sup> and Cu-Cl<sup>114</sup> and in polycrystalline Co-I, Ni-Br, and Mn-I.<sup>115</sup>

Two magnetic transitions exist in Ni-Cl boracite: to the antiferromagnetic phase at 25 K and a transition from the antiferromagnetic to a weakly ferromagnetic state at 9 K. The ME susceptibility  $\alpha_{32}^{EM}$  ("3" and "2" are the directions of spontaneous polarization and spontaneous magnetization) shows a peak near the tempera-

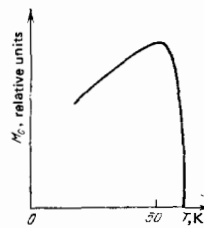


FIG. 10. Temperature-dependence of the spontaneous magnetization of Ni-I boracite.<sup>23</sup>

ture of the transition from the antiferromagnetic to the weakly ferromagnetic state (Fig. 11).<sup>113</sup> This peak fits in with the ideas<sup>87</sup> concerning the anomalous behavior of the ME susceptibility near the temperature of a transition to the weakly ferromagnetic state in a ferroelectric orthorhombic crystal. The maximum value of  $\alpha_{EM}$  in Ni-Cl boracite is smaller by a factor of two than in Ni-I boracite.

A break in the dielectric permittivity at the magnetic-transition temperature that had been previously predicted theoretically<sup>66</sup> has been found<sup>116</sup> in Co-I and Cu-Br boracites.

The trigonal boracites Fe-Cl, Fe-Br, Fe-I and Co-Cl belong to the type of ferroelectromagnets whose symmetry does not allow a  $180^\circ$  rotation of the electric polarization.<sup>117</sup> Co-Cl boracite shows a FE response of the system to an applied constant magnetic field.<sup>41</sup> Induction of magnetization by an alternating field  $\bar{E}$  in Fe-Br, Co-Cl, Co-I, and Fe-Cl boracites has also been observed.<sup>118-120</sup>

2)  $BaMF_4$  below 25 K—pyroelectric—weak ferromagnet<sup>121</sup> with two-dimensional magnetic order.<sup>122</sup> The crystal lattice in the high-temperature phase is orthorhombic. An incommensurate phase possibility precedes the magnetically ordered phase.<sup>123</sup> An anomaly in the static dielectric permittivity  $\epsilon$  along the pyroelectric axis is found at the temperature of the magnetic transition<sup>124,125</sup> (Fig. 12). Fox *et al.*,<sup>126</sup> ascribe the break in  $\epsilon(T)$  at  $T = \Theta_M = 30$  K to weak ferromagnetism and an anisotropic ME interaction of the form  $F_{an} = \lambda_{ik} L_i M_k P^2$  ( $L$  is the antiferromagnetism vector and  $M$

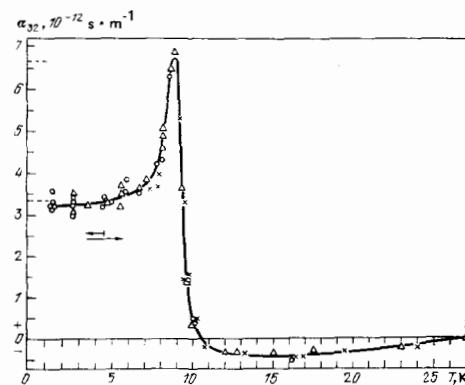


FIG. 11. Temperature-dependence of the ME susceptibility  $\alpha_{32}^{EM} = \alpha_{32}$  in Ni-Cl boracite.<sup>113</sup>

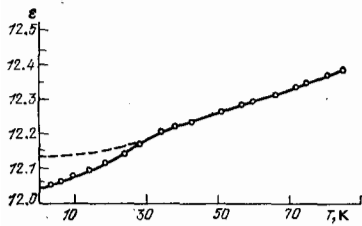


FIG. 12. Dielectric permittivity along the pyroelectric axis as a function of the temperature in BaMnF<sub>4</sub>.<sup>125</sup>

is the magnetization). However, general theoretical precepts (see Sec. 3) imply that a break in  $\epsilon$  ( $\Theta_M$ ) arises even in the isotropic case, and require no extra conditions on the magnetic symmetry of the crystal. In any ferroelectric-antiferromagnet, whether allowing weak ferromagnetism or not, there is an exchange ME term of the form  $F_{\text{exch}} = \gamma L^2 P^2$ , which gives rise to a change in the dielectric permittivity.

$$\Delta\epsilon \sim \gamma L^2 \sim \gamma M_0^2 \sim \gamma (\Theta_M - T)^{2\beta} \quad (T \leq \Theta_M). \quad (5.2)$$

Here  $M_0$  is the magnetic moment of the sublattice. The ME energy  $F_{\text{exch}}$  is of exchange origin, rather than relativistic as for  $F_{\text{an}}$ . In any case, it exceeds the anisotropic energy  $F_{\text{an}}$  by a factor of  $M_0/M$  ( $M$  is the weak ferromagnetic moment). Comparison of the experimental values of  $\Delta\epsilon$  in BaMnF<sub>4</sub> with those calculated taking into account the exchange ME interaction<sup>127</sup> yields a value of the parameter  $\gamma \sim 10^{-7}$  dyne<sup>-1</sup> cm<sup>2</sup>. A rough estimate of the magnetic critical index  $\beta$  from the temperature-dependence of  $\epsilon$  below  $\Theta_M$  yields the value  $\beta \approx 0.35$ . Neutron-diffraction measurements<sup>128</sup> yield the value  $\beta \approx 0.32$ .

3) *Lead manganate*. PbMn<sub>2</sub>O<sub>4</sub> manifests weak ferromagnetic properties below  $\Theta_M = 63$  K. The type of order as well as the space group of the paramagnetic phase have not been established exactly.<sup>129</sup> These circumstances impede the interpretation of the linear ME effect that has been found.<sup>130</sup> Al'shin *et al.*,<sup>131,132</sup> interpret the experimental results under the assumption of FE ordering and a symmetry group  $C_{3v}$  of the paraphase. In that case the experimental data can be explained if it is assumed that the ME interaction makes the fundamental contribution to the magnitude of the Dzyaloshinskii field.

4) *Perovskite-type compounds*. In the first ferroelectromagnetic compound Pb(Fe<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub>, for which the temperature of FE ordering lies below the Néel temperature, a manifestation of ME interaction is noted near  $\Theta_E$ . Studies of the Mössbauer effect show a considerable increase in the magnetic field at the iron nuclei in the FE transition.<sup>133</sup> A spontaneous magnetization in the FE phase has also been noted.<sup>134</sup>

A spontaneous magnetization arose in the compounds Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> and Pb(Mn<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> when specimens were taken through the temperature of antiferromagnetic ordering ( $\Theta_M < \Theta_E$ ) in the presence of electric and magnetic fields.<sup>135</sup> Its magnitude depended weakly on the constant electric field, but varied considerably under the action of an alternating electric field applied

near  $\Theta_M$ . Apparently the latter situation indicates a role of domain effects in the manifestation of ME interactions: FE repolarization alters the magnetic structure.<sup>134</sup>

A weak ME effect has been found in the ferroelectric-ferromagnet CO<sub>1.75</sub>Mn<sub>1.25</sub>O<sub>4</sub>.<sup>136</sup> The data given in Ref. 136 indicate a magnitude of the ME susceptibility  $\chi^{\text{ME}} \sim 10^{-6}$ .

## b) ME measurements in polycrystals and in solid solutions

BiFeO<sub>3</sub> has a rhombohedrally distorted perovskite-type structure. It manifests FE properties at low temperatures.<sup>137</sup> The type of electric order at room temperature (FE or antiferroelectric) has not been fully established. BiFeO<sub>3</sub> has a high temperature of the transition to the antiferromagnetic state,  $\Theta_M = 643$  K.<sup>9</sup> A weak anomaly in the dielectric permittivity is observed at  $T = \Theta_M$ .<sup>138,139</sup> The high electric conductivity of the specimens impedes the study of both the dielectric and the ME properties. Study of the Mössbauer effect revealed a coupling of the directions of the magnetic and electric fields at the iron nuclei below the magnetic-transition temperature.<sup>140</sup> In Ref. 141 a study was made of the dependence of the induced electric signal on the magnitude of the constant magnetic field imposed on BiFeO<sub>3</sub>. A maximum of the signal was observed at a certain value of the magnetic-field intensity, which was identified with the spin-flop field. These results agree with the theoretical views<sup>73</sup> on the jump in the value of the polarization, and hence, in the electric field, in spin-flop.

Induction of an electric signal by a constant magnetic field has been observed in the antiferroelectric-antiferromagnet Bi<sub>0.7</sub>La<sub>0.3</sub>Fe<sub>0.986</sub>Mn<sub>0.014</sub>O<sub>3</sub>,<sup>142</sup> in the ferroelectric-antiferromagnet with a layer structure Bi<sub>3</sub>Ti<sub>3</sub>Fe<sub>5</sub>O<sub>27</sub>,<sup>16</sup> and in the ferroelectric-antiferromagnet with a pseudoilmenite structure Li(Fe<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>2</sub>.<sup>143</sup>

Anomalies in the dielectric permittivity at the temperature of a magnetic transition in ferroelectromagnets having  $\Theta_M < \Theta_E$  have been observed in the perovskite compounds Pb(Mn<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub>, Pb(Fe<sub>1/2</sub>Mn<sub>1/4</sub>W<sub>1/4</sub>)O<sub>3</sub>,<sup>144</sup> and in the solid solutions Pb<sub>2</sub>CoWO<sub>6</sub>-BaTiO<sub>3</sub> with 5 mole % BaTiO<sub>3</sub>,<sup>145</sup> Pb<sub>2</sub>CoWO<sub>6</sub>-CdMnO<sub>3</sub> with 30 mole % CdMnO<sub>3</sub>,<sup>144</sup> (Bi<sub>1-x</sub>La<sub>x</sub>)FeO<sub>3</sub> with  $0 \leq x \leq 0.3$ .<sup>146</sup> An anomaly arises in the region of the FE transition in the temperature-dependence of the spontaneous magnetization (Fig. 13)<sup>147</sup> in the ferroelectric-ferrimagnetic solid solution 0.9 Pb(Fe<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub>-0.1 Pb(Yb<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> having  $\Theta_M > \Theta_E$ .

The temperature-dependence of the ME signal arising in constant magnetic field has been studied in the solid solutions BiFeO<sub>3</sub>-BaTiO<sub>3</sub> and BiFeO<sub>3</sub>-LaFeO<sub>3</sub>.<sup>148</sup> A jump in the spin-flop field at the temperature of the FE transition has been observed in the ferroelectric-antiferromagnets BiFeO<sub>3</sub>-BaTiO<sub>3</sub> and the antiferroelectric-antiferromagnets BiFeO<sub>3</sub>-LaFeO<sub>3</sub> having  $\Theta_E < \Theta_M$ . Since the spin-flop field in ferroelectric-antiferromagnets depends on the value of the equilibrium polarization,<sup>74</sup> the jump in it at  $T = \Theta_E$  can stem from a first-order FE transition.



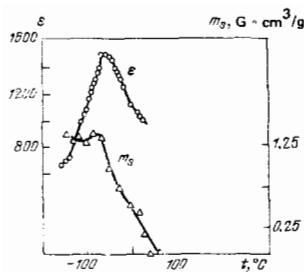


FIG. 13. Temperature-dependence of the dielectric permittivity  $\epsilon$  and the spontaneous magnetization  $m_s$  in the solid solution  $0.9 \text{ Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3 - 0.1 \text{ Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ .<sup>147</sup>

## 6. EXPECTED EFFECTS AND POSSIBLE APPLICATIONS

The material presented here shows that studies of ferroelectromagnets have just begun. Yet the existence of new magnetoelectric effects that can be used in technology (some of them are given in Table II) is already becoming obvious. Experimental proofs have been obtained of the interaction of magnetization and polarization and of the possibility of controlling the magnetization with an electric field, or the electric polarization by a magnetic field. An appreciable ME interaction is observed also in heterophase systems.<sup>149</sup> Therefore we can assume that, just like the ferroelectromagnetic crystals, they will find application in technology. Let us give some examples of the use of the new ME effects for scientific and practical purposes.

Measurements of the linear ME effect in magnetoelectrics and in ferroelectromagnets are employed to establish the type of magnetic ordering in a crystal.<sup>112, 150</sup> The dependence of the ME susceptibility on the orientation of the moments in the domains makes it possible to determine the domain structure of a crystal by studying the behavior in external fields.<sup>151</sup> In magnetoelectrics the study of the temperature-dependence of the ME susceptibility is used to investigate magnetic transitions: determination of the magnetic critical index,<sup>152</sup> study of spin-flop and metamagnetic transitions.<sup>153</sup> Analogous measurements can be performed also in ferroelectromagnets. Moreover, potentialities arise of determining the magnetic critical index from the temperature-dependence of the dielectric permittivity (and the FE index from the temperature-dependence of the magnetic susceptibility, effect No. 9) and studying other phase transitions induced by the ME interaction (effects No. 2-8).

In order to employ ferroelectromagnets for practical purposes, compounds are desirable that have low losses, low electric conductivity, a considerable magnetic moment and ME susceptibility and sufficiently high values of the electric and magnetic transition temperatures (above room temperature). At present there are no ferroelectromagnets that satisfy all these requirements, although individual compounds satisfy several of the listed conditions.

One can classify devices employing ferroelectromagnetic crystals into three types: 1) devices that employ

TABLE II. ME effects in ferroelectromagnets.

| Effect  | Notes   |
|---|---|
| 1. Values of the ME susceptibility near the temperatures of second-order phase transitions<br>$\chi^{\text{ME}} \sim (\Theta_{\text{E}} - T)^{-1/2}$<br>$\chi^{\text{ME}} \sim (\Theta_{\text{M}} - T)^{-1/2}$                    | In a ferroelectric-ferromagnet, at $T \lesssim \Theta_{\text{E}} < \Theta_{\text{M}}$ ; in a FE-(weak) ferromagnet at $T \lesssim \Theta_{\text{M}} < \Theta_{\text{E}}$ and $m_c \sim (\Theta_{\text{M}} - T)^{1/2}$ . Observed experimentally   |
| 2. Switching of polarization or induction of a FE transition by a magnetic field  | Can occur upon changing the magnitude or direction of a constant magnetic field. When the values of the polarization are not very large, i.e., near $\Theta_{\text{E}}$ or in an improper FE transition, the required magnetic fields are not large. Experimentally observed                              |
| 3. Break in the temperature-dependence of the magnetic-anisotropy constant at $T = \Theta_{\text{E}}$ . Orientational "easy magnetic axis" → "easy magnetic plane" transition at $T < \Theta_{\text{E}}$ .                        | No experiment   |
| 4*. Transition from the antiferromagnetic to the ferromagnetic state with decreasing temperature  | No experiment   |
| 5. Induction of a second-order magnetic transition by a second-order FE transition.   | In a ferroelectric-ferromagnet in a magnetic field, with a smaller magnetic-anisotropy field and in a ferroelectric-antiferromagnet, with a larger spin-flop field and a smaller spin-collapse field. No experiment   |
| 6*. Replacement of a second-order transition from an antiferromagnetic to a ferromagnetic state by a first-order transition   | Effects 6 and 7 can occur in ferroelectric-antiferromagnets with $\Theta_{\text{E}} < \Theta_{\text{M}}$ , $\gamma > 0$ , and $\gamma^2 \rho_0^2 \sim \Delta$ . The latter condition implies that the exchange ME interaction energy must be of the order of the intrinsic magnetic energy. No experiment |
| 7*. Replacement of spin-flop by a metamagnetic transition   | The effect has been observed experimentally   |
| 8. Jump in the equilibrium electric polarization in spin-flop   | Anomalies in $\epsilon$ ( $\Theta_{\text{M}}$ ) have been observed experimentally   |
| 9*. Break in the temperature-dependence of the dielectric permittivity at the temperature of a magnetic transition, and in the temperature-dependence of the magnetic susceptibility at the temperature of an electric transition | No experiment   |
| 10*. Shift of $\Theta_{\text{M}}$ in an electric field and a shift in $\Theta_{\text{E}}$ in a magnetic field   | No experiment   |
| 11. Existence of coupled ferroelectromagnetic waves   | No experiment   |
| 12. Existence of a ME gap in the spin-wave spectrum in the absence of external electric and magnetic fields   | No experiment   |
| 13*. Magnetolectric frequency doubling  | A ME signal has been experimentally observed at a frequency twice that of the alternating electric field  |
| 14*. Excitation of spin waves by an alternating electric field, and FE oscillations by an alternating magnetic field  | Most effective in a ferroelectric-ferromagnet under the condition of resonance approach of the FE and upper spin frequencies, and also in strong constant magnetic fields. No experiment  |
| 15*. Parametric excitation of spin waves by an electric field   | Apparently the value of the threshold excitation field can be small. No experiment  |
| 16*. Excitation of spin waves by a rapidly oscillating electric field that slowly varies in space   | The value of the threshold excitation field is from one to two orders of magnitude higher than in the previous effect. No experiment  |
| 17. Electrostatic excitation of spin waves by a flux of electrons   | No experiment   |

Notes: The asterisks denote the effects that can arise not only in ferroelectromagnets.

the FE or the magnetic properties separately; 2) devices that employ the FE and magnetic properties simultaneously, but without ME interaction; 3) devices whose action is based on ME effects. We shall not take up the first type of devices, since the use of FE crystals as well as magnetically ordered crystals is widely known.

The review of Ref. 154 gives a detailed table of the possible applications of magnetoelectric crystals and characterizes 15 different devices in a working range from audio to optical frequencies, including modulators, phase inverters, switches, rectifiers, stabilizers,

etc. We shall take up only certain of these.

The second type of devices includes a Faraday phase inverter operating in the microwave range. Its quality of operation is determined by the quantity  $\epsilon' M_e / \epsilon''$ , where  $M_e$  is the component of the magnetization in the direction of propagation of the electromagnetic waves, and  $\epsilon'$  and  $\epsilon''$  are the real and imaginary components of the dielectric permittivity. The observed small values of  $M_e$  in ferroelectromagnets may have no effect on the quality of operation of the device for large values of the dielectric permittivity  $\epsilon'$ . Such values of  $\epsilon'$  are observed, e.g., in perovskite compounds and in heterophase solid solutions.<sup>155</sup>

It seems possible to employ ferroelectromagnets in reversing optical modulators and optical processors, whose principles of operation are based on the electrooptic and magneto-optic Kerr, Pockels, and Faraday effects and birefringence.

The use of ME interaction (devices of the third type), e.g., switching or modulation of the electric polarization by a magnetic field (effect No. 2) makes it possible to obtain a magnetically switchable optical device in the visible and infrared regions of the spectrum. Its principle of operation consists in altering the linear birefringence by changing the polarization under the action of a magnetic field. The magnetic field required to switch the polarization may not be very high, e.g., in Ni-I boracite it is of the order of several kilooersteds. This type of switching of  $\mathbf{P}$  would require strong electric fields of the order of several kV/cm. To produce these, one needs specimens in the form of thin plates. One can use massive specimens in the magnetic method of switching the electric polarization. As estimates show, the magnetic method of switching  $\mathbf{P}$  will be effective at values of the absorption coefficient  $K < 10^2 \text{ cm}^{-1}$ .<sup>154</sup> The requirement for low values of the absorption coefficients is the main difficulty in realizing such a device. The values of the absorption coefficient in the boracites and other ferroelectromagnetic compounds having 3d transition ions are of the order of  $10^3$ – $10^4 \text{ cm}^{-1}$  in the visible part of the spectrum. The value of  $K$  can be smaller in the infrared and in purer specimens.

Ferroelectromagnetic crystals can also be applied as film waveguides in integrated optics and in fiber communications technology.

Effects Nos. 14–17 can be employed to produce ME generators and spin-wave amplifiers using an alternating electric field or electric current, and effect No. 11 for generating new types of coupled waves—ferroelectromagnetic waves. One can use the nonlinear ME interaction, which is especially strongly manifested near transition temperatures, to produce a ME nonlinear optical device that gives rise, for example, to frequency doubling (effect No. 13).

## 7. CONCLUSION

This review has demonstrated a set of new and interesting effects arising in ferroelectromagnets owing to the ME interactions. An interrelation has been found between the spontaneous electric and magnetic mo-

ments, with an influence of the magnetic field on the electric moment, and of the electric field on the magnetization. It has been shown theoretically that the ME interaction leads to additional first- and second-order phase transitions in the spin and FE subsystems, to excitation of spin waves by an alternating electric field, and FE oscillations by a magnetic field, and to a gap in the spin-wave spectrum in the absence of external fields. Most of these effects await experimental confirmation.

At present the experimental data are mainly qualitative in nature. Further studies are needed of the values of the ME constants and the ME energy in different crystals. In contrast to magnetoelectrics having weak induced ME effects, in ferroelectromagnetic crystals a strong ME effect exists and is manifested near the phase-transition temperatures.

Since the ME interaction is most strongly manifested near phase-transition temperatures, for measurements and possible practical applications it is preferable to use ferroelectromagnets having close-lying values of  $\Theta_E$  and  $\Theta_M$  and sufficiently clearly marked magnetic and ferroelectric properties, i.e., ferro- and ferrimagnets with proper FE ordering. Synthesis of ferroelectromagnets of this type will render promising their application in technology.

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