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Magnetically Ordered Ferroelectrics

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(24. III. 68)

For the last twenty years the extensive development of solid state physics has been applied to such fields as ferromagnetism and ferroelectricity. In so doing not only concepts on the nature of these phenomena have been deepened but the number of known substances exhibiting magnetic or electric ordering has been considerably extended. This development has resulted in the possibility of creating substances having ferroelectric properties and magnetic ordering simultaneously. It might be anticipated that such type materials showed new effects due to the mutual influence of electric and magnetic subsystems.

The first investigations in this direction [1–3] were made in the U.S.S.R. where a number of ferroelectric-antiferromagnets with the perovskite-type structure was discovered. Then hexagonal ferroelectric-antiferromagnets were obtained in France and recently a family of ferroelectric boracites with antiferromagnetic or weakly ferromagnetic properties were synthesized in Switzerland.

Before reviewing experimental data on these compounds we shall briefly describe some basic results of the thermodynamic theory of ferroelectric-ferromagnets.

1. Thermodynamic Theory of Ferroelectric-Ferromagnets

Thermodynamic properties of ferroelectric-ferromagnets were studied in some of our work [4–6]. In the first of these papers [4] the second order phase transition from ferromagnetic (or ferroelectric) to a ferroelectric-ferromagnetic state has been considered under the assumption that the transition temperature is close to the temperature of transition from the para- to the ferromagnetic state (or from the para- to the ferroelectric one). It was shown [5] that the results of this work have a general character and are not due to the closeness of both transition temperatures.

In the ferroelectric-ferromagnetic phase a magnetoelectric effect appears which gives rise to the following linear dependence of electric and magnetic moments on magnetic and electric fields when the fields are weak:

$$\boldsymbol{P} = \chi^e \boldsymbol{E} + \chi^{em} \boldsymbol{H}\,, \qquad \boldsymbol{\mu} = \chi^m \boldsymbol{H} + \chi^{me} \boldsymbol{E}\,, \tag{1}$$

where $\boldsymbol{P}$ is the polarization, $\boldsymbol{\mu}$ is the magnetization, χ^e is the tensor of electric susceptibility, χ^m is the tensor of the magnetic susceptibility, and $\chi^{em} = \chi^{me} = -\,\partial^2\Phi/\partial E \partial H$

is the tensor of the mixed susceptibility. Note that near the transition point the following dependence is valid:

$$\chi^{em} = \frac{\partial P}{\partial H} = \chi^{me} = \frac{\partial M}{\partial E} \cong (T - T_c)^{-1/2} . \tag{2}$$

In these papers the case of magnetic and electric fields parallel to magnetic and electric moments, respectively, was investigated in which case the fields change only the magnitude of the moments but not their directions. If the field directions are arbitrary the thermodynamic theory must be developed for every individual crystal taking into account the crystal symmetry.

During the transition from a ferromagnetic (ferroelectric) to a ferroelectric-ferromagnetic phase a positive jump of magnetic (electric) susceptibility occurs, so that

$$(\chi^m)\, sf > (\chi^m)\, f \quad \text{or} \quad (\chi^e)\, sf > (\chi^e)\, s . \tag{3}$$

Here indices (f), (s), (sf) stand for a ferromagnetic, ferroelectric, and ferroelectric-ferromagnetic medium, respectively.

In the paper [6] the thermodynamics of a ferroelectric-ferromagnetic substance was studied taking into account the anisotropy of suitable properties. The crystal considered was of cubic symmetry in the paraelectric and paramagnetic states. The appearance of electric (magnetic) ordering was shown to cause the development of uni-axial magnetic (electric) anisotropy.

Elastic properties of ferroelectric-ferromagnets were also investigated in the above work. The authors have shown that the interaction between magnetic and electric subsystems might be considered as a result of electro- or magnetostriction. The appearance of the electric moment gives rise to some electrostrictive deformation which influences the magnetic moment through the magnetostriction and vice versa. As a result, new terms of the type $M_e M_j P_i P_k$ appear in the expression for the thermodynamic potential describing the interaction of the electric and magnetic subsystems.

In the above mentioned work ferroelectric-ferromagnets are treated. However, some of the presently known magnetically ordered ferroelectrics are antiferromagnets. Generally, the development of the thermodynamic theory for such crystals is possible with the knowledge of their crystal symmetry, the positional parameters of the magnetic ions, and the character of magnetic ordering. Thus every substance requires special consideration. Nevertheless it is possible to draw certain conclusions which are valid for a wide range of ferroelectric-antiferromagnetic structures.

NEDLIN [7] has studied the second order transition of a more general type from a ferroelectric to a ferroelectric and magnetically ordered state. We considered a magnetic ordering in which magnetic and chemical cells coincided, but were arbitrary in all other respects.

In the papers [8, 9] the symmetry of ferroelectric-ferromagnets was studied theoretically.

In the following some experimental facts will be considered.

2. Ferroelectric-antiferromagnets

For the first time the possibility of synthesis of compounds with simultaneous magnetic and electric ordering was shown in 1958 on an example of so called complex compounds $PbFe_{1/2}Nb_{1/2}O_3$ and $PbFe_{2/3}W_{1/3}O_3$ having a perovskite-type structure [1]. In these compounds the ions Fe^{3+}, W^{6+}, and Nb^{5+} occupy octahedral positions without any order. $PbFe_{2/3}W_{1/3}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ are ferroelectric-antiferromagnets with the Curie temperatures of 178° and 387°K and with the Neel points at 363° and 143°K, respectively [3].

The temperatures of the magnetic transition were determined by a sharp change in the slope of magnetic susceptibility curves (Fig. 1). The increase of magnetic susceptibility below the Neel temperature can be explained by the fact that the magnetic moments of Fe^{3+} ions, surrounded by a considerable number of diamagnetic ions, are not ordered. In a first approximation the behaviour of these ions in the external magnetic field is paramagnetic which leads to an increase in χ with decreasing temperature. Neutron diffraction studies made on these substances [10, 11] confirmed later the existence of long range magnetic order of G type. It is known that in the G-type magnetic structure each magnetic ion has six nearest neighbours with opposite spins. Magnetic moments of the sublattices in $PbFe_{2/3}W_{1/3}O_3$ determined from neutron diffraction data are in sufficiently good agreement with moments calculated by the GOODENOUGH and GILLEO method [10, 12, 13].

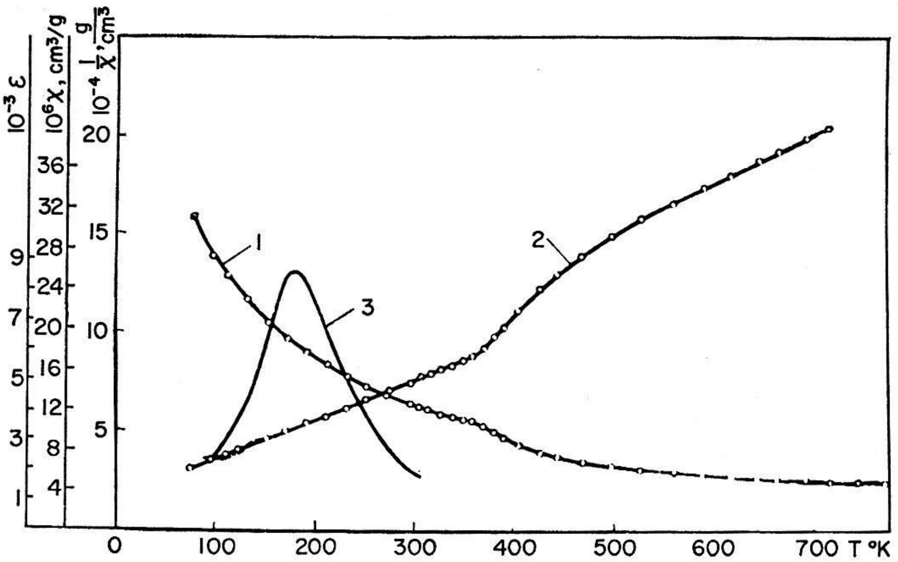

Figure 1

The temperature dependence of the magnetic susceptibility (χ(1), $1/\chi$(2)) and of the dielectric permeability (ε(3)) for $PbFe_{2/3}W_{1/3}O_3$ [3].

$PbCo_{1/2}W_{1/2}O_3$ is one of the most interesting complex-composition perovskites. The Co^{2+} and W^{6+} ions occupy octahedral sites in ordered way and that leads to a doubling of the unit cell [14–16]. $PbCo_{1/2}W_{1/2}O_3$ transforms into antiferroelectric state at 305°K [16]. The antiferroelectric-state stability decreases with temperature and from about 170°K a transition into the ferroelectric state can be induced by moderate electric fields. The field in which this transition occurs decreases due to the fact that at 68°K $PbCo_{1/2}W_{1/2}O_3$ becomes ferroelectric [17]. In this compound the exchange interaction between Co^{2+} ions is weak since it acts via Co–O–W–O–Co linkage. The magnetic ordering occurs at 9°K, the 4.2°K spontaneous magnetization being 0.15 gauss · $cm^3 \cdot g^{-1}$ (see Fig. 2) [18]. Thus below 9°K $PbCo_{1/2}W_{1/2}O_3$ is a ferroelectric and a weak ferromagnet simultaneously.

Dielectric and magnetic properties of $BiFeO_3$ have been treated in three articles which independently appeared in 1960. $BiFeO_3$ was reported to have a perovskite-type structure with rhombohedral distortion [19–21]. It was found that dissolving $BiFeO_3$ in ferroelectric $PbTiO_3$ [19, 22] and $PbFe_{2/3}W_{1/3}O_3$ [23] increases the Curie temperatures of the latter compounds. On this account it was suggested that $BiFeO_3$ was a ferro- or an antiferroelectric with a high Curie temperature. From a general point of view it might be expected that $BiFeO_3$ is ferro- or antiferroelectric because the Bi^{3+} ion has the same electron shell as Pb^{2+} ion which causes a high electron polarizability connected, in particular, with the existence of the undivided pair of 6 *s* electrons [24]. Actually, the $(Bi_{1/2}K_{1/2})TiO_3$ and $(Bi_{1/2}Na_{1/2})TiO_3$ compounds are ferroelectrics with high Curie temperatures [23].

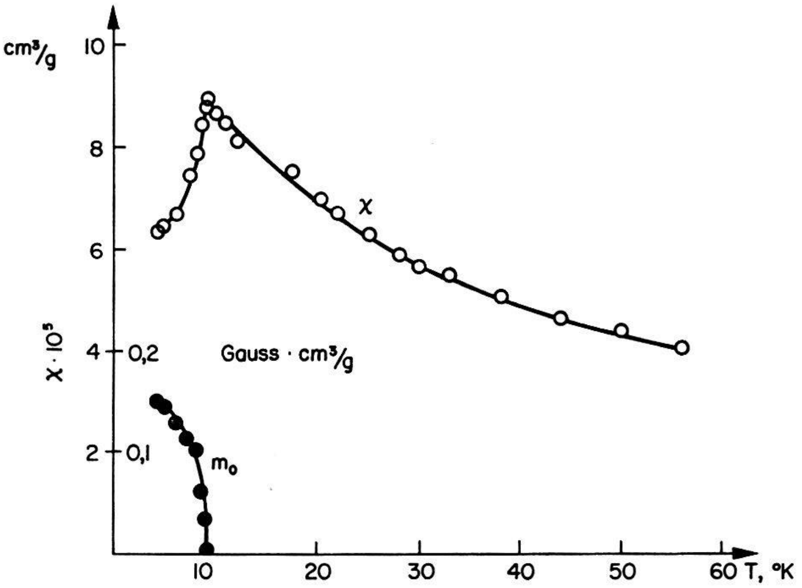

Figure 2

The temperature dependence of the magnetic susceptibility and of the spontaneous magnetic moment for $PbCo_{1/2}W_{1/2}O_3$ [18].

Magnetic [25] and neutron diffraction [11, 26] measurements have shown that $BiFeO_3$ is an antiferromagnet with a Néel temperature of 370°C. Up to the present several investigations of the structure of $BiFeO_3$ have been published. Neutron diffraction data [10] indicate that $BiFeO_3$ has a crystallographic superstructure the unit cell containing no less than two formula units. However, other authors consider the presence of superstructure as open to question [26–28]. If the structure of $BiFeO_3$ is rhombohedral, the comparison of physical and structural investigations gives two possible space groups. One of them, namely R3c($R\bar{3}c$) [29], allows the superstructure whereas for R3m [28, 30] it is forbidden.

According to Tomashpolskii et al. [31], an anomaly in cell parameters occurs in the region of 400°C. It is accompanied by the appearance of a maximum in the dielectric permeability. In [31] this fact is considered to be due to mutual influence of magnetic and electric subsystems. Further work [32–35] has confirmed that in this temperature range the maximum of ε as well as anomalies in the thermal expansion and in lattice parameters are observed. However, these peculiarities are considered to be a result of the phase transition between states with different electric ordering. In the investigations [34, 35] other phase transitions between similar states were observed. The temperature dependence of dielectric permeability for $BiFeO_3$ is given in Figure 3.

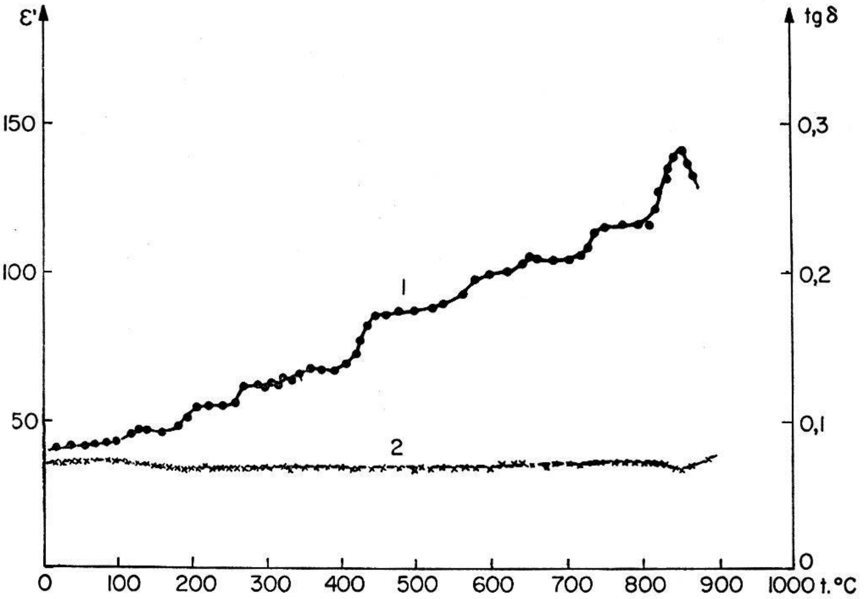

Figure 3

The temperature dependence of the dielectric permeability for $BiFeO_3$ at $9.4 \cdot 10^9$ Mc/sec [34].

In the series of solid solutions based on $BiFeO_3$ two systems were studied in more detail, viz. $BiFeO_3$–$PbTiO_3$ [19, 22, 36] and $BiFeO_3$–$PbFe_{1/2}Nb_{1/2}O_3$ [32–35, 37]. $BiFeO_3$ and $BiFeO_3$ rich solid solutions $BiFeO_3$–$PbFe_{1/2}Nb_{1/2}O_3$ were shown to have a superstructure, a small value of ε_{max} but no hysteresis loops and no field dependence of the permeability. These findings permit us to conclude that the transition in $BiFeO_3$ is caused by the change from a para- to an antiferroelectric state.

The free energies of ferro- and antiferroelectric states seem to be nearly equal. This assumption is confirmed by the fact that ferroelectric phases occur in those solid solutions which have an increased tolerance-factor, for example, in the solid solutions with $PbTiO_3$, $PbFe_{1/2}Nb_{1/2}O_3$, and $BaFe_{1/2}Nb_{1/2}O_3$. In other solid solutions with $LaFeO_3$ a decrease of the tolerance-factor was found to be followed by a decrease of ε_{max}. The character of the temperature dependence of ε suggests that these solid solutions have antiferroelectric properties [38]¹). It is to be noted that our opinion on this point differs from that of ZHDANOW, VENEVTSEW et al. who consider $BiFeO_3$ to exhibit the transition from a para- to a ferroelectric state.

As it has been shown by magnetic investigations of the systems $BiFeO_3$–$PbTiO_3$ and $BiFeO_3$–$PbFe_{1/2}Nb_{1/2}O_3$, in certain concentration ranges a weak ferromagnetism is observed [36, 39].

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¹) For $BiFeO_3$ a more general case is possible when antiparallel and parallel displacements of ions are present simultaneously. $PbZrO_3$, for example, shows such a phenomenon.

In 1963 Bertaut et al. [40] have found further oxyde ferroelectrics with new type of a crystal structure. So far it was well known that manganites of rare earths with the general formula $AMnO_3$ (where A is a rare earth from La to Dy) have a perovskite-type structure. But it turned out that rare earth metals from Ho to the end of the row with small ionic radii gave an alternative structure, the chemical formula being the same. X-ray data have shown that these compounds are of the space group Pbcm [40, 41]. The structure is shown in Figure 4. Besides the rare earths, this structure can be formed with Y and Sc ions [42]. The Y ion has a maximum ion radius for this row of elements and also forms a perovskite type structure, i.e. $YMnO_3$ is a bimorphic compound. According to Bertaut et al., the causes for the formation of the new structure are not only entirely geometric. For example, the ionic radius of Fe^{3+} which differs a little from that of the Mn^{3+} ion, forms only a perovskite-type structure with all rare earths. In this case the covalent bonds Mn–O resulting from the dsp^3 orbital of hybrid type are responsible for the coordination number of Mn^{3+} ions.

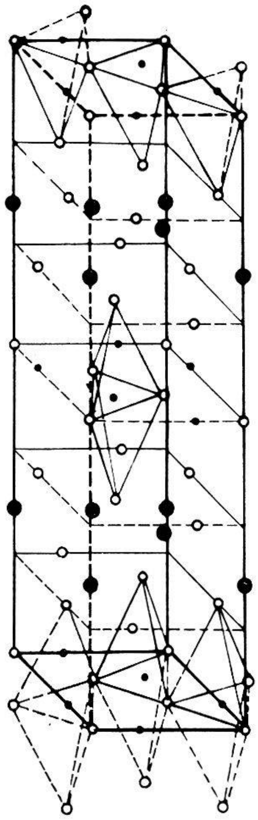

Figure 4

The unit cell of $YMnO_3$. ● Mn^{3+}, ⬤ Y^{3+}, ○ O^{2-}.

It was found that yttrium and rare earths manganites (from Ho to Lu) show ferroelectric properties with a polar axis coinciding with the axis of six-fold symmetry [40]. The magnitudes of spontaneous polarization and cohesive field quoted by various authors [43–46] are variable within the limits 5 to 5.6 cm^{-2} and 15 to 34 $kv \cdot cm^{-1}$, respectively. The Curie temperatures for $YMnO_3$ and $YbMnO_3$ were first suggested by the sharp change in cell parameters obtained from x-ray diffraction and by the maximum of the pyroelectric current [47]. Subsequently Kizhaev [48]

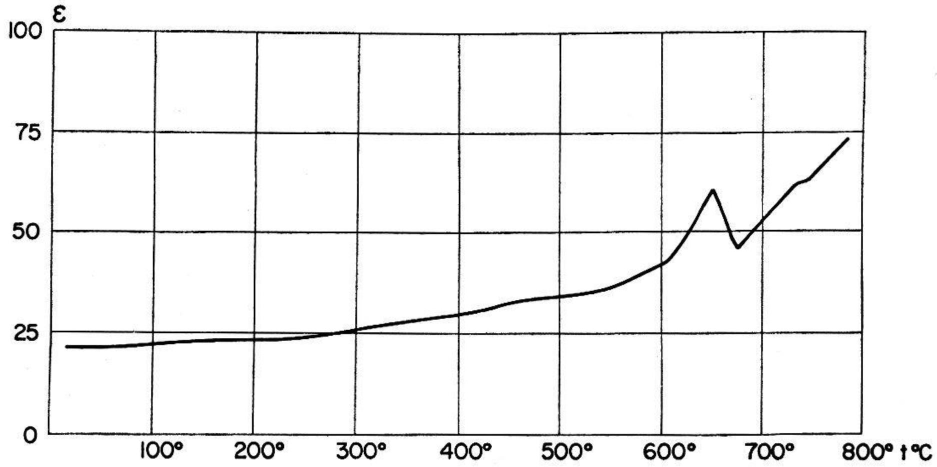

Figure 5

The temperature dependence of the dielectric permeability for $YMnO_3$ at 70 Mc/sec.

and COEURÉ et al. [45] measured the temperature dependence of the dielectric permeability for a number of manganites. The curve for $YMnO_3$ is shown in Figure 5. It is characterized by rather low values of dielectric permeability even at the Curie point. $YMnO_3$ is the most thoroughly investigated example of these compounds. This compound is a pure antiferromagnet with no anomaly of magnetic susceptibility at the Néel point [49–51]. The magnetic structure of $YMnO_3$ was treated both theoretically [52] and experimentally with the aid of neutron diffraction [53–55]. Almost for all compounds the Néel temperatures were suggested by neutron diffraction investigations [43]. $YMnO_3$ was not measured but, as Mössbauer investigations have shown, the Néel temperature of samples with substituted Fe^{3+} for 10% Mn^{3+} [56] is about 77 °K. Data concerning ferroelectric Curie points and Néel points are listed in the Table .

Ferroelectric Curie points (θ_F) and Néel points (θ_N) for some hexagonal manganites.

Phase transition temperature	Compounds						
	$YMnO_3$	$HoMnO_3$	$ErMnO_3$	$TuMnO_3$	$YbMnO_3$	$LuMnO_3$	$ScMnO_3$
θ_F °C	660 [48] 640 [45]	600 [45]	560 [45]		720 [45]		
θ_N °C	~77 [56]	76 [42]	79 [42]	86 [42]	—	91 [42]	120 [42]

The group of boracites is the third group of ferroelectrics in which a magnetic order was found. The first compound that was observed to have a ferroelectric character was a mineral boracite $Mg_3B_7O_{13}Cl$ [57]. The crystal structure of the boracite was studied by ITO et al. [58]. This work was followed by others in which ferroelectricity in the boracite was doubted [59, 60]. However, ASHER, SCHMID et al. [61–65] synthesized and investigated a number of compounds with this structure and for some of these evidence of ferroelectricity has been found. A general formula for these compounds may be written as $Me_3B_7O_{13}X$ where Me = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and X = Cl, Br, I. Probably, all the compounds are ferroelectrics with Curie points between 60° and 800 °K depending upon the composi-

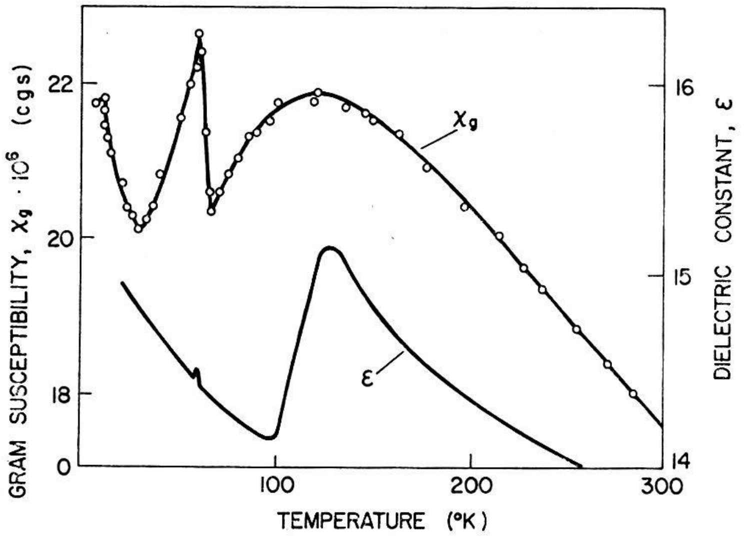

Figure 6

The temperature dependence of the dielectric permeability (ε) and of the magnetic susceptibility (χ_g) (H = 27,00 Oe) for $Ni_3B_7O_{13}I$ [64].

tion [62], and simultaneously they are antiferromagnets with the Néel points below liquid nitrogen temperature [63]. $Ni_3B_7O_{13}I$ is the most interesting compound. This compound has a high-temperature piezoelectric phase with a cubic structure (T_d^5) just as boracite $Mg_3B_7O_{13}Cl$ and below 64 °K [64] it becomes ferroelectric. The Néel point is about 120 °K. In the non-polar range between 64° and 120 °K $Ni_3B_7O_{13}I$ has no spontaneous magnetic moment but in its polar state it is a weak ferromagnet with the magnetic point group *m′ m 2′*. The temperature dependence of the dielectric permeability and magnetic susceptibility taken from reference [62] are given in Figure 6. The spontaneous magnetization is directed along ⟨001⟩ (in the pseudocubic

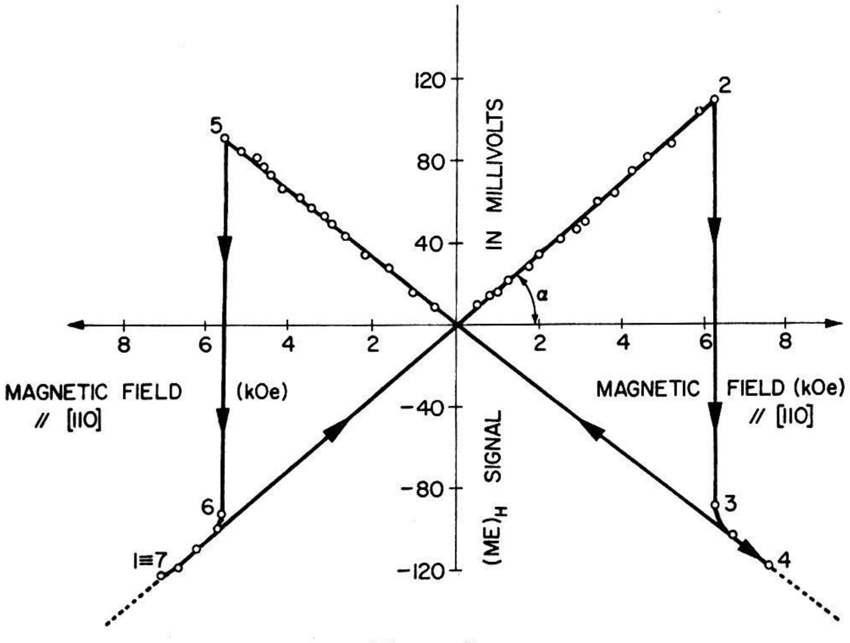

Figure 7

Example of a quadratic magnetoelectric hysteresis loop for $Ni_3B_7O_{13}I$ with H along ±⟨110⟩ and P along ⟨001⟩ at 46 °K [64].

indices) and the spontaneous magnetization is either along $\langle 110\rangle$ or $\langle \bar{1}\bar{1}0\rangle$. Thus $\boldsymbol{P}_s \perp \boldsymbol{M}_s$. The direction of $\boldsymbol{M}_s$ in this compound can be changed by the electric field [62]. An electric switching of $\boldsymbol{P}_s$ from $\langle 001\rangle$ to $\langle 00\bar{1}\rangle$ results in a 90° change of $\boldsymbol{M}_s$ from $\langle 110\rangle$ to $\langle 1\bar{1}0\rangle$. A rotation of magnetic field from $\langle 110\rangle$ to $\langle 1\bar{1}0\rangle$ leads to a reversal of the polarization $\boldsymbol{P}_s$ from $\langle 001\rangle$ to $\langle 00\bar{1}\rangle$. Aside from these pure domain effects a linear magnetoelectric effect is observed with a susceptibility of about 3.3×10^{-4} at 15°K. The domain effects combined with the linear magnetoelectric effect give a quadratic magnetoelectric hysteresis loop which is observed experimentally (Fig. 7).

3. Ferroelectric-ferromagnets

Ordinary ferrimagnets[2]) contain magnetic ions in two or more non-equivalent crystallographic sublattices. The well known examples are represented by spinels, garnets, hexaferrites and others. However, ferroelectrics of this type are unknown so far. Therefore in order to synthesize ferrimagnets with ferroelectric properties some other way must be found. The way consists in introducing two or more kinds of ions into the same sublattice and in forming a certain order in their distribution. The work of Reference [66] was the first one where the ferrimagnetic state in the perovskite-type structure was formed in this manner and the ferroelectric-ferromagnets were obtained.

We shall consider an example of solid solutions $(1-x)\, A'\, B'\, O_3 - xA''\, B''_{0.5}\, B'''_{0.5}\, O_3$. The second compound has an ordered distribution of B'' and B''' ions and the B'' and B''' alternate along all three four-fold axes of the cubic lattice. When x is small the ions in octhahedral positions are distributed randomly. However, when the content of the second component increases, a partial ordering of the ions develops. At sufficiently high contents of the second component the ions may be ordered completely. We shall study the case where B' and B'' ions possess some magnetic moments and the B''' ion has no magnetic moment. Then under the condition that the magnetic order is of G type, the solid solution may be presented by the formula:

$$A'_{1-x}\, A_x\, (\vec{B}{}'_{(1-x)/2}\, \vec{B}{}''_{x/2})\, (\overset{\leftarrow}{B}{}'_{(1-x)/2}\, B'''_{x/2})\, O_3\,,$$

where the arrows show the directions of the magnetic moments. In this case the magnetic sublattices coincide with the sublattices of (B', B'') and (B', B''') ions. If the magnetic moments of sublattices have opposite directions but are not equal, the net moment will not vanish.

A similar way for the synthesis of ferrimagnetics was used to obtain ferroelectric-ferromagnets [66], e.g., solid solutions of the type

$$(1-x)\, Pb\, (Fe_{2/3}\, W_{1/3})\, O_3 - x\, Pb\, (Mg_{1/2}\, W_{1/2})\, O_3\,.$$

The first component is ferroelectric and antiferromagnetic, the second is antiferroelectric with an ordered distribution of diamagnetic Mg^{2+} and W^{6+} ions. This differs from the above considered case in that the second component does not contain magnetic ions, but causes some ordering of Fe^{3+} and W^{6+} ions in the solid solutions.

---

[2]) We shall denote by this non-compensated antiferromagnets.

When this ion ordering is complete the formula of the solid solution may be written in the following way:

$$Pb\ (\overrightarrow{Fe}_{3/6\,(1-x)}\ Mg_{3/6\,x})\ (\overleftarrow{Fe}_{1/6\,(1-x)}\ W_{1/6\,(2-x)})\ O_3\ ,$$

where, as before, the expression in brackets represents the composition of (Fe, Mg) and (Fe, W) sublattices and simultaneously the composition of the magnetic sublattices. The different number of ferric ions in magnetic sublattices causes the non-vanishing magnetic moment, and ferrimagnetism results.

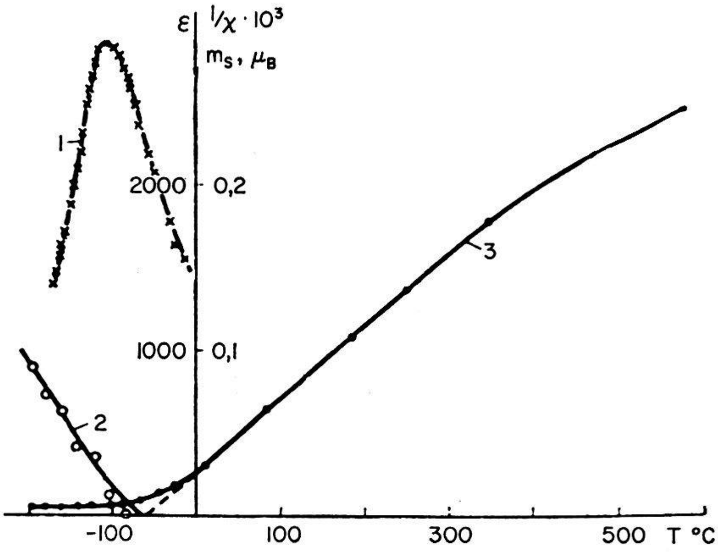

Figure 8

The temperature dependence of the dielectric permeability (1), of the spontaneous magnetic moment (2), and of the reciprocal magnetic susceptibility (3) for solid solution 0.7 $PbFe_{2/3}W_{1/3}O_3$ $- 0.3$ $PbMg_{1/2}W_{1/2}O_3$ [66].

X-ray investigations have shown that when the content of the second component is 20% and more, the ion ordering in octahedral positions is in fact observed, and this leads to the doubling of cell parameters along the three cubic axes. The examined solid solutions containing $PbMg_{1/2}W_{1/2}O_3$ from 0 to 88 mol % are ferroelectrics, but at higher concentrations they become antiferroelectrics. The temperature dependence of dielectric permeability of the solid solution containing 30% mol of $PbMg_{1/2}W_{1/2}O_3$ (curve 1), the temperature dependence of spontaneous magnetic moment (curve 2) and of reciprocal magnetic susceptibility (curve 3) are shown in Figure 18. As can be seen from curve 3, the temperature dependence of reciprocal magnetic susceptibility is typical for a ferrimagnet. The experimentally determined Néel temperatures are in good agreement with values calculated by the GOODENOUGH and GILLEO technique [12, 13].

4. Conclusions

As a result of the investigations of the last year a new group of materials (ferroelectric-ferromagnets) has been found in which the ordering of electric as well as magnetic moments is observed. In the perovskite-type structures, in hexagonal structures of $YMnO_3$ type, and in boracites, different coupling of electric and magnetic ordering can be observed. The principles of thermodynamical theory are developed for these crystals and new phenomena are predicted, i.e. a magnetoelectric effect, a jump of the magnetic (electric) permeability at the transition into a ferroelectric (magnetically ordered) state and some others.

The example of boracite demonstrates the mutual interaction of the magnetic and electric subsystems.

Further investigations of a new group of materials taken up in order to experimentally verify phenomena predicted by the thermodynamical theory, some developments of microscopic theory, synthesis of new ferroelectric-ferromagnets with sufficiently high magnetic moments and high Curie temperatures are of great interest.

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