

19. Balents L, Fisher M P A, Nayak C *Int. J. Mod. Phys. B* **12** 1033 (1998)
20. Franz M, Tešanović Z *Phys. Rev. Lett.* **87** 257003 (2001)
21. Franz M, Tešanović Z, Vafek O *Phys. Rev. B* **66** 054535 (2002)
22. Volovik G E *Pis'ma Zh. Eksp. Teor. Fiz.* **58** 457 (1993) [*JETP Lett.* **58** 469 (1993)]
23. Chakravarty S et al. *Phys. Rev. B* **63** 094503 (2001)
24. Gutzwiller M C *Phys. Rev. Lett.* **10** 159 (1963)
25. Zhang F C et al. *Supercond. Sci. Technol.* **1** 36 (1988)
26. Paramakanti A, Randeria M, Trivedi N *Phys. Rev. Lett.* **87** 217002 (2001)
27. Laughlin R B, cond-mat/0209269
28. Baskaran G, Zou Z, Anderson P W *Solid State Commun.* **63** 973 (1987)
29. Affleck I et al. *Phys. Rev. B* **38** 745 (1988)
30. Wen X-G, Lee P A *Phys. Rev. Lett.* **76** 503 (1996)
31. Lee P A et al. *Phys. Rev. B* **57** 6003 (1998)
32. Bernevig B A et al., cond-mat/0312573
33. Bernevig B A, Laughlin R B, Santiago D I, cond-mat/0303045
34. Zhang F C, cond-mat/0209272
35. Haas S et al., cond-mat/0311537
36. Nayak C *Phys. Rev. B* **62** 4880, R6135 (2000)
37. Volkov B A et al. *Zh. Eksp. Teor. Fiz.* **81** 729 (1981) [*Sov. Phys. JETP* **54** 391 (1981)]
38. Marston J B, Affleck I *Phys. Rev. B* **39** 11538 (1989)
39. Hsu T C, Marston J B, Affleck I *Phys. Rev. B* **43** 2866 (1991)
40. Kaminski A et al., cond-mat/0203133
41. Chakravarty S *Phys. Rev. B* **66** 224505 (2002)
42. Damascelli A, Hussain Z, Shen Z-X *Rev. Mod. Phys.* **75** 473 (2003)
43. Chakravarty S, Nayak C, Tewari S *Phys. Rev. B* **68** 100504(R) (2003); cond-mat/0306084
44. Ivanov D A, Lee P A, Wen X-G *Phys. Rev. Lett.* **84** 3958 (2000)
45. Leung P W *Phys. Rev. B* **62** R6112 (2000)
46. Yang C N *Phys. Rev. Lett.* **63** 2144 (1989)
47. Japaridze G I et al. *Phys. Rev. B* **65** 014518 (2002)
48. Belyavsky V I, Kopaev Yu V *Phys. Rev. B* **67** 024513 (2003)
49. Belyavskii V I, Kopaev V V, Kopaev Yu V *Zh. Eksp. Teor. Fiz.* **118** 941 (2000) [*JETP* **91** 817 (2000)]
50. Shen Z-X et al. *Science* **267** 343 (1995)
51. Lozovik Yu E, Yudson V I *Fiz. Tverd. Tela* **17** 1613 (1975) [*Sov. Phys. Solid State* **17** 1613 (1975)]
52. Abrikosov A A *Physica C* **341** – **348** 97 (2000)
53. Maksimov E G *Usp. Fiz. Nauk* **170** 1033 (2000) [*Phys. Usp.* **43** 965 (2000)]
54. Belyavskii V I et al. *Zh. Eksp. Teor. Fiz.* **124** 1149 (2003) [*JETP* **97** 1032 (2003)]
55. Belyavsky V I et al. *Zh. Eksp. Teor. Fiz.* (2004) (in press)
56. Brandow B H *Phys. Rev. B* **65** 054503 (2002)
57. Hirsch J E *Phys. Rev. B* **59** 11962 (1999)
58. Babaev E, Faddeev L D, Niemi A J *Phys. Rev. B* **65** 100512(R) (2002)

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Phase transitions and the giant magnetoelectric effect in multiferroics

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1. Introduction

It has long been noted that despite the different nature of structural phase transitions in them, the three classes of crystalline solid bodies — ferromagnets, ferroelectrics, and ferroelastics — have a whole series of similarities such as the existence of specific domains, anomalous physical properties in the neighborhood of a transition, hysteresis, etc. In 1969, K Aizu unified them into a single class of materials collectively named ferroics, due to the prefix ‘ferro’ they

share [1]. Multiferroics are a class of crystalline solids in which at least two of the three order parameters — magnetic, electrical, or mechanical — coexist.

The subject matter of this work is ferromagnetoelectrics, i.e., materials with magnetic and electric order simultaneously present [2, 3]. The relationship between magnetic and electric subsystems in ferromagnetoelectrics manifests itself as *magnetoelectric (ME) effects* and opens up the possibility of using an electric field to control the magnetic properties of a material or, vice versa, to use a magnetic field to modulate the electrical properties. All this makes ferromagnetoelectrics likely candidate materials for magnetic field sensors and writing/reading devices.

Although this theme is not new (the first ferromagnetoelectric was synthesized back in 1961 [4]), it has long been of purely academic interest because of the relatively small values of the observed magnetoelectric effects and because these effects have usually only been seen at low temperatures. For example, for the classical magnetoelectric material Cr₂O₃ (chromite) the magnitude of the magnetoelectric effect is $\alpha = P/H = 3 \times 10^{-10}$ C (m² Oe)⁻¹ (3.7×10^{-12} s m⁻¹ or 10^{-4} in the CGS system). ME effects two orders of magnitude stronger were observed in TbPO₄ [5]: 10^{-2} (in the CGS system) or 3×10^{-10} s m⁻¹. In current terminology such effects are referred to as *giant*. However, in this particular compound the magnetoelectric effect only exists at temperatures below 2 K. It is only recently that materials showing giant magnetoelectric effects at room temperature have been obtained [6].

The discovery of giant ME effects is of particular interest in the light of the rapid development of *spin electronics*, a new branch of microelectronics which makes use of the transport properties of spin-polarized electrons. The main concern of spin electronics is converting information in the form of magnetization into an electrical voltage. Currently, this problem is being solved by using the phenomenon of *giant magnetic resistance (GMR)* [7]. With the alternative offered by the giant magnetoelectric effect, devices working on the giant magnetoelectric effect can possibly present competition to GMR devices in the future.

Also of interest are prospects for using magnetoelectric materials in magnetic memory devices. The major limiting factor in increasing the data-recording density is the magnetic dipole interaction, and this gives promise to the use of magnetoelectrics, most of which are antiferromagnets in which magnetoelectric domains can act as information bits.

Thus, for a ferromagnetoelectric to be used for practical purposes, the following are simultaneously required: (1) high (above room) electric and magnetic transition temperatures, (2) a large ME effect, and (3) low electrical conductivity at room temperature.

2. The ferromagnetoelectric bismuth ferrite BiFeO₃

Among various ferromagnetoelectric materials, one of the most attractive is bismuth ferrite BiFeO₃. There are both fundamental science and applied aspects of interest in this material. The relatively simple chemical and crystal structure of bismuth ferrite makes it interesting as a model object for first-principles studies. Moreover, bismuth ferrite is of practical interest as the basis for creating magnetoelectric materials — to a large measure due to its record high temperatures for electric ($T_c = 1083$ K) and magnetic ($T_N = 643$ K) ordering.

Bismuth ferrite crystallizes in a rhombohedrically distorted perovskite structure with lattice parameters $a_{\text{hex}} = 5.58$ and $c_{\text{hex}} = 13.9$ Å (in hexagonal setting). Early neutron diffraction studies [8] showed bismuth ferrite to possess antiferromagnetic G-type order, in which each atom is surrounded by six others with opposite spin directions. More precise time-of-flight neutron diffraction measurements [9] revealed the presence of a more complex spatially modulated structure, with a large period $\lambda = 620 \pm 20$ Å incommensurate with that of the crystal lattice. The magnetic moments of iron ions, while maintaining the local antiferromagnetic G-type alignment, rotate along the propagation direction of the modulated wave in a plane perpendicular to the hexagonal basal plane.

Although bismuth ferrite belongs to the space group $R3c$, its magnetoelectric properties are conveniently analyzed in terms of first-order perturbation theory using a centrosymmetric group $R3\bar{c}$ as the zero approximation. The irreducible representations of the space group $R3\bar{c}$ are listed in the table below. There are eight of them: four one-dimensional ($\Gamma_1, \Gamma_2, \Gamma_5, \Gamma_6$) and four two-dimensional ($\Gamma_3, \Gamma_4, \Gamma_7, \Gamma_8$). The symmetry elements of group $R3\bar{c}$ are produced by the identical transformation E^+ , spatial inversion I^- , a 3-fold symmetry axis $3z^+$, and a 2-fold symmetry axis $2x^+$. The plus-sign superscript on a symmetry operator indicates that the magnetic sublattice transforms into itself; the minus-sign superscript means that it transforms into a sublattice with opposite spin direction under the symmetry transformation. While these features of the symmetry operators have no effect on the transformation rules of electric and magnetic fields, they do affect the transformation rules for the antiferromagnetism operator \mathbf{L} , which is defined as the difference of the sublattice magnetization vectors,

$$\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2. \quad (1)$$

The vector components of the electric field \mathbf{E} , magnetic field \mathbf{H} , electric polarization \mathbf{P} , and magnetization \mathbf{M} , and the components of the antiferromagnetism vector \mathbf{L} are placed in the table according to their transformation properties. It is readily seen that the following combinations of the vector components correspond to the irreducible representation Γ_1 , i.e., are invariant under symmetry transformations: $E_z(H_y L_x - H_x L_y)$, $L_z(H_y E_x - H_x E_y)$, $H_z(E_x L_y - E_y L_x)$, $E_x(H_y L_y - H_x L_x) + E_y(H_x L_y + H_y L_x)$. This means that the expression for the free energy will contain terms proportional to these invariants.

Since the polarization is the derivative of the free energy with respect to the electric field,

$$P_i = -\frac{\partial F}{\partial E_i}, \quad (2)$$

it follows that for the linear magnetoelectric effect tensor, which relates the vector of the magnetic-field-induced polarization with the magnetic field vector,

$$P_i^{\text{induced}} = \alpha_{ij} H_j, \quad (3)$$

we have [10]

$$\alpha_{i,j} = \begin{vmatrix} -a_1 L_x & -a_4 L_z + a_1 L_y & -a_2 L_y \\ a_1 L_y + a_4 L_z & a_1 L_x & a_2 L_x \\ -a_3 L_y & a_3 L_x & 0 \end{vmatrix}. \quad (4)$$

Note also that from the table of irreducible representations it follows that there exist a fundamental magnetoelectric interaction between spontaneous magnetization and spontaneous polarization, $P_z^0(M_y L_x - M_x L_y)$; an invariant $E_z(M_y L_x - M_x L_y)$, which gives rise to spontaneous polarization

$$P_z^0 \sim (0; 0; M_y L_x - M_x L_y); \quad (5)$$

and an invariant $P_z^0(H_y L_x - H_x L_y)$, which gives rise to spontaneous magnetization,

$$\mathbf{M} = -\frac{\partial F}{\partial \mathbf{H}} \sim (P_z L_y; -P_z L_x; 0). \quad (6)$$

Equations (5) and (6) contain only the z component of spontaneous polarization, since it is known from experiments that spontaneous polarization is directed along the 3-fold axis in bismuth ferrite.

Besides the ME effect and spontaneous magnetization, the magnetic symmetry of bismuth ferrite also allows the existence of a special type of magnetic order known as *toroidal* [11, 12]. The existence of a toroidal moment is due to the presence in the free energy of a term proportional to the invariant

$$(\mathbf{T} \cdot [\mathbf{E} \times \mathbf{H}]). \quad (7)$$

From this it follows that the vector components of the toroidal moment are proportional to the antisymmetric part of the linear ME-effect tensor,

$$T_i = \varepsilon_{ijk} \alpha_{jk}. \quad (8)$$

It is easily verified by comparing Eqns (8) and (4) that for bismuth ferrite the vector components of the toroidal moment are proportional to the components of the antiferromagnetism vector,

$$\begin{pmatrix} T_x \\ T_y \end{pmatrix} \sim \begin{pmatrix} L_x \\ L_y \end{pmatrix}, \quad T_z \sim L_z. \quad (9)$$

Thus, crystal symmetry allows the existence in bismuth ferrite of a linear ME effect (4), spontaneous magnetization (6), and a toroidal moment (9). However, under normal conditions these effects are not observed due to the existence of a spatially modulated spin structure. As is seen from Eqns (4), (6), and (9), for the ferromagnetism vector varying periodically in space the volume-averaged values of the magnetoelectric-effect tensor components, magnetization, and toroidal moment are zero. When the spatially modulated structure is destroyed, however, all three effects do manifest themselves, as will be discussed below.

Note that the presence of a modulated structure does not rule out the existence of the quadratic ME effect $P_i = \beta_{ijk} H_j H_k$. This is confirmed experimentally in Refs [13, 14].

3. Spatially modulated spin structure

The existence of a spatially modulated spin structure discovered in Ref. [9] was given a theoretical justification in Ref. [15], in which it is shown that the formation of the modulated structure is due to the presence in the free-energy-density expression of the Lifshitz invariant

$$f_L = \gamma P_z (L_x \nabla_x L_z + L_y \nabla_y L_z - L_z \nabla_x L_x - L_z \nabla_y L_y), \quad (10)$$

Table 1. Irreducible representations (IR) of the space group $R\bar{3}c$. R is the matrix for a 120° rotation about the z axis (c axis in hexagonal setting).

IR	E^+	I^-	$3z^+$	$2x^+$	H_i, E_i	L_i
Γ_1	1	1	1	1		
Γ_2	1	1	1	-1	H_z, M_z	
Γ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	R	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} H_x \\ H_y \end{pmatrix}; \begin{pmatrix} M_x \\ M_y \end{pmatrix}$	
Γ_4	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	R	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} H_y \\ -H_x \end{pmatrix}; \begin{pmatrix} M_y \\ -M_x \end{pmatrix}$	
Γ_5	1	-1	1	1		
Γ_6	1	-1	1	-1	E_z, P_z	L_z
Γ_7	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	R	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} E_x \\ E_y \end{pmatrix}; \begin{pmatrix} P_x \\ P_y \end{pmatrix}$	$\begin{pmatrix} L_x \\ L_y \end{pmatrix}$
Γ_8	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	R	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$		$\begin{pmatrix} L_y \\ -L_x \end{pmatrix}$

where γ is a coefficient of magnetoelectric nature. This invariant combination of vectors can be obtained from Table 1 by noting that the vector

$$\mathbf{V} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

transforms by the same rules as the polar vectors \mathbf{E} and \mathbf{P} . It is worthwhile noting that combination (10) is called the Lifshitz invariant by analogy with the invariant of the form

$$L_i \frac{\partial L_j}{\partial x} - L_j \frac{\partial L_i}{\partial x},$$

but what is different about combination (10) is that it requires the presence of spontaneous polarization for its existence.

The total expression for the free-energy density is written in the form

$$f = f_L + f_{\text{exch}} + f_{\text{an}}, \quad (11)$$

where

$$f_{\text{exch}} = A \sum_{i=x,y,z} (\nabla_i)^2 = A [(\nabla\theta)^2 + \sin^2\theta(\nabla\varphi)^2] \quad (12)$$

is the exchange energy, $A = 3 \times 10^7$ erg cm $^{-1}$ is the nonuniform exchange constant (also known as exchange stiffness),

$$f_{\text{an}} = K_u \sin^2\theta \quad (13)$$

is the anisotropy energy, and θ and φ are the polar and azimuthal angles of the unit antiferromagnetism vector $\mathbf{l} = (\sin\theta \cos\varphi, \sin\theta \sin\varphi, \cos\theta)$ in a spherical coordinate system with the polar axis along the principal axis (hexagonal setting).

Minimizing the free energy functional $F = \int f dV$ by the Lagrange–Euler method and neglecting anisotropy, the functions $\theta(x, y, z)$ and $\varphi(x, y, z)$ are found to be [10, 15]

$$\varphi_0 = \text{const} = \arctan\left(\frac{q_y}{q_x}\right), \quad \theta_0 = q_x x + q_y y, \quad (14)$$

where \mathbf{q} is the wave vector of the spatially modulated spin structure. Solution (14) is a cycloid whose plane is perpendicular to the basal plane and is oriented along the modulation-wave propagation direction.

Refining the calculation by allowing for anisotropy, K_u is given by the formula [15, 16]

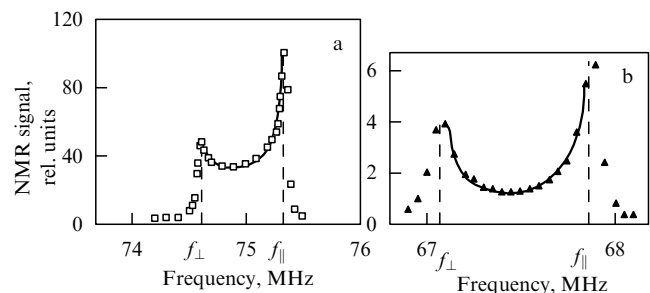
$$\cos\theta = \text{sn}\left(q_x x, m = -\frac{K_u}{E}\right), \quad (15)$$

which corresponds to an anharmonic cycloid. For an anisotropy constant much smaller than the exchange energy, $K_u \ll E \sim Aq^2$, the modulus parameter of the elliptic sine m tends to zero, and solution (15) goes over to Eqn (14).

The point to note here is that in addition to neutron diffraction methods, NMR observations lend support to the existence of the spatially modulated structure [17–19]. Instead of a single peak corresponding to a uniform structure, these observations have revealed a spectral line of complex shape with its two maxima corresponding to spin alignments perpendicular and parallel to the principal axis (Fig. 1). The shape analysis of the line has not only revealed the presence of the cycloid but has also yielded the spin distribution over its length, which at low temperatures ($T = 4.2$ K) was found to be essentially anharmonic in that over most of the cycloid period spins are at a small angle to the axis, thus increasing the intensity of the high-frequency peak. As the temperature is increased, the line shape becomes increasingly symmetric, the anharmonicity decreases, and at room temperature the coordinate dependence of the angle tends to a linear one [17] (see Fig. 1a, 1b).

Substituting Eqn (14) into Eqn (11) and assuming the cycloid to be harmonic, the volume-averaged free-energy density is

$$\langle F \rangle = Aq^2 - (\gamma P_z)q + \frac{K_u}{2}. \quad (16)$$

**Figure 1.** NMR spectra of ^{57}Fe nuclei in BiFeO_3 at 77 K (a) and 304 K (b) [17].

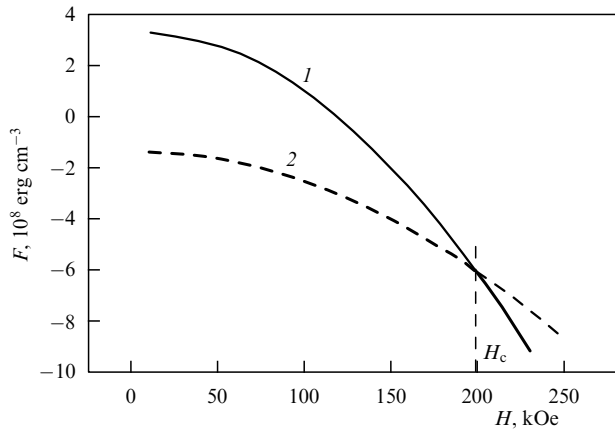


Figure 2. Magnetic field variation of the free energy density: 1, uniform state; 2, spatially modulated state.

The wave vector corresponding to the energy minimum is

$$q = \frac{2\pi}{\lambda} = \frac{\gamma P_z}{2A}. \quad (17)$$

Knowing the period of the structure ($\lambda = 620 \text{ \AA}$) and assuming the polarization $P_z = 6 \times 10^{-6} \text{ C cm}^{-2}$ and the exchange constant $A = 3 \times 10^{-7} \text{ erg cm}^{-1}$, the nonuniform magnetoelectric coefficient is estimated to be $\gamma = 10^5 \text{ erg C}^{-1} = 10^{-2} \text{ V}$.

4. Magnetic-field-induced phase transition

Since the volume-averaged magnetoelectric effect, spontaneous magnetization, and toroidal moment are all zero due to the presence of the cycloid, the destruction of the spatially modulated structure is the necessary condition for the existence of all the effects. One of the ways of suppressing the modulated structure is applying a strong magnetic field. This means introduction of an additional term to the expression for the anisotropy constant, giving (the magnetic field is applied along the 3-fold axis c)

$$K_u = K_u^0 - \chi_{\perp} \frac{H_z^2}{2}, \quad (19)$$

where χ_{\perp} is the magnetic susceptibility in the direction perpendicular to the antiferromagnetism vector, and K_u^0 is the uniaxial anisotropy constant in the absence of a field. For a field greater than a certain critical value, the existence of a spatially modulated structure may become unfavorable compared to the uniform state, whose energy is defined by

$$F_{\text{hom}} = K_u, \quad (20)$$

where K_u is the constant of effective anisotropy (19).

Figure 2 shows the dependence of the free-energy density on the applied field for the spatially modulated structure (16) and the uniform state (20). Although at low fields the spatially modulated structure is more favorable energetically than the modulated state, for high fields the situation is different. The critical field H_c for the phase transition to the uniform state is found from Eqns (16) and (20) to be

$$H_c = \sqrt{\frac{2(K_u^0 + 2Aq^2)}{\chi_{\perp}}}. \quad (21)$$

Assuming $K_u^0 \ll Aq^2$ and taking $A = 3 \times 10^{-7} \text{ erg cm}^{-1}$ and $\chi_{\perp} = 4.7 \times 10^{-5}$, the critical field is estimated to be $\sim 200 \text{ kOe}$. A theoretical treatment of phase transitions in bismuth ferrite with allowance for the anharmonic nature of the cycloid is given in Ref. [16].

The destruction of the spatially modulated structure and the appearance of a linear magnetoelectric effect and of a toroidal moment in bismuth ferrite have been confirmed experimentally by measuring the magnetic-field variation of polarization in pulsed fields [10, 20, 21]. For $H < H_c$, the polarization depends almost linearly on the field; however, in a field equal to the critical one the polarization experiences a sudden jump, which is accompanied by the appearance of a linear ME effect and by the renormalization of the quadratic ME-effect tensor (Fig. 3). The critical field and the linear magnetoelectric effects were found to be $\sim 200 \text{ kOe}$ and $\sim 10^{-10} \text{ C (m}^2 \text{ Oe)}^{-1}$, respectively. It was also found from the polarization variations that at the critical field a toroidal moment appears in the material [21]. Magnetization measurements in strong magnetic fields revealed the presence of a spontaneous magnetization of $0.25 \text{ G cm}^3 \text{ g}^{-1}$ in fields above H_c [22]. Thus, in a field above the critical value all three effects

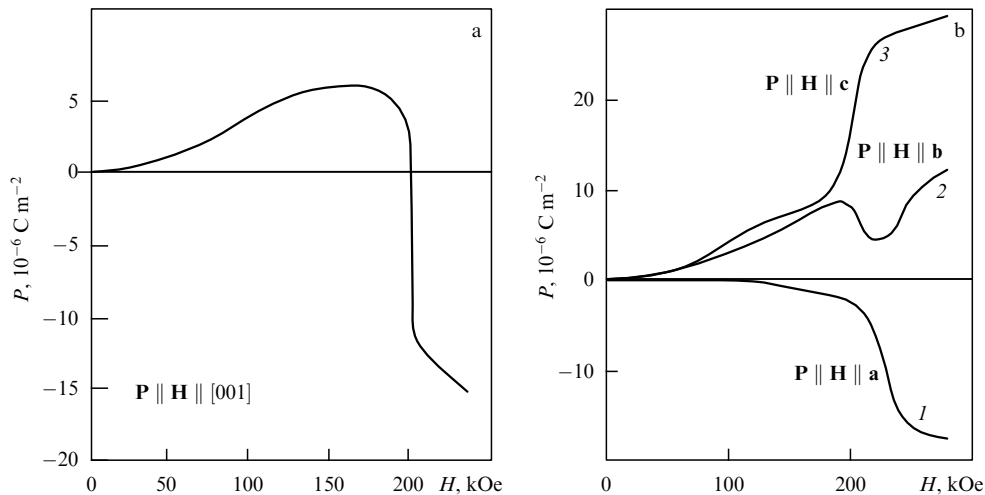


Figure 3. Longitudinal electric polarization versus magnetic field for various crystallographic directions: (a) along the [001] cubic axis; and (b) along the axes **a**, **b**, **c** in the hexagonal setting [10, 20].

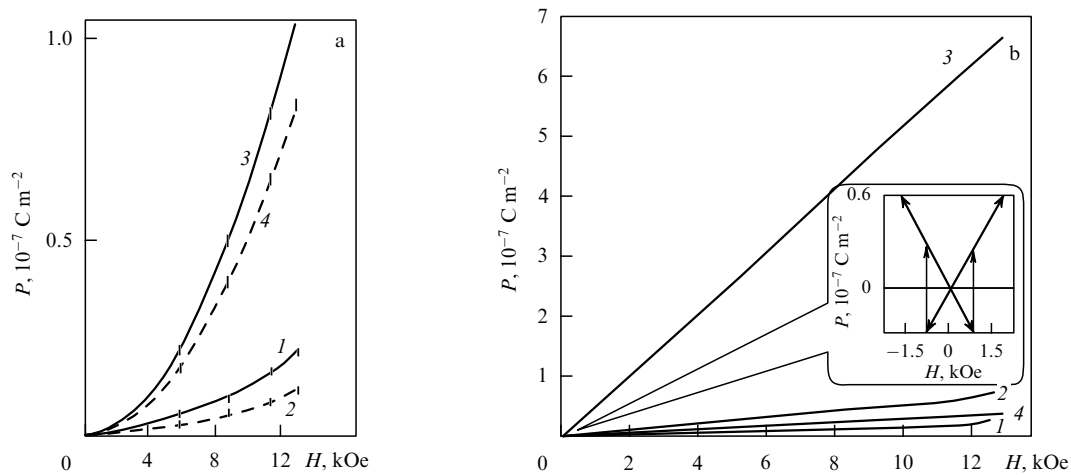


Figure 4. Polarization versus magnetic field for rare-earth solid solutions in bismuth ferrite after Ref. [24]: (a) crystals of BiFeO_3 (curves 1, 2) and $\text{Bi}_{0.92}\text{La}_{0.08}\text{FeO}_3$ (curves 3, 4) at temperatures of 4.2 K (1, 3) and 77 K (2, 4); and (b) crystals of $\text{Bi}_{0.45}\text{La}_{0.55}\text{FeO}_3$ (1), $\text{Bi}_{0.55}\text{Gd}_{0.45}\text{FeO}_3$ (2), $\text{Bi}_{0.45}\text{Dy}_{0.55}\text{FeO}_3$ (3, 4) at temperatures of 4.2 K (1–3) and 77 K (4).

allowed by the symmetry of the crystal — the linear ME effect, spontaneous magnetization, and toroidal moment — were observed.

The measurements of Refs [10, 20–22] were carried out in pulsed fields. In recent years, experiments on electron spin resonance in bismuth ferrite in a static magnetic field have yielded a more accurate value for the transition field, $H_c = 180 \text{ kOe}$. Also, it is shown that at the phase transition the resonance line shows a large hysteresis as the field increases and decreases [23]. The magnetoelectric coefficient value of $3.3 \text{ V (cm Oe)}^{-1}$ found by approximating the experimental dependences above the critical field is in good agreement with the value of the giant ME effect in thin bismuth ferrite films [6].

5. Bismuth ferrite–based materials and the giant magnetoelectric effect

The spatially modulated structure can be suppressed in ways other than by applying strong magnetic fields. One such way is to substitute rare-earth ions for bismuth ions. Compounds of formula $R\text{FeO}_3$ (rare-earth orthoferrites) also have a perovskite-like structure but distorted orthorhombically. Introducing rare-earth impurities can increase the anisotropy constant of bismuth ferrite to the point where the existence of a spatially modulated structure becomes energetically unfavorable.

The ME-effect measurements of Refs [14, 24–27] were made on bismuth ferrite compounds of the form $\text{Bi}_{1-x}\text{R}_x\text{FeO}_3$, in which rare-earth ions of lanthanum, gadolinium, and dysprosium were substituted for bismuth ions. Figure 4a shows the field dependence of polarization for pure bismuth ferrite and $\text{Bi}_{0.92}\text{La}_{0.08}\text{FeO}_3$. Both materials display quadratic dependences, but even a relatively small concentration of lanthanum leads to a significantly increased quadratic effect. Results on the ME effect in bismuth ferrite compounds with a high concentration of rare-earth impurities are given in Fig. 4b. The magnetic field variations are found to be linear. The linear magnetoelectric effect was largest [$0.05 \times 10^{-9} \text{ C (m}^2 \text{ Oe)}^{-1}$] in dysprosium compounds at the liquid-helium temperature (4.2 K). As the temperature is increased, the linear magnetoelectric effect decreases, and at the liquid-nitrogen temperature it is only observed in

dysprosium compounds. A further interesting feature of the bismuth ferrite–based solid solutions is the low-field polarization switching effect with a characteristic ‘butterfly’ hysteresis (Fig. 4b). High-field polarization measurements on bismuth ferrite with a low lanthanum content ($x < 0.3$) showed that although at such impurity concentrations the spatially modulated structure persists, adding lanthanum decreases the value of the field required for the transition from the spatially modulated to the uniform state [26, 27]. However, the relatively small values of the observed effects and the loss of magnetoelectric and dielectric properties at room temperatures preclude speaking of the practical use of these materials.

Recently, however, encouraging results have been obtained on thin films of BiFeO_3 , in which a giant magnetoelectric effect $dE/dH = 3 \text{ V (cm Oe)}^{-1}$ was observed [6]. The destruction of the spatially modulated structure in the films is possibly due to epitaxial stresses which, whether working through the magnetostriction or piezoelectric effects, can create magnetic and electric fields critical for phase transitions. In addition to the large magnetoelectric effect, the films also displayed anomalously high values of polarization (0.6 C m^{-2}), an order of magnitude higher than for bulk samples (0.061 C m^{-2}).

Large values of ME effects can be obtained in composite materials, i.e., in structures consisting of alternate magnetostriction and piezoelectric layers [28–31]. Such a composite material behaves as an effective magnetoelectric medium in which the ME interaction is mediated by the mechanical subsystem. The effects reach $0.1 \text{ V (cm Oe)}^{-1}$ in a static magnetic field and $90 \text{ V (cm Oe)}^{-1}$ in a magnetic field alternating at the electromechanical resonance frequency dependent on sample dimensions and composite parameters [31].

We cannot conclude without mentioning the optical methods used in the study of magnetoelectric materials. Reference [32] introduces the concept of the *electromagneto-optical effect*, which manifests itself as a change in the rotation angle of the polarization of light due to the applied electrical and magnetic fields [32, 33].

A study of the temperature variation of the intensity of the second optical harmonic in bismuth ferrite [34] showed that

the appearance of electrical and magnetic order affects the nonlinear magneto-optical response. The experiment revealed a sharp increase in the intensity of the second optical harmonic with decreasing temperature below the Curie point, and demonstrated a nonlinear variation of the intensity with the temperature close to the Néel point.

6. Conclusions

Bismuth ferrite BiFeO_3 is a multiferroic material with uniquely high temperatures for electric ($T_c = 1083$ K) and magnetic ($T_N = 643$ K) ordering, which makes it attractive for practical applications. A necessary condition for observing a linear magnetoelectric effect, spontaneous magnetization, and a toroidal moment in the BiFeO_3 compound is that the spatially modulated spin structure be destroyed. One way of suppressing the spin cycloid is applying strong magnetic fields in which the system makes a phase transition from a spatially modulated to a uniform state, during which all three effects appear. Other methods of suppressing the spin cycloid (such as replacing bismuth ions by rare-earth ions or preparing epitaxial films of bismuth ferrite) led to the ME effect an order of magnitude stronger than previously observed. These effects are known as giant in current terminology.

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References

1. Aizu K *Phys. Rev. B* **2** 754 (1970)
2. Smolenskiĭ G A, Chupis I E *Usp. Fiz. Nauk* **137** 415 (1982) [*Sov. Phys. Usp.* **25** 475 (1982)]
3. Venevtsev Yu N, Gagulin V V, Lyubimov V N *Segnetomagnetiki* (Ferromagnetoelectrics) (Moscow: Nauka, 1982)
4. Smolenskiĭ G A et al. *Izv. Akad. Nauk SSSR Ser. Fiz.* **25** 1333 (1961)
5. Rado G T, Ferrari J M, Maisch W G *Phys. Rev. B* **29** 4041 (1984)
6. Wang J et al. *Science* **299** 1719 (2003)
7. Johnson M *Proc. IEEE* **91** 652 (2003)
8. Kiselev S V, Ozerov R P, Zhdanov G S *Dokl. Akad. Nauk SSSR* **145** 1255 (1962) [*Sov. Phys. Dokl.* **7** 742 (1963)]
9. Sosnowska I, Neumaier T P, Steichele E J. *Phys. C: Solid State Phys.* **15** 4835 (1982)
10. Popov Yu F et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **57** 65 (1993) [*JETP Lett.* **57** 69 (1993)]
11. Ginzburg V L et al. *Solid State Commun.* **50** 339 (1984)
12. Schmid H *Ferroelectrics* **252** 41 (2001)
13. Tabares-Munoz C et al. *Jpn. J. Appl. Phys.* **24** 1051 (1985)
14. Murashov V A et al. *Fiz. Tverd. Tela* **32** 2156 (1990) [*Sov. Phys. Solid State* **32** 1255 (1990)]
15. Sosnowska I, Zvezdin A K *J. Magn. Magn. Mater.* **140–144** 167 (1995)
16. Tehranchi M M, Kubrakov N F, Zvezdin A K *Ferroelectrics* **204** 181 (1997)
17. Zaleskiĭ A V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **71** 682 (2000) [*JETP Lett.* **71** 465 (2000)]
18. Zaleskiĭ A V et al. *Europhys. Lett.* **50** 547 (2000)
19. Zaleskiĭ A V et al. *Zh. Eksp. Teor. Fiz.* **122** 116 (2002) [*JETP* **95** 101 (2002)]
20. Popov Yu F et al. *Ferroelectrics* **162** 135 (1994)
21. Popov Yu F et al. *Fiz. Nizk. Temp.* **21** 649 (2001) [*Low Temp. Phys.* **27** 478 (2001)]
22. Popov Yu F et al., in *Magnetoelectric Interaction Phenomena in Crystals: MEIPIC-5, Sudak, Crimea, Ukraine, 21–24 September, 2003*, Abstracts, p. 31
23. Ruetter B et al. *Phys. Rev. B* **69** 064114 (2004)
24. Murashov V A et al. *Kristallografiya* **35** 912 (1990) [*Sov. Phys. Crystallogr.* **35** 538 (1990)]
25. Gabbasova Z V et al. *Phys. Lett. A* **158** 491 (1991)
26. Kadomtseva A M et al. *Physica B* **211** 327 (1995)
27. Vorob'ev G P et al. *Fiz. Tverd. Tela* **37** 2428 (1995) [*Phys. Solid State* **37** 1329 (1995)]
28. Srinivasan G et al. *Phys. Rev. B* **64** 214408 (2001)
29. Bichurin M I et al. *Phys. Rev. B* **66** 134404 (2002)
30. Bush A A et al. *J. Magn. Magn. Mater.* **258–259** 45 (2003)
31. Laletin U et al., in *Magnetoelectric Interaction Phenomena in Crystals: MEIPIC-5, Sudak, Crimea, Ukraine, 21–24 September, 2003*, Abstracts, p. 22
32. Krichevskii B B, Pisarev R V, Selitskiĭ A G *Pis'ma Zh. Eksp. Teor. Fiz.* **41** 259 (1985) [*JETP Lett.* **41** 317 (1985)]
33. Kovalenko V F, Koronovskii V E *Ukr. Fiz. Zh.* **47** 855 (2002)
34. Agal'tsov A M et al. *Kratk. Soobshch. Fiz. FIAN* (5) 37 (1989)