Linear magnetoelectric effect and phase transitions in bismuth ferrite, $BiFeO_3$

Yu. F. Popov, A. K. Zvezdin, G. P. Vorob'ev, A. M. Kadomtseva, V. A. Murashev, and D. N. Rakov
M. V. Lomonosov Moscow State University

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A new phase transition has been observed in $BiFeO_3$. It is a transition from a state with a spatially nonuniform cycloid structure to an antiferromagnetic phase. This transition is induced by a high magnetic field and is accompanied by a large increase in the electric polarization of the sample. The linear magnetoelectric effect has been measured in $BiFeO_3$.

Bismuth ferrite is a ferromagnet with high electric and antiferromagnetic ordering temperatures,[1-3] $T_c=1083$ K and $T_N=673$ K. Although the crystal symmetry of $BiFeO_3$ is consistent with the existence of a linear magnetoelectric effect, this effect cannot be seen experimentally because of the cycloid antiferromagnetic structure.[4-6] The quadratic magnetoelectric effect in $BiFeO_3$ has been studied in detail.[7,8] Our purpose in the present study was to learn about the magnetoelectric effect in $BiFeO_3$ in high magnetic fields, up to 280 kOe, at which a phase transition can occur from a spatially modulated structure to a uniform antiferromagnetic structure. We would expect a significant increase in the electric polarization of the sample as a result of the onset of a linear magnetoelectric effect.

Experimental results. The electric polarization P induced by a pulsed magnetic field up to 280 kOe was studied over the temperature range 10–180 K. The $BiFeO_3$ crystals were grown by spontaneous crystallization from molten solution. The crystal habit is approximately cubic and corresponds to {001} faces (in an orthorhombic arrangement). Small cubes were cut from the $BiFeO_3$ single crystals. The edges of the cubes were oriented along the a, b, and c axes in a hexagonal coordinate system (a is the twofold axis). For the measurements of the ith polarization component ($i=a$, b, c), electrodes were applied by means of epoxy resin with a conducting filler to the planes perpendicular to the i axis. The voltage ($V \propto P$) across the electrodes was fed through a special amplifier to an oscilloscope. The triaxial input of the amplifier made it possible (at $K \sim 0.99$) to cancel the input capacitance of the amplifier, so the sensitivity of the apparatus was improved to 10^{-8} C/m^2. The high input resistance (10^{13}–$10^{14}\Omega$) of the amplifier made the time constant of the measurement system long (in comparison with the length of the magnetic field pulse) and prevented charge drainage.

Figure 1 shows the field dependence of the longitudinal polarization in the case in which the field is along the [001] axis. At $H<H_c$ the polarization is an essentially quadratic function of the field. At $H_c=200$ kOe, there is a sharp change in $P(H)$, which apparently means a destruction of the cycloid spin structure. This event should

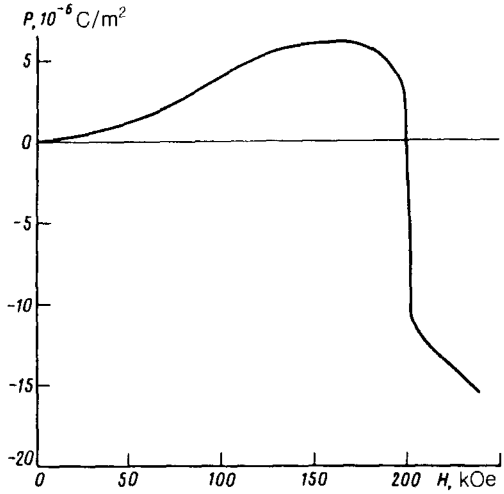

FIG. 1. Longitudinal polarization versus the strength of the magnetic field along the [001] axis at $T = 10$ K.

be accompanied by the onset of a linear magnetoelectric effect and a renormalization of the tensor of the quadratic magnetoelectric effect.

A similar field dependence was observed for the polarization in measurements of the magnetoelectric effect along the *c* axis of the crystal with the magnetic field along the *a*, *b*, and *c* axes (curves 1–3, respectively, in Fig. 2).

The most abrupt changes in the polarization at H_c were observed in measurements of the longitudinal magnetoelectric effect along the *c* axis. In the cases $H \| a$ and $H \| b$ the changes in *P* are smaller and consist of two steps. The reason may be the presence of blocks in the sample. As the temperature is varied, there is no qualitative

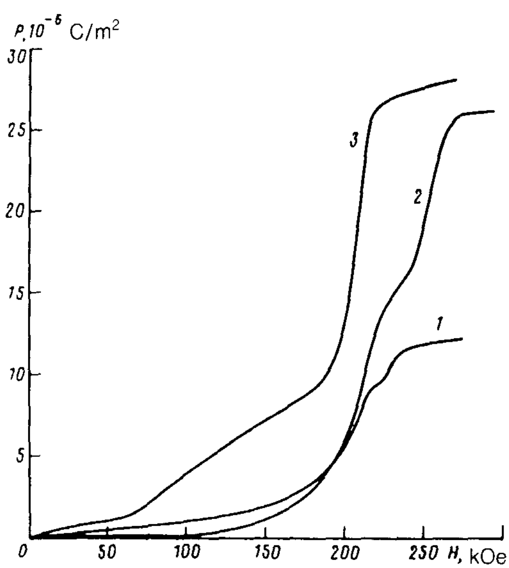

FIG. 2. Polarization along the *c* axis at $T = 18$ K. The magnetic field is along the *a*, *b*, and *c* axes (curves *1–3*, respectively).

change in the $P(H)$ curves. The magnitude of the polarization varies by less than 20% over the temperature range studied, while the critical field remains essentially constant. Measurements of P at $T > 180$ K are complicated by the sharp increase in the conductivity of the sample.

Discussion of results. Below T_c, $BiFeO_3$ has the space group $R3c - C_{3v}^6$. The antiferromagnetic order of type G can be characterized by ferromagnetic and antiferromagnetic vectors:

$$\mathbf{m} = V_0^{-1} \sum_j \mathbf{M}_j, \quad \mathbf{L} = V_0^{-1} \sum_j (-1)^{-j} \mathbf{M}_j, \tag{1}$$

where $\mathbf{M}_j$ are the magnetic moments of the iron ions of the unit cell of the crystal, and V_0 is the volume of this cell. To analyze the magnetic properties of $BiFeO_3$ we use the reduced group D_{3d}^6, which is obtained from the overall space group of the paraphase of $BiFeO_3$ ($T > T_c$) by replacing all translations over an integer number of lattice constants by the unit element. The sole electric order parameter is P_z, which is the projection of the polarization onto the C_3 axis. The origin of the spatially modulated structure in bismuth ferrite can be explained in terms of the existence of relativistic Lifshitz invariants in the group D_{3d}^6 of the form $\alpha_{ij} L_i \partial_j L_k$, of which only one is important for our purposes:

$$\tilde{\alpha} P_z (L_x \partial_x L_z + L_y \partial_y L_z). \tag{2}$$

It is easy to verify directly that this combination is indeed an invariant of the D_{3d}^6 group. The vector $\mathbf{L}$ can be written in the form $L_x = L \sin\theta \cos\phi$, $L_y = L \cos\theta \sin\phi$, $L_z = L \cos\theta$, where θ and ϕ are the polar and azimuthal angles, defined in the usual way in the coordinate system in which the c axis is the polar axis.

Minimizing the free energy of the crystal, taking the Lifshitz invariant into account, we find the spatially modulated spin structure (SMSS) to be[9]

$$\theta = q_x x + q_y y, \quad \phi = \arctan(q_x / q_y), \tag{3}$$

where the vector $\mathbf{q} = (q_x, q_x, 0)$ belongs to the star of wave vectors (rays) obtained from an arbitrary q by applying all elements of the $R3c$ group.

There is another solution which minimizes the free energy:

$$\theta = \text{const}, \quad \phi = \text{const}. \tag{4}$$

This solution describes a spatially uniform antiferromagnetic structure (SUAS). However, the minimum of the free energy corresponds to the SMSS. The energy advantage over the SUAS is

$$\Delta F(q) = F_{\text{SMSS}} - F_{\text{SUAS}} = -Aq^2 + K_u/2 < 0, \tag{5}$$

where A is the inhomogeneous-exchange constant (the exchange stiffness), K_u is the constant of the uniaxial magnetic anisotropy, $q = \alpha/4A$, and α is the constant of relativistic inhomogeneous exchange, which is assumed to be proportional to P_z in accordance with (2).

Let us estimate $\Delta F(q)$, using the parameter values[4-6]

$$A \sim (2\text{–}4) \times 10^{-7}\ \text{erg/cm}, \quad q = 2\pi/\lambda, \quad \lambda = 620\ \text{Å}. \tag{6}$$

Substituting these values into (5), we find $\Delta F = 2 \times 10^5$ erg/cm^3.

In a magnetic field, the free energy of the SUAS falls off more rapidly than that of the SMSS; an SMSS–SUAS phase transition may occur as a result. The critical field for this transition can be calculated by comparing the free energies of the SMSS and SUAS phases. With the magnetic field along the c axis $[\mathbf{H} = (0, 0, H_z)]$, for example, we have

$$F_{\text{SUAS}} = K_u - \chi_\perp H^2/2, \tag{7}$$

where $\chi_\perp$ is the transverse magnetic susceptibility of the antiferromagnetic structure. We assume (quite naturally) $\theta = \pi/2$ in the SUAS phase.

Assuming $K_u \ll Aq^2$, and equating the free energies of the SMSS, (3), and of the SUAS, (4), we find a rough estimate of the critical field for the SMSS–SUAS transition:

$$H_c^z = (4Aq^2/\chi_\perp)^{1/2}. \tag{8}$$

The critical fields H_c for $\mathbf{H} = (H_x, H_y, 0)$ can be found from an expression like (8) if $m_s \ll (K_u \chi_\perp)^{1/2}$, where m_s is the spontaneous magnetization of $BiFeO_3$. Assuming $\chi_\perp = 10^{-5}$, and taking the value of Aq^2 from (6), we find $H_c^z = (2\text{–}3) \times 10^5$ kOe, in agreement with the value found from experimental data.

The polarization vector $\mathbf{P}$ can be written

$$P_i = P_{si} + \alpha_{ij} H_j + 1/2 \beta_{ijk} H_j H_k, \tag{9}$$

where $\mathbf{P}_s = (0, 0, P_s)$ is the spontaneous-polarization vector, and α_{ij} is the tensor of the linear magnetoelectric susceptibility,

$$\alpha = \begin{vmatrix} -a_1 L_x & -a_4 L_z + a_1 L_y & -a_2 L_y \\ a_1 L_y + a_4 L_z & a_1 L_x & a_2 L_x \\ -a_3 L_y & a_3 L_x & 0 \end{vmatrix}. \tag{10}$$

The exact expressions for the components of the tensor β_{ijk} are quite lengthy. As examples, we write out three components of this tensor, emphasizing their angular dependence:

$$\begin{aligned} \beta_{xxx} &= b_1 + b_2 \sin^2\theta \cos 2\phi + b_3 \sin\theta \cos\theta \cos\phi, \\ \beta_{yyy} &= b_2 \sin^2\theta \sin 2\phi + b_2 \sin\theta \cos\theta \sin\phi, \\ \beta_{zzz} &= b_4 + b_5 \sin^2\theta. \end{aligned} \tag{11}$$

It follows from (10) that when the cycloid structure is destroyed by a magnetic field, a linear magnetoelectric effect should arise. This effect vanishes in the original structure. In addition, there should be a renormalization of the tensor of the quadratic magnetoelectric effect, which leads in turn to the abrupt change in the polarization seen experimentally at $H = H_c$.

In conclusion we would like to repeat that this study has revealed a new phase transition in the magnetic ferroelectric $BiFeO_3$, from a cycloid spin-modulated phase to a uniform antiferromagnetic phase. This transition is induced by a magnetic field and is accompanied by a sharp change in the electric polarization. We attribute this effect to a contribution of the linear magnetoelectric effect to the polarization of the crystal.

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