Origin of the giant linear magnetoelectric effect in perovskitelike multiferroic $BiFeO_3$

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(Received 29 November 2015; revised manuscript received 6 March 2016; published 29 March 2016)

In this article the mechanism of the linear magnetoelectric (ME) effect in the rhombohedral multiferroic $BiFeO_3$ is considered. The study is based on the symmetry approach of the Ginzburg-Landau type, in which polarization, antiferrodistortion, and antiferromagnetic momentum vectors are viewed as ordering parameters. We demonstrate that the linear ME effect in BFO is caused by reorientation of the antiferrodistortion vector in either electric or magnetic field. The numerical estimations, which show quantitative agreement with the results of the recent measurements in film samples, have been performed. A possibility of significant enhancement of the magnetoelectric effect by applying an external static electric field has been investigated. The considered approach is promising for explaining the high values of the ME effect in composite films and heterostructures with BFO.

DOI: 10.1103/PhysRevB.93.094435

I. INTRODUCTION

Magnetoelectric (ME) effect opens up wide prospects for practical applications of multiferroic materials in various fields of nanoelectronics, microwave electronics, and optoelectronics [1–6]. Intense investigation of the magnetoelectric effect dates back to the 2000s, with the advent of perspective film oxide perovskite multiferroics ABO_3. The pseudocubic multiferroic $BiFeO_3$ (BFO) stands out among other materials, since it has both ferroelectric and magnetic ordering at room temperature [7,8]. However, for a long time the linear magnetoelectric effect in BFO was not found. The bismuth ferrite is an antiferromagnet with the structure, which is not fully G type, but shows a cycloidal spin structure with a period of 62 nm [9,10]. Canting of the Fe^{3+} sublattices leads to a weak local magnetization, which averages to zero over a period of the spin cycloid structure [11]. Due to the spin cycloid structure, the volume average of the linear magnetoelectric effect also equals to zero. Therefore, first only the quadratic ME effect had been observed, and the value of the obtained magnetoelectric susceptibility tensor elements of the order of 10^{-19} sA^{-1} had been found [12]. In 2003, the article [13] by Wang *et al.* was published, in which a giant value of magnetoelectric coefficient of an order of 3 V/(cm Oe) was found in heteroepitaxially constrained thin BFO films, and the interest in the bismuth ferrite was revived. The spin cycloid structure can be destroyed and the linear ME effect can be recovered by applying an external magnetic field of a large magnitude [14–17] and using chemical doping [18,19]. In recent years, more experimental studies have been conducted, which indicate the giant magnetoelectric effect, enhanced in composites and multilayer heterostructures based on BFO [20–23]. Latest studies report the value of the linear magnetoelectric coefficient of approximately 4.2 V/(cm Oe) in $BiFeO_3$ films and 24 V/(cm Oe) in composite films with BFO [24]. However, the origin of the large values of the ME effect observed by numerous experiments in BFO remains unexplained, and the attempts to provide theoretical grounding to it have failed.

Pioneering works introduced an atomisticlike approach, where first the value of the intrinsic ME coefficient of the order of 10^{-2} V/(cm Oe) was obtained [25], which was close to experimental values [26] known at that time, but is much lower than the values observed in the recent experiments. As well, in [27], using a similar method, it was concluded that the magnetoelectric properties of BFO can be explained without resorting to the linear ME coefficients. In light of the latest experiments it has become evident that these results need reconsideration. To the best of our knowledge, there are no theoretical publications that consider the linear ME effect in BFO and give the value of the ME coefficient close to experimental.

In our study we provide theoretical background and explain the large value of the intrinsic linear ME coefficient of BFO in the absence of the cycloidal antiferromagnetic phase. As it was mentioned, this situation can be achieved using high magnetic fields, epitaxial films with strain $\gtrsim 10^{-2}$ [28] or by chemical doping. The obtained value of the linear ME coefficient is close to the maximum measured value in recently published articles [24]. We demonstrate that the antiphase oxygen octahedra rotation is responsible for occurrence of magnetoelectricity in BFO. Our approach is based on the symmetry representation of the thermodynamic potential in the Ginzburg-Landau approach. We use an invariant expansion of the thermodynamic potential in powers of the ordering parameters, namely antiferrodistortion ($\mathbf{\Omega}$), polarization ($\mathbf{P}$), and antiferromagnetic ($\mathbf{L}$) vectors. In Fig. 1 the rhombohedral perovskite-type doubled unit cell is shown with corresponding illustrations of order parameters. The doubling of the unit cell of the crystal structure occurs due to the antiphase rotation of the oxygen octahedra, which surround the Fe^{3+} ions (antiferrodistortion). Displacement of oxygen and iron ions within the double cell is responsible for the spontaneous polarization [29] (see Fig. 1).

II. ANTIFERRODISTORTION AND MAGNETOELECTRIC TENSOR

There are two alternative ways to derive the tensor of the linear magnetoelectric effect $\hat{\alpha}$ (the magnetoelectric tensor): either using the definition $\alpha_{ij} = 4\pi \frac{\delta P_i}{\delta H_j}$ or the definition $\alpha_{ji} =$

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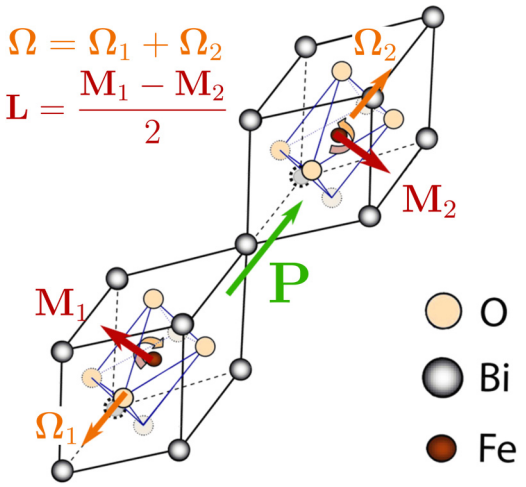

FIG. 1. Bismuth ferrite rombohedrally distorted perovskite cell doubled by antiparallel rotation of oxygen octahedra.

$4\pi\frac{\delta M_i}{\delta E_j}$, where $\mathbf{M}=(\mathbf{M}_1+\mathbf{M}_2)/2$ is the magnetic moment per formula unit, and $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetic moments of the two iron atoms in the aligned unit cell (see Fig. 1). In our work, we find the tensor $\hat{\alpha}$ through modulation of the magnetic moment $\mathbf{M}$ in the external electric field $\mathbf{E}$. Due to weak ferromagnetism of bismuth ferrite, the spontaneous magnetic moment can be expressed as $\mathbf{M}=\chi_\perp\mathbf{H}_D$, where $\chi_\perp$ is the component of the magnetic susceptibility, which is perpendicular to the antiferromagnetic vector $\mathbf{L}=(\mathbf{M}_1-\mathbf{M}_2)/2$ (see Fig. 1), and $\mathbf{H}_D$ is the Dzyaloshinskii field. The latter is defined by the expression $\mathbf{H}_D=\mathbf{D}\times\mathbf{L}$, where $\mathbf{D}$ is the Dzyaloshinskii vector [30]. The direction of the Dzyaloshinskii vector coincides with the direction of the antiferrodistortion vector $\mathbf{\Omega}$ [31]. Later, it was shown [32] that this dependency can be written as $\mathbf{D}=K\mathbf{\Omega}$, where $K=M_S/(\chi_\perp\Omega_0M_0)$, M_S denotes the equilibrium magnetization, M_0 is the magnetic moment of one iron atom in the unit cell, and Ω_0 is the magnitude of the AFD vector in the equilibrium state. All the physical values mentioned can be determined from experiment. Therefore, using the equations above and introducing the normalized antiferromagnetic vector $\mathbf{l}=(\mathbf{M}_1-\mathbf{M}_2)/2M_0$, we express the magnetoelectric tensor with the following formula:

$$\alpha_{ji}=\frac{4\pi M_S}{\Omega_0}\epsilon_{inm}\frac{\delta\mathbf{\Omega}_n}{\delta E_j}l_m. \tag{1}$$

Thus we have shown that the mechanism of the occurrence of the ME effect can be interpreted using the change of the AFD vector $\mathbf{\Omega}$ in the external electric field. Namely, one has to find the value of the tensor of the electric susceptibility of the antiferrodistortion $\eta_{ij}=\delta\Omega_i/\delta E_j$ in order to obtain the magnetoelectric tensor from (1).

III. THERMODYNAMIC POTENTIAL AND LINEAR MAGNETOELECTRIC EFFECT IN $BiFeO_3$

In order to obtain the expressions for the components of the ME tensor we introduce the ferroelectric part of the thermodynamic potential $\Phi_{st}(\mathbf{\Omega},\mathbf{P},\mathbf{E})$. In the coordinate system $Ox\parallel[001]$, $Oy\parallel[010]$, $Oz\parallel[100]$ the ferroelectric part of the thermodynamic potential has following form [33]:

$$\begin{aligned}\Phi_{st}(\mathbf{\Omega},\mathbf{P},\mathbf{E})=&\,a_1\left(P_x^2+P_y^2+P_z^2\right)+a_{11}\left(P_x^4+P_y^4+P_z^4\right)+a_{12}\left(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2\right)-\mathbf{PE}+b_1\left(\Omega_x^2+\Omega_y^2+\Omega_z^2\right)\\&+b_{11}\left(\Omega_x^4+\Omega_y^4+\Omega_z^4\right)+b_{12}\left(\Omega_x^2\Omega_y^2+\Omega_y^2\Omega_z^2+\Omega_z^2\Omega_x^2\right)-t_{11}\left(\Omega_x^2P_x^2+\Omega_y^2P_y^2+\Omega_z^2P_z^2\right)-t_{12}\left(\Omega_x^2\left(P_y^2+P_z^2\right)\right.\\&\left.+\Omega_y^2\left(P_x^2+P_z^2\right)+\Omega_z^2\left(P_x^2+P_y^2\right)\right)-t_{44}(\Omega_xP_y\Omega_yP_x+\Omega_yP_z\Omega_zP_y+\Omega_zP_x\Omega_xP_z),\end{aligned} \tag{2}$$

where a_1, b_1, a_{ij}, b_{ij}, and t_{ij} are parameters that are defined later in the article.

The dependencies of the equilibrium order parameters $\mathbf{\Omega}_0$ and $\mathbf{P}_0$ on the applied static external magnetic and electric fields $(\mathbf{H}_0,\mathbf{E}_0)$ are found by minimization of the thermodynamic potential of the crystal Φ using the variational equations $\delta\Phi(\mathbf{H}_0,\mathbf{E}_0)/\delta\mathbf{P}=0$ and $\delta\Phi(\mathbf{H}_0,\mathbf{E}_0)/\delta\mathbf{\Omega}=0$. After that, we consider the small deviation of the external electric field: $\mathbf{E}=\mathbf{E}_0+\delta\mathbf{E}$. In the linear approximation the polarization can be naturally represented as $\mathbf{P}=\mathbf{P}_0+\hat{\kappa}\delta\mathbf{E}$, where $\hat{\kappa}$ is the electric susceptibility tensor, and $\mathbf{P}_0=\mathbf{P}(\mathbf{H}_0,\mathbf{E}_0)$ is the equilibrium polarization. We introduce the same representation for the AFD vector: $\mathbf{\Omega}=\mathbf{\Omega}_0+\hat{\eta}\delta\mathbf{E}$, $\mathbf{\Omega}_0=\mathbf{\Omega}(\mathbf{H}_0,\mathbf{E}_0)$ is the equilibrium antiferrodistortion vector. Below we consider the bismuth ferrite in the absence of external fields (unperturbated crystal), $(\mathbf{E}_0,\mathbf{H}_0)=(0,0)$. In this case the equilibrium ordering parameters $\mathbf{P}_0$, $\mathbf{\Omega}_0\parallel(1,1,1)$. Now we consider the variation of the thermodynamic potential due to the deviation of the external electric field. We introduce three tensors $A_{ij}=\frac{\delta^2\Phi}{\delta P_i\delta P_j}$, $B_{ij}=\frac{\delta^2\Phi}{\delta\Omega_i\delta P_j}$, and $C_{ij}=\frac{\delta^2\Phi}{\delta\Omega_i\delta\Omega_j}$, which describe the quadratic form of the expansion of the thermodynamic potential at the point of equilibrium. The variational equations may be rewritten as the following:

$$\begin{aligned}A_{ij}\delta P_j+B_{ij}\delta\Omega_j&=-\frac{\delta^2\Phi}{\delta P_i\delta E_j}\delta E_j,\\B_{ij}\delta P_j+C_{ij}\delta\Omega_j&=-\frac{\delta^2\Phi}{\delta\Omega_i\delta E_j}\delta E_j.\end{aligned} \tag{3}$$

The three introduced tensors have similar structure, namely $A_{ij}=A_1\delta_{ij}+A_2(1-\delta_{ij})$ (δ_{ij} is the Kronecker symbol), where

$$\begin{aligned}A_1&=2a_1+\left(4a_{11}+\tfrac{4}{3}a_{12}\right)P_0^2-\left(\tfrac{2}{3}t_{11}+\tfrac{4}{3}t_{12}\right)\Omega_0^2,\\A_2&=\tfrac{4}{3}a_{12}P_0^2-\tfrac{1}{3}t_{44}\Omega_0^4,\\B_1&=-\tfrac{4}{3}t_{11}P_0\Omega_0-\tfrac{2}{3}t_{44}P_0\Omega_0,\\B_2&=-\tfrac{4}{3}t_{12}P_0\Omega_0-\tfrac{1}{3}t_{44}P_0\Omega_0,\\C_1&=2b_1+\left(4b_{11}+\tfrac{4}{3}b_{12}\right)\Omega_0^2-\left(\tfrac{2}{3}t_{11}+\tfrac{4}{3}t_{12}\right)P_0^2,\\C_2&=\tfrac{4}{3}b_{12}\Omega_0^2-\tfrac{1}{3}t_{44}P_0^2.\end{aligned} \tag{4}$$

TABLE I. Numerical values of the parameters in thermodynamic potential (2) of BFO, which have been used in calculations.

a_1(J m/C^2)	a_{11}(J m^5/C)	a_{12}(J m^5/C^4)	b_1(J/m^3)	b_{11}(J/m^3)	b_{12}(J/m^3)	t_{11}(J m/C^2)	t_{12}(J m/C^2)	t_{44}(J m/C^2)
-8.05×10^7	5.22×10^7	6.87×10^7	-3×10^8	1.3×10^9	1.9×10^9	-2.6×10^8	-2.5×10^8	5×10^7

Given that $\delta^2\Phi/\delta P_i\delta E_j=-\delta_{ij}$ and $\delta^2\Phi/\delta\Omega_i\delta E_j=0$, we obtain the following expressions for tensors of the linear expansion:

$$\kappa_{ik}=\Delta_{ij}^{-1}C_{jk},\quad \eta_{ik}=\Delta_{ij}^{-1}B_{jk}, \tag{5}$$

where $\hat{\Delta}=\hat{A}\hat{C}-\hat{B}^2$.

Note that the magnetoelectric tensor (1) can be expressed using tensor $\hat{\eta}$, for which is true $\eta_{ij}=\delta\Omega_i/\delta E_j$. We find the last tensor using (5), and transfer to the "rhombohedral" coordinate system with $Ox\parallel[11\bar{2}]$, $Oy\parallel[1\bar{1}0]$, $Oz\parallel[111]$. In this system the tensor $\hat{\eta}$ has the diagonal form,

$$\hat{\eta}=\begin{pmatrix}\eta_\perp & 0 & 0\\ 0 & \eta_\perp & 0\\ 0 & 0 & \eta_\parallel\end{pmatrix}, \tag{6}$$

where $\eta_\perp$ and $\eta_\parallel$ characterize the electric susceptibility of the AFD vector in the longitudinal and the transverse directions in relation to the unit vector $\mathbf{e}_P=\mathbf{P}_0/P_0$. These components are defined by the following equations:

$$\eta_\parallel=\frac{((\mu_1-\nu_1)-(\mu_2-\nu_2))(B_1+B_2)}{(\mu_1-\nu_1)(\mu_1-\nu_1+\mu_2-\nu_2)-2(\mu_2-\nu_2)^2},$$
$$\eta_\perp=\frac{((\mu_1-\nu_1)+2(\mu_2-\nu_2))(B_1-B_2)}{(\mu_1-\nu_1)(\mu_1-\nu_1+\mu_2-\nu_2)-2(\mu_2-\nu_2)^2}, \tag{7}$$

where $\mu_1=A_1C_1+2A_2C_2$, $\mu_2=A_1C_2+A_2C_1+A_2C_2$, $\nu_1=B_1^2+2B_2^2$, $\nu_2=2B_1B_2+B_2^2$. For reference we present the expression for the tensor $\hat{\eta}$ in the pseudocubic coordinate system:

$$\eta_{ij}=\eta_1\delta_{ij}+\eta_2(1-\delta_{ij}), \tag{8}$$

where $\eta_1=\frac{1}{3}(\eta_\parallel+2\eta_\perp)$ and $\eta_2=\frac{1}{3}(\eta_\parallel-\eta_\perp)$.

Thus, we obtained the magnetoelectric tensor in the coordinate system $O\tilde{x}\parallel[1\bar{1}0]$, $O\tilde{y}\parallel[11\bar{2}]$, and $O\tilde{z}\parallel[111]$ using the definition of $\hat{\eta}$ and (1):

$$\hat{\alpha}=4\pi\frac{M_S}{\Omega_0}\begin{pmatrix}0 & \eta_\perp l_z & -\eta_\perp l_y\\ -\eta_\perp l_z & 0 & \eta_\perp l_x\\ -\eta_\parallel l_y & \eta_\parallel l_x & 0\end{pmatrix}. \tag{9}$$

This tensor depends linearly on the components of the vector $\mathbf{l}$, and its diagonal elements are equal to zero. It corresponds to the ME tensor from [14], where the approach was based on symmetry properties of the rhombohedral ferroelectric phase of the BFO, if we take $a_1=0$ and $a_4=-a_2=\eta_\perp$, $a_3=\eta_\parallel$. The difference is due to the fact that a_1 is proportional to l_i in the second or higher degree, and in our calculations we assume elementary cells, which are rhombohedral, to be cubic. The difference is small, because the rhombohedral angle is approximately 89.3°.

According to expression (9) for the ME tensor, the ME energy depends on $\mathbf{l}$ also linearly. It can be shown that beyond the linear approximation some of the components of the tensor (9) are no longer equal to zero. In the case of $BiFeO_3$ these are components α_{11} and α_{22}. The situation is similar for magnetoelectric tensor in well-known magnetoelectric Cr_2O_3 where $\alpha_{33}=0$ in linear approximation. However, α_{33} differs from zero in the third-order approximation in respect to $\mathbf{l}$ [34]. Usually these moments are small, because they arise when perturbation theory of higher order is used. In this connection, a consideration of the magnetic anisotropy energy, which is linear in respect to $\mathbf{E}$, becomes an important issue. In $BiFeO_3$ these effects have been studied both experimentally and theoretically [35,36]. In these works the influence of an external electric field $\mathbf{E}$ upon magnon spectra has been studied and the influence of the magnetic anisotropy on properties of the spin cycloid has been analyzed theoretically. However, the magnetoelectric effect has not been considered in these studies. It can be shown that taking into account the electric-field-induced magnetic anisotropy leads to the magnetoelectric effect in third or higher order in respect to $\mathbf{l}$. This question should be a matter of further consideration.

Our numerical calculations are based on the thermodynamic potential (2) with parameters a_i, b_i,a_{ij},b_{ij}, and t_{ij}, which are present in Table I. The values of these parameters have been selected [37] to fit to the available experimental data [11,38] and *ab initio* calculations [39]. The values of the ME tensor can be estimated as $\alpha_\parallel=4\pi\frac{M_S}{\Omega_0}|\eta_\parallel|$ and $\alpha_\perp=4\pi\frac{M_S}{\Omega_0}|\eta_\perp|$. We assume that $M_S=H_D^0\chi_\perp, H_D^0\approx1.4\times10^5$ Oe is the magnitude of the Dzyaloshinskii field in the equilibrium, $\chi_\perp\approx5\times10^{-5}$, and $\Omega_0=0.21$, and obtain $\alpha_\perp\approx2.2\times10^{-3}$ (in Gaussian units), or 0.67 V/(cm Oe), and $\alpha_\parallel\approx3.27\times10^{-2}$ (in Gaussian units), or 9.81 V/(cm Oe) (with accuracy up to the components of the normalized vector $\mathbf{l}$,$|\mathbf{l}|\approx1$). The order of the magnitude of the last value is consistent with the value of the linear magnetoelectric effect $\alpha\approx1.4\times10^{-2}$ (in Gaussian units), present in [24]. It is more than an order of magnitude greater than the value of the ME coefficient $\alpha_\parallel\approx1.24\times10^{-3}$ in the well-known multiferroic Cr_2O_3 [40,41], but is less than the effect in $TbPO_4$ giving 720 ps/m ($T=1.50$ K) [2]. We should note that the obtained result is suitable for a single-domain sample, while for a multidomain sample the ME effect would be smaller.

IV. CRITICAL ENHANCEMENT OF MAGNETOELECTRIC EFFECT NEAR PHASE TRANSITION

As an illustration of applications of our approach for investigation of mechanisms of enhancement of the linear ME effect, let's consider the following idea. Due to (1) and (9) the giant values of the ME effect are expected to occur when the derivatives of the AFD vector with respect to the electric field are experiencing critical behavior. In particular, the studies of the electric-field-induced structure and magnetic changes in BFO [27,37] have shown that at certain magnitudes of the external electric field a reorientation of the antiferromagnetic structure occurs. In the vicinity of the

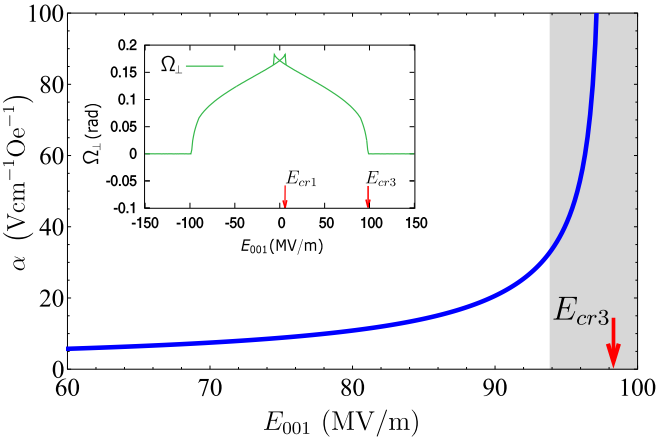

FIG. 2. Dependence of the ME coefficient α on the external electric field, which is applied in [001] direction. (Inset) Dependence of the $\Omega_\perp$ on the applied external electric field.

critical fields the derivatives of the AFD vector components may approach infinity, which, in turn, leads to an unlimited increase of the magnetoelectric effect in theory. The BFO films in experiments are often oriented perpendicularly to [001] [28,42,43], therefore as an example we consider the case of a phase transition in $\mathbf{E} \parallel [001]$.

In the external electric field $\mathbf{E} \parallel [001]$ there are three critical points, namely E_{cr1}, E_{cr2}, and E_{cr3}, at which phase transitions occur [33,37]. Here we present an example of analysis of the asymptotic behavior of the ME tensor near E_{cr3} (see the insertion in Fig. 2). At the large values of the electric field ($E > E_{cr3}$) polarization is aligned with the direction of the electric field ($P = P_\parallel$), and the AFD vector consists only of the perpendicular component $\Omega_\perp$. We assume that $\Omega_\perp$ is parallel to the [110] direction, which is not the only direction due to symmetry. In this case the thermodynamic potential in the coordinate system $Ox \parallel [001], Oy \parallel [010], Oz \parallel [100]$ acquires the following form:

$$\Phi(\mathbf{\Omega},\mathbf{P},\mathbf{E}) = \alpha_1 P_\parallel^2 + \alpha_{11} P_\parallel^4 - P_\parallel E_{001} + \beta_1 \Omega_\perp^2 + (2\beta_{11} + \beta_{12})\Omega_\perp^4 - t_{12} P_\parallel^2 \Omega_\perp^2. \quad (10)$$

At E_{cr3} a phase transition of the second order occurs: The expression standing in front of the term $\Omega_\perp^2$ changes its sign, and the coefficient in front of $\Omega_\perp^4$ remains positive. Solving the minimization problem in the approximation of the small value of $\Omega_\perp$, we obtain the following expressions near the equilibrium point: $P_\parallel \approx P_\parallel^0 + \gamma_P \Delta E_{001}, \Omega_\perp \approx \gamma_\Omega \sqrt{\frac{\Delta E_{001}}{E_{cr3}}}$, where $P_\parallel^0 \approx 1.1$ C/m^2, $\gamma_P \approx -1.69 \times 10^{-9}$ C^2/(J m), $\gamma_\Omega \approx 0.21$ rad, the deviation of the electric field magnitude from the critical value is $\Delta E_{001} = E_{cr3} - E_{001}, E_{cr3} \approx 9.81 \times 10^7$ V/m. For estimation of the ME tensor components using (1), we introduce the magnetoelectric coefficient α, which is proportional to the elements of the tensor $\hat{\alpha}$ with accuracy up to the components of the vector $\mathbf{l}$. The following expression indicates the unlimited growth of the ME effect:

$$\alpha \propto \frac{\partial \Omega_\perp}{\partial E_{001}} = -\frac{\gamma_\Omega}{2\sqrt{E_{cr3}}} \times \frac{1}{\sqrt{E_{cr3} - E_{001}}}. \quad (11)$$

The same asymptotic behavior may be obtained near other critical points. In Fig. 2 is shown the dependence of the magnetoelectric coefficient α on the electric field E_{001}. Thus we have shown that the search of the similar setups, when the derivatives of the AFD vector with respect to the electric field components become considerably large, may lead to significantly enhanced results for the magnetoelectric effect in BFO.

In order to ensure that the system is thermodynamically stable [44] the next condition must be satisfied:

$$\alpha_{ij} < 4\pi \sqrt{\chi_{ii} \kappa_{jj}}, \quad (12)$$

where $\hat{\chi}$ and $\hat{\kappa}$ are magnetic and electric susceptibility tensors correspondingly. For the upper boundary of the value of the α_{ij}, at which the condition (12) is still satisfied, approximate estimation gives the order of 10^{-1} Gaussian units. This sets the limit to the external electric fields in our approach (the limitation area is denoted by gray filling in Fig. 2).

V. CONCLUSION

In conclusion, we have shown that the nature of the magnetoelectric effect in $BiFeO_3$ lies in the orientation change of the AFD vector in the external electric field. We note that the developed model for the magnetoelectric interaction in BFO indicates the prospect of the ME effect enhancement. The enhancement mechanism may lie in the softening of the mode of the reorientation of the antiferrodistortion vector, for example, under the elastic stresses in film heterostructures. Also, our investigations have shown that in the presence of the external electric field of critical magnitude (at which phase transition of the second order occur), the giant ME effect may be observed. Our study may be relevant, in particular, for explanation of recent experimental observations of the growth of the ME effect in thin-film heterostructures with BFO [13,21,22,24,45], and for the search for tools of enhancement of the linear magnetoelectric effect in BFO.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (Grants No. 16-02-00494 A and No. 14-29-08216 ofi_m) and 5-100 Initiative, Moscow Institute of Physics and Technology (MIPT).

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