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Structural Transformations and Magnetic Changes in Multiferroic $BiFeO_3$ under External Electric Field

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The influence of electric field on the structure parameters and magnetic states in $BiFeO_3$ multiferroic is studied using the Landau theory of phase transitions taking into account experimental data and results of *ab initio* calculations. Main features of structure transitions near critical electric fields and a concomitant rearrangement of the magnetic structure are discussed.

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1. Introduction

Multiferroics like $BiFeO_3$ (BFO) having spontaneous polarization and magnetic ordering attract a wide attention due to theirs possible applications in UHF electronics, computing techniques and optoelectronics [1, 2]. Substantial part of researches of BFO magnetoelectric properties is based on phenomenological approach using invariants which are obtained from the symmetry of ferroelectric crystal phase [3]. It is interesting to consider interplay between structural phase transformations and concomitant magnetic changes on the basis of multiparametric Landau–Ginzburg theory of phase transitions in BFO single crystal taking into account *ab initio* calculations and experimental data.

2. Thermodynamic potential

Considered multiferroic corresponds to the $R3c$ symmetry group, but its paraphase is close to a perovskite-like structure having $Pm3M$ symmetry group. It is convenient to present original thermodynamic potential in the form [4]:

$$\Phi(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{M},\boldsymbol{L})=\Phi_{\rm me}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{M},\boldsymbol{L})+\Phi_{\rm st}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{E}), \quad (1)$$

where $\Phi_{\rm me}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{M},\boldsymbol{L})$ is the potential of magnetoelectric interaction, $\Phi_{\rm st}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{E})$ is the potential of ferroelectric ordering, $\boldsymbol{P}$ is the polarization vector, $\boldsymbol{\omega}$ is the rotation vector of oxygen octahedrons, $\boldsymbol{M}$ is the magnetization vector, and $\boldsymbol{L}$ is the antiferromagnetic vector. For the coordinate system $Ox\|$ [100], $Oy\|$ [010], and $Oz\|$ [001] the actual part of $\Phi_{\rm st}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{E})$ can be written as follows:

$$\begin{aligned}\Phi_{\rm st}(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{E}) &= \beta_1(\omega_x^2+\omega_y^2+\omega_z^2)\\ &+\beta_{11}(\omega_x^4+\omega_y^4+\omega_z^4)+\beta_{12}(\omega_x^2\omega_y^2+\omega_y^2\omega_z^2+\omega_z^2\omega_x^2)\\ &+\beta_2\omega_x^2\omega_y^2\omega_z^2+\alpha_1(P_x^2+P_y^2+P_z^2)+\alpha_{11}(P_x^4+P_y^4+P_z^4)\\ &+\alpha_{12}(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2)+\alpha_2P_x^2P_y^2P_z^2-\boldsymbol{P}\times\boldsymbol{E}\\ &-t_{11}(P_x^2\omega_x^2+P_y^2\omega_y^2+P_z^2\omega_z^2)\\ &-t_{12}\left[(P_y^2+P_z^2)\omega_x^2+(P_z^2+P_x^2)\omega_y^2+(P_x^2+P_y^2)\omega_z^2\right]\\ &-t_{44}(P_x\omega_yP_y\omega_x+P_y\omega_zP_z\omega_y+P_z\omega_xP_x\omega_z). \quad (2)\end{aligned}$$

Invariant parameters can be considered here as the constants having ferroelastic renormalization.

3. Structure transitions in electric field

We assume that the anisotropy of the crystal is such that in the absence of electric field, the equilibrium polarization direction will be given along the diagonals of the cube. Potential minimum conditions for $E \neq 0$ allow to find the equilibrium values of $\boldsymbol{P}$ and ω. Figure 1 shows an example of calculation of hysteretic changes of equilibrium orientation of the spontaneous polarization in the electric field in the case $\boldsymbol{E}\|[\bar{1}\bar{1}0]$. In this case the equilibrium azimuthal direction of polarization $\boldsymbol{P}$ is coinciding with the electric field azimuth. In the region $|E| < E_{\rm c1}$ a monotonic change of electric polarization is going close to the original direction along one of the diagonals of the perovskite cube.

At the point $|E| = E_{\rm c1}$ there is an abrupt change of polarization vector component which is parallel to the direction of electric field.

After that a smooth increase of parallel component of polarization and decrease of perpendicular component are coming in the region $E_{\rm c1} < |E| < E_{\rm c2}$ until its complete disappearance at the second critical field $|E| = E_{\rm c2}$.

The change of polarization components leads to the change of rotation axis of octahedrons $\boldsymbol{\omega}(\boldsymbol{P})$. Perpendicular component of polarization vector $\boldsymbol{P}(\boldsymbol{E})$ plays the same role of an external force for the axial vector $\boldsymbol{\omega}(\boldsymbol{P})$ as the electric field for the polarization $\boldsymbol{P}(\boldsymbol{E})$. Figure 2 shows an expected hysteresis loop of concomitant change

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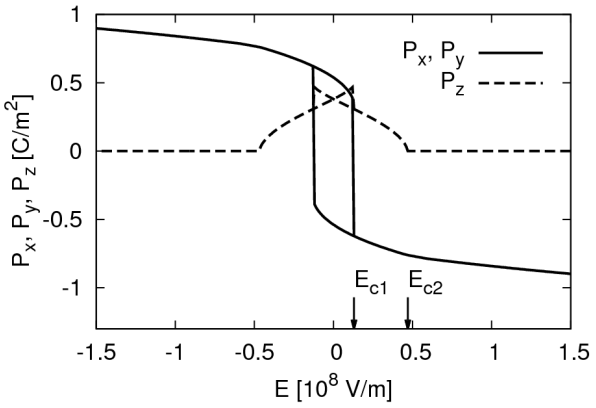

Fig. 1. Hysteresis of polarization $\boldsymbol{P}$ in electric field $\boldsymbol{E}||[\bar{1}\bar{1}0]$. Solid line shows components P_x, P_y, dashed line shows P_z.

of parallel and perpendicular components of $\boldsymbol{\omega}(\boldsymbol{E})$ vector. The first critical field E_{c1} is responsible for a jump of polarization to the closest anisotropy axis. At the second critical field E_{c2} the perpendicular components of polarization and rotation vector of octahedrons vanish. In the region $E_{c2} < |E| < E_{c3}$ polarization vector and rotation axis of octahedrons are not coincident. At last, above E_{c3} the rotation vector of octahedron fully vanishes. Sharp change of polarization vector accompanies with a jump of the rotation axis. For given values of the parameters $P_0 = 1$ C/m^2, $\omega_0 = 0.2$ rad, $\beta_1 = -3 \times 10^8$ J/m^3, $\beta_2 = 0$, $\beta_{11} = -1.3 \times 10^9$ J/m^3, $\beta_{12} = -1.9 \times 10^9$ J/m^3, $\alpha_1 = -8.05 \times 10^7$ Jm/C^2, $\alpha_2 = 0$, $\alpha_{11} = -5.22 \times 10^7$ Jm/C^2, $\alpha_{12} = -6.87 \times 10^7$ Jm/C^2, $t_{11} = -2.6 \times 10^8$ Jm/C^2, $t_{12} = -2.5 \times 10^8$ Jm/C^2, $t_{44} = 5 \times 10^7$ Jm/C^2 the critical fields of phase transitions E_{c1}, E_{c2}, E_{c3} are close to the values 16.2 MV/m, 42.6 MV/m, 55.0 MV/m, respectively, which are obtained in Ref. [3] from *ab initio* calculations of BFO in the electric field.

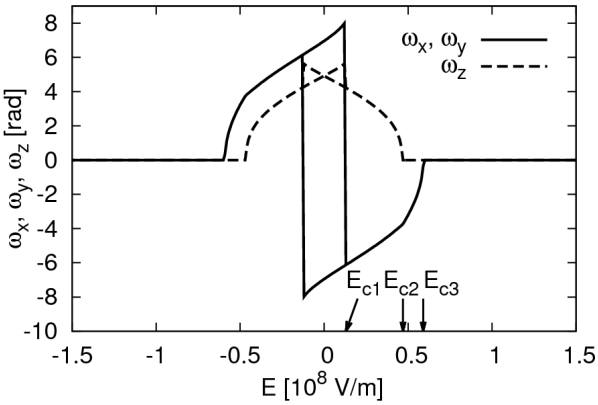

Fig. 2. Hysteresis of rotation angle of octahedrons in electric field $\boldsymbol{E}||[\bar{1}\bar{1}0]$. Solid line shows ω_x, ω_y; dashed line shows ω_z.

4. Concomitant change of spatially modulated antiferromagnetic structure

Rearrangement of ω and $\boldsymbol{P}$ give an appropriate change of magnetization vector $\boldsymbol{M}$ and antiferromagnetic vector $\boldsymbol{l}$. A free energy of magnetoelectric interaction of multiferroic can be presented in the form [5, 6]:

$$\Phi(\boldsymbol{P},\boldsymbol{\omega},\boldsymbol{m},\boldsymbol{l}) = \Phi_0(\boldsymbol{P},\boldsymbol{\omega}) + A\sum_{i=x,y,z}(\nabla l_i)^2 + \beta \boldsymbol{e}_p \times [\boldsymbol{l}(\nabla \times \boldsymbol{l}) - (\boldsymbol{l}\times\nabla)\boldsymbol{l}] - \frac{1}{2}\chi_\perp H_{\rm D}^2(\boldsymbol{e}_\omega \times \boldsymbol{l})^2 + K_u l_z^2, \quad (3)$$

where $H_{\rm D}$ is a Dzyaloshinskii field, β is a magnetoelectric constant, $\boldsymbol{e}_p = \boldsymbol{P}/P_0$, $\boldsymbol{e}_\omega = \boldsymbol{\omega}/\omega_0$, $P_0 = P(E=0)$, $\omega_0 = \omega(E=0)$.

At low magnetic fields the ground state of BFO-like single crystal is characterized by the presence of incommensurate spatially modulated spin structure in a form of antiferromagnetic cycloid. In this state the plane of spin rotation passes through the equilibrium polarization vector $\boldsymbol{P}_0||$ [111] and the direction of spin spatial modulation (see e.g. [5]).

When electric field is applied in the $[00\bar{1}]$-direction, antiferromagnetic cycloid modulated along $[1\bar{1}0]$-direction with the turn in the $(11\bar{2})$-plane at the first critical field $E = E_{c1}$ is abruptly transformed into a cycloid with the turn in the (112)-plane (see Fig. 3). With further increase of the field to the second critical value $E = E_{c2}$, the cycloid gradually becomes flat with the plane turn (110).

In (001)-oriented films with high anisotropy constant (for values $K_u \geq 1.8$ Merg/cm^3) at fields exceeding the critical value $E = E_{c2}$, cycloid may be suppressed up to its complete disappearance. Note that the anisotropy constant can change in a wide range in doped BFO by rare earth ions [7].

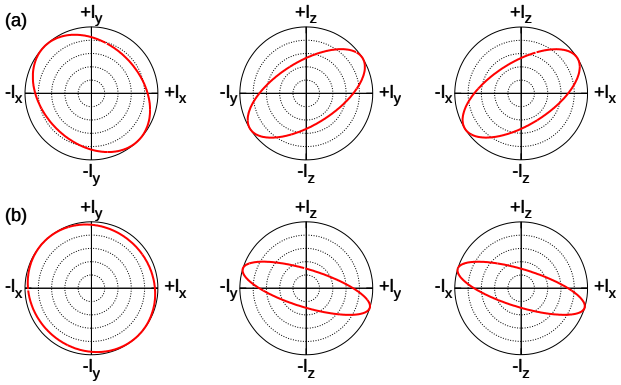

Fig. 3. Projections of antiferromagnetic vector trajectory for antiferromagnetic cycloid modulated along $[1\bar{1}0]$-direction on Cartesian coordinate planes. (a) E is close to E_{c1}, $E < E_{c1}$, (b) E is close to E_{c1}, $E > E_{c1}$. Calculated with the values $H_{\rm D} = 1.4 \times 10^5$ Oe, $M_0 = 640$ Gs, $A = 2 \times 10^{-7}$ erg/cm, $\chi_\perp = 5 \times 10^{-5}$, $\beta = 0.6$ erg/cm^2.

5. Conclusion

Thus, we have shown that when an electric field is applied in the pseudocubic BFO-like multiferroic, the reorientation of ferroelectric ordering parameters occurs, and the symmetry of the crystal may decline to monoclinic in the process of multiferroic repolarization. In a region below the first critical field the metastable domains of polarization can appear for a given ω vector. These domains can significantly decrease the critical fields of transitions. The coupling constants of the polarizing mode and of the oxygen octahedrons rotation mode can be varied, when an elastic stress are induced in the multiferroic film. In this case, a different types of hysteresis, and different types of symmetry of the crystal can be realized in the films with variation of the mismatch in the lattice parameters of the film and the substrate. Abrupt change of the polarization that occurs under the action of electric field at the critical point is accompanied by the sudden change of the plane of spatial modulation of the antiferromagnetic vector. Change in the magnetic anisotropy induced by electrostrictive stresses may alter the degree of cycloid anharmonicity and lead to the full disappearance of the cycloid in the electric field after the transformation of the rhombohedral crystal to the tetragonal.

Acknowledgments

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