Antiferromagnetic states of BiFeO$_3$ single crystal multiferroic in external magnetic field

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Abstract. Room-temperature multiferroics take special attention due to possibilities for applications in technology, but they are also interesting from fundamental point of view. Bismuth ferrite is the most studied multiferroic demonstrating high ordering temperatures and fascinating properties in thin films and could be used as a functional element in magnetoelectric memory. For better utilization of bismuth ferrite in spintronic devices the detailed understanding of its properties is of great importance. In this work we apply the developed thermodynamic model for description of magnetic states and magnetic field driven transformation of magnetic structure of single crystal BiFeO$_3$. Presence of magnetic field may lead to a situation, when the transition from inhomogeneous magnetic state having cycloidal structure into homogeneous state proceeds through emergence of intermediate magnetic state with conical-like structure. Magnetic field transitions emerging under influence of magnetic field should somehow lead to alternation of magnetization. For revealing this influence the magnetization curves were calculated for three directions of magnetic field and the comparison with experimental results was carried out. Good agreement with experimental curves allows us to say, that peculiarities of magnetization curves may be caused by the emergence of intermediate conical state.

1. Introduction

High ordering temperatures of magnetic and ferroelectric phase transitions of bismuth ferrite make this crystal a great object for investigations of magnetoelectric properties, along with possible applications of bismuth ferrite and derivative compounds it can explain a huge number of publications dedicated to this material. Close attention is dedicated to magnetic structure of bismuth ferrite, because achieving the desired effects requires an opportunity to manipulate magnetic structure by means of external magnetic field [1–8], elastic deformations in films [9,10], or by ion substitution [11]. Magnetic ordering of bismuth ferrite is characterized by presence of incommensurate spatially-modulated spin structure (SMSS), which was observed by neutron diffraction [12], NMR [13,14] and Mössbauer spectroscopy [14]. The origin of this structure can be explained by antirotation of oxygen octahedrals and related Dzyaloshinskii-Moriya interaction [15], which determines the weak ferromagnetism as well, hidden by the presence of spin modulation. The linear magnetoelectric effect is also hidden. Such hidden phenomena
could be revealed by, for example, magnetic field, which must be high enough to suppress
cycloidal spin structure, when magnetization of sublattices becomes homogeneous. In early
work [16] the critical field of transition to homogeneous state as well as specific magnitude of
linear magnetoelectric effect were established. Then, in Refs. [2, 3, 8] the weak ferromagnetic
moments were observed. The results on resonant frequencies in external magnetic field [4, 7]
confirm the nature of transition from inhomogeneous magnetic state to homogeneous state.

In recent experimental works [3, 6] the peculiarities of magnetization and polarization
alternation of single crystal BiFeO$_3$ (BFO) in external magnetic field were considered. In
Ref. [3] the observed hysteretic phenomena may be connected with reconfiguration of
antiferromagnetic domains, and additional investigations in Ref. [6] indicate the emergence of
intermediate inhomogeneous state having conical-like magnetization spatial distribution, what
was theoretically predicted before in Ref. [17].

In this work we analyse the stability of magnetic states and transformation of incommensurate
spin structure of BFO single crystal in external magnetic field for three orthogonal directions
using the developed thermodynamic model.

2. Considered model
We rely on the model of antiferromagnet with two sublattices taking into account the
approximation of reduced description of magnetization dynamics [17, 18]. We consider
thermodynamic potential, which includes flexomagnetoelectric interaction [19] responsible for
emergence of spin cycloid structure. In this case we assume, that the full magnetization
m = (M$_1$ + M$_2$)/2M$_0$ normalized on sublattice magnetization M$_0$ is low in relation to the
antiferromagnetic vector l = (M$_1$ + M$_2$)/2M$_0$, what allows us to express m through l and simplify
the analysis of magnetic states. This approach was successfully used before for description of
magnetic phase transitions for BFO single crystal [20] and films [9].

For analysis of magnetic states of single crystal BFO we use the thermodynamic potential in
the following form

$$\Phi = A \sum_{\xi=x,y,z} \left( \frac{\partial l}{\partial \xi} \right)^2 + \beta e_P \cdot [(l \cdot \nabla)l - l(\nabla \cdot l)] - K_u(e_P \cdot l)^2 - \frac{1}{2} \chi_\perp [H_{\text{tot}}^2 - (H_{\text{tot}} \cdot l)^2],$$  \hspace{1cm} (1)

where A is the exchange stiffness, $\beta$ is the constant of flexomagnetoelectric interaction, $e_P$
is the unit vector of polarization, $K_u$ is the constant of uniaxial anisotropy, $\chi_\perp$ is the
antiferromagnetic susceptibility, H$_{\text{tot}}$ = H - H$_D$[e$_\Omega$, l], H is the magnetic field vector, H$_D$
is the Dzyaloshinskii field, e$_\Omega$ is the unit vector of antidistortion $\Omega$. Vectors of polarization and
antidistortion are assumed to be known and constant.

In this approach the magnetization can be expressed as follows

$$\mathbf{M} = \chi_\perp \{ \mathbf{H} - (\mathbf{H} \cdot \mathbf{l})\mathbf{l} + H_D[\mathbf{e}_\Omega, \mathbf{l}] \}. \hspace{1cm} (2)$$

In further calculations we use a normalized notation. Multiplying (1) by 2A/$\beta^2$ after some
transformations we get

$$\tilde{\Phi} = \frac{1}{2} \sum_{\xi=x,y,z} \left( \frac{\partial l}{\partial \xi} \right)^2 + e_P \cdot [(l \cdot \nabla)l - l(\nabla \cdot l)] - \frac{1}{2} \kappa_u(e_P \cdot l)^2 + \frac{1}{2} \kappa_d(e_\Omega \cdot l)^2$$

$$+ \frac{1}{2} \kappa_M (h \cdot l)^2 - \sqrt{\kappa_u \kappa_d} h \cdot [e_\Omega, l], \hspace{1cm} (3)$$

where we use notations $\tilde{\Phi} = \Phi \cdot 2A/\beta^2$, $\tilde{x} = x \cdot \beta/2A$, $\kappa_u = K_u \cdot 4A/\beta^2$, $\kappa_d = \chi_\perp H_D^2 \cdot 2A/\beta^2$, $\kappa_M = \chi_\perp M_0^2 \cdot 2A/\beta^2$, and $h = H/M_0$. We will drop the tilde in further formulas.
Table 1. Values of model parameters

| $A$, erg/cm | $\beta$, erg/cm$^2$ | $K_u$, erg/cm$^3$ | $H_D$, Oe | $\chi_\perp$ | $M_0$, emu/cm$^3$ |
|------------|-----------------|-----------------|----------|----------|-----------------|
| $2.8 \cdot 10^{-7}$ | 0.78 | $10^9$ | $1.2 \cdot 10^9$ | 5.6 $\cdot 10^{-9}$ | 442 |

The stationary equation minimizing the potential (3) has a form of the Brown equation:

\[
\frac{l}{\delta l} = 0. \tag{4}
\]

Stability of homogeneous antiferromagnetic states can be determined by calculation of spin wave spectrum in linear approximation, when antiferromagnetic vector can be expressed in a form $l(r, t) = l_0 + l_1(r, t)$, where $|l_1| \ll 1$ is small oscillation around a stationary solution $l_0$. Determination of dispersion relation $\omega = \omega(k)$ can be derived from linearised equations of magnetization dynamics. Stability loss of homogeneous state corresponds to zero-point of spin wave frequency, what is caused by presence of soft mode oscillations discussed in Ref. [18].

Extensive experimental investigation of magnetization curves of single crystal BFO in Ref. [3] showing a mark of magnetic phase transitions require an additional theoretical consideration including calculation of magnetization curves using the proposed thermodynamic model, what can help to establish the character of magnetic state change and estimate values of model parameters. For this purpose we will analyse possible homogeneous states for three directions of magnetic field, along axes [111], [1 ¯10] and [11¯2], and find stability boundaries of their existence, after that we will carry out calculation of inhomogeneous states. A comparison of calculated curves with experimental data will be provided for measurements at $T = 4.2$ K. Decent agreement is attained with parameter values listed in Tab. 1.

3. Results

We begin consideration with the case, when the magnetic field is oriented along axis [111]. For convenience of homogeneous states calculations we introduce Cartesian coordinate system, where the coordinate axes are directed along crystallographic axes of pseudocubic cell: $Ox \parallel [110], Oy \parallel [112], Oz \parallel [111]$. We also use the spherical coordinate system: $l_x = \sin \theta \cos \varphi$, $l_y = \sin \theta \sin \varphi$, $l_z = \cos \theta$. We can express the homogeneous part of the potential (3) by excluding non-uniform terms in the following form

\[
\Phi = -\frac{1}{2}(\kappa_c - \kappa_d - \kappa_M h_z^2)l_z^2 = -\frac{1}{2}(\kappa_c - \kappa_d - \kappa_M h_z^2) \cos^2 \theta, \tag{5}
\]

Applying the minimum conditions of this potential we get two solutions:

(i) the easy-axis state (EA) having $l = (0, 0, \pm 1)$, when $|h| < \sqrt{(\kappa_c - \kappa_d)/\kappa_M}$,

(ii) the easy-plane state (EP) having $l \perp [111]$ when $|h| < \sqrt{(\kappa_c - \kappa_d)/\kappa_M}$,

which must be unstable at the low field. A schematic image of homogeneous states is depicted in Fig. 1.

The dispersion equation for the solution $l_z = \pm 1$ (red arrow in Fig. 1-a) has a form

\[
\omega^2 = k^2 + \kappa_c - \kappa_d - \kappa_M h_z^2 \tag{6}
\]

and gives the stability condition for this homogeneous solution: $|h| < \sqrt{(\kappa_c - \kappa_d)/\kappa_M}$.

For the solution $l_y = \pm 1$ (green arrows in Fig. 1-a) the dispersion equation has a form

\[
(\omega^2 - k^2)(\omega^2 - k^2 + \kappa_c - \kappa_d - \kappa_M h_z^2) - 4(k_x^2 \sin^2 \varphi_0 - k_y^2 \cos^2 \varphi_0) = 0. \tag{7}
\]
Figure 1. Configuration of antiferromagnetic vector $\mathbf{l}$ in geometry of pseudocubic BFO cell for (a) homogeneous states (green arrows – EP states; red arrows – EA states; tilted states are not shown) and two inhomogeneous states: (b) cycloidal state propagating along axis $[1 \bar{1} 0]$; (c) conical state with the same propagation direction. The inset picture shows that in the conical state the antiferromagnetic vector is out of the plane.

And the stability condition is given by inequality $|h| > \sqrt{(4+\kappa_c - \kappa_d)/\kappa_M}$.

Violation of given conditions leads to stability loss of corresponding homogeneous states and emergence of incommensurate magnetic structure. In absence of external magnetic field this structure has a form of cycloid, which has a spatial dependence of antiferromagnetic vector depicted in Fig. 1-b for a case, when spin modulation direction is collinear with axis $[1 \bar{1} 0]$. Presence of magnetic field directed along axis $[111]$ leads to alternation of anharmonicity level and period of cycloidal structure. But after reaching magnitude of $\mu_0 H = 24.5$ T the cycloidal structure losses stability, in the point of stability loss two solutions having conical-like spatial distribution of antiferromagnetic vector emerge (see Ref. [17]). Further increase of magnetic field leads to transition to the EP state, in which the antiferromagnetic vector is oriented along or against axis $[11 \bar{2}]$.

Described transformations of magnetic states manifest themself on magnetization curve in Fig. 2-a calculated for considered magnetic field direction. Comparison with the experimental curve from Ref. [3] shows a good agreement of the model and the experiment. Alternation of monotone level in the region of magnetic field between 24 and 31 T on both curves may be interpreted as a transition from cycloidal state into conical state. It should be noted, that the calculated curve is lower that experimental one, what signifies the existence of additional
magnetic moment which is not predicted by the model.

In the case, when magnetic field is oriented along axis [112] and non-uniform terms in thermodynamic potential are excluded, we can earn two homogeneous states:

(i) the easy-plane state (EP) having \( l = (\pm 1, 0, 0) \) when \( |h| > (\kappa_c - \kappa_d)/\sqrt{\kappa_d \kappa_M} \),

(ii) the tilted state (T) having \( l = (\pm \sin \theta_0, 0, \cos \theta_0) \) where \( \sin \theta_0 = \sqrt{\kappa_d \kappa_M} h/(\kappa_c - \kappa_d) \) when \( |h| < (\kappa_c - \kappa_d)/\sqrt{\kappa_d \kappa_M} \).

Analysis of the dispersion equation for EP state allows to establish condition of stability loss, which has a form of inequality

\[
(\kappa_c - \kappa_d - \kappa_M h_y^2 + 2\sqrt{\kappa_d \kappa_M} h_y + 4)^2 + 4(\kappa_c - \kappa_d + \sqrt{\kappa_d \kappa_M} h_y)(\kappa_M h_y^2 - \sqrt{\kappa_d \kappa_M} h_y) < 0. \tag{8}
\]

In presence of magnetic field oriented along [112] the ground antiferromagnetic state characterized by cycloidal spin structure having modulation direction along [11\bar{2}] axis undergoes distortions of increase of cycloid period and nucleation of homogeneously magnetized domains with antiferromagnetic vector \( l = (1, 0, 0) \) (when \( h_y > 0 \)) or \( l = (-1, 0, 0) \) (when \( h_y < 0 \)). In the point of transition into homogeneous state the rotation period of antiferromagnetic vector increases up to infinity forming a domain of uniform magnetization. It leads to a different magnetization dependence on magnetic field, which can be seen in Fig. 2-b. Good agreement with the experimental curve allows to say, that for this case the corresponding magnetic state is characterized by calculated cycloidal structure.

A similar situation takes place for magnetic field oriented along [1\bar{1}0] axis, when in absence of non-uniform terms in the thermodynamic potential we can express the following homogeneous states:

(i) the easy-plane state (EP) having \( l = (0, \pm 1, 0) \) and existing when \( |h| > (\kappa_c - \kappa_d)/\sqrt{\kappa_d \kappa_M} \),

(ii) the tilted state (T) having \( l = (0, \pm \sin \theta_0, \cos \theta_0) \) when \( |h| < (\kappa_c - \kappa_d)/\sqrt{\kappa_d \kappa_M} \), where \( \sin \theta_0 = \sqrt{\kappa_d \kappa_M} h/(\kappa_c - \kappa_d) \).

The stability condition of the EP state is the same as for the case of \( H \parallel [112] \), namely it is described by the inequality (8) taking into account \( z \)-component of magnetic field. In the region of low magnetic field the ground state is characterized by the conical structure, which emerges from the cycloidal structure by detachment of transverse component of antiferromagnetic vector \( l \) from the plane of cycloid after applying even low magnetic field oriented along [11\bar{0}] axis. Instead of steeply growing magnetization in this case a smooth growth takes place until the transition point, where the magnetization dependence is linear and caused by canting of sublattices (see Fig. 2-c). Such dependence was not observed at \( T = 4.2 \text{K} \) in Ref. [3], but there are similar dependencies for higher temperatures, what was reported in Ref. [6], where authors relate this peculiarity to emergence of conical state.
4. Conclusion
Presented results attest the availability of at least two mechanisms of transition from inhomogeneous antiferromagnetic state into homogeneous one: (i) through emergence of intermediate inhomogeneous state having conical-like distribution of antiferromagnetic vector, or (ii) through domain formation of uniform magnetizations accompanied by increase of period of cycloidal structure. Good agreement of calculated magnetization curves with experimental results for magnetic field directed along [111] and [11 2] axes supports the aforementioned statements. But the discrepancy in results for direction of magnetic field along [1 10] axis requires an additional analysis, in particular the case of spin cycloids having different propagation directions should be examined.

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