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Influence of Magnetoelectric Interaction on the Elementary Excitation In $BiFeO_3$

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ABSTRACT

This paper discusses the microscopic theory of magnetoelecrtic (ME) effects in multiferroic substance $BiFeO_3$ (BFO). Ferroelectric properties are described within the transverse Ising model with the pseudo-spin S = 7/2. Considering the influence of the polar lattice shifts on symmetric and antisymmetric exchange interactions, two types of coupling between magnetic and ferroelectric subsystems are defined. The first magnetoelecrtic interaction is quadratic regarding spin and pseudo-spin operators. The second, called antisymmetric, is induced by appearance of spontaneous polarization in $BiFeO_3$. The increase of quadratic interaction leads to increase in the energy of the ferroelectric mode, while the increase of antisymmetric interaction leads to decrease of its energy. This paper examines the influence of the direction and magnitude of an external magnetic field is on the hardening and softening of the ferroelectric mode. ME mechanisms appear to be in competition in relation to the energy of the pseudo-spin excitation. An analytical expression is obtained (derived) for damping of pseudo-spin and spin excitations, for the first time. The influence of ME interactions on the processes of damping in $BiFeO_3$ is also examined. In the vicinity of the point of magnetic phase transition, an anomaly is observed in the damping of ferroelectric modes. It has been proven that anomalies in the width of the Raman lines are a result of ME interactions.

Keywords: Multiferroism, Magnetoelecrtic Interactions, Green's Functions, Energy And Attenuation Of Elementary Excitations.

I. INTRODUCTION

In the last 10-15 years there has been an increasing interest in the theoretical investigation of various spin-ordered systems where (in one phase) magnetic and ferroelectric arrangement can exist simultaneously [1-3]. Such substances are called multiferroics. In these compounds, due to magnetoelecrtic interaction, their magnetic properties can be manipulated through an electric field and vice versa – the ferroelectric arrangement can be manipulated through a magnetic field. This type of interaction is only possible at given point groups of symmetries of the crystals, corresponding to invariance concerning time and space.

In accordance with [4] multiferroics are divided into two groups: type I and type II. Multiferroics of type I are characterized by different temperatures of phase transitions from paraelectric in ferroelectric state and from paramagnetic in magnetic-ordered state. At temperature below that of the magnetic phase transition, we observe spontaneous polarization and magnetization. The temperature of the ferroelectric phase transition is always higher than the temperature of the magnetic phase transition. In these multiferroics independent structural units of elementary cell are responsible for the occurrence of polarization and magnetization. Such compounds are $BiFeO_3$, hexagonal $RMnO_3$, where R is a rare earth ion, etc. At multiferroics of type II, appearance of ferroelectric phase is due to the magnetic phase transition in the frustrated spin systems [5-7]. At temperature lower than that of the magnetic phase transition, spiral magnetic arrangement is usually observed. It leads to violation of the centrosymmetry of the crystal and occurrence of spontaneous polarization at a temperature of the magnetic transition. It is well known that in such systems antisymmetric interaction Dzhelodzhinski-Moria (DM) plays an important role in the occurrence of the so-called weak magnetism [8, 9]. The connection between the ferroelectricity and DM

interaction has been discussed in [10-12] from a theoretical point of view.

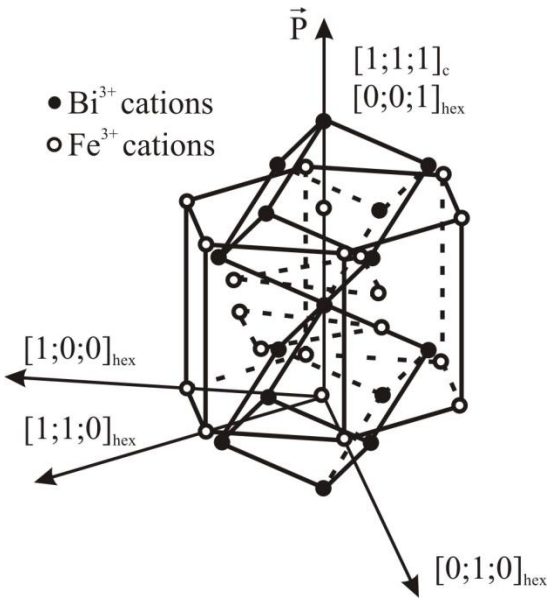


Figure 1. Crystallographic structure of $BiFeO_3$.

For a new generation of electric and magnetically - controlled multifunctional devices it is important to study the mechanisms of ME interactions theoretically. One approach is so called "First-principles studies", which is based on double-functional theory [13, 14]. Rovillain et al. [15] showed that the spin-wave energy in BFO can be renormalized up to 30 % in an energy-independent manner, with almost no energy consumption. Theoretical studies indicate that this effect is a consequence of the linear ME interaction, which is connected to the change of the spin-orbit coupling, induced by an external electric field. Fishman et al. [16] create quantitative microscopic theory of ME coupling in multiferroics using spin's Hamiltonian with two DM interactions taking into account single-ion anisotropy. Recently, Lee et al. [17], on the ground of "first-principles studies", systematically investigate possible ME interactions responsible for the occurrence of polarization based on the spin-current and magnetostriction. [18] have presented a microscopic model for the explanation of the origin of the additional polarization in RCrO$_3$, where R is a rare earth ion. The authors examine the various contributions in polarization due to antisymmetric DM interaction and magnetostriction. It has been shown that the appearance of an additional polarization below the point of the magnetic phase transition is due to the interaction between magnetic R- and Cr-ions. The influence of magnetic field on the polarization and of the electric field on the magnetization is numerically calculated as evidence for the strong ME connection in RCrO$_3$.

The properties of solids are characterized by their elementary excitations. In this paper we examine the elementary excitations in BFO, which define macroscopic behaviour of polarization and magnetization. $BiFeO_3$ is multiferroic of type lone pair and is structurally characterized by two distorted perovskite cells connected in direction [1,1,1] of their diagonals (Fig.1). In BFO ferroelectricity and weak ferromagnetism with temperatures of the phase transitions T_C = 1 100K and T_N = 643K are simultaneously observed. Ferroelectricity is obtained as a result of the shift of Bi ions concerning FeO_6 octahedrons, that define eight possible directions in four cubic diagonals [19-21]. The type of magnetic arrangement is incommensurable spiral structure with a period of 6300 nm in the direction [1,1,0] (Fig.1). The magnetic structure is of G-type, composed of Fe^{3+} magnetic ions, as each Fe^{3+} ion is surrounded by six Fe^{3+} nearest neighbours with antiparallel spins [22]. We describe the magnetic subsystem through a modified model of Heisenberg, taking into account isotropic exchange interaction up to second neighbours, antisymmetric DM interactions and single-ion anisotropy. While the ferroelectric system is characterized by a process of charge arrangement, we describe it through a transverse Ising model presenting in pseudo-spin operators for pseudo-spin S = 7/2 [23]. We prove that the connection between both subsystems (ME interaction) is determined by two different mechanisms. The first is quadratic to spins and pseudo-spin operators, while the second is induced by spontaneous polarization and we call it antisymmetric ME mechanism [24]. The system will be investigated using the method of two-time thermodynamic functions of Green (FG). This will allow us to present the energy of elementary excitations and their mutual influence on the temperature range above and below the phase transition temperature analytically.

II. METHODS AND MATERIALS

The Hamiltonian which describes the common multiferroic properties of BFO compounds can be written as follows:

$$H = H_e + H_m + H_{me}. \quad (1)$$

H_e defines the ferroelectric subsystem based on the Transverse Ising model with pseudo-spin S=7/2:

$$H_e = -\Omega \sum_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - \mu \sum_i \vec{E}.\vec{S}, \quad (2)$$

where S_i^x and S_i^z are the components of the pseudo-spins of spontaneous polarization, J_{ij} is the exchange pseudospin interaction, Ω is the tunneling frequency and $\vec{E}$ is an external electric field.

H_m describes the magnetic properties of BFO. The weak ferromagnetism of G-type depends on the symmetry of the lattice. The canted magnetic moments and the antiferromagnetic axis lie perpendicular to each other in the (1,1,1) plane. The magnetization is along the [−1;2;1] direction (fig.2).

$$H_m = -\sum_{ij} A_{ij}(\vec{B}_i.\vec{B}_i) - \sum_{<i\,l>} A'_{il}(\vec{B}_i.\vec{B}_l) - \\ -\sum_{ijalongx'} \vec{D}_{ij}^{y'}.(\vec{B}_i \times \vec{B}_j) - K\sum_i \left(B_i^{z'}\right)^2 - \\ -g\mu_B \sum_i \vec{h}.\vec{B}_i, \quad (3)$$

In this equation $\vec{B}_i$ is the Fe^{3+} spin, A_{ij} and A'_{il} are the symmetry exchange interactions between the nearest-neighbours (nn) along the Fe–O–Fe bond and the next-nearest-neighbours (nnn) along the Fe–O–O–Fe bond, respectively. $\vec{D}_{ij}^{y'}$ represents the DM vector along y' responsible for the cycloid periodicity and the DM interaction between spins along the [1;0;−1] direction. These spins rotate into the plane defined by the *P*s direction and the propagation vector in [1;0;−1] direction. $\vec{D}_{ij}^{y'}$ produces a weak ferromagnetic moment along y' due to the canting of the uniform moments of each (1,1,1) plane. The fourth term gives the single-ion (easy-axis) anisotropy (SIA) along z' ($K > 0$) (fig.2). The last term in (3) determines the influence of the external magnetic field on the magnetic subsystem.

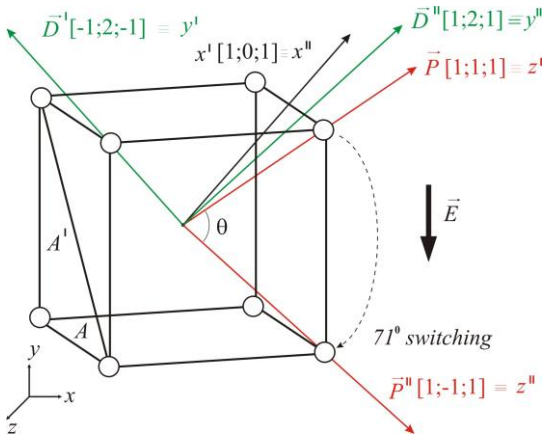


Figure 2. Presentation of spatial location of the main parameters which characterize the multiferroic properties of BFO. The red arrows denote the direction of the spontaneous polarization $\vec{P}$; the green arrows present the direction of a DM vector $\vec{D}^{y'}$ and the black thick arrow the direction of an external electric field *E*, responsible for the rotation of the spontaneous polarization by 71° (so-called 71° in-plane switching).

Now we discuss the third member of (1). It is well known that symmetrical and antisymmetrical exchange interactions depend on the distance between magnetic ions and the angle of the Fe-O-Fe bond. The relative shift of Bi^+ and Fe^{3+} ions in the direction [1,1,1] modulates exchange interactions. If we denote shift of the Fe ion from its equilibrium position with u (<u> = 10^{-3}Å [25]) and expand DM vector in this shift we will obtain:

$$\sum_{ijalongx'} \vec{D}_{ij}^{y'}.(\vec{B}_i \times \vec{B}_j) \approx \sum_{ijalongx'} \vec{D}_{ij}^{y'0}.(\vec{B}_i \times \vec{B}_j) + \lambda^* \sum_{ijalongx'} (\vec{P} \times \vec{e}_{ij}).(\vec{B}_i \times \vec{B}_j), \quad (4)$$

where $\lambda^* = \frac{\lambda}{e^*}$, λ is the spin-lattice interaction, which is a consequence of the relativistic spin-orbital coupling, e^* is the ionic charge of Born, and $P = e^* < u >$ is the polarization in the pseudo-spin presentation as $\vec{P} = [\frac{1}{N}\sum_i < S_i^x >; 0; \frac{1}{N}\sum_i < S_i^z >]$. The last term in (4) defines ME interaction, which depends on the direction. This term is similar to the Peierls-type spin-phonon interaction. The last term in (6) can be regarded as induced DM interaction by the spontaneous polarization. This means that the cycloid spiral structure in the BFO is not a consequence of the strong magnetic geometric frustration, but of the the large value of the constant of the DM interaction. Experimental studies [26] show that

the spontaneous polarization increases with increasing external magnetic field. This effect can be described by taking into account the modulation of symmetrical exchange interaction of the magnetic polar shifts ions.
This can be accounted by adding the following members to the ME interaction:

$$-\gamma \sum_{ij}\left(\vec{P}\right)^2\left(\vec{B}_i.\vec{B}_j\right) - \gamma' \sum_{ij}\left(\vec{P}\right)^2\left(\vec{B}_i.\vec{B}_j\right), \qquad (5)$$

where γ and γ' are the second derivatives of A_{ij} and A'_{il} from the polar displacements of Fe^+ ions.
From the above mentioned arguments the term of the Hamiltoian (1) which describes ME interaction in BFO has the form:

$$H_{me} = -\lambda^* \sum_{ijalongx'}\left(\vec{P}\times\vec{e}_{ij}\right).\left(\vec{B}_i\times\vec{B}_j\right) - \gamma \sum_{ij}\left(\vec{P}\right)^2\left(\vec{B}_i.\vec{B}_j\right) - \gamma' \sum_{ij}\left(\vec{P}\right)^2\left(\vec{B}_i.\vec{B}_j\right). \qquad (6)$$

III. RESULTS AND DISCUSSION

For the theoretical calculations we are using the method of retarded Green functions [27]. This method is widely used for investigation of multiparticulate complex systems whose subsystems interact with each other intensively. This leads to occurrence of nonlinear interactions where the small coupling parameter is absent. Green's functions are the universal approach in calculating the static and dynamic characteristics of the different systems. Formalism is very convenient because it does not use operators, but rather complex functions with simple analytical properties. GF allows for a single solution of all quantum statistical problems of many systems. The method is suitable for investigating low-dimensional systems because it is applicable to the real space. The obtained expressions are in analytical form and they are convenient for numerical calculations. The thermodynamic Green's function technique allows us to determine the elementary excitations and the temperature-dependent magnetization and polariza-tion.

For the theoretical calculations instead of the x, y, z components of the vectors $\vec{S}_i, \vec{B}_i$ and $\vec{D}_{ij}$, we introduce the following operators:

$$S_i^{\pm} = \frac{1}{\sqrt{2}}\left(S_i{}^x \pm iS_i{}^y\right); S_i{}^z = S_i{}^z;$$
$$B_i^{\pm} = \frac{1}{\sqrt{2}}\left(B_i{}^x \pm iB_i{}^y\right); B_i{}^z = B_i{}^z; \qquad (7)$$
$$D_{ij}^{\pm} = \frac{1}{\sqrt{2}}\left(D_{ij}{}^x \pm iD_{ij}{}^y\right); D_{ij}{}^z = D_{ij}{}^z.$$

In order to calculate the necessary corre-lation functions we use retarded Green's function in Heisenberg's presentation:

$$G_{AB} = \ll \hat{A}(t); \hat{B}(t') \gg = -\Theta(t-t').\left[\hat{A}(t); \hat{B}(t')\right]_- > \qquad (8)$$

We define the following GFs and average values of the following commutators:

(a) For the pseudo-spin subsystem:

$$G_{fg}^{(ps)+z-} = \ll S_f^+; \left(S_g^z\right)^n S_g^- \gg;$$
$$\Phi^{+z-} = < \left[S_f^+; \left(S_g^z\right)^n S_g^-\right] >$$
$$G_{fg}^{(ps)-z-} (= \ll S_f^-; \left(S_g^z\right)^n S_g^- \gg;$$
$$\Phi^{-z-} = < \left[S_f^-; \left(S_g^z\right)^n S_g^-\right] > \qquad (9)$$
$$G_{fg}^{(ps)zz-} = \ll S_f^z; \left(S_g^z\right)^n S_g^- \gg;$$
$$\Phi^{zz-} = < \left[S_f^z; \left(S_g^z\right)^n S_g^-\right] >$$

(b) For the magnetic subsystem:

$$G_{fg}^{(ss)+z-} = \ll B_f^+; \left(B_g^z\right)^n B_g^- \gg;$$
$$\Xi^{+z-} = < \left[B_f^+; \left(B_g^z\right)^n B_g^-\right] >$$
$$G_{fg}^{(ss)-z-} = \ll B_f^-; \left(B_g^z\right)^n B_g^- \gg;$$
$$\Xi^{-z-} = < \left[B_f^-; \left(B_g^z\right)^n B_g^-\right] > \qquad (10)$$
$$G_{fg}^{(ss)zz-} = \ll B_f^z; \left(B_g^z\right)^n B_g^- \gg; .$$
$$\Xi^{zz-} = < \left[B_f^z; \left(B_g^z\right)^n S_g^-\right] >$$

Based on Tyablikov's method for $G_{ij}^{(ps)\zeta z-}$ and $G_{ij}^{(ss)\zeta z-}$, where $\zeta = +, -, z$ and using the spectral theorem [27] we find a system of self-consistent equations to calculate the average values of $< \left(S_g^z\right)^n >$ and $< \left(B_g^z\right)^n >$. The poles of Green's functions determine the energy of elementary pseudo-spin excitations.

$$\omega_3 = 0$$
$$\omega_1 = -\omega_2 = \pm\sqrt{\Lambda_{eff}^2 - 2\Omega_{eff}\left(\frac{1}{2}\Omega_{eff} + S\right) - T^2}\ , \qquad (11)$$

where:

$$\Lambda_{eff} = \sum_j \{J_{ij} + 4[\gamma \sum_{kl} < \left(\vec{B}_k \cdot \vec{B}_l\right) > + \gamma' \sum_{<kl>} < \left(\vec{B}_k \cdot \vec{B}_l\right) >]\delta_{ij}\} < S_j^z > + \frac{\lambda^*}{\sqrt{2}} \sum_{kl} < \left(\vec{B}_k \times \vec{B}_l\right)^y > ;$$
$$\Omega_{eff} = \Omega + \frac{\lambda^*}{\sqrt{2}} \sum_{kl} < \left(\vec{B}_k \times \vec{B}_l\right)^y > \qquad (12)$$
$$T = 2 < S_g^z > [\gamma \sum_{kl} < \left(\vec{B}_k \cdot \vec{B}_l\right) >$$

$$+\gamma' \sum_{<kl>} <(\vec{B}_k \cdot \vec{B}_l)>]$$

$$S = \frac{\Omega_{eff}[\gamma \sum_{kl} <(\vec{B}_k \cdot \vec{B}_l)> + \gamma' \sum_{<kl>} <(\vec{B}_k \cdot \vec{B}_l)>]}{\Lambda_{eff} - T} \cdot$$

$$. < S_g^z >$$

The equation:

$$E^3 - (\mathrm{M}_+ - \mathrm{M}_-)E^2 + (P_+Q_+ + P_-Q_- - M_+M_-)E + (P_+Q_+M_- - P_-Q_-M_+) = 0 \qquad (13)$$

determines the energy of magnetic elementary excitations, introducing following notations:

$$A_{ij}^{eff} = A_{ij} + \gamma P^2 \delta_{ij}; \quad A_{ij}^{\prime eff} = A_{ij}' + \gamma' P^2 \delta_{ij}; \quad D_{eff} = D + \lambda^* P$$

$$M_\pm = 4 \sum_{\substack{i \\ nn}} A_{if}^{eff} < B_i^z > +4 \sum_{\substack{l \\ nnn}} A_{lf}^{\prime eff} < B_i^z > \pm 2 g \mu_B h_z$$

$$P_\pm = 4 \sum_{\substack{i \\ nn}} A_{if}^{eff} < B_i^\pm > +4 \sum_{\substack{l \\ nnn}} A_{lf}^{\prime eff} < B_i^\pm > +2 D_{eff} \pm \sqrt{2} g \mu_B h_x \qquad (14)$$

$$Q_\pm = 4 \sum_{\substack{i \\ nn}} A_{if}^{eff} < B_i^\mp > +4 \sum_{\substack{l \\ nnn}} A_{lf}^{\prime eff} < B_i^\mp > -2 D_{eff} \mp \sqrt{2} g \mu_B h_x \, .$$

As a final step in our calculations, based on the equation of motion of the operator in the Heisenberg representation $i\dot{\hat{A}} = [\hat{A}; H]$ for $< S_g^x >$, $< (S_g^x)^2 >$, $< B_g^x >$, $< B_g^y >$, $< (B_g^x)^2 >$ and $< (B_g^y)^2 >$ we derive:

$$< S_g^x > = \frac{\Omega_{eff}}{(\Lambda_{eff} - T)} < S_g^z >$$

$$< (S_g^x)^2 > = \frac{1}{2} \left(\frac{\Omega_{eff}}{\Lambda_{eff} - T} \right)^2 < (S_g^z)^2 >$$

$$< B_g^x > = (\frac{P_+}{M_+} + \frac{P_-}{M_-}) < (B_g^z) > \qquad (15)$$

$$< B_g^y > = i(\frac{P_-}{M_-} - \frac{P_+}{M_+}) < (B_g^z) >$$

$$< (B_g^x)^2 > = 12 \mathrm{D}_{eff} (\frac{P_+}{(M_+)^2} + \frac{P_-}{(M_-)^2}) < (B_g^z)^2 >$$

$$< (B_g^y)^2 > = -2 \mathrm{D}_{eff} (\frac{P_+}{(M_+)^2} + \frac{P_-}{(M_-)^2}) < (B_g^z)^2 > .$$

The detailed procedure for calculating $< (S_g^z)^n >$ and $< (B_g^z)^n >$ is presented in [28]. Spontaneous polarization and magnetization are determined by:

$$P_s = \frac{1}{N} \sqrt{\sum_\alpha (\sum_i < S_i^\alpha >)^2} \, , \qquad (16)$$

$$\mathrm{M} = \frac{1}{N} \sqrt{\sum_\alpha (\sum_i < B_i^\alpha >)^2} \, , \qquad (17)$$

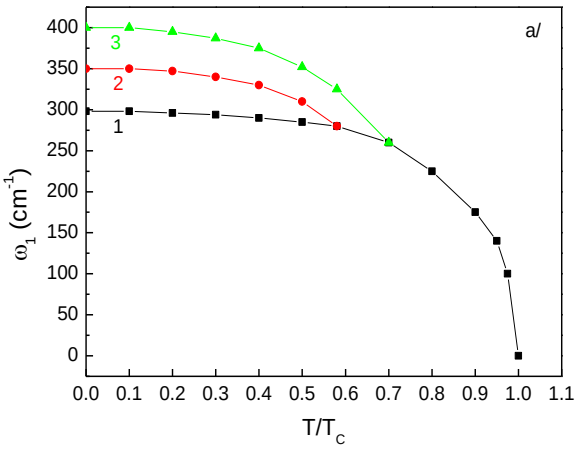
where $\alpha = x, y, z$.

The numerical calculations are made using the following model parameters appropriate for BFO:

a/ For the electric subsystem: pseudo-spin $S = 7/2$; $T_C = 1065$ K; $\Omega = 15{,}34$ cm^{-1}; $J_{ij} = 1342{,}26$ cm^{-1}. Here the interaction of the pseudo-spin coupling J_{ij} and the tunneling frequency Ω are determined by minimizing the free energy of the pseudo-spin system for $T < T_C$ [29].

b/ For the magnetic subsystem: S = 5/2; T_N = 650 K; A_{ij} = 54,34 cm^{-1}; A_{il}' = 1,86 cm^{-1}; D = 0,87 cm^{-1}; K = 0,027 cm^{-1} [30].

c/ As constants of the ME interaction we use: γ = 113,33 cm^{-1}Å^{-1}; γ' = 3,73 cm^{-1}Å^{-1}; λ^* = 6,08 cm^{-1}Å^{-1}. These constants are determined by the following procedure: following [31] we calculate <u> and renormalized phonon energy omitting the effects of DM interaction. From the experimental data for magnetization [32], the polarization [33] and Raman spectra for BFO [34] for two different temperatures $T < T_N$ we obtain the system of equations for determining the constants of ME interactions.



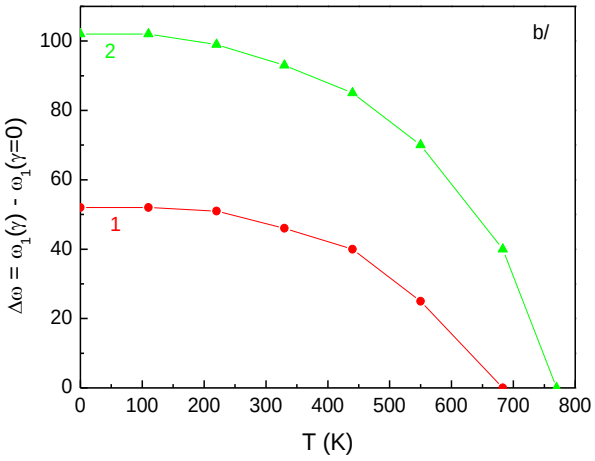


Figure 3. Temperature dependence a/ pseudo-spin energy ω_1 for different values of quadratic ME interaction 1/ $\gamma = 0$ cm^{-1}Å^{-1}; 2/ $\gamma = 113{,}33$ cm^{-1}Å^{-1} and 3/ $\gamma = 170{,}00$ cm^{-1}Å^{-1}; b/ the change in energy of ferroelectric exitation $\Delta\omega = \omega_1(\gamma \neq 0) - \omega_1(\gamma = 0)$ in comparison with the case of absence of ME interaction 1/ $\gamma = 113{,}33$ cm^{-1}Å^{-1} и 2/ $\gamma = 170{,}00$ cm^{-1}Å^{-1}.

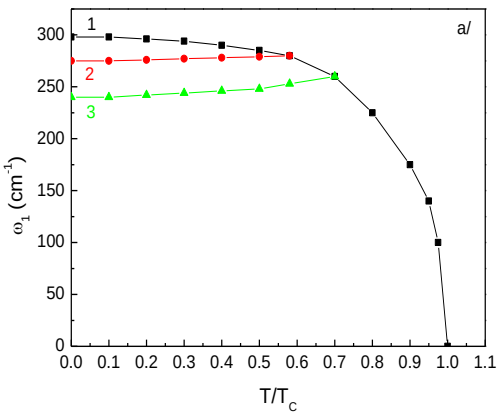
Figure 3 presents the energy of ferroelectric elementary excitations ω_1 as a function of temperature for different values of magnetoelecrtic constant γ, which determines the intensity of quadratic coupling between the spin and pseudo-spin operators (second and third term in (6)). ω_1 shows the typical behavior of soft mode at ferroelectric phase transition, i.e. energy approximates zero when approaching T_C. In the multiferroic phase (below T_N) when γ increase, the energy of the ferroelectric mode increases accordingly. At the point of phase transition "positive kink" in ferroelectric mode is observed. Experimental confirmation of this behavior is the occurrence of anomaly in the Raman spectrum in the BFO in vicinity of the point of the magnetic phase transition [34]. When $T > T_N$ magnetic subsystem is in paramagnetic state, there is not any influence of the magnetic system on the ferroelectric mod. Growth in γ leads to an increase of the effective pseudo-spin interaction. Theoretical calculations show that J_{eff} is temperature-dependent:

$$J_{eff} = J + 4\gamma \sum_i [8D_{eff}(\frac{P_+}{(M_+)^2} - \frac{P_-}{(M_+)^2}) + 1]. \\ .< B_i^z >^2 \qquad (18)$$

The quadratic ME interaction stabilizes ferroelectric phase in T_N and causes the extraordinary polarization by magnetostriction. Fig.3b shows that by lowering the temperature, the influence of quadratic ME interaction increases.

Figure 4 presents the energy of ferroelectric elementary excitation ω_1 as a function of temperature for different values of magnetoelecrtic constant λ*, which determines the intensity of antisymmetric coupling between the spin and the pseudo-spin operators (the first term (6)). As noted, this ME interaction can be characterized as induced DM interaction caused by polarization of the system. The first term in Hamiltonian of the system (6) depends on the direction. It has a minimum when the vectors of the polarization and the magnetization are perpendicular. Under the influence of an external electric field in the direction [0,-1,0] polarization is oriented from the direction [1,1,1] in the direction [1,-1,1]. Due to the antisymmetric ME connection, the magnetization will rotate together with the polarization so that the first term (6) always has a minimum value (fig.2). This rotation of the spins in the magnetic sublattice under the influence of an external electric field is experimentally observed in [35, 36]. Based on this term the possibility of occurrence of spin-reorientation transition in BFO is theoretically proven [24]. In multiferroic phase (below T_N) when the value of λ* increases the ferroelectric excitation energy decreases. At the point of phase transition "negative kink" to ferroelectric mode is observed. This behavior can be explained by the fact that the induced antisymmetric ME interaction renormalizes the tunneling frequency Ω and makes it temperature dependent. Theoretical calculations determine the following expression of this relationship:

$$\Omega_{eff} = \Omega + \frac{\lambda^*}{\sqrt{2}} \sum_i \left(\frac{P_+}{M_+} - \frac{P_-}{M_-}\right) < B_i^Z > . \qquad (19)$$



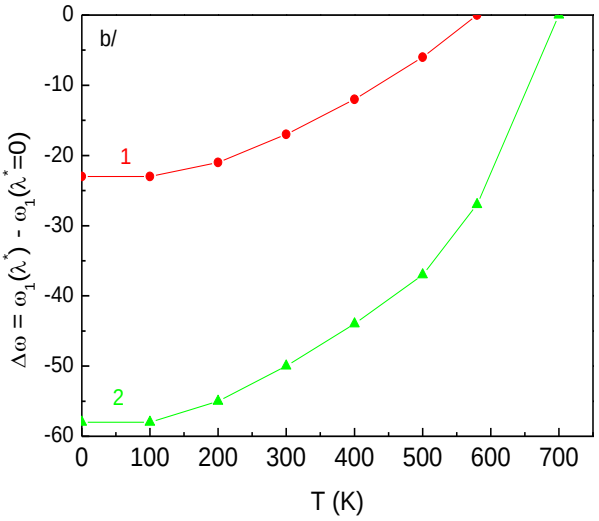


Figure 4. Temperature dependence of a/ pseudo-spin energy ω_1 for different values of induced antisymmetric ME interaction 1/ λ^* = 0 cm^{-1}Å^{-1}; 2/ λ^* = 6,08 cm^{-1}Å^{-1} и 3/ λ^* = 12,16 cm^{-1}Å^{-1}; b/ the change of the energy in ferroelectric exitation $\Delta\omega = \omega_1(\lambda^* \neq 0) - \omega_1(\lambda^* = 0)$ in comparison with the case of absence of ME interaction 1/ λ^* = 6,08 cm^{-1}Å^{-1} и 2/ λ^* = 12,16 cm^{-1}Å^{-1} .

It is clear that at a given temperature when the value of λ^* increases, the tunneling frequency Ω_{eff} grows, as according to (11), the energy of pseudo-spin excitations decreases. Fig. 4b shows that at low temperatures the influence of λ^* increases.

In summary, we can make the following conclusion: antisymmetric ME interaction destabilizes the ferroelectric phase. The first term of equation (6) is responsible for the appearance of incommensurable magnetic structure. This magnetic structure is due to the spontaneous polarization of the ferroelectric phase. This leads to symmetry in ME interaction in the following sense: usually magnetic phase transition, accompanied by a structural one, is responsible for the occurrence of spontaneous polarization. The reason for the structural phase transition in this system is the strong magnetic frustration (RMnO$_3$). Now spontaneous polarization BFO is responsible for inducing antisymmetric DM interaction into the magnetic system. DM interaction is responsible for the appearance of incommensurable cycloidal structure although the magnetic system is not highly frustrated. DM interaction is strong and increases with rising temperature. In our opinion based on the above conclusions we can introduce a new definition of multiferroics from I-type: these are substances in which the appearance of multiferroic properties is due to induced DM interaction and induced magnetostriction. Spontaneous polarization is responsible for the induced ME interactions in these substances.

Figure 5 shows for $T < T_N$ the dependence of the energy of the ferroelectric excitation on an external magnetic field a/ applied in a direction, parallel to the spontaneous polarization [1,1,1] and b/ perpendicular to the polarization and the easy-axis of magnetization at [-1,2,-1].

In case a/ An increase in the magnetic field leads to a hardening of the ferroelectric mode, only when the quadratic interactions is included, i.e. the pseudo-spin energy grows reaching saturation.

This behavior is explained by the increase in the exchange pseudo-spin interaction (18) which leads to an increase in $< B_i^Z >$. When taking into account only antisymmetric magnetic interaction an increase of the magnetic field leads to the energy of the ferroelectric mode to decrease, i.e. to soften. With the increase of the magnetic field, $< B_i^Z >$ increases and according to (19) it leads to an increase in tunneling field Ω_{eff} and reduces the ferroelectric energy. It is clear that there is a competition between the two ME mechanisms, defined in (6).

The opposite behavior in the energy of the pseudo-spin excitations is observed in case b / (a magnetic field applied perpendicularly to the easy-axis of magnetization). With the growth of the magnetic field, $< B_i^Z >$ decreases, which leads to a reduction in Ω_{eff} and J_{eff}. The antisymmetric ME interaction hardens the ferroelectric energy, while quadratic mechanism softens the pseudo-spin mode.

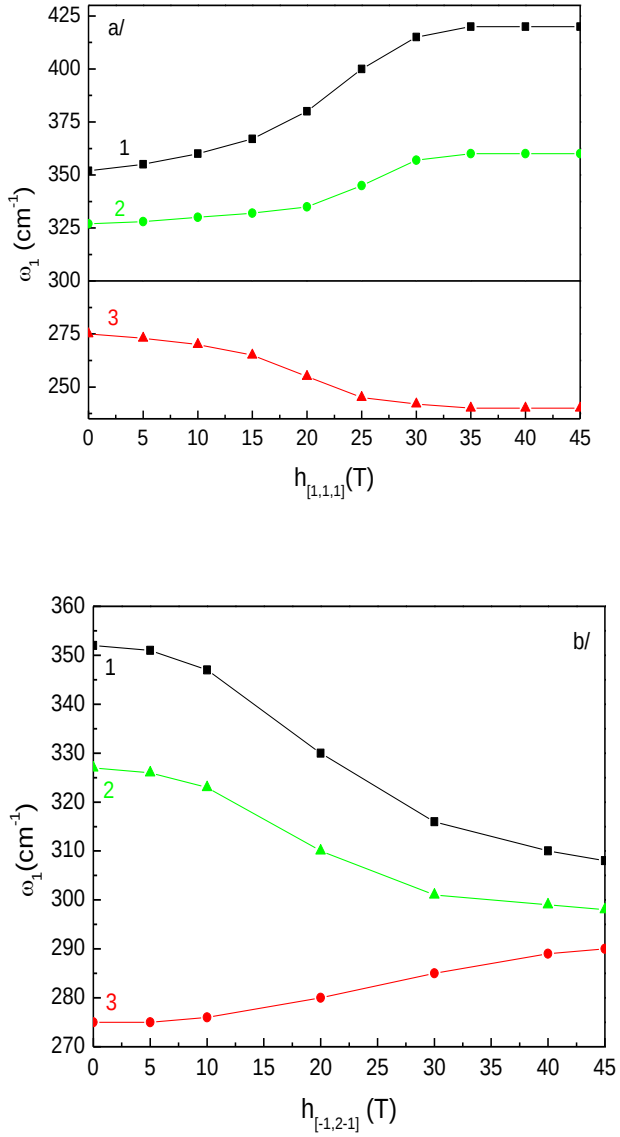


Figure 5. Energy of pseudo-spin excitations ω as a function of an external magnetic field *h* in a direction a/ [1,1,1] and b/ [-1,2-1] for $T = 0.2T_C$ including: 1/ only quadratic ME interaction ($\gamma \neq 0$ and $\lambda^* = 0$); 2/ both ME interactions ($\gamma \neq 0$ and $\lambda^* \neq 0$); 3/ only induced antisymmetric ME interaction ($\gamma = 0$ and $\lambda^* \neq 0$).

From the above discussion it becomes clear that there is a competition between the two ME mechanisms in BFO. This competition is a consequence of the renormalization of the main microscopic parameters of ferroelectric system – the tunneling frequency Ω and the exchange pseudo-spin interaction *J*.

Figure 6 shows the temperature dependence of the energy of the spin excitations E for different values of γ and λ^*. When the values of quadratic and antisymmetric exchange interaction increase, the temperature of the magnetic phase transition increases. The shift on the temperature of the magnetic phase transition to higher values shows that ME interactions stabilize the magnetic phase.

So far we have discussed the static properties of elementary excitations in BFO. To study the dynamic characteristics, i.e. the damping of pseudo-spin and spin waves we will apply the method of Tserkovnikov [37]. After the formal integration of the equation of motion for the Green's function (8), using the term depending on the time, we calculate the effects of damping beyond the random phase approximation (RPA).

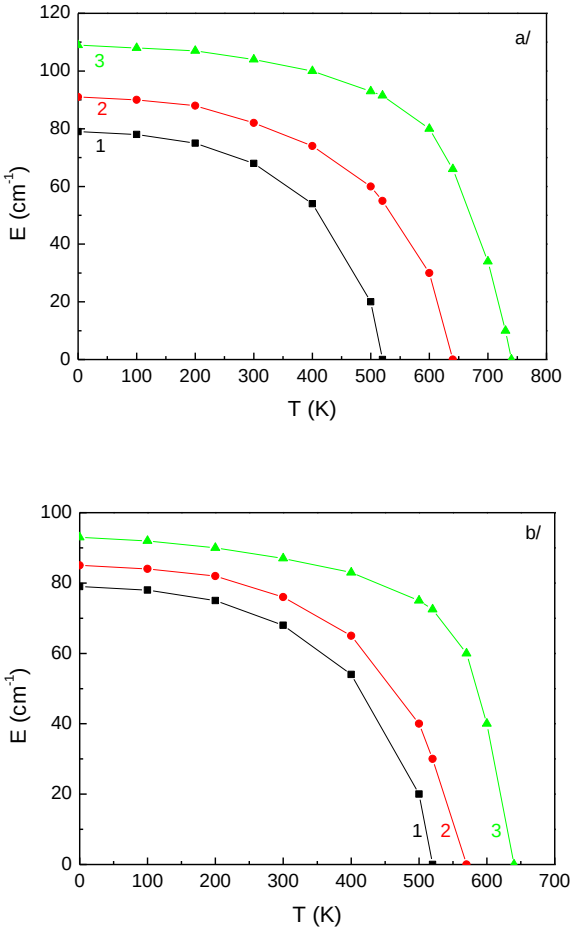


Figura 6. Temperature dependence of a/ spin energy *E* for different values of quadratic ME interaction 1/ γ = 0 cm^{-1}Å^{-1}, 2/ γ = 113,33 cm^{-1}Å^{-1} and 3/ γ = 170,00 cm^{-1}Å^{-1}; b / spin energy *E* for different values of induced antisymmetric ME interaction 1/ λ^* = 0 cm^{-1} Å^{-1}; 2/ λ^* = 6,08 cm^{-1} Å^{-1} and 3/ λ^* = 12,16 cm^{-1}Å^{-1}

For the damping of the pseudo-spin excita-tions we get:

$$\Gamma_{ij}^{sp} = \Gamma_{ij}^{sp-sp} + \Gamma_{ij}^{sp-me}\ , \qquad (20)$$

where Γ_{ij}^{sp-sp} is the part of the damping in the ferroelectric subsystem due to pseudo-spin interactions and Γ_{ij}^{sp-me} is the part of the damping of pseudo-spin mode due to interactions between ferroelectric excitations and the magnetic subsystem.

For Γ_{ij}^{sp-sp} we have:

$$\Gamma_{ij}^{sp-sp} = \frac{\pi}{4N^2}\sum_{kl}\frac{(J_{kl})^2}{< S_i^Z >}[\left(n_i + 2 < S_i^Z >\right)\left(3n_k + 2 < S_k^Z >\right) < S_l^Z > + +n_k\left(n_l + 2 < S_l^Z >\right) < S_i^Z >]\delta_{ij}\delta\left(\omega_j - \omega_k - \omega_l + \omega_i\right) + \frac{\pi}{2N}\sum_l \frac{\left(J_{ij}\right)^2}{<S_i^Z>}[4\left(n_i + 2 < S_i^Z >\right)\left(n_j + 2 < S_j^Z >\right) < S_l^Z > +\left(n_l + 2 < S_l^Z >\right)n_j < S_i^Z >]\delta\left(\omega_i - \omega_j - \omega_l + \omega_i\right), \qquad (21)$$

where $n_i =< S_i^- S_i^+ >$ is the pseudo-spin correla-tion function.

Γ_{ij}^{sp-sp} has only terms related to processes of dispersion of a spin wave by another, which satisfy the law of conservation of energy and the law of conservation of momentum. The remaining processes associated with damping of a spin wave in two or three spin waves and reverse processes are omitted because they are essential for $T = T_C$ [38].

Γ_{ij}^{sp-me} we will present in the following way:

$$\Gamma_{ij}^{sp-me} = \Gamma_{ij}^{sp-me}(\gamma) + \Gamma_{ij}^{sp-me}(\lambda^*). \qquad (22)$$

$\Gamma_{ij}^{sp-me}(\gamma)$ gives the part of the damping of the pseudo-spin waves due to quadratic ME interaction and has the form:

$$\Gamma_{ij}^{sp-me}(\gamma) = \frac{\pi(\gamma^2+\gamma'^2)}{4N^2<S_i^Z>}\sum_{kl}[n_i\left(n_k + 2 < S_k^Z > + L_l\right) - L_j n_k]\ \delta\left(E_l - \omega_k - E_j + \omega_i\right). \qquad (23)$$

$\Gamma_{ij}^{sp-me}(\lambda^*)$ determines the part of Γ_{ij}^{sp} depending on antisymmetric ME interaction and has the form:

$$\Gamma_{ij}^{sp-me}(\lambda^*) = \frac{\pi(\lambda^*)^2}{4N^2}\sum_{kl}\frac{<B_i^Z><B_j^Z>}{<S_i^Z>}L_l. \cdot\left(n_k + 2 < S_k^Z >\right)\delta\left(E_l - \omega_k - E_j + \omega_i\right) \qquad (24)$$

where $L_i =< B_i^- B_i^+ >$ is spin correlation function.

In (23) and (24) again included only members that satisfy the laws of conservation of momentum and energy.

The expressions of the damping of the ferroelectric modes are suitable for numerical calculations. Figure 7 presents the temperature dependence of the damping of pseudo-spin excitations. The influence of each of the mechanisms on Γ_{ij}^{sp} is shown. The damping, due to antisymmetric ME interaction (fig.7, curve 3) increases as temperature increases, reaching a maximum value to a temperature less than the temperature of magnetic phase transition. After that it decreases and becomes zero in T_N. The damping associated with the quadratic ME interaction (fig.7, curve 2) increases with rising temperature as in the vicinity of T_N reaches a maximum value, then decreases and at the point of the magnetic phase transition has a final value. The damping due to the pseudo-spin interaction (fig.7, curve 1) increases with increasing temperature to the ferroelectric phase transition. This behavior of Γ_{ij}^{sp-sp} is in accordance with the damping of the ferroelectric modes within the transverse Ising model for small values of tunneling field [39]. The damping Γ_{ij}^{sp-sp} prevails over Γ_{ij}^{sp-me}. The total damping of pseudo-spin waves Γ_{ij}^{sp} is represented in figure 7, curve 4. In the multiferroic phase there is an anomaly in the vicinity of the point of the magnetic phase transition at $T < T_N$. This means that, in the Raman spectra of the BFO, an anomaly is expected to occur in the width of the spectral line. This has been proven experimentally in [34].

Figures 8a and 8b present temperature dependence of $\Gamma_{ij}^{sp-me}(\gamma)$ and $\Gamma_{ij}^{sp-me}(\lambda^*)$ for different values of the constants of ME interaction, γ and λ^*. It is clear that when the ME constants for the different mechanisms of ME interaction increase, the damping increases, as the peaks in the curves are shifted to higher temperatures.

For the damping of the spin excitation we get:

$$\Gamma_{ij}^{ss} = \Gamma_{ij}^{ss-ss} + \Gamma_{ij}^{ss-me}, \qquad (25)$$

where Γ_{ij}^{ss-ss} is the damping of the spin energy due to the spin-spin interaction, Γ_{ij}^{ss-me} is the part of the spin's damping depending on the interaction between spin waves and the excitations of the ferroelectric subsystem.

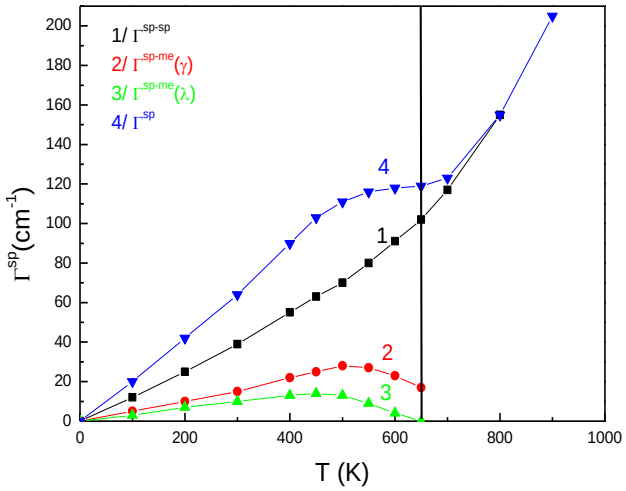


Figure 7. Temperature dependence of the damping of the pseudo-spin excitations and its components as: 1/ Γ_{ij}^{sp-sp}; 2/ $\Gamma_{ij}^{sp-me}(\gamma)$; 3/$\Gamma_{ij}^{sp-me}(\lambda^*)$ and 4/ Γ_{ij}^{sp} (the total damping).

We present Γ_{ij}^{ss-ss} in the following way:

$$\Gamma_{ij}^{ss-ss} = \frac{4\pi}{N}\sum_{l}[(A_{il})^2 + (A'_{il})^2] < S_l^z > \left[L_l\left(2 < B_j^z > + L_j + L_i\right) - L_i L_l\right]\delta(E_l - E_i - E_i + E_l) + \quad (26)$$
$$+2\pi D_i^2 < S_i^z > L_i\left(2 < B_j^z > + L_i\right)\delta_{ij}\delta(E_j - E_i)\,.$$

We write Γ_{ij}^{ss-me} in the following form:

$$\Gamma_{ij}^{ss-me} = \Gamma_{ij}^{ss-me}(\gamma) + \Gamma_{ij}^{ss-me}(\lambda^*). \quad (27)$$

$\Gamma_{ij}^{ss-me}(\gamma)$ gives the part of the damping of the spin waves due to quadratic ME interaction and has the form:

$$\Gamma_{ij}^{ss-me}(\gamma) = \frac{\pi(\gamma^2+\gamma'^2)}{4N^2}\sum_{kl} n_k\left(n_l + 2 < S_l^Z >\right)\left(L_l + 2 < B_l^Z >\right)\delta\left(\omega_l - \omega_l - E_j + E_i\right) +$$
$$+ \pi(\gamma^2 + \gamma'^2)\left(< S_i^Z >\right)^2 L_i\,\delta_{ij}\delta\left(E_j - E_i\right). \quad (28)$$

$\Gamma_{ij}^{ss-me}(\lambda^*)$ determines the part of Γ_{ij}^{ss} depending on antisymmetric ME interaction and has the form:

$$\Gamma_{ij}^{ss-me}(\lambda^*) = \frac{\pi(\lambda^*)^2}{2N}\sum_l < S_i^Z > L_l\delta_{ij}\delta(E_i - E_l) +$$
$$+\frac{\pi(\lambda^*)^2}{4N^2}\sum_{kl} L_l n_k \delta_{ij}\,\delta(E_l + \omega_k - E_i). \quad (29)$$

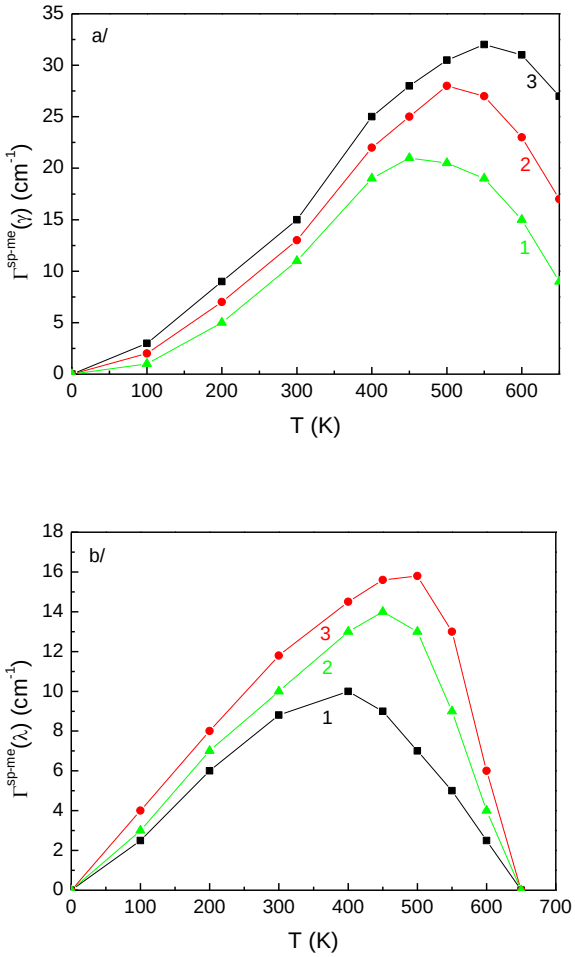


Figure 8. Temperature dependence of the part of the damping of the ferroelectric modes due to a/ quadratic ME interaction as: $1/\gamma$ = 75,55 cm^{-1}Å^{-1}; $2/\gamma$ = 113,33 cm^{-1}Å^{-1} and $3/\gamma$ = 170,00 cm^{-1} Å^{-1}; b/ induced antisymmetric ME interaction as: $1/\lambda^*$ = 3,04 cm^{-1}Å^{-1}; $2/\lambda^*$ = 6,08 cm^{-1}Å^{-1} и $3/\lambda^*$ = 12,16 cm^{-1}Å^{-1}.

The obtained expressions for the damping of spin excitations are convenient for numerical calculations. Figure 9 presents the temperature dependence of Γ_{ij}^{ss}. It shows the influence of each of the mechanisms on the damping of spin modes. The part of the damping $\Gamma_{ij}^{ss-me}(\lambda^*)$, due to the antisymmetric ME interaction (fig.9, curve 3) increases with temperature and reaches a maximum value of a temperature less than the temperature of magnetic phase transition. It then decreases and reaches final value in T_N. $\Gamma_{ij}^{ss-me}(\gamma)$, which depends on the quadratic ME interaction (fig.9, curve 4), increases with rising temperature as in the vicinity of T_N reaches a maximum value. It then

decreases and becomes zero at the point of the magnetic phase. The damping Γ_{ij}^{ss-ss}, due to the spin-spin interaction (fig.9, curve 2), increases with increasing temperature up to the temperature of the magnetic phase transition. This behavior is consistent with the damping of spin modes within the Heisenberg model [40]. It is clear that Γ_{ij}^{ss-ss} prevails over Γ_{ij}^{ss-me}. Figure 9, curve 1 depicts the total damping of spin waves Γ_{ij}^{ss}. An anomaly is observed in the vicinity of the point of the magnetic phase transition at $T < T_N$. Thus, we expect to observe an anomaly in the in the width of the spectral line in the Raman spectra of the BFO.

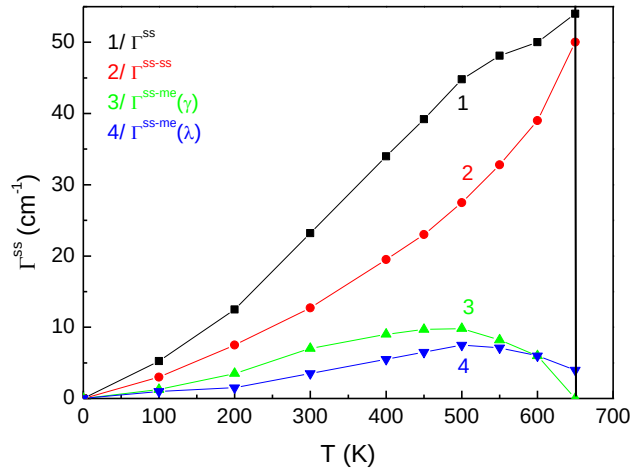


Figure 9. Temperature dependence of the damping of spin excitations and its components as 1/ Γ_{ij}^{ss} (the total damping); 2/ Γ_{ij}^{ss-ss}; 3/ $\Gamma_{ij}^{ss-me}(\gamma)$ and 4/ $\Gamma_{ij}^{ss-me}(\lambda^*)$.

IV. CONCLUSION

This paper calculates the spectrum of elementary excitations for BFO on the base of two types of ME interactions in a wide temperature range. The theoretical calculations used are temperature-dependent retarded Green's functions and Tyablikov's procedure for splitting of the higher Green's functions. The Ising model in a transverse field for pseudo-spin S = 7/2 has been applied, for the first time. ME interaction between the magnetic and ferroelectric subsystems are described with quadric terms in regards to spin and pseudo-spin operators $-\gamma\sum_{ij}(\vec{P})^2(\vec{B}_i.\vec{B}_j) - \gamma'\sum_{ij}(\vec{P})^2(\vec{B}_i.\vec{B}_j)$ and antisymmetric term, describing induced DM interaction by polar shifts in Bi ions with respect to Fe ions: $-\lambda^*\sum_{ijalongx'}(\vec{P}\times\vec{e}_{ij}).(\vec{B}_i\times\vec{B}_j)$. It was found that ME interactions renormalized elementary excitations in multiferroic phase. Below the T_N, with increasing γ, the energy of the ferroelectric excitation increases. At the point of phase transition "positive kink" in the ferroelectric mode is observed. On the contrary, with an increase in the value of λ*, the energy of the ferroelectric excitation decreases and a "negative kink" to pseudo-spin mode is observed at T_N. In BFO the multiferroic properties due to induced DM interactions and magnetostriction below T_N are a result of the spontaneous polarization. In our opinion, this can be used for a new definition of multiferroics from I-type. When an external magnetic field is applied, the mechanisms of ME interactions appear to be in competition. According to the orientation of the external magnetic field with respect to the direction of the spontaneous polarization a hardening or softening of the ferroelectric mode is observed.

The damping of elementary excitations in BFO is calculated, for the first time. The obtained expressions are in analytical form and are suitable for numerical calculations. The influence of ME interactions on the damping of spin and pseudo-spin excitations is discussed. In the vicinity of the magnetic phase transition, there appears to be an anomaly in the damping of ferroelectric and magnetic excitations. It has been shown that the anomalies in widths of Raman lines in BFO are a result of ME interaction. Our results are in a quality agreement with the published experimental data.

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