

Vibronic Magnetolectric Effects in the Bi-Based Multiferroics

P. KONSIN* AND B. SORKIN

Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

The detailed magneto-electron-lattice (vibronic) theory of ferroelectricity in the Bi-based multiferroics (BiFeO₃ etc.) is developed further. The vibronic admixture of the empty oxygen 2*p* states to the Bi 6*s* lone electron pair state leads to ferroelectricity. These interactions are the driving and restoring forces of the structural phase transformations of the Bi-based multiferroics. The free energy of the BiFeO₃-type multiferroics with the ferroelectric and the *G*-type antiferromagnetic phase transitions are derived. The Zeeman splitting and spin-transversal optical phonon couplings are also important.

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1. Introduction

Multiferroics are multifunctional materials, in which two or more order parameters (ferroelectric, ferro(antiferro) magnetic and ferroelastic) coexist in a single compound [1–5]. The vibronic theory of ferroelectric displacive phase transitions with an order-disorder component in the BaTiO₃-type perovskite oxides is developed, see [6–8]. In [9] a vibronic approach is proposed for explaining of ferroelectric properties of the Bi-based multiferroics.

In this contribution we take into account vibronic and magnetic couplings in the BiFeO₃-type multiferroics. Magnetism and ferroelectricity are involved with local spins (Fe, Mn) and off-center structural distortions (Bi), respectively [1–5, 9]. We obtained the free energy of the Bi-based multiferroics in external electric and magnetic fields. On the base of this free energy the magnetolectric effects can be studied in this type material.

2. Free energy

Using the results of the papers [9, 10] we obtained the free energy of the BiFeO₃-type multiferroics

$$F = F_e + F_m, \quad (1)$$

where F_e is the density of the free energy of the ferroelectric subsystem and F_m is the free energy of the magnetic subsystem including direct magnetolectric couplings [10].

In comparison with [9] in [11] and in this paper all actual vibronic couplings, including the electron-lattice vertex corrections and phonon-phonon couplings are taken into account. The influence of the magnetic field \mathbf{H} on the electronic states is considered. We have

$$F_e = F_0 + \left[\frac{1}{N} V^2 (\alpha_1 + \alpha_2 \Delta) + \frac{M \bar{\omega}_0^2}{2} \right] (x^2 + y^2) + \left[(\alpha_1 + \alpha_2 \Delta) \frac{(V^2 + V_\beta^2)}{N} + \frac{M \bar{\omega}_0^2}{2} + \frac{1}{2} k_{0\beta} \right] z^2$$

$$+ \left[(\beta_1 + \beta_2 \Delta) \frac{(V^2 + V_\beta^2)^2}{N^2} \right] z^4 - \frac{e_\beta^\perp}{\sqrt{N}} \eta_\perp E_\perp - \frac{Q^*}{\sqrt{N}} z E_\parallel - V^2 \frac{(\mu_B H)^2 \kappa_{1,2}}{2 \Delta^3} (x^2 + y^2) - (V^2 + V_\beta^2) \frac{(\mu_B H)^2 \kappa_{1,2}}{2 \Delta^3} z^2. \quad (2)$$

The vibronic coupling constants

$$V = \left\langle \psi(^1A'_1(\text{Bi } 6s^2)) \left| \frac{\delta H}{\delta x} \right| \psi(p_x(\text{O})) \right\rangle$$

and

$$V_\beta = \left\langle \psi(^1A'_1(\text{Bi } 6s^2)) \left| \frac{\delta H}{\delta \tau_\beta} \right| \psi(R_{15}(\text{O})) \right\rangle.$$

The quantity $\tau_\beta \approx z$ [9] and x, y, z are the Cartesian coordinates, N is the number of unit cells, Δ is the averaged gap between the bands. The coefficients: $\alpha_1 = \alpha_{10} f_s \frac{N_0}{\Delta}$, $\alpha_2 = \alpha_{20} f_s \frac{N_0}{\Delta^2}$, $\beta_1 = \beta_{10} f_s \frac{N_0}{\Delta^3}$ and $\beta_2 = \beta_{20} f_s \frac{N_0}{\Delta^4}$ (N_0 is the number of electrons in the bands). The calculated in [9] coefficients are the following: $\alpha_{10} = -0.4131$, $\alpha_{20} = -0.6498$, $\beta_{10} = 17.6455$ and $\beta_{20} = -10.29$. The quantity $\bar{\omega}_0$ is the frequency of the potential optical vibrations with the wave vector $\mathbf{q} = 0$ renormalized by the phonon-phonon couplings and the contribution from higher order electron-phonon interactions (i.e., vertex corrections)

$$M \bar{\omega}_0^2 = M \omega_0^2 + 12 \sum_{\mathbf{q}} \sum_{i=1,2} \frac{B \begin{pmatrix} 0 & 0 & \mathbf{q} & -\mathbf{q} \\ 1 & 1 & i & i \end{pmatrix}}{M_i \omega_{i\mathbf{q}}^2} \left(n_{i\mathbf{q}} + \frac{1}{2} \right) + M^{-1} \frac{V^4}{\Delta^3} \sum_{\mathbf{q}} \frac{\hbar}{\omega_{\mathbf{q}}} \coth \frac{\hbar \omega_{\mathbf{q}}}{k_B T} + \frac{V_\beta^4}{\kappa_{0\beta} \Delta^3} k_B T. \quad (3)$$

Here, M is the mass factor, the index 1 belongs to the transversal optical (TO) and 2 to the transversal acoustic (TA) branches, B corresponds to the 4th order anharmonicity (renormalized in respect of the 3rd order one), $\kappa_{0\beta}$ is the corresponding force constant, ω_0 is the bare phonon frequency of the active long wave transverse optical vibration. The g -factors corresponding to the Zeeman

*corresponding author; e-mail: konsin@fi.tartu.ee

man effect in Eq. (2) for the valence band are g_v and the conduction band $g_c^{(1,2,3)}$.

Here [11]:

$$\begin{aligned} \kappa_1 = \kappa_2 = & \frac{1}{2}(g_c^{(1)} - g_v)^2 + \frac{1}{6}(g_c^{(2)} - g_v)^2 \\ & + + 2t^2 - \frac{4}{\sqrt{18}}t [g_c^{(2)} + g_c^{(3)} + 2g_v]. \end{aligned} \quad (4)$$

The dynamic Born effective charge, Q^* equals [9, 11]:

$$Q^* = Q + \Delta Q \frac{a_0 \sqrt{N}}{z_0}. \quad (5)$$

Here, a_0 is the cell constant, Q is the ionic charge and $\frac{z_0}{\sqrt{N}}$ is the ionic displacement (Bi^{3+}). We obtained in [11]:

$$\Delta Q = \frac{2|e|}{N} \sum_{\mathbf{k}} \frac{V(\mathbf{k}) \frac{z_0}{\sqrt{N}}}{E_p(\mathbf{k} + \mathbf{q}) - E_s(\mathbf{k})} (f_s - f_p), \quad (6)$$

where $E_{p,s}$ are the renormalized by the vibronic coupling [9] electronic spectra of the Bi $6s^2$ state and $2p$ states of O, correspondingly, f_s and f_p are the band filling numbers. The quantity in Eq. (2) $\eta_{\perp} = \sqrt{x^2 + y^2}$ and the electric fields $E_{\perp,||}$ (E_{\perp} : \mathbf{E} perpendicular to the c -axis, $E_{||}$: $\mathbf{E}||c$). A certain part of the oxygen p orbital is admixed to Bi $6s^2$ states. We have calculated for the spontaneous polarization of $BiFeO_3 P_s = 6.02 \mu C/cm^2$, close to the measured in [12]. For the $BiFeO_3$ films higher values of P_s are obtained. In $BiFeO_3$ - $PbTiO_3$ -based multiferroics-ceramics [10] significantly enhanced multiferroic properties are established. Favouring of the ferroelectric order takes place. It is supported by the vibronic coupling covalent hybridization of the Pb $6s^2$ electronic states with the oxygen $2p$ states which leads to the displacement of the equilibrium positions of the Pb ions. At this, the free energy of the ferroelectric subsystem analogous to Eq. (2) can be obtained. For attempts to understand magnetoelectric effects the free energy F_m can be used (see also [10]):

$$F_m = F_{\text{exch}} + F_L + F_{\text{an}} + F_M, \quad (7)$$

where F_{exch} is the inhomogeneous exchange energy, F_L is the magnetoelectric coupling that is linear in gradient, F_{an} is the magnetic anisotropy energy, and F_M is the magnetic energy [10]. The influence of the spin-TO phonon coupling on the magnetic properties of the Bi-based multiferroics using the Heisenberg model for anti-ferromagnetic properties can be calculated.

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