Electromagnetically controlled multiferroic thermal diode

L. Chotorlishvili, S. R. Etesami, and J. Berakdar
Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle/Saale, Germany
R. Khomeriki
Physics Department, Tbilisi State University, 0128 Tbilisi, Georgia
Jie Ren
Center for Phononics and Thermal Energy Science, School of Physics Science and Engineering, Tongji University, 200092 Shanghai, China and Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

(Received 10 March 2015; revised manuscript received 28 September 2015; published 30 October 2015)

We propose an electromagnetically tunable thermal diode based on a two-phase multiferroic composite. Analytical and full numerical calculations for a prototypical heterojunction composed of iron on barium titanate in the tetragonal phase demonstrate a strong heat rectification effect that can be controlled externally by a moderate electric field. This finding is important for thermally based information processing and sensing and can also be integrated in (spin) electronic circuits for heat management and recycling.

DOI: 10.1103/PhysRevB.92.134424 PACS number(s): 44.10.+i, 05.20.–y, 05.60.–k, 66.70.–f

I. INTRODUCTION

A diode, i.e., a device that controls the electrical current flow direction, is an integral part of everyday electronics. The sonic counterpart governs the propagation of mechanical vibrations and has wide-ranging applications in acoustics, medical sensing, and heat management. Acoustic (sound waves) diodes were recently demonstrated [1,2]. Thermal diodes are more challenging, however. Even though heat and sound are of phononic nature, the frequency range of the latter is typically in the range of kilohertz to gigahertz (hypersound). Heat, on the other hand, is mediated by a broad spectrum of terahertz vibrations. Controlling heat diodes is therefore more delicate, but on the plus side the relevant scale for material structuring is the nanometer, therefore allowing us, as shown below, to exploit the marked achievements of nanotechnology in tuning the material compositions and the associated electric, magnetic, and optical properties. Applications are diverse. For instance, in spintronics it was shown that a thermal gradient may generate a direction-dependent spin current that can be utilized for information handling [3]. Such thermal magnetic diodes would add therefore an essential element towards thermally based spintronic circuits.

Generally, substantial research has been devoted in recent years to phononic-based diodes [4–8]. Our aim here is to add a different facet, namely, the external control of thermal diodes via electric and/or magnetic fields. In view of an experimental implementation we consider a well-tested system composed of a two-phase multiferroic (MF), i.e., a ferroelectric (FE) structure interfacially coupled to a ferromagnet (FM). The interfacial coupling changes the transmission and conversion of magnetic excitations into ferroelectric ones. The thermal energy in the proposed multiferroic thermal diode is carried by elementary excitations of electric polarization and magnetization (rather than by vibrational excitation in a conventional thermal diode), both of which are susceptible to external electric or magnetic fields. As shown below, the performance of the thermal diode is then controllable electromagnetically. Multiferroics, in general, are intensively investigated in view of a variety of applications in electronics and sensing [9–18]. Thus, the current study augments these applications with the possibility of a controlled heat recycling.

II. MULTIFERROIC THERMAL DIODE

The physics of a thermal diode is a resonance phenomenon [8] relying on the overlapping of the temperature-dependent power spectra of thermal excitations (mediated by polarization, magnetization, and other types of excitations) of the two different diode segments. In addition, the dependence of frequency on the oscillation amplitude, i.e., the nonlinear nature of excitations, is a key factor. A perfect thermal conductance hints at power spectra overlapping. Our aim here is to demonstrate that thermal bias applied on the edges of a MF thermal diode generates a heat flux that can be rectified and controlled by temperature, electric field, and interface ME coupling. To this end, we assume that the FM part of the thermal diode is a normal ferromagnetic metal (e.g., Fe). As a prototypical FE we employ BaTiO3. For this experimentally realized composite an interfacial magnetoelectric coupling [14,19,20] was demonstrated. The ferroelectric dynamics of BaTiO3 is captured by the Ginzburg-Landau-Devonshire (GLD) potential [21] valid at temperatures ~280–400 K (tetragonal phase) in which case the polarization switches bidirectionally. In the spirit of a coarse-grained approach, the FE order parameter is discretized into N cells (also called sites), each with a size of 1 nm [22]. The coarse-grained polarization at site n is referred by \( p_n \). In the tetragonal phase, realized also at room temperature, we have one component (Ising-type) polarization vector \( \vec{p}_n = (0,0,p_n^z) \), \( n = 1,\ldots,N \) (here n is the site number) entering the ferroelectric free-energy functional [21]. In the context of a thermal diode an important fact is that, by applying an external electric field, the temperature range of the tetragonal phase can be extended [23,24]. Taking the general cubic paraelectric phase as a reference, we performed numerical calculations which
turned out to be in line with the experimentally determined phase diagram [23]. The result of our calculations is shown in Fig. 1. As we see by applying an electric field with an amplitude $E = 100$ MV/m, the lower limit of the tetragonal phase is reduced from $T = 280$ K to $T = 200$ K, while the upper limit of the tetragonal phase exceeds $T = 500$ K.

For FM we employ the well-established classical Heisenberg model to describe transversal excitations of the coupled (coarse-grained) magnetic moment $\vec{M}_n$ at site $n$. Experiments done for different materials [25] show the dominant role of magnons for the thermal heat conductance at relatively high temperatures $T > 20$ K. The relevance of magnons to thermal heat conductance was also confirmed by the spin Seebeck effect [26]. The multiferroic interaction between the interfacial heat conductance was also confirmed by the spin Seebeck effect [23].

\[ \frac{d E}{d t} = -\frac{1}{1 + \alpha_k} \vec{M}_k \times (\vec{B}_k^{\text{eff}} + \alpha_k \vec{M}_k \times \vec{B}_k^{*\text{eff}}). \quad (3) \]

Here $\alpha_k = \alpha \delta_{k,0}$ and $\vec{B}_k^{\text{eff}}$ are the total effective (electric polarization-dependent) magnetic field acting on the $k$th magnetic moment $k \in [N + 1, M]$, $\vec{B}_k^{*\text{eff}} = \vec{i}_k \cdot J(\vec{M}_{k-1} + \vec{M}_{k+1}) + \vec{i}_k \cdot 2 \delta_{k,0} \vec{M}_k^2$ and the contributions from exchange $J(\vec{M}_{k-1} + \vec{M}_{k+1})$ and magnetic anisotropy $\vec{i}_k \cdot 2 \delta_{k,0} \vec{M}_k^2$. Due to its interfacial nature the magnetoelectric coupling $\vec{i}_k \cdot g_1 \vec{p}_N \delta_{k,N+1} + \vec{i}_k \cdot 2 \delta_{k,N} \vec{M}_k^2$ acts only on the interfacial FM and FE cells. The random magnetic field $\vec{n}_k$ enters the dynamic of only the edge cells (thermal bias is applied at the end of the FM chain), while the heat propagation through the structure is evaluated self-consistently.

The magnetization dynamics of the FM part is governed by a set of coupled polarization-dependent LLG equations as follows:

\[ \frac{d \vec{M}_k}{d t} = \frac{1}{1 + \alpha_k} \vec{M}_k \times (\vec{B}_k^{\text{eff}} + \alpha_k \vec{M}_k \times \vec{B}_k^{*\text{eff}}). \quad (3) \]

Here $\alpha_k = \alpha \delta_{k,0}$ and $\vec{B}_k^{\text{eff}}$ are the total effective (electric polarization-dependent) magnetic field acting on the $k$th magnetic moment $k \in [N + 1, M]$, $\vec{i}_k \cdot J(\vec{M}_{k-1} + \vec{M}_{k+1}) + \vec{i}_k \cdot 2 \delta_{k,0} \vec{M}_k^2$ and the contributions from exchange $J(\vec{M}_{k-1} + \vec{M}_{k+1})$ and magnetic anisotropy $\vec{i}_k \cdot 2 \delta_{k,0} \vec{M}_k^2$. Due to its interfacial nature the magnetoelectric coupling $\vec{i}_k \cdot g_1 \vec{p}_N \delta_{k,N+1} + \vec{i}_k \cdot 2 \delta_{k,N} \vec{M}_k^2$ acts only on the interfacial FM and FE cells. The random magnetic field $\vec{n}_k$ enters the dynamic of only the edge cells (thermal bias is applied at the end of the FM chain), while the heat propagation through the structure is evaluated self-consistently. The random magnetic field $\vec{n}_k$ is quantified via the correlation function

\[ \langle n_k^i(t) n_k^j(t') \rangle = 2 \alpha_k T_k \delta_{ij} \delta(t - t'). \quad (5) \]

Here $j$ and $d$ define the Cartesian components of the random magnetic field, $k$ numbers the cell, and $T_k$ is the cell-dependent local temperature. $\alpha_k$ is the dimensionless Gilbert damping constant. Values of the FM and FE parameters used in the calculations are given in Table I in the Appendix. Following the continuity equation for the local energy and the equipartition theorem, the heat current and the temperature profile can be evaluated self-consistently [8]. In particular, the expression for the heat current in the FE part reads

\[ J_{k}^h = -(p_k (p_{k+1} - p_k)). \]

The time derivative of the polarization $p_k$ plays the role of a canonical momentum. In the FE part the local (site-dependent) temperature follows from its relation to the average

\[ J_{k}^h = -(p_k (p_{k+1} - p_k)). \]

The time derivative of the polarization $p_k$ plays the role of a canonical momentum. In the FE part the local (site-dependent) temperature follows from its relation to the average

\[ J_{k}^h = -(p_k (p_{k+1} - p_k)). \]
TABLE I. Parameters of an unstrained bulk BaTiO3 single crystal [30,46] and bulk bcc Fe [31].

| Parameter | SI units | Dimensional unit (d.u.) |
|-----------|----------|------------------------|
| $P_0$     | $0.265$ C/m$^2$ | $p_{in} = P_0/P_k$ |
| $\alpha_1$ | $2.770 \times 10^4$ V m/C | $\alpha_{FE}^0 = \alpha_{FM}^0 \approx 0.213$ |
| $\alpha_2$ | $1.7 \times 10^4$ Vm$^2$/C$^3$ | $\alpha_{FE} = \alpha_{FM} \approx 0.0918$ |
| $\gamma_{L}$ | $2.5 \times 10^{-3}$ V m/s | $\gamma_{L} = \frac{\gamma_{L}}{\kappa} \approx 0.192$ |
| $\alpha_{FE}$ | $1.02 \times 10^{-7}$ m | $\kappa = 1.3 \times 10^4$ V m/C |
| $E$ | (V/m) | $E \rightarrow \frac{\Delta E}{k_B T} \approx 3.4 \times 10^7 E$ |
| $T$ | (K) | $T \rightarrow \frac{\Delta T}{k_B T} \approx 1.4 \times 10^{-4} T$ |
| $J$ | joules/s | $J \rightarrow \frac{\Delta J}{k_B T} \approx 10^6 J$ |

Bulk bcc Fe

| Parameter | SI units | Dimensional unit (d.u.) |
|-----------|----------|------------------------|
| $M_5$ | $1.71 \times 10^6$ A/m | $\tilde{S}_5 = \tilde{M}_5/M_5 = (\tilde{S}_5/S)$ |
| $\gamma$ | $1.76 \times 10^{10}$ (T s)$^{-1}$ | $D = \frac{\gamma_{L} K_{FM}}{\mu_{FM}^0} = 0.206$ |
| $\alpha_{FM}$ | $1.0 \times 10^{-9}$ m | $A = \frac{\gamma_{L} K_{FM}}{\mu_{FM}^0} = 2.16$ |
| $\mu_{FM}$ | $1.71 \times 10^{-21}$ J/T | $B = \frac{\gamma_{L} K_{FM}}{\mu_{FM}^0} = 0.17B$ |
| $T$ | (K) | $T \rightarrow \frac{\Delta T}{k_B T} \approx 1.4 \times 10^{-4} T$ |
| $J$ | joules/s | $J \rightarrow \frac{\Delta J}{k_B T} \approx 10^6 J$ |

local kinetic energy [8], which in our scaled units implies $T_k = \left( \frac{2\mu_0 J_1^2}{\kappa} \right)^2$. Note that here average means the long-time average, which in numerical simulations is implemented as the ensemble average. We derive the expression for the local heat current in the FM part by using the Heisenberg equation of motion $\frac{dH_{total}}{dt} = i[H_S, H_{total}]$. Here $H_S = -J \sum \tilde{M}_k \cdot \tilde{M}_{k+1} - D \sum \nabla^2 (\tilde{M}_k^2) - B \sum \tilde{M}_k^2$ is the Hamiltonian of the system, and $H_{total} = -J \tilde{M}_k \cdot \tilde{M}_{k+1} - D (\tilde{M}_k^2)^2 - B \tilde{M}_k^2$ is the local Hamiltonian. After straightforward calculations the heat current in the FM part is obtained as

$$J_k^{FE} = \left< \frac{db_k}{dt} \right> = 2D\tilde{J}(\tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8 - \tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8) + DB(\tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8 - \tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8) - J^2(\tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8 - \tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8) - J^2(\tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8 - \tilde{M}_k^1 \tilde{M}_k^2 \tilde{M}_k^8)$

(6)

The equilibrium temperature $T_k$ is evaluated self-consistently via the relation $\tilde{M}_k^L = L(\tilde{M}_k^L \tilde{M}_k^L)$, where $L(\cdot \cdot \cdot)$ is the Langevin function and $\tilde{M}_k^L$ is the component of the magnetization vector parallel to the effective field $\tilde{B}_k^{eff}$.

III. INTERFACE EFFECT AND HEAT RECTIFICATION

An important element of the thermal diode is the interface thermal resistance (ITR), usually referred to as the asymmetric Kapitza resistance [8] as it quantifies the asymmetry in interfacial resistance. We will consider the cases in which the hot thermal bath is applied to the FE part $T_{FE} > T_{FM}$ and to the FM part $T_{FE} < T_{FM}$. Inverting the sign of the thermal bias for a constant temperature difference $\Delta T = T_{FE} - T_{FM}$ drastically changes the heat flux $J_+ \neq J_-$ and the resistance $R_+ = \Delta T/J_+$, $R_- = \Delta T/J_-$. The ratio between the two different resistances $R_+/R_-$ measures the rectification effect. The rectification effect of the MF diode stems from the overlapping of the spectra of the FE and FM subsystems. The frequency of the linear excitations in FM $\omega_{FM}$ is set by the anisotropy constant $\approx 2D$ [34]. The applied electric field substantially modifies the frequency of linear excitations in the FE part, $\omega_{FE}$. Basically, the electric field shifts the minimum of the GLD potential derived from the relation $\partial_j H_p = 0$. In the limit of weak coupling between the dipoles, FE frequency takes the form $\omega_{FE}(E) = \omega_{FE}(0) + \Delta \omega_{FE}(E) + \omega_{FM}(0)$ where $\omega_{FM}(E) = \omega_{FE}(0)$ in the even electric field (for more details we refer to the Appendix). Therefore, the current heat is symmetric with respect to the change of the electric field’s sign $E \rightarrow -E$. On the other hand, maximal heat conductance occurs when FM and FE frequencies $\omega_{FM} \approx \omega_{FE}(0) + \Delta \omega_{FM}$ match. Thus, the electric field can be utilized to enhance the heat current. From the frequency-matching condition and for the parameters listed in Table I in the Appendix, we obtain an estimation of the optimum electric field as $|E| \approx \frac{2\mu_0 J}{k_B T} \sqrt{\frac{2D J}{2\mu_0 J T_{FM} - \Delta T}}$, which in conventional units this corresponds to an electric field of $E = 3.4 \times 10^7$ V/cm. Increasing the electric field strength results in a mismatch of FE and FM spectra and hence a decrease of the heat current. This analytical estimation is confirmed by full numerical calculations as well (Fig. 3 below). Interface ME coupling leads to a small shift between analytically estimated and numerically calculated values of the optimum electric field. However, we see a prominent maximum in the heat current for optimal electric field.

IV. TEMPERATURE EFFECTS ON MF DIODE

We implemented full numerical simulations for a MF thermal diode consisting of 50 dipolar and 50 magnetic cells. Calculations are also done for a larger system (not shown) up to 500 dipolar and 500 magnetic cells, and we did not observe significant size effects. Of special interest is the rectification effect. We present the edge temperatures in the following form: $T_1 = T_0 + T_3 \Delta$, $T_{FE} = T_0 - T_3 \Delta$, where $M$ is the total number of sites. Thus, the difference between the edges temperatures is $T_1 - T_{FE} = 2T_3 \Delta$. Inverting the thermal bias simply means $\Delta \rightarrow -\Delta$. The heat current as a function of $\Delta$ for different values of $T_0$ is shown in Fig. 2(a). We observe that at larger temperature $T_0$ the asymmetry becomes stronger. The other hand, due to the different heat capacities of the FE and FM systems and the different heat exchange rates with the environment, the temperatures formed self-consistently in the FE and FM parts are different. In the case of an applied positive thermal bias the heat flux $J_+ = 0.8$ d.u., while for a negative
FIG. 2. (Color online) (a) Diode heat current under different edge temperatures. The multiferroic diode includes 50 FE cells (from 1 to 50) and 50 FM cells (from 51 to 100). In dimensional units, the applied electric and magnetic fields are $E = 1.74$ d.u. and $B = 0.0$ d.u., and FE-FM coupling coefficients are $g_1 = g_2 = -1$ d.u. Other employed parameters and reduced unit coefficients are tabulated in Table I in the Appendix. (b) Heat current profile for forward temperature bias ($\Delta = 1.4$), reverse temperature bias ($\Delta = -1.4$), and $T_0 = 400$ K. (c) Temperature profiles for forward temperature bias ($\Delta = 1.4$) and reverse temperature bias ($\Delta = -1.4$), $T_0 = 400$ K. In both cases temperature formed in the FE part corresponds to the tetragonal phase.

thermal bias the flux reaches $J = 2.5$ d.u. and therefore $R_+ / R_- < 1$. This rectification is also characterized by distinct temperature profiles for opposite thermal differences [see Fig. 2(c)].

V. ELECTRIC FIELD EFFECT ON THE MF DIODE

The heat current as a function of $\Delta$ is displayed in Fig. 3. We note that the change of the sign of $\Delta$ corresponds to the inverted thermal bias. In addition, we consider different amplitudes of the applied electric field in order to see whether an electric field may enhance the heat rectification effect. As shown in Fig. 3(a) the rectification effect becomes stronger upon increasing the electric field strength. However, the role of the electric field is not trivial. As shown in the inset, there is an optimum electric field for which the asymmetry of the diode is maximal. The optimal value $E \approx 0.75$ d.u. corresponds to the frequency-matching condition $\omega_{FM} \approx \omega_{FE}(0) + \Delta \omega_{FE}$ and is quite close to the analytical value that we estimated above without interface ME coupling. Further increasing the electric field destroys the spectra-matching condition and reduces the heat current. Magnetic field $B$, however, monotonically decreases the heat flux, as shown in Fig. 3(b). This is due to the fact that the stronger the magnetic field is, the stiffer the magnetization is in the FM part, which suppresses the energy transport.

VI. INTERFACIAL ME COUPLING EFFECTS ON THE MF DIODE

Figure 4 shows the heat current as a function of the interfacial ME coupling constant ($g = g_1 = g_2$ d.u.) for forward and reverse biases, respectively. Without magnetoelectric coupling the heat current across the MF diode diminishes. In the range of $g = [-1, 0]$ d.u. the rectifying effect is magnified monotonically when increasing $g$ from 0 to $-1$, and the maximum rectifying effect (asymmetry) is achieved at $g = -1$ d.u., which is the value we have used in all other simulations. Surprisingly, a different picture emerges in the positive range of $g = [0, 0.8]$ d.u., where a large coupling strength near 0.8 d.u. deteriorates the heat current in both directions. The optimal transport and rectification are achieved at an intermediate strength of $g$ around 0.4 d.u. This distinct response upon the sign change of the coupling constant can be traced back to the fact that such a change influences the ground state of the polarization and the magnetization configurations of the MF diode system. For a different sign of the coupling constant, slightly different configurations correspond to the
ground state with a minimal energy. For the explicit form of the interface coupling term \( V = -g(\bar{P}_n M^z) - g(\bar{P}_n M^z)^2 \) we find that the positive coupling constant \( g > 0 \) favors large values of the magnetization component \( M^z \). Aligning the magnetic moment along the \( z \) axis naturally decreases the current, which is consistent with the picture in the inset of Fig. 3(b). In the case of a negative \( g < 0 \) the situation is different. A small \( M^z \) means larger transversal components, and this enhances the current.

In summary, we proposed and demonstrated a thermal diode based on a two-phase multiferroic composite. The heat transfer through it can be rectified and controlled by a thermal bias and an electromagnetic field. In particular, the external electric field applied to the ferroelectric part of the multiferroic thermal diode can substantially enhance the heat conductance and the rectification. On the other hand, we found that an applied magnetic field decreases the heat current. We demonstrated and discussed how the interfacial magnetoelectric coupling influences the thermal diode operation in a dynamical way. In view of contemporary advances in engineering composite multiferroic structures, the present findings are potentially interesting for applications, such as elements in thermal switches and thermal memories [33] and thermal management via multifunctional caloric materials [37].

**APPENDIX**

1. Definitions of the dimensionless units

The total energy of the ferroelectric subsystem \( H_P \) as a function of the coarse-grained polarization \( P_n \) and corresponding equations of motion read \( H_P = \sum_{n=1}^{N} \frac{2}{\kappa} P_n^2 + \frac{\alpha_0^2 P_n^4}{2} - \frac{\alpha_1^2 P_n^6}{2} - E_P a \) and \( \alpha_0 \bar{P}_n = \alpha_1 P_n - \alpha_3 P_n^3 - k[\bar{P}_n - (P_n - P_{n-1})] + E_n \). These equations are normalized by introducing \( p_n = P_n / P_0, E \to E / k P_0 \). Dividing both parts by \( \kappa \) leads to the new reduced time \( t' = t \sqrt{\kappa / \alpha_0} \) or \( t' = \omega_0 t \), where \( \omega_0 = \sqrt{\frac{2}{\kappa}} \). Finally, we obtain the equation for the polarization dynamics in fully dimensionless units for \( n \neq N \) [see Eq. (1)] with \( \alpha^F = \alpha_1 / \kappa, \beta^F = \alpha_2 P_0^2 / \kappa \).

2. Time scales

The frequency of oscillations associated with the mode-plasma frequency \( \omega_{pl} \) is higher than the inverse relaxation time \( \alpha_1 / \gamma c \) [38] (see Table I). The overdamped case yields the Landau-Khalatnikov equation [39] employed for modeling the polarization hysteresis [22,38]. An overview of the real parameters and their dimensionless counterparts for the ferroelectric subsystem is given in Table I. The time scale within the present calculations is set by the frequency \( \omega_{pl} \), which is related to the mode-plasma frequency or the fast oscillations (also known as “eigendisplacements” or Slater modes [30]) of the Ti atom in BaTiO3.

3. Parameters of the FM part

For the FM part we employ the Landau-Lifshitz-Gilbert equation of motion [43,44] [see Eq. (3)]. Bulk parameters for Fe are the anisotropy strength \( K_1 \approx 5.0 \times 10^3 \text{ J/m}^3 \) given in Ref. [31] and the saturation magnetization \( M_s = 1.7 \times 10^6 \text{ A/m} \) given in Ref. [31]. The Larmor (precessional) frequency in the local anisotropy field scales as \( \omega_{pre} / (2 \pi) = \gamma K_1 / (2 M_s) \approx 8 \times 10^{12} \text{ Hz} \), and the frequency associated with the relaxation scales as \( \omega_{rel} / (2 \pi) = \alpha_3 M_0 \omega_{pre} / (2 \pi) \approx 0.08 \times 10^{12} \text{ Hz} \). The autocorrelation functions of the thermal fields in the FE and FM parts in standard units are given as \( \langle \xi_k(t) \xi_k(t') \rangle = \frac{E_{pl}}{\omega_0^2} T_k \delta(t - t') \) and \( \langle \eta_k(t) \eta_k(t') \rangle = \frac{E_{pl}}{\omega_0^2} T_k \delta(t - t') \delta(t - t') \), where \( T_k \) is the site-dependent local temperature in degrees Kelvin.

4. Shift of ferroelectric frequency

We consider one unit cell in the FE Hamiltonian: \( H_P = \frac{1}{2} \bar{P}^2 + \frac{\alpha_0^2}{2} P^4 + \frac{\alpha_1^2}{2} P^6 - E_P \). Equilibrium properties are given by the condition \( \partial H_P / \partial P_0 = 0 \). After solving the cubic equation, we obtain \( p_{10}^{(0)} = \sqrt{\frac{2}{\kappa}} \sqrt{\frac{\omega_{pl}}{\omega_0^2}} \cos \left( \frac{\theta}{2} \right), p_{10}^{(0)} = \frac{2}{\sqrt{\alpha_0}} \sqrt{\frac{\omega_{pl}}{\omega_0^2}} \cos \left( \frac{\theta}{2} + \frac{\pi}{4} \right), \) and \( p_3^{(0)} = \frac{2}{\sqrt{\alpha_0}} \sqrt{\frac{\omega_{pl}}{\omega_0^2}} \cos \left( \frac{\theta}{2} + \frac{\pi}{4} \right) \). Here \( \theta = \arccos \left( \frac{3 \sqrt{E_p}}{2 \sqrt{\omega_0^2}} \right) \), and the minimum of the energy reads \( H(p_{10}^{(0)}(E)) = -\omega_{pl}^2 / 2 \pm \sqrt{\frac{\omega_{pl}^2}{2} E} \). As we can see, if \( E > 0 \), then the minimum of the energy corresponds to the solution \( p_{10}^{(0)}(E) \), while if \( E < 0 \), then the energy minimum corresponds to the solution \( p_3^{(0)}(E) \). Taking into account the fact that the
system is even in the electric field, we express the minimum of the energy in the form valid for both the $E > 0$ and $E < 0$ cases: $H(p_1^{0,0}(E)) = -\frac{w_0^{(2)}}{4}\sqrt{\frac{3E}{2\pi n}} |E|$. In order to evaluate the dependence of the FE frequency on the electric field $E$, we expand the linearized Hamiltonian $\widetilde{p} = -(-\alpha FE + 3\beta FE p_0^2) + E$ enters the electric-field-dependent frequency: $\omega_p(E) = (-\alpha FE + 3\beta FE p_0^2)$. Considering the small electric field $E$ in the first-order approximation from $p_1^{0,1,2,3}$, we obtain

$$\omega_p(E > 0) = \sqrt{2\alpha FE + \frac{3E}{2\pi n} \sqrt{\frac{3E}{2\pi n}}}, \quad \omega_p(E < 0) = \sqrt{2\alpha FE - \frac{3E}{2\pi n} \sqrt{\frac{3E}{2\pi n}}}, \quad \omega_p(E = 0) = \sqrt{2\alpha FE}.$$
Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolichnov, A. K. Tagantsev, D. V. Taylor, and T. Yamada, J. Appl. Phys. 100, 051606 (2006); S. Sivasubramanian, A. Widom, and Y. N. Srivastava, Ferroelectrics 300, 43 (2004).

[31] J. M. D. Coey, Magnetism and Magnetic Materials (Cambridge University Press, Cambridge, 2010).

[32] A. Klümp and K. Sakai, J. Phys. A 35, 2173 (2002).

[33] J. Cheng, J. Ren, X. Moya, J. Li, J. Sun, and E. K. H. Salje, Sci. Rep. 4, 6375 (2014).

[34] L. Chotorlishvili, R. Khomeriki, A. Sukhov, S. Ruffo, and J. Berakdar, Phys. Rev. Lett. 111, 117202 (2013).

[35] S. Nambu and D. A. Sagala, Phys. Rev. B 50, 5838 (1994); E. Klotins, Ferroelectrics 370, 184 (2008).

[36] D. Viehland and Y. H. Chen, J. Appl. Phys. 88, 6696 (2000).

[37] X. Moya, S. Kar-Narayan, and N. D. Mathur, Nat. Mater. 13, 439 (2014).

[38] D. Ricinschi, C. Harnagea, C. Papusoi, V. Tura, and M. Okuyama, J. Phys. Condens. Matter 10, 477 (1998).

[39] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR 96, 469 (1954).

[40] Ph. Ghosez, E. Cockayne, U. V. Waghmare, and K. M. Rabe, Phys. Rev. B 60, 836 (1999).

[41] J. L. Servoin, F. Gervais, A. M. Quittet, and Y. Luspin, Phys. Rev. B 60, 2038 (1980).

[42] W. Cao, J. Phys. Soc. Jpn. 63, 1156 (1994).

[43] L. D. Landau and E. M. Lifshitz, Phys. Z. Sowjetunion 8, 153 (1935).

[44] T. L. Gilbert, Phys. Rev. 100, 1243 (1955); IEEE Trans. Magn. 40, 3443 (2004).

[45] J. L. Doman, D. Fiorani, and E. Tronc, Adv. Chem. Phys. 98, 283 (1997).

[46] J. Hlinka, J. Petzelt, S. Kamba, D. Noudin, and T. Ostapchuk, Phase Transitions 79, 41 (2006).