Origin of the linear term in the pseudo-spin Hamiltonian of compositionally graded ferroelectrics

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Abstract This paper is devoted to the microscopic theory of compositionally graded ferroelectrics (CGF). From a simple microscopic picture of CGF we deduce the so called transverse Ising pseudo-spin model. However the Hamiltonian used in recent papers does not contain a linear term in pseudo-spins. We show that for inhomogeneous material it is necessary to modify the Ising Hamiltonian by addition of the linear term in pseudo-spins. This linear term is equivalent to introduction of an external bias field. The influence of long-range forces is discussed.

1 Introduction

Since publishing of the pioneering work [1] many papers [2–15] have been devoted to investigation of compositionally graded ferroelectrics (CGF). One of the most interesting results of experimental observation on CGF is discovery of a new type of the pyroelectric effect. Although our main aim is to contribute to a semi-microscopic theory of CGF, we start with several

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remarks on the phenomenological approach (see brief review [7]). At the beginning it was assumed [1–3] that the properties of CGF can be explained by spatially dependence of all macroscopic quantities introduced by means of the spatially dependent stochiometric ratio c. Namely according to this supposition polarization $\mathbf{P}$ is a function of space coordinates x, y, z of the form $\mathbf{P} = \mathbf{P}(c(x, y, z))$. Similarly it was assumed that the Landau free energy density expansion appropriate for CGF differs from the homogeneous case only by the spatial dependence of the coefficients. But from the point of symmetry consideration it is clear that such modification of the free energy is not sufficient when gradient of c (or of the others fields such as temperature or deformation) is present. Indeed, it is necessary to change the classical Landau expansion of the free energy density by adding the term, which perturbs the centrosymmetric symmetry (that means the transformation $\mathbf{P} \to -\mathbf{P}$). It can be done by introducing the term $\gamma \mathbf{P} \cdot \mathbf{grad} c$ [5, 6, 11] to the volume part of the free energy density. Although the magnitude of this term can be small its influence can be important because due to this term one of the possible polarization direction is preferred. The magnitude of γ was estimated in [14].

The basic aim of this paper is to extend the existing microscopic theory of CGF proposed in Gao et al. [12] and Cao et al. [13], where the pseudospin transverse Ising model was considered. The authors supposed that the inhomogeneous ferroelectrics ($\mathbf{grad} c \neq 0$) can be described by an assumption that the spin-spin interaction coefficient varies along one direction. However, it was shown in [14] that this assumption is not sufficient and a new linear term in pseudospins should be introduced in the pseudospin Hamiltonian. It turns out that this term is proportional to the gradient of

concentration. The compositional gradient plays analogical role as the electric force.

The present paper improves our previous work [14] in these points: (a) long-range forces are considered, (b) free boundary conditions are used, and (c) the origin of the fourth order interaction term in Hamiltonian of the free (non-clamped) crystal is clarified.

Considering the sample of finite thickness, the spatial dependence of polarization (at given temperature and **grad**c) is derived within the framework of mean-field theory. We have divided the next section into two parts: in the first part we consider a clamped crystal where fourth order interaction term is not taken into account; in the second part a free crystal is considered.

2 Microscopic model

2.1 Clamped crystal

We are going to extend the single-ion model of a diatomic crystal that is described for example in Strukov and Levanyuk [16]. In this model the cubic lattice is considered and the displacements of ions in a double-well potential are investigated. These ions interact with themselves by a harmonic force. For the clamped crystal the rigid lattice should be considered. Although this model is very simple, it allows to describe qualitatively the main ferroelectric properties.

Our aim is to study the sample which is inhomogeneous in the direction z. Homogenous layers perpendicular to the axis z are labelled by a discrete index ζ. The layer is characterised by the stochiometric ration c_ζ only. The two-minimum potential is expressed as the power series in the displacements $u_{i\zeta}$ where index i denotes i-th ion inside the layer ζ.

For description of an inhomogeneous system we suppose that coefficients of our Hamiltonian are functions of the stochiometric ratio c_ζ only [13], hence they also depend on the layer number ζ. The lattice constant a also depends only on the ζ. The Hamiltonian describing our model is

$$H_M = \sum_{\zeta,i} -\frac{A_\zeta}{2} u_{i\zeta}^2 + \frac{B_\zeta}{4} u_{i\zeta}^4$$
$$+ \frac{1}{2} \sum_{\zeta,\zeta',i,j} k_{\zeta\zeta'}(u_{i\zeta} - u_{j\zeta'} - \Delta a_{\zeta\zeta'})^2 \quad (1)$$

where $A_\zeta > 0$ and $B_\zeta > 0$ are single-site constants of the double-well potential, $k_{\zeta\zeta'}$ are elastic constants, which couple the nearest neighbour cells by the harmonic interaction. The change of the lattice constant is introduced as $\Delta a_{\zeta\zeta'} = 1/2(\Delta a_\zeta + \Delta a_{\zeta'})$, $\Delta a_\zeta = a_\zeta - a_0$,

where a_0 is the lattice constant in the first layer. The similar variation of the lattice constant was used in the work [17] where it originates from inhomogeneous deformation. The sum is taken over the nearest neighbour pairs.

The double-well model can be approximated by an appropriate pseudospin model. For that, displacements of the ions are expressed as

$$u_{i\zeta} = b_\zeta 2 s_{i\zeta}^z + y_{i\zeta} \quad (2)$$

where s_ζ^z are pseudo-spin variables with values $\pm 1/2$ and $\pm b_\zeta$ are the positions of the minima of the symmetrical single-site potential; $b_\zeta \equiv (A_\zeta/B_\zeta)^{1/2}$. Local deviations from the minima y_ζ are further neglected.

Substituting Eq. 2 into Eq. 1 and omitting all constant terms we obtain the modified Hamiltonian Eq. 1 in terms of the pseudospin variables, which consists of two parts, $H_M = H_2 + H_L$.

The double-spin interaction part H_2 is

$$H_2 = -\sum_{\zeta,\zeta',i,j} J_{\zeta\zeta'} s_{i\zeta}^z s_{j\zeta}^z, \quad (3)$$

where

$$J_{\zeta\zeta'} \equiv 4k_{\zeta\zeta'} b_\zeta b_{\zeta'} \quad (4)$$

are double-spin interaction coupling constants. The linear term H_L appears due to the change of the lattice constant:

$$H_L = -\sum_{\zeta,\zeta',i,j} k_{\zeta\zeta'} \left(2s_{i\zeta}^z b_\zeta - 2s_{j\zeta'}^z b_{\zeta'} \right) \Delta a_{\zeta\zeta'}. \quad (5)$$

For the quantum system the pseudospin variables $s_{i\zeta}^z$ are replaced with pseudospin operators $s_{i\zeta}^z$ with eigenvalues $\pm 1/2$ and the tunnelling term

$$H_\Omega = -\sum_{\zeta,i} \Omega_\zeta s_{i\zeta}^x \quad (6)$$

should be added to the Hamiltonian. The operator $s_{i\zeta}^x$ plays the role of the tunnelling operator through the barrier and Ω_ζ is the tunnelling frequency.

2.2 Free crystal

For the free crystal we must take into account the elastic energy and the coupling of pseudospins with elastic modes. It will finally lead to the multispin interaction. For this purpose the elastic energy is introduced in the form $\sim K_{\alpha\beta}(x_{i\zeta}^\alpha - x_{j\zeta'}^\beta - a)^2$ and the pseudospin-phonon interaction term can be obtained assuming dependence of the coupling constant $k_{\zeta\zeta'}$ on the lattice constant. For one-dimensional case we consider replacement $k_{\zeta\zeta'} \to k_{\zeta\zeta'} + k'_{\zeta\zeta'}(x_{i\zeta} - x_{j\zeta'} - a)$, where $k_{\zeta\zeta'}$ and $k'_{\zeta\zeta'}$ are constants and $x_{i\zeta}$ are coordinates of lattice

sites. In the original Hamiltonian Eq. 1 the additional term H' appears:

$$H' = \frac{K}{2} \sum_{i\zeta \, j\zeta'} (x_{i\zeta} - x_{j\zeta'} - a)^2$$

$$+ \sum_{i\zeta \, j\zeta'} k'_{\zeta\zeta'} (x_{i\zeta} - x_{j\zeta'} - a)(u_{i\zeta} - u_{j\zeta'} + \Delta a_{\zeta\zeta'})^2. \quad (7)$$

Completing the square with regard to the coordinate $x_{i\zeta}$ we obtain a new term of the 4th order in $u_{i\zeta}$

$$H_4 = \sum_{\zeta\zeta'} \frac{k'^2_{\zeta\zeta'}}{2K} (u_{i\zeta} u_{j\zeta'})^2 \quad (8)$$

and the term corresponding to the modified elastic energy. The latter represents the harmonic contribution to the free energy and can be integrated out over $x_{i\zeta}$ in the partition sum so we need not to keep it in our Hamiltonian. In general three dimensional case [18] the interaction term H_4 is the sum of $u_{i\zeta} u_{j\zeta} u_{k\zeta'} u_{l\zeta'}$ over all such distinct indices i, j, k, l that set out square-facets of elementary lattice cubes. We can write H_4 in the form

$$H_4 = -\sum_{\zeta\zeta'} \sum_{<i,j,k,l>} J^{\zeta\zeta'}_{ijkl} s^z_{i\zeta} s^z_{j\zeta} s^z_{k\zeta'} s^z_{l\zeta'}. \quad (9)$$

where $J^{\zeta\zeta'}_{ijkl}$ are four-spin interaction coupling constants and sum run over only distinct round-a-plaquette spins. For simplicity, these coupling constants will be further expressed through double-spin coupling constants, i.e. $J_{ijkl} = \beta J_{ij}$, where β is a positive nonzero parameter when elastic coupling is considered. This interaction is responsible for the first order phase transition of the pure BaTiO$_3$ crystal.

The complete Hamiltonian H that will be used in our calculations is given by relation

$$H = H_M + H_\Omega + H_4 - \sum_\zeta P(\zeta) E(\zeta) \quad (10)$$

where the last term represents the electrostatic energy of dipoles in the inhomogeneous electric field $E(\zeta)$. It is considered in order to account for depolarising field effects which will be introduced afterwards. H_4 is zero in the case of the clamped crystal.

3 Meanfield approximation

Within the mean-field approximation the pseudospins $s_{i\zeta}$ are expressed as $s_{i\zeta} = m_\zeta + \delta s_{i\zeta}$ where $m_\zeta \equiv \langle s_{i\zeta} \rangle$ represents a mean value of pseudospin in the ζ layer, and interactions of fluctuations are neglected;

$(\delta s_\zeta)^2 \sim 0$. The linear term H_L can be expressed in compact form

$$H_L = -\sum_\zeta k_{\zeta\zeta+1} (2m_\zeta b_\zeta - 2m_{\zeta+1} b_{\zeta+1}) \Delta a_{\zeta\zeta+1} \quad (11)$$

or it can be rewritten as

$$H_L = -\sum_\zeta \left(k_{\zeta\zeta+1} \Delta a_{\zeta\zeta+1} - k_{\zeta\zeta-1} \Delta a_{\zeta\zeta-1} \right) 2m_\zeta b_\zeta. \quad (12)$$

Further we investigate composition of Ba$_c$Sr$_{1-c}$TiO$_3$ (BST). Firstly we express all intra-layer quantities through the stochiometric ratio c_ζ. In real samples the linear dependence of the stochiometric ratio c_ζ on the ζ-coordinate is realised. Then grad$c$ (grad$c \equiv dc/dz$) is constant in the whole sample (grad$c \cong (c_\zeta - c_0)/(\zeta a_0)$; $a_0 = a_{\zeta=0}$). According to the linear Vegard law [12] the dependence of the lattice constant a_ζ on the stochiometric ratio c_ζ is $a_\zeta = a_{Sr} + c_\zeta \alpha$ where in the first approximation $\alpha = 0.1$Å. So we can write down the dependence of Δa_ζ on the coordinate number ζ

$$\Delta a_\zeta = a_{Sr} + c_\zeta \alpha - a_0 \cong a_0 \alpha \text{grad}c \cdot \zeta. \quad (13)$$

Within linear approximation the coefficients $J_{\zeta\zeta'}$ and b_ζ are:

$$J_{\zeta\zeta} = c_\zeta J_{Ba} + (1 - c_\zeta) J_{Sr} \quad (14)$$

$$b_\zeta = c_\zeta b_{Ba} + (1 - c_\zeta) b_{Sr} \quad (15)$$

and similarly for $k_{\zeta\zeta}$ and Ω_ζ. For inter-layer interaction $J_{\zeta\zeta+1}$ we use arithmetic average value: $J_{\zeta\zeta+1} = 1/2(J_{\zeta\zeta} + J_{\zeta+1,\zeta+1})$ (and in the same way for $k_{\zeta\zeta+1}$). The change of the lattice constant between two adjacent layers $\Delta a_{\zeta\zeta+1}$ is approximated by

$$\Delta a_{\zeta\zeta+1} = \Delta a_\zeta + \frac{1}{2} a_0 (\text{grad}c) \alpha. \quad (16)$$

Substituting these relations into H_L Eq. 12 we obtain (up to the first order of grad$c$):

$$H_L = -a_0 \text{grad}c \sum_\zeta \left(\Delta a_\zeta \delta k + k_{\zeta\zeta} \alpha \right) 2m_\zeta b_\zeta$$

$$= -\sum_\zeta E_L(\zeta) 2m_\zeta b_\zeta e \quad (17)$$

where $\delta k = k_{Ba} - k_{Sr}$ and a new space dependent effective electric field is introduced

$$E_L(\zeta) = - \left(2c_\zeta \delta k + (k_{Sr} - c_0 \delta k) \right) \frac{\alpha}{e} a_0 \text{grad}c. \quad (18)$$

Here e means an effective charge that sets up an effective local dipole moment eb_ζ. The thermodynamic mean value of the local dipole moment is given by
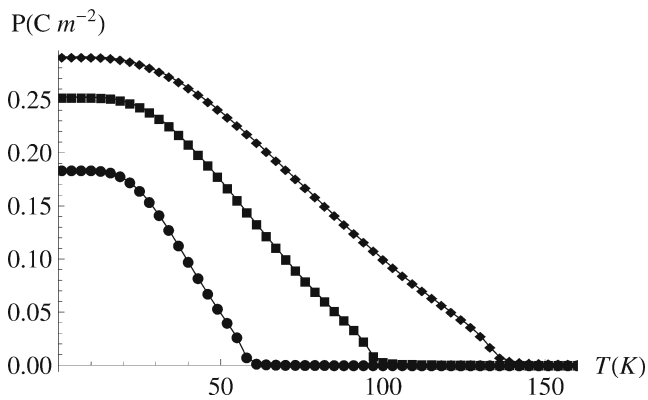
P(C m^{-2})

Fig. 1 The dependence of overall mean polarization on the temperature without long-range forces considered. The initial concentration of Ba is constant $c(1) = 0$ and final concentrations $c(10)$ are different: $c(10) = 0.1$ (*circles*), 0.2 (*squares*), 0.3 (*diamonds*); (ST → BST)

ΔP(C m^{-2})

Fig. 3 The temperature dependence of the contribution ΔP of the linear term H_L to overall mean polarization without long-range forces considered. The initial concentration of Ba is constant $c(1) = 0$ and final concentrations $c(10)$ are different: $c(10) = 0.1$ (*circles*), 0.2 (*squares*), 0.3 (*diamonds*); (ST → BST)

$m_\zeta 2eb_\zeta$. The mean-field equation for the mean value m_ζ in the ζ layer is given as

$$m_\zeta = \frac{L_\zeta}{2\sqrt{\Omega_\zeta^2 + L_\zeta^2}} \tanh \frac{1}{2k_B T}\sqrt{\Omega_\zeta^2 + L_\zeta^2} \qquad (19)$$

where

$$\begin{aligned} L_\zeta &\equiv 4J_\zeta m_\zeta + J_{\zeta\zeta+1}m_{\zeta+1} + J_{\zeta\zeta-1}m_{\zeta-1} + \\ &+ 4\beta\left(J_\zeta m_\zeta^3 + J_{\zeta\zeta+1}m_\zeta m_{\zeta+1}^2 + J_{\zeta\zeta-1}m_\zeta m_{\zeta-1}^2\right) \\ &- (E_L(\zeta) + E(\zeta))2b_\zeta e. \end{aligned} \qquad (20)$$

Mean polarization in the layer ζ is given by the density of the thermodynamically averaged effective local dipole moment eb_ζ

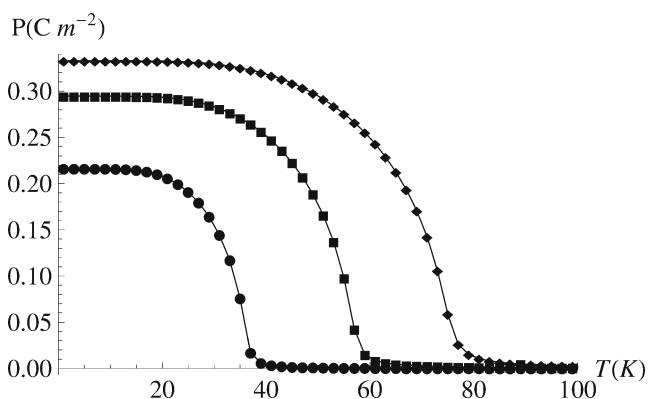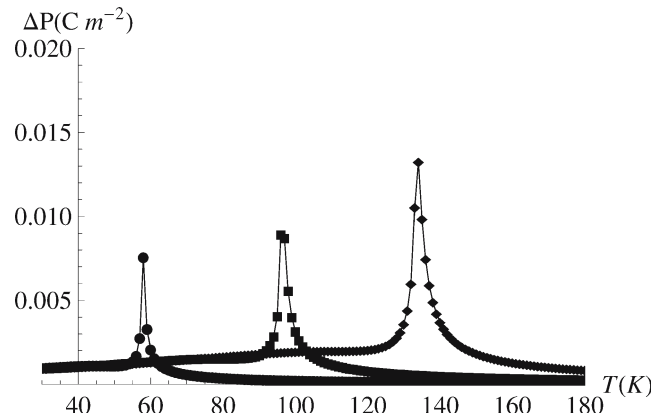$$P(\zeta) \equiv \frac{2m_\zeta eb_\zeta}{v_c(\zeta)} \qquad (21)$$

where v_c is the volume of the elementary cell which also varies with the stochiometric ratio. The overall mean polarization $\bar{P}$ is the average of $P(\zeta)$ over the layers:

$$\bar{P} = \frac{1}{N}\sum P(\zeta). \qquad (22)$$

Since polarization is inhomogeneous bound electric charges exist in the sample and the long-range electric forces should be also taken into account. From the macroscopic theory of electrostatics follows [11] that the electric field in the ζ-layer can be expressed as

$$E(\zeta) = E_0 - \frac{1}{\epsilon_0}(P(\zeta) - \bar{P}), \qquad (23)$$

where E_0 is an external electric field. Equation 23 should be substituted into Eq. 20. Further the short-circuited sample is considered, then $E_0 = 0$.
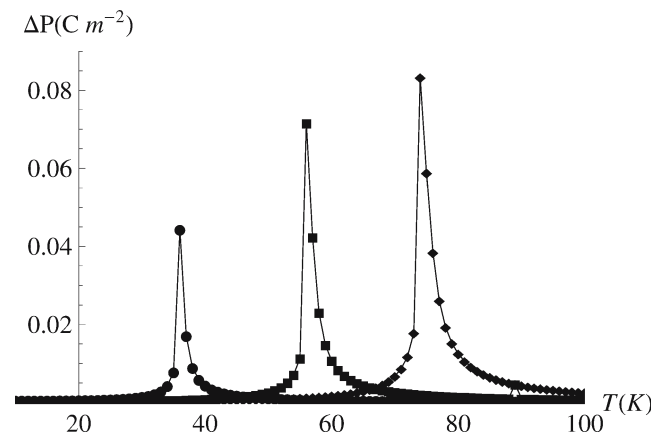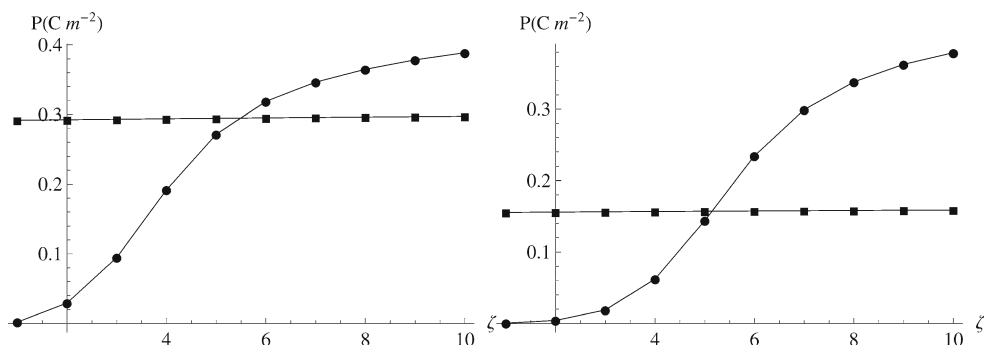
P(C m^{-2})

Fig. 2 The same parameters as in Fig. 1, but with long-range forces considered

ΔP(C m^{-2})

Fig. 4 The same parameters as in Fig. 3, but with long-range forces considered

Fig. 5 The dependence of mean polarization on the space coordinate ζ considering long-range forces (*squares*) and without long-range forces (*circles*). The *left picture* is for $T_1 = 50K$ and the *right one* is for $T_2 = 70K$; concetration gradient is in both the same: c(1)=0 and c(10)=0.3

For numerical calculations we use the free boundary condition in the form $m_0 = 2m_1 - m_2$ and $m_{N+1} = 2m_N - m_{N-1}$ contrary to our previous work [14] where the fixed boundary conditions were used.

4 Numerical results

The numerical calculations are made for ten layers, $N = 10$. We used the following values of parameters for pure BaTiO$_3$: $J_1 = 38.3 \times 10^{-22}$ J, $\beta = 0.9$, $eb_1 = 2.17e$ Å, $\Omega_1 = 4.9 \times 10^{-21}$ J, and for pure SrTiO$_3$: $J_2 = 3.26 \times 10^{-22}$ J, $eb_2 = 1.51e$ Å, $\Omega_2 = 1.1 \times 10^{-21}$ J, which were obtained from the fitting of experimental results [12].

In Figs. 1 and 2 the temperature dependence of the overall mean polarization is shown. The stochiometric ratio of Ba linearly increase from $c(1) = 0$ in the first layer up to the values 0.1, 0.2 and 0.3 in the last layer (here $c(10)$, i.e. in the 10th layer). It corresponds to 3 different grad$c$. In Fig. 2 contrary to Fig. 1 the long-range forces are considered.

The part of polarization which is induced by the gradient term, we will denote it by ΔP, is depicted in Figs. 3 and 4. In Fig. 3 the contribution ΔP of overall polarization without considering long-range forces (as in [14]) is shown. The corrections due to the long-range forces essentially change the previous result as can be seen from comparison of Fig. 3 with Fig. 4, where the long-range forces are considered. As it is expected the transition temperature is decreased. On the other hand the magnitude of ΔP is more pronounced when long-range forces are taken into account. According to our theory ΔP depends on the temperature via the susceptibility χ only. It means that graphs in Figs. 3 and 4 show the temperature dependence of the susceptibility χ. The sharp maximum in dependence of susceptibility on temperature is typical for the phase transition of thick sample. Smearing of the phase transition known in films [11] is a result of specific properties of the sample surface, which is not considered in this investigation. Though our calculation has been performed for

small number of layers our results describe rather the behaviour of thick sample than thin film.

In Fig. 5 the profile of mean polarization $P(z)$ through sample is shown for two different temperatures below the phase transition ($T_1 = 50K$—the left picture, $T_2 = 70K$—the right picture) for particular initial stochiometric ratio $c(1) = 0$ and final stochiometric ratio $c(10) = 0.3$. The stochiometric ratio increase along the z direction; ST $\rightarrow$ BST. There are two cases plotted: the first case with long-range forces considered is marked by squares and the second one without long-range forces is marked by circles.

5 Conclusion

The Ising type Hamiltonian describing the CGF was derived from the simple microscopic model and the origin of fourth order term was clarified. In contrast to the assumption given in Gao et al. [12] and Cao et al. [13], the Hamiltonian describing CGF involves the term that is linear in both pseudospins and **grad**c. Using the mean-field approximation the dependence of polarization on space coordinate, temperature and **grad**c was derived. In addition to our previous results [14], the role of long-range electric fields was studied. It is shown that they are essential for discussed results, e.g. the polarization profile is strongly influenced by the presence of internal electric fields, see Fig. 5, and from the same cause the polarization contribution ΔP of the linear term H_L is stronger pronounced, see Figs. 3 and 4.

In this paper the specific properties of surface was not taken into account and hence our results describe better the thick sample than the thin film. But we used more appropriate free boundary conditions instead of fixed boundary conditions (as in [13, 14]) in our present numerical calculations.

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