

**Enhanced ferroelectric phase-transition temperature in perovskite-based solid solutions**V. A. Stephanovich,<sup>1,\*</sup> M. D. Glinchuk,<sup>2,†</sup> and C. A. Randall<sup>3</sup><sup>1</sup>*Opole University, Institute of Mathematics and Informatics, Opole 45-052, Poland*<sup>2</sup>*Institute for Problems of Materials Science, National Academy of Science of Ukraine, Krjijanovskogo 3, 03142 Kiev, Ukraine*<sup>3</sup>*The Pennsylvania State University, 144 Materials Research Laboratory Building, University Park, Pennsylvania 16802, USA*

(Received 6 May 2004; published 5 October 2004)

We explain how the phenomena of ferroelectric phase transition temperature  $T_c$  enhancement beyond the end members in perovskite solid solution such as  $\text{BiMO}_3\text{-PbTiO}_3$  ( $M=\text{Sc, In, etc.}$ ) is related to nonlinear and spatial correlation effects. The explanation is based on the calculation of  $T_c$  in the framework of our random field theory with additional account for nonlinear effects in the above substances. We show that the maximum of  $T_c$  for certain  $\text{PbTiO}_3$  content takes place when coefficient of nonlinearity is positive, the value of this coefficient is found from best fit between theory and experiment. This nonlinearity coefficient is the only adjustable parameter of the theory. We show that enhancement of positive nonlinearity coefficients enhances greatly the  $T_c$  maximum over its value for end members. The theory lays the foundation to calculate not only  $T_c$  for above solid solutions but virtually any equilibrium and/or nonequilibrium thermodynamic characteristics such as static and dynamic dielectric susceptibility, specific heat, etc., as a function of  $\text{PbTiO}_3$  content, temperature, electric field, and other external parameters.

DOI: 10.1103/PhysRevB.70.134101

PACS number(s): 77.80.Bh, 77.84.Lf, 77.84.Dy

**I. INTRODUCTION**

Over the last few years considerable effort has been spared to synthesize the dielectric materials with controllable properties for many technical applications. The most promising substances are believed to be compound materials consisting of solid solutions of different combinations of ferroelectrics with different dielectric properties. One of the examples is a perovskite solid solutions such as  $\text{BiMO}_3\text{-PbTiO}_3$  ( $M=\text{Sc, In, etc.}$ ), which have high ferroelectric phase transition temperatures  $T_c$  at the morphotropic phase boundaries with enhancement beyond the end members. Such materials can be used as the materials with excellent high-temperature piezoelectric properties.<sup>1-6</sup>

A common feature of the above solid solutions is the existence of numerous random fields sources due to substitutional disorder, unavoidable impurities, vacancies in anion and cation sublattices, etc. These random fields play a crucial role in the properties of disordered ferroelectric and magnetic materials (see, e.g., Refs. 7-9) and the above substances in particular. This means that observable physical properties of the above systems depend strongly on the form of the random field distribution function. Namely, the relation between the width of the distribution function (the dispersion of random fields) and its first moment (mean value of random field) generates all observable features of the phase diagram of a disordered dielectric and/or magnetic materials, i.e., realization of the ferroelectric (ferromagnetic in the case of magnetic materials) dipole (spin) glass, and mixed ferroglass phases. Also, a so-called paraglass (Griffiths) phase may occur in disordered dielectrics (see, e.g., Ref. 10).

On the other hand, both ordered and disordered dielectrics have intrinsic nonlinearities, consisting of, e.g., dielectric hysteresis. The “interaction” between these nonlinearities

and random fields lead to their renormalization so that the distribution function of random fields will also include a nonlinear contribution of random fields. Such calculation had been carried out in a different context in Ref. 11.

The calculations in Ref. 11 incorporate a self-consistent dependence of distribution function of random fields on the third order nonlinearity coefficient  $\alpha_3$ . It has been shown that when the nonlinear coefficient is sufficiently large and positive, the results are strongly different than those in the linear case.<sup>7</sup> In particular, for  $\alpha_3 > 0$ , the phase transition temperature exceeds its mean field asymptotic value, while for  $\alpha_3 < 0$  the results are qualitatively the same as in the linear case. As we found out earlier, this phenomenon is due to the “generation of order by disorder” (or more precisely, a specific positive feedback generated by positive nonlinearity) taking place at  $\alpha_3 > 0$ .

**II. GENERAL FORMALISM****A. The distribution function of random fields**

Here we briefly review the main facts about the shape of distribution function of random fields with respect to nonlinear effects, a more detailed discussion can be found, e.g., in Refs. 7 and 11 for disordered dielectrics and in Refs. 12 and 13 for disordered magnetic semiconductors.

The distribution function of random field  $\vec{E}$  can be represented in the form

$$f(\vec{E}) = \overline{\langle \delta(\vec{E} - \vec{E}(\vec{r}_i)) \rangle}. \quad (1)$$

Here the overbar denotes averaging over spatial configurations of random fields sources (e.g., electric dipoles, “responsible” for emergence of ferroelectricity in the above com-

pounds),  $\langle \cdots \rangle$  means the averaging over dipoles orientations,  $\vec{E}(\vec{r}_i)$  is the internal electric field induced by electric dipoles, and other sources in the observation point  $\vec{r}_i$ . In a disordered ferroelectric this field already contains the intrinsic nonlinearity and can be written in the form (see Ref. 11 for details)

$$E_\gamma(\vec{r}_i) = \mathcal{E}_\gamma(\vec{r}_i) + \sum_{m=2}^{\infty} \alpha_m \prod_{j=1}^m \mathcal{E}_{\gamma_j}(\vec{r}_i), \quad (2)$$

where  $\gamma=x,y,z$  so that  $\mathcal{E}_\gamma$  simply denotes the  $\gamma$  component of vector  $\vec{\mathcal{E}}$ . Here  $\vec{\mathcal{E}}$  is an internal electric field induced by electric dipoles and  $\alpha_m$  is a coefficient of nonlinearity of  $m$ th order. Note that the first term in Eq. (2) can be generalized to account for other possible sources of random fields such as point charges, elastic dipoles etc.<sup>5,7,11</sup>

The calculation of the distribution function (1) with respect to Eq. (2) in the framework of statistical theory (see Refs. 14 and 15 for details of this theory) for the so-called disordered Ising model (when the dipole has only two admissible orientations) yields the following rigorous result for any electric field component  $E_\alpha \equiv E$ .<sup>16</sup>

$$f(E) = \int_{-\infty}^{\infty} f_1(E') \delta\left(E - E' - \sum_{m=2}^{\infty} \alpha_m E'^m\right) dE', \quad (3)$$

where  $f_1(E)$  is the distribution function that takes into account only the first linear term in Eq. (2) (distribution function of the first order).

A more detailed version of Eq. (3) reads

$$f(E) = \int_{-\infty}^{\infty} f_1(E') \delta\left(E - E' - \sum_{m=2}^{\infty} \alpha_m E'^m\right) dE', \quad (4)$$

$$f_1(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iEt - nF(t)} dt, \quad (5)$$

$$F(t) = \int d^3r \langle (1 - e^{-it\mathcal{E}(\vec{r})}) \rangle. \quad (6)$$

Here  $n$  and  $\mathcal{E}(\vec{r})$  are the concentration and electric field of the dipoles. Equation (5) determines the function  $f_1(E)$ , calculated earlier in Ref. 7 for the case of two-orientable electric dipoles. We note here that in general case (e.g., arbitrary interaction between the above dipoles, their arbitrary concentration, etc., see Ref. 7 and references therein for discussion) function  $f_1(E)$  has non-Gaussian form. It can be shown that for our case of compound ferroelectrics it is sufficient to use its Gaussian asymptotics, which reads

$$f_1(E) = \frac{1}{2\sqrt{\pi n B}} \exp\left[-\frac{(E - E_0 L)^2}{4nB}\right]. \quad (7)$$

Here  $L = \langle \vec{d}^* \rangle / d^*$  and  $E_0 = 4\pi(n d^{*2}) / \epsilon_0$  are the order parameter (number of coherently oriented impurity electric dipoles or dimensionless spontaneous polarization) and the mean value of random field of electric dipoles (in the energy units),

$d^* = (1/3)d\gamma(\epsilon_0 - 1)$  is the effective electric dipole moment,  $\gamma$  and  $\epsilon_0$  are, respectively, Lorentz factor and static dielectric permittivity of the host lattice, and  $n$  is the concentration of electric dipoles. Coefficient  $B$  determines the width of the distribution function (dispersion of random fields) and depends on host lattice parameters such as its correlation radius  $r_c$ , see Ref. 7 for details.

## B. The equation for long-range order parameter

In our approach, an average value  $\bar{A}$  of any physical quantity can be represented in the form

$$\bar{A} = \int_{-\infty}^{\infty} f(E) A(E) dE, \quad (8)$$

where  $f(E)$  is determined by Eq. (4) and  $A(E)$  is the above quantity for the single random field constituent, averaged over its internal degrees of freedom. In our case this is the average value over the orientations of the single electric dipole.

To calculate  $T_c$  for the disordered ferroelectric compound we need to calculate the long-range order parameter  $L$  first. In the spirit of Eq. (8) we obtain the following self-consistent equation for this parameter:

$$L = \int_{-\infty}^{\infty} f_1(E) \tanh\left[\left(E + \sum_{m=2}^{\infty} \alpha_m E^m\right) / kT\right] dE. \quad (9)$$

Here we use the fact that for two-orientable dipoles ( $l_z = \pm 1$ ,  $l_x = l_y = 0$ )  $A(E) = \langle l \rangle = \tanh(E/kT)$ ,  $E \equiv E_z$ .

The self-consistency of Eq. (9) is revealed by substitution of Eq. (7) into it, which yields

$$L = \frac{1}{2\sqrt{\pi n B}} \int_{-\infty}^{\infty} \exp\left[-\frac{(E - E_0 L)^2}{4nB}\right] \times \tanh\left[\left(E + \sum_{m=2}^{\infty} \alpha_m E^m\right) / kT\right] dE. \quad (10)$$

In the linear case ( $\alpha_m = 0$ ), Eq. (10) transforms into that derived in Ref. 7. It is seen that the order parameter is self-consistently expressed through itself and is a function of temperature, dipole concentration, and nonlinearity coefficients.

Further simplifications of Eq. (10) are possible on symmetry grounds. Namely, for the lattice with the center of inversion in paraelectric phase, the order parameter has to be an odd function of electric field, i.e.,  $m$ 's in Eq. (10) are odd numbers. Conserving only the first nonlinear term in the tanh argument, we obtain

$$L = \frac{1}{2\sqrt{\pi n B}} \int_{-\infty}^{\infty} \exp\left[-\frac{(E - E_0 L)^2}{4nB}\right] \tanh[(E + \alpha_3 E^3) / kT] dE. \quad (11)$$

It is now instructive to consider the mean field limit of Eq. (11). This limit corresponds to the case of an ordered ferroelectric, where the distribution function of random fields de-

generates into a  $\delta$  function  $\delta(E-E_0L)$ . Formally, in our method this limit corresponds to  $nr_c^3 \rightarrow \infty$ . Substitution of this  $\delta$  function into Eq. (11) gives the desired mean field equation for order parameter

$$L_{\text{MF}} = \tanh \left[ \frac{T_{\text{CMF}}}{T} (L_{\text{MF}} + \alpha_0 L_{\text{MF}}^3) \right], \quad (12)$$

where  $E_0 = kT_{\text{CMF}}$ ,  $T_{\text{CMF}}$  is the transition temperature in a mean field approximation (see below),  $\alpha_0 \equiv \alpha_3 E_0^2$  so that  $\alpha_0$  is dimensionless. We now use Eq. (11) to derive the equation for the ferroelectric phase transition temperature beyond the mean field approximation.

### C. Ferroelectric phase transition temperature

The phase transition temperature is defined as a temperature when a nonzero order parameter  $L$  appears. In other words, to get an equation for  $T_c$  from Eq. (11), we should put in it  $L \rightarrow 0$ . This is accomplished by noting that at small  $L$

$$\exp \left[ -\frac{(E-E_0L)^2}{4nB} \right] \approx e^{-E^2/4nB} \left( 1 + \frac{EE_0L}{2nB} \right). \quad (13)$$

Subsequent substitution of Eq. (13) into Eq. (11) yields after some algebra

$$\frac{\lambda}{\tau_c} \int_0^\infty \frac{(1+3\alpha_0 x^2)e^{-(\pi/4)x^2\lambda^2}}{\cosh^2 \frac{x+\alpha_0 x^3}{\tau_c}} dx = 1. \quad (14)$$

Here we introduced the following dimensionless variables:

$$\lambda = \frac{E_0}{\pi nB} \equiv \sqrt{15nr_c^3},$$

$$x = \frac{E}{E_0}, \quad \tau_c = \frac{kT_c}{E_0} \equiv \frac{T_c}{T_{\text{CMF}}}. \quad (15)$$

Equation (14) is the main theoretical result of this work. It predicts the existence of the critical concentration of dipoles

$$n_{\text{cr}} r_c^3 = \frac{\lambda_{\text{cr}}^2}{15},$$

such that for  $n < n_{\text{cr}}$ , the long-range order in the system would never be realized. Thus, the critical concentration is determined from the condition that  $\lambda = \lambda_{\text{cr}}$  at  $\tau_c = 0$ . Taking the limit  $\tau_c \rightarrow 0$  (Ref. 17) in Eq. (14), we obtain  $\lambda_{\text{cr}} = 1$ , which justifies the choice of dimensionless parameter  $\lambda$ . It is seen that the critical concentration does not depend on the coefficient of nonlinearity and it is completely the same as in linear case (see Refs. 7 and 11).

Now we demonstrate that in a mean field approximation  $\tau_{\text{CMF}} = 1$ , i.e., that  $E_0 = kT_{\text{CMF}}$ . For that we notice that this approximation corresponds to  $\lambda \rightarrow \infty$  in Eq. (14), which after some transformations<sup>17</sup> gives  $\tau_{\text{CMF}} = 1$ . This value also does not depend on the coefficient of nonlinearity.

The plot of dependence  $\tau_c(\lambda^{-1})$  at different  $\alpha_0$  is shown in Fig. 1. It is seen that at  $\alpha_0 > 0$  the dependence  $\tau_c(\lambda^{-1})$

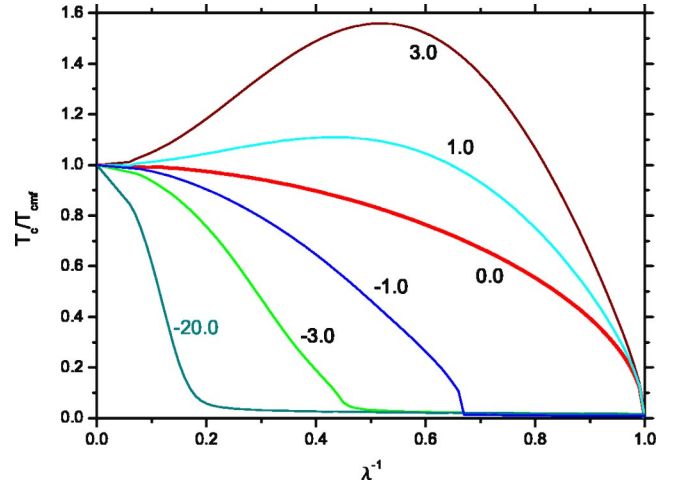


FIG. 1. Theoretical dependence  $\tau_c(\lambda^{-1})$ . Numbers near curves denote magnitudes of nonlinear coefficient  $\alpha_0$ .

has a maximum, while at  $\alpha_0 < 0$  it does not. Moreover, for negative nonlinearity there is a sharp lowering (but not to zero) of  $\tau_c$  at certain  $\lambda^{-1}$ . This demonstrates that negative feedback almost destroys long-range order especially at small dipoles concentrations. This behavior shows that at  $\alpha_0 > 0$  nonlinear effects produce positive feedback thus enhancing the long-range order in the system, while at  $\alpha_0 < 0$  the feedback is negative so that long-range order is inhibited but not completely destroyed even for large negative  $\alpha_0$ , see curve for  $\alpha_0 = -20$  in Fig. 1. Also, at sufficiently large positive  $\alpha_0$  we can achieve very large enhancement of  $T_c$  as compared to its mean field value (see curve for  $\alpha_0 = 3$  in Fig. 1). Since in our model we suppose that the value of  $T_{\text{CMF}}$  is equivalent to  $T_c$  for pure  $\text{PbTiO}_3$  (the end member of compound), we conclude that large positive  $\alpha_0$  give substantial increase of  $T_c$  as compared to the end members of ferroelectric compound.

### III. COMPARISON WITH THE EXPERIMENT: DISCUSSION

In our model, the ferroelectric compounds are considered as an ensemble of electric dipoles embedded in some virtual paraelectric host, its nature we will discuss later. It can be supposed that in the considered system  $(\text{BiScO}_3)_{1-x}(\text{PbTiO}_3)_x$  electric dipoles are originated from  $\text{PbTiO}_3$ , i.e., their number increase with  $x$  increasing. The nondipolar random field sources such as point charges, elastic dipoles, etc., are also present in such compositions due to the mixed valency of Bi and the difference in charges and ionic radii of  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$  and  $\text{Ti}^{4+}$  and  $\text{Sc}^{3+}$ . These defects could easily be incorporated in the consideration (see Ref. 11 for details), but we do not consider their contribution here to have the minimal number of adjustable parameters when fitting the theory with experiment.

For quantitative description of experiment in above ferroelectric compounds in the framework of our random field theory (in linear or nonlinear approximation) we should have precise information about the concentrations

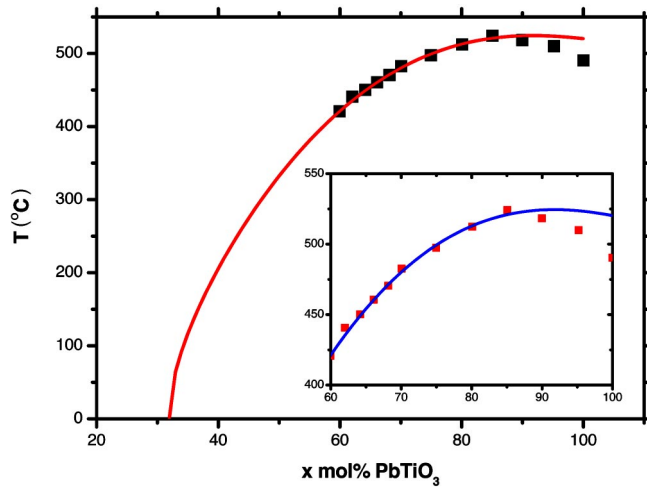


FIG. 2. Comparison of our theory (line) with experiment (Ref. 2) (squares). The inset shows the fit in more detail.

of electric dipoles and other random fields sources as well as the parameters  $\epsilon_0$ ,  $r_c$ , etc. Unfortunately the available data are strongly restricted for above compounds. That is why we recalculated our dimensionless parameters (15) from the best fit to the experiment.<sup>2</sup> Namely, from the position and “amplitude” of maximum of experimental curve  $T_c(x)$  we determine our nonlinearity coefficient  $\alpha_0 = 0.81$  and coefficient of recalculation of parameter  $\lambda$  into  $x$ . Latter coefficient gives us the value and a critical content of  $\text{PbTiO}_3$   $x_{cr} = 32\%$ . The result of such a fitting is shown in the Fig. 2.

It is seen in Fig. 2 that there is a pretty good coincidence between theory and experiment. This coincidence shows that the physical mechanism of enhancement of ferroelectric phase transition temperature beyond the end members in the ferroelectric compounds is the enhancement of initial (i.e., that of end members) long-range ferroelectric order in them caused by positive feedback generated by the nonlinear effects with positive coefficient. The obtained value is very close to transition temperature of  $\text{PbTiO}_3$ . This speaks in favor of the statement that  $\text{PbTiO}_3$  paraelectric phase can be considered as a host lattice.

As we mentioned above, the origin of nonlinear effects in compound ferroelectrics is quite naturally related to its intrinsic nonlinearities, reflected, for instance, in their hysteresis loop. The physical origin of these nonlinearities may be the nonlinear coupling of the ions in the unit cell as well as the clusterization of dipoles in diluted ferroelectric compounds. Each cluster has its own mesoscopic dipole moment (polarization of cluster) and such clusters can interact between each other. If interaction between such clusters is of positive sign, which may be manifested in the almost rectangular shape of hysteresis loop, we have the positive feedback with enhancement of initial (i.e., that of end member) long-range order with positive nonlinear coefficient. If the interaction is of negative sign, we have negative feedback and inhibition of ferroelectric order. But such negative feedback cannot destroy ferroelectricity completely, probably except for the case of extremely small dipole concentration. So, to achieve high positive values of nonlinear coefficients (which are necessary to strongly enhance  $T_c$ ), we should have (or prepare) the end members of ferroelectric compound with “as much as possible rectangular” hysteresis loop. The contribution of nonlinearities to dielectric response and hysteresis loop in mixed perovskites PZT with impurities was discussed in Ref. 18. The essential role of nonlinearity effect in explanation of phase diagram peculiarities in mixed ferroelectrics  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ,  $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ , and mixed systems of ferroelectric relaxors was shown recently in Refs. 19 and 20, respectively.

To make more precise prediction of which components in ferroelectric compound to use to increase  $T_c$  beyond end members value, the measurements of correlation radius, Lorentz factor, and ions shifts in both end members and entire above ferroelectric compounds are highly desirable. It should finally be noted that the theory outlined here permits one to calculate not only  $T_c$  for above substances but virtually any equilibrium and/or nonequilibrium thermodynamic characteristics such as static and dynamic dielectric susceptibility, specific heat, etc., as a function of  $\text{PbTiO}_3$  content, temperature, electric field, and other external parameters.

\*Electronic address: stef@math.uni.opole.pl; URL: http://cs.uni.opole.pl/~stef

†Electronic address: glin@materials.kiev.ua

<sup>1</sup>R. E. Eitel, C. A. Randall, T. R. Shrout, W. Hackenberger, and S. E. Park, *Jpn. J. Appl. Phys., Part 1* **40**, 5999 (2001).

<sup>2</sup>R. E. Eitel, C. A. Randall, T. R. Shrout, and S. E. Park, *Jpn. J. Appl. Phys., Part 1* **41**, 2099 (2001).

<sup>3</sup>C. A. Randall, R. E. Eitel, T. R. Shrout, D. Woodward, and I. M. Reaney, *J. Appl. Phys.* **93**, 9271 (2003).

<sup>4</sup>T. H. Song, R. E. Eitel, T. R. Shrout, C. A. Randall, and W. Hackenberger, *Jpn. J. Appl. Phys., Part 1* **42**, 5181 (2003).

<sup>5</sup>J. Inigues, D. Vanderbilt, and L. Bellaiche, *Phys. Rev. B* **67**, 224107 (2003).

<sup>6</sup>Inaguma, A. Miyaguchi, M. Yoshida, T. Katsumata, Y. Shimojo,

R. P. Wang, and T. Sekiya, *J. Appl. Phys.* **95**, 231 (2004).

<sup>7</sup>M. D. Glinchuk and V. A. Stephanovich, *J. Phys.: Condens. Matter* **6**, 6317 (1994).

<sup>8</sup>M. D. Glinchuk and V. A. Stephanovich, *Ferroelectrics* **169**, 281 (1995).

<sup>9</sup>J. Ya. Korenblit and E. F. Shender, *Usp. Fiz. Nauk* **157**, 267 (1989).

<sup>10</sup>V. A. Stephanovich, *Eur. Phys. J. B* **18**, 17 (2000).

<sup>11</sup>M. D. Glinchuk, R. Farhi, and V. A. Stephanovich, *J. Phys.: Condens. Matter* **9**, 10247 (1997).

<sup>12</sup>Yu. G. Semenov and V. A. Stephanovich, *Phys. Rev. B* **66**, 075202 (2002).

<sup>13</sup>Yu. G. Semenov and V. A. Stephanovich, *Phys. Rev. B* **67**, 195203 (2003).

- <sup>14</sup>A. M. Stoneham, *Rev. Mod. Phys.* **41**, 82 (1969).
- <sup>15</sup>M. D. Glinchuk, V. G. Grachev, M. F. Deigen, A. B. Roitcin, and L. A. Syslin, *Electrical Effects in Radiospectroscopy* (Nauka, Moscow, 1981) (in Russian).
- <sup>16</sup>M. D. Glinchuk and I. V. Kondakova, *Solid State Commun.* **96**, 529 (1995).
- <sup>17</sup>We perform the asymptotic analysis at  $\tau_c \rightarrow 0$  by changing the variable  $y=x/\tau_c$  in Eq. (14) and expanding in small parameter  $\tau_c$ . The analysis for the case  $\lambda \rightarrow \infty$  is performed by substitution  $z^2 = \pi\lambda^2 x^2/4$  and further expansion in small parameter  $\lambda^{-1}$ .
- <sup>18</sup>Qi Tan and D. Viehland, *Phys. Rev. B* **53**, 14103 (1996).
- <sup>19</sup>M. D. Glinchuk, E. A. Eliseev, and V. A. Stephanovich, *Ferroelectrics* **254**, 27 (2001).
- <sup>20</sup>M. D. Glinchuk, E. A. Eliseev, V. A. Stephanovich, and B. Hilzner, *Ferroelectrics* **254**, 13 (2001).