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Theory of phase transitions in disordered ferroelectrics allowing for nonlinear and spatial correlation effects

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Abstract. The order parameter, ferroelectric phase transition temperature, and critical concentrations of random-site electric dipoles, point charges and dilatational centres in disordered ferroelectrics are calculated. The calculations are carried out by the random-field method with a random-electric-field distribution function, allowing for nonlinear and spatial correlation effects. Essential differences from the linear case are revealed. First, the aforementioned effects lead to the transformation of the second-order phase transition into one of first order and vice versa for $\alpha_3 > 0$ and $\alpha_3 < 0$ respectively, where α_3 is the third-order nonlinearity constant. Second, for $\alpha_3 > 0$ the phase transition temperature T_c has a maximum as a function of the random-field-source concentration; its maximal value appears to be larger than that in the mean-field approximation. At the same time, for $\alpha_3 < 0$ the maximum is absent and the T_c-value is smaller than that in the linear case (i.e. at $\alpha_3 = 0$). This means that nonlinear and spatial correlation effects enhance the long-range order in disordered ferroelectrics for $\alpha_3 > 0$ and inhibit it for $\alpha_3 < 0$.

It is shown that the critical concentrations of electric dipoles, point charges and dilatational centres are the same as in the linear case. The application of the theory developed to various disordered ferroelectrics is discussed.

1. Introduction

Disordered ferroelectrics, such as the relaxors $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), and $Pb_{1-x}La_xZr_{1-y}Ti_yO_3$ (PLZT $x/1-y/y$), incipient ferroelectrics with off-centre impurities, e.g. $KTaO_3$:Li, Nb, Na, PbTe:Ge, and mixed systems of the KDP family, attract much scientific attention due to the anomalies in the physical properties of these systems. Their common feature is the existence of numerous random-field sources due to substitutional disorder, unavoidable impurities, vacancies in anion and cation sublattices, etc. The random fields, produced by material imperfections, are known to play a crucial role in the properties of disordered ferroelectric and magnetic systems (see e.g. [1–3]). Hence, all observable properties of such systems depend strongly on the random-field characteristics, and the forms of their distribution functions in particular. For example, for disordered magnetic systems the ranges of existence of the paramagnetic, ferromagnetic, spin-glass and mixed ferromagnetic–spin-glass phases depend on the ratios T/J and J_0/J [3], where J_0 and J are respectively the position of the distribution function maximum and its width. Qualitatively, the phase diagrams of disordered ferroelectrics have the same features, but,

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quantitatively, the influence of the random electric fields may be stronger than for disordered magnets due to larger number of these field sources in the material. Since defects are distributed randomly in the host crystal lattice, their spatial correlations are of importance for the random-electric-field distribution function. On the other hand, a nonlinear dependence of the spontaneous polarization on the external electric field (dielectric hysteresis) is a characteristic feature of both ordered and disordered ferroelectrics. This means that nonlinear effects are also important for the systems under consideration. However, up to now all of the calculations have been carried out only in the linear approximation—that is within the framework of the statistical theory of the first order [1, 2, 4–6]. Such an approach may be valid for systems with small enough coefficients of nonlinearity and/or random-field-source concentrations. In the general case, however, the nonlinear and correlation effects have to be taken into account. A method of distribution function calculation allowing for both of these effects was proposed in [7].

In this paper we use the random-local-field method, developed earlier (see [8, 9] and references therein). The comparison with other mathematical techniques for investigation of disordered systems (the method of virial expansion of the inverse dielectric susceptibility, the method of random mean fields, Monte Carlo numerical methods, percolation theory, etc) as well as with results of classical works (e.g. [10]) can be found in the above-mentioned references. The advantage of the random-local-field method lies in its comparative simplicity and universality, due to it being based on a statistical physics approach. It can be applied for arbitrary forms of random electric fields to real three-dimensional disordered ferroelectrics outside the critical region. Note that this approach is more general than the mean-field approximation, which can be obtained from our results as a special case.

This method is applied in the present work to the case of several random-field sources, namely point charges, dilatational centres and electric dipoles. The temperature dependence of the order parameter, the concentrational dependence of the ferroelectric phase transition temperature, and the critical concentration of the random-field sources have been calculated. The calculations incorporate the dependence of the aforementioned parameters on the concentrations of point charges and dilatational centres as well as on the third-order nonlinearity coefficient α_3. It has been shown that when the magnitude of the nonlinear coefficient is large enough, the results obtained are very different from those obtained within the linear approximation [1]. In particular, the second-order phase transition transforms into a first-order one, and a maximum in the dependence of the transition temperature on the random-field-source concentration appears.

2. The random-field distribution function allowing for nonlinear and correlation effects

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

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

Here the bar denotes averaging over spatial configurations of random-field sources, and $\langle\langle\cdots\rangle\rangle$ indicates averaging both over dipole orientations and over the random-field distribution, so the distribution function is expressed in terms of itself in a self-consistent manner. $\boldsymbol{E}(\boldsymbol{r}_i)$ is the internal electric field induced by electric dipoles, point charges, and other sources at the observation point $\boldsymbol{r}_i$, i.e.

$$E_\gamma(\boldsymbol{r}_i) = \varepsilon_\gamma(\boldsymbol{r}_i) + \sum_{m=2}^{p} \alpha_m \varepsilon_\gamma^m(\boldsymbol{r}_i) \tag{2}$$

and

$$\varepsilon_\gamma(\boldsymbol{r}_i) = \sum_k \sum_j \varepsilon_{\gamma k}(\boldsymbol{r}_{ij}) \tag{3}$$

where $\varepsilon_{\gamma k}$ is the γ-component of the field, produced at the observation point $\boldsymbol{r}_i$ by a source of the kth type (e.g. dipoles, point charges, or dilatational centres) situated at the point $\boldsymbol{r}_j$. Note that the last term in equation (2) determines the nonlinear contribution of any power of the internal fields $\varepsilon_\gamma(\boldsymbol{r})$, allowing for both nonlinear and spatial correlation effects. Indeed any nonlinear term in equation (2) can be rewritten in a form similar to that for $m = 2$:

$$\alpha_2 \left[\sum_{j=1}^{N} \varepsilon_\gamma^2(\boldsymbol{r}_{ij}) + \sum_{l \neq j}^{N} \varepsilon_\gamma(\boldsymbol{r}_{ij}) \varepsilon_\gamma(\boldsymbol{r}_{il}) \right] \tag{4}$$

where the first and the second sums are respectively the nonlinear and spatial correlation contribution, and N is the number of random-field sources under consideration.

In accordance with a recently proposed model [6], the sources of random fields are supposed to be embedded into the material's paraelectric phase (the host lattice); α_m is the coefficient of nonlinearity of this lattice with the dimension of inverse electric field to the power $(m-1)$ (i.e., the dimension of α_m is inverse to $E^{(m-1)}$), which characterizes the corresponding contribution of the nonlinear term.

Rigorous calculation of the distribution function in the form $F(\boldsymbol{E}) = \overline{\delta(\boldsymbol{E} - E'(r_{ij}))}$ with respect to equation (2) in the framework of the statistical theory approach yields the following result for any electric field component $E_\alpha \equiv E$ [7]:

$$f(E) = \int_{-\infty}^{\infty} f_1(\varepsilon)\, \delta\left(E - \varepsilon - \sum_{m=2}^{p} \alpha_m \varepsilon^m \right) \mathrm{d}\varepsilon \tag{5}$$

$$f_1(\varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left(\mathrm{i}\varepsilon t - \sum_{m=2}^{p} n_k F_k(t) \right) \mathrm{d}t \tag{6}$$

$$F_k(t) = \int \mathrm{d}^3 r \ (1 - \exp(-\mathrm{i}t\varepsilon_k(\boldsymbol{r}))) \tag{7}$$

where $f_1(\varepsilon)$ is the distribution function that takes into account only the linear term in (2) (the distribution function of the first order). This means that spatial averaging in $f_1(\varepsilon)$ can be carried out within the framework of the statistical theory of the first order, which gives the exact solution for many types of random electric fields [11, 12].

In equations (5)–(7), n_k and $\varepsilon_k(\boldsymbol{r})$ are the concentration and electric field of the kth type of source respectively. It is seen that only the integrand in equation (7) depends on the source coordinates and electric dipole orientations due to the dependence of $\varepsilon_k(r)$ on these parameters (see [1] for details). Thus thermal averaging over the dipole orientations and over random fields can be fulfilled by substitution of

$$F_k^T(t) = \int \mathrm{d}^3 r \ \left\langle\!\left\langle 1 - \mathrm{e}^{-\mathrm{i}t\varepsilon_k(\boldsymbol{r})} \right\rangle\!\right\rangle \tag{8}$$

for equation (7).

Equations (6) and (8) determine $f_1(\varepsilon)$, calculated earlier in [1] for the case of two-orientation electric dipoles, point charges, and dilatational centres, acting as the random-field sources. It was obtained in the form

$$f_1(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[\mathrm{i}t(E - E_0 L) - n_1 B_1 |t| - n_2 B_2 |t|^{3/2} - n_3 B_3 t^2] \, \mathrm{d}t \tag{9}$$

$$B_1 = \frac{\Omega_0}{9} \frac{1+\nu}{1-\nu} p \qquad B_2 = \frac{32}{15} \left(\frac{\pi Z e}{2\varepsilon_0} \right)^{3/2} \qquad B_3 = \frac{16\pi}{15} r_c^3 \left(\frac{d^*}{\varepsilon_0 r_c^3} \right)^2.$$

Here $L = \overline{\langle\langle d^* \rangle\rangle}/d^*$ and $E_0 = 4\pi(n_3 d^{*2})/\varepsilon_0$ are the order parameter (the number of coherently oriented impurity electric dipoles) and the mean value of the electric dipole random field (in energy units), $d^* = \frac{1}{3} d\gamma(\varepsilon_0 - 1)$ is the effective electric dipole moment, γ and ε_0 are respectively the Lorentz factor and static dielectric permittivity of the host lattice, n_1, n_2, and n_3 are respectively the concentrations of dilatational centres, point charges, and electric dipoles, Ze and Ω_0 are the point defect charge and elastic moment, and p and ν are the host-lattice piezoelectric tensor component and Poisson coefficient respectively. Note that equation (9) corresponds to the case of a Gaussian distribution function of random electric fields induced by electric dipoles, i.e. to the case where $n_3 r_c^3 \gg 1$ (see [1] and references therein).

3. Average values of the physical quantities

3.1.

In the general case, the average value of any physical quantity $A(E)$ can be represented in the form

$$\bar{A} = \int_{-\infty}^{\infty} f(E) A(E)\ \mathrm{d}E. \tag{10}$$

Substitution of (5) into (10) with further integration over $\mathrm{d}E$ gives

$$\bar{A} = \int_{-\infty}^{\infty} f_1(\varepsilon) A\left(\varepsilon + \sum_{m=2}^{p} \alpha_m \varepsilon^m\right) \mathrm{d}\varepsilon. \tag{11}$$

Equation (11) makes it possible to calculate the average value of any physical quantity with respect to nonlinear and correlation effects with the help of the distribution function of the first order.

3.2.

One of the most important physical quantities which determines the main characteristics of a disordered ferroelectric is the order parameter L. To calculate it we have to substitute $\langle l \rangle$ ($\boldsymbol{l} \equiv \boldsymbol{d}^*/|d|$) for $A(E)$ in equation (10), where $\langle \cdots \rangle$ indicates thermal averaging over possible dipole orientations (see [1] for details). In the case of two-orientation dipoles ($l_z = \pm 1$, $l_x = l_y = 0$) $\langle l \rangle = \tanh(E/kT)$, where $E \equiv E_z$. With the help of equation (11) one obtains for the order parameter $L_z \equiv L$

$$L = \int_{-\infty}^{\infty} f_1(\varepsilon) \tanh\left[\left(\varepsilon + \sum_{m=2}^{p} \alpha_m \varepsilon^m\right) \Big/ kT\right] \mathrm{d}\varepsilon. \tag{12}$$

Substitution of equation (9) into equation (12) and some simple transformations of the integrand give

$$L = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}\varepsilon\ \tanh\left[\left(\varepsilon + \sum\nolimits_{m=2}^{p} \alpha_m \varepsilon^m\right) \Big/ kT\right] \int_0^{\infty} \mathrm{e}^{-F(t)} \cos t(\varepsilon - E_0 L)\ \mathrm{d}t \tag{13}$$

where

$$F(t) = n_1 B_1 t + n_2 B_2 t^{3/2} + n_3 B_3 t^2.$$

In the linear case ($\alpha_m = 0$), equation (13) transforms into that derived in [1]. It is seen that order parameter is self-consistently expressed in terms of itself, and is a function of the temperature, concentrations and parameters of random-field sources, and host-lattice characteristics.

3.3.

The result of the calculation of equation (13) depends strongly on the form of the argument of the tanh function. The latter can be simplified on the basis of the following symmetry considerations. Consider a lattice with a centre of inversion in the paraelectric phase. In this case the order parameter has to be an odd function of the electric field, i.e. the values m in equation (13) are odd numbers. Retaining only the first nonlinear term in the argument of the tanh function, one obtains

$$L = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\varepsilon \ \tanh[(\varepsilon + \alpha_3\varepsilon^3)/kT] \int_0^{\infty} \mathrm{e}^{-F(t)} \cos t(\varepsilon - E_0 L) \ \mathrm{d}t. \qquad (14)$$

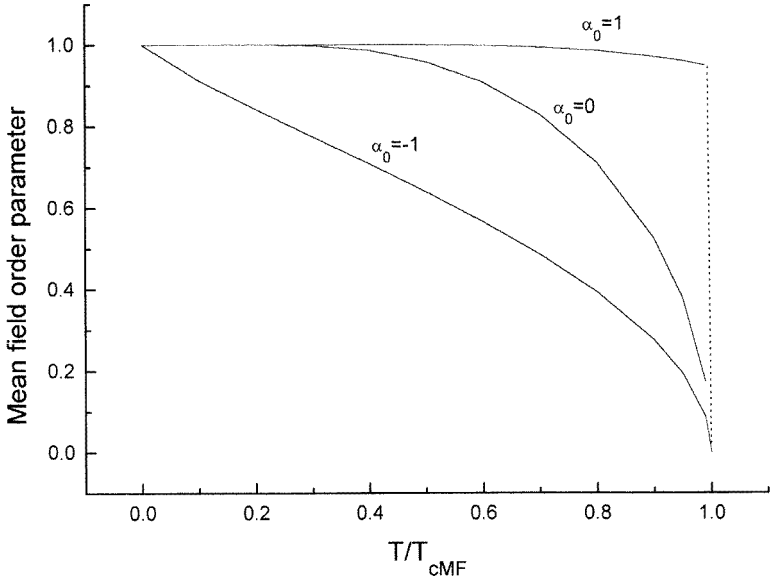


Figure 1. The order parameter in the mean-field approximation for several values of the dimensionless nonlinearity coefficient α_0.

4. The order parameter, phase transition temperature, and critical concentration

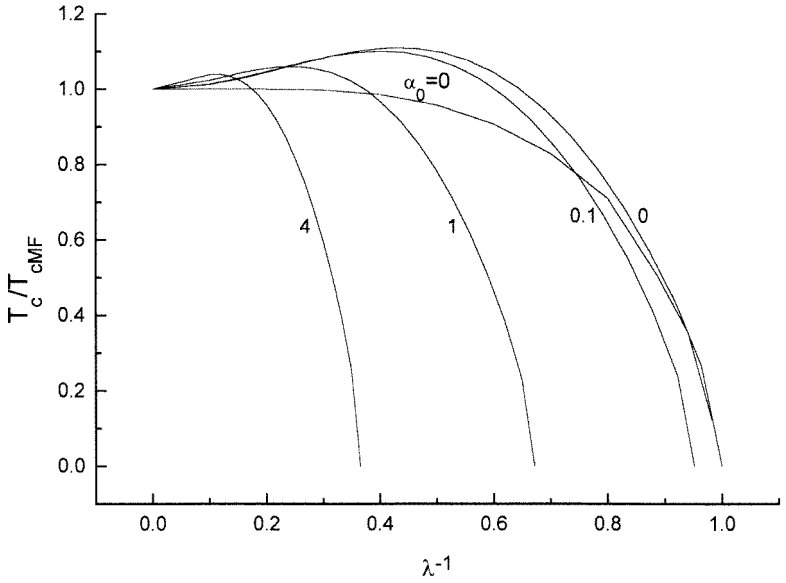
4.1.

Let us first consider the order parameter in the mean-field approximation, where the width of the distribution function is much less than its first moment, i.e. in equation (14) $F(t) \ll E_0 L$, so that

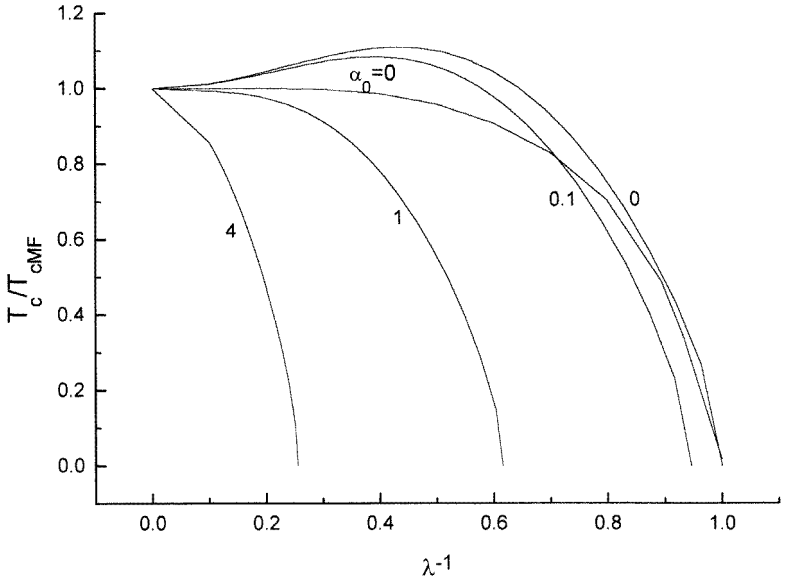
$$\frac{1}{\pi}\int_0^{\infty} \mathrm{e}^{-F(t)} \cos t(\varepsilon - E_0 L) \ \mathrm{d}t \to \delta(\varepsilon - E_0 L).$$

Substitution of this δ-function into equation (14) gives the equation for the order parameter within the mean-field approximation:

$$L_{mf} = \tanh\left[\frac{T_{cmf}}{T}(L_{mf} + \alpha_0 L_{mf}^3)\right] \qquad (15)$$



(a)



(b)

Figure 2. The phase transition temperature for $\alpha_0 = 1$ as a function of the concentration of electric dipoles for different concentrations of (a) point charges and (b) dilatational centres. The numbers near the curves correspond to the values of μ (a) and of Δ (b). The additional curve corresponds to the linear case ($\alpha_0 = 0$, $\mu = \Delta = 0$).

where $E_0 = kT_{cmf}$, T_{cmf} is the transition temperature in the mean-field approximation, $\alpha_0 \equiv \alpha_3 E_0^2$, and α_0 is dimensionless. The temperature dependence of L_{mf} (equation (15)) is depicted in figure 1 for $\alpha_0 = \pm 1$. The linear case ($\alpha_0 = 0$) is represented also for the

sake of comparison with nonlinear cases. It is seen that the second-order phase transition of the linear case transforms into a phase transition of first order for $\alpha_0 > 0$ and is of second order for $\alpha_0 < 0$. Note that for the sake of simplicity we have depicted a phase transition of second order for the case where $\alpha_0 = 0$; however, $\alpha_0 < 0$ corresponds to a phase transition of first order in the linear case, i.e. nonlinear effects transform the first-order phase transition into a second-order one.

It is seen that for $\alpha_0 > 0$ ($\alpha_0 < 0$) the mean-field order parameter is larger (smaller) than that in the linear case ($\alpha_0 = 0$). Therefore, correlation effects strengthen ($\alpha_0 > 0$) or weaken ($\alpha_0 < 0$) the long-range order induced by random-site electric dipoles. Estimations have indicated that qualitatively the same behaviour and phase transition order change are characteristic for the general case, described by equation (14). Indeed, as was shown recently [7], at large enough α_3-values, the distribution function $f(E)$ has a sharp maximum ($\alpha_3 > 0$) or minimum ($\alpha_3 < 0$) at $E = E_0 L$, so one can expect increasing or decreasing of the phase transition order parameter.

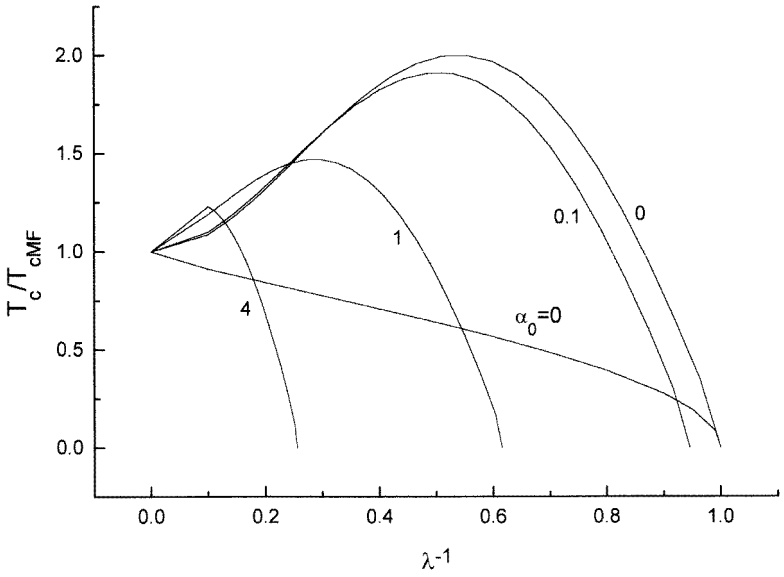
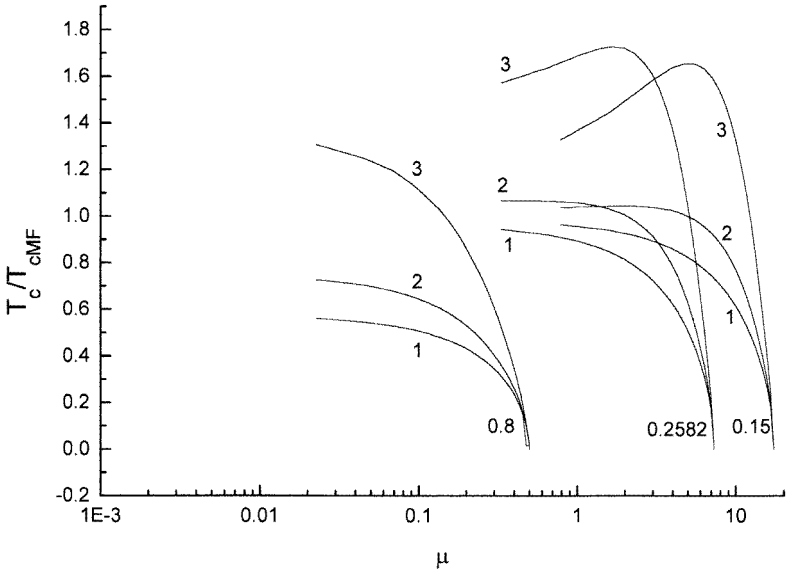


Figure 3. The phase transition temperature for $\alpha_0 = 5$ versus the concentration of electric dipoles for different concentrations of dilatational centres. The numbers near the curves correspond to values of Δ, and the additional curve corresponds to the linear case ($\alpha_0 = 0$, $\Delta = 0$).

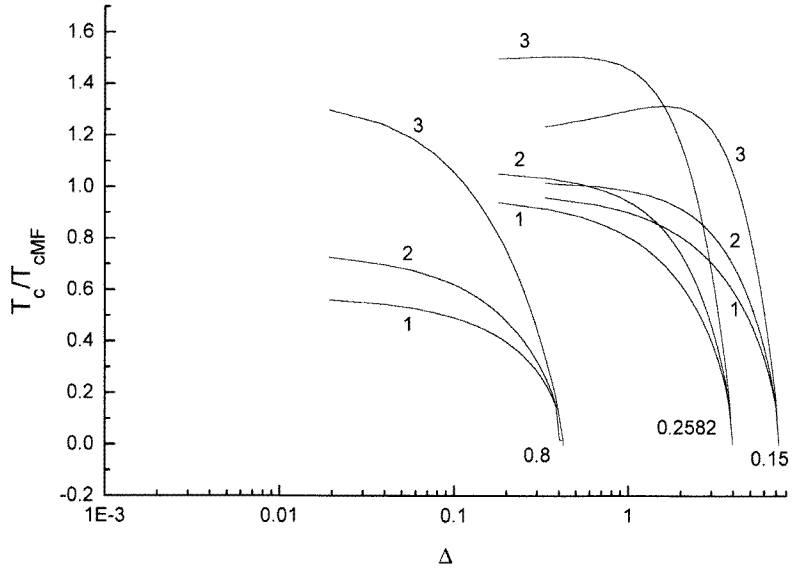
4.2.

Formula (14) makes it possible to calculate the transition temperature T_c. For the phase transition of second order, it is the temperature at which the order parameter appears. Putting $E - E_0 = x$ in (14) and expanding the integrand near $T = T_c$ in the small parameter L up to the first nonvanishing term, we find the following equation for T_c:

$$\frac{T_c}{T_{cmf}} = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{(1+3\alpha_0 x^2)\ \mathrm{d}x}{\cosh^2((x+\alpha_0 x^3)/kT_c)} \times \int_0^{\infty} (\cos tx)\exp(-n_1 B_1 t - n_2 B_2 t^{3/2} - n_3 B_3 t^2)\ \mathrm{d}t. \tag{16}$$



(a)



(b)

Figure 4. The phase transition temperature as a function of the concentrations of (a) point charges and (b) dilatational centres for different values of α_0: 0.1 (curves 1), 1 (curves 2), and 5 (curves 3). The numbers near the curve families correspond to values of λ^{-1}.

Equation (16) determines the phase transition temperature for the cases in which, in addition to electric dipoles, which induce ferroelectric long-range order, there are point charges and dilatational centres, which tend to destroy long-range order. To obtain a quantitative description of this process, equation (16) had been solved numerically for the cases where $n_1 = 0$ (the random-field sources are electric dipoles and point charges) and

where $n_2 = 0$ (the random-field sources are electric dipoles and dilatational centres). To discover the influence of correlation effects in the systems with random-site electric dipoles as the main sources of random electric fields, we solved (16) for the case where $n_3 \neq 0$, $n_1 = n_2 = 0$. The results of the numerical solution are depicted in figure 2 ($\alpha_0 = 1$), figure 3 ($\alpha_0 = 5$), and figure 4 ($\alpha_0 = 0.1$, 1, and 5) for different sets of dimensionless parameters $\Delta = (n_1 B_1)/\sqrt{n_3 B_3}$, $\mu = (n_2 B_2)/(n_3 B_3)^{3/4}$, and $\lambda = E_0/\sqrt{\pi n_3 B_3} = \sqrt{15 n_3 r_c^3}$.

It is seen from figures 2 and 3 that α_0 increasing leads to a significant increase of the value of T_c/T_{cmf} (compare the curves with those for $\alpha_0 = 0$ in figures 2 and 3). So nonlinear and spatial correlation effects in the system of random-site and random-orientation electric dipoles tend to order the system more strongly. Meanwhile, point charges and dilatational centres destroy the long-range order and decrease the value of T_c/T_{cmf} (compare the curves marked 0.1, 1, and 4 in figures 2 and 3) like in the linear case [1]. However, the appearance of a maximum in the T_c-curves, where $T_c/T_{cmf} > 1$, is a completely new feature, caused by nonlinear effects. The fact that $T_c/T_{cmf} > 1$ for a certain range of values of λ^{-1}, μ, and Δ (see figures 2–4) may be the result of long-range order 'amplification' by nonlinear effects. It is seen from equation (15) that one may consider $E_0(1 + \alpha_0 L^2)$ as an effective mean field, which is larger than that in the linear case, $E_0 \equiv kT_{cmf}$, in figures 1–4. For the same reason, in the case where $\alpha_0 < 0$, $T_c/T_{cmf} < 1$ for all of the values of λ^{-1}, μ, and Δ. Calculations confirm this supposition. It is seen from the figures that the maximum position is shifted towards smaller λ^{-1}, i.e. to larger concentrations of electric dipoles with increase in the concentrations of point charges or dilatational centres. So there is an optimal concentration of electric dipoles at which the transition temperature has its maximal value. It follows from figure 4 that this maximum is absent at small dipole concentrations (see the curves for $\lambda^{-1} = 0.8$ ($nr_c^3 \approx 0.1$). The maxima are also absent for small α_0-values (see the curves marked '1', where $\alpha_0 = 0.1$). But maxima are clearly seen at $\alpha_0 = 1$ and $\alpha_0 = 5$ (curves '2' and '3' for $\lambda^{-1} = 0.2582$ and $\lambda^{-1} = 0.15$ respectively), their positions being shifted towards larger values of μ or Δ with increasing α_0 at a constant value of λ^{-1} .

4.3.

The value of λ at which $T_c = 0$ corresponds to the critical concentration of electric dipoles n_{3c}, so for $n_3 < n_{3c}$ there is no long-range order ($L = 0$), and only short-range order (dipole glass) may exist ($L = 0, L^2 \neq 0$). The limit of equation (16) for $T_c \to 0$ leads to the following equation for the critical concentration of electric dipoles:

$$\frac{2E_0}{\pi} \int_0^\infty \exp(-n_1 B_1 t - n_2 B_2 t^{3/2} - n_3 B_3 t^2)\ \mathrm{d}t \geqslant 1. \tag{17}$$

It is seen that this equation is independent of the coefficient of nonlinearity, and it is exactly the same as in the linear case (see [1]). It can be easily seen from (17) that for $B_1 = B_2 = 0$ long-range order can appear only for $\lambda \geqslant 1$. That is why we used $0 \leqslant \lambda^{-1} \leqslant 1$ for the calculations.

Note that $\lambda^{-1} = 0$ ($n_3 r_c^3 \to \infty$) corresponds to the mean-field approximation for all values of μ and Δ. The critical concentrations of electric dipoles for arbitrary values of $n_1 \neq 0$ and $n_2 \neq 0$ were calculated in [1]. In the same way one can introduce the critical concentration of point charges, n_{2c}, or dilatational centres, n_{1c}, at which $T_c = 0$, so that for $n_1 > n_{1c}$ and $n_2 > n_{2c}$ long-range order is completely destroyed, and only the dipole glass state may exist. The values of n_{1c} and n_{2c} for arbitrary concentrations of electric dipoles were calculated recently with the help of equation (17) (see [6]).

5. Discussion

5.1.

In the framework of a recently proposed model [6], any disordered ferroelectric is considered as random-site electric dipoles, point charges, dilatational centres and other impurities and defects, embedded in the paraelectric phase as a host lattice. In relaxors like PMN, all of the ions were shown to be shifted from their equilibrium positions in the ideal perovskite structure [13], the values and directions of their shifts being random values [14]. Since this ideal structure can be supposed to be the PMN paraelectric phase, the shifted ions are random-site electric dipoles in the system. Substitutional disorder (Nb^{5+} is substituted for Mg^{2+} and vice versa) vacancies of lead and oxygen leads to a great number of randomly distributed point charges, dilatational centres, and other imperfections. The latter may be defect complexes like $Nb^{5+}(Mg^{2+})$–$V(Pb^{2+})$ or $Mg^{2+}(Nb^{5+})$–$V(O^{2-})$, where $A^{n+}(B^{m+})$ is an A^{n+} ion substituted for a B^{m+} ion, and $V(C^{k+})$ is a vacancy for a C^{k+} ion. Since Nb dipoles were shown to be the sources of the system's polar regions with the observed polarization along [111]-type directions [13, 15], all other random-field sources tend to destroy this ordering. On the other hand, in relaxors like PSN, the complexes $Nb^{5+}(Sc^{3+})$–$V(Pb^{2+})$ and $Sc^{3+}(Nb^{5+})$–$V(O^{2-})$ are electric dipoles with orientations along [111]-type and [100]-type directions respectively. Since the direction of the polarization in PSN is known to be along a [100]-type direction [16], impurity dipoles with the same orientations may be considered as sources of long-range order enhancement rather than its destruction.

In the PLZT system, Ti, Zr, and Pb ions are known to be shifted from their equilibrium positions in the PZT paraelectric phase, i.e. they are electric dipoles; meanwhile La^{3+} ions are point charges or dilatational centres, which destroy ferroelectric long-range order, familiar for PZT. Some other sources of random electric fields in PLZT can be considered also [6].

The simplest disordered systems are incipient ferroelectrics with off-centre impurity ions. These materials (e.g. KTL) can be considered as random-site electric dipoles (e.g. off-centre Li^{+}) in a $KTaO_3$ lattice. Vacancies of oxygen and potassium, and some unavoidable impurities (e.g. iron ions [17]) are the sources of random fields which tend to destroy long-range order, induced by off-centre ions [1, 5].

Therefore, in all of the aforementioned disordered ferroelectrics, the number of random-field sources can be large, so nonlinear and correlation effects can be very important. On the other hand, these effects are known to be large in the vicinity of the dielectric susceptibility maximum. More precisely, the coefficients α_m in equation (2) can be estimated from the consideration of the Landau expansion of the host-lattice free energy: $\alpha_m \propto \alpha_m^0 {\varepsilon_0}^m$, where α_m^0 is the coefficient in front of the mth power of the polarization in the Landau expansion. Thus, the parameter $\alpha_0 = \alpha_3 E_0^2 \sim \alpha_3^0(n_3^2\varepsilon_0^3)$, i.e. it is proportional to the concentration of the impurity electric dipoles and the dielectric permittivity of the host lattice; the latter should be divergent at the host-lattice phase transition points. This means that nonlinear and correlation effects have to be larger both near the ε_0-maximum and in systems with large numbers of electric dipoles. Therefore the peculiarities of the phase diagrams, described in previous sections, must depend on the temperature and the concentration of electric dipoles in all of the aforementioned disordered systems.

The most prominent features of the nonlinear and correlation effects are the changing of the order of the phase transition (see figure 1), and the appearance of a maximum in T_c/T_{cmf} for $\alpha_3 > 0$, i.e. the existence of an optimal concentration of electric dipoles (see figures 2 and 3) or point charges and dilatational centres (see figure 4) at which the 'degree

of ordering' is maximal. Note that the origin of these maxima may be connected with the transformation of the second-order phase transition into a first-order one. Contrary to the case for $\alpha_3 > 0$, in the systems with $\alpha_3 < 0$ one can expect the destruction of long-range order with increase of $|\alpha_0|$.

5.2.

The transformation of the second-order phase transition into a first-order one with reduction of the temperature was observed earlier for KTL with 3.5% and 8% Li^+ ions [18]. Since for $KTaO_3$ ε_0 increases with decreasing temperature and $\alpha_3^0 > 0$ [19], one can assume that this phenomenon is a manifestation of nonlinear and correlation effects. Unfortunately, it is impossible to compare our theory and experiment for KTL with 3.5% and 8% of Li, because there are no quantitative measurements available for 8% Li ions (see [18]). It follows from the theory developed that at larger concentrations the phase transition order transformation in KTL may occur at higher temperatures, where ε_0 is smaller. Recently a sign change of α_3^0 near the dielectric permittivity maximum was observed for PMN single crystal in investigations of the dependence of the nonlinear dielectric permittivity on an external dc electric field [20]. This experiment seems to provide direct confirmation of our theoretical predictions.

In the $Pb_{1-x}La_xZr_{0,65}Ti_{0,35}O_3$ system the transition temperature from the paraelectric to the ferroelectric phase in the host PZT lattice is known to be $T_d = 640$ K [21]. Thus for $T < 640$ K, α_0 has to decrease with reduction in the temperature. Perhaps this fact is the main reason for the fairly good quality of the description of the $T_c(x)$ dependence obtained recently within the linear approximation [6].

To obtain a quantitative description of the peculiarities of the phase diagram and properties of relaxor ferroelectrics like PMN and PSN within the framework of random-field theory within the linear or nonlinear approximation, one has to know the concentrations of electric dipoles and other random-field sources, and their characteristics, as well as the host-lattice parameters b, ε_0, r_c, T_d, etc. Unfortunately, the available data are very sparse for these relaxors. Qualitatively, one can suppose that systems like PSN are more ordered than PMN due to the smaller magnitudes of the random fields of point charges there ($Z_{Nb} - Z_{Sc} < Z_{Nb} - Z_{Mg}$; Z_A is the A-ion charge) and the existence of additional electric dipoles such as $Sc^{3+}(Nb^{5+})$–$V(O^{2-})$ with orientations along [100] directions. Another possible type of dipole pair, $Nb^{5+}(Sc^{3+})$–$V(Pb^{2+})$, with orientation along a [111]-type direction, has to compete with the system's tendency to order along [100] [4], i.e. these dipoles will destroy the polarization of PSN along the [100] direction. That is why annealing of PSN in lead vapour makes the material more ordered [22]. For a quantitative description of disordered ferroelectric phase transitions and peculiarities of properties within the framework of random-field theory, additional experimental investigations of these materials are extremely desirable.

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