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Random fields and their influence on the phase transitions in disordered ferroelectrics

M D Glinchuk† and V A Stephanovich‡

† Institute for Materials Science, Krjijanovskogo str. 3, 252180 Kiev, Ukraine

‡ Institute of Physics of Semiconductors, prospect Nauki 45, 252650 Kiev, Ukraine

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Abstract. Calculations of the phase transition temperature and the critical concentration of electric dipoles which induce in the host crystal lattice the phase transition with the appearance of long-range order are carried out. These calculations are made by considering the additional static random electric fields owing to defects of other types: elastic dipoles and point electric charges. The distribution function of the joint action of the aforementioned random fields is also calculated. It is shown that the presence of the defects of other types inhibits phase transition so that, for the occurrence of long-range order, in this case larger concentrations of electric dipoles are necessary. The theoretical results obtained are found to be important for a description of the experimental situation in $K_{1-x}Li_xTaO_3$, $PbMg_{1/3}Nb_{2/3}O_3$ and other disordered ferroelectrics.

1. Introduction

The problem of phase transitions in disordered ferroelectrics is one of the most widely investigated and discussed problems of phase transition physics. This is due both to large number of phases in these systems (e.g. ferroelectric and ferroelastic phases, dipole and quadrupole glass states, and ferroglass intermediate phases) and to the unusual physical properties of these systems.

The disordered ferroelectrics of different types have different phase transitions. For example in incipient ferroelectrics such as $KTaO_3$:Li,Nb,Na; $SrTiO_3$:Ca or PbTe:Ge with dipole impurities, the ferroelectric phase and the dipole glass state are realized at $n > n_{cr}$ and $n < n_{cr}$, respectively, where n_{cr} is the critical concentration of dipole impurities [1]. In ferroelectrics such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) or $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) with diffuse phase transitions, only a transition to the dipole glass state was observed (see, e.g., [2, 3]). The largest number of phase transitions was observed in mixed ferroelectrics of the KDP family, e.g. $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP). There are ferroelectric, antiferroelectric, dipole glass and intermediate ferroglass phases [4].

The explanation of such a rich phase transition picture is usually based on the common feature of the aforementioned systems, namely the presence of electric dipoles with random sites and orientations in the host crystal lattice. The constant-sign electric fields arising because of indirect interaction of electric dipoles via host lattice soft phonons [5] lead mainly to the possible appearance of long-range ferroelectric order in these systems. However, the real occurrence of phases with long-range or short-range (glassy) order depends on the competition of the aforementioned fields with various types of random field of alternating sign. They are random electric fields due to direct interaction of impurity electric dipoles, random electric fields created by point charge defects (e.g. excess point charges in the PMN

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lattice [6]) and random elastic fields created both by the aforementioned defects and by unavoidable defects of another type [6].

Nevertheless up to now, only random electric fields of impurity dipoles have been considered as those competing with constant-sign electric fields. The calculated value of the critical concentration [7] in this model turns out to be much lower than the experimentally observed value [8]. The variation in the latter quantity due to additional impurity electric dipoles which create additional random electric fields was considered in [9]. The qualitative results of this consideration are quite obvious, but the question about the probable phase transition due to these additional dipoles of unknown nature is still left unanswered.

In the present paper, calculations of the critical concentration of electric dipoles, which induce in the host crystal a lattice phase transition with the appearance of long-range order together with a concentration dependence of the phase transition temperature are carried out. The calculations are made with respect to random electric fields of both electric dipoles and defects of other types, i.e. elastic dipoles and point electric charges. The distribution functions of the above-mentioned random fields are also calculated. It is shown that the presence of defects of other types inhibits the phase transition so that, for the appearance of long-range order, in this case larger concentrations of electric dipoles are necessary.

2. Random electric fields in disordered ferroelectrics

Let us consider a highly polarizable dielectric with soft phonon modes and with randomly situated electric dipoles oriented in the crystal lattice and point defects with electric charge or elastic dipoles. The Hamiltonian of such system can be written as follows:

$$\mathcal{H} = \sum_{i\beta}\left(\sum_{j\alpha} K^{\alpha\beta}(r_{ij})l_j^{\alpha} + \mathcal{E}^{\beta}(r_i)\right)\cdot l_i^{\beta} \equiv \sum_{i\beta} E^{\beta}(r_i)\cdot l_i^{\beta} \tag{1}$$

where $l_i = d_i^*/d_i^*$ is a unit vector pointing along the direction of ith defect effective dipole moment, $\boldsymbol{E}(r_i)$ is the internal electric field so that the first and second terms in the large parentheses of equation (1) denote a random electric field acting on the ith dipole site both from other dipoles of the same type and from defects of another type, $r_{ij} = r_j - r_i$ and $\alpha, \beta = x, y, z$. The function $K^{\alpha\beta}(r_{ij})$ for crystals with soft phonon modes in a harmonic approximation has the form [1]

$$K^{\alpha\beta}(r_{ij}) = -\frac{d^{*2}}{\varepsilon_0}[f_1(r_{ij})\delta_{\alpha\beta} + (3n_\alpha n_\beta - \delta_{\alpha\beta})f_2(r_{ij})] \tag{2a}$$

$$\begin{aligned} n &= \frac{r_{ij}}{r_{ij}},\ f_1(x) = \frac{2}{3}\frac{\exp(-x/r_c)}{xr_c^2} + \frac{4\pi}{3V} \\ f_2(x) &= \frac{1}{x^3}\left[1 - \exp\left(-\frac{x}{r_c}\right)\left(1 + \frac{x}{r_c} + \frac{x^2}{3r_c^2}\right)\right] \end{aligned} \tag{2b}$$

where ε_0, r_c and V are the pure crystal dielectric permittivity, the correlation radius and the volume, respectively. Note that the second term in the function f_1 is added so that the boundary conditions for a shorter sample are correct [10]. As was shown in [11], this term is completely defined by the host lattice anharmonicity coefficient. In the same reference the expressions for $f_1(x)$ and $f_2(x)$ with respect to anharmonicity are calculated. Here we do not give them because they are in a cumbersome form.

The sources of the internal electric field $\mathcal{E}(r_i)$ could be point charge defects, charged dislocations and, in crystals with a piezoeffect, elastic dipoles, dislocations and disclinations. The number of some of the above-mentioned defects, e.g. vacancies, impurity ions and dislocations, depends on the sample preparation technology and hence should vary from sample to sample. At the same time, point charge defects should be present, e.g. in ferroelectrics with diffuse phase transitions because of site disorder in the B-sublattice ions and because of lead and oxygen vacancies. It is well known that the presence of an equilibrium quantity of oxygen vacancies is peculiar to lattices with a perovskite structure and to $KTaO_3$ and $SrTiO_3$ in particular. For mixed systems of the KDP family the presence of elastic dipoles due to the difference between ionic radii of substitutional and host lattice ions is possible [12]. Owing to static shifts of the ions the elastic dipoles can play an important role in ferroelectrics with diffuse phase transitions where any lattice ion can be shifted from its equilibrium position in one of the lattice symmetry directions [13].

Thus we shall consider the random fields created by point charge defects and elastic dipoles, because these defects are peculiar to the above-mentioned disordered systems and do not depend on the sample preparation method. We shall write $\mathcal{E}(r_i) = \mathcal{E}_1(r_i) + \mathcal{E}_2(r_i)$, where $\mathcal{E}_1$ and $\mathcal{E}_2$ are fields from point defects and elastic dipoles, respectively.

The electric field from point defects with a charge $z_j e$ can be written in the usual form

$$\mathcal{E}_1(r_i) = \sum_j \frac{z_j e}{\varepsilon_0} \frac{|r_{ij}|}{r_{ij}^3}. \tag{3}$$

For lattices with a piezoeffect in the paraelectric phase the electric field $\mathcal{E}_2(r_i)$ of elastic dipoles has the form

$$\mathcal{E}_{2\alpha}(r_i) = \sum_{j,\beta,\gamma} d_{\alpha\beta\gamma} u_{\beta\gamma}(r_{ij}) \tag{4}$$

where $d_{\alpha\beta\gamma}$ are the piezoelectric tensor components and $u_{\beta\gamma}(r_{ij})$ are the components of the deformation tensor, created at the r_i point by elastic dipoles $\Omega_{\alpha\beta}$ situated at the points r_j. The relation between $u_{\beta\gamma}$ and $\Omega_{\beta\gamma}$ for the general case is cited in [14]. Below we shall limit ourselves to the most usual case of elastic dipoles as dilatation centres, because all point defects are dilatation centres, and consider only the dilatation properties of the elastic dipole, i.e. put $\Omega_{\alpha\beta} = \Omega_0 \delta_{\alpha\beta}$. The deformation tensor components in the isotropic approximation for a space without boundaries can be written in the form [14]

$$u_{\alpha\beta}(r_{ij}) = \frac{\Omega_0}{12\pi} \frac{1+\nu}{1-\nu} \frac{1}{r_{ij}^3} (\delta_{\alpha\beta} - 3m_\alpha m_\beta) \tag{5}$$

where $m = r_{ij}/r_{ij}$ and ν is Poisson's ratio. Note that in highly polarized dielectrics with soft modes the components of the deformation tensor at sufficiently high elastic dipole concentrations may contain terms of a constant sign proportional to $\exp(-2r/r_c)$ together with terms of type (5) [15]. In our work, however, we shall limit ourselves to the case of not very high concentrations when the deformation tensor components can be well described by equation (5).

3. Distribution function of random fields

The observable physical quantities for disordered ferroelectrics depend strongly on random field realizations and for their calculation it is necessary to introduce a distribution function of random fields.

This distribution function has the form

$$f(\boldsymbol{E}) = \overline{\langle\langle \delta(\boldsymbol{E} - \boldsymbol{E}(\boldsymbol{r}_i))\rangle\rangle} \tag{6}$$

where the bar denotes averaging over spatial configurations of random field sources, $\langle\langle \ldots \rangle\rangle$ means thermal averaging both over orientations and over the random field distribution so that the distribution function can be expressed through itself in a self-consistent manner. The value $\boldsymbol{E}(\boldsymbol{r}_i)$ is determined from equation (1). The calculation of $f(\boldsymbol{E})$ from equation (6) will be carried out by a statistical method widely used for the calculations of absorption lineshapes in radio and optical spectroscopy [16]. In the framework of this method we shall introduce the integral representation of the δ-function. We have from (6)

$$f(\boldsymbol{E}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp(\mathrm{i}\boldsymbol{E}\cdot\boldsymbol{\rho}) \overline{\left\langle\left\langle \exp\left(-\mathrm{i}\rho_\beta \sum_{m=1}^{k} E_{\beta m}\right)\right\rangle\right\rangle} \mathrm{d}^3\rho \tag{7}$$

where we use summation over repeated Greek indices and m is the number of random field sources (see (1)). If we can calculate the quantity under the averaging signs exactly, we would obtain a rigorous solution of the problem. Unfortunately we cannot calculate this quantity exactly and to calculate it we neglect the correlations in the impurity sites, i.e. we shall use the first-order statistical method [16]. This permits us to consider the impurities as independent sources of a random field so that for the mth source

$$\overline{\langle\langle \exp(-\mathrm{i}\rho_\beta E_{\beta m})\rangle\rangle} = \left(\frac{1}{V}\int_V \langle\langle \exp(-\mathrm{i}\rho_\beta E_{\beta m})\rangle\rangle \,\mathrm{d}V\right)^{N_m}$$

$$\equiv \left(1 + \frac{1}{V}\int_V \langle\langle \exp(-\mathrm{i}\rho_\beta E_{\beta m}) - 1\rangle\rangle \,\mathrm{d}V\right)^{N_m}$$

where N_m is the number of impurities of mth type and V is the crystal volume. Then we consider the conventional thermodynamic limit, i.e. put $n_m = N_m/V = \text{constant}$, while N_m, $V \to \infty$. This gives

$$\overline{\langle\langle \exp(-\mathrm{i}\rho_\beta E_{\beta m})\rangle\rangle} = \exp\left(n_m \int_V \langle\langle \exp(-\mathrm{i}\rho_\beta E_{\beta m}) - 1\rangle\rangle \,\mathrm{d}^3 r\right). \tag{8}$$

To be more specific, let us rewrite equations (7) and (8) in the form which explicitly takes into account k independent random field sources $E(r) = \sum_{m=1}^{k} E_m(r)$:

$$f(\boldsymbol{E}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left(\mathrm{i}\boldsymbol{E}\cdot\boldsymbol{\rho} - \sum_{m=1}^{k} F_m(\boldsymbol{\rho})\right)\mathrm{d}^3\rho \tag{9}$$

$$F_m(\boldsymbol{\rho}) = n_m \int_V \langle\langle \exp[-\mathrm{i}\boldsymbol{\rho}\cdot\boldsymbol{E}_m(\boldsymbol{r})] - 1\rangle\rangle \,\mathrm{d}^3 r \tag{10}$$

where $\boldsymbol{E}_m(\boldsymbol{r})$ is determined by equations (1)–(4) and n_m is the concentration of mth-type defects. To fulfil the self-consistent thermal averaging, let us take into account the fact that only random fields of electric dipoles determined by the first term in (1) depend on the direction $\boldsymbol{l}$.

Until now, only the case of two orientable dipoles has been considered in detail [17]; we shall make detailed calculations just in this model ($l_z = \pm 1, l_x = l_y = 0$). This model,

being relatively simple, gives a clear illustration of the influence of additional defects on the ferroelectric phase transition, induced by electric dipoles. At the same time, as analysis [16] has shown, the latter model gives a qualitatively correct description of the situation in dielectrics with electric dipole impurities.

Then the sign $\langle\langle \ldots \rangle\rangle$ means averaging over l directions with the one-particle Hamiltonian $\mathcal{H}_0 = l \cdot \boldsymbol{E}$, where $\boldsymbol{E}$ is the argument of function (9), and then averaging over $\boldsymbol{E}$. For two orientable dipoles this gives

$$\langle\langle \exp(-i\rho_z K^{zz} l_z) - 1 \rangle\rangle = \frac{\cosh[E_z/kT - iK^{zz}(r)\rho_z]}{\cosh(E_z/kT)}$$
$$\equiv \cos[K^{zz}(r)\rho_z] - 1 - i\tanh(E_z/kT)\sin[K^{zz}(r)\rho_z]. \tag{11}$$

Self-consistent averaging over $\boldsymbol{E}$ in (11) can be made by the substitution $\tanh(E_z/kT) = \langle l \rangle$ to $L_z \equiv L$, where

$$L = \int f(\boldsymbol{E}, L)\langle l \rangle \, d\boldsymbol{E} \tag{12}$$

is the ferroelectric phase transition order parameter [17] arising at $T = T_c$ (phase transition of the second order) or at the critical concentration of dipoles ($T = 0$).

It is seen from equations (10) and (11) that $F_m(\rho)$ are complex quantities so that $\mathrm{Re}[F_m(\rho)] = \int\{1 - \cos[\boldsymbol{E}_m(r) \cdot \rho]\}\, d^3r$ determines the width of the distribution function (random field dispersion), while $\mathrm{Im}[F_m(\rho)] = \int\{\sin[\boldsymbol{E}_m(r) \cdot \rho]\}\, d^3r$ determines the position of the distribution function maximum (most probable value of the random field). It follows from equation (9) that to obtain the distribution function it is necessary to calculate $F_m(\rho)$ by (10) for each type of random field source.

Substituting $\mathcal{E}_1(r)$ from (3) into (10) and calculating the integral, we obtain for point charge defects

$$\mathrm{Re}[F_1(\rho)] = \tfrac{32}{15} n_1 \left(\frac{\pi}{2}\frac{ze}{\varepsilon_0}|\rho|\right)^{3/2} \qquad \mathrm{Im}[F_1(\rho)] = 0. \tag{13}$$

Calculation of $F_2(\rho)$ for dilatation centres depends on the number of coefficients $d_{\alpha\beta\gamma}$ and hence on the lattice symmetry. For mixed crystals of the KDP family, only those $d_{\alpha\beta\gamma}$ for which α, β and γ are different, differ from zero, and $d_{zxy} \gg d_{xyz}, d_{yzx}$ (z is the polar axis) [18]. Calculations for this case with respect to equations (10), (4) and (5) give

$$\mathrm{Re}[F_2(\rho)] = \frac{\Omega_0}{9}\frac{1+\nu}{1-\nu} d_{zxy}|\rho| n_2 \qquad \mathrm{Im}[F_2(\rho)] = 0. \tag{14}$$

The fact that imaginary parts of $F_m(\rho)$ for these defects are equal to zero tells us that they make a contribution to random field dispersion only and thus should inhibit the creation of long-range order.

For electric dipoles we can find from (11) that

$$\mathrm{Re}[F_3(\rho_z)] = \int\{1 - \cos[K^{zz}(r)\rho_z]\}\, d^3r$$
$$\mathrm{Im}[F_3(\rho_z)] = L_z \int\{\sin[K^{zz}(r)\rho_z]\}\, d^3r. \tag{15}$$

The calculation of integrals (12) for K^{zz} in the form (2) for arbitrary values of the parameter $n_3 r_c^3$ were carried out numerically [7]; analytical calculation can be made in two limiting cases: $n_3 r_c^3 \ll 1$ and $n_3 r_c^3 \gg 1$ (Lorentzian and Gaussian limits, respectively, for the distribution function). In the first case the long-range order in the system with impurity electric dipoles does not appear even without defects of another type. That is why we shall consider the most interesting case of a Gaussian distribution function of electric dipole random fields, when a phase transition without defects of another type is firmly realized. In this case,

$$\mathrm{Re}[F_3(\rho_z)] = \frac{16\pi}{15}\frac{1}{r_c^3}\left(\frac{d^*\rho_z}{\varepsilon_0}\right)^2 n_3 \qquad \mathrm{Im}[F_3(\rho_z)] = 4\pi n_3 \frac{d^*\rho_z}{\varepsilon_0} L_z. \tag{16}$$

If both point charge defects and dilatation centres are present in the system, we can obtain by substitution of (13), (14) and (16) into (9) the following expression for the distribution function:

$$f(E) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp[\mathrm{i}(E_x\rho_x + E_y\rho_y) + \mathrm{i}\rho_z(E_z - E_0 L_z)]$$
$$\times \exp(-A|\rho|^{3/2} - B|\rho| - C\rho_z^2)\,\mathrm{d}\rho_x\,\mathrm{d}\rho_y\,\mathrm{d}\rho_z,\ E_0 = 4\pi\frac{n_3 d^*}{\varepsilon_0}$$

$$A = \frac{32}{15}\left(\frac{\pi}{2}\frac{ze}{\varepsilon_0}\right)^{3/2} n_1 \qquad B = \frac{\Omega_0}{9}\frac{1+\nu}{1-\nu} d_{zxy} n_2$$

$$C = \frac{16\pi}{15} n_3 r_c^3 \left(\frac{d^*}{\varepsilon_0 r_c^3}\right)^2 \qquad |\rho| = (\rho_x^2 + \rho_y^2 + \rho_z^2)^{1/2}. \tag{17a}$$

Since in our model the long-range order parameter is oriented along the z axis, we can convert in equation (17*a*) $|\rho| \to \rho_z$. Then it follows from (17*a*) that

$$f(E) = \delta(E_x)\delta(E_y) f_1(E_z)$$
$$f_1(E_z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp[\mathrm{i}\rho(E_z - E_0 L_z) - A|\rho|^{3/2} - B|\rho| - C|\rho|^2]\,\mathrm{d}\rho. \tag{17b}$$

In the general case the function $f_1(E_z)$ is a convolution of Gaussian, Lorentzian and Holtzmarkian distribution functions. This function was calculated numerically and tables of dependences of its parameters, namely the width, first moment and maximal amplitude, on A, B and C are presented in [16].

Here we shall make detailed calculations for the important case for disordered systems, when only one source of random fields, additional to electric dipoles, exists: either point charges or dilatation centres. For the first case we have to put $B = 0$ in (17*a*), and for the second case we have $A = 0$. Taking into consideration the characteristic expression for the aforementioned distribution functions convolution [16] given by

$$(\delta|\rho|)^{k_3} = (\eta|\rho|)^{k_1} + (\zeta|\rho|)^{k_2}$$

where η, ζ and δ are parameters characterizing the widths of the convoluted and resulting distribution functions, respectively, we can find that (putting $|\rho| = 1/\delta$)

$$\left(\frac{\eta}{\delta}\right)^{k_1} + \left(\frac{\zeta}{\delta}\right)^{k_2} = 1. \tag{18}$$

Comparison between (17*b*) and (18) gives $k_1 = 2$, $\eta = \sqrt{C}$, while $k_2 = \frac{3}{2}$, $\zeta = A^{2/3}$ or $k_2 = 1$, $\zeta = B$ for point charges and dilatation centres, respectively. So we can rewrite (18) for these two types of defect as follows:

$$\frac{C}{\delta^2} + \frac{A}{\delta^{3/2}} = 1 \qquad \frac{C}{\delta^2} + \frac{B}{\delta} = 1 \tag{19}$$

Equations (19) permits us to calculate quite easily the width δ of the resulting distribution function, which is a parameter of great importance.

Below we shall use these results to calculate the critical concentration and phase transition temperature.

4. Ferroelectric phase transition temperature and critical concentration

The phase transition temperature can be obtained from equation (12) as the temperature for which $L \neq 0$. Rewriting (12) for our model with two possible orientations of the vector l and taking into account that in this model $\langle l \rangle = \tanh(E/kT)$, we obtain

$$L = \int_{-\infty}^{\infty} \tanh\left(\frac{E}{kT}\right) f_1(E - E_0 L)\,\mathrm{d}E \tag{20}$$

where $E \equiv E_z$, $L \equiv L_z$. Putting $E - E_0 L = x$ in (20) and expanding the result near $T = T_c$ in the small parameter L up to the first non-vanishing term, we find the following equation for T_c:

$$\frac{T_c}{T_{cmf}} = \int_{-\infty}^{\infty} \frac{f_1(x)}{\cosh^2(x/kT_c)}\,\mathrm{d}x \tag{21}$$

where $T_{cmf} = E_0$ is the phase transition temperature in the mean-field approximation. Taking into account that the phase with long-range order exists at $T < T_c$ only, then this condition is the temperature criterion for the existence of long-range order. At $T_c \to 0$ we obtain from (21) the concentration criterion in the form

$$2E_0 f_1(0) \geqslant 1. \tag{22}$$

To obtain (22) from (21) we put $x/kT_c = y$ and took the limit $T_c \to 0$. The inequality in (22) reflects the fact that long-range order exists at $n_3 \geqslant (n_3)_{cr}$ only. The latter criterion includes two main parameters of the distribution function, which in turn are functions of the defect concentrations.

Substituting (17*b*) into (21) and integrating over x, we find the explicit form of equations for T_c:

$$\frac{1}{kT_c} = E_0 \int_0^{\infty} \frac{\rho \exp(-C\rho^2 - A\rho^{3/2})}{\sinh(\frac{1}{2}\pi kT_c\rho)}\,\mathrm{d}\rho \tag{23a}$$

$$\frac{1}{kT_c} = E_0 \int_0^{\infty} \frac{\rho \exp(-C\rho^2 - B\rho)}{\sinh(\frac{1}{2}\pi kT_c\rho)}\,\mathrm{d}\rho. \tag{23b}$$

Equations (23*a*) and (23*b*) determine the phase transition temperature for the cases when additional sources of random fields are point charges and dilatation centres, respectively.

The concentration criterion has the forms

$$\frac{2E_0}{\pi}\int_0^\infty \exp(-C\rho^2 - A\rho^{3/2})\,\mathrm{d}\rho \geqslant 1 \tag{24a}$$

$$\frac{2E_0}{\pi}\int_0^\infty \exp(-C\rho^2 - B\rho)\,\mathrm{d}\rho \geqslant 1. \tag{24b}$$

The integrals (23) and (24) were calculated numerically and the results are presented in figures 1 and 2 for the set of dimensionless parameters $\mu = A/C^{3/4}$, $\Delta = B/\sqrt{C}$ and $\lambda = E_0/\sqrt{\pi C}$. It can be easily seen from (24) that, without additional defects ($A = B = 0$), long-range order can appear only at $\lambda \geqslant 1$. That is why we used $0 \leqslant \lambda^{-1} \leqslant 1$ for the calculations. The case $\lambda^{-1} = 0$ at any values of μ and Δ corresponds to the mean-field approximation ($n_3 r_c^3 \to \infty$) and gives $T_c/T_{cmf} = 1$. It follows from (17a) that $\lambda^{-1} = (15 n_3 r_c^3)^{-1/2}$ and so to make the figures clearer we put one more scale in the units $n_3 r_c^3$.

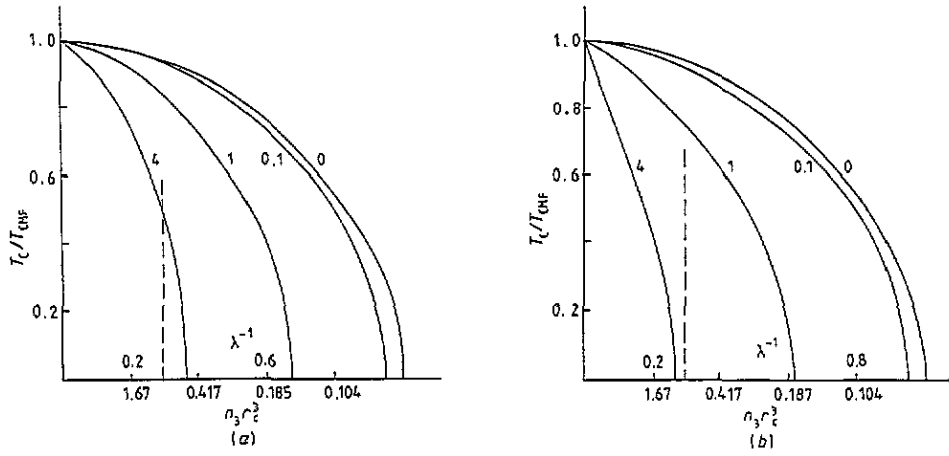

Figure 1. Phase transition temperature versus electric dipole concentration at different concentrations of (*a*) point charges and (*b*) dilatation centres. The numbers near the curves corresponds to values of μ in (*a*) and values of Δ in (*b*). For the meaning of vertical broken lines see the text.

Note that, while the parameter λ depends only on the dipole concentration n_3, the parameters μ and Δ depend not only on the concentration but also on the dipole moment d^*:

$$\mu = \frac{4\sqrt{\pi}}{15}\left(\frac{ze\lambda}{d^* n_3^{1/3}}\right)^{3/2}\frac{n_1}{n_3} \qquad \Delta = \frac{\Omega_0 d_{zxy}}{36\sqrt{\pi}}\frac{1+\nu}{1-\nu}\frac{\varepsilon_0\lambda}{d^*}\frac{n_2}{n_3}.$$

Thus for smaller values of the electric dipole moment the contribution of additional sources is larger. This makes it possible to obtain large values of μ and Δ even at small concentrations of additional sources.

It is seen from the figures that both point charges and dilatation centres have a similar qualitative influence to T_c and $(n_3 r_c^3)_{cr}$. So, with increase in n_1 or n_2 (increase in μ and

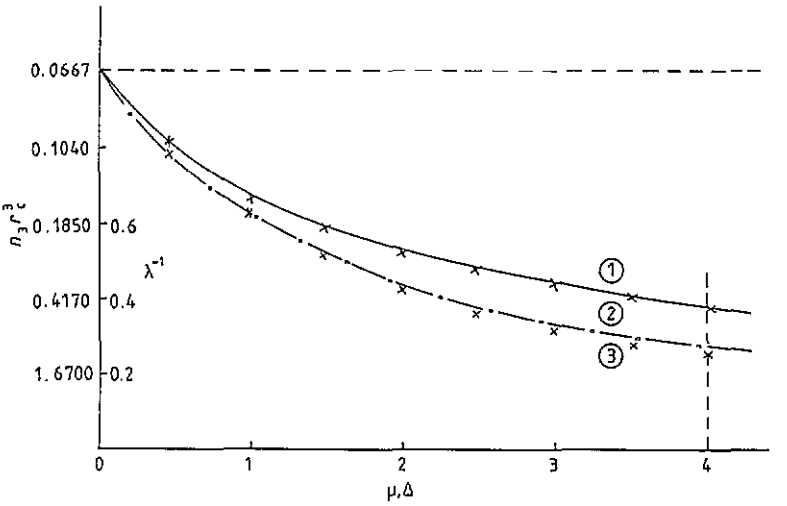

Figure 2. Critical concentration of electric dipoles versus μ (full curve) and Δ (chain curve). The horizontal broken line corresponds to the case $\mu = \Delta = 0$. Long-range order exists in regions 1, 2 and 3 at $\mu = \Delta = 0$, in the regions 2 and 3 at $\mu \neq 0$, $\Delta = 0$ and in region 3 at $\mu = 0$, $\Delta \neq 0$. The crosses on the curves represent the results of calculations using (24*a*) and (24*b*), respectively. The meaning of the vertical broken line is clear from the text.

Δ, respectively), T_c decreases and the critical concentration increases, but variations in the latter are larger for dilatation centres (compare full and chain curves in figure 2). It is also seen from figure 1 that for example for $\Delta = \mu = 4$ and a fixed concentration of electric dipoles, e.g. $\lambda^{-1} = 0.3$, the dilatation centres have destroyed long-range order, while point charges only make T_c approximately half its mean-field value (see the vertical broken lines in figure 1). We can suppose that the disappearance of long-range order at certain concentrations of defects of another type can qualitatively explain the absence of long-range order in ferroelectrics with a diffuse phase transition, for which concentrations of defects of another type are rather large. The vertical broken line in figure 2 shows that, for the same $\Delta = \mu = 4$, $(n_3 r_c^3)_{cr} \simeq 0.37$ for point charges and $(n_3 r_c^3)_{cr} \simeq 1.07$ for dilatation centres, while, in the absence of additional defects, $(n_3 r_c^3)_{cr} \simeq \frac{1}{15} \simeq 0.067$.

It follows that the critical concentration of electric dipoles can be changed by additional defects by more than one order of magnitude according to the experimental results for $K_{1-x}Li_xTaO_3$, where $(x_{Li})_{cr} \simeq 0.02$ was obtained [8], while calculation with respect to random fields of electric dipoles only and two possible orientations of the vector l gave $(x_{Li})_{cr} \simeq 0.001$ [7]. Thus the random fields created by dilatation centres destroy long-range order more effectively than do point charge fields. This could be due to the slower decrease in the Lorentzian function than in the Holtzmarkian function. In other words, the shorter the range of the fields induced by the additional source, the more strongly does it inhibit the long-range order.

Note that a critical concentration evaluation can be made with good accuracy on the basis of (19) without numerical integration in (24). Really, for the case of dilatation centres the width δ of the resulting distribution function can be written in the following explicit form (see (19)):

$$\delta = \sqrt{C}[\tfrac{1}{2}\Delta + (1 + \tfrac{1}{4}\Delta^2)^{1/2}]. \tag{25a}$$

For the case of point defects we have the equation

$$C + A\sqrt{\delta} - \delta^2 = 0. \tag{25b}$$

Taking into account the fact that for the occurence of long-range order the width of distribution function should not exceed the most probable field value E_0, we can obtain from (25*a*) the equation for the concentration criterion in the form

$$\lambda \geqslant \tfrac{1}{2}\Delta + (1 + \tfrac{1}{4}\Delta^2)^{1/2}. \tag{26a}$$

The same condition for point defects has the form $\lambda \geqslant \lambda_m$, where λ_m is determined from the equation

$$1 + \mu\sqrt{\lambda_m} - \lambda_m^2 = 0. \tag{26b}$$

Equations (26*a*) and (26*b*) describe correctly the cases $\Delta \to 0$ and $\mu \to 0$. The plots of λ^{-1} versus Δ and μ are shown by crosses on the corresponding curves in figure 2. There is very good coincidence between the results of calculations due to (26*a*) and (26*b*) and the more complicated formulae (24*a*) and (24*b*). Moreover, at large μ and Δ it follows from (24*a*) and (24*b*) that $\lambda^{-1} \leqslant 1.02\mu^{-2/3}$ and $\lambda^{-1} \leqslant 1.13\Delta^{-1}$, respectively, while in the same limiting case we obtain from (26*a*) and (26*b*) $\lambda^{-1} \leqslant \mu^{-2/3}$ and $\lambda^{-1} \leqslant \Delta^{-1}$, respectively. This means that the simplified approach (19) can be readily used to describe the concentration criterion for the realization of long-range order for arbitrary (and not only for small) values of parameters Δ and μ.

It should be noted also that, if several independent random field sources with distribution functions of the same shape are present in the host lattices, then A, B and C should be considered as the resulting parameters and $B = \sum_K B_k$, $C = (\sum_k C_k)^{1/2}$, $A = (\sum_k A_k)^{2/3}$, as follows from (18) and (19). The increase in the parameters A, B and C will lead to a decrease in T_c and an increase in the critical concentration, which is seen from the figures.

5. Conclusions

The main physical result of the present paper is as follows. The variety of phase transitions in disordered ferroelectrics with electric dipoles (impurities as in $KTaO_3$:Li or intrinsic as in PMN) is due to the presence in these ferroelectrics of a number of unavoidable defects, which create random electric fields additional to those of electric dipoles. The proof of this result was obtained by consideration of the influence of these additional defects and their fields on the ferroelectric long-range order induced by electric dipoles. We showed that, on increase in the contribution from these additional fields, $(n_3)_{cr}$ increases and T_c decreases, i.e. ferroelectric order inhibits, being replaced by the dipole glass state. In the n_3 range, where $T_c < T_{cmf}$, we have a mixed ferroglass phase, because in this range, even at $T = 0$, $L < 1$, which means that dipoles are not completely coherently oriented. Because additional defects increase the range where $T_c < T_{cmf}$, they promote the occurrence of a mixed state. Note that, as we showed, for shorter-range fields induced by defects, they have a larger influence on long-range order.

The calculations made above also explain the large difference between the $(n_3)_{cr}$-values measured and those calculated without consideration of the presence of additional defects in $KTaO_3$:Li. It follows from the aforementioned results that a sufficiently large contribution from the additional fields can completely inhibit ferroelectric order. This gives a qualitative explanation of the existence of only the dipole glass state in PMN. Quantitative results for crystals with a larger unavoidable defect content (e.g. PMN) when correlation effects become considerable can be obtained in the framework of the statistical theory of the second order [19] for distribution function calculation.

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References

[1] Vugmeister B E and Glinchuk M D 1990 *Rev. Mod. Phys.* **82** 993–1026
[2] Vakchrushev S B, Kvyatkovsky O E, Nabereznov A A, Okuneva N M and Toperverg B P 1989 *Physica* B **156–7** 90–2
[3] Viehland D, Li J F, Jang S J and Cross L E 1991 *Phys. Rev.* B **43** 8316–22
[4] Trybula Z, Schmidt V H and Drumheller J E 1991 *Phys. Rev.* B **41** 1287–90
[5] Vugmeister B E and Glinchuk M D 1980 *Zh. Eksp. Teor. Fiz.* 79 947–52 (Engl. Transl. 1980 *Sov. Phys.–JETP* **52** 482–4)
[6] Leung K M and Liu S T 1979 *J. Appl. Phys.* **50** 4471–5
[7] Vugmeister B E and Stephanovich V A 1987 *Solid State Commun.* **67** 323–7
[8] Kleemann W, Kutz S and Rytz D 1987 *Europhys. Lett.* **4** 239–43
[9] Vugmeister B E 1991 *Ferroelectrics* **120** 133–9
[10] Vugmeister B E and Glinchuk M D 1985 *Usp. Fiz. Nauk.* **146** 459–89 (Engl. Transl. 1985 *Sov. Phys.–Usp.* **28** 589–607)
[11] Stephanovich V A 1993 *Phys. Rev.* B **47** 9084–6
[12] Smolyaninov I M and Glinchuk M D 1994 *J. Phys.: Condens. Matter* **6** 2869–80
[13] Bonneau P, Garnier P, Calvarin G, Husson E, Gavarri J R, Hewat A W and Morell A 1991 *J. Solid State Chem.* **91** 350–9
[14] Kosevich A M 1972 *Osnovy Mekhaniki Kristallicheskoi Reshetki (Introduction to Crystalline Lattice Mechanics)* (Moscow: Nauka) (in Russian)
[15] Glinchuk M D and Smolyaninov I M 1988 *Fiz. Tverd. Tela* **30** 1197–9
[16] Glinchuk M D, Grachev V G, Deigen M F, Roitsin A B and Suslin L A 1981 *Elektrisheskie Effekty v Radiospektroskopii (Electrical Effects in Radiospectroscopy)* (Moscow: Nauka) (in Russian)
[17] Vugmeister B E and Stephanovich V A 1990 *Zh. Eksp. Teor. Fiz.* **97** 1867–81 (Engl. Transl. 1990 *Sov. Phys.–JETP* **70** 1053–60)
[18] Jona F and Shirane G 1962 *Ferroelectric Crystals* (New York: Macmillan)
[19] Stoneham A M 1969 *Rev. Mod. Phys.* **41** 82–170