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Phase transitions in disordered ferroelectrics with two types of random site electric dipole

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Abstract. Phase transitions in a highly polarizable crystal of cubic symmetry induced by two types of random site electric dipole orientated correspondingly along the [100]- and [111]-type directions are considered. The distribution function of random electric fields produced by these dipoles was calculated. This function made it possible to obtain the order parameters, the critical concentrations of dipoles and the transition temperatures for ferroelectric phase transitions with tetragonal and rhombohedral symmetries. All these quantities were calculated as functions of the ratio of dipole moments and the concentrations of the two types of dipole considered. It was shown that, at certain concentrations and dipole moment ratio, the order parameters of both aforementioned ferroelectric phases had to coexist. The mean values of random elastic fields produced by the random electric fields considered through the electrostriction effect are calculated. It was found that in crystals such as KTaO_3 the elastic fields of E_g symmetry may be larger than those of T_{2g} symmetry. The eight-well adiabatic potential of the cluster, which includes the impurity dipole and its nearest neighbours, was shown to be transformed into a six-well potential under the action of E_g symmetry deformations. This transformation was supposed to be the main reason for the tetragonal symmetry phase transitions observed earlier in $\text{K}_{1-\eta}\text{Li}_\eta\text{Ta}_{1-\xi}\text{Nb}_\xi\text{O}_3$ ($\eta \leq 0.06$; $\xi \leq 0.028$) even at very low lithium ion concentrations. The calculation of the transition temperature confirmed this supposition and made it possible to explain qualitatively the transition temperature concentrational dependence observed in the aforementioned mixed disordered system.

1. Introduction

At present, investigations of the disordered ferroelectrics have attracted much attention because many problems concerning the physical nature of the various phase transitions in these materials are still far from solution (see e.g. [1–3], and references therein). It was shown recently [4–6] that random electric and elastic fields produced by unavoidable defects and impurities in disordered ferroelectrics influence strongly the transition temperature and critical concentration of electric dipoles, which induce the ferroelectric phase transition. The distribution function of these random fields was shown to determine the distribution function of relaxation times and thus the dynamic dielectric susceptibility [7]. Random site point charges and dilatation centres [4], elastic dipoles [5] and electric dipoles [6, 7] were considered as the sources of the random electric fields. These random fields were shown to destroy the long-range order induced by electric dipoles of one type only, e.g. those pointing along either [100]- or [111]-type directions. Meanwhile there are a great number of disordered ferroelectrics in which several types of random site electric dipole coexist and thus they tend to induce long-range order along the orientations of their moments. This means that they tend to establish ferroelectric phases of different symmetries (tetragonal or

rhombohedral for [100]- or [111]-type dipole moment orientations, respectively). Examples of such materials are numbers: $K_{1-\eta}Li_{\eta}Ta_{1-\xi}Nb_{\xi}O_3$ (KLTN), $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $Pb_{1-\eta}La_{\eta}Zr_{1-\xi}Ti_{\xi}O_3$ (PLZT), $PbZr_{1-\eta}Ti_{\eta}O_3$ (PZT), $KH_2P_{1-\eta}As_{\eta}O_4$, etc. In PMN (a ferroelectric with a diffused phase transition) the niobium, lead and even oxygen ions were shown to produce electric dipoles with [111]-, [110]- and [100]-type orientations [8]. The existence of polarization along the [111]- or [100]-type directions produced by the zirconium or titanium sublattices as well as the coexistence of these polarizations in a definite range of η (morphotropic region) in PZT and PLZT is well known [9, 10]. The competition between the two types of long-range order with different symmetries is the main reason for the phase diagram peculiarities in the mixed systems of the KDP family [11, 12]. Incipient ferroelectric $KTaO_3$ doped with Li^+ and Nb^{5+} ions (KLTN system) can be considered as the model system with two types of electric dipole. Each type of dipole is able to induce ferroelectric phases with tetragonal symmetry at $\eta > \eta_{cr}$, $\xi = 0$, or rhombohedral symmetry at $\xi > \xi_{cr}$, $\eta = 0$ (see [3, 13]). Unfortunately information about the properties of the KLTN system is poor (see [14], and references therein). It was shown [14] that even a small addition of lithium ions transforms the rhombohedral phase induced by niobium ions into a tetragonal phase. In this work we shall consider a system such as $KTaO_3$ with two types of independent electric dipole with their dipole moments oriented along the [100]- or [111]-type directions. In the framework of the first-order statistical theory [15], the distribution function of electric fields produced by these dipoles will be calculated. This function made it possible to calculate the transition temperature, critical concentrations and order parameters for two types of ferroelectric phase symmetry. It will be shown that for a certain ratio of electric dipole moments the above-mentioned order parameters coexist in a definite range of dipole concentrations. The observed transformation of the rhombohedral-symmetry ferroelectric phase into the tetragonal phase in KLTN was explained by supposing that the deformation of E_g symmetry, produced by Li^+ ions, transforms the eight-well Nb^{5+} potential into a six-well potential. Calculations of the transition temperature confirmed this supposition and made it possible to explain qualitatively the transition temperature concentration dependence observed for KLTN [14].

2. The competition between the two types of ferroelectric ordering

Let us consider a highly polarizable medium with a soft mode such as $KTaO_3$ with two types of electric dipole, the first being oriented along six of the [100]-type directions and the second along eight of the [111]-type directions. Their dipole moments are d_1 and d_2 , respectively, and their concentrations n_1 and n_2 , respectively. It was shown earlier [1] that in the system with dipoles of one type ($n_1 \neq 0, n_2 = 0$, or $n_2 \neq 0, n_1 = 0$) at concentrations higher than the critical value ($n_1 > n_{1cr}$ or $n_2 > n_{2cr}$) the ferroelectric phase has to appear at $T = T_{c1}$ or $T = T_{c2}$, its symmetry being tetragonal or rhombohedral, respectively. One can expect that the addition of another type of dipole influences n_{cr} , T_c and the order parameter of the phase transition induced by the previous type of dipole and can induce ferroelectric order with another symmetry. This type of mutual influence of the dipoles may result in competition between two types of ferroelectric phase symmetry as well as between the ferroelectric phase and dipole glass state. The main way in which this mutual influence can be shown is the appearance of additional random electric fields produced by another type of electric dipole, which has to change the distribution function of the internal electric fields in the system.

Since all the physical quantities in the ferroelectric disordered systems depend strongly on the form and parameters of the distribution function, we shall begin with its calculation.

Both types of dipole can be considered as independent sources of random electric fields if their concentration is small enough, so that it is possible to neglect the correlation effects. In this case the distribution function calculation can be carried out in the framework of a statistical method of the first order [15]. Calculations similar to those described in [5] give for the distribution function $f(E)$:

$$f(E) = \frac{1}{(2\pi)^3} \int \int \int_{-\infty}^{+\infty} \exp[iE\rho - F_1(\rho) - F_2(\rho)] d^3\rho \quad (1)$$

$$F_k(\rho) = n_k \int \langle \langle \exp[-i\rho \cdot E_k(r)] - 1 \rangle \rangle d^3r \quad (2)$$

where $k = 1, 2$ and $\langle \langle \exp[-i\rho \cdot E_k(r)] - 1 \rangle \rangle$ means thermal averaging both over dipole orientations and over the distribution of the random fields. Thus the distribution function is expressed through itself in a self-consistent manner.

The electric field $E(r_i)$ produced by the dipoles of one type at the point r_i can be represented in the form [1]

$$E_\alpha(r_i) = - \sum_{j,\beta} \frac{d^{*2}}{\varepsilon_0} [f_1(r_{ij})\delta_{\alpha\beta} + (3k_\alpha k_\beta - \delta_{\alpha\beta})f_2(r_{ij})] \quad (3)$$

$$k_\alpha = \frac{r_{ij}^\alpha}{r_{ij}} \quad f_1(x) = \frac{2}{3} \frac{\exp(-x/r_c)}{xr_c^2} + \frac{4\pi}{3V} \quad (4)$$

$$f_2(x) = \frac{1}{x^3} \left[1 - \exp\left(-\frac{x}{r_c}\right) \left(1 + \frac{x}{r_c} + \frac{x^2}{3r_c^2} \right) \right] \quad (5)$$

where ε_0 , r_c and V are the pure crystal dielectric permittivity, the correlations radius and the volume, respectively. d^* is the effective dipole moment given by $d^* = \gamma(\varepsilon_0 - 1)/3$, where γ is the Lorentz field factor, which depends on the lattice site.

Since until now only the case of two-orientable dipoles has been considered in detail [16], we shall make the detailed calculations just in this model ($l_{1z} = \pm 1$, $l_{1x} = l_{1y} = 0$, $l_{2z'} = \pm 1$, $l_{2x'} = l_{2y'} = 0$, where l is the unit vector of the dipole moment orientation, and z and z' correspond to the [001] and [111] directions, respectively). In spite of this model's simplicity, it gives a qualitatively correct description of physical properties in dielectrics with electric dipoles [16].

Even for two-orientable dipoles the calculation of integral (1) in the case of one type of dipole with $E_z(r)$ in the form (3)–(5) for arbitrary values of nr_c^3 was carried out numerically [17]. Analytical calculation can be done in two limiting cases only: $nr_c^3 \ll 1$ and $nr_c^3 \gg 1$ (Lorentzian and Gaussian limits, respectively). In the first case, long-range order does not appear because the half-width of the distribution function turns to be larger than the most probable electric field value [1]. That is why we shall carry out all the calculations in the Gaussian limit for the distribution function.

In this case, calculations of integrals (2) yield

$$\begin{aligned} F_1(\rho_z) &= \exp(-\xi_1 \rho_z^2 - iE_{01} L_1 \rho_z) \\ F_2(\rho_{z'}) &= \exp(-\xi_2 \rho_{z'}^2 - iE_{02} L_2 \rho_{z'}). \end{aligned} \quad (6)$$

Here

$$L_1 = \overline{\langle\langle d_1^* \rangle\rangle} / d_1^* \quad (7a)$$

$$L_2 = \overline{\langle\langle d_2^* \rangle\rangle} / d_2^* \quad (7b)$$

are the numbers of coherently oriented dipoles (the bar means averaging over spatial disorder, and the angular brackets have the same meaning as in (2)), i.e. L_1 and L_2 are the dimensionless order parameters of ferroelectric phase transitions with tetragonal and rhombohedral symmetries, respectively.

The other parameters in equation (6) have the form:

$$\begin{aligned} \xi_1 &= \frac{16\pi n_1 d_1^{*4}}{5 \varepsilon_0^2 r_c^3} & \xi_2 &= \frac{2\pi n_2 d_2^{*4}}{3 \varepsilon_0^2 r_c^3} \\ E_{01} &= \frac{4\pi}{\varepsilon_0} n_1 d_1^{*2} & E_{02} &= \frac{4\pi}{\varepsilon_0} n_2 d_2^{*2}. \end{aligned} \quad (8)$$

The calculation of the order parameters L_k ($k = 1, 2$) determined by (7a) and (7b) was carried out by integration over random electric fields with the help of the distribution functions (1) and (6), i.e. L_k was represented as a sixfold integral over $d^3\rho d^3E$. After thermal averaging with respect to the two dipole orientations and the transformation of the z' axis into the x, y, z axes by rotation of the axes between the z' and z axes by the angle ($\cos(z'z) = 1/\sqrt{3}$; $\sin(z'z) = \pm\sqrt{2/3}$) the integration yields

$$L_k = \frac{1}{\beta} \int_0^\infty \frac{\exp[-\rho^2(\xi_k + \frac{1}{3}\xi_{k'})] \cos(E_{0k'} L_{k'} \rho / \sqrt{3}) \sin(E_{0k} L_k \rho)}{\sinh(\pi\rho/2\beta)} d\rho. \quad (9)$$

Here $\beta = 1/k_B T$, $k \neq k'$ and $k, k' = 1, 2$. It is easy to see that (9) can be transformed correctly to the equation for order parameter in the case where there is one type of dipole ($n_1 \neq 0, n_2 = 0$, or $n_1 = 0, n_2 \neq 0$) (see e.g. [16]):

$$\begin{aligned} L_k &= \frac{1}{\beta} \int_0^\infty \frac{\exp(-\xi_k \rho^2) \sin(E_{0k} L_k \rho)}{\sinh(\pi\rho/2\beta)} d\rho \\ L_{k'} &= 0 \quad (n_k \neq 0, n_{k'} = 0). \end{aligned} \quad (10)$$

In the general case, L_k is a function of n_1, n_2, d_1^* and d_2^* , and thus the transition temperatures and critical concentrations of dipoles must depend on these parameters. So, at $n_1 \neq 0, n_2 \neq 0$, it should be competition between two order parameters if $L_1 \neq 0$ and $L_2 \neq 0$. Existence of the ferroelectric phase with tetragonal or rhombohedral symmetries depends on the ratio of the transition temperatures T_{c1} to T_{c2} and of the critical concentrations n_{cr1} to n_{cr2} . For example, if $T_{c1} > T_{c2}$, tetragonal long-range order will appear; at $T_{c1} = T_{c2}$, both order parameters coexist. Let us proceed to the calculations of T_{ck} and $(n_k)_{cr}$.

3. Transition temperatures and critical concentrations

The transition temperature can be obtained from (9) at $L_k \rightarrow 0, L_{k'} \rightarrow 0$, which gives

$$\begin{aligned} \beta_{ck} &= E_{0k} \int_0^\infty \frac{\exp(-\rho^2 \lambda_{kk'}) \rho d\rho}{\sinh(\pi\rho/2\beta_{ck})} \\ \lambda_{kk'} &= \xi_k + \frac{1}{3}\xi_{k'}. \end{aligned} \quad (11)$$

Here $T_{c1} = 1/k_B\beta c_1$ and $T_{c2} = 1/k_B\beta c_2$ correspond to the appearances of L_1 and L_2 , respectively.

In the mean-field approximation, equation (11) takes the simple form

$$(\beta_k)_{CMF} = \frac{1}{E_{0k}} \quad (12)$$

which coincides with the equation for one type of dipole. This result tells us that there may be only one type of long-range order in the mean-field approximation. That is because it is impossible to reach simultaneously the concentrations of both dipole types sufficient for the realization of the mean-field approximation. The critical concentration value can be obtained from equation (11) at $T_{ck} \rightarrow 0$. In this limit, one obtains

$$\sqrt{\pi\lambda_1} = E_{01} \quad (13a)$$

$$\sqrt{\pi\lambda_2} = E_{02}$$

$$\lambda_1 = \xi_1 + \frac{1}{3}\xi_2 \quad (13b)$$

$$\lambda_2 = \xi_2 + \frac{1}{3}\xi_1.$$

Equations (13) determine the critical concentration n_{cr} of one type of dipole as a function of another type of dipole concentration, the quantities n_{1cr} and n_{2cr} being the concentrations at which L_1 and L_2 , respectively, appear.

For numerical calculations we rewrite (9), (11) and (13) in dimensionless parameters as follows:

$$L_1 = \tau^{(1)} V_{11} T_{12} \quad (14a)$$

$$L_2 = \tau^{(2)} V_{22} T_{21}$$

$$1 - \tau_c^{(1)} (V_{11})^2 T_{11} = 0 \quad (14b)$$

$$1 - \tau_c^{(2)} (V_{22})^2 T_{22} = 0$$

$$T_{kk'} = \int_0^\infty \frac{\exp(-t^2) \sin(V_{kk} L_k t) \cos(V_{k'k} L_{k'} t / \sqrt{3}) dt}{\sinh(\pi t V_{kk} \tau^{(k)} / 2)} \quad k \neq k' \quad (14c)$$

$$T_{kk} = \int_0^\infty \frac{\exp(-t^2) t dt}{\sinh(\pi t V_{kk} \tau^{(k)} / 2)}$$

$$\frac{V_{11}}{\sqrt{\pi}} = \frac{x \Delta^2}{\sqrt{x \Delta^4 + \frac{25}{192} y}} \quad \frac{V_{22}}{\sqrt{\pi}} = \frac{y}{\sqrt{y + \frac{64}{75} x \Delta^4}} \quad (14d)$$

$$\frac{V_{12}}{\sqrt{\pi}} = \frac{x \Delta^2 \sqrt{3}}{\sqrt{x \Delta^4 + \frac{75}{64} y}} \quad \frac{V_{21}}{\sqrt{\pi}} = \frac{y \sqrt{3}}{\sqrt{y + \frac{192}{25} x \Delta^4}}$$

$$\frac{x_{cr} \Delta^2}{\sqrt{x_{cr} \Delta^4 + \frac{25}{192} y}} = 1 \quad \frac{y_{cr}}{\sqrt{y_{cr} + \frac{64}{75} x \Delta^4}} = 1 \quad (14e)$$

$$\Delta = \frac{d_1^*}{d_2^*} \quad x = \frac{z_1}{z_1^0} \quad y = \frac{z_2}{z_2^0} \quad z_k = n_k r_c^3 \quad (14f)$$

Here $z_k^0 = (z_k)_{cr}$ are the dimensionless critical concentrations when there is only one type of electric dipole, i.e. $z_1^0 = 1/15$ and $z_2^0 = 1/24$.

The definition of dimensionless temperatures is as follows:

$$\tau^{(k)} = \frac{kT}{E_{0k}} = \frac{T}{T_{CMF}^{(k)}} \quad (15)$$

$$\frac{\tau^{(1)}}{\tau^{(2)}} = \frac{5}{8} \frac{y}{x\Delta^2} = \alpha. \quad (16)$$

It is seen from (14e) that x_{cr} or y_{cr} increased when $y \neq 0$ or $x \neq 0$, respectively. This means that the addition of another type of dipole makes the conditions for realization of ferroelectric phase transition (induced, of course, by the first type of dipole) more severe. One can expect that at some values of x , y and Δ it may turn out that $x_{cr} = y_{cr}$ and $T_c^{(1)} = T_c^{(2)}$, so that the order parameters L_1 and L_2 have to coexist. Since such coexistence seems to be the most interesting part of the phase diagram, we shall begin with the consideration of this case.

It follows from (15) and (16) that $T_c^{(1)} = T_c^{(2)}$ at $\alpha = 1$ and $\tau_c^{(1)} = \tau_c^{(2)}$. The latter can be obtained at $V_{11} = V_{22}$ (see (14b) and (14c)) which gives the following connection between the parameters Δ and α :

$$\Delta^2 = \frac{5}{8} \alpha \frac{-\alpha^2 + 3}{-1 + 3\alpha^2}. \quad (17)$$

The condition $\alpha = 1$ leads to $\Delta^2 = 5/8$ and $x = y$ (see (17) and (15)).

On the other hand, because $\alpha > 0$, $\Delta^2 > 0$, the numerator and denominator in (17) must have the same signs, which is possible if

$$\frac{1}{\sqrt{3}} < \alpha < \sqrt{3}. \quad (18)$$

Since for all α in this region $T_c^{(1)}/T_c^{(2)} = 1/\alpha$ (see (16)), so that $T_c^{(1)} > T_c^{(2)}$ at $1 > \alpha > 1/\sqrt{3}$ or $T_c^{(2)} > T_c^{(1)}$ at $1 < \alpha < \sqrt{3}$, thus the ferroelectric order with order parameters L_1 or L_2 , respectively, should appear. At $\Delta^2 = 5/8$ and $\alpha = 1$, it follows from (14d) and (14e) that $x_{cr} = y_{cr}$ and $L_1 = L_2$ because $V_{11} = V_{22} = V_{12} = V_{21}$. Note that this peculiar point corresponds to $n_1/n_2 = 8/5$, i.e. for the coexistence of phases $n_1/n_2 = (d_2^*/d_1^*)^2$.

To check whether $\Delta^2 = 5/8$ is the only point with the coexistence of phases, we carried out a numerical calculation of the critical concentrations as functions of each other. This was done by solving the system of equations (14e) with respect to x_{cr} and y_{cr} at arbitrary Δ -values. The results are depicted in figure 1. It is seen that $\Delta = \Delta_0 = \sqrt{5/8}$ is really the only point where $x_{cr} = y_{cr}$. If $\Delta < \Delta_0$, then $y_{cr} < x_{cr}$ or if $\Delta > \Delta_0$, then $x_{cr} < y_{cr}$ so that the ferroelectric order of rhombohedral or tetragonal symmetries, respectively, appears. The dependence of the critical concentration of one type of dipole on the concentration of another type of dipole for several Δ^2 is depicted in figure 2. It is seen that the addition of the second type of dipole inhibits the ferroelectric phase induced by the first type of dipole. This influence is strongly dependent on the dipole moment ratio.

The transition temperatures $\tau_c^{(1)}$ and $\tau_c^{(2)}$ (14b) in the form $\tau_c = f(V/\sqrt{\pi})$ are presented in figure 3. Keeping in mind that $\tau_c^{(1)}$ depends only on V_{11} and that $\tau_c^{(2)}$ depends only on V_{22} , one can obtain the $\tau_c^{(1)}$ and $\tau_c^{(2)}$ dependences on the dipole concentrations and Δ by changing the scale of the abscissa axis on the base of (14d). As an example we gave two

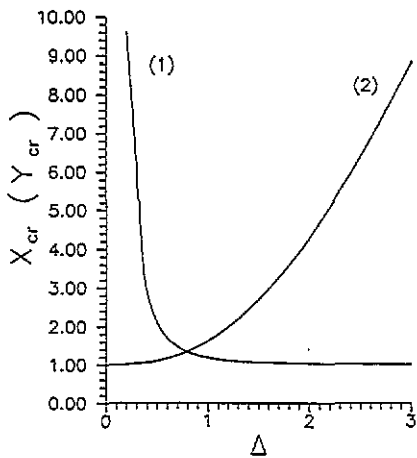


Figure 1. Dependences of the critical concentration x_{cr} of one type of dipole (curve (1)) and the critical concentration y_{cr} of another type of dipole (curve (2)) on their dipole moment ratio $\Delta = d_1^+/d_2^+$.

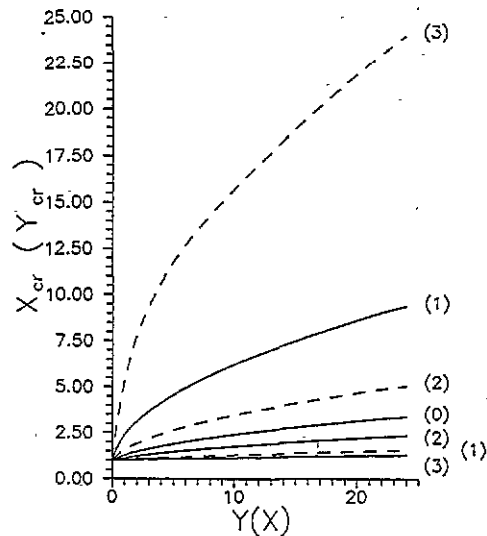


Figure 2. Dependences of the critical concentration of one type of dipole on the concentration of another type of dipole for different Δ -values: curve (0), $\Delta^2 = 5/8$; curve (1), $\Delta^2 = 0.2$; curve (2), $\Delta^2 = 1$; curve (3), $\Delta^2 = 3$; —, x_{cr} ; ---, y_{cr} .

extra scales for the special cases $x \neq 0$, $y = 0$ or *vice versa* and $x = y$, $\Delta^2 = 5/8$. It follows from (14d) that, for any Δ -value, V_{11} increases when x increases or y decreases and *vice versa* for V_{22} . Since τ_c increases on increasing V , it follows from figure 3 and (14d) that $\tau_c^{(1)}$ increases and $\tau_c^{(2)}$ decreases with increasing x . Thus the points of intersection of the $\tau_c^{(1)}$ and $\tau_c^{(2)}$ curves may lead to $T_c^{(1)} = T_c^{(2)}$ in certain regions of x -, y - and Δ -values (coexistence of L_1 and L_2). This region is expected to be near the point $x_{cr} = y_{cr}$ in figure 1. As an example we represent the $\tau_c^{(1)}$ and $\tau_c^{(2)}$ concentrational dependences for $\Delta = 1$ in figure 4. It is seen that $T_c^{(1)} = T_c^{(2)}$ near the points $x \approx 1, 4$, $y = 2$ and $x \approx 2$, $y = 3$; meanwhile this equality appeared to be invalid for $y = 5$.

The temperature and concentrational dependences of the order parameters L_1 and L_2 can be obtained by solving equations (14a) for $x > x_{cr}$, $y > y_{cr}$ (see figure 1) and $\tau < \tau_c$ for any Δ -value.

4. Influence of the elastic fields induced by one type of dipole on the multiwell potential of another type of dipole

Off-centre impurity ions are known to be random site electric dipoles in the lattices such as KTaO_3 . The rotational motion of the dipoles can be described by a multiwell potential with, for example, eight or six minima. It was shown [15] that the adiabatic potential of a cluster which includes an off-centre ion and its nearest neighbours can be represented in the form

$$W = \frac{m\omega^2 R^2}{2} - \sqrt{\delta^2 + a^2 R^2} - \frac{a[(c-b)(R_x^4 + R_y^4 + R_z^4) + bR^4]}{\sqrt{\delta^2 + a^2 R^2}}. \quad (19)$$

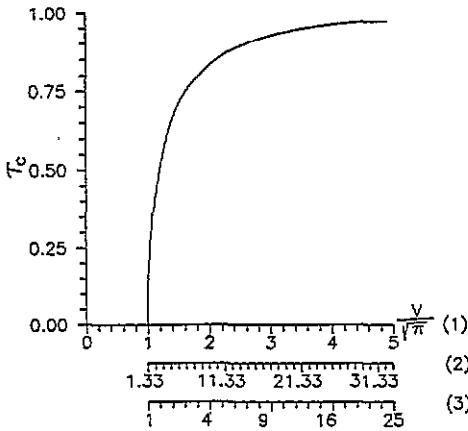


Figure 3. Dependences of the transition temperatures $\tau_c^{(1)}$ and $\tau_c^{(2)}$ of the ferroelectric phase of tetragonal and rhombohedral symmetries on the parameter V (see (14d)) (scale (1)) the dipole concentrations for $x = y$, $\Delta = \Delta_0 = \sqrt{5}/8$ (scale (2)) and the concentration of one type of dipole, i.e. $x \neq 0$, $y = 0$, or $y \neq 0$, $x = 0$ (scale (3)).

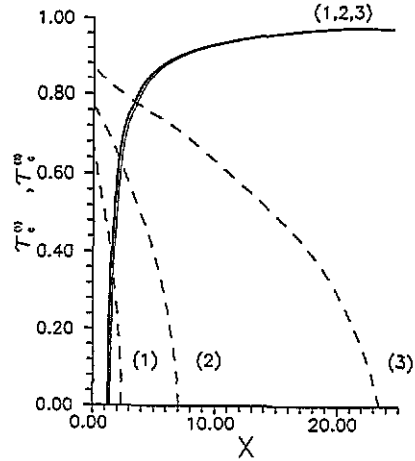


Figure 4. Concentrational dependences of $\tau_c^{(1)}(x)$ (—) and $\tau_c^{(2)}(x)$ (---) for $y = 2$ (curves (1)), $y = 3$ (curves (2)) and $y = 5$ (curves (3)) with $\Delta = 1$.

Here R , m and ω are the off-centre ion displacement, mass and oscillational frequency, respectively; $\pm\delta$ are the energies of two cluster electronic levels ψ_1 and ψ_2 with opposite parities; $a = \langle \psi_1 | (\partial V / \partial R_\alpha) | \psi_2 \rangle$ (V is the potential of the electron-ion interaction); c and b are connected with cluster anharmonicity and are determined by $\langle \psi_1 | (\partial^3 V / \partial R_\alpha^3) | \psi_2 \rangle$ and $\langle \psi_1 | [\partial^3 V / (\partial R_\alpha \partial^2 R_\beta)] | \psi_2 \rangle$ ($\alpha, \beta = x, y, z$). The number of minima of (19) can be obtained by the conventional differential method. When the electronic levels considered are sufficiently close ($\delta < a^2/m\omega^2$), (19) has a maximum at $R_x = R_y = R_z = 0$ and minima on the surface of the sphere with radius $R_0 = (a^2/m^2\omega^4 - \delta^2/a^2)^{1/2}$ if $c = b = 0$. Anharmonicity produces barriers for these freely orientable dipoles; thus, if $a(c - b) < 0$ or $a(c - b) > 0$, we obtained eight or six minima, respectively, which correspond to dipole orientations along [111]- or [100]-type directions.

The same minima were produced by even-parity cluster deformation [15]. In the case of T_{2g} and E_g deformations the adiabatic potential has the same form as (19) even without the contribution from anharmonicity, but we have to replace $c - b$ by $c_1 - b_1$, where

$$c_1 - b_1 = c_0 \left(\frac{9A_1^2}{2\kappa_{E_g}} - \frac{A_2^2}{\kappa_{T_{2g}}} \right). \quad (20)$$

Here $c_0 > 0$, $A_1 = \langle \psi_{2\alpha} | (\partial V / \partial Q_{E_g}) | \psi_{2\alpha} \rangle$, $A_2 = \langle \psi_{2\alpha} | (\partial V / \partial Q_{T_{2g}}) | \psi_{2\alpha} \rangle$, Q_{E_g} , κ_{E_g} and $Q_{T_{2g}}$, $\kappa_{T_{2g}}$ are the normal coordinates, the elastic modulus of E_g and T_{2g} symmetries, respectively. It follows from (20) that, if the contribution of E_g deformation is larger than that of T_{2g} , there should be six minima and, when the T_{2g} contribution is larger than the E_g contribution, there should be eight minima. One can suppose that in the cases of the shallow minima produced by cluster anharmonicity the addition of the elastic field sources, e.g. impurities, can change the number of potential minima, i.e. the directions of electric dipoles. The electric dipoles can be considered as the sources of these elastic fields because

the random electric fields induced by the electric dipoles have to be transformed into elastic fields through the electrostriction effect in cubic crystals.

Let us proceed to calculate the elastic fields of E_g and T_{2g} symmetry induced by the two types of electric dipole considered to find out whether the deformations produced by one of them can change the potential shape of another type of dipole.

The normal coordinates of E_g and T_{2g} symmetry deformations can be written for cubic crystals in the form

$$\begin{aligned} Q_{E_g} &= (q_1 - q_2)(\bar{E}_x^2 - \bar{E}_y^2) \\ Q_{E_{2g}} &= (q_1 - q_2)(2\bar{E}_z^2 - \bar{E}_x^2 - \bar{E}_y^2) \\ Q_{T_{2g}}^{\alpha\beta} &= q_3 \overline{E_\alpha E_\beta} \end{aligned} \quad (21)$$

where $q_1 = q_{\alpha\alpha\alpha\alpha}$, $q_2 = q_{\alpha\alpha\beta\beta}$, and $q_3 = q_{\alpha\beta\alpha\beta}$ ($\alpha \neq \beta$) are the electrostriction constants. Bars denote averaging with the random electric field distribution function. This function is determined from equations (1), (6) and (8).

After transformation of the z' axis into the x, y, z axes in (6) by their rotation by the angle between the z and z' axes, integration of (1) gives the distribution function as a function of E_x, E_y, E_z , which makes it possible to calculate \bar{E}_α^2 and $\overline{E_\alpha E_\beta}$. They can be represented in the form

$$\begin{aligned} \bar{E}_x^2 &= \bar{E}_y^2 = \frac{1}{3}(E_{02}^2 L_2^2 + 2\xi_2) \\ \bar{E}_z^2 &= 2\xi_1 + E_{01}^2 L_1^2 + \bar{E}_x^2 \pm E_{01} L_1 \bar{E}_x \\ \overline{E_x E_z} &= \overline{E_y E_z} = E_{01} L_1 \bar{E}_x \pm \bar{E}_x^2 \quad \bar{E}_x = \frac{E_{02} L_2}{\sqrt{3}} \\ \overline{E_x E_y} &= \bar{E}_x^2 \end{aligned} \quad (22)$$

where the signs \pm relate to the cases of acute and obtuse angles, respectively, between the [001] and [111] directions at which the double-well potentials are chosen.

The substitution of (22) into (21) shows that $Q_{E_g} = 0$ and that $Q_{E_{2g}}/Q_{T_{2g}}$ has the form

$$\begin{aligned} \frac{Q_{E_{2g}}}{Q_{T_{2g}}^{xy}} &= \frac{6(q_1 - q_2)}{q_3} \frac{(E_{01}^2 L_1^2 + 2\xi_1 \pm 2E_{01} L_1 (E_{02} L_2)/\sqrt{3})}{E_{02}^2 L_2^2 + 2\xi_2} \\ \frac{Q_{E_{2g}}}{Q_{T_{2g}}^{yz}} &= \frac{6(q_1 - q_2)}{q_3} \frac{(E_{01}^2 L_1^2 + 2\xi_1 \pm 2E_{01} L_1 (E_{02} L_2)/\sqrt{3})}{\sqrt{3} E_{01} E_{02} L_1 L_2 \pm (E_{02}^2 L_2^2 + 2\xi_2)} \end{aligned} \quad (23)$$

Taking into account (8), (14f) and (15), one can rewrite (23) through the dipole dimensionless concentrations x, y and α :

$$\begin{aligned} \frac{Q_{E_{2g}}}{Q_{T_{2g}}^{xy}} &= \frac{6(q_1 - q_2)}{q_3} \frac{1}{\alpha^2} \frac{L_1^2 + 6/\pi x \pm 2\alpha L_1 L_2/\sqrt{3}}{L_2^2 + 2/\pi y} \\ \frac{Q_{E_{2g}}}{Q_{T_{2g}}^{yz}} &= \frac{6(q_1 - q_2)}{q_3} \frac{1}{\alpha^2} \frac{L_1^2 + 6/\pi x \pm 2\alpha L_1 L_2/\sqrt{3}}{\sqrt{3} L_1 L_2/\alpha \pm (L_2^2 + 2/\pi y)} \end{aligned} \quad (24)$$

It is seen that, in the case of one type of dipole, i.e. $x \neq 0, y = 0$ or $x = 0, y \neq 0$, $Q_{E_{2g}} \gg Q_{T_{2g}}$ or $Q_{T_{2g}} \gg Q_{E_{2g}}$, respectively. This is because the dipoles oriented along

the [001]- or [111]-type directions induce the E_g or T_{2g} deformations, respectively. In the general case $x \neq 0$, $y \neq 0$, there may be a sufficiently wide region of x -, y - and α -values when $Q_{E_{2g}} > Q_{T_{2g}}$ at $x > y$, $\alpha < 1$, as well as at $x < y$, $\alpha > 1$, because the factor $6(q_1 - q_2)/q_3$ may be large enough for incipient ferroelectrics with the perovskite structure (see e.g. [18, 19]). On the other hand even in the case unfavourable for E_{2g} deformations, $x < y$, $x < x_{cr}$ ($L_1 = 0$), $y \gg y_{cr}$ ($L_2 \neq 0$, $L_2 \approx 1$) the factor in (24) which depends on x , y , and α tends to $5x\Delta^4/y^2$ and so it may be not much less than 1 at some Δ -values. At the peculiar point $x > x_{cr}$, $y > y_{cr}$, $\Delta^2 = 5/8$, $x = y$, $L_1 = L_2$ (see section 3) this factor is larger than 1. Thus one can expect that under some conditions the eight-well potential will be transformed into a six-well potential, so that both types of dipole will be oriented along [001]-type directions. In this case the system may have only one transition temperature τ_c and order parameter L , which can be calculated similarly to section 3. They have the following forms:

$$L = \tau V \int_0^\infty \frac{\exp(-t^2) \sin(VLt) dt}{\sinh(\pi t V \tau / 2\beta)} \quad (25a)$$

$$1 - \tau_c V^2 \int_0^\infty \frac{\exp(-t^2) t dt}{\sinh(\pi t V \tau_c / 2\beta)} = 0 \quad (25b)$$

$$\frac{V}{\sqrt{\pi}} = \frac{x\Delta^2 + y}{\sqrt{x\Delta^4 + y}}$$

$$\tau = \frac{T}{T_{CMF}} \quad k_B T_{CMF} = E_{01} + E_{02}. \quad (25c)$$

The definition of dimensionless concentrations are $x = z_1/z_1^0$, $y = z_2/z_1^0$ (see (14f) and (15)); the condition $V/\sqrt{\pi} = 1$ gives the critical concentration value. It is seen that (25a) and (25b) have the same form as in the case of one type of dipole, but their parameters depend on both the dipole concentrations and the dipole moment ratio $\Delta = d_1^*/d_2^*$.

5. Discussion

Let us begin with the experimental results obtained for KTaO_3 doped with Li and Nb ions [14]. Raman scattering and optical depolarization measurements on $\text{K}_{1-\eta}\text{Li}_\eta\text{Ta}_{1-\xi}\text{Nb}_\xi\text{O}_3$ KLTN with $\xi \leq 0.028$ and $\eta \leq 0.06$ have shown that the addition of Li to $\text{KTa}_{1-\xi}\text{Nb}_\xi\text{O}_3$ destabilizes the niobium-induced rhombohedral ferroelectric phase and changes its symmetry to tetragonal down to a very low Li concentration (0.025 at.%). These experimental results can be explained if E_{2g} deformations appeared to be larger than those of T_{2g} symmetry. A large value of the factor $6(q_1 - q_2)/q_3$ (about 20 in KTaO_3 [19]) in (24) favours such a possibility. On the other hand, Nb eight-well potential minima in KTN are known to be sufficiently shallow (the height of barrier is about 100 K [20]). Thus one can suppose that in KLTN both Li^+ and Nb^{5+} dipoles are six-orientable with dipole moments along one of the [001]-type directions. The dimensionless transition temperature τ_c can be calculated with the help of (25b). Its concentrational dependence is displayed in figure 5 for the case $\Delta = 1$.

It is seen that τ_c increases with increase in dipole concentrations. Meanwhile, in the case of eight-orientable Nb dipoles induced by them the transition temperature $\tau_c^{(2)}$ decreases with Li concentration increase contrary to the case of orientation of the same dipoles

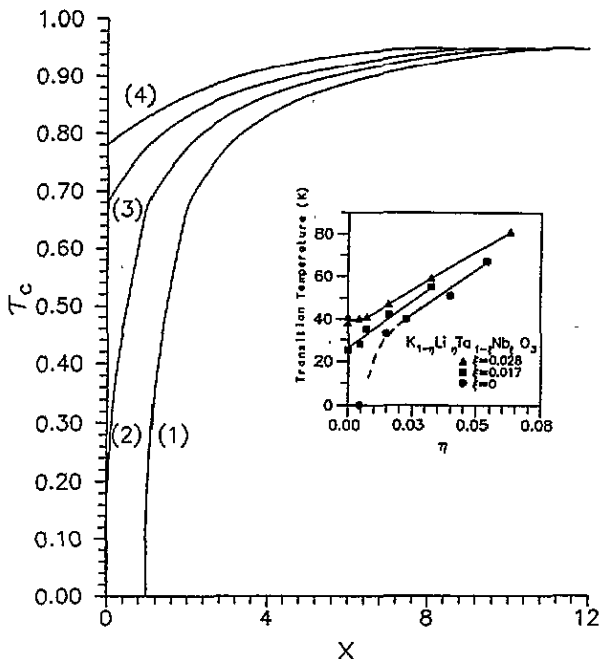


Figure 5. Concentrational dependence of $\tau_c(x)$ for $y = 0$ (curve (1)), $y = 1$ (curve (2)), $y = 2$ (curve (3)) and $y = 3$ (curve (4)) with $\Delta = 1$, in the case when both dipoles are oriented along the [001] direction. The inset represents the experimental results [14].

(compare figures 4 and 5). Thus one can suppose that for $x < 1$ it can be the region where $\tau_c(x)$ decreases and then begins to increase when the eight-well potential transforms into the six-well potential, i.e. $\tau_c(x)$ will have a minimum; the probability of appearance of this minimum increases with increase in Nb concentration. In our view the difference in behaviour observed in [14] for $T_c(\eta)$ for $\xi = 0.017$ and 0.028 at Li concentrations less than the critical value ($\eta_{cr} \approx 0.02$ [21]) favours this supposition. Indeed, $T_c(\xi = 0.017)$ increases but $T_c(\xi = 0.028)$ is constant at $\eta \leq 0.01$ (see inset in figure 5). So we can suppose that the τ_c minimum appears at $\xi > 0.028$, where the contribution of rhombicity has to increase. However, we have to emphasize that there are different opinions about the pure KTN phase diagram, namely about the Nb concentration value ξ_0 , corresponding to the rhombohedral-tetragonal phase transition: $\xi_0 = 0.05$ [2] and $\xi_0 = 0.03$ [3]. If the latter value is correct, the behaviour of $T_c(\eta, \xi)$ at $\xi > 0.028$ will look like figure 5 without any plateau at $\eta < 0.01$. In the case when $\xi_0 > 0.03$ it may be the minimum discussed earlier. It follows from figure 5 that the behaviour of the concentrational dependences of the calculated transition temperatures at $y = 0$ (pure KTL system), $y > 1$ ($y_{cr} = 1$ for pure KTN) and the observed dependences are in qualitative agreement.

Note that, in the dimensionless transition temperature $\tau_c = T_c/T_{cMF}$, the T_{cMF} -value depends on the concentration (see section 3). In particular, T_{cMF} increases linearly with concentration increase. This can explain the smaller rate of $\tau_c(x)$ increase in comparison with $T_c(\eta)$ (see inset to figure 5). This rate also depends on $\Delta = d_1^*/d_2^*$. So the ratio $T_c^{y \neq 0}/T_c^{y=0} = (\tau_c^{y \neq 0}/\tau_c^{y=0})(1 + y/x\Delta^2)$ ($x > 1$, $y > 1$) may be useful for Δ determination by fitting the observed and calculated values. To fit the experimental and dimensionless theoretical concentration scales we used the observed critical concentration value ($\eta_{cr} \approx 0.02$

and $\xi_{cr} \approx 0.01$ [13, 21]). With these fitting parameters the aforementioned procedure gives $\Delta = d_1^*/d_2^* \approx 2.5$, i.e. the transformation of the Nb eight-well potential to the six-well potential also leads to a change in the Nb dipole moment.

In other disordered systems such as PMN, PZT and PLZT the number of electric dipoles is large, i.e. the calculations have to take into account correlation effects (e.g. in the framework of the statistical theory of second order [15]). However, the coexistence of tetragonal and rhombohedral order parameters obtained at $x = y$, $\Delta^2 = 5/8$ (see section 3) may be supposed to have something to do with the morphotropic region observed in PZT when the Zr and Ti concentrations are close to each other. On the other hand, such systems as KTaO_3 doped with several impurities with electric dipole moments can be considered as a model system for more complicated disordered ferroelectrics (e.g. PMN).

Additional theoretical and experimental investigations are extremely desirable to check this calculation forecast and to clear up the many puzzles concerning various disordered systems.

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