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A random field theory based model for ferroelectric relaxors

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Abstract. A model for ferroelectric relaxors such as PMN, PSN and PLZT giving a quantitative description of their properties and phase diagrams is proposed within the framework of the random field theory. In this model, the relaxors are considered as systems with random sites and orientations of electric dipoles, lattice vacancies, antisite ions and other defects as well as impurities embedded into the paraelectric phase, which is proposed to be the ‘host’ lattice for these materials.

The calculations of the temperature T_c which corresponds to the transition from the paraelectric to the ferroelectric phase is carried out as a function of the concentration of lattice defects (point charges and dilatational centres). On the basis of these calculations, the peculiarities of the ferroelectric relaxor phase diagram are discussed. The main features of the phase transition sequence when decreasing the temperature in relaxors with constant dipole and defect concentrations are described.

The Cross superparaelectric model and Burns temperature T_d have been shown to appear in a natural way in the proposed model.

A comparison between calculated and experimental data has been made for the model ferroelectric relaxor PLZT $x/65/35$. Fairly good agreements between calculated and measured $T_c(x)$ and critical concentrations of lanthanum have been obtained from the model.

1. Introduction

Relaxor ferroelectrics are numerous. They belong to the family of disordered materials and most particularly to the group of mixed-cation ferroelectrics of perovskite structure with general chemical formula $A_{1-x}A'_x B_{1-y}B'_y O_3$. The most intensively studied relaxors are $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $PbSc_{1/2}Ta_{1/2}O_3$ (PST), $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) and $Pb_{1-x}La_x Zr_{1-y}Ti_y O_3$ (PLZT $x/1 - y/y$). The relaxors PMN and PST, PSN are representatives of the 1:2 and 1:1 groups respectively. The relaxor properties of 1:2 systems were shown to be independent of technology; meanwhile it appeared possible to prepare 1:1 compounds with any level of order and disorder, i.e. with any mixture of the materials with conventional ferroelectric and relaxor properties depending on technological conditions (see [1, 2] and references therein).

At first glance PLZT $x/1 - y/y$ seems to be more complex due to disorder both on A and B cation sublattices. However, the existence of PLZT materials with any content of Ti and Zr ($0 < y < 1$) for many x values makes it possible to investigate systems with different levels of order which seems to be important for clearing up the nature of disordered

systems and their property anomalies. So far, PLZT has been shown to be a relaxor for several x and y values of a given temperature region. As judged from the published phase diagram [3] and different property measurements [4] the compositions $x/65/35$ begin to exhibit significant relaxor character only for $x \gtrsim 5$. This 65/35 series with rhombohedral symmetry of the ferroelectric phase at $x = 0$ has been extensively studied [5–8]. The series with tetragonal symmetry of the ferroelectric phase for $x = 0$ has been shown to behave like a relaxor only above $x = 12$ (see [9] and references therein).

The most important feature of relaxors is known to be dielectric permittivity dispersion, which cannot be described using a conventional Debye relaxation with only one relaxation time. The existence of long-time (up to infinity) relaxation modes seems to be the peculiar feature of any relaxor. As a result, many anomalies of relaxor material properties can be observed in these systems. For instance, in contrast to ordinary ferroelectrics many properties show a maximum within a broad temperature region located around $T = T_m$, where T_m corresponds to the maximum in the real part of the dielectric permittivity, i.e. the transition is referred to as ‘diffused’. Due to the property anomalies, relaxor materials find a variety of applications as ceramics, particularly as electrostrictive actuators and capacitor dielectrics [10].

In spite of the great effort which has been applied to the understanding of the origin and mechanisms of the relaxor property anomalies, this problem has not been cleared up to date.

Firstly Smolenskii and coworkers [11] proposed that the origin of the phase transition diffuseness in PMN could be related to chemical heterogeneities which result in a smearing of local Curie temperatures. Some years later, Burns and Dacol [12] showed that only short-range order polar clusters would be present, i.e. the system could be considered as a dipole glass rather than a ferroelectric with a distribution of local regions with long-range order. Nowadays a large number of experimental data speak in favour of a dipole glass state in relaxors (see e.g. [1], [6], [13] and [14]). However some measurements were discussed in the framework of long-range ferroelectric order (see e.g. [15]). In our opinion, this discrepancy is related to the lack of any quantitative description of the phenomena in relaxors, which makes it difficult to pour light on the origin and driving forces of dipole glass or ferroelectric phase appearance. More likely chemical heterogeneities, random sites and orientation of electric dipoles, unavoidable lattice defects such as vacancies of lead, oxygen and antisite ions etc as the sources of random electric field distribution in any disordered ferroelectric play a crucial role in the phase diagram and the particular properties of these materials [16–19].

In the present work we propose for the first time a model of relaxor ferroelectrics based upon the random field theory. A comparison between calculated and experimental data will be performed for PLZT $x/65/35$ relaxor ferroelectrics.

2. The model

It is well known that many properties of ordinary ferroelectrics can be explained within the framework of the mean-field approximation. In this approach, any ion of the lattice ‘feels’ the same average field induced by other lattice ions. Due to this, at $T < T_c$, where T_c is the ferroelectric phase transition temperature, ions are shifted in the same way, giving rise to macroscopically large regions called domains, the size of which is mainly fixed by electrostatic energy considerations. In contrast to this description, in disordered ferroelectrics with random sites and orientations electric dipoles, lattice defects and unavoidable impurities, a distribution of random fields has to be introduced, i.e.

different ions 'feel' different random electric fields induced by other lattice ions, defects and impurities. It is clear that the physical properties of such a system have to be calculated in this case using this distribution function, and more particularly its maximum position and width, being defined by average E_0 and mean squared electric field ΔE respectively. The indirect interaction between random site electric dipoles through the soft mode of the 'host' lattice has been shown [20] to be the source of constant-sign electric field, i.e. non-zero average field which tends to order the system. This field is defined by the dipole subsystem characteristics (concentrations, dipole moment values and orientations) as well as the 'host' lattice parameters (dielectric permittivity and correlation radius). Direct dipole-dipole interactions, point charges, dilatational centres etc are known to be the sources of alternating-sign electric fields and contribute to the distribution functions width [16, 19]. It is clear that the average field has to be larger than its dispersion (i.e. $E_0 \gg \Delta E$) for long-range order appearance with a non-zero order parameter P , where P is the average polarization. In the opposite case, i.e. $E_0 \ll \Delta E$ or $E_0 \leq \Delta E$, a dipole glass or mixed ferroglass phase with coexistence of long- and short-range orders can appear.

These suppositions were confirmed by the calculations of phase diagram characteristics of model disordered systems such as $K_{1-x}Li_xTaO_3$ with the help of the random field distribution function [16–19, 21] i.e. in the random field theory framework. In KTL as well as in KTN ($KTa_{1-x}Nb_xO_3$) and KTNa ($K_{1-x}Na_xTaO_3$), Li, Nb and Na ions are known to be off-centre ions, i.e. random electric dipoles in the incipient ferroelectric $KTaO_3$ host lattice [22, 23]. Vacancies of oxygen, potassium and unavoidable impurities were supposed to be the additional sources of random electric fields.

To find out whether a similar random field theory approach can be applied to the calculations of relaxor ferroelectric properties, one has to know whether they can be considered as systems of electric dipoles and other random electric field sources. The question arises of what material should be considered as the host lattice.

Let us begin with PLZT $x/1 - y/y$ relaxor ferroelectric. We suppose that $PbZr_{1-y}Ti_yO_3$ (PZT) paraelectric phase can be considered as the host lattice for PLZT. It is well known that a conventional ferroelectric transition occurs in PZT on cooling, the temperature of which depends on the y value. In this phase all PZT cations are shifted from their equilibrium position in the paraelectric phase, i.e. all of them can be considered as electric dipoles embedded in the paraelectric phase. It was shown recently through NMR measurements [24] that in both PZT and PLZT the values of the ionic displacements are distributed in a wide region around average shifts. In our opinion this phenomenon is the consequence of the random substitution of Zr for Ti and vice versa for any y value, which corresponds only to an average titanium concentration. Keeping in mind that the relative concentration of the configurations with k ions of Ti as nearest neighbours of any Zr or Ti ion can be written as

$$P_6^k = [6!/k!(6-k)!]y^k(1-y)^{6-k} \quad k = 1, \dots, 6 \quad (1)$$

one can see that the probabilities of having configurations with $k = 1, 2, 3$ are close to one another; meanwhile the probability of having $k = 6$ or 0 is much smaller than the most probable value P_m (e.g. for $y = 0.35$, $P_m = 0.328$, which corresponds to $k = 2$). The distribution of ions around any cation and lattice defects may result in a y -dependent random distribution of both values and directions of the cation displacements in contrast to what happens for the end members of the PZT diagram, $PbTiO_3$ and $PbZrO_3$, for which the same values of the displacements of all Ti or Zr and Pb ions along [100] or [111] and [110] type directions respectively take place. The peculiarities of the PZT phase diagram [25] seem to speak in favour of random sites and orientations of the electric dipoles in PZT. Though it is cumbersome to estimate the parameters of the dipole distribution, the

existence of an ordinary (i.e. without dielectric dispersion) ferroelectric phase transition in PZT gives evidence that the average electric field is larger than its dispersion. The La ions in PZT induce random electric fields which tend to destroy the PZT long-range order. PLZT can thus be considered as a system constituted of electric dipoles, La ions and different defects embedded in the PZT paraelectric phase. Among these defects should be mentioned vacancies of Pb, Zr and Ti as well as dipole pairs $\text{La}^{3+}(\text{Pb}^{2+})\text{--}\text{La}^{3+}(\text{Zr}^{4+} \text{ or } \text{Ti}^{4+})$, the concentration of all these defects being dependent upon La concentration (the notation $\text{A}^{n+}(\text{B}^{p+})$ represents an A^{n+} ion substituted for a B^{p+} ion). The essential influence of La ions on the PLZT conductivity up to the changing of p-type into n-type at 6–8% La in PLZT $x/52/48$ [27] speaks in favour of the La influence on other defects. The existence of Ti^{3+} ions and of $\text{La}^{3+}(\text{Pb}^{2+})\text{--}\text{Ti}^{3+}(\text{Ti}^{4+})$ dipoles can also be supposed at least in illuminated samples [28, 29].

The relaxors belonging to the 1:1 group (e.g. PSN and PST) may have an ordinary ferroelectric phase transition dependent on the sample preparation technology. Assuming that in all samples the paraelectric phase is the same, we propose to consider it as the host lattice in the random field model of the 1:1 group of relaxors. Unfortunately nothing is known about a ferroelectric–paraelectric phase transition in any material of the 1:2 group of relaxors (see however section 4 in this paper). We can only assume that in PMN it might be somewhere near 900 or 600 K where Pb or Nb ion displacements appear respectively [1]. In PMN all the ions, including oxygen, are shifted from their equilibrium positions in the ideal perovskite structure, i.e. they are electric dipoles in the host lattice. Their orientations are shown to be one of the following: [111] for Nb and Mg, [110] for Pb and [100] for O [1, 26]. NMR measurements [26] gave evidence that the values of Nb and Pb dipole moments were also distributed.

The main defects of other types in these materials are vacancies of Pb and O and antisite ions (e.g. Nb substituted for Mg and vice versa). Since local polarization in PMN is along [111] it has to be induced by Nb(Mg) ions [14]. Under these conditions lead and oxygen dipoles may be considered as defects which tend to destroy [111] type polarization and to order the system in their own directions [17].

3. Order parameter and transition temperature in the random field theory

The ferroelectric phase transition order parameter in the random field theory can be represented as [16]

$$L = \int_{-\infty}^{\infty} \langle l \rangle f(\mathbf{E}, L) d\mathbf{E}. \quad (2)$$

Here $L = \overline{\langle \langle d^* \rangle \rangle} / d^*$ is a dimensionless order parameter which characterizes the number of coherently oriented dipoles (the bar denotes averaging over spatial disorder and brackets signify both quantum statistical averaging over possible dipole orientations and self-consistent averaging over random electric fields). $d^* = d\gamma(\epsilon_0 - 1)/3$ is the effective dipole moment, γ is the Lorentz factor, ϵ_0 is the host lattice static permittivity and $\langle l \rangle$ is the quantum statistical average of the dimensionless single dipole moment $l = d^*/d^*$. The distribution function $f(\mathbf{E}, L)$ has been calculated in the statistical theory framework by averaging over spatial configurations of random field sources [30] as well as thermal averaging both over orientations and the random field distribution function so that it is expressed through itself in a self-consistent manner. The ferroelectric phase transition order parameter has to arise at $T = T_c$ (second-order phase transition) or at a critical

concentration of defects at zero temperature. The transition temperature can thus be obtained from expression (2) at the limit where $\mathbf{L} \rightarrow \mathbf{0}$.

In the simplest model with two possible orientations of the vector \mathbf{l} ($l_z = \pm 1$, $l_x = l_y = 0$), its thermal average value $\langle l \rangle = \tanh(E/kT)$ and the distribution function $f(E, L) = f(E - E_0L)$ where $L \equiv L_z$, $E \equiv E_z$ and E_0 is the most probable random electric field value. Therefore expression (2) can be rewritten in the form

$$L = \int_{-\infty}^{\infty} \tanh(E/kT) f(E - E_0L) dE. \tag{3}$$

Expanding the result near $T = T_c$ in the small parameter L up to the first non-vanishing term we obtain the equation for T_c :

$$T_c/T_{cmf} = \int_{-\infty}^{\infty} f(x)/\cosh^2(x/kT_c) dx \tag{4}$$

where $T_{cmf} = E_0$ is the phase transition temperature in the mean field approximation. It should be noted that the obtained equations are valid also for dipoles with eight possible orientations, e.g. of the [111] type, if a factor $\sqrt{3}$ is entered into expression (4) (see for instance [21]).

The form of the distribution function $f(x)$ is strongly dependent on the form of the electric fields (created by the other dipoles, lattice defects and impurities) which act on the considered dipole. We have calculated it in the framework of the statistical theory of first order allowing for a linear electric field contribution. For independent sources of the random fields the calculations similar to those in [16] yield

$$f(x) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \exp\left(i\mathbf{E} \cdot \mathbf{t} - \sum_m^k F_m(\mathbf{t})\right) dt \tag{5}$$

$$F_m(\mathbf{t}) = n_m \int \langle \langle \exp(-i\mathbf{t} \cdot \mathbf{E}_m(\mathbf{r})) - 1 \rangle \rangle d^3r. \tag{6}$$

Here n_m and $E_m(\mathbf{r})$ are respectively the concentration and electric field of m th type defects. Since angular brackets in (6) include the averaging over possible dipole orientation it is essential when $E_m(\mathbf{r})$ is the field of electric dipoles. In the crystals with soft modes it has the form [22]

$$E^\alpha(\mathbf{r}) = - \sum_\beta \frac{d^{*2}}{\epsilon_0} [f_1(\mathbf{r})\delta_{\alpha\beta} + (3q_\alpha q_\beta - \delta_{\alpha\beta})f_2(\mathbf{r})] l^\beta \tag{7}$$

$$\begin{aligned} f_1(\mathbf{r}) &= \frac{2}{3} (\exp(-r/r_c)/rr_c^2) + 4\pi/3V & \mathbf{q} &= \mathbf{r}/r \\ f_2(\mathbf{r}) &= (1/r^3)[1 - \exp(-r/r_c)(1 + r/r_c + r^2/3r_c^2)] \end{aligned} \tag{8}$$

where r_c and V are the host lattice correlation radius and volume respectively, $\alpha, \beta = x, y, z$. The complex form of field (7) allows us to make an analytical calculation of the distribution function in the two limiting cases $nr_c^3 \ll 1$ (Lorentzian limit) and $nr_c^3 \gg 1$ (Gaussian limit) where n is the dipole concentration. Since at $nr_c^3 \gg 1$ the ferroelectric phase transition induced by electric dipoles in the host lattice without defects of other types is firmly realized we shall consider the case of the Gaussian distribution function form when $\text{Re}F_1(\mathbf{t}) \sim t^2$, $\text{Im}F_1(\mathbf{t}) = E_0Lt$. Note that the Gaussian limit seems to be valid for relaxor ferroelectrics, e.g. PLZT $x/65/35$, in which at $x = 0$ a ferroelectric phase transition occurs. Keeping in mind La^{3+} in PLZT, let us assume that additional defects in the lattice are point charges and dilatational centres, their fields being respectively

$$E_1^\alpha = (Ze/\epsilon_0)q_\alpha/r^2 \tag{9}$$

$$E_2^\alpha = \sum_{\alpha\beta} p_{\alpha\beta\gamma} U_{\beta\gamma}(r) \quad (10)$$

$$U_{\beta\gamma} = (\Omega_0/12\pi)[(1+\nu)/(1-\nu)]l/r^3(\delta_{\alpha\beta} - 3q_\alpha q_\beta)$$

where Ze and Ω_0 are the point defect charge and elastic moment, and $p_{\alpha\beta\gamma}$ and ν are the host lattice piezoelectric tensor component and Poisson coefficient respectively.

Substitution of (9) or (10) into (6) and integration leads to $F_2(t) \sim |t|^{3/2}$ or $F_3(t) \sim |t|$ [30], i.e. a Holtzmarkian or Lorentzian form of distribution function for point charges or dilatational centres respectively. As a result the distribution function can be represented in the following form:

$$f(E - E_0L) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[it(E - E_0L) - A|t|^{3/2} - B|t| - Ct^2] dt \quad (11)$$

Here $E \equiv E_z$, $L \equiv L_z$, $E_0 = 4\pi nd^*/\varepsilon_0$, $A = \frac{32}{15}((\pi/2)Ze/\varepsilon_0)^{3/2}n_1$, $B = (\Omega_0/9)[(1+\nu)/(1-\nu)]pn_2$ and $C = (16\pi/15)nr_c^3(d^*/\varepsilon_0r_c^3)^2$ where n_1 and n_2 are the concentrations of point charges and dilatational centres respectively. In order to take into account all the defects already mentioned in section 2 we have to consider A , B and C in expression (11) as the global parameters $B = \sum_k B_k$, $C = \sum_k C_k$ and $A = \sum_k A_k$ where k enumerates the sources of the same type, B_k , C_k and A_k being proportional to the concentration of the k th type of defect. Because of the lack of information about these concentrations we shall consider one type of electric dipole, point charge or dilation centre. Substituting (11) into (3) and (4) and integrating over x we find the explicit form for T_c

$$1/kT_c = E_0 \int_0^\infty \frac{\exp(-Ct^2 - At^{3/2} - Bt) dt}{\sinh((\pi/2)kT_c t)}. \quad (12)$$

We have to underline that transition temperature T_c at which the long-range order parameter L appears was calculated in the random local field theory framework [21], which is more general than the mean-field approximation. In the latter approximation $kT_{cmf} = E_0$, i.e. to the most probable random field value.

The results of the numerical calculation of the integral (12) are reported in figures 1 and 2 for point charges ($B = 0$) or dilatational centres ($A = 0$) respectively. At any constant concentration of electric dipoles dimensionless parameters $\mu = A/C^{3/4} = (4\sqrt{\pi}/15)(Ze\lambda/d^*n)^{3/2}n_1$ and $\Delta = B/C^{1/2} = (\Omega_0/36\sqrt{\pi})P[(1+\nu)/(1-\nu)](\varepsilon_0\lambda/d^*n)n_2$ are proportional to the concentration of point charges n_1 and dilatational centres n_2 respectively. The parameter $\lambda = \sqrt{15}nr_c^3$ is the measure of the nr_c^3 value. It is seen from figures 1 and 2 that increasing defects concentration decreases the T_c/T_{cmf} ratio more strongly than decreasing nr_c^3 (compare this ratio for $\mu = \Delta = 0$ with the values for points $\mu \neq 0$, $\Delta \neq 0$). Note that L increases smoothly with increasing λ and at $T_c = T_{cmf}$ all the dipoles have to be coherently oriented ($L = 1$) [18], i.e. T_c/T_{cmf} can be considered as the measure of the coherently oriented dipoles. The decrease in this ratio with Δ or μ increasing is larger for small nr_c^3 values, and dilatational centres influence it more strongly than point charges do (compare figures 1 and 2). The $\mu = \mu_c$ or $\Delta = \Delta_c$ values at which $T_c = 0$, corresponding to critical concentrations of point charges n_{1c} or dilatational centres n_{2c} are reported in figure 3. At critical concentration of defects (e.g. La^{3+} in PLZT) the ferroelectric phase transition with long-range order is completely destroyed ($T_c = 0$, $L = 0$). At $n_1 > n_{1c}$ or $n_2 > n_{2c}$ a dipole glass state appears. We have to underline that for dipole glass property description we have to consider dynamic order parameter $L(\omega)$, which can be obtained from expression (2) allowing for a Debye-like single dipole l relaxation with barriers depending upon random electric fields. This approach makes it possible to describe $\varepsilon(\omega)$ behaviour without introducing any relaxation time distribution function [18]. However

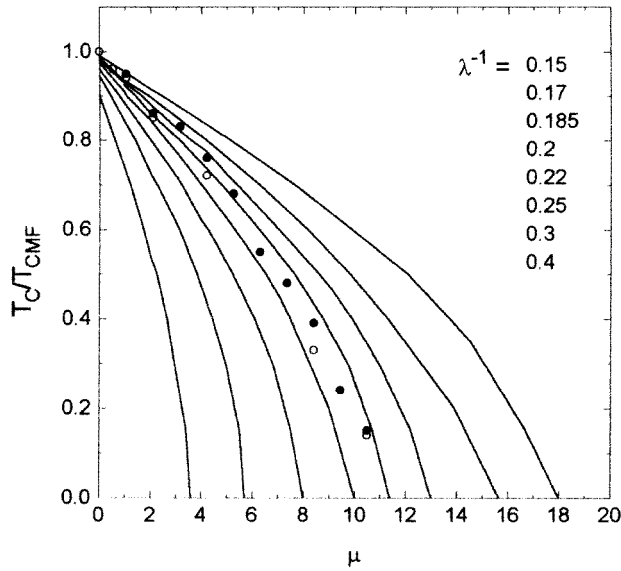


Figure 1. The dependence of the ratio T_c/T_{cmf} on point charge dimensionless concentration $\mu = an_1$ for different $\lambda = \sqrt{15nr_c^3}$ values (λ^{-1} numerates the curves from the right- to the left-hand side). ● and ○ are experimental data for PLZT $x/65/35$ from [5] and [32] respectively.

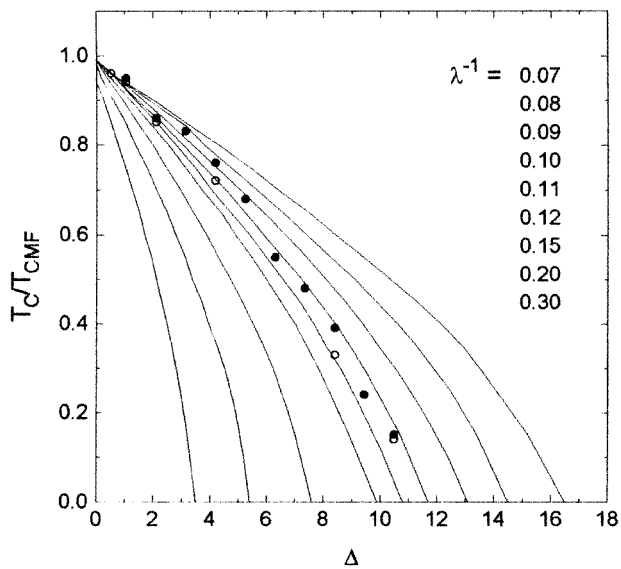


Figure 2. The dependence of the ratio T_c/T_{cmf} on dilatational centre dimensionless concentration $\Delta = bn_2$ for different $\lambda = \sqrt{15nr_c^3}$ values (λ^{-1} numerates the curves from the right- to the left-hand side.)● and ○ are experimental data for PLZT $x/65/35$ from [5] and [32] respectively.

we shall restrict the discussion in this paper to the consideration of relaxor phase diagram peculiarities and their static properties only.

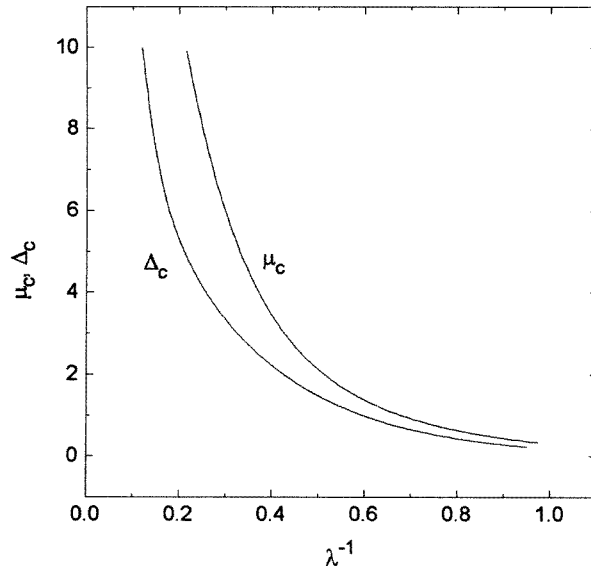


Figure 3. Dependence of dimensionless critical concentrations of point charges μ_c and dilatation centres Δ_c on the parameter $\lambda^{-1} = (15nr_c^3)^{-1/2}$.

It follows from figure 3 that n_{1c} and n_{2c} increase for increasing nr_c^3 and at the limit $\lambda^{-1} \rightarrow 0$, ($nr_c^3 \rightarrow \infty$) we have $\mu, \Delta \rightarrow \infty$ so that the ordinary ferroelectric phase transition which appears in the mean-field approximation may be destroyed only by large defect concentrations. Note that the nr_c^3 value depends both on electric dipole concentration and temperature because of the correlation radius temperature dependence.

4. Discussion

Let us begin with the comparison of calculated and experimental data. The conditions of the performed calculations are very close to the PLZT $x/1 - y/y$ relaxor. In agreement with the proposed model (see section 2) the transition temperature in the mean-field approximation T_{cmf} has to be the transition temperature from the paraelectric to the ferroelectric phase of the pure PZT system, which has been referred to as T_d (the Burns temperature) [31], and depends on the y value. Since the PLZT $x/65/35$ series is the most studied one, we have reported in figures 1 and 2 the experimental T_c/T_{cmf} ratios for two different series of samples with lanthanum compositions between 0 and 10% [5, 32] where T_c was measured as dielectric susceptibility maximum position. To transform μ and Δ values into x values we fitted the calculated and experimental ratio for one composition and obtained the proportionality relations $\mu = 1.05x$, $\Delta = 1.05x$ where x is a percentage. The constant λ curves of these figures fit the experimental results rather well, despite the scattering of the data of [5] and [32], which is probably related to differences in the sample preparation. It should be noticed moreover that for La concentrations larger than about 6% in 65/35 ceramics, the temperature at which dielectric susceptibility is maximum acquires a dynamic character which forbids any use as a static transition temperature T_c . This could explain why the curves do not fit the experimental data so nicely for $x > 6$. Critical concentrations of point charges or dilatational centres can be obtained by using the λ values which fit the observed data. It can be seen

from figure 3 that the corresponding critical concentrations of lanthanum are 9.5–10.5% from data from both [5] and [32]. Note that the existence of other defects in the lattice would contribute to a decrease of these numbers. Since e.g. in PLZT 8/65/35 the concentrations of Pb and Ti or Zr vacancies are about 3–4% [33], they may decrease the obtained value of the lanthanum critical concentration by a value proportional to their concentration. The obtained critical concentration is thus in good agreement with the observed one ($x_x \approx 6$). Therefore the calculations in the framework of the random field theory lead to a correct description of the T_c concentration dependence with only one adjustable parameter. It should be noticed that in ferromagnetic disordered systems with non-magnetic impurities (which seem to be the magnetic analogue to PLZT) the observed transition temperature shows an exponential decrease with non-magnetic impurity concentration increase [34] in contrast to the essentially different observed in PLZT. This could be explained by the fact that non-magnetic ions do not introduce any random magnetic field but only disturb the magnetic dipole–dipole interaction.

In agreement with the proposed model, r_c is the correlation radius of the host lattice. For PLZT this host lattice has been suggested to be pure PZT paraelectric phase. At $T \leq T_d$, the variation of r_c can be estimated from $r_c \approx \sqrt{\epsilon_0}$. Since $\epsilon_0(T)$ and thus r_c are large at $T \approx T_d$, local ferroelectric regions (remanent from the PZT ferroelectric phase) have to exist even at defect concentrations larger than the critical ones. Actually, nr_c^3 may be a maximum near the Burns temperature and at $nr_c^3 \gg 1$ defects are unable to destroy the ferroelectric ordering (see figure 3). The existence of such ferroelectric regions in 8–9/65/35 has been shown from x-ray [35], Raman scattering [7, 8] and refractive index measurements [31]. Notice that at $n_{1,2} < n_{1c,2c}$ the size of these ferroelectric regions may be larger so at $n_{1,2} \rightarrow 0$ they transform into pure PZT ferroelectric domains. To our mind the existence of ferroelectric regions at $T \leq T_d$ at any concentration of La^{3+} seems to be the main reason for the sharp break of the optical index of refraction in PLZT $x/65/35$ at $T = T_d$ for any x [31]. The assumption that this phenomenon speaks in favour of pure PZT region existence in PLZT for any concentration of lanthanum [31] contradicts the NMR and ESR data [24]. In accordance with ESR measurements, PZT local regions exist at $x \leq 4\%$ only. Since the measurements of the refractive index in PMN and PZN exhibit an effect similar to those observed in PLZT with T_d several hundred degrees above T_c (see [31] and references therein), the same model has to be valid for these materials and very likely to other relaxor ferroelectrics. Note that T_d measurements in the relaxors of the 1:2 family may pour light on the unobservable paraelectric–ferroelectric phase transition in these relaxors.

Figures 1–3 can be considered as relaxor ferroelectric phase diagrams. It is seen that at large nr_c^3 values ($nr_c^3 \gg 1$), T_c/T_{cmf} is close to unity for a wide enough concentration range of defects, e.g. $0.8 \leq T_c/T_{cmf} \leq 1$ when $0 \leq \mu \leq 4.5$ or $0 \leq \Delta \leq 4$, for PLZT $x/65/35$ these μ and Δ values being close to the defect concentrations as percentages. Since at T_c near T_{cmf} a large fraction of the dipoles has to be coherently oriented, the order parameter L can be close to unity, i.e. the ferroelectric phase transition is realized. When nr_c^3 decreases, even small concentrations of defects decrease T_c/T_{cmf} strongly. For instance for $nr_c^3 = 0.74$ and $\Delta = 2$, $T_c/T_{cmf} = 0.5$ (see figure 2). Under these conditions, $L < 1$ and only a fraction of the dipoles is coherently oriented. The other fraction is gathered in short-range order clusters of typical size r_c . We have thus a system which can be described as a mixed ferroglass state. On further decreasing of nr_c^3 ($nr_c^3 \ll 1$), $T_c/T_{cmf} \rightarrow 0$ even at small defect concentrations, i.e. $L \rightarrow 0$, and we are faced with the dipole glass picture in which only short-range order clusters exist. The same dipole glass state has to be at defect concentrations larger than critical, which strongly depend on the nr_c^3 value (see figure 3). Since, for all the relaxors, concentrations of dipoles, lattice defects and impurities are constant, nr_c^3 has

to change with temperature, i.e. the critical concentration of defects as well as the phase transition picture may change. Let us consider the possible sequence of phase transitions in the relaxors on cooling, at any constant concentration of defects, e.g. $n_{1,2} \geq n_{1c,2c}$.

As discussed above, in the high-temperature region close to the Burns temperature T_d where the correlation radius is large ($nr_c^3 \gg 1$, $L \approx 1$), ferroelectric regions with sizes depending on the defect concentration are present.

When $nr_c^3 \approx 1$, a mixed ferroglass phase may appear. In this phase infinite clusters coexist with short-range order clusters. As a result, this state is characterized by a long-range order parameter $L \neq 0$ but smaller than unity (only a fraction of the dipoles are coherently oriented) together with long relaxation times which are evidenced through dynamic dielectric susceptibility dispersion. Some hints of ferroglass phase existence has been obtained in 1:1 relaxors [2].

In the intermediate temperature range $T_c < T < T_d$ where the host lattice correlation radius is small enough that $nr_c^3 < 1$, short-range clusters may appear. The size of these clusters is determined by the r_c value, i.e. it is temperature dependent. If $nr_c^3 \ll 1$, it becomes possible to neglect the interactions between dipoles and we are faced with the picture of random site and orientation effective dipoles $d^* = \gamma(\epsilon_0 - 1)d/3$ with a temperature dependent value determined by the static dielectric susceptibility of the host lattice ϵ_0 . This value d^* may be even two orders of magnitude larger than the real dipole moment d , e.g. about 30–50 e A. Because of the small values of r_c or d^* , in the high enough temperature region considered the clusters or effective dipoles may have large reorientational velocity, which is expected to decrease on decreasing the temperature. In this temperature region, $L = 0$ and $\sqrt{L^2} = 0$. This picture of small movable clusters corresponds quite well to the Cross superparaelectric phase model [36].

At $T < T_c$ some of the clusters or effective dipoles may freeze; the complete freezing of all of them appears at $T = T_g$ where T_g is the transition temperature to the dipole glass state ($L = 0$, $\sqrt{L^2} \neq 0$, $L(\omega) \neq 0$; long-time relaxation modes up to infinity determine the system dynamic properties). This dipole state has to exist at temperatures below T_g and higher than zero provided that $n_{1,2} \geq n_{1c,2c}$. The T_g value can be estimated from the random field distribution function width $\Delta E \approx T_g$. In the case of dilatational centres, the distribution function is a convolution of Gaussian and Lorentzian functions (see equation (5)) i.e. $\Delta E = C^{1/2}(\frac{1}{2}\Delta + (1 + \frac{1}{4}\Delta^2)^{1/2})$. Since $\Delta > \Delta_c$ ($\Delta_c \approx 10$ for PLZT 65/35) we obtain $\Delta E > 10\sqrt{C}$. Defining $T_g^0 = \sqrt{C}$ as the dipole glass transition of the system without any dilatational centre, we can see that the defects increase T_g very strongly. Keeping in mind that in diluted systems such as KTN $T_g^0 \sim 3$ K [37] we can expect relaxors with larger concentrations of dipoles to have T_g^0 values around 20 K, which gives $T_g = 200$ K for PLZT. This is very close to the observed value [6, 8]. For a more accurate T_g estimation we should know additional parameters determining the \sqrt{C} value (see section 3). The dipole glass is also expected to occur in other relaxor systems of 1:2 type such as PMN because of their previously discussed large number of defects (see section 2). The glass state in PMN has been confirmed by many experimental data [1]. The dynamic properties of dipole glasses $L(\omega)$ and $\epsilon(\omega)$ can be calculated also within the frame of the model proposed in this paper.

5. Conclusion

We have proposed in this paper a model which allows us to describe the physical properties and phase diagram peculiarities of the relaxor ferroelectrics within the framework of a

random field theory. The Cross superparaelectric state as well as the Burns temperature T_d naturally appear in our model. The calculations based on the statistical theory of first order involving the linear random field contribution permitted us to give a fair explanation of the T_c dependence on La concentration in $x/65/35$ PLZT as well as the value of La concentration at which the dipole glass state appears below T_g . The preliminary calculations have shown that non-linear random electric field contributions to the distribution function and to the order parameter in relaxors with a centrosymmetric paraelectric phase have to be involved only through their odd powers due to symmetry considerations, i.e. the first non-linear term is proportional to E^3 . Its contribution can be supposed to be rather small in some cases. The exact calculation of these non-linear term contributions both to the random field distribution function and to the system order parameter is in progress.

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