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Theory of the nonlinear susceptibility of relaxor ferroelectrics

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Abstract. The theory of the nonlinear dielectric response to an external dc electric field is developed in the random-field-theory framework. The equations describing the dependence of the order parameter and the dielectric susceptibility (both linear and nonlinear) on the temperature, dc electric field, frequency, parameters of the host lattice and random-field sources are obtained. The numerical solution of these equations for several random-field-source concentrations and other parameters has shown that in the dipole-glass phase the dc electric field always decreases the dielectric response, while in the mixed ferroelectric–glass phase the dc field can either decrease or increase this response. Approximation of the numerical results for the nonlinear part of the susceptibility leads to $\Delta\chi'(\xi, T)/\chi'(0, T) = -b_0(T)\xi^2 + b_1(T)\xi^{7/2}$ with $b_1(T) < b_0(T)$ (ξ is the dimensionless dc-field value). It was shown that, for all of the cases considered, $b_0(T = T_g)$ remains finite and $b_1(T = T_g)$ has a maximum (T_g is the dipole-glass freezing temperature). The absence of critical divergency of the nonlinear susceptibility both in theory and experiment proves that, unlike conventional spin glass, the dipole-glass state in relaxors is a metastable state with long (up to infinite) relaxation times. A comparison of the theoretical results obtained with available experimental data for PMN and PMN–10PT is carried out. The calculated temperature and dc-field dependences of the nonlinear susceptibility are in agreement with observed data.

1. Introduction

The influence of external fields on the dielectric (magnetic) susceptibilities of disordered dielectric (magnetic) systems has attracted much attention for many years. This is because the investigation of this phenomenon can shed some light on the nature of the phase transitions in the disordered systems. Phase diagrams of such disordered systems can contain ferroelectric (ferromagnetic) phases with long-range order, mixed ferroelectric–glass (ferromagnetic–spin-glass) phases with the coexistence of long- and short-range order and also dipole-glass (spin-glass) states [1–4]. One of the most interesting questions of glassy-state physics is the question of whether glasses are truly equilibrium phases or whether they are just metastable states with long-time (up to infinite) relaxation modes. In the search for a solution of this problem, the investigation of nonlinear susceptibility appears to be of particular interest, because this quantity is more sensitive to dipole- or spin-glass order than linear susceptibility. In spite of the existence of experimental data on critical divergence of the nonlinear susceptibility of spin glasses such as AgMn at the freezing temperature T_g, the question of whether a static phase transition is realized at T_g has not yet been resolved for all spin glasses [1]. The investigation of the nonlinear susceptibility in the 'classical' dipole glasses KCl:OH^- gave no divergency at T_g in experiment [5] or in theory [6]. The

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nature of the dielectric response of relaxor ferroelectrics (relaxors) such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $PbSc_{1/2}Ta_{1/2}O_3$ (PST) and $Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$ (PLZT 8/65/35) has been the subject of intensive study for many years (see, e.g., [7–14]). Establishing the dependence of the nonlinear susceptibility on T and the external electric field was the main goal of these investigations. The dependence obtained of the dielectric response on the mode of field application (that is, field application during sample cooling or sample heating, with possible subsequent zero-field heating or cooling (FC, FH, ZFH, ZFC)) speaks in favour of nonergodic behaviour of relaxors, which is known to be a characteristic feature of the glassy state and of the mixed ferroelectric–glass phase [1–4]. However, the observed properties of the relaxors have been discussed in terms of several models, including that of ferroelectric long-range order (see, e.g., [15]). The absence of a quantitative description of the observed anomalies seems to be the main reason for the difficulties in achieving an understanding of the nature of the relaxors. Recently, a theoretical approach for use in the description of relaxors was proposed [16] in the random-field-theory framework [17]. The theory developed was shown to fit fairly well several observed static [16, 18] and dynamic [19] properties of relaxors. The nonlinear contribution of random internal electric fields to the properties of relaxors was also taken into account recently [18, 20].

In the present work the theory of the nonlinear dielectric response of the relaxors to an external dc field is developed. We calculated the influence of a dc external electric field $\mathcal{E}$ on the polarization and the nonlinear susceptibility (which is a linear function of the alternating field). A comparison of the data obtained with available experimental results is carried out.

2. Theory

Relaxor ferroelectrics such as PMN, PST, PLZT can be considered as systems containing random-site and random-orientation electric dipoles, antisite ions (which appear due to substitutional disorder) and vacancies of lead and oxygen. All of these are sources of random electric fields.

According to a recently proposed model [16], these random-field sources are embedded in a host lattice, which was shown to coincide with the Burns and Dacol reference phase [21]. The local physical properties of the relaxors can depend on specific random-field values, so the average macroscopic properties have to be calculated with the help of a random-field distribution function. This leads to a dependence of the relaxor properties (including the phase diagram [1, 2]) on the distribution function characteristics—its maximum position (mean field E_0) and width ΔE.

2.1. General equations

2.1.1. The order parameter. Self-consistent averaging over spatial configurations of random-field sources and subsequent thermal averaging over possible dipole orientations permits one to obtain the equation for the ferroelectric order parameter (the dimensionless polarization $\boldsymbol{L}$) in the form [17]

$$\boldsymbol{L} = \int_{-\infty}^{\infty} \langle \boldsymbol{l}(\boldsymbol{E} + \boldsymbol{\mathcal{E}}) \rangle f(\boldsymbol{E}, \boldsymbol{L})\ \mathrm{d}\boldsymbol{E} = \int_{-\infty}^{\infty} \langle \boldsymbol{l}(\boldsymbol{E}) \rangle f(\boldsymbol{E} - \boldsymbol{\mathcal{E}}, \boldsymbol{L})\ \mathrm{d}E. \qquad (1)$$

Here $\boldsymbol{L}$ characterizes the number of coherently oriented dipoles, the polarization $\boldsymbol{P} = nd^*\boldsymbol{L}$, $\langle l \rangle$ is the quantum statistical (thermal) average of the dimensionless single-dipole moment $\boldsymbol{l} = \boldsymbol{d}^*/d^*$, $d^* = d\gamma(\varepsilon_0 - 1)/3$ is the effective-impurity dipole moment, γ is the Lorenz

factor, ε_0 is the host-lattice static permittivity, $\boldsymbol{E}$ and $\mathcal{E}$ are internal random and external fields respectively. The random-field distribution function $f(E, L)$ has been calculated self-consistently (see [17] for details) in the framework of statistical theory [22].

Calculations of the distribution function of the random fields induced by electric dipoles, point charges and dilatational centres were carried out in [17] for two-orientable electric dipoles ($l_z = \pm 1$, $l_x = l_y = 0$) in the Gaussian limit for the electric dipole random-field partial distribution function. It can be shown that the Gaussian limit for this function is valid for $nr_c^3 > 1$, where n and r_c are the electric dipole concentration and the host-lattice correlation radius respectively. This distribution function has the form

$$f(E, L) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\left[\mathrm{i}\rho(E - E_0 L) - A|\rho|^{3/2} - B|\rho| - C\rho^2\right]\,\mathrm{d}\rho \qquad (2)$$

where

$$\begin{aligned} A &= \frac{32}{15}\left(\frac{\pi}{2}\frac{Ze}{\varepsilon_0}\right)^{3/2} n_1 \qquad B = \frac{\Omega_0}{9}\frac{1+\theta}{1-\theta}pn_2 \\ C &= \frac{16\pi}{15}\left(\frac{d^*}{\varepsilon_0 r_c^3}\right)^2 nr_c^3 \qquad E_0 = \frac{4\pi n d^*}{\varepsilon_0} \end{aligned} \qquad (3)$$

where $E \equiv E_z$, $L \equiv L_z$, n_1 and n_2 are the concentrations of point charges and dilatational centres respectively, Ze and Ω_0 are the point defect charge and elastic moment respectively, p and θ are the host-lattice piezoelectric tensor component and Poisson coefficient respectively.

Since the random field E enters the exponent in equation (2) linearly, the distribution function $f(E, L)$ corresponds to the case of a linear contribution of the random fields. Note that calculations of the distribution function of the random field induced by electric dipoles for arbitrary values of nr_c^3, i.e. beyond the Gaussian limit, were performed in [23].

The distribution function allowing for both linear and nonlinear random-field contributions was calculated in references [18, 20]. In the case of host-lattice cubic symmetry and when one retains only the first nonlinear term, the distribution function has the form

$$f_{nL}(E, L) = \int_{-\infty}^{\infty} f(x, L)\delta(E - x - \alpha_3 x^3)\,\mathrm{d}x \qquad (4)$$

where α_3 is the third-order nonlinear coefficient of the host lattice and $f(x, L)$ is given by equations (2), (3).

To describe the frequency dependence of the order parameter, one has to consider the relaxation of a single dipole $\langle l\rangle$ to its equilibrium value $\langle l\rangle_{eq}$. For a two-orientable dipole, such a dependence has a simple Debye form [23]:

$$\langle l(E+\mathcal{E})\rangle = \frac{\langle l(E+\mathcal{E})\rangle_{eq}}{1 + \mathrm{i}\omega\langle\tau(E+\mathcal{E})\rangle} \qquad \langle l(E+\mathcal{E})\rangle_{eq} = \tanh\left(\frac{E+\mathcal{E}}{kT}\right) \qquad (5)$$

$$\langle\tau(E+\mathcal{E})\rangle = \overline{\tau}\frac{\cosh(2(E+\mathcal{E})/kT)}{\cosh((E+\mathcal{E})/kT)}. \qquad (6)$$

Here $\overline{\tau} = \tau_0 \exp(U/kT)$ is the Arrhenius law for a dipole reorientation between two equivalent positions with barrier height U. Substituting equations (2)–(6) into equation (1), one can obtain (after some simple transformations) the following self-consistent equation for the order parameter:

$$L = \frac{2}{\pi}\int_0^{\infty}\int_0^{\infty} \tanh\left(\frac{E + \alpha_3 E^3}{kT}\right)\exp\left[-A\rho^{3/2} - B\rho - C\rho^2\right] \times \sin(\rho E)\frac{\sin(\rho(\mathcal{E} + E_0 L))}{1 + \mathrm{i}\omega\tau_1(E)}\,\mathrm{d}E\,\mathrm{d}\rho \qquad (7)$$

where

$$\tau_1 = \overline{\tau}\frac{\cosh(2(E+\alpha_3 E^3)/kT)}{\cosh((E+\alpha_3 E^3)/kT)}.$$

Equation (7) describes the dependence of the order parameter on the temperature, frequency and external electric field, as well as on the characteristics of the random-field sources and host lattice.

Since equation (7) can be solved only numerically, let us rewrite it in the following dimensionless variables:

$$L = \frac{2}{\pi}\int_0^\infty\int_0^\infty \tanh\left(\frac{x+\alpha_0 x^3}{\tau}\right)\exp\left[-\mu y^{3/2} - \Delta y - y^2\right] \times \sin(\lambda xy)\frac{\sin(\lambda y(\xi+L))}{1+\mathrm{i}\nu\tau_1(x)}\,\mathrm{d}x\,\mathrm{d}y \tag{8}$$

where

$$\tau_1(x) = \overline{\tau}\frac{\cosh(2(x+\alpha_0 x^3)/\tau)}{\cosh((x+\alpha_0 x^3)/\tau)}.$$

Here

$$\begin{array}{lll} x = E/E_0 & y = \rho\sqrt{C} & \tau = kT/E_0 = T/T_{cmf} \\ \alpha_0 = \alpha_3 E_0^2 & \xi = \mathcal{E}/E_0 & \nu = \omega\tau_0 \\ \mu = A/C^{3/4} & \Delta = B/\sqrt{C} & \lambda = E_0/\sqrt{C} \equiv \sqrt{15\pi n r_c^3}. \end{array} \tag{9}$$

2.1.2. The dielectric susceptibility. The dielectric susceptibility is known to be the first derivative of the polarization $\boldsymbol{P} = nd^*\boldsymbol{L}$ with respect to the external field $\mathcal{E}$, i.e.

$$\chi_{\alpha\beta} = nd^*\frac{\partial L_\alpha}{\partial \mathcal{E}_\beta} \tag{10}$$

where $\alpha, \beta = x, y, z$.

For two-orientable dipoles, $L = L_z \neq 0$ and $L_x = L_y = 0$, so the dielectric susceptibility $\chi \equiv \chi_{zz}$. Keeping in mind that both the left- and right-hand sides of equation (8) depend on L, and performing the differentiation in equation (10), we obtain

$$\frac{4\pi}{\varepsilon_0}\chi = \frac{Q}{1-Q} \tag{11}$$

$$Q = \frac{2\lambda^2}{\pi}\int_0^\infty\int_0^\infty \tanh\left(\frac{x+\alpha_0 x^3}{\tau}\right)\exp\left[-\mu y^{3/2} - \Delta y - y^2\right] \times \sin(\lambda xy)\frac{y\cos(\lambda y(\xi+L))}{1+\mathrm{i}\nu\tau_1(x)}\,\mathrm{d}x\,\mathrm{d}y. \tag{12}$$

Equations (11), (12) (together with (9)) describe the dependence of the dielectric susceptibility on the temperature, external electric field, frequency, parameters of the host lattice and random-field sources. Note that equation (12) can be represented as an infinite series in powers of ξ, its coefficients being linear and nonlinear susceptibilities of the corresponding order. To obtain the linear susceptibility, we should retain just the zeroth term in this expansion [19, 23, 25].

2.2. The mean-field approximation

In the general case, equations (8) and (12) can be solved only numerically. Let us consider the limiting case where $E_0 \to \infty$ ($nr_c^3 \to \infty$) of the equations (8) and (12), i.e. the mean-field approximation. Keeping in mind that, in this limit,

$$\exp(-\mu y^{3/2} - \Delta y - y^2) \to 1$$

and

$$[1/(2\pi)] \int_{-\infty}^{\infty} \cos(kx)\ \mathrm{d}k = \delta(x) \qquad \delta(ax) = \delta(x)/a$$

one obtains after some transformations

$$L_{mf} = \frac{\tanh V}{1 + \mathrm{i}\nu\tau_1(V)} \qquad \tau_1 = \frac{\cosh 2V}{\cosh V} \tag{13}$$

where

$$V = \frac{\xi + L_{mf} + \alpha_0(\xi + L_{mf})^3}{\tau}$$
$$\frac{4\pi}{\varepsilon_0}\chi_{mf} = \frac{Q_{mf}}{1 - Q_{mf}} \qquad Q_{mf} = \frac{1 + 3\alpha_0(\xi + L_{mf})^2}{\tau\,[1 + \mathrm{i}\nu\tau_1(V)]\cosh^2 V}. \tag{14}$$

In the static case ($\nu = 0$), equation (13) transforms to $L_{mf} = \tanh V$, which at $\alpha_0 = 0$ completely coincides with the well known expression for the ferroelectric transition order parameter derived from the conventional type of free energy of the Ising model for the order–disorder phase transition (see, e.g., [24]). The same coincidence is also found for the dielectric susceptibility. At $\alpha_0 \neq 0$, additional nonlinear terms appear in the equation for the order parameter and that for the dielectric susceptibility. In the general case, equations (13), (14) describe the temperature, frequency and electric field dependence of these quantities in the mean-field approximation, i.e. for the ordinary ferroelectric phase transition of order–disorder type.

3. The electric field and temperature dependence of the nonlinear susceptibility

Numerical calculations of the real part of the dependence of the susceptibility on $\mathcal{E}$, T and ν were performed on the basis of equations (8), (11), (12) for several values of λ, Δ and μ. In the calculations we chose the following impurity dipole parameters: $U/T_{cmf} = 1.143$, $\tau_0 = 10^{-13}$ s^{-1}. Also, we took $\omega = 200$ Hz ($\omega\tau_0 = \nu = 2 \times 10^{-11}$). Note that even at $\alpha_0 = 0$ there is a contribution that is nonlinear in ξ due to the nonlinear dependence on ξ of the integrands of equations (8) and (12). This can be also seen from the mean-field expressions for L and χ (equations (13), (14)). In the case where $\alpha_0 \neq 0$, additional nonlinearity appears due to the nonlinear contribution of the internal random electric field to the distribution function. We shall call this the 'intrinsic' nonlinearity of the system.

The phase diagram of the disordered systems depends on the random-field-source concentrations. It may contain ferroelectric phases, mixed ferromagnetic–glass phases and a dipole-glass state (see, e.g., [2, 18]). The concentrations of electric dipoles, point charges and dilatational centres which correspond to the aforementioned phases were calculated recently [17, 18]. To capture the nonergodic behaviour of the relaxor ferroelectrics, we performed our numerical calculations for the parameters corresponding to the dipole-glass state and those corresponding to the mixed ferromagnetic–glass phase. Note that the 'intrinsic' nonlinearity ($\alpha_0 \neq 0$) does not influence the critical concentrations of random-field sources, but it changes T_c and the order parameter [20].

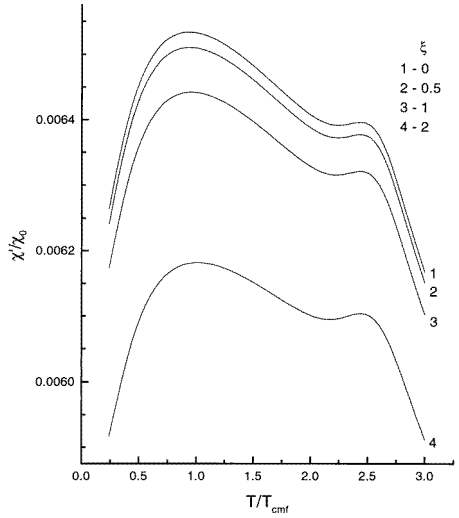

Figure 1. The temperature dependence of the dielectric susceptibility for $\lambda = 1$, $\Delta = 8$, $\alpha_0 = 0$ for several dimensionless dc-field values ξ (indicated by the numbers near the curves).

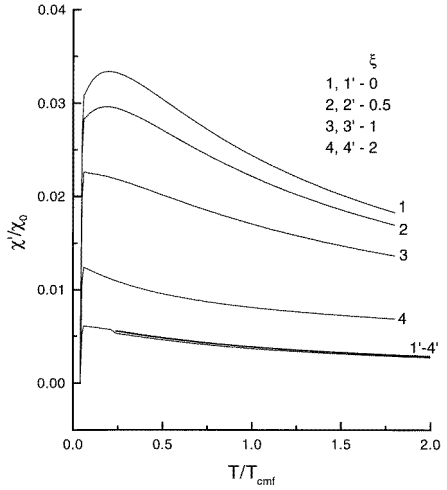

Figure 2. The temperature dependence of the dielectric susceptibility, allowing for a nonlinear random-field contribution, at $\omega = 200$ Hz, $\Delta = 8$, $\alpha_0 = 1$ for several dc-field values ξ; the curves labelled 1–4 and the corresponding ones labelled $1'$–$4'$ are for $\lambda = 5$ and $\lambda = 1$ respectively.

3.1. The dipole-glass state

The temperature dependences of the dielectric susceptibility χ' at the frequency $\omega = 200$ Hz for several values of the external electric field are depicted in figures 1 and 2 for $\alpha_0 = 0$ and $\alpha_0 = 1$ respectively. It is seen that increase of the external electric field leads to the dielectric susceptibility decreasing, i.e. the electric field suppresses the dielectric response of the system. Meanwhile, the shape of $\chi'(T)$ at $\xi \neq 0$ looks like that at $\xi = 0$. We have to draw attention to the fact that the shapes of $\chi'(T)$ for $\alpha_0 = 0$ and $\alpha_0 = 1$ are significantly

different (compare figures 1 and 2). Indeed, there are two maxima at $\alpha_0 = 0$ (named the LT and HT maxima in [19], where a detailed consideration of the linear susceptibility of relaxors was performed) and only one maximum for $\alpha_0 = 1$, at a temperature much lower than that of the LT maximum. This means that the 'intrinsic' nonlinearity of the system, which is due to the nonlinear contribution of the random field, including spatial correlation effects [18, 20], influences the dielectric response more strongly than the external dc field. Since the curves for $\xi = 0$ in figures 1, 2 correspond to linear susceptibility, we may conclude that the 'intrinsic' nonlinearity significantly changes both the linear and the nonlinear susceptibilities: it shifts the positions of their maxima towards lower temperatures and changes the temperature dependence of the dielectric response. This phenomenon may be the main reason for the shift of the dielectric susceptibility maximum towards lower T for relaxors such as PST with a higher level of disorder [26].

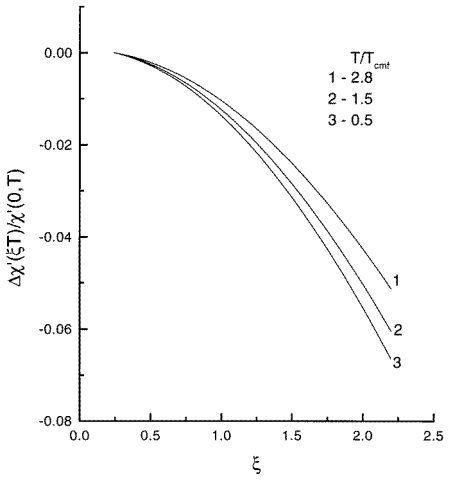

Figure 3. The dependence of the nonlinear dielectric susceptibility on the dc external field for $\lambda = 1$, $\Delta = 8$, $\alpha_0 = 0$ for several temperatures T/T_{cmf} (indicated by the numbers near the curves).

The relative nonlinear part of the susceptibility can be expressed as

$$\Delta\chi'(\xi, T)/\chi'(0, T) = (\chi'(\xi, T) - \chi'(0, T))/\chi'(0, T).$$

The dependence of this quantity on the external electric field is represented in figure 3 for $\alpha_0 = 0$ and several temperatures. These curves proved to be fitted fairly well by the expression

$$\Delta\chi'(\xi, T)/\chi'(0, T) = -b(T)\xi^2 \tag{15}$$

with $b = 1.12 \times 10^{-2}$, 1.34×10^{-2}, 1.4×10^{-2} for $T/T_{cmf} = 2.8$, 1.5, 0.5 respectively. The calculations had shown that at smaller temperatures $0.1 \leqslant T/T_{cmf} \leqslant 0.3$ (this interval includes the T_g-value [19]), b remains finite. Therefore there is no divergency in the value of $b(T)$ in the low-temperature region (and this region includes the freezing temperature T_g). To check whether the results obtained depend on the concentrations of the dipoles and the nonlinear contribution of the random field, we performed calculations of $\Delta\chi'$ for several α_0 and $\lambda = 5$, i.e. for an electric dipole concentration 25 times that used in the previous case with $\lambda = 1$ (see equation (9)). The results of the calculations are depicted in figure 4. It is seen that for all of the cases considered at $\alpha_0 = 0$ (figure 4(a)), $\alpha_0 = 1$ (figure 4(b)) and $\alpha_0 = -1$ (figure 4(c)), $b(T)$ is independent of ξ over the region $\xi \leqslant 0.25$ and has a finite value in the low-temperature region including $T = T_g$ ($T_g/T_{cmf} \approx 0.1$ [19]). The most important difference between the cases where $\lambda = 1$ (figure 3) and $\lambda = 5$ (figure 4) is

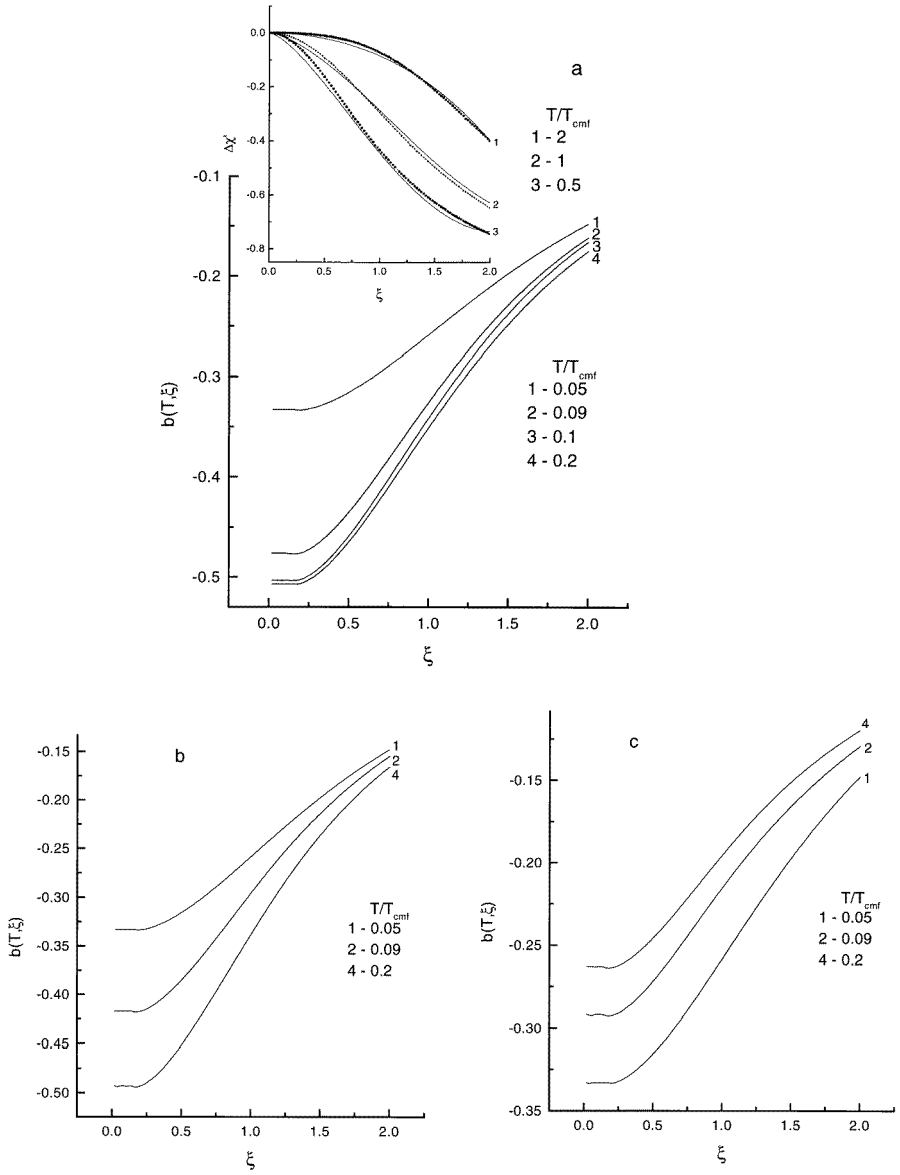

Figure 4. The field dependence of the coefficient $b(T)$ in equation (15) for $\lambda = 5$, $\Delta = 8$ and $\alpha_0 = 0$ (a); 1 (b); -1 (c) for several temperatures T/T_{cmf}. Inset in (a): the nonlinear dielectric susceptibility for several temperatures T/T_{cmf}: 2 (curve 1); 1 (curve 2); 0.5 (curve 3). The points represent the results of calculations; the solid line was obtained by fitting with equation (17)

the appearance of a significant dependence of b in equation (15) on ξ at $\xi > 0.25$. For all ξ, the coefficient b can be represented as

$$b(\xi, T) = b_0(T) - b_1(T)\xi^{3/2}. \tag{16}$$

Equation (16) fits the $b(\xi, T)$ dependence fairly well with $b_1(T) < b_0(T)$. Substitution

of equation (16) into (15) gives

$$\Delta\chi'(\xi, T)/\chi'(0, T) = -\left[b_0(T)\xi^2 - b_1(T)\xi^{7/2}\right]. \tag{17}$$

Equation (17) also describes the field dependence of $\Delta\chi'(\xi, T)/\chi'(0, T)$ at larger temperatures than those depicted in figure 4(a) (see the inset to the figure, where the solid lines correspond to equation (17) with $b_0 = 8.3 \times 10^{-2}$, $b_1 = 0$ ($T/T_{cmf} = 2$); $b_0 = 3.3 \times 10^{-1}$, $b_1 = 4.1 \times 10^{-2}$ ($T/T_{cmf} = 1$); $b_0 = 5.1 \times 10^{-1}$, $b_1 = 8.6 \times 10^{-2}$ ($T/T_{cmf} = 0.5$)). These data show that $b_1(T)$ has a sharp enough maximum near $T = T_g$ while $b_0(T)$ has a smeared maximum (if it has one at all) near $T = T_g$. Note that equation (17) fits the data obtained much better than the equation

$$\Delta\chi'(\xi, T)/\chi'(0, T) = -b_0(T)\xi^2 + b_1(T)\xi^4$$

with integer powers which follow from the ordinary form of the free-energy expression.

For $\lambda = 5$, the nonlinear susceptibility appeared to be more than ten times that for $\lambda = 1$ (compare figures 3 and 4(a)). Therefore, increasing the electric dipole concentration increases the nonlinear susceptibility. The increase of the linear susceptibility with growth of λ was demonstrated in reference [19]. Note that the case with $\lambda = 5$, $\Delta = 8$ is close to the boundary between the glass and the mixed phase (see [16]). Calculations also show that increasing the parameters Δ and μ decreases the linear and the nonlinear response of the system.

3.2. The mixed ferromagnetic–glass phase

The temperature dependence of the nonlinear dielectric susceptibility in the mixed phase appeared to be significantly different from that in the dipole-glass state. The main difference is that both $\Delta\chi' > 0$ and $\Delta\chi' < 0$ occur for some ranges of the temperature and dc electric field (see figures 5(a), 5(b)). For the dipole glass, $\Delta\chi' < 0$, because $\chi'(0, T)$ is always larger than $\chi'(\xi, T)$ (see figures 1, 2). It is seen from figure 5 that there are two maxima in the nonlinear part of the susceptibility, these maxima having heights that are especially large at small dc electric fields. Note that for the mixed-phase parameters considered, $\Delta\chi' < 0$ at $\xi = \mathcal{E}/T_{cmf} \geqslant 1$, where the second maximum becomes less pronounced. For smaller ξ, we have $\Delta\chi' > 0$ near both maxima and $\Delta\chi' < 0$ in the temperature regions away from the maxima.

Analysis shows that the aforementioned peculiarities are the consequence of the co-existence of long- and short-range order in the mixed phase. Indeed, calculations within the mean-field approximation (long-range order), with the help of equation (14), have shown that, in addition to the main maximum at $T/T_{cmf} = 1$, new maxima appeared at sufficiently small dc electric fields, the sharpest one being at $T/T_{cmf} < 1$ (see figure 6). These new maxima are due to there being several roots of the denominator in equation (14). Because of the similarity of equations (14) and (11), one can expect the same peculiarities when the mean-field approximation is not used, i.e. for the mixed-phase and dipole-glass states. However, there is no sharp maximum for the dipole-glass state (see figures 1, 2), because the random field suppresses and smears the dielectric response. Since in the mixed phase the randomness is 'smaller' than in the dipole-glass state, two groups of maxima appeared for this phase, at $\xi \neq 0$ (see the right-hand inset in figure 5(a), where the positions of the maxima are indicated by arrows). The details of the behaviour of the susceptibility near the high-temperature maxima are depicted in the left-hand inset in figure 5(a). It is seen that the height of the low-temperature maximum (LTM) is 25 times that of the high-temperature one (HTM). Therefore one might guess that the origins of the LTM and HTM are, respectively, long-range order and short-range order in the mixed phase.

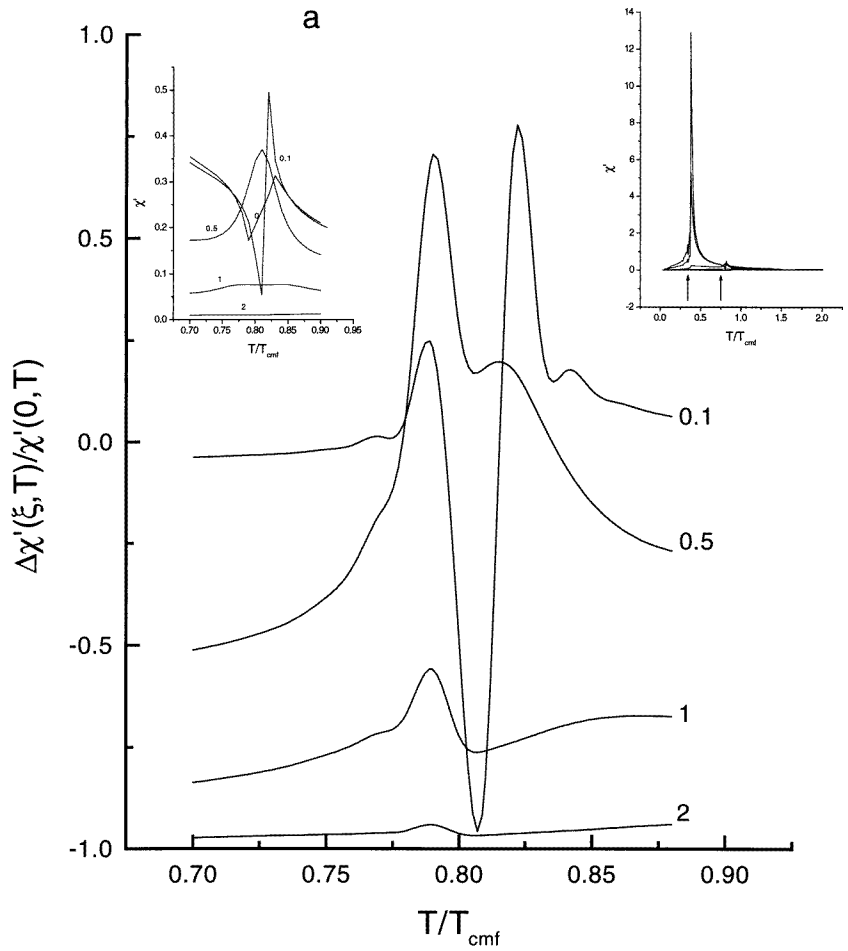

Figure 5. The temperature dependence of the nonlinear susceptibility for the mixed phase (parameters: $\Delta = 1$, $\lambda = 3.3$ and $\alpha_0 = 0$) in the regions with soft ($\Delta\chi' > 0$) and stiff ($\Delta\chi' < 0$) dielectric responses for several values of the dc electric field ξ indicated by the numbers near the curves. Insets to (a): the susceptibility with the HTM and LTM indicated by arrows and that near the HTM; inset to (b): the observed [12] nonlinear part $\Delta\varepsilon'$ of the dielectric permittivity of PMN single crystal at $\omega = 100$ Hz and several dc fields applied along the [111] direction.

The field dependence of the susceptibility is depicted in figure 7. It can be fitted with the same expression, equation (17), as for dipole glass. Thus the dc-field dependence of the nonlinear susceptibility in the mixed phase looks like that of a dipole glass.

4. Discussion and comparison with experiment

4.1. Discussion

The nonlinear dielectric response is known to be particularly interesting for disordered systems because it is more sensitive to short-range order than the linear (zero-field)

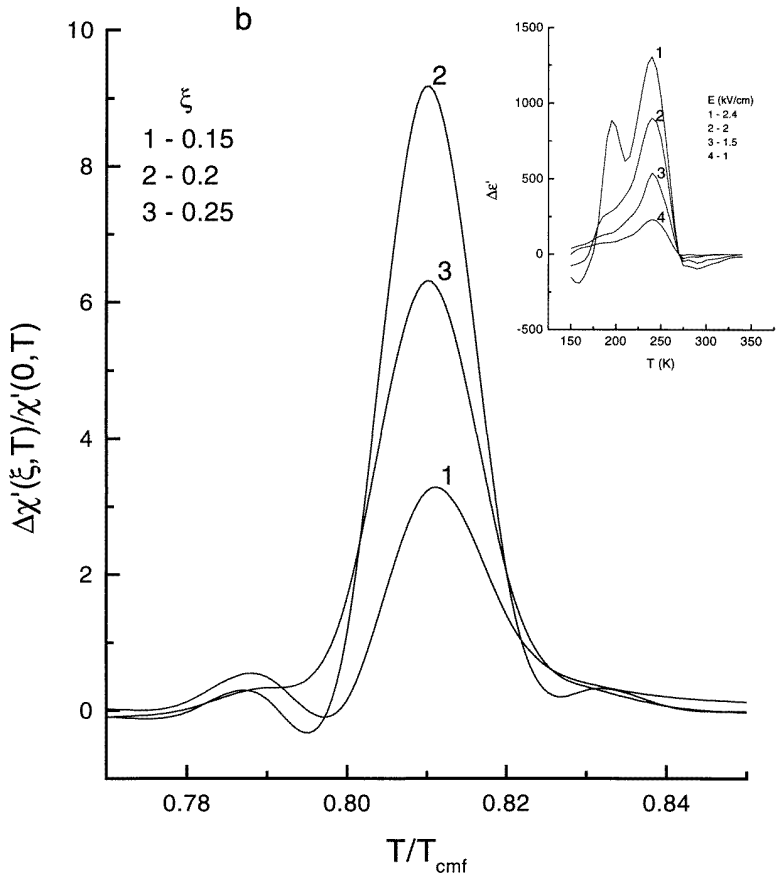

Figure 5. (Continued)

susceptibility. For spin glasses, much attention has been paid to the temperature dependence of coefficients such as $b(T)$ in equation (15), i.e. to terms with a quadratic variation of the susceptibility in the external magnetic field.

Theory (see [1] and references therein) predicts a critical divergence of $b(T)$ at the spin-glass freezing temperature if there is an equilibrium phase transition to a spin-glass state. Data obtained for systems such as AgMn are now taken as evidence that real spin glasses have an equilibrium phase transition at the freezing temperature. However, due to the scatter of the available critical exponent values and the difficulties encountered in attempting to compare theory and experiment for some disordered magnetic systems, this problem is not yet absolutely resolved [1].

Measurements of the nonlinear dielectric susceptibility in KCl:OH^-, which is known to be a dipole glass, gave no evidence concerning the possible dielectric susceptibility divergency at the freezing temperature. The experiment described in [5], as well as its theoretical description [6], speaks against realization of a static phase transition into a dipole-glass state. These results cannot be applied directly to disordered ferroelectrics such as PMN, PST, PLZT because of their high polarizability and higher chemical complexity in comparison with relatively simple systems such as KCl:OH^- (see [4]), and, consequently,

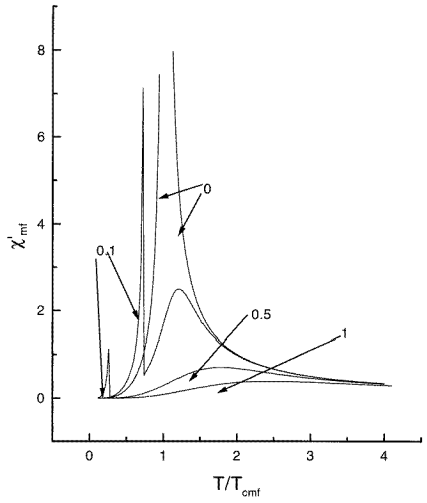

Figure 6. The temperature dependence of the static mean-field susceptibility for $\alpha_0 = 0$ and several values of the dc field ξ, given near the arrows.

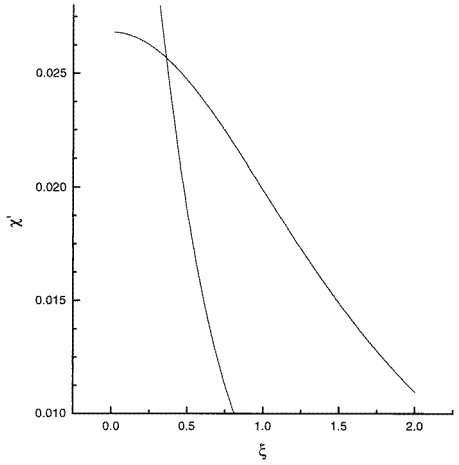

Figure 7. The field dependence of the dielectric susceptibility for the parameters $\Delta = 1$, $\lambda = 3.3$, which correspond to a mixed phase at $\alpha_0 = 0$, $T/T_{cmf} = 0.05$.

because electric dipoles are not the only source of random fields in the relaxors. Note that the important role of the additional (to electric dipoles) random-field sources is a feature peculiar to disordered ferroelectrics, because, in magnetic systems, random spins are the main source of random magnetic fields.

The available experimental data for relaxors show no divergency of the nonlinear susceptibility [7, 12, 14]. In view of this, the question arises of whether relaxors must belong to the group of dipole glasses if we make the supposition that all of the properties of spin and dipole glasses have to be exactly the same [13]. Another question that arises here is that of whether the dipole-glass states (if there are any) in relaxors are truly equilibrium phases or whether they are metastable states with long-time (up to infinity) relaxational modes.

The calculations carried out in this work have shown that the nonlinear susceptibility of the relaxors has a finite value in the vicinity of the freezing temperature and at T_g (see figures 3, 4), so dipole glass is a metastable state rather than an equilibrium phase, and does exist in conventional spin glasses. The main reason for this difference seems to be the stronger disorder in the relaxors due to the large number of random-field sources. Note also that a random electric field is of electrostatic nature, i.e. the radius of its action is longer than that of a random magnetic field. This results in a difference in some phenomena, including a stronger (as compared to that for magnetic disordered systems) influence of random fields on the physical properties of the substances under consideration. It is obvious, however, that more detailed consideration of the physical reasons for the difference between spin and dipole glasses is desirable.

4.2. Comparison with experiment

The dependence of the dynamic dielectric response on the dc electric field and temperature was measured for PMN ceramics with 10 at.% $PbTiO_3$ (PMN–10PT) [7], PMN single crystals and ceramics [12], and PLZT (9/65/35) [14]. The measurements were performed in a

field-cooled (FC) regime [7, 12] and under zero-field heating after field cooling (the ZFH/FC regime) [14]. Since the FC regime is known to be reversible, we can use our theory to explain the experimental data for this regime. The temperature dependence of $\Delta\chi'$ measured for PMN single crystal [12] for several dc fields applied along the [111] direction (i.e. along the direction of the local polarization of PMN) is depicted in the inset to figure 5(b). One can see that both theory (see figure 5) and experiment indicate the temperature regions with $\Delta\chi' > 0$ and $\Delta\chi' < 0$. The second low-temperature maximum was observed only at sufficiently large dc field, and its origin was thought to be the ferroelectric phase induced by the electric field [12]. This supposition is in agreement with the one discussed earlier (see section 3), namely that the origin of the LTM is connected with long-range order. The observed intensities of the HTM increase with increasing field (see the inset to figure 5(b)). This behaviour is in agreement with the calculated behaviour only for $0.1 \leqslant \xi \leqslant 0.2$, because for $\xi \geqslant 0.25$ the intensity of the HTM decreases and smears with increasing field (see figure 5). Note that for $\boldsymbol{\mathcal{E}} \parallel [100]$ only $\Delta\chi' < 0$ was observed [12]. In our view, this is because the polarization is not directed along the dc-field direction, so the $\boldsymbol{\mathcal{E}}$-field suppresses the dielectric response of the crystal. Since our calculations were performed within the model where the dc field is directed along the direction of orientation of the dipoles, only the case where $\boldsymbol{\mathcal{E}} \parallel [111]$ can be considered in our model. The improvement of the model for arbitrary electric field orientation is in progress now.

Positive and negative signs of $\Delta\chi'$ were observed also for PMN–10PT [7]. The measured dependence of the dielectric susceptibility on the dc field looks like that depicted in figure 8. The observed $\chi'(\mathcal{E})$ curve was fitted in [7] with the expression

$$\chi'(\mathcal{E}, T) = \chi_0(T) + \chi_2(T)\mathcal{E}^2 + \chi_4(T)\mathcal{E}^4.$$

The corresponding theoretical result (equation (17)) differs from it in sign and in having the power 3.5 instead of 4 in the second nonlinear term. Since the contribution of the latter term is sufficiently small, equation (17) also fits the observed $\chi'(\mathcal{E})$ dependence. On the other hand, it would be interesting to measure $\chi'(\mathcal{E})$ with greater accuracy. This could make it possible to clarify whether an expression with $\mathcal{E}^{7/2}$ in the third term fits the observed data better than one with $\mathcal{E}^4$. Note that the equation which expresses $\chi'(\mathcal{E})$ in terms of integer powers of $\mathcal{E}$ used to be stated as the equation for the order parameter expansion in a power series in $\mathcal{E}$. In such an approximation, the coefficients of the series are the derivatives of the corresponding order taken at $\mathcal{E} = 0$. In our view, calculation of the nonlinear susceptibility on the basis of equations (11), (17) seems to be more general, because it takes into account all possible nonlinear contributions to $\chi'(\mathcal{E})$ without any approximations. Measurements of the temperature dependences $\chi_2(T)$ and $\chi_4(T)$ have shown that $\chi_2(T)$ increases as $T \to T_g$ and $\chi_4(T)$ has a maximum at $T = T_g$ [7]. Analysis of the data for $b_0(T)$ and $b_1(T)$ obtained by fitting the curves in figure 4(a) with equation (17) showed that $b_0(T)$ slowly increases when T approaches T_g from above and then decreases for $T < T_g$. The value of $b_1(T)$ has a maximum in the region $0.1 \leqslant T/T_{cmf} \leqslant 0.2$, which includes the T_g-value. Note that some experimental evidence in favour of the coexistence of short- and long-range order in PMN–10PT was obtained recently [27].

The observed dependence of the nonlinear dielectric susceptibility on the dc field for PMN single crystal has been described by the expression $\chi \sim \mathcal{E}^2$ at temperatures near the susceptibility maximum [12]. This behaviour is also in agreement with our theoretical results, predicting $\Delta\chi' \sim \mathcal{E}^2$ for both the dipole-glass state (see, e.g., figure 3) and for high enough temperatures, when some admixture of long-range order might be expected.

Therefore, one can see that, despite the model's limitations, random-field theory describes the main features of the behaviour of the nonlinear susceptibilities of relaxors.

5. Conclusions

The explanation of the most important experimental results—the absence of a nonlinear susceptibility divergency at the freezing temperature and the existence of both positive (soft) and negative (stiff) nonlinear susceptibilities—seems to shed light on the physical nature of relaxors. That is, the first phenomenon speaks in favour of the statement that dipole glass is a metastable phase with long-time relaxation modes, in contrast to ordinary spin glasses, and the second phenomenon provides evidence of the existence of some admixture of ferroelectric long-range order with the glassy state in relaxors such as PMN and PMN–10PT. This mixed phase is known to be a nonergodic one [1, 2], with long-time relaxation [23], which is a feature peculiar to glasses. Therefore the main characteristics of relaxors—the dependence of the dielectric response on the regime of cooling and heating, and the peculiarities of their dynamics—do not rule out the existence of a mixed phase in the relaxors. For clarifying the question of the precise values of the short- and long-range-order contributions in any particular relaxor, additional experimental and theoretical investigations are extremely desirable.

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