Nonlinear dielectric response of relaxor ferroelectrics

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The behavior of the third-order nonlinear dynamic dielectric susceptibility $\chi_3(\omega)$ in relaxor ferroelectrics is investigated in the framework of the spherical random-bond–random-field model. It is shown that there are two distinct contributions to $\chi_3(\omega)$: The first one $\chi_3(\omega)^I$, which has been studied earlier, is due to the intrinsic nonlinearity of the rigid spherical model; the second contribution $\chi_3(\omega)^{II}$ arises from the field modulation of the average coupling between polar clusters. The frequency and temperature dependence of $\chi_3(\omega)^{II}$ is calculated and compared with $\chi_3(\omega)^I$. In the static limit, the results for $\chi_3(\omega)^{II}$ are in qualitative agreement with the measured field-cooled static nonlinear dielectric permittivity in $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ ceramics.

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I. INTRODUCTION

Relaxor ferroelectrics are structurally disordered polar materials, which are characterized by the occurrence of nanosized polar clusters of various sizes below a certain temperature, typically in the range of several hundred K.[1,2] According to the recently proposed spherical random-bond–random-field (SRBRF) model[3–5] the dipole moments of polar clusters interact via a spin-glass-type random exchange coupling, and are also subject to random local electric fields. In the dynamic SRBRF model,[5] one assumes that polar clusters reorient by means of stochastic flips[6] described by the relaxation time τ. Empirically, the temperature dependence of τ can be determined from the positions of the maxima of the linear dielectric susceptibility $\chi_1(\omega)$ at different frequencies, and is thus found to obey the Vogel-Fulcher (VF) law $\tau=\tau_0\exp[U/(T-T_0)]$, where the VF temperature T_0 is commonly taken as a measure of the freezing temperature T_f.

The behavior of the third-order nonlinear dielectric susceptibility $\chi_3(\omega)$ of relaxors has been attracting considerable attention during the past few years.[7–9] The crucial quantity, which is capable of discriminating between the static behavior of normal ferroelectrics and relaxors, is the dielectric nonlinearity coefficient[7] $a_3=\chi_3/\chi_1^4$. In relaxors, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT) ceramics,[9] a_3 was found to exhibit a crossover from a paraelectriclike behavior at high temperatures to a dipolar-glass-like behavior on approaching T_f. The original SRBRF model[5] can qualitatively describe such a crossover behavior, however, it also predicts that in the quasistatic limit a_3 should have a peak near $T\approx T_f$. So far, this peak could not be observed in any system. Moreover, in a recent experiment carried out under true static conditions both in PMN and PLZT the peak at T_f has not been found.[11] This fact necessitates a search for alternative mechanisms of nonlinear response not studied so far, and calls for a refinement and generalization of the static and dynamic SRBRF model.

The mechanism of nonlinear response originally proposed within the SRBRF model in Ref. 5 (to referred to here as mechanism I) has been derived under the assumption that polar clusters are embedded in a rigid lattice; the nonlinearity effects are thus entirely due to the intrinsic nonlinearity of the rigid SRBRF model. A possible alternative mechanism, characteristic of the generalized SRBRF model and explored in the present work, is based on the fact that polar clusters can be displaced from their equilibrium positions by the applied electric field; this then leads to the field modulation of the intercluster coupling (mechanism II). A similar idea was used in connection with the field-temperature (E,T) phase diagram of PLZT,[12] and was found to lead to the correct description of the observed phase boundary between the ferroelectric and glassy phases. Here we will consider both the static and dynamic nonlinear responses resulting from the above mechanism, and compare it with the effects of the intrinsic nonlinearity of the rigid spherical model. The criteria for the mechanism to be dominant will generally depend on the parameters of the system, such as the average dipole moment and volume of the cluster and the critical electric field E_c, which is required to transform the relaxor into an inhomogeneous ferroelectric.

In Sec. II of this paper we discuss the microscopic origin of field variation of intercluster coupling, and derive its contribution to the static nonlinear response, which is compared with experiments. In Sec. III we study the dynamic nonlinear response, and in Sec. IV we summarize our conclusions.

II. MECHANISMS OF NONLINEAR RESPONSE

A. Field variation of intercluster coupling

For simplicity, we consider the uniaxial SRBRF model with a scalar order parameter field $-\sqrt{N}<S_i<\sqrt{N}$ satisfying the spherical condition

$$\sum_{i=1}^{N} S_i^2=N, \tag{1}$$

where N is the number of polar clusters. The model Hamiltonian has the usual form[5]

$$\mathcal{H}=-\frac{1}{2}\sum_{ij} J_{ij}S_iS_j-\sum_i h_iS_i-\varphi gE\sum_i S_i, \tag{2}$$

where the random bonds J_{ij} and random fields h_i are specified by the random cumulant averages

$$[J_{ij}]_{av}=J_0/N, \quad [J_{ij}^2]_{av}^c=J^2/N \tag{3}$$

and

$$[h_i]_{av}=0, \quad [h_ih_j]_{av}=\Delta\delta_{ij}. \tag{4}$$

Also, E is the applied electric field, φ the local-field factor, and g the average dipole moment of a polar cluster. It should be noted that in this paper we consider only the case $J_0<J$.

We now introduce a new concept into the above model, namely, we assume that the coupling J_{ij} depends on the displacements of clusters from their equilibrium positions. This could be rigorously formulated by introducing a coupling[13] between a set of lattice displacements $\vec{u}_i$ and the order parameter field S_i. After integrating out these additional degrees of freedom in the long-wavelength limit one would obtain an effective coupling $J_{ij}=J_{ij}(u_{\mu\nu})$, which depends on the lattice strains $u_{\mu\nu}$. These can be generally written as functions of the stress tensor $\sigma_{\kappa\lambda}$ and electric field E_κ,

$$u_{\mu\nu}=\sum_{\kappa\lambda}(-s_{\mu\nu\kappa\lambda}\sigma_{\kappa\lambda}+L_{\mu\nu\kappa\lambda}E_\kappa E_\lambda), \tag{5}$$

where $s_{\mu\nu\kappa\lambda}$ and $L_{\mu\nu\kappa\lambda}$ are components of the elastic compliance and electrostriction tensor, respectively. Assuming the existence of a hydrostatic pressure p and a field E along one of the principal axes in a cubic system, one obtains the simple relation $u_{11}\equiv u=-p/B+LE^2$, where B is the bulk modulus and $L=L_{1111}+2L_{1122}$.

Turning now to the coupling J_{ij}, we consider the variation of the parameters J_0 and J with pressure p and field E. Since J measures the fluctuations of J_{ij}, the effects of p and E on it are expected to be much smaller than the variation of its average J_0. To lowest nontrivial order the latter can be expressed as $J_0(u)=J_0(0)+(\partial J_0/\partial u)u+\cdots$, and the pressure and field dependence thus becomes

$$J_0(p,E)=J_0(0)+\frac{\partial J_0}{\partial u}\left[-\frac{p}{B}+LE^2\right]. \tag{6}$$

The effects of pressure on J_0 and on the phase diagram of PLZT were already discussed in Ref. 13, whereas the effects of E on the phase diagram in PMN and PLZT were described in Ref. 12. We will consider the case of atmospheric pressure ($p=0$) and write the remaining field dependence in the form[12]

$$J_0(E)=J_{0c}+J_1\left[\left(\frac{E}{E_c}\right)^2-1\right]. \tag{7}$$

Here J_{0c} is the value of J_0 at the critical field E_c, which corresponds to the onset of long-range order, and $J_1=(\partial J_0/\partial u)LE_c^2$.

B. Static nonlinear response

The linear and nonlinear static susceptibilities are defined in terms of the expansion of the dielectric polarization P, i.e.,

$$P=\chi_{1s}E-\chi_{3s}E^3+\cdots. \tag{8}$$

This can be formally rewritten by introducing a field-dependent susceptibility $\chi_s(E)$ as

$$P=\chi_s(E)E, \tag{9}$$

leading to the following relation for the third order static nonlinear susceptibility:

$$\chi_{3s}=-\frac{1}{2}\frac{\partial^2\chi_s(E)}{\partial E^2}\bigg|_{E=0}. \tag{10}$$

Now $\chi_s(E)$ can be calculated from the solutions $S_i(t)$ of the Langevin equations of motion discussed in detail in Ref. 5. Equation (16) of Ref. 5 in the static case $\omega=0$ yields

$$\chi_s(E)=\frac{\varphi g^2}{v_c}\frac{z-r-\beta J_0}{\beta(J^2+J_0^2)-2J_0z}, \tag{11}$$

where v_c is the average volume of a polar cluster and $r\equiv\sqrt{z^2-\beta^2J^2}$. The parameter z is a Lagrange multiplier enforcing spherical condition (1). It is determined by the equation[5]

$$z-r+\frac{\beta^2\Delta}{2}\frac{z}{r}+\frac{(\beta J\varphi g)^2E^2}{2(J^2+J_0^2-2J_0z/\beta)}\left[\frac{z-r}{r}-\frac{2J_0(z-r-\beta J_0)}{\beta(J^2+J_0^2)-2J_0z}\right]=\beta^2(J^2+\Delta/2). \tag{12}$$

Since both z and J_0 are functions of E^2, from Eqs. (10) and (11) we obtain the general relation

$$\chi_{3s}\equiv\chi_{3s}^I+\chi_{3s}^{II}=-\frac{1}{2}\left(\frac{\partial\chi_s(E)}{\partial z}\frac{\partial^2z}{\partial E^2}+\frac{\partial\chi_s(E)}{\partial J_0}\frac{\partial^2J_0}{\partial E^2}\right)_{E=0}, \tag{13}$$

where χ_{3s}^I and χ_{3s}^{II} refer to the first and second terms, respectively, of the last expression. Note that χ_{3s}^I is the part of the static nonlinear response, which was calculated in Ref. 5, and agrees with the result of replica theory derived in Ref. 3. Here we will focus on the second term χ_{3s}^{II}. Combining Eqs. (13), (10), and (7), we find

$$\chi_{3s}^{II}=\frac{J_1\varphi g^2}{E_c^2v_c}\left\{\frac{\beta}{\beta(J^2+J_0^2)-2J_0z}+2\frac{(z-r-\beta J_0)(\beta J_0-z)}{[\beta(J^2+J_0^2)-2J_0z]^2}\right\}. \tag{14}$$

The static dielectric nonlinearity coefficient $a_{3s}=\chi_{3s}/\chi_{1s}^4$ can also be written as a sum of two terms

$$a_{3s}\equiv a_{3s}^I+a_{3s}^{II}=\frac{\chi_{3s}^I}{\chi_{1s}^4}+\frac{\chi_{3s}^{II}}{\chi_{1s}^4}, \tag{15}$$

where a_{3s}^I was calculated in Ref. 3.

It should be noted that the sign of χ_{3s}^{II}—and hence of a_{3s}^{II}—is negative in a broad temperature range, in contrast to χ_{3s}^I and a_{3s}^I which were found to be positive quantities. The relative size of $|\chi_{3s}^{II}|$ versus χ_{3s}^I is measured by the ratio of the second derivatives of z and J_0 appearing in Eq. (13). It is

possible to derive analytical expressions for $|\chi_{3s}^{I}|$ and χ_{3s}^{II} at $T=0$. From Eq. (27) of Ref. 5, we have

$$\chi_{3s}^{I}(0)=\frac{1}{2}\varphi v_c\left(\frac{\varphi g^2}{v_c}\right)^2\frac{J}{(J-J_0)^4}, \tag{16}$$

whereas from Eq. (14) above, in the limit $T\to 0$, we find

$$\chi_{3s}^{II}(0)=-\frac{\varphi g^2}{v_c}\frac{J_1}{E_c^2(J-J_0)^2}. \tag{17}$$

Thus we may introduce the dimensionless amplitude ratio

$$A=\left|\frac{\chi_{3s}^{II}(0)}{\chi_{3s}^{I}(0)}\right|=2\frac{(J_1/J)(J-J_0)^2}{\varphi v_c(\varphi g^2/v_c)E_c^2}. \tag{18}$$

If $A<1$, then χ_{3s}^{I} will be larger than $|\chi_{3s}^{II}|$. On the other hand, if $A>1$ one can expect that $|\chi_{3s}^{II}|>\chi_{3s}^{I}$, i.e., the main contribution to the nonlinear response will be due to mechanism II, i.e., the field variation of the average coupling strength J_0.

For 9/65/35 PLZT ceramics we have the following parameter values estimated from the (E,T) phase diagram[12]: $J/k=261$ K, $J_0/k\simeq 214$ K, $J_1=0.04J$, $\Delta/J^2=0.01$, and $E_c=4.8$ kV/cm, and the static dielectric constant at low temperatures is $\epsilon_s\simeq 5.7\times 10^4$. The value of the quantity $\varphi g^2/v_c$ can be estimated from the $T=0$ static linear dielectric susceptibility [Eq. (13)]; for $\Delta\ll J^2$ one has $z\approx\beta J$, and thus

$$\chi_{1s}=\frac{\varphi g^2}{v_c}(J-J_0)^{-1}. \tag{19}$$

Since $\chi_{1s}=\epsilon_0(\epsilon_s-1)\approx\epsilon_0\epsilon_s$, where ϵ_0 is the permittivity of the vacuum, from Eq. (19) we find $\varphi g^2/v_c\simeq 4\times 10^{-28}$ C^2 m^{-1}.

From Eq. (17) we can now calculate the $T=0$ nonlinear static susceptibility due to mechanism II, $\chi_{3s}^{II}(0)$, and the corresponding nonlinearity coefficient a_{3s}^{II}. The results are $\chi_{3s}^{II}(0)=-9.6\times 10^{-19}$ $\mathrm{Cm\,V^{-3}}$ and $a_{3s}^{II}=-1.5\times 10^{7}$ $\mathrm{V\,m^5C^{-3}}$.

To determine χ_{3s}^{I} and the ratio A, however, we must also know the values of the parameters v_c and φ. According to the Onsager reaction field theory[14] the value of φ lies in the range $1.5<\varphi<(n^2+2)/3$, where n^2 is the "internal refraction index." For PLZT one can estimate $n^2\sim 30$ from the high-frequency dielectric data at low temperatures, and thus $1.5<\varphi\lesssim 11$. Assuming that the average cluster is a sphere of radius $R\simeq 15$ nm—or a cylinder of the same volume—and choosing the average value $\varphi\sim 6.5$, from Eq. (18) we find that in PLZT the ratio A is of the order $A\simeq 200$. This implies that mechanism II is much stronger than mechanism I at $T=0$—and possibly at other temperatures as well—and thus $|\chi_{3s}^{II}|\gg\chi_{3s}^{I}$.

In fact, we can now calculate the temperature dependence of χ_{3s}^{II} and χ_{3s}^{I} from Eq. (14) and the corresponding expression from Ref. 5, respectively. The result is plotted in Fig. 1. In contrast to χ_{3s}^{I}, which shows a peak near $T_f\approx J$, the absolute value of the contribution to the static nonlinear response $|\chi_{3s}^{II}|$ increases monotonically with decreasing temperature and levels off gradually on approaching $T=0$. A similar situation occurs in the case of the dielectric nonlinearity coefficients a_{3s}^{I} and a_{3s}^{II}, which are displayed in Fig. 2. Here a_{3s}^{I} also has a pronounced peak near $T_f\approx J$, whereas $-a_{3s}^{II}$ decreases monotonically with decreasing temperature. It should be stressed that χ_{3s}^{II} and a_{3s}^{II} both have negative signs in the entire temperature range. This is possible in a thermodynamic sense provided that the signs of higher order coefficients in expansion (8) are such that stability of the free energy $F(P)$ is not violated.

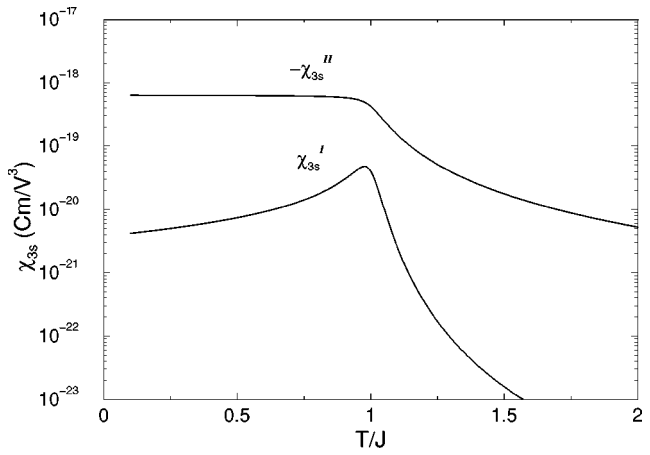

FIG. 1. Calculated temperature dependence of the static field-cooled third order nonlinear response due to the intrinsic nonlinearity of the rigid spherical model (mechanism I) (lower curve) and field modulation of intercluster coupling (mechanism II) (upper curve), plotted on a logarithmic vertical scale. Parameter values appropriate to PLZT ceramics were used, as explained in the text.

C. Comparison with experiments

The nonlinear static dielectric response has been investigated experimentally in PLZT ceramics by using the same charge accumulation technique as previously applied to the

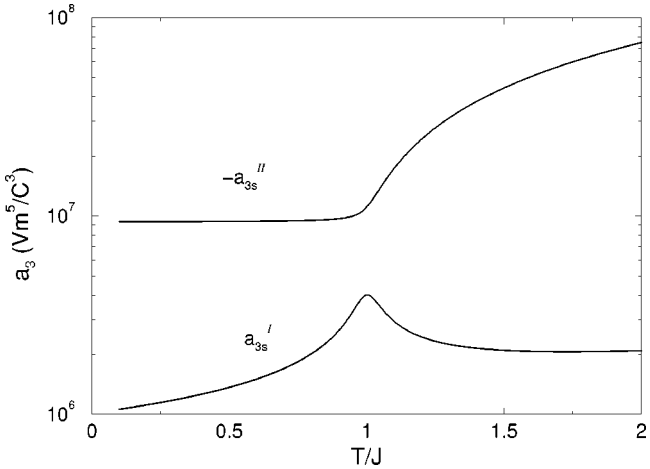

FIG. 2. Calculated temperature dependence of the static dielectric nonlinearity coefficient $a_{3s}=\chi_{3s}/\chi_{1s}^4$ plotted on a semilogarithmic scale, using the same parameters as in Fig. 1.

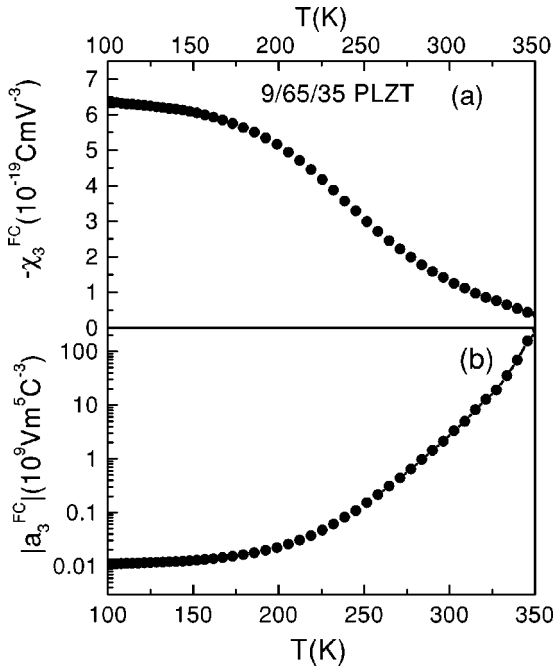

FIG. 3. (a) Field-cooled static nonlinear response χ_{3s} of PLZT 9/65/35 ceramics measured by the charge accumulation technique by cooling slowly (~ 1 K/min) in a field $E=0.3$ kV/cm. (b) Experimental nonlinearity coefficient a_{3s} in PLZT plotted on a semilogarithmic scale.

PMN relaxor system.[10,11] The PLZT system was cooled slowly (- 1 K/min) in an applied d.c. electric field $E<E_c=4.4$ kV/cm and the effective field-cooled (FC) dielectric susceptibility $\chi_{eff}=P_{FC}(E,T)/E$ was determined from the observed dielectric polarization $P_{FC}(E,T)$. The corresponding polarization charge was measured by the Keithley 617 programmable electrometer. The nonlinear field-cooled dielectric susceptibility χ_{3s}^{FC} was then obtained by means of the relation $\chi_{3s}^{FC}=[\chi_{eff}(0)-\chi_{eff}(E)]/E^2$. In Fig. 3(a) the measured values of $-\chi_{3s}^{FC}$, and in Fig. 3(b) the dielectric nonlinearity coefficient $|a_{3s}|=|\chi_{3s}|/\chi_{1s}^4$ in 9/65/35 PLZT ceramics, are shown as functions of temperature. At low temperatures we find the following limiting values: $\chi_{3s}^{FC}\simeq -6.4\times10^{-19}$ Cm V^{-3} and $|a_{3s}^{FC}|\simeq10^7$ Vm^{5}C^{-3}. These results are close to the estimated values of $\chi_{3s}^{II}(0)$ and $a_{3s}^{II}(0)$ given above, suggesting that mechanism II is dominant in PLZT. Actually, the theoretical estimates can be brought much closer to the experimental values if the value of J_0 is slightly readjusted to $J_0/k\simeq224$ K, yielding a corrected value $\varphi g^2/v_c=2.64\times10^{-28}$ C^{2}m^{-1}. From this we can now also estimate the value of the average cluster dipole moment, i.e., $g\simeq2.2\times10^{-26}$ Cm$\simeq1500$ D.

It should be stressed that the measured temperature dependences of χ_{3s}^{FC} and a_{3s}^{FC} agree qualitatively with the corresponding theoretical results for mechanism II, which appears to be stronger than mechanism I at all temperatures. Since the weak anomaly due to mechanism I could not be observed in the experiment, we conclude that its contribution must be about two orders of magnitude smaller, and hence below the present experimental resolution.

III. DYNAMIC NONLINEAR RESPONSE

The time dependence of the order parameter field $S_i(t)$ is governed by the Langevin equations of motion[5]

$$\tau\frac{\partial S_i(t)}{\partial t}=-\frac{\partial(\beta\mathcal{H})}{\partial S_i}-2z(t)S_i(t)+\xi_i(t), \tag{20}$$

where τ is the relaxation time, assumed for simplicity to be independent of the site index i, and $z(t)$ the Lagrange multiplier enforcing spherical condition (1) at all times. The ensemble averages of the stochastic Langevin forces $\xi_i(t)$ satisfy the Einstein relation

$$\langle\xi_i(t)\xi_j(t')\rangle_{av}=2\tau\delta_{ij}\delta(t-t'), \tag{21}$$

thus ensuring the proper equilibrium limit of correlation functions. As discussed in detail in Ref. 5, Eq. (20) can be decoupled by introducing a set of normal modes S_λ, where λ labels the eigenvalues J_λ of the random bond matrix J_{ij}. The resulting equations of motion for $S_\lambda(t)$ can be solved exactly in the asymptotic limit $t\gg2\tau JT/\Delta$. The dynamic dielectric polarization of the system under the influence of an oscillating external field $E(t)=E_0\cos(\omega t)$ can be expressed as[5]

$$P(t)=\frac{g\beta E_0}{2v_c}\int_0^t\frac{dt_1}{\tau}\langle\langle e^{\beta J_\lambda(t-t_1)/\tau}\rangle\rangle e^{-2J\int_{t_1}^t dt' z(t')/\tau}e^{-i\omega t_1}+\text{c.c.} \tag{22}$$

Here $z(t')$ represents the solution of the equation for the time-dependent spherical condition in the presence of the applied field $E(t)$. The symbol $\langle\langle\cdots\rangle\rangle$ denotes the average over the appropriate Wigner density of states, i.e.,

$$\langle\langle f(J_\lambda)\rangle\rangle=\int_{-2J}^{+2J}dJ_\lambda\frac{\sqrt{4J^2-J_\lambda^2}}{2\pi(J^2+J_0^2-J_0J_\lambda)}f(J_\lambda). \tag{23}$$

In Ref. 5, the nonlinear response due to the modulation of $z(t)$ by the oscillating field $E(t)$ was calculated; in the present study we will focus on on the effects of the modulation of $J_0=J_0[E(t)]$. The response $P(t)$ in the asymptotic regime $t/\tau\gg1$ can in general be written as a sum of first, third, etc., harmonic responses, i.e.,

$$P(t)\sim[P_\omega e^{-i\omega t}+P_{3\omega}e^{-3i\omega t}+\cdots]+\text{c.c.}, \tag{24}$$

where the amplitudes P_ω, $P_{3\omega}$, etc. are expanded in powers of E_0:

$$P_\omega=\chi_{1,0}(\omega)\left(\frac{E_0}{2}\right)+\chi_{1,1}(\omega)\left(\frac{E_0}{2}\right)^3+\cdots, \tag{25}$$

$$P_{3\omega}=\chi_{3,0}(\omega)\left(\frac{E_0}{2}\right)^3+\chi_{3,1}(\omega)\left(\frac{E_0}{2}\right)^5+\cdots. \tag{26}$$

The third order nonlinear susceptibilities $\chi_{1,1}(\omega)$ and $\chi_{3,0}(\omega)$ can be calculated by expanding $P(t)$ in Eq. (24) in powers of E_0 and comparing the corresponding terms. Since both $z(t)$ and $J_0(t)$ are quadratic in E_0, it is obvious that we can write the E_0^3 terms in Eq. (24) as a sum

$$P_3(t)=P_3(t)^I+P_3(t)^{II}, \tag{27}$$

where in analogy to Eqs. (13) and (15) the first and third terms represent the contributions of $z(t)$ and $J_0[E(t)]$, respectively. Equation (27) implies that we can also write

$$\chi_{1,1}(\omega)=\chi_{1,1}(\omega)^I+\chi_{1,1}(\omega)^{II}, \tag{28}$$

$$\chi_{3,0}(\omega)=\chi_{3,0}(\omega)^I+\chi_{3,0}(\omega)^{II}. \tag{29}$$

The nonlinear response $\chi_{3,0}(\omega)^I$ was calculated in Ref. 5. To determine $\chi_{3,0}(\omega)^{II}$ we now set $z(t')=z=$ const in Eq. (22), and write

$$P_3(t)^{II}=\frac{E_0}{2}[\chi(\omega,E)^{II}e^{-i\omega t}+\text{c.c.}], \tag{30}$$

where in analogy with Eq. (9) we define

$$\chi(\omega,E)^{II}=\beta\frac{\varphi g^2}{v_c}\int_0^t\frac{dt_1}{\tau}\langle\langle e^{(\beta J_\lambda-2z)(t-t_1)/\tau}\rangle\rangle e^{-i\omega t_1}, \tag{31}$$

and it is understood that the average needs to be evaluated only up to $O[E(t)^2]$. We can then expand

$$\chi(\omega,E)^{II}=\chi(\omega,0)+\left.\frac{\partial\chi(\omega,E)}{\partial E}\right|_{E=0}E(t)+\frac{1}{2}\left.\frac{\partial^2\chi(\omega,E)}{\partial E^2}\right|_{E=0}E(t)^2+\cdots. \tag{32}$$

The zeroth-order term is given by[5]

$$\chi(\omega,0)=\chi_1(\omega)=\frac{\varphi g^2}{v_c}\frac{z(\omega)-r(\omega)-\beta J_0}{\beta(J^2+J_0^2)-2J_0z(\omega)}, \tag{33}$$

with $z(\omega)\equiv z-i\omega\tau/2$, $r(\omega)\equiv\sqrt{z(\omega)^2-\beta^2J^2}$ and $J_0=J_0(0)$. Since $\chi(\omega,E)^{II}$ depends on E only via $J_0(E)$, it is easy to see that the second term on the right-hand side of Eq. (32) vanishes, while the second derivative in the last term becomes

$$\left.\frac{\partial^2\chi(\omega,E)}{\partial E^2}\right|_{E=0}=\frac{\partial\chi(\omega,0)}{\partial J_0}\frac{J_1}{2E_c^2}. \tag{34}$$

The last two expressions are then inserted into Eq. (32). Collecting all the E_0^3 terms which oscillate as $e^{-i\omega t}$, $e^{-3i\omega t}$, etc., returning to Eq. (30) and comparing it with Eqs. (27)–(29), we finally obtain the two third-order nonlinear susceptibilities:

$$\chi_{1,1}(\omega)^{II}=\frac{J_1}{E_c^2}\left[2\frac{\partial\chi_1(\omega)}{\partial J_0}+\frac{\partial\chi_1(\omega)^*}{\partial J_0}\right], \tag{35}$$

$$\chi_{3,0}(\omega)^{II}=\frac{J_1}{E_c^2}\frac{\partial\chi_1(\omega)}{\partial J_0}. \tag{36}$$

It is convenient to define the third-order susceptibility $\chi_3(\omega)$ with an opposite sign,

$$\chi_3(\omega)=-\chi_{3,0}(\omega)=\chi_3(\omega)^I+\chi_3(\omega)^{II}, \tag{37}$$

so that $\chi_3(0)$ agrees with χ_{3s} from Eq. (8).

The partial derivative in Eq. (36) is calculated from Eq. (33), and the final result for $\chi_3(\omega)^{II}$ is

$$\chi_3(\omega)^{II}=\frac{J_1\varphi g^2}{E_c^2v_c}\left\{\frac{\beta}{\beta(J^2+J_0^2)-2J_0z(\omega)}+2\frac{[z(\omega)-r(\omega)-\beta J_0][\beta J_0-z(\omega)]}{[\beta(J^2+J_0^2)-2J_0z(\omega)]^2}\right\}. \tag{38}$$

For $\omega=0$ this reduces to the static nonlinear response [Eq. (14)]. The total static nonlinear response can be obtained from Eqs. (24)–(26) in the form

$$\chi_{3s}^{II}=-\frac{1}{4}[\chi_{1,1}(0)^{II}+\chi_{3,0}(0)^{II}]. \tag{39}$$

By setting $\omega=0$ in Eqs. (35) and (36) and comparing with Eq. (37) in the static limit, we have

$$\chi_{3s}^{II}=-\frac{1}{4}\frac{J_1}{E_c^2}\left[3\frac{\partial\chi_1(\omega)}{\partial J_0}+\frac{\partial\chi_1(\omega)^*}{\partial J_0}\right]_{\omega=0}=\chi_{3s}, \tag{40}$$

i.e., the nonlinear susceptibility $\chi_3(\omega=0)^{II}$ determines the total static response.

To evaluate $\chi_3(\omega)^{II}$ from Eq. (38) one needs to know the temperature dependence of the relaxation time τ. A constant τ cannot reproduce even qualitatively the observed behavior of either the linear response $\chi_1(\omega)$ or the nonlinear response. If the empirical VF relation $\tau=\tau_0\exp[U/(T-T_0)]$ at $T>T_0$ is employed, then $\chi_1(\omega)$ agrees qualitatively with experiments in the high-temperature region $T\gg T_0$, but cannot be extended into the region near and below T_0. Formally τ diverges as $T\to T_0$ and thus $\chi_1(\omega)\to0$, contrary to observation. This problem cannot be removed by performing an average over the barrier heights U; however, as argued in Ref. 5 a reasonable description is obtained if one averages $\chi_1(\omega)$ over a distribution $w(T_0)$ of VF temperatures T_0. Physically this would correspond to the assumption that each cluster relaxes with its own relaxation time τ_i in analogy with the concept of dynamic heterogeneity in relaxors.[15,16] Unfortunately, nothing is known about τ_i, neither can the coupled equations of motion (20) be solved for even a simple functional dependence $\tau_i=\tau_i(S_i)$. On the other hand, in analyzing the experimental data in relaxors and other polydispersive systems it is common to introduce a probability distribution of relaxation times $g(\ln\tau)$, of which $w(T_0)$ is just a special case.

A reasonably good description of the average response can be achieved by choosing a linear distribution of T_0, i.e., $w(T_0)=(2/J^2)(T_0-J)$ for $0\leqslant T_0\leqslant J$ and $w(T_0)=0$ otherwise.[5,13] The resulting averaged complex response is written as

$$\overline{\chi_n}(\omega)=\int_0^J dT_0w(T_0)\chi_n(\omega), \tag{41}$$

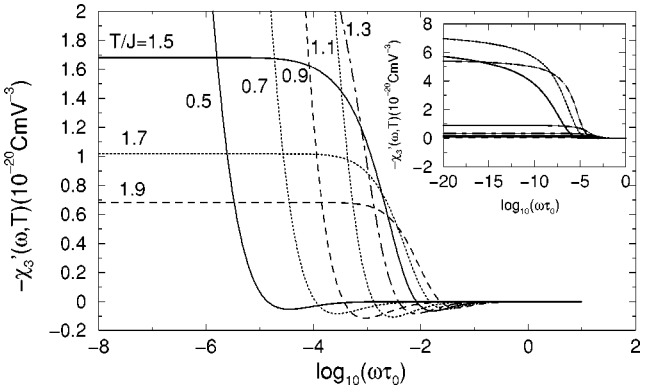

FIG. 4. Calculated frequency dependence of the real part of the third-order nonlinear susceptibility due to field modulation of intercluster coupling (mechanism II), averaged over a linear distribution of T_0 and using the same parameters as in Figs. 1 and 2. Inset: Same, but for a wider frequency range. Top to bottom (at $x=-10$): $T/J=0.7$, 0.9, 0.5, 1.1, 1.3, 1.5, 1.7, and 1.9.

where $n=1$ or 3 for the linear and third-order nonlinear responses, respectively. The calculated frequency dependence of the real part of $\overline{\chi_3}(\omega,T)^{II}$ is shown in Fig. 4 in the region of strongest frequency dispersion for a number of temperatures, as indicated. The inset shows the behavior of $\overline{\chi_3'}(\omega,T)^{II}$ in a wider frequency range. In Fig. 5, the imaginary part of $\overline{\chi_3}(\omega,T)^{II}$ is plotted on a double-logarithmic scale. At small frequencies it shows a power-law behavior $\overline{\chi_3}(\omega,T)^{II}\sim(\omega\tau_0)^{\nu}$, where ν varies between $\nu\simeq 0.125$ at $T/J=0.5$ and $\nu=1$ at high temperatures.

This behavior is similar to that of $\overline{\chi_3'}(\omega,T)^{I}$ studied earlier,[5] however, there are some important differences. To see more clearly the difference between the two contributions to the nonlinear response it is instructive to consider the dynamic dielectric nonlinearity function, defined for convenience as

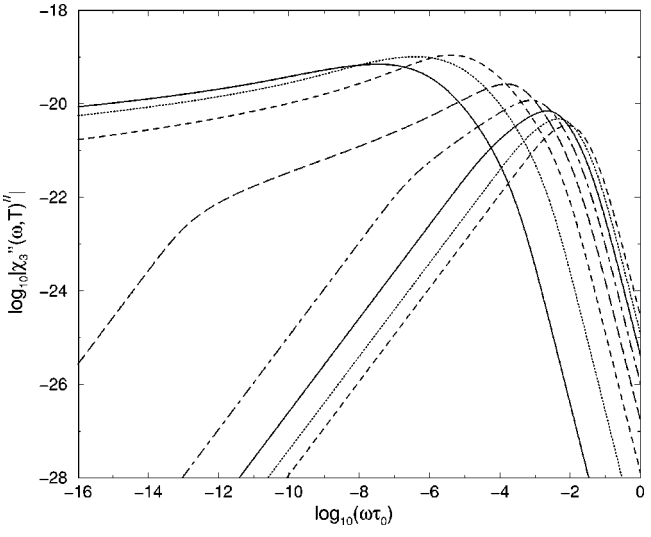

FIG. 5. Calculated frequency dependence of the imaginary part of the third-order nonlinear susceptibility (mechanism II) plotted on a double-logarithmic scale (χ_3 in units $\mathrm{Cm\,V}^{-3}$). Top to bottom (left side): $T/J=0.5$, 0.7, 0.9, 1.1, 1.3, 1.5, 1.7, and 1.9.

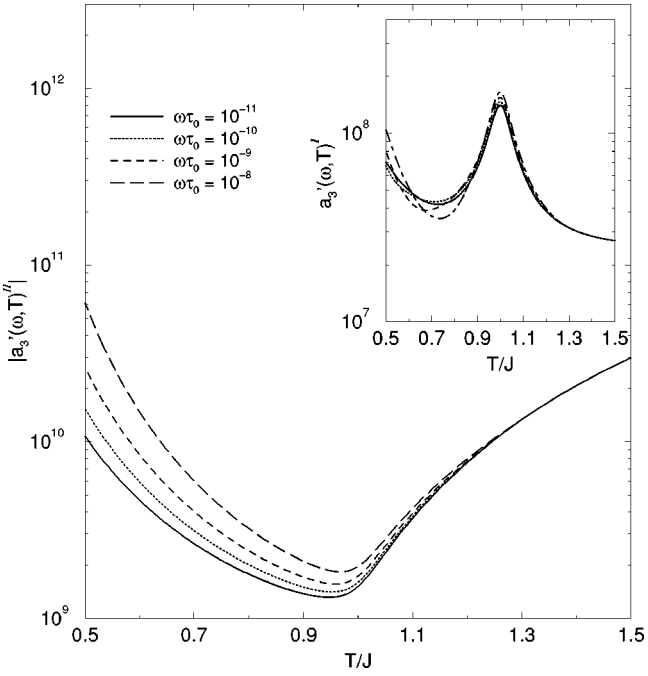

FIG. 6. Calculated temperature dependence of the dynamic nonlinearity function for mechanism II, $|a_3'(\omega,T)^{II}|$ (in units $\mathrm{Vm}^5\mathrm{C}^{-3}$), at various frequencies as indicated. Inset: same, but for mechanism I.

$$a_3'(\omega,T)^{II}=\frac{\overline{\chi_3'}(\omega)^{II}}{\overline{\chi_1'}(\omega)^4}. \tag{42}$$

Other definitions of $a_3'(\omega,T)$ have been in use[8,5]; however, in the low-frequency limit which is of prime interest to us, they all lead to similar results. In Fig. 6, $|a_3'(\omega,T)^{II}|$ is plotted for several frequencies using a double logarithmic scale. In the temperature interval displayed, $a_3'(\omega,T)^{II}$ is negative and reaches extremely large values at lower temperatures in view of the smallness of the term $\overline{\chi_1'}(\omega)^4$ in the denominator. The behavior of $|a_3'(\omega,T)^{II}|$ is qualitatively similar to that of a related quantity $|\beta|$ determined experimentally in PMN.[8,9] For comparison, the inset of Fig. 6 shows the behavior of the dielectric nonlinearity function $a_3'(\omega,T)^{I}$ defined in terms of mechanism I, which is due to the intrinsic nonlinearity of the rigid spherical model.[5] In contrast to $|a_3'(\omega,T)^{II}|$, this contribution shows a peak near $T\approx J$, which could not be confirmed experimentally.[8] This is not surprising, since the contribution of the mechanism is at least one order of magnitude larger in the peak region and even larger at other temperatures.

The above behavior depends on the type of average over T_0 as defined in Eq. (41). At small values of ω the dynamic nonlinearity $a_3'(\omega,T)^{II}$ differs significantly from the static field-cooled value a_{3s}^{FC} given by Eq. (15), which is displayed in Fig. 2. This happens even in the limit $\omega\tau_0\ll 1$. The reason is that the average over T_0 contains values of τ which can become extremely large, and thus $\omega\tau\gg 1$ in spite of the fact that $\omega\tau_0\ll 1$. Therefore, in the limit $\omega\tau_0\ll 1$, the dynamic

nonlinearity function $a_3'(\omega,T)^{II}$ corresponds to the zero-field-cooled quasistatic value of the dielectric nonlinearity coefficient a_{3s}^{ZFC}.

By contrast, the analogous quantity $a_3'(\omega,T)^{I}$ calculated in Ref. 5 as the contribution of mechanism I has a peak near $T \approx J$, and at small values of frequency approaches the static limit a_{3s}^{I}, i.e., there is no difference between the field-cooled and zero-field-cooled dynamic dielectric nonlinearity functions in that case.

IV. CONCLUSIONS

It has been shown in the framework of the generalized SRBRF model that there are two main mechanisms of nonlinear response in relaxor ferroelectrics: Mechanism I is due to the intrinsic nonlinearity of the rigid spherical model, and mechanism II to the field modulation of the intercluster coupling. The main result of the present study is that the contribution of mechanism II to the third-order nonlinear dielectric susceptibility $\chi_3(\omega)$ is more than one order of magnitude stronger than that of mechanism I in systems such as PMN and PLZT ceramics. Also, the sign of $\chi_3(\omega)^{II}$ turns out to be opposite to the sign of $\chi_3(\omega)^{I}$. In the static limit $\omega=0$, the corresponding result for $\chi_3(0)^{II}$ agrees qualitatively with the experimental value for the third-order field-cooled static dielectric susceptibility in PLZT ceramics. The zero-field-cooled quasistatic nonlinearity function $a_3'(\omega,T)^{II}$, which is obtained in the low-frequency limit $\omega\tau_0 \ll 1$, differs from $a_3'(\omega,T)^{I}$. In particular, $a_3'(\omega,T)^{I}$ shows a peak near the freezing temperature, while $a_3'(\omega,T)^{II}$ has a broad minimum in the same temperature range, in qualitative agreement with the observed behavior in PMN.

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