Anisotropic nonlinear dielectric response of relaxor ferroelectrics

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The anisotropy of the nonlinear static dielectric response of inorganic relaxor ferroelectrics of lead magnesium niobate (PMN) type is studied in the framework of the spherical random bond–random field model. Assuming that the shape of a polar nanoregion (PNR) and thus its dipole moment is modified by the action of homogeneous lattice strains, the anisotropic part of the interaction between the PNRs is derived. This interaction is bilinear in the electric field as well as in the order parameter field components, and gives rise to an effective field-dependent interaction strength, which depends both on the magnitude and the direction of the electric field. In addition to the isotropic intrinsic nonlinearity of the system studied earlier, we thus obtain an anisotropic part of the nonlinear response. By comparing the results with the experimental data of Tagantsev and Glazounov [Appl. Phys. Lett. **74**, 1910 (1999)] for PMN we calculate the temperature dependence of the anharmonicity coefficients in the effective free energy of the system.

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I. INTRODUCTION

Relaxor ferroelectrics have long been attracting considerable attention not only in view of their potential applicability to a number of practical devices, but also because of their interesting physical properties.[1] In contrast to conventional ferroelectrics, relaxors are characterized by slow relaxation and a strong frequency dispersion of the dielectric permittivity, and by the absence of macroscopic symmetry change down to the lowest temperatures. Typical representatives are the mixed ABO_3 perovskite oxides such as $PbMg_{1/3}Nb_{2/3}O_3$ (or PMN), but in recent years a number of inorganic and organic materials have been found to exhibit the same kind of relaxor behavior. In addition to the above normal or proper relaxors, there is a group of materials such as strontium barium niobate (SBN),[2] in which ferroelectric long range order and a relaxorlike dispersion coexist. It is believed that in the case of these "improper" relaxors the concept of diffuse phase transition, originally proposed for PMN and related systems,[3] may be applicable.

A common feature of relaxor systems is the existence of polar clusters or nanoregions (PNRs),[4] which appear as a result of compositional fluctuations in a highly polarizable lattice. Similar to dipolar glasses, these PNRs are coupled through long range random dipolar interactions or random bonds and are subject to local random electric fields. In contrast to dipolar glasses, however, the lengths of the dipolar moments of PNRs are not fixed, but rather have a broad statistical distribution. By assuming a generalized gamma distribution one obtains the so-called spherical random bond–random field (SRBRF) model of relaxor ferroelectrics,[5,6] which is exactly solvable. The SRBRF model has several limitations. Specifically, the model is static and thus applicable to phenomena occurring in the ergodic relaxor phase or to quasistatic phenomena in the nonergodic phase. The linear static dielectric susceptibility χ_1 calculated from the SRBRF model corresponds to the field-cooled static susceptibility, which is measured by cooling the system slowly in a small bias field and monitoring the surface charge.[7] Thus the calculated static susceptibility will not exhibit a broad temperature maximum, which is a typical feature of the low frequency response of relaxors and is essentially a dynamic effect.[8] Since random fields are present, the Edwards-Anderson (EA) order parameter q is nonzero at all temperatures, and does not mark the transition into the nonergodic relaxor state. For the same reason, the isotropic part of the third order nonlinear susceptibility χ_3 does not diverge at the ergodic-nonergodic transition, but only exhibits a peak whose width depends on the strength of the random fields.

Here and in the following, the linear and nonlinear susceptibilities are defined, as usual, in terms of an expansion of the physical polarization $\vec{\mathcal{P}}$ in powers of the applied static electric field $\vec{E}$. For a general orientation of the field we can write

$$\mathcal{P}_\mu = \mathcal{P}_{s,\mu} + \sum_\nu \chi_1^{\mu\nu} E_\nu + \sum_{\nu\kappa} \chi_2^{\mu\nu\kappa} E_\nu E_\kappa - \sum_{\nu\kappa\lambda} \chi_3^{\mu\nu\kappa\lambda} E_\nu E_\kappa E_\lambda + \cdots . \quad (1)$$

In relaxors, the spontaneous polarization $P_{s,\mu}(\mu=x,y,z)$ is zero, and in case of inversion symmetry the second order nonlinear response $\chi_2^{\mu\nu\kappa}$ will be zero as well. Note that we have introduced the third order nonlinear susceptibility tensor $\chi_3^{\mu\nu\kappa\lambda}$ with a negative sign though sometimes the opposite sign is chosen.

In a cubic relaxor, the linear susceptibility $\chi_1^{\mu\nu}$ is replaced by a scalar, χ_1. It should be noted, however, that in PMN the quasistatic linear susceptibility measured in a weak applied field is slightly anisotropic[9] because the field breaks the average cubic symmetry. Here we will consider the linear susceptibility in cubic systems in zero applied field, which is isotropic. For fields along a symmetry direction $[p]$, say, [100], [110], or [111], we expect that $\vec{\mathcal{P}}$ will be parallel to $\vec{E}$ and Eq. (1) will contain a single component of $\vec{\mathcal{P}}$ and $\vec{E}$ along $[p]$.

It has been found experimentally in PMN that the longitudinal nonlinear susceptibility χ_3 shows a strong anisotropy

with respect to the orientation of the field.[9,10] For a field along [100] one finds $\chi_3^{[100]}>0$, whereas $\chi_3^{[111]}<0$ for $\vec{E}\|[111]$. Thus for PMN and related systems, Eq. (1) can be written in a simplified form[10]

$$\mathcal{P}=\chi_1 E-\chi_3^{[p]}E^3+\cdots . \tag{2}$$

The purpose of the present work is to discuss the origin of the anisotropic nonlinear dielectric response of relaxor ferroelectrics within the framework of the SRBRF model. We propose a mechanism based on the deformation of PNRs due to lattice strain fluctuations, which gives rise to a change of magnitude and orientation of the PNR dipole moment. This then leads to a field-dependent effective interaction between the PNRs, from which the anisotropic part of the nonlinear susceptibility can be derived. According to this mechanism, the anisotropy of χ_3 is intimately related to the existence of PNRs and thus seems to be a unique feature of relaxor ferroelectrics, which so far has not been observed in spin and dipolar glasses.

II. LINEAR AND NONLINEAR RESPONSE OF RELAXORS

It has been recognized a long time ago that the linear susceptibility χ_1 of a relaxor deviates from the Curie-Weiss (CW) behavior over a wide temperature range.[3] Viehland *et al.*[11] pointed out that there exists a close analogy between relaxors and spin—or rather dipolar—glasses and that the linear susceptibility of a relaxor can be described by the well-known formula derived originally for spin glasses,[12]

$$\chi_1=C_0\frac{1-q(T)}{T-\Theta[1-q(T)]}. \tag{3}$$

Here C_0 is an effective CW constant, and $q(T)$ is a generalized EA order parameter, which is nonzero at all temperatures. The temperature dependence of $q(T)$ can be extracted from the experimental data, and C_0 and the effective CW temperature Θ are determined from the asymptotic high-temperature behavior of χ_1. Note that Eq. (3) is analogous to the static susceptibility of conventional ferroelectrics if we set $\Theta=T_c$, and assume that $q=0$ for $T\geqslant T_c$, and $q=P^2$ for $T<T_c$, where P is a dimensionless dielectric polarization proportional to $\mathcal{P}$.

In relaxor ferroelectrics, the order parameters q and P can be introduced in the framework of the replica approach applied to the SRBRF model. They are then obtained as solutions of two coupled equations[5,6]

$$q=\beta^2J^2(q+\Delta/J^2)(1-q)^2+P^2/3, \tag{4a}$$

$$P=\beta(J_0P+gE)(1-q). \tag{4b}$$

The SRBRF model is based on infinite range random interactions J_{ij} and random fields $\vec{h}_i$ acting on the PNRs. The mean interaction strength is given by $[J_{ij}]_{av}=J_0/N$, the random field variance is defined by $[h_{i\mu}h_{j\nu}]_{av}=\Delta\delta_{ij}\delta_{\mu\nu}$, whereas J measures the degree of bond randomness, i.e.,

$$J^2/N=[J_{ij}^2]_{av}-J_0^2. \tag{5}$$

Throughout, we will consider the case without long range order, namely, $J_0<(J^2+\Delta)^{1/2}$.

Writing $\mathcal{P}=(g/v_0)P$, the linear susceptibility is obtained from Eq. (4b) in terms of J_0, q, dipole moment g, and average volume $v_0=V/N$ of a PNR as follows:

$$\chi_1=\left(\frac{g^2}{v_0}\right)\frac{\beta(1-q)}{1-\beta J_0(1-q)}. \tag{6}$$

Comparing with Eq. (3), we readily see that the SRBRF model implies $C_0=g^2/(k\epsilon_0v_0)$ and $\Theta=J_0/k$. In the presence of an external field $\vec{E}$, the order parameter q becomes field dependent, $q\rightarrow q(E,T)$, and thus $\chi_1\rightarrow\chi_1(E,T)$. Note that since Eqs. (4) are independent of the orientation of the field, both q and χ_1 are fully isotropic. Also, q is an even function, and P an odd function of E, implying that $\chi_2=0$. The longitudinal third order nonlinear susceptibility χ_3 can then be calculated using the relation

$$\chi_3=-\frac{1}{2}\left[\frac{\partial^2\chi_1(E)}{\partial E^2}\right]_{E=0}. \tag{7}$$

As discussed in more detail below, the directional dependence of χ_3 can be introduced into the model by considering a new coupling mechanism, which leads to a field dependent coupling parameter J_0, namely,

$$J_0^{[p]}(E)=J_0(0)+G_pE^2, \tag{8}$$

where the index p specifies the direction of the field ($[p]=[100],[110],[111]$) and G_p is the corresponding proportionality parameter. A field dependence of this type had earlier been found empirically[7,13] by studying the $(E-T)$ phase diagram of PMN and PLZT. We can split χ_3 into its isotropic and anisotropic part and write

$$\chi_3^{[p]}=\chi_{3,is}+\chi_{3,an}^{[p]}, \tag{9}$$

with

$$\chi_{3,is}=-\frac{1}{2}\left[\frac{\partial\chi_1}{\partial q}\frac{d^2q}{dE^2}\right]_{E=0}=\frac{kTv_0^3}{3g^4D(q)}\chi_1^4, \tag{10}$$

where $D(q)\equiv(1-q)^2[1-\beta^2J^2(1-q)(1-3q-2\Delta/J^2)]$, and

$$\chi_{3,an}^{[p]}=-\frac{1}{2}\left[\frac{\partial\chi_1}{\partial J_0}\frac{d^2J_0}{dE^2}\right]_{E=0}=-G_p\frac{v_0}{g^2}\chi_1^2. \tag{11}$$

To illustrate the behavior of the linear and nonlinear static response, $\chi_{3,is}$ and $\chi_{3,an}$ are plotted in Fig. 1 as functions of temperature for five different values of the random field strength Δ. The remaining parameters of the SRBRF model were chosen as $J/k=219\pm4$ K and $\Delta/J^2=0.001$, which are the representative values for PMN.[14] The remaining parameter J_0 is given by $J_0/k=79.7$ K as shown in Sec. IV. Since, as discussed below, the relative magnitudes of $\chi_{3,is}$ and $\chi_{3,an}$ are not known *a priori*, the sign of $\chi_{3,an}$ was chosen as positive and the vertical scales are in arbitrary units. Also shown in the inset is the behavior of the quasistatic linear field-cooled susceptibility. As expected, by increasing the random field strength Δ, the anomaly in $\chi_{3,is}$ is smeared, and both

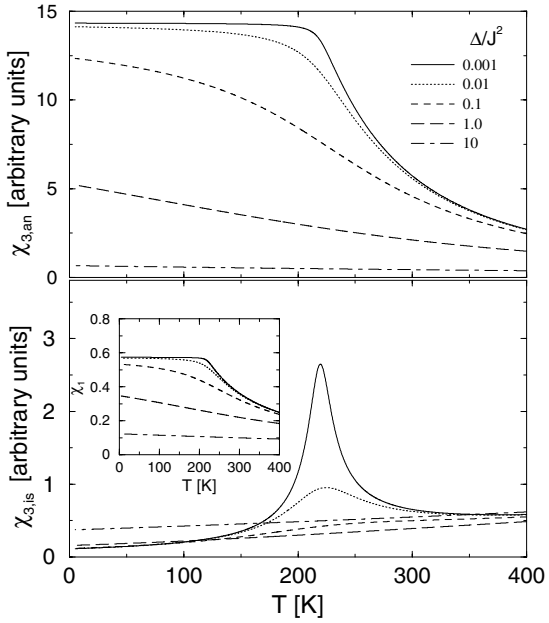

FIG. 1. Isotropic (lower) and anisotropic (upper graph) quasistatic nonlinear response as functions of temperature, calculated from Eqs. (10) and (11), respectively, and plotted for several values of random field strength Δ/J^2. The inset shows the corresponding temperature dependence of the linear susceptibility.

$\chi_{3,an}$ and χ_1 become monotonically decreasing functions of temperature.

The remaining task is to calculate the anisotropy parameters G_p from the SRBRF model. It should be noted that instead of the replica approach used here, one can formulate the problem in terms of exact eigenstates and eigenvalues of the random matrix J_{ij}.[15] The present formulation has the advantage that the EA order parameter q appears explicitly in the results, thus facilitating a comparison with the empirical formula, Eq. (3).

III. MECHANISM OF ANISOTROPIC NONLINEAR RESPONSE

We consider a model system of PNRs, which are characterized by the order parameter field $\vec{S}_i$, $i=1,2,\ldots,N$, assuming that the dipole moment of the ith PNR is equal to $\vec{p}_i = g\vec{S}_i$, where g is a unit dipole moment. In the SRBRF model, the components $S_{i\mu}$ span the entire space, but are restricted by the global spherical condition $\Sigma_{i=1}^{N}(\vec{S}_i)^2=3N$. The interaction with an external electric field $\vec{E}$ is formally described by the Hamiltonian

$$\mathcal{H}_{ext} = -\sum_{i=1}^{N}\sum_{\mu,\nu=1}^{3} g_{\mu\nu}E_\mu S_{i\nu}, \tag{12}$$

where $g_{\mu\nu}=g\delta_{\mu\nu}$. We now assume that the dipole moment is deformed by the homogeneous strain fluctuations $u_{\mu\nu}$, giving rise to a modified interaction

$$\tilde{\mathcal{H}}_{ext} = -\sum_{i}\sum_{\mu\nu\kappa\lambda} u_{\mu\nu}g_{\mu\nu\kappa\lambda}E_\kappa S_{i\lambda}. \tag{13}$$

The tensor $g_{\mu\nu\kappa\lambda}$ represents the strain derivative of $g_{\mu\nu}$ and can be regarded as a measure of the local electrostriction effect due to the deformation of PNRs by the strain. The microscopic mechanism of this deformation has not yet been proposed, however, similar effects due to an external electric field have been investigated earlier.[16] Note that $g_{\mu\nu\kappa\lambda} = g_{\nu\mu\kappa\lambda}$, etc., but $g_{\mu\nu\kappa\lambda} \neq g_{\kappa\lambda\mu\nu}$.

The elastic energy is given by

$$\mathcal{H}_{el} = \frac{1}{2}V\sum_{\mu\nu\kappa\lambda} u_{\mu\nu}C_{\mu\nu\kappa\lambda}u_{\kappa\lambda}, \tag{14}$$

introducing the elastic constants $C_{\mu\nu\kappa\lambda}$. In equilibrium, the strains are eliminated from $\tilde{\mathcal{H}}_{ext}+\mathcal{H}_{el}$, transforming $\tilde{\mathcal{H}}_{ext}$ into

$$\tilde{\mathcal{H}}_{\text{ext}} = -\frac{1}{2V}\sum_{ij}\sum_{\mu\nu\kappa\lambda} b_{\mu\nu\kappa\lambda}E_\mu E_\kappa S_{i\nu}S_{j\lambda}, \tag{15}$$

where

$$b_{\mu\nu\kappa\lambda} = \sum_{\mu'\nu'\kappa'\lambda'} g^{T}_{\mu\nu\mu'\nu'}C^{-1}_{\mu'\nu'\kappa'\lambda'}g_{\kappa'\lambda'\kappa\lambda}, \tag{16}$$

and $g^{T}_{\mu\nu\mu'\nu'}=g_{\mu'\nu'\mu\nu}$.

The $i\neq j$ terms in Eq. (15) represent an additional interaction between the PNRs due to homogenous strain fluctuations under the influence of an external field $\vec{E}$. Thus $\tilde{\mathcal{H}}_{ext}$ can be regarded as a field-dependent contribution to the unperturbed isotropic SRBRF Hamiltonian. The resulting effective SRBRF Hamiltonian can be written as

$$\mathcal{H}_{eff} = -\frac{1}{2}\sum_{ij}\sum_{\mu\nu} J^{\mu\nu}_{ij}S_{i\mu}S_{i\nu} - \sum_{i\mu} h_{i\mu}S_{i\mu}, \tag{17}$$

introducing a new field-dependent random bond interaction

$$J^{\mu\nu}_{ij} = J_{ij}\delta_{\mu\nu} + \frac{1}{V}\sum_{\kappa\lambda} b_{\mu\kappa\nu\lambda}E_\kappa E_\lambda. \tag{18}$$

In a system with macroscopic cubic symmetry, $b_{\mu\nu\kappa\lambda}$ will have the full cubic symmetry. Thus we can use the Voigt notation b_{ij}, $i,j=1,2,\ldots,6$, where $b_{11}=b_{1111}$, $b_{12}=b_{1122}$, $b_{1212}=b_{44}$, etc. We will be interested in the special case where the applied field is along one of the cubic symmetry directions $[p]$. The coordinate system can then be rotated in such a manner that $\vec{E}=(E,0,0)$. The relevant components of $b^{[p]}_{\mu\nu\kappa\lambda}$ in the new system along $[p]$ are then

$$[100]:\ b^{[p]}_{1111} = b_{11}, \tag{19a}$$

$$b^{[p]}_{1212} = b^{[p]}_{1313} = b_{44}; \tag{19b}$$

$$[110]:\ b^{[p]}_{1111} = (b_{11}+b_{12}+2b_{44})/2, \tag{20a}$$

$$b^{[p]}_{1212} = (b_{11}-b_{12})/2, \tag{20b}$$

$$b^{[p]}_{1313} = b_{44}; \tag{20c}$$

$$[111]: b_{1111}^{[p]} = (b_{11} + 2b_{12} + 4b_{44})/3, \tag{21a}$$

$$b_{1212}^{[p]} = b_{1313}^{[p]} = (b_{11} - b_{12} + b_{44})/3. \tag{21b}$$

The field-dependent interaction (18) can thus be written

$$J_{ij}^{\mu\mu} = J_{ij} + \frac{1}{V} b_{\mu 1 \mu 1}^{[p]} E^2, \tag{22}$$

and for the mean interaction strength J_0 appearing in Eq. (6) we recover Eq. (8) with

$$G_p = b_{1111}^{[p]}/v_0. \tag{23}$$

The contribution of homogeneous strains considered above is expected to be dominant provided that the average size of PNRs is large compared to the lattice constant. For example, in PMN the lattice constant is $a \simeq 0.404$ nm, whereas the average PNR size is $R \sim 3.2$ nm.[17]

IV. COMPARISON WITH EXPERIMENTS

The quasistatic nonlinear susceptibility χ_3 as given by Eqs. (9)–(11) can be measured directly by cooling the system slowly in a small static field.[7,9] A number of dynamic techniques are also in use, yielding a frequency dependent complex nonlinear permittivity $\chi_3(\omega)$.[10,18] In the ergodic relaxor phase above the freezing temperature, the $\omega \to 0$ limit of the real part of $\chi_3(\omega)$ is expected to converge towards the quasistatic value χ_3. For any orientation of the field $\vec{E}$, the measured χ_3 is always a sum of an isotropic and an anisotropic component.

In conventional ferroelectrics, Landau theory predicts that the isotropic part of χ_3 diverges as $\sim (T - T_c)^{-4}$ at the critical temperature T_c. For $T > T_c$, this follows from Eq. (6) after setting $J=0$ and $\Delta=0$, i.e., no randomness, which also implies $q=0$. Thus the divergence is due entirely to the factor χ_1^4. For $T < T_c$, however, one must include the spontaneous polarization as well as the fact that $\chi_2 \neq 0$. This then leads to a negative value of χ_3 below T_c. The anisotropic part of χ_3, as given by Eq. (11), is not expected to be applicable to ferroelectrics, however, it may be relevant to improper relaxors where long range order exists.

In proper relaxors, random fields ($\Delta \neq 0$) prevent $\chi_{3,is}$ from diverging near $T_f \simeq J/k$, whereas $\chi_{3,an}$ is always expected to be finite.

Equation (2) can formally be inverted to yield the equation of state[10]

$$E_\mu = A\mathcal{P}_\mu + \sum_{\nu\kappa\lambda} B_{\mu\nu\kappa\lambda} \mathcal{P}_\nu \mathcal{P}_\kappa \mathcal{P}_\lambda + \cdots \tag{24}$$

for a general direction of the polarization $\vec{\mathcal{P}}$ and field $\vec{E}$. From Eq. (2) we see that $A = A(q) = 1/\chi_1$, where χ_1 is given by Eq. (6).

Equation (24) can formally be derived from the effective free energy

$$\mathcal{F}(\vec{\mathcal{P}}, q) = \frac{3}{2} F(q) + \frac{1}{2} A(q) \mathcal{P}^2 + \frac{1}{4} \sum_{\mu\nu\kappa\lambda} B_{\mu\nu\kappa\lambda}(q) \mathcal{P}_\mu \mathcal{P}_\nu \mathcal{P}_\kappa \mathcal{P}_\lambda + \cdots - \vec{E} \cdot \vec{\mathcal{P}} \tag{25}$$

by applying the equilibrium condition $\partial \mathcal{F}/\partial \mathcal{P}_\mu = 0$. Here, the zero-field free energy $F(q)$ is given by[6]

$$\beta v_0 F(q) = \frac{\beta^2 J^2 q^2}{2} - \frac{1}{1-q} - \log(1-q) - \beta^2 \Delta (1-q). \tag{26}$$

The effective functional (25) could, in principle, be derived from the exact free energy of a relaxor in the SRBRF model, $\mathcal{F}_0 = \mathcal{F}_0(\vec{\mathcal{P}}, q_{\mu\nu}, r_{\mu\nu}, z)$, where $q_{\mu\nu}$ and $r_{\mu\nu}$ are two generalized order parameter tensors.[6] The EA order parameter is here given by $q = (1/3)\mathrm{Tr}\,\mathbf{q}$, whereas $\mathrm{Tr}\,\mathbf{r} = 3$. Furthermore, z is a Lagrange multiplier enforcing the spherical condition. It is easily verified that the stability conditions $\partial \mathcal{F}_0(\vec{\mathcal{P}}, q)/\partial P_\mu = \partial \mathcal{F}_0(\vec{\mathcal{P}}, q)/\partial q = 0$, where $\mathcal{F}_0(\vec{\mathcal{P}}, q)$ is the functional (25) without the $B_{\mu\nu\kappa\lambda}$ term, simply lead to Eqs. (4). The stable solutions of these equations must obey the saddle-point conditions $\partial^2 \mathcal{F}_0/\partial P_\mu^2 > 0$ and $\partial^2 \mathcal{F}_0/\partial q^2 < 0$, in accord with standard spin glass theories.[19]

In a system with cubic symmetry we can write[10]

$$B_{\mu\nu\kappa\lambda} = B_{12}(\delta_{\mu\nu}\delta_{\kappa\lambda} + \delta_{\mu\kappa}\delta_{\nu\lambda} + \delta_{\mu\lambda}\delta_{\nu\kappa}) + (B_{11} - 3B_{12}) e_{\mu\nu\kappa\lambda}, \tag{27}$$

where B_{11} and B_{12} are two independent parameters, introduced here in such a manner that $B_{1111} = B_{11}$ and $B_{1122} = B_{1212} = B_{12}$, etc. Furthermore, $e_{\mu\nu\kappa\lambda} = 1$ if $\mu = \nu = \kappa = \lambda$ and 0 otherwise. Inserting Eq. (24) into Eq. (1) we find

$$B_{\mu\nu\kappa\lambda} = \frac{\chi_3^{\mu\nu\kappa\lambda}}{\chi_1^4}. \tag{28}$$

For a symmetry direction $[p]$, and with the aid of Eqs. (9)–(11), this leads to

$$B_{1111}^{[p]} = \frac{\chi_3^{[p]}}{\chi_1^4} = \frac{k T v_0^3}{3 g^4 D(q)} - G_p \frac{v_0}{g^2} \chi_1^{-2}, \tag{29}$$

and using Eq. (23) we finally have

$$B_{1111}^{[p]} = \frac{k T v_0^3}{3 g^4 D(q)} - \frac{b_{1111}^{[p]}}{g^2} \chi_1^{-2}. \tag{30}$$

The coefficients $B_{1111}^{[p]}$ for the three symmetry directions are given by

$$B_{1111}^{[100]} = B_{11}, \tag{31}$$

$$B_{1111}^{[110]} = \frac{1}{2}(B_{11} + 3B_{12}), \tag{32}$$

$$B_{1111}^{[111]} = \frac{1}{3}(B_{11} + 6B_{12}). \tag{33}$$

Thus the anisotropic nonlinear response is determined by just two independent parameters, B_{11} and B_{12}.[20]

By measuring $\chi_3^{[p]}$ and χ_1 one can thus obtain the parameters B_{11} and B_{12} appearing in the free energy functional (25), and from these one can, in principle, deduce the values of the coefficients b_{ij}. Note that $B_{1111}^{[p]}$, just like $\chi_3^{[p]}$, consists of an isotropic and an anisotropic part, each having a different temperature dependence. The isotropic part can be eliminated by forming the differences between the corresponding values of $\chi_3^{[p]}$ for two different directions,[10] for example,

$$\frac{\chi_3^{[100]} - \chi_3^{[110]}}{\chi_1^4} = B_{1111}^{[100]} - B_{1111}^{[110]} = \frac{1}{2}(B_{11} - 3B_{12}). \quad (34)$$

It then follows from Eq. (30) that

$$B_0 \equiv B_{11} - 3B_{12} = \frac{b_0}{g^2 \chi_1^2}, \quad (35)$$

where $b_0 \equiv 2b_{44} + b_{12} - b_{11}$. It is easily shown that for any pair of directions $[p],[p']$, the difference $B_{1111}^{[p]} - B_{1111}^{[p']}$ is always proportional to B_0, or equivalently to b_0.

The so-called scaled nonlinear susceptibility $a_3 = \chi_3/\chi_1^4$ is readily obtained from the measured χ_3 and χ_1 and is often used to discriminate between the normal ferroelectric and relaxor behavior of a system under study. For example, in a uniaxial ferroelectric above T_c, one has $a_3 = B$, where B is the fourth order coefficient in the free energy expansion, and a_3 is thus expected to behave as $a_3 \sim (T - T_c)^{\gamma - 2\beta}$. In mean field, $\gamma = 2\beta$ and $a_3 \sim$ const as $T \to T_c + 0$. Below T_c, however, $a_3 = -8B$, implying that a_3 makes a jump to a negative value at T_c, since B is expected to be continuous at T_c.

In a normal relaxor, a_3 consists of an isotropic and an anisotropic part according to Eq. (9). The isotropic component shows a peak anomaly due to the factor $1/D(q)$ in Eq. (10), whereas the anisotropic part behaves as $a_3 \sim \chi_1^{-2}$, and hence increases monotonically with temperature. Estimates based on an empirical model[9] suggested that in PMN the isotropic part might be much smaller than the contribution from the field dependent coupling as given by Eq. (8). Since $\chi_3^{[100]} > 0$ for $\vec{E} \| [100]$, it follows that $B_{11} > 0$ as indeed observed.[10,20] On the other hand, $\chi_3^{[111]} < 0$ implies that $B_{11} + 4B_{12} < 0$.

Assuming the parameters b_{ij} to be approximately constant, the temperature dependence of the parameter B_0 can be determined by Eqs. (35) and (6). We find

$$B_0 = a_0[T/(1-q) - J_0/k]^2, \quad (36)$$

where $a_0 = b_0 k^2 v_0^2 / g^6$.

In PMN, Tagantsev and Glazounov[10] determined B_0 experimentally as a function of temperature in the range $270\ \mathrm{K} < T < 325\ \mathrm{K}$ and found $B_0 > 0$, implying that $B_{11} > 3B_{12}$ and $b_{11} < b_{12} + 2b_{44}$ in this temperature range.

In Fig. 2 we plot the calculated temperature dependence of the coefficient B_0 in PMN using the parameter values[14] $J/k = 219 \pm 4$ K and $\Delta/J^2 = 0.001$. The inset shows a fit to the data of Tagantsev and Glazounov,[10] from which the remaining parameters $J_0/k = 79.67$ K and $a_0 = 2.79 \times 10^3\ \mathrm{m^5\ V\ C^{-3}\ K^2}$ have been determined. The agreement appears to be good in the available temperature range. For the above values of the parameters J, J_0, and Δ/J^2 the order parameter q in Eq. (36) has a rather small but finite value at temperatures $T > J/k$, and does not contribute significantly to the calculated value of B_0. The fact that the measured coefficient B_0 agrees with the calculated temperature dependence does not constitute a proof that the experiment in PMN supports the SRBRF model at all temperatures. The experiment merely proves the mean field type interaction J_0 between polar nanoregions, rather than the regime of applicability of the SRBRF model. New experiments in a broader temperature range would be necessary to test the predictions of the present calculation.

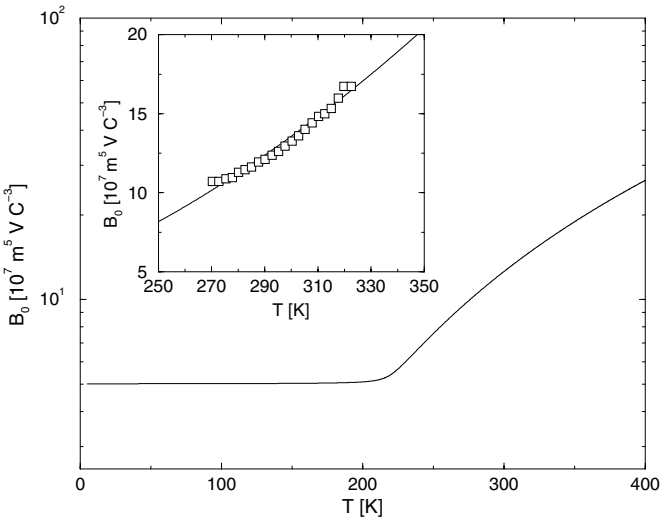

FIG. 2. Calculated temperature dependence of the coefficient $B_0 = B_{11} - 3B_{12}$ in relaxor ferroelectric PMN, plotted on a logarithmic vertical scale. The inset shows a fit to the data from Ref. 10.

From a_0 we can estimate the value of the coefficient b_0 appearing in Eq. (35). Using the value[11] $C_0 \sim 1.25 \times 10^5$ K to obtain the ratio g^2/v_0, and assuming that $g \sim 10e_0$ nm, where e_0 is the elementary charge, we find $b_0 \cong 54.8 e_0\ \mathrm{nm^5/V}$. This corresponds to an average PNR volume $v_0 \cong 19.8\ \mathrm{nm^3}$, in reasonable agreement with the estimates from inelastic neutron scattering data.[17]

Quasistatic measurements of the field-cooled nonlinear response in PMN revealed no anomaly at the freezing temperature T_f,[7,9] suggesting that $\chi_{3,an}$ is the dominant component of the static response. On the other hand, earlier dynamic measurements[14] have shown an increase of χ_3 on approaching T_f, which has been attributed to the isotropic part of the response. This apparent inconsistency can be explained in the framework of a dynamic approach by considering the experimental frequency dependent nonlinear response and by assuming that it is essentially given by its anisotropic component $\chi_{3,an}(\omega)$. This response should then be proportional to $\chi_1(\omega)^2$ according to Eq. (11), and its temperature dependence will thus exhibit the typical broad frequency peak structure and dispersion of the zero-field-cooled dynamic linear response.

V. CONCLUSIONS

We have proposed a mechanism of anisotropic nonlinear dielectric response in relaxor ferroelectrics, which is based

on the deformation of polar nanoregions and corresponding changes in their dipole moments by homogeneous strain fluctuations. The corresponding expressions for the linear and third order nonlinear field-cooled static susceptibilities were obtained within the framework of the SRBRF model of relaxor ferroelectrics. The isotropic component of the static third order nonlinear response, $\chi_{3,is}$, has a peak anomaly at the static freezing temperature, but remains finite due to the presence of random fields. The anisotropic component $\chi_{3,an}$ depends on the direction of the applied field, and was evaluated for fields along the cubic [100], [110], and [111] directions. A general expression for the nonlinear response in terms of the anharmonicity coefficients of an effective free energy functional for the SRBRF model has been obtained. The temperature dependence of the anharmonicity coefficients in relaxor ferroelectric PMN has been calculated and compared to the experimental data by Tagantsev and Glazounov.[10]

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[1] G. A. Samara, *Solid State Physics*, Vol. 56, edited by H. Ehrenreich and R. Spaepen (Academic, New York, 2001), p. 1.
[2] W. Kleemann, P. Licinio, Th. Woike, and R. Pankrath, Phys. Rev. Lett. **86**, 6014 (2001).
[3] G. A. Smolensky, J. Phys. Soc. Jpn. **28**, 26 (1970).
[4] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998).
[5] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13470 (1999).
[6] R. Pirc, R. Blinc, V. Bobnar, and A. Gregorovič, Phys. Rev. B **72**, 014202 (2005).
[7] Z. Kutnjak, R. Pirc, and R. Blinc, Appl. Phys. Lett. **80**, 3162 (2002).
[8] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **61**, 14448 (2000).
[9] Z. Kutnjak, C. Filipič, and A. Levstik, Ferroelectrics **261**, 101 (2001).
[10] A. K. Tagantsev and A. E. Glazounov, Appl. Phys. Lett. **74**, 1910 (1999).
[11] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, Phys. Rev. B **46**, 8003 (1992).
[12] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **26**, 1792 (1975).
[13] V. Bobnar, Z. Kutnjak, R. Pirc, and A. Levstik, Phys. Rev. B **60**, 6420 (1999).
[14] V. Bobnar, Z. Kutnjak, R. Pirc, R. Blinc, and A. Levstik, Phys. Rev. Lett. **84**, 5892 (2000).
[15] R. Pirc, R. Blinc, and Z. Kutnjak, Phys. Rev. B **65**, 214101 (2002).
[16] A. K. Tagantsev and A. E. Glazounov, Phys. Rev. B **57**, 18 (1998).
[17] P. M. Gehring, S. Wakimoto, Z.-G. Ye, and G. Shirane, Phys. Rev. Lett. **87**, 277601 (2001).
[18] Y. Ishibashi, J. Korean Phys. Soc. **32**, S407 (1998).
[19] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[20] Our B_{11} corresponds to β_{11} of Ref. 10, and $B_{12}=\beta_{12}/3$.