Spherical random-bond–random-field model of relaxor ferroelectrics

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A model of relaxor ferroelectrics based on the interacting polar clusters picture has been formulated. The electric dipole moment of a nanosized polar domain is allowed a large number of discrete orientations and its length is assumed to fluctuate in a broad interval. Introducing a set of quasicontinuous order parameter fields and imposing a global spherical constraint, the spherical random-bond–random-field (SRBRF) model is written down and its static properties are investigated. It is found that for weak random fields the scaled third-order nonlinear susceptibility $a_3=\chi_3/\chi_1^4$ shows a nearly divergent behavior in the spherical glass phase, but there is no such anomaly in a random-field frustrated ferroelectric state. The probability distribution of local cluster polarization is calculated and its relation to the quadrupole perturbed NMR line shape of ^{93}Nb in PMN is discussed. The fact that the observed line shape is Gaussian at all temperatures provides strong support to the SRBRF model. [S0163-1829(99)06943-X]

I. INTRODUCTION

Since the discovery of relaxor ferroelectrics more than 50 years ago,[1] a number of concepts have been introduced to account for their unusual physical behavior: diffuse phase transition,[1] superparaelectric[2] and dipolar glass models,[3] random-field frustrated ferroelectric,[4,5] and reorienting polar clusters.[6,7] In a recent experimental study[8] based on the quadrupole perturbed NMR and nonlinear dielectric response techniques it has been suggested that the observed behavior in lead niobium manganate (PMN) could be well described within the framework of the spherical random-bond–random-field (SRBRF) model. This brings relaxors close to the category of dipolar glasses; however, there are important differences between these two classes of systems. In particular, the ^{93}Nb NMR line shape and the associated probability distribution of local polarization in PMN was shown to remain Gaussian at all temperatures. This is incompatible with the assumption of a fixed-length order parameter field typically made in dipolar glasses. Rather, in a relaxor the order parameter field is described as a continuous vector field of variable length, which is associated with the dipole moment of reorientable polar clusters, and is subject to a global spherical constraint on the square of the total polarization. Thus a relaxor corresponds to a new type of dipolar glass, namely, the spherical vector glass.

The purpose of the present paper is to derive the basic ideas of the SRBRF model in a concise way and calculate the predicted temperature and electric-field dependencies of some crucial physical properties, such as the nonlinear dielectric response and the probability distribution of local polarization, which is related to the inhomogeneous NMR line shape. The SRBRF model may be regarded as the simplest generic model of relaxor ferroelectrics of the PMN type. Since the random interactions—or bonds—between polar clusters are by assumption infinitely ranged with a Gaussian distribution, and local random fields are similarly Gaussian and uncorrelated, this will lead to a mean-field-type theory analogous to the case of spin[9,10] and dipolar[11] glasses.

In Sec. II we adopt a semimicroscopic description of a typical relaxor based on the interacting polar clusters picture and write down the model Hamiltonian. In Sec. III we present the solution of the SRBRF model obtained by the replica method and derive the basic equations for the glass order parameter and polarization. The predictions for the nonlinear susceptibility are given in Sec. IV, and in Sec. V the probability distribution of local polarization and the line shape of the quadrupole perturbed NMR are explicitly derived. Section VI contains the conclusions.

II. INTERACTING POLAR CLUSTERS

We will consider $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) as a representative relaxor ferroelectric system. On the mesoscopic level PMN is a structurally inhomogeneous material consisting of Nb-rich regions or polar clusters embedded in a quasiregular array of chemically ordered 1:1 regions[12] or chemical clusters. The polar clusters have typically the size of a few nanometers and are reorientable, and are thus responsible for the observed dielectric behavior.[3,6,7] In contrast, the chemical clusters are essentially static and act as sources of random electric fields. Each polar cluster C_i consists of a number of pseudocubic unit cells containing either Nb or Mg ions. Here $i=1,2,\ldots,N$ and N denotes the total number of polar clusters. If $\vec{u}_k(il)$ is the displacement of the kth ion in the lth cell in C_i from its ideal perovskite cubic position and $e_k(il)$ its charge, then the dipole moment of the cell is

$$\vec{m}(il)=\sum_k e_k(il)\vec{u}_k(il). \tag{1}$$

X-ray and neutron scattering studies of PMN reveal that each ion in the unit cell can occupy a large number of equivalent off-center equilibrium positions.[13–15] In single-crystal PMN the positions of the Pb ions were found to be uniformly distributed over a spherical layer.[16] It has been argued[17] that the dominant contribution to $\vec{m}(il)$ is due to the displacements of the Nb^{5+} and Pb^{2+} ions, so that Eq. (1) can be simplified to

$$\vec{m}(il)=\frac{3}{2}e_0[\vec{u}_{\mathrm{Nb}}(il)-\vec{u}_{\mathrm{Pb}}(il)]+\cdots, \tag{2}$$

where e_0 is the unit charge and the dots represent the contributions of the remaining terms. Since Mg and Pb ions have the same charge, the contribution of a Mg-type cell is much smaller and only Nb-type cells are relevant. Let n_i represent the number of Nb cells in cluster C_i. The dipole moment of C_i can then be written as

$$\vec{M}_i=\sum_l \vec{m}(il)\cong n_i\vec{m}_0(i), \tag{3}$$

assuming that the dipole moment $\vec{m}(il)$ is the same for each Nb cell in C_i, and can thus be replaced by $\vec{m}_0(i)=(3/2)e_0[\vec{u}_{\mathrm{Nb}}(i)-\vec{u}_{\mathrm{Pb}}(i)]$.

Let us now introduce a dimensionless order parameter field, which is proportional to $\vec{M}_i$ and thus scales with the number of Nb ions n_i

$$\vec{S}_i=\left(\frac{3}{[n^2]_{av}}\right)^{1/2}\frac{\vec{M}i}{m_0(i)}. \tag{4}$$

Here $[n^2]_{av}=(1/N)\Sigma_i n_i^2$. It is easily verified that the order parameter field then satisfies the closure relation

$$\sum_i (\vec{S}_i)^2=3N. \tag{5}$$

The model Hamiltonian of a system of interacting polar clusters is formally written as

$$\mathcal{H}=-\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i\cdot\vec{S}_j-\sum_i \vec{h}_i\cdot\vec{S}_i-g\sum_i \vec{E}_i\cdot\vec{S}_i. \tag{6}$$

Here J_{ij} are random interactions or bonds and $\vec{h}_i$ random local electric fields. Following the theories of spin[9,10] and dipolar[11] glasses we will assume that the random bonds are infinitely ranged with a Gaussian probability distribution characterized by the cumulant averages

$$[J_{ij}]^c_{av}=J_0/N, \quad [(J_{ij})^2]^c_{av}=J^2/N. \tag{7}$$

The random fields similarly obey an independent Gaussian distribution such that

$$[h_{i\mu}]^c_{av}=0, \quad [h_{i\mu}h_{j\nu}]^c_{av}=\Delta\delta_{ij}\delta_{\mu\nu}; \quad (\mu=x,y,z). \tag{8}$$

In the last term of Eq. (6), $\vec{E}$ is an applied external field and $g=(4\pi/3\epsilon)(\epsilon+2)\gamma_{eff}([n^2]_{av}/3)^{1/2}m_0$, where γ_{eff} represents an effective local field factor and we assume that the length of the dipole moment of a Nb cell is the same in all clusters, i.e., $m_0(i)\simeq m_0$.

It should be noted again that the order parameter field $\vec{S}_i$ is a discrete vector restricted to a large but finite number of equilibrium orientations. Its magnitude scales with the cluster size n_i, implying that $|\vec{S}_i|$ can vary over a large interval. Since the distribution of the number of polarized cells n_i in a cluster is not known, an exact evaluation of the free energy of model (6) is far from trivial. We will therefore deal here with a simplified model, assuming that each component of $\vec{S}_i$ fluctuates continuously over the entire space,

$$-\infty<S_{i\mu}<+\infty; \tag{9}$$

however, condition (5) should be strictly satisfied. This then leads to a spherical vector model, which is referred to as the spherical random-bond–random-field (SRBRF) model.

III. EQUILIBRIUM PROPERTIES OF THE SRBRF MODEL

The spherical model of a uniaxial spin glass has been solved a long time ago by Kosterlitz et al.[18] using the representation of eigenstates of the random matrix J_{ij}. The same method is, in principle, applicable to the SRBRF model; however, as shown in Ref. 18 one can also apply the replica method. This method has several advantages in the present case and will be adopted here. Introducing the familiar replica indices $\alpha=1,2,\ldots,n$ and a Lagrange multiplier z to enforce the spherical condition (5), we can formally write down the expression for the free energy $\mathcal{F}$:

$$\beta\mathcal{F}=\lim_{n\to 0}\frac{1}{n}\left\{\int_{-\infty}^{+\infty}\left[\prod_{i\mu\alpha} dS^\alpha_{i\mu}\right]\int_{c-i\infty}^{c+i\infty}\frac{dz}{2\pi i}\exp\left[-z\sum_\alpha\left(\sum_{i\mu}(S^\alpha_{i\mu})^2-3N\right)\right]\right.$$
$$\left.\times\exp\left[\beta\sum_\alpha\left(\frac{1}{2}\sum_{ij\mu}J_{ij}S^\alpha_{i\mu}S^\alpha_{j\mu}+\sum_{i\mu}h_{i\mu}S^\alpha_{i\mu}+g\sum_{i\mu}E_\mu S^\alpha_{i\mu}\right)\right]-1\right\}. \tag{10}$$

As usual, $\beta=1/kT$ and we will set $k=1$.

In the next step, the random averages over J_{ij} and $h_{i\mu}$ are performed, to be followed by the usual manipulations of replica theory. This procedure is standard and parallels the theory of spin glasses.[9,10] Therefore, the intermediate steps in the derivation will not be reproduced here. In analogy to the uniaxial case[18] the replica symmetric solution is exact in a spherical glass. The immediate objective is to calculate the order parameters such as the polarization

$$P_\mu=\frac{1}{N}\sum_i\langle S_{i\mu}\rangle, \tag{11}$$

and the dipolar glass order parameter, written here in its Cartesian components,

$$q_\mu = \frac{1}{N}\sum_i \langle S_{i\mu}\rangle^2, \tag{12}$$

as functions of the electric field $\vec{E}$ and temperature. For an arbitrary direction of $\vec{E}$ this is a nontrivial problem, which cannot be solved analytically. In order to analyze the basic equilibrium properties of the model we will, therefore, assume that the electric field is parallel to the [111] direction. In this case, including the choice $E \equiv |\vec{E}| = 0$, the Cartesian components are μ independent by symmetry, i.e., $P_\mu = P$ and $q_\mu = q$. Introducing an infinitesimal generating field $\vec{\lambda}^\alpha$ parallel to $\vec{E}$ we obtain the following expression for the free energy per cluster $f \equiv \mathcal{F}/N$:

$$\beta f = -\frac{3}{2}\beta J_0 P^2 + \frac{3}{4}\beta^2 J^2 q^2 + \lim_{n\to 0}\frac{1}{n}\left\{ \int_{-\infty}^{+\infty}\left[\prod_\mu \frac{dx_\mu}{\sqrt{2\pi}}\exp\left(-\frac{1}{2}x_\mu^2\right)\right]\int_{-\infty}^{+\infty}\prod_{\mu\alpha} dS_\mu^\alpha \exp\{-z[(S_\mu^\alpha)^2-1]\}\right.$$

$$\left.\times \exp\left[\beta(J_0 P + gE + x_\mu\sqrt{J^2 q + \Delta} + \lambda_\mu^\alpha)S_\mu^\alpha - \frac{1}{2}\beta^2 J^2 q (S_\mu^\alpha)^2\right] - 1\right\}. \tag{13}$$

This expression will be used later to evaluate random averages of the type $\langle S_{\mu_1}^{\alpha_1} S_{\mu_2}^{\alpha_2}\cdots S_{\mu_r}^{\alpha_r}\rangle$. In the limit $\vec{\lambda}^\alpha \to 0$ we find

$$-\frac{2}{3}\beta f = \beta J_0 P^2 - \frac{1}{2}\beta^2 J^2 q^2 - 2z + \ln(2z + \beta^2 J^2 q) - \frac{\beta^2}{2}\frac{J^2 q + \Delta + (J_0 P + gE)^2}{2z + \beta^2 J^2 q}. \tag{14}$$

Finally, the equilibrium values of P, q, and z are obtained from the saddle-point condition $\partial f/\partial P = \partial f/\partial q = \partial f/\partial z = 0$ after some rearranging:

$$P = \beta(1-q)(J_0 P + gE), \tag{15a}$$

$$q = \beta^2(1-q)^2(J^2 q + \Delta) + P^2, \tag{15b}$$

$$2z + \beta^2 J^2 q = 1/(1-q). \tag{15c}$$

It should again be stressed that Eqs. (14) and (15) were obtained for a special field direction of the field $\vec{E}\|[111]$. Formally, Eqs. (15) also apply in the case of an isotropic relaxor system. The effects of cubic anisotropy could, in principle, be studied after one has solved the SRBRF model for a general direction of the field.

In the following we will first discuss the case without external fields, i.e., $E = 0$ but $\Delta \neq 0$. Equations (15) then have two sets of solutions: (a) $P = 0$, $q \neq 0$, corresponding to a phase without long-range order, to be referred to as the spherical glass (SG) phase; and (b) $P \neq 0$, $q \neq 0$, i.e., the long-range order or ferroelectric (FE) phase. The FE phase can only exist if $J_0 > J_{0c}$, where the critical value is given by $J_{0c} = \sqrt{J^2 + \Delta}$. Assuming $P \neq 0$, Eq. (15a) yields

$$q = 1 - T/J_0. \tag{16}$$

Inserting into Eq. (15b) one finds that the spontaneous polarization is determined by the equation

$$P^2 = [1 - (J/J_0)^2](1 - T/J_0) - \Delta/T^2. \tag{17}$$

The critical temperature T_c is obtained from the condition $P^2 = 0$, i.e.,

$$T_c = J_0\left(1 - \frac{\Delta}{J_0^2 - J^2}\right)\theta(J_0/J - 1), \tag{18}$$

where $\theta(x)$ is the unit step function. Obviously, $P = 0$ for $T > T_c$.

At $T \to 0$ the polarization is given by

$$P^2(0) = 1 - (J^2 + \Delta)/J_0^2. \tag{19}$$

This implies that a critical value $\Delta_c = J_0^2 - J^2$ exists such that for $\Delta > \Delta_c$ there can be no long-range order at any temperature. The value of q at the critical temperature is simply $q(T_c) = \Delta/\Delta_c$.

For $J_0 < J_{0c}$ there is no long-range order and the glass order parameter is determined by the equation

$$q = \beta^2(1-q)^2(J^2 q + \Delta). \tag{20}$$

The solutions $q(T)$ for various values of the random field strength Δ are shown in Fig. 1.

It should be noted that since the replica symmetric solution is exact in the SRBRF model, q is equal to the Edwards-Anderson order parameter q_{EA}.

The phase diagram of the SRBRF model, compared with the spin glass case $\Delta = 0$, is shown as an inset in Fig. 1. As already noted for the case of a uniaxial spherical spin glass[18] without long-range order ($J_0 = 0$), there is no phase transition in the presence of an external field; the same is true of the present model with nonzero random fields ($\Delta \neq 0$). In terms of a replica theory, there is no replica symmetry breaking and no Almeida-Thouless line[9,10] in the SRBRF model. Thus, in general, for $\Delta \neq 0$ and $J_0 < J_{0c}$ there is no sharp freezing transition into into a low-temperature spherical glass state within the static SRBRF model.

IV. NONLINEAR DIELECTRIC RESPONSE

In a system with average cubic symmetry the phenomenological relation between the applied electric field E_μ ($\mu = 1,2,3$) and polarization P_μ can be written, assuming small amplitudes, as a power series

$$P_1 = \chi_1 E_1 - \chi_{122} E_1(E_2^2 + E_3^2) - \chi_{111} E_1^3 + \cdots. \tag{21}$$

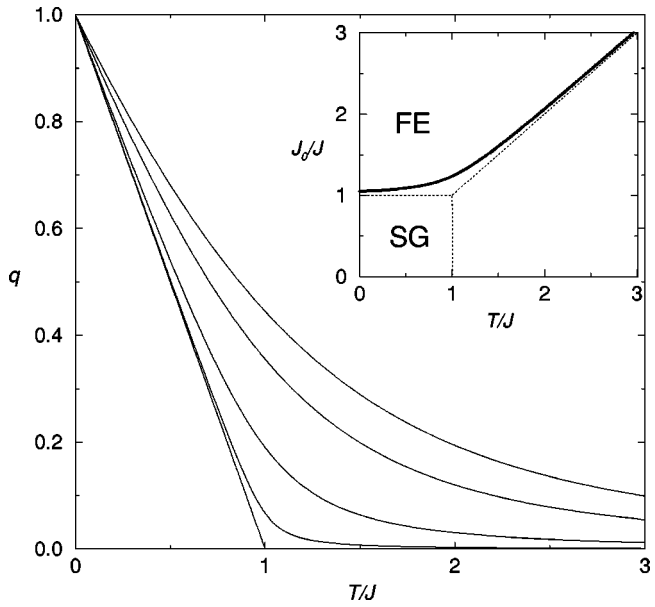

FIG. 1. Temperature dependence of the SG order parameter q in the SG phase ($J_0=0$) for various values of the random-field strength Δ. Top to bottom: $\Delta/J^2=1.0,0.5,0.1,0.01,0$. Inset: Phase diagram of the SRBRF model in zero-bias field. Solid line: Phase boundary between the ferroelectric (FE) and spherical glass (SG) phase for random-field strength $\Delta/J^2=0.1$. Dotted line: Spherical spin glass ($\Delta=0$).[17]

The inverse relation is formally

$$E_1=a_1P_1+a_{122}P_1(P_2^2+P_3^2)+a_{111}P_1^3+\cdots. \tag{22}$$

Here and in the following we redefine the fields E_μ by absorbing into them the local field factor g, which is formally accomplished by setting $g=1$ in Eqs. (15).

Comparing the above two relations yields

$$a_1=1/\chi_1;\quad a_{122}=\chi_{122}/\chi_1^4;\quad a_{111}=\chi_{111}/\chi_1^4. \tag{23}$$

Here χ_1 is the linear susceptibility and χ_{122}, χ_{111}, etc. the third-order nonlinear susceptibilities. For a field $\vec{E}\|[111]$ and $P_1=P_2=P_3=P$ Eqs. (21) and (22) simplify to

$$P=\chi_1E-\chi_3E^3+\cdots, \tag{24a}$$

$$E=a_1P+a_3P^3+\cdots, \tag{24b}$$

where $\chi_3=2\chi_{122}+\chi_{111}$ and

$$a_3=\chi_3/\chi_1^4. \tag{25}$$

The same relations formally hold for an isotropic system.

Experimentally, χ_3 can be determined, for example, by measuring the third-harmonic nonlinear response to an oscillating external field in zero-bias field. The scaled nonlinear response a_3 is obtained from Eq. (25) provided one has also determined the linear response χ_1 in zero bias.

If a nonzero-bias field E is applied, one measures the modified field-dependent linear and third-harmonic nonlinear responses, which will be denoted by $\chi_1(E)$ and $\chi_3(E)$, respectively. The field-dependent scaled third-order nonlinear response is then defined as

$$a_3(E)=\chi_3(E)/\chi_1^4, \tag{26}$$

where $\chi_1\equiv\chi_1(0)$. Obviously, $a_3=a_3(0)$.

Alternatively, in some experiments a different definition of the scaled nonlinear response is being used, namely,[5]

$$\hat{a}_3(E)=\frac{\chi_1(0)-\chi_1(E)}{3E^2\chi_1(0)^4}. \tag{27}$$

Using Eqs. (24) one can show that in the case without long-range order $\lim_{E\to0}\hat{a}_3=a_3$; however, in general, $\hat{a}_3(E)$ will differ from $a_3(E)$. It should be noted that the relation (27) is not applicable in the FE phase.

We can now calculate the nonlinear response $\chi_3(E)$ from the solution of Eq. (15a), i.e.,

$$\chi_3(E)=-\frac{1}{6}\frac{\partial^3P}{\partial E^3}, \tag{28}$$

where χ_3 in Eqs. (24a) and (25) corresponds to $\chi_3(0)=\lim_{E\to0}\chi_3(E)$.

The linear susceptibility $\chi_1(E)$ is obtained as the derivative of the solution $P(E,T)$ of Eq. (15a),

$$\chi_1(E)=\frac{\beta(1-q)}{1-\beta J_0(1-q)+D(E,P)}, \tag{29}$$

where $D(E,P)\equiv2\beta P(J_0P+E)/[1+2\beta^2(J^2q+\Delta)(1-q)-\beta^2J^2(1-q)^2]$. In the SG phase ($J_0<J_{0c}$) with $E=0$ one has $D=0$, but for $E\neq0$ or in the FE phase at $T<T_c$ it follows that $D\neq0$.

One can easily calculate $\chi_1(E)$ from Eqs. (15) and (29). In the FE phase, $\chi_1\equiv\chi_1(0)$ is found to diverge at $T=T_c$, where T_c is given by Eq. (18). In the SG phase, however, χ_1 is nonsingular.

In experiments, χ_1 is typically measured at some finite frequency ω. Thus a comparison with the predictions of a static theory is not straightforward in view of the strong frequency dispersion observed in relaxor ferroelectrics. Special techniques such as the frequency-temperature plots[19] have been used to extract the ''static'' freezing temperature T_f from the apparent divergence of the longest relaxation time. Clearly, the results of a static theory are applicable only in the temperature region where frequency dispersion is negligible, namely, at sufficiently high temperatures. A dynamic version of the SRBRF model has not yet been worked out. The dynamics of a uniaxial spherical spin glass in random fields has been studied in Ref. 20.

The frequency dispersion also plays a role in the temperature dependence of the third-order nonlinear susceptibility χ_3. As already suggested for dipolar glasses[21] the scaled nonlinear response a_3 is a suitable quantity to be compared with the static theory. In principle, by measuring $a_3(T)$ one can discriminate between the FE and SG behavior more easily than on the basis of χ_1 or χ_3 alone. The phenomenological theory predicts that in the FE phase χ_3 diverges as $\sim|T-T_c|^{-3\bar{\gamma}-2\bar{\beta}}$, so that a_3 should behave as

$$a_3^{FE}\sim|T-T_c|^{\bar{\gamma}-2\bar{\beta}}, \tag{30}$$

where in general $\bar{\gamma}-2\bar{\beta}>0$ for a cubic system,[22] and $\bar{\gamma}=2\bar{\beta}$ in the mean-field approximation. Thus in a random-

field frustrated ferroelectric a_3^{FE} should not diverge at T_c, but should fall off to a constant value or zero at T_c. In contrast, for a dipolar glass (DG) one expects a divergent behavior,

$$a_3^{DG} \sim |T - T_c|^{-\gamma_3}, \tag{31}$$

where the mean-field value of the exponent is $\gamma_3 = 1$.

These results can now be matched with the predictions of the SRBRF model. By calculating successively the derivatives of $P(E)$ and $q(E)$ from Eqs. (15), we find from Eq. (28) in the limit $E \to 0$ and for $P = 0$:

$$\chi_3 = \frac{\beta \chi_1^2 (J_0 \chi_1 + 1)}{[1 - \beta^2 J^2 (1-q)(1-3q-2\Delta/J^2)][1 - \beta J_0 (1-q)]}. \tag{32}$$

Here $\chi_1 = \chi_1(0)$ is given by Eq. (29). The last result is applicable in the SG phase at all temperatures and in the FE phase ($J_0 > J_{0c}$) for $T > T_c$.

The scaled nonlinear susceptibility $a_3 = \chi_3 / \chi_1^4$ is thus given by

$$a_3 = \frac{T}{(1-q)^2 [1 - \beta^2 J^2 (1-q)(1-3q-2\Delta/J^2)]}. \tag{33}$$

Notice that this expression is independent of the value of J_0.

We now investigate the behavior of a_3 and $a_3(E)$ in two characteristic cases, i.e., the SG phase where $J \gg J_0$, and the FE phase with $J \ll J_0$ corresponding to a random-field frustrated ferroelectric.

A. Spherical glass phase

Here we will set $J_0 = 0$. In Fig. 2, a_3 as a function of temperature is plotted for various values of the random field strength Δ. If $\Delta = 0$, corresponding to a spherical vector spin glass, a_3 diverges at $T_f = J$ according to $a_3 \sim |T - T_f|^{-1}$. For $\Delta \neq 0$ the denominator in Eq. (33) never vanishes and the divergence of a_3 does not occur; however, for $\Delta/J^2 \ll 1$, a_3 shows a sharp peak near T_f. At $\Delta/J^2 \gtrsim 0.1$ the peak starts to broaden and completely disappears at larger values of Δ/J^2.

In experiments, a_3 can be determined in the region above the expected value of T_f, where the dispersion is weak and one is essentially observing the high-temperature tail of $a_3(T)$. This behavior mimics a diverging a_3; however, only a fit to Eq. (33) may reveal the true nature of the singularity and yield the parameters of the model.[8] The narrow peak occurring near $T \approx J$ is unlikely to be observed in practice in view of the dynamic effects which become dominant close to T_f.

In the presence of a bias field ($E \neq 0$) we consider the temperature dependence of $a_3(E)$ as defined by Eq. (26). Figure 3 shows a_3 at $E = 0$ compared with $a_3(E)$ for various values of the field E at fixed random-field strength $\Delta/J^2 = 0.01$. With increasing field strength the peak in $a_3(T)$ gradually disappears. This effect is similar to that occurring in a_3 when the value of Δ is increased. Thus in an experiment under a bias field[5] one can miss the nearly divergent behavior observed under the zero field conditions. It is not trivial to predict the magnitude of the effects of a bias field,

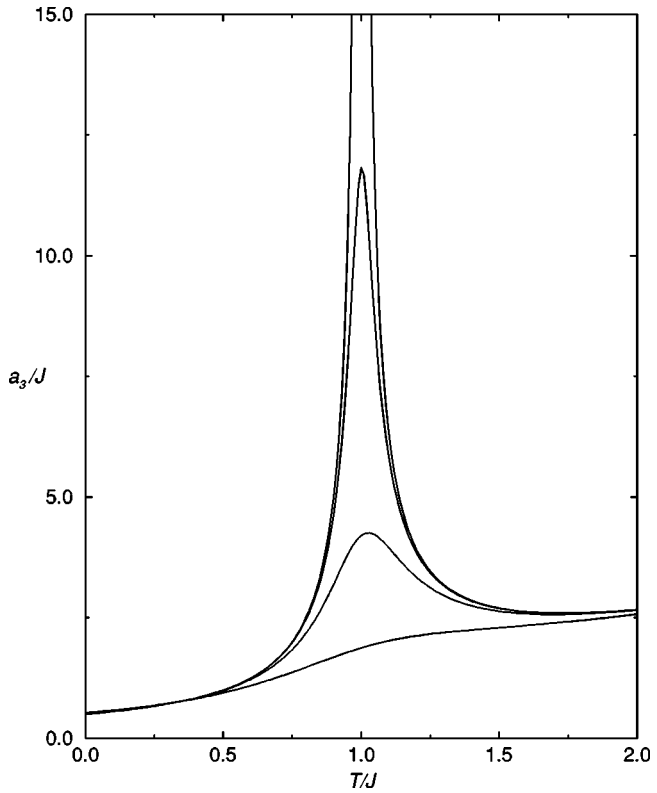

FIG. 2. Scaled third-order nonlinear response $a_3 = \chi_3 / \chi_1^4$ in the SG phase ($J_0 = 0$) as a function of temperature, plotted for various values of the random-field strength Δ. Top to bottom: $\Delta/J^2 = 0, 0.001, 0.01, 0.1$.

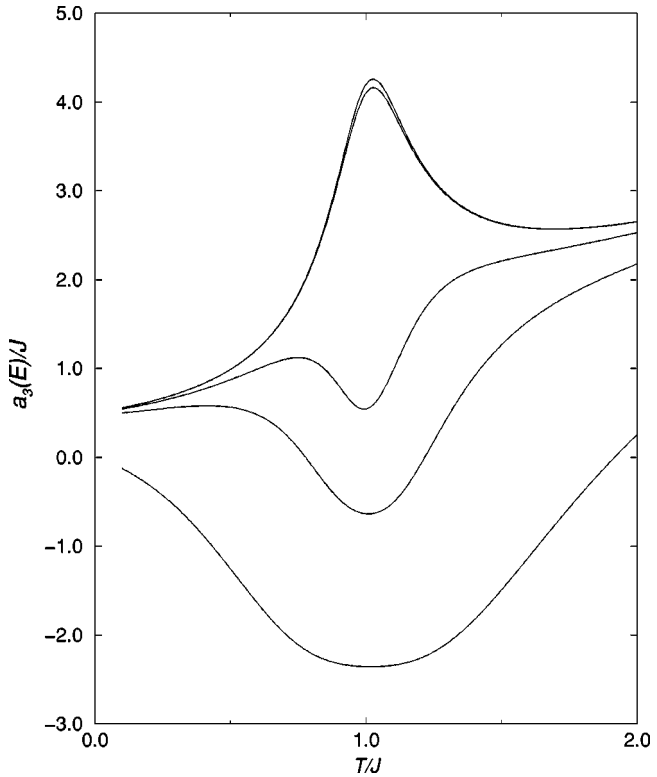

FIG. 3. Temperature and field dependence of the nonlinear response $a_3(E)$ in the SG phase ($J_0 = 0$) and for fixed value of $\Delta/J^2 = 0.01$. Top to bottom: $E/J = 0, 0.01, 0.1, 0.2, 0.5$.

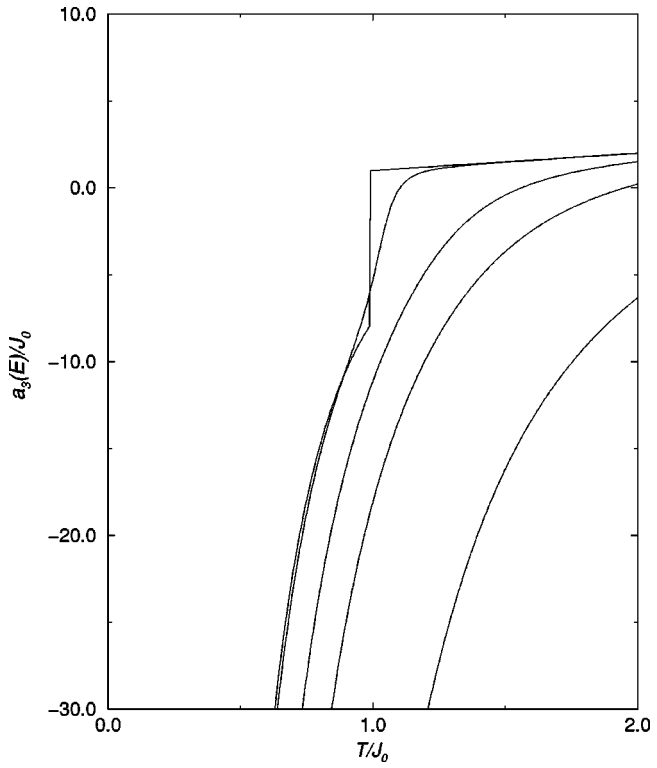

FIG. 4. Temperature and field dependence of the nonlinear response in the FE phase ($J=0$) and fixed $\Delta/J_0^2=0.01$. Top to bottom: $E/J_0=0,0.01,0.1,0.2,0.5$.

since the relevant energy shift will depend on the unknown local field parameter g in Eq. (15a).

B. Ferroelectric in random fields

This corresponds to the case $J \ll J_0$ and we will set $J=0$ without much loss of generality. We can distinguish between the paraelectric (PE) phase $T>T_c$ and the FE phase $T \leqslant T_c$, where from Eq. (18) we find $T_c=J_0(1-\Delta/J_0^2)$. For $T>T_c$, Eq. (15b) yields

$$q_{>}=\frac{1}{2\beta^2\Delta}(1+2\beta^2\Delta-\sqrt{1+4\beta^2\Delta}). \tag{34}$$

The linear susceptibility χ_1 is given by Eq. (29) with $D=0$, and one can easily check that it diverges as $\sim(T-T_c)^{-1}$.

The nonlinear susceptibility χ_3 diverges as $\sim(T-T_c)^{-4}$; however, the scaled nonlinear response a_3 is given by

$$a_{3>}=\frac{T}{(1-q)^2[1+2\beta^2\Delta(1-q)]} \tag{35}$$

and remains finite at $T \to T_c$.

For $T \leqslant T_c$ one has from Eq. (15b)

$$P^2=1-T/J_0-\Delta/J_0^2, \tag{36}$$

whereas $q_{<}(T)$ is given by the solution of Eq. (16). The scaled nonlinear response $a_{3<}$ can be calculated numerically after deriving a set of the appropriate field derivatives of $P(E,T)$. The result for a_3 with $\Delta/J_0^2=0.01$ at temperatures both above and below T_c is shown in Fig. 4. Also shown is the nonlinear response $a_3(E)$ at $T>T_c$ and various values of the external field E. Obviously, a_3 remains finite as $T \to T_c$, but makes a jump at T_c in accordance with mean-field theory.

In contrast to the SG case, a_3 in a random-field frustrated ferroelectric does not show any anomalous peak even at the smallest values of Δ. Thus by determining the scaled nonlinear response a_3 without a bias field one can readily decide whether the system under investigation behaves as a spherical glass or a ferroelectric. In PMN, $a_3(T)$ was determined in the temperature range 220 K $\lesssim$ T $\lesssim$ 320 K and found to increase sharply on approaching the lower end of this interval. A fit to the SRBRF model[8] yielded the model parameters $J=220$ K and $\Delta/J^2=2\times10^{-4}$. The value of J was found to agree reasonably well with the Vogel-Fulcher temperature $T_0=215$ K characterizing the temperature dependence of the longest relaxation time, which was obtained by means of the frequency-temperature plots.[19]

V. PROBABILITY DISTRIBUTION OF LOCAL POLARIZATION

The local polarization of a cluster C_i is defined as $\vec{p}_i=\langle\vec{S}_i\rangle$, where $\langle\cdots\rangle$ is the thermal average. The probability distribution of local polarization is formally written as

$$W(\vec{p})=\frac{1}{N}\sum_i \delta(\vec{p}-\vec{p}_i). \tag{37}$$

This quantity is useful in describing NMR and related experiments in dipolar and quadrupolar glasses.[23,25,24] It is trivial to show that the first moment of $W(\vec{p})$ is just the total polarization $\vec{P}$ of the system, and the diagonal part of the second moment gives the glass order parameter q.

To evaluate $W(\vec{p})$ for the SRBRF model we consider the case $J_0=0$. First we introduce, as usual, the Fourier transform of the δ function in Eq. (37), i.e.,

$$W(\vec{p})=\int_{-\infty}^{+\infty}\frac{d^3k}{(2\pi)^3}\exp(-i\vec{k}\cdot\vec{p})[\exp(i\vec{k}\cdot\langle\vec{S}\rangle)]_{av}. \tag{38}$$

Next, we expand the last exponential into a power series and in order to evaluate the random averages assign each component $S_{i\mu}$ a different replica index. The random average can then be expressed in terms of the appropriate derivatives of the generating field λ_μ^α in Eq. (13). Since all replicas are independent, the averages of different Cartesian components $S_{i\mu}^\alpha$ will decouple. This then implies

$$W(\vec{p})=w(p_x)w(p_y)w(p_z), \tag{39}$$

where

$$w(p_\mu)=[\delta(p_\mu-\langle S_\mu\rangle)]_{av}. \tag{40}$$

The last expression can again be rewritten as

$$w(p_\mu)=\int_{-\infty}^{+\infty}\frac{dk_\mu}{2\pi}\exp(-ik_\mu p_\mu) \times\sum_{r=0}^{\infty}\frac{(ik_\mu)^r}{r!}[\langle S_\mu^{\alpha_1}\rangle\langle S_\mu^{\alpha_2}\rangle\cdots\langle S_\mu^{\alpha_r}\rangle]_{av}, \tag{41}$$

where the limit $n \to 0$ is understood. The averages $\langle S_\mu^\alpha \rangle$ are all equal and evaluating them with the aid of Eq. (13) we find for the random average in Eq. (41):

$$[\cdots]_{av} = \int_{-\infty}^{+\infty} \frac{dx_\mu}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}x_\mu^2\right)\left(x_\mu \frac{\beta\sqrt{J^2q+\Delta}}{2z+\beta^2J^2q}\right)^r. \tag{42}$$

After performing the summation in Eq. (41), carrying out the remaining Gaussian integration, and using Eqs. (15c) and (15b), we obtain the result

$$w(p_\mu) = (2\pi q)^{-1/2} \exp\left(-\frac{p_\mu^2}{2q}\right). \tag{43}$$

Equation (39) then yields

$$W(\vec{p}) = (2\pi q)^{-3/2} \exp\left(-\frac{\vec{p}^2}{2q}\right). \tag{44}$$

This result shows that $W(\vec{p})$ for the SRBRF model is Gaussian at all temperatures and its width is determined by the spherical glass order parameter q. In contrast, $W(p)$ of an Ising dipolar glass is characterized by a single-peak form at high temperatures, which changes to a double-peak structure at low temperatures.[23] Similarly, in a quadrupolar glass the low-temperature shape of $W(\vec{p})$ consists of two or three peaks, depending on the symmetry considered.[24]

Equation (43) can readily be extended to the case of nonzero polarization P occurring either for $J_0 > J_{0c}$ and $T < T_c$ or with nonzero-bias field $\vec{E} \| [111]$, i.e.,

$$w(p_\mu) = [2\pi(q-P^2)]^{-1/2} \exp\left[-\frac{(p_\mu - P)^2}{2(q-P^2)}\right]. \tag{45}$$

The complete probability distribution of local polarization $W(\vec{p})$ is then given by Eq. (39).

A. Application to the NMR line shape

A convenient way of measuring the probability distribution of local polarization is by means of the quadrupole pertubed NMR. As an example we consider the ^{93}Nb ($I = 9/2$) nucleus in PMN having a nonzero electric quadrupole moment, which couples to the local electric field gradient (EFG) tensor.[8] Relaxors exhibit giant electrostriction in the region of the relaxor transition, i.e., anomalously large deformations of the lattice in an electric field, indicating the long-range nature of interactions on a microscopic level. Therefore, we will assume that the EFG tensor at a given Nb site is a function of the displacements $\vec{u}_k(il)$ of every ion in the cluster. These displacements are in turn related to the cluster dipole moment $\vec{M}_i$ via Eqs. (1)–(3), as we assume perfect long-range order within a cluster. From this it follows that all Nb nuclei have the same quadrupole shift, which depends on $\vec{M}_i$ and hence on the order parameter field $\vec{S}_i$. In the fast motion limit the observed quadrupole shift depends on the time average of $\vec{S}_i$, which is equal to the local polarization $\vec{p}_i = \langle \vec{S}_i \rangle$. The quadrupole perturbed NMR resonance frequency of ^{93}Nb in the lth cell in C_i can thus be expanded into a power series

$$\nu_{il} = \nu^{(0)} + \nu_{il}^{(1)} + \vec{\alpha}\cdot\vec{p}_i + \vec{p}_i \cdot \boldsymbol{\beta} \cdot \vec{p}_i + \cdots, \tag{46}$$

where $\nu^{(0)}$ is the unperturbed resonance frequency and $\nu_{il}^{(1)}$ represents the static shift due to the distortion of the cell from its high symmetry (cubic) perovskite structure. The coefficients $\vec{\alpha}$ and $\boldsymbol{\beta}$ depend on the orientation of the magnetic field $\vec{B}$.

The inhomogeneous NMR line shape is given in terms of the frequency distribution function

$$f(\nu) = \frac{1}{N}\sum_i \frac{1}{n_i}\sum_l \delta(\nu - \nu_{il}). \tag{47}$$

The site averages can be replaced by an average over the probability distribution of $\nu_{il}^{(1)}$ and the distribution of local polarization $W(\vec{p})$. Assuming that the cluster average of $\nu_{il}^{(1)}$ is the same for all clusters, i.e., $(1/n_i)\Sigma_l \nu_{il}^{(1)} = \nu^{(1)}$ and absorbing it into $\nu_0 \equiv \nu^{(0)} + \nu^{(1)}$ we have

$$f(\nu) = \int d^3p\, W(\vec{p})\, \delta(\nu - \nu_0 - \vec{\alpha}\cdot\vec{p} - \vec{p}\cdot\boldsymbol{\beta}\cdot\vec{p}). \tag{48}$$

The integral can be evaluated analytically in two special cases. The *linear* case corresponds to the orientation of the magnetic field $\vec{B} \| [111]$ for which $|\vec{\alpha}| \gg \|\boldsymbol{\beta}\|$. Neglecting the last term in the δ function we can write

$$f(\nu) = \int \frac{dk}{2\pi} \exp[-ik(\nu-\nu_0)] \int d^3p (2\pi q)^{-3/2} \times \exp\left(-\frac{\vec{p}^2}{2q} + ik\vec{\alpha}\cdot\vec{p}\right). \tag{49}$$

Evaluating the triple Gaussian integral and the Fourier transform we find the result

$$f(\nu) = (2\pi q \alpha^2)^{-1/2} \exp\left[\frac{(\nu-\nu_0)^2}{2q\alpha^2}\right]. \tag{50}$$

This shows that the line shape is Gaussian at all temperatures and its width depends on the glass order parameter q and the coupling coefficient $\alpha = |\vec{\alpha}|$. The second moment of $f(\nu)$ is proportional to the glass order parameter, i.e.,

$$M_2 = \int d\nu f(\nu)(\nu-\nu_0)^2 = \alpha^2 q. \tag{51}$$

Thus by measuring the line shape $f(\nu)$ and its second moment in the linear case, one can directly obtain the probability distribution of local polarization $W(\vec{p})$ and the temperature dependence of the glass order parameter $q(T)$.

The *bilinear* case is characterized by $|\vec{\alpha}| \ll \|\boldsymbol{\beta}\|$ and therefore the linear term in the δ function of Eq. (48) is negligible. This occurs, for example, when $\vec{B} \| [100]$ and we may assume that

$$\boldsymbol{\beta}=\beta_0\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix}, \tag{52}$$

leading to

$$f(\nu)=\int dp_x(2\pi q)^{-1/2}\exp\left(-\frac{p_x^2}{2q}\right)\delta(\nu-\nu_0-\beta_0 p_x^2). \tag{53}$$

For $\beta_0>0$ we thus find

$$f(\nu)=\theta(\nu-\nu_0)[2\pi q\beta_0(\nu-\nu_0)]^{-1/2}\exp\left(-\frac{\nu-\nu_0}{2\beta_0 q}\right). \tag{54}$$

For $\beta_0<0$, $f(\nu)$ is simply mirrored around $\nu=\nu_0$.

In contrast to the linear case, the line shape $f(\nu)$ is now strongly asymmetric and diverges when $\nu\rightarrow\nu_0$. The glass order parameter is related to the first moment of $f(\nu)$, i.e.,

$$M_1=\int d\nu f(\nu)(\nu-\nu_0)=\beta_0 q. \tag{55}$$

Experiments in PMN with $\vec{B}\|[100]$ (Ref. 26) have confirmed the predicted asymmetric form (54). In general, the NMR line shape in PMN can be decomposed into a narrow temperature-dependent Gaussian component and a broad *T*-independent Gaussian background.[8,26] Both components turn out to be inhomogeneously broadened. The narrow line refers to the central $\frac{1}{2}$ and $\rightarrow-\frac{1}{2}$ transition and can be well described by the above theory. The broad Gaussian background is due to unresolved satellite transitions (Ref. 26). The ratio of the intensities of the two components was found to be temperature independent throughout the investigated temperature interval.[8]

It should be noted that the time scale of a NMR experiment is essentially determined by the inverse of the maximum linewidth, which is in PMN typically of the order $t_{exp}\sim10^{-5}$ s, while in dielectric experiments one can, in principle, extrapolate the data to quasistatic values. Due to the strong frequency dispersion observed in relaxors at low temperatures, the model parameters deduced from the NMR data have to be regarded in the context of their time-scale dependence, and cannot be directly compared with the values obtained from dielectric measurements in a different temperature range. Again, these discrepancies could be resolved only within the framework of a dynamic model

VI. CONCLUSIONS

We have presented a simple semimicroscopic model of relaxor ferroelectrics based on the vector spherical random-bond–random-field (SRBRF) model of dipolar glasses. The relevant degrees of freedom are associated with the dipole moments of the reorientable polar clusters, which are embedded in a quasiregular array of chemically 1:1 ordered regions. The static SRBRF is exactly solvable by the replica method and predicts the existence of two phases, namely, the spherical glass (SG) phase without long-range order and the long-range ordered polarized ferroelectric (FE) phase. In case of nonzero random fields there is no phase transition within the SG phase; however, one can show that for weak random fields the scaled third-order nonlinear susceptibility $a_3=\chi_3/\chi_1^4$ shows a sharp peak near a temperature T_f, which corresponds to the freezing temperature of the spherical spin-glass model without random fields. Thus in experiments one should be able to observe a quasidivergent behavior of a_3 on the high-temperature side of the peak, where the frequency dispersion is weak. This has indeed been found in PMN (Ref. 19) and PLZT ceramics,[27] supporting the assumption that these systems can be described as a special kind of dipolar glass, namely, the spherical glass. If a bias electric field is applied, the behavior changes dramatically and the peak disappears at relatively weak-bias fields. In the FE phase, which corresponds to a random-field frustrated ferroelectric, there is no peak in the scaled nonlinear response both in a nonzero-bias field or without bias.

As an application of the theory the quadrupole perturbed NMR line shape of ^{93}Nb has been considered. The frequency shift can be expressed in terms of the EFG tensor components at the Nb site, which are expanded into a power series with respect to the order parameter field. For special orientations of the magnetic field, the frequency shift can be either a linear or bilinear function of the time average of the order parameter field $\vec{S}_i$ or equivalently the local cluster polarization $\vec{p}_i$. In the linear case, the NMR line shape $f(\nu)$ is simply related to the probability distribution of local polarization $W(\vec{p})$. It turns out that a special feature of the SRBRF model is the fact that $W(\vec{p})$—and hence $f(\nu)$—is Gaussian at all temperatures. Its second moment is proportional to the glass order parameter q. Thus by measuring $f(\nu)$ one can simply determine the probability distribution of local polarization and the temperature dependence of the glass order parameter, from which the values of the model parameters can be extracted. In the bilinear case, the NMR line shape is an asymmetric function of frequency, which diverges at the unperturbed resonance frequency, and the glass order parameter is given by its first moment. The observed NMR line shape in both the linear and bilinear regime lends strong support to the SRBRF model, since models other than spherical cannot reproduce a Gaussian form of $f(\nu)$ at all temperatures.

As already noted the above model is completely static. A dynamic theory is clearly needed to describe the frequency dispersion observed in real systems both in the linear and nonlinear susceptibilities χ_1 and χ_3, respectively. The present static SRBRF model could possibly be extended to include dynamic effects by introducing Langevin-type equations of motion.[20] It should also be mentioned that a dynamic theory based on a random-site–random-field model has been proposed by Vugmeister and Rabitz,[6,7] which provides good agreement with the experimental results on the frequency-dependent and zero-field-cooled linear permittivity. The relation between the Vugmeister-Rabitz dynamic model and the dynamic extension of our SRBRF model will be discussed in full detail in a forthcoming publication.

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[1] G. A. Smolenskii and V. A. Isupov, Dokl. Akad. Nauk SSSR **97**, 653 (1954).
[2] L. E. Cross, Ferroelectrics **76**, 241 (1987); **151**, 305 (1994).
[3] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, J. Appl. Phys. **68**, 2916 (1990); Phys. Rev. B **46**, 8003 (1992).
[4] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[5] A. K. Tagantsev and A. E. Glazounov, J. Korean Phys. Soc. **32**, S951 (1998).
[6] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998).
[7] B. E. Vugmeister and H. Rabitz, cond-mat/9906403 (unpublished).
[8] R. Blinc, J. Dolinšek, A. Gregorovič, B. Zalar, C. Filipič, Z. Kutnjak, A. Levstik, and R. Pirc, Phys. Rev. Lett. **83**, 424 (1999).
[9] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[10] K. H. Fischer and J. A. Hertz, *Spin Glasses* (Cambridge University Press, Cambridge, 1991).
[11] R. Pirc, B. Tadić, and R. Blinc, Phys. Rev. B **36**, 8607 (1987).
[12] C. Boulesteix, F. Varnier, A. Llebaria, and E. Husson, J. Solid State Chem. **108**, 141 (1994).
[13] N. de Mathan, E. Husson, G. Calvarin, J. R. Gavarri, A. W. Hewatt, and A. Morell, J. Phys.: Condens. Matter **3**, 8159 (1991).
[14] P. Bonneau, P. Garnier, G. Calvarin, E. Husson, J. R. Gavarri, A. W. Hewatt, and A. Morell, J. Solid State Chem. **91**, 350 (1991).
[15] A. Verbaere, Y. Piffard, Z. G. Ye, and E. Husson, Mater. Res. Bull. **27**, 1227 (1992).
[16] S. Vakhrushev, S. Zhukov, G. Fetisov, V. Chernyshev, J. Phys.: Condens. Matter **12**, 4021 (1994).
[17] V. A. Isupov, Ferroelectrics **90**, 113 (1989).
[18] J. M. Kosterlitz, D. J. Thouless, and R. C. Jones, Phys. Rev. Lett. **36**, 1217 (1976).
[19] A. Levstik, Z. Kutnjak, C. Filipič, and R. Pirc, Phys. Rev. B **57**, 11 204 (1998).
[20] L. F. Cugliandolo and D. S. Dean, J. Phys. A **28**, L453 (1995).
[21] J. Hemberger, H. Ries, A. Loidl, and R. Böhmer, Phys. Rev. Lett. **76**, 2330 (1996).
[22] Here, $\overline{\gamma}$ and $\overline{\beta}$ are the susceptibility and polarization exponent, respectively. See H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, 1971).
[23] R. Blinc, J. Dolinšek, R. Pirc, B. Tadić, B. Zalar, R. Kind, and O. Liechti, Phys. Rev. Lett. **63**, 2248 (1989).
[24] B. Tadić, R. Pirc, and R. Blinc, Phys. Rev. B **55**, 816 (1997).
[25] B. Zalar, R. Blinc, W. Albert, and J. Petersson, Phys. Rev. B **56**, R5709 (1997).
[26] R. Blinc, J. Dolinšek, A. Gregorovič, B. Zalar, C. Filipič, Z. Kutnjak, A. Levstik, and R. Pirc, J. Phys. Chem. Solids (to be published).
[27] Z. Kutnjak, C. Filipič, R. Pirc, A. Levstik, R. Farhi, and E. El Marssi, Phys. Rev. B **59**, 294 (1999).