Local Polarization Distribution and Edwards-Anderson Order Parameter of Relaxor Ferroelectrics

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The temperature dependence of the Edwards-Anderson order parameter q_{EA} and the local polarization distribution function $W(\vec{p})$ have been determined in a PMN single crystal via 2D ^{93}Nb NMR. A glasslike freezing of reorientable polar clusters occurs in the temperature range of the diffuse relaxor transition, whereas the NMR spectra corresponding to pinned nanodomains do not change with temperature. The obtained form of $W(\vec{p})$ as well as the temperature dependence of q_{EA} and the nonlinear dielectric susceptibility can be well described by a newly proposed spherical random bond–random field model of relaxor ferroelectrics.

Relaxor ferroelectrics [1,2] have been attracting considerable attention in recent years as they are believed to provide a conceptual link between ferroelectrics and dipolar glasses. In addition, they have found use in numerous applications. In spite of intensive investigations, the nature of the diffuse phase transition in relaxors has remained the subject of some controversy [3–6]. The basic open question is whether the relaxor state in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and related systems in zero field is either (i) a ferroelectric state broken up into nanodomains under the constraint of quenched random electric fields [4], or (ii) a dipolar glass state with randomly interacting polar microregions in the presence of random fields [3,5].

In this Letter, we report a direct determination of the temperature dependence of the Edwards-Anderson order parameter q_{EA} and the local polarization distribution function $W(\vec{p})$ in a PMN single crystal via two-dimensional (2D) ^{93}Nb NMR. A two-phase behavior is seen. Within the pinned nanodomains q_{EA} is temperature independent in the region of the diffuse phase transition, whereas it is strongly T dependent in the reorientable clusters. The obtained results are well described by a newly proposed spherical random bond–random field (SRBRF) model of relaxor ferroelectrics. The measured shape of the local polarization distribution function, in particular, is very different from that previously measured for dipolar glasses or quadrupolar glasses, but agrees very well with the form predicted by the SRBRF glass model. This model can in addition to other glassy features also quantitatively reproduce the previously observed peak in the temperature dependence of the dielectric nonlinearity $a_3 = \chi_3/\chi_1^4$ in PMN in zero field, which cannot be explained in terms of a random-field frustrated ferroelectric state. Here χ_1 is the linear and χ_3 the third-order nonlinear dielectric susceptibility. The model also predicts that the peak in a_3 disappears in the presence of a nonzero electric field E as indeed observed [7], and that a ferroelectric long range ordered state appears for $E > E_c$ [5].

Polar regions [8–10] are formed when two or more Nb ions moving in a multisite potential around the high temperature perovskite sites begin to respond along with their surroundings as a single reorientable polar unit. Compositional fluctuations will also induce randomly oriented pinned nanodomains—"chemical clusters," which act as sources of random fields. We adopt the physical picture of reorientable interacting polar clusters [2,3,6] embedded in a random array of pinned nanodomains [11]. There are n_i Nb-type unit cells in a cluster C_i, where $i = 1, 2, \ldots, N$ and N is the total number of reorientable clusters. The main contribution to the dipole moment $\vec{m}_0(i)$ of the lth cell in C_i is due to the relative displacements of the Nb^{5+} and Pb^{2+} ions from their pseudocubic positions [8,12]. The cluster dipole moment is thus $\vec{M}_i = n_i\vec{m}_0(i)$. Introducing $\vec{S}_i = \{[m_0(i)^2]_{av}/3\}^{-1/2}\vec{M}_i/n_i$ as a dimensionless order parameter field, where $[m_0(i)^2]_{av} = (1/N)\sum_i m_0(i)^2$, we find that its components satisfy the closure relation

$$\sum_{i=1}^{N} \vec{S}_i^2 = 3N. \tag{1}$$

The Edwards-Anderson order parameter is defined as

$$q_\mu^{EA} = \frac{1}{N}\sum_{i=1}^{N}\langle S_{i\mu}\rangle^2 = [\langle S_{i\mu}\rangle^2]_{av}; \qquad (\mu = x, y, z). \tag{2}$$

In zero field, due to the average cubic symmetry q_μ^{EA} does not depend on μ and will be simply written as q_{EA}.

The average probability distribution of local polarization $\vec{p}_i \equiv \langle\vec{S}_i\rangle$ is defined as

$$W(\vec{p}) = \frac{1}{N}\sum_i \delta(\vec{p} - \vec{p}_i). \tag{3}$$

It is trivial to verify that the first moment of $W(\vec{p})$ is the total polarization $\vec{P}$, which in the glass phase is zero in the absence of an external electric field, while its second moment is just q_{EA}.

The quadrupole perturbed NMR frequency of the ^{93}Nb nucleus ν_{il} depends on the value of the electric field gradient (EFG) tensor at the site (il), which is determined by the ionic displacements. The dimensionless order parameter $\vec{S}_i$ is proportional to the local distortion $\vec{m}_0(i)$, which influences the NMR resonance frequency. For a special orientation of the magnetic field $\vec{B} \parallel [111]$ the frequency shift will be a linear function of the relative displacements of the Nb and Pb ions or equivalently of the order parameter field $\vec{S}_i(t)$. In the fast motion limit the time average of $\vec{S}_i(t)$ enters the expression for ν_{il}, and by replacing it by the thermodynamic average $\langle \vec{S}_i \rangle = \vec{p}_i$ we can write

$$\nu_{il} = \nu_{il}^0 + \vec{\alpha} \cdot \vec{p}_i, \tag{4}$$

where the unperturbed resonance frequency ν_{il}^0 is site dependent due to disorder. The coefficients $\vec{\alpha}$ depend on the orientation of $\vec{B}$ and are nonzero due to the structural disorder, i.e., they would strictly vanish if the Nb and Pb ions were at sites with perfect cubic symmetry.

The inhomogeneous NMR line shape is characterized by the average frequency distribution function

$$f(\nu) = \frac{1}{N} \sum_i \frac{1}{n_i} \sum_l \delta(\nu - \nu_{il}), \tag{5}$$

which is related to the local polarization distribution function via

$$f(\nu) = \int d^3 p \, W(\vec{p}) \, \delta(\nu - \nu_0 - \vec{\alpha} \cdot \vec{p}). \tag{6}$$

The second moment of the NMR line shape is given by

$$M_2 = \int f(\nu)(\nu - \nu_0)^2 \, d\nu = \alpha^2 \frac{1}{N} \sum_i \vec{p}_i^2, \tag{7}$$

where ν_0 is the cluster average of ν_{il}^0 and $\alpha = |\vec{\alpha}|$. Comparing with Eq. (2) we see that

$$M_2 = \alpha^2 q_{\text{EA}}. \tag{8}$$

The temperature dependence of $f(\nu)$ and the Edwards-Anderson order parameter $q_{\text{EA}}(T)$ in a PMN single crystal have been measured by 2D separation of interactions ^{93}Nb $1/2 \to -1/2$ quadrupole perturbed NMR [13] at a Larmor frequency $\nu_L = 93.5$ MHz. The spectra have been measured (Fig. 1) at an orientation where the NMR frequency is mainly determined by a linear term in the expansion of the EFG tensor at the Nb site in powers of the local displacements from the ideal perovskite sites so that expression (4) applies. The ^{93}Nb NMR spectrum consists here—as already observed by Glinchuk *et al.* [14] with 1D NMR—of a relatively broad and temperature independent component and a relatively narrow temperature dependent component. Both lines are inhomogeneously broadened. The inhomogeneous width of the narrow line is, at this orientation, 16 kHz at 270 K, whereas the homogeneous width is only 720 Hz. The inhomogeneous width increases to 53 kHz at 130 K, whereas the homogeneous width is
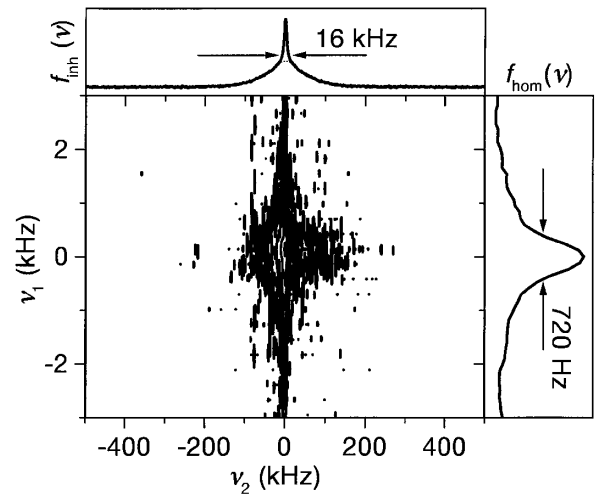

FIG. 1. 2D separation of interactions ^{93}Nb $1/2 \to -1/2$ quadrupole perturbed NMR spectra of a PMN single crystal at $T = 270$ K. The projection on the horizontal axis represents the inhomogeneous line shape, whereas the projection on the vertical axis yields the homogeneous line shape.

smaller by a factor of 76, and amounts to only 700 Hz. We believe that the broad temperature independent line is due to pinned nanodomains, whereas the relatively narrow line is due to the reorientable Nb^{5+} clusters.

The temperature dependences of the ^{93}Nb spin-lattice and spin-spin relaxation rates show that the average correlation time for the fluctuations of the EFG tensor at the ^{93}Nb sites is short as compared to the inverse inhomogeneous NMR linewidth above 100 K both within the reorientable polar clusters as well as within the pinned nanodomains. We are thus in the fast motion regime and Eqs. (4)–(8) apply.

The temperature dependence of the second moment of the inhomogeneous frequency distribution corresponding to the narrow ^{93}Nb NMR line is shown in Fig. 2. We see that the Edwards-Anderson order parameter $q_{\text{EA}}(T)$, which is proportional to M_2, is—within the limits of experimental error—nonzero in the whole investigated temperature range between 400 and 30 K. It is rather small and weakly T dependent above 300 K. Below 260 K it increases nearly linearly with decreasing temperature down to $\sim$100 K. On the other hand, the second moment of $f(\nu)$ corresponding to the broad line as well as the q_{EA} deduced from it, are nearly independent of temperature.

It should be stressed that the observed forms of the inhomogeneous frequency distribution $f(\nu)$ and the related local polarization distribution function $W(\vec{p})$ in PMN are completely different (Fig. 1) from those previously found in rubidium-ammonium-dihydrogen-phosphate-type (RADP-type) Ising dipolar [15] and cyanide-type quadrupolar glasses [16,17]. In PMN $W(\vec{p})$ is Gaussian, whereas it is double peaked in dipolar and triple peaked in quadrupolar glasses below the freezing temperature T_f. This shows that the glassy features in PMN cannot be
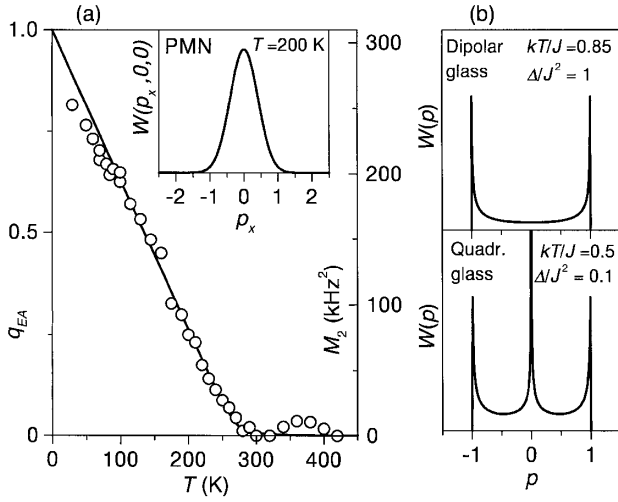
FIG. 2. (a) Temperature dependence of the Edwards-Anderson order parameter q_{EA} of the reorientable part of the inhomogeneous frequency distribution in PMN. The solid line is a fit to the SRBRF model with parameters as specified in the text. The inset shows the corresponding local polarization distribution function $W(\vec{p})$ along the p_x axis as obtained from Eq. (12). (b) Examples of $W(p)$ functions for RADP dipolar [15] and cyanide-type quadrupolar glasses [17] are shown for comparison.

described as a dipolar or quadrupolar glass as suggested earlier [5], and that we are dealing with a new type of glass.

Another feature specific for the reorientable clusters in PMN is that the break in the temperature dependence of q_{EA} around T_f is much more pronounced than in dipolar or quadrupolar glasses. Thus the random-field contribution to the glass transition is here much weaker than the contribution of the random bonds. In the pinned nanodomains, on the other hand, random-field effects may be dominant.

Let us now try to describe the above features in terms of a new microscopic model for relaxor ferroelectrics. Since the number of allowed orientations of $\vec{S}_i$ is rather high, we can consider $\vec{S}_i$ as a continuous vector $-\infty < S_{i\mu} < +\infty$ subject to the spherical constraint (1). Thus we obtain the SRBRF model of relaxor ferroelectrics

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - \sum_i \vec{h}_i \cdot \vec{S}_i - \sum_i \vec{E} \cdot \vec{S}_i,$$
(9)

assuming that the interactions J_{ij} are randomly frustrated and infinitely ranged. The last assumption is also supported by the long range nature of the acoustic and optic phonon mediated strain-polarization intercluster interactions. The random bonds J_{ij} are characterized by the mean value of the coupling J_0/N and the rms variance $J/\sqrt{N}$, and the random fields $\vec{h}_i$ by the variance Δ [15,18]. The average free energy can be calculated in a standard manner by applying the replica trick and im-

posing the spherical constraint (1) [19]. If $J_0 < J$ we have a spherical glass without long range order, whereas we have an inhomogeneous ferroelectric with a nonzero spontaneous polarization if $J_0 > J$. This can occur due to field induced polarization-strain coupling, resulting in $J_0 = J_0(E)$ and $J_0 > J$ for $E > E_c$. For $\vec{E} \parallel [111]$ the components of polarization P_μ, and the spin glass order parameter q_μ, are μ independent and the resulting equations for $P = P_\mu$ and $q = q_\mu$ are ($\beta = 1/kT$)

$$q = \beta^2 J^2 (q + \Delta/J^2)(1 - q)^2 + P^2,$$
(10)

$$P = \beta(1 - q)(J_0 P + E).$$
(11)

The probability distribution of local polarization (3) is surprisingly simple and found to be Gaussian over the whole temperature interval. For $J_0 < J$ we obtain

$$W(\vec{p}) = (2\pi q)^{-3/2} \exp(-\vec{p}^2/2q).$$
(12)

Inserting $W(\vec{p})$ into Eq. (5) we find that the inhomogeneous NMR frequency distribution $f(\nu)$ is also Gaussian:

$$f(\nu) = (2\pi q\alpha^2)^{-1/2} \exp[-(\nu - \nu_0)^2/2q\alpha^2].$$
(13)

Thus, $W(\vec{p}) = (\alpha/2\pi q)f(\nu_0 + \alpha|\vec{p}|)$.

By evaluating $q(T)$ from Eq. (10) for the case $E = 0$ and $P = 0$ we can compare the theoretical results with the NMR spectra. The observed temperature variation of q_{EA} from the narrow line can be fitted with Eq. (10) using $J/k = 265$ K and $\Delta/J^2 = 0.002$ (Fig. 2a). The temperature dependence of the inhomogeneous line shape can be quantitatively described by the local polarization distribution function $W(\vec{p})$ according to the SRBRF model using the above values of J and Δ. It should be stressed that the form of $W(\vec{p})$ used to describe the temperature dependence of $f(\nu)$ is completely different from those in dipolar and quadrupolar glasses (Fig. 2b). The T independence of $W(\vec{p})$ of the broad line means that this component is not directly involved in the diffuse relaxor transition in PMN.

Whereas the local polarization distribution function $W(\vec{p})$ discriminates between dipolar, quadrupolar, and spherical glassy behavior, the third-order dielectric nonlinearity $a_3 = \chi_3/\chi_1^4$ [20] discriminates between a glassy state and a ferroelectric state broken up into nanodomains due to the presence of random fields. In the case of no long range order the SRBRF glass model yields

$$a_3 = \frac{T}{(1 - q)^2[1 - \beta^2 J^2(1 - q)(1 - 3q - 2\Delta/J^2)]}.$$
(14)

For a random-field frustrated ferroelectric ($J_0^2 < \Delta$) without random bonds ($J = 0$), a_3 is found to be a monotonically increasing function of temperature. For a random-bond glass ($J_0 \ll J$) without random fields
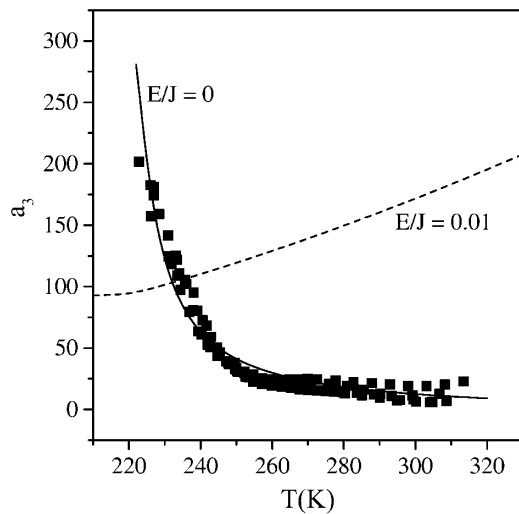
FIG. 3. Temperature dependence of the quasistatic nonlinear susceptibility $a_3 = \chi_3/\chi_1^4$ in PMN [21,22] for $E = 0$ and fit (solid line) to the SRBRF model Eq. (14). Dashed line: Temperature dependence of a_3 evaluated for $E/J = 0.01$.

($\Delta = 0$) a_3 diverges at a freezing temperature $T_f = J/k$. In the presence of weak random fields, i.e., for $\Delta/J^2 \ll 1$, a_3 does not diverge, but shows a sharp peak near $T \approx J/k$. This last behavior corresponds to the case of a relaxor ferroelectric.

The quasistatic $\chi_3(T)$ [21] has been measured in a PMN single crystal in zero field [22]. The corresponding $a_3(T)$ was found to increase sharply on lowering the temperature between 320 and 220 K [23]. This is incompatible with the case of a random-field frustrated ferroelectric, but quantitatively agrees with the above predictions of the SRBRF model for a random-bond glass as shown in Fig. 3. In the presence of a nonzero electric field the behavior completely changes, i.e., the peak in a_3 disappears [7], in agreement with the SRBRF model (Fig. 3).

In summary, we have directly determined the temperature dependence of the local polarization distribution function $W(\vec{p})$ and of the Edwards-Anderson order parameter q_{EA} in PMN. Within the pinned nanodomains q_{EA} is temperature independent in the range of the diffuse phase transition, whereas it shows a T dependence characteristic of a glasslike freezing in the reorientable part of the crystal. The form and T dependence of $W(\vec{p})$ and q_{EA} as well as the peak in the quasistatic nonlinear dielectric susceptibility in PMN can be well described by a newly proposed spherical random bond–random field model of relaxor ferroelectrics.

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