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Field Cooled and Zero Field Cooled ^{207}Pb NMR and the Local Structure of Relaxor $PbMg_{1/3}Nb_{2/3}O_3$

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An isotropic ^{207}Pb NMR spectrum corresponding to the glassy matrix with spherical shell type Pb shifts from the cubic sites, as well as an anisotropic spectral component corresponding to polar nanoclusters with a Pb shift parallel to the [111] direction, have been observed in a $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) single crystal. This represents a microscopic confirmation of the model of relaxors first proposed by Burns and Dacol. A sudden increase in the intensity of the anisotropic cluster line is seen for electric fields larger than the critical field around 210 K. This demonstrates the occurrence of an orientational percolation type transition to the field-induced ferroelectric phase with about 50% of the Pb nuclei still remaining in the spherical glass matrix. A similar though smaller increase of the intensity of this line is also seen in the zero field cooled data, demonstrating that relaxor PMN is an incipient ferroelectric.

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Perovskite relaxors [1,2] such as lead magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) are intermediate between dipolar glasses and classical ferroelectrics and exhibit both substitutional and charge disorder. They exhibit very large dielectric, piezoelectric, and electromechanical responses and are important for many applications [1,2]. The key to the understanding of the nature of relaxors is their local structure. At any temperature between 1000 and 4 K the average symmetry of PMN, for instance, is cubic. This is true even on the micrometric scale. Experiments on the nanometric scale have, however, shown that the local structure is different from the average structure. Burns and Dacol [3] suggested that randomly oriented polar nanoclusters appear below 925 K [2]. The size of the nanoclusters should be smaller than 500 Å so that they cannot be seen on the profile of the x-ray diffraction lines [3,4]. In spite of years of investigations, very little is known about the microscopic nature of these nanoclusters [1–8].

Here we report on an investigation of polar nanoclusters in a PMN single crystal with the help of ^{207}Pb NMR in an electric field. A characteristic difference between dipolar glasses such as rubidium-ammonium dihydrogen phosphate [5] and relaxors is that in relaxors a ferroelectric state appears [6] for fields larger than a critical field, $E > E_c$, whereas this is not the case in glasses. This difference, which is obviously due to polar nanoclusters, has been so far studied mainly on the macroscopic level. We decided to study it on the microscopic level by measuring the field cooled (FC) and zero field cooled (ZFC) ^{207}Pb NMR spectra at different temperatures and orientations of the crystal in the magnetic and electric field. Our results show for the first time the presence and structure of both the polar clusters and of the pseudocubic spherical shell type matrix into which the polar ferroelectriclike clusters are embedded. This represents a direct microscopic proof of the existence of these two entities. The NMR method also allows for the determination of their relative intensities. The sudden increase in the intensity of the anisotropic NMR line corresponding to polar clusters with a Pb shift parallel to the polar direction [111] which appears for $E > E_c \approx 1.8$ kV/cm and $T < T_c \approx 210$ K together with a dielectric peak [9] demonstrates the occurrence of a first-order ferroelectric phase transition. About 50% of the crystal volume, however, still remains in the spherical glass matrix state. With decreasing temperature the volume percentage of the [111] oriented polar clusters remains constant. This seems to show that the electric field-induced transition to the ferroelectric state in PMN is an orientational percolation transition. Below T_c the electric field aligns the domains and increases their size along the [111] direction so that they become visible by x rays but does not change their total volume. It should be noted that a similar, though smaller, increase in the intensity of the line corresponding to [111] oriented polar clusters occurs in the vicinity of T_c also in the absence of the electric field. PMN is thus an incipient ferroelectric. The anisotropic chemical shift perturbed ^{207}Pb NMR line characteristic of nanoclusters oriented along the polar [111] direction abruptly disappears above 210 K.

If the Pb nuclei in the polar clusters are displaced from their high symmetry cubic perovskite sites, the ^{207}Pb chemical shift tensors become anisotropic and can be written as a sum of a scalar part σ_0 and a traceless second rank tensor part $\boldsymbol{\sigma}_a$:

$$\boldsymbol{\sigma} = \sigma_0 \cdot \mathbf{1} + \boldsymbol{\sigma}_a. \tag{1}$$

The eigenvalues of the traceless part are $-\sigma_a/2$, $-\sigma_a/2$, σ_a. The largest principal axis of $\boldsymbol{\sigma}_a$ should be parallel to the direction of the average shift of the Pb nucleus, i.e., to the direction of the polarization p_i of a given polar cluster i.

For a general orientation of the crystal with respect to the direction of the magnetic field B_0 specified by (θ, ϕ), the ^{207}Pb NMR transition frequency will be given by

$$\nu_{\mathrm{Pb}} = \nu_L[1 + \sigma_0(p) + \sigma_{ZZ}(p, \vartheta, \varphi, \theta, \phi)], \qquad (2)$$

where ν_L is the unperturbed Pb Larmor frequency, σ_0 is the isotropic part of the chemical shift tensor, and σ_{ZZ} is the component of $\boldsymbol{\sigma}_a$ along the magnetic field direction. The angles ϑ, φ determine the orientation of the eigenframe of $\boldsymbol{\sigma}_a$ with respect to the crystal fixed frame.

The ^{207}Pb ($I = 1/2$) chemical shift perturbed spin echo Fourier transform spectra of the PMN single crystal have been measured in a superconducting magnet at 9.1 T, i.e., at a Larmor frequency 79.4 MHz. The width of the 90° pulse was ≈ 4 μs. The orientation of the crystal was determined by x rays. The sample was first cooled down to 20 K in the presence of an applied electric field of 3 kV/cm. The FC spectra were then measured on heating both with the electric field on and with the electric field turned off. The field-induced changes in the spectra were stable for at least several days for temperatures lower than 210 K. After that the crystal was heated to 430 K and allowed to anneal. The annealed sample was cooled down and the ZFC spectra were measured. A large difference between FC and ZFC spectra was seen below 210 K at $\mathbf{E} \parallel [111]$, i.e., when the electric field was applied along the rhombohedral polar axis. No effects were seen with $\mathbf{E} \parallel [100]$.

Some representative ZFC and FC ^{207}Pb NMR spectra of PMN are shown in Fig. 1 for $\mathbf{B} \parallel [111]$ and $\mathbf{E} \parallel [111]$. A single isotropic Gaussian spectrum is seen for both ZFC and FC spectra at temperatures above 210 K. Its half-width at 410 K is about 30 kHz, i.e., much larger than what can be accounted for by nuclear dipolar interactions [7]. The observed line shape is thus here due to a spherical shell type distribution of chemical shift tensors and the structure is pseudocubic. The spectral shape does not correspond to a random orientational distribution of chemical shift tensors of equal magnitude, as no singularities characteristic of such a distribution are seen. Below 210 K an anisotropic line appears in addition to the isotropic component in both the FC and the ZFC spectra. The ratio of the intensities of the two components is about 1:5 in the ZFC spectra. In the FC spectra the anisotropic component is much stronger. The angular dependence of the anisotropic lines is the same in the FC and ZFC spectra.

Whereas the isotropic spectrum can be understood on the basis of the spherical shell Pb displacement model based on the x-ray data [10], this is not the case for the anisotropic line, which requires a Pb shift in a given preferred direction. The width of both the isotropic and the anisotropic components increases with decreasing temperature as predicted by the spherical random bond-random field model of relaxors [7]. At 80 K, the width of the isotropic component reaches 100 kHz, whereas the anisotropic component is 40 kHz wide. Below $T_c = 210$ K and for electric fields larger than the critical value $E > E_c$, a sudden increase of the intensity of the anisotropic polar cluster line corresponding to Pb shifts along the [111] direction is seen (Fig. 2). At the same temperature, a peak in the dielectric constant appears for $E > E_c$

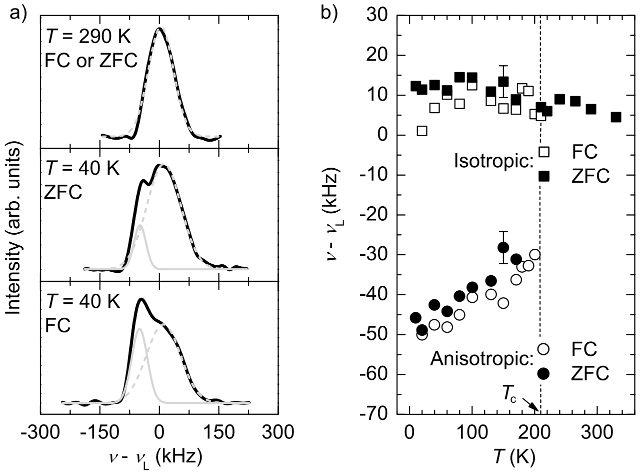

FIG. 1. (a) Decomposition of the field cooled and zero field cooled ^{207}Pb NMR spectra of a PMN single crystal, taken at $\mathbf{B} \parallel \mathbf{E} \parallel [111]$ at different temperatures, into an isotropic (dashed grey line) and anisotropic (solid grey line) component. (b) Temperature dependence of the positions of isotropic and anisotropic ^{207}Pb NMR lines. The anisotropic line disappears above 210 K for both the FC ($E = 3$ kV/cm) and the ZFC spectra.

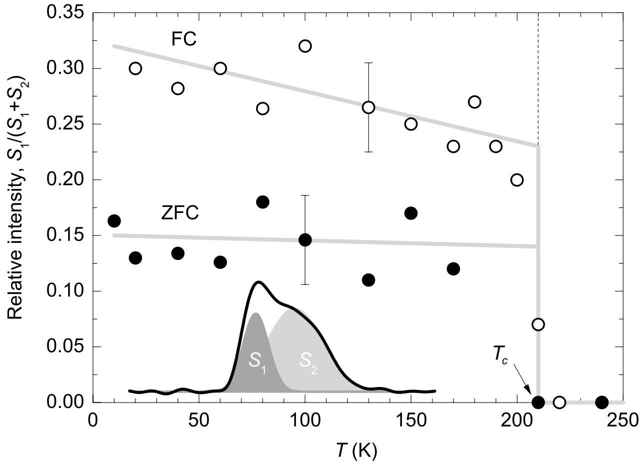

FIG. 2. Temperature dependence of the relative integral intensity of the anisotropic cluster line with a Pb shift—and local polarization—parallel to the [111] direction. The sharp increase in the intensity of this line at $T_c = 210$ K and $E = 3$ kV/cm $> E_c = 1.7$ kV/cm (open circles) signals the first order transition to the field-induced ferroelectric phase. The observed smaller increase in the intensity of this line in the ZFC data (solid circles) demonstrates that PMN is an incipient ferroelectric. Solid lines are guides for the eye.

[9]. This means that the sudden increase in the intensity of the [111] oriented polar cluster line signals the transition to the ferroelectric phase [6]. According to the intensities of the NMR lines, about 50% of the Pb nuclei still reside in the isotropic spherical glass matrix. The transition at T_c seems to correspond to an orientational percolation transition of ferroelectric polar clusters with the polarization and Pb shifts parallel to the [111] direction. It is interesting to note that a similar but about 2 times smaller increase in the intensity of this cluster line is also seen in the ZFC spectra (Fig. 2). This means that PMN is an incipient ferroelectric, as in the absence of the electric field the concentration of polar clusters is below the threshold for a percolation type ferroelectric transition.

To check on the nanocluster dynamics we performed FC and ZFC ^{207}Pb spin-spin relaxation time (T_2) measurements with the Carr-Purcell-Meiboom-Gill technique [11] using a pulse separation of $\tau = 100\ \mu$s. The measurements were made for $\mathbf{B} \parallel \mathbf{E} \parallel [111]$ using a frequency offset of -40 kHz as well as 20 kHz with respect to the Larmor frequency. On cooling from 400 K, T_2 initially decreases with temperature, demonstrating the rapid slowing down of the nanocluster dynamics in the spherical glass matrix (Fig. 3). The decrease of T_2 is similar to the decrease [7] of the spin lattice relaxation time T_1 but the values of T_2 are by 3 orders of magnitude shorter than the T_1 values. A very pronounced Bloembergen-Pound-Purcell type T_2 minimum [11] appears around 255 K. This closely matches the nominal freezing temperature $T_M \approx 250$ K, i.e., the temperature where a maximum of the dielectric susceptibility is found [9]. The same mechanism, i.e., fluctuations in the orientation of the nanocluster polarization, is therefore responsible for dielectric losses and for the T_2 data. At the position of the minimum the mean correlation frequency of nanocluster orientational polarization fluctuations is about 10 kHz. At $T > 250$ K, T_2 only weakly depends on the frequency offset, demonstrating that the nanocluster dynamics is similar in different parts of the crystal.

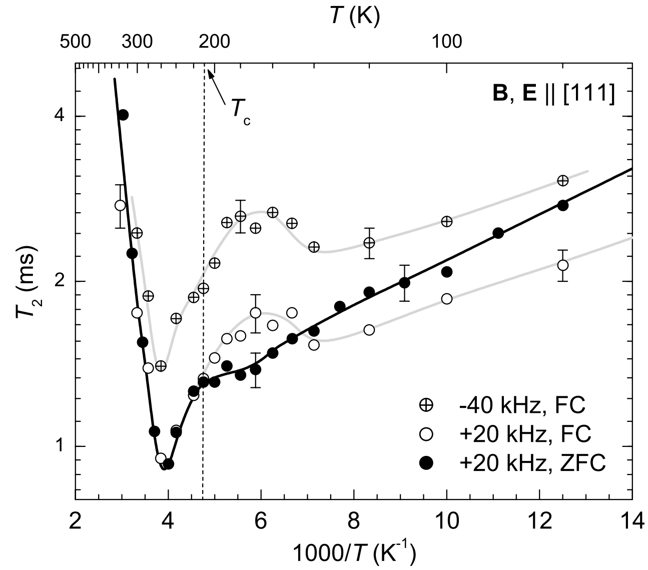

FIG. 3. Temperature dependence of the spin-spin relaxation time T_2. The minimum at 250 K corresponds to the well-known freezing of polar clusters. At about 140 K there is a second shallow minimum in the FC ($E = 3$ kV/cm) data, which could be related to the motion of domain walls at $T < T_c$.

Above $T_c \approx 210$ K there is no difference between the FC and ZFC $T_2(T)$ dependencies, whereas below T_c a significant mismatch is observed. A second rather flat T_2 minimum appears in the FC data around 140–150 K (Fig. 3), i.e., below the transition to the ferroelectric phase. A new reorientation process thus appears. It seems to be due to the motion of the domain walls of [111] clusters at the percolation transition. T_2 here depends on the frequency offset, i.e., the nanocluster dynamics is different in different parts of the crystal, as expected for a two-component system.

It should be noted that the dynamic NMR width $\Delta\nu_{\mathrm{dyn}} = (\pi T_2)^{-1}$ of the NMR line is always small compared to the static "glassy" NMR width induced by the inhomogeneous nature of the spectrum. Therefore, the cluster dynamics can be seen only by T_2 measurements and not by 1D line shape data, which reflect the static glassy nature of the relaxor state corresponding to the Edwards-Anderson order parameter [5,7].

We have thus for the first time observed separately the anisotropic ^{207}Pb NMR spectra of ferroelectriclike polar clusters and the isotropic spectra of the spherical glass matrix into which the polar clusters are embedded. This provides for a microscopic confirmation of the model of relaxors first proposed by Burns and Dacol [3]. We have observed as well an electric field-induced transition to the ferroelectric state, which is due to the sudden increase in the concentration of clusters with a Pb shift and polarization along the [111] direction. About 50% of the crystal still remains in the glassy matrix state. A similar though smaller increase in the intensity of this cluster line is seen also in the absence of an electric field. The concentration, however, does not seem to be large enough to induce a ferroelectric state. PMN thus seems to be an incipient ferroelectric.

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