Electric-field effects on the diffuse scattering in $PbZn_{1/3}Nb_{2/3}O_3$ doped with 8% $PbTiO_3$

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We report measurements of the neutron diffuse scattering from a single crystal of the relaxor ferroelectric $PbZn_{1/3}Nb_{2/3}O_3$ doped with 8% $PbTiO_3$ (PZN-8%PT) for temperatures 100 K$\leqslant$T$\leqslant$530 K and electric fields 0 kV/cm$\leqslant E\leqslant$10 kV/cm. The field-cooled diffuse scattering measured transverse to the (003) Bragg peak is strongly suppressed in the tetragonal phase at 400 K for E=2 kV/cm applied along the [001] direction. However, no change is observed in the diffuse scattering measured transverse to (300), even for field strengths up to 10 kV/cm. Thus the application of an external electric field in the tetragonal (ferroelectric) phase of PZN-8%PT does not produce a uniformly polarized state. This unusual behavior can be understood within the context of the model of Hirota *et al.* of phase-shifted polar nanoregions in relaxors, since an electric field applied along [001] below T_c would reduce the shifts of the nanoregions along [001] while preserving those along the orthogonal [100] direction.

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I. INTRODUCTION

The shape, size, density, and orientation of the polar nanoregions (PNR) that form below the Burns temperature T_d (Ref. 1) in the lead-oxide class of relaxors $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and their solid solutions with $PbTiO_3$ (PZN-xPT and PMN-xPT, respectively) are key parameters of interest to many researchers attempting to clarify the various mechanisms responsible for the exceptional piezoelectric properties exhibited by these materials.[2] The existence of these PNR was first inferred through optical measurements of the index of refraction by Burns and Dacol,[1] and has since been correlated with the onset of strong neutron diffuse scattering in PMN,[3] a saturation of the PMN unit cell volume,[4] and the overdamping of long-wavelength phonon modes in PMN, PZN and PZN-8%PT near T_d.[5–7] More recently an important model concerning the relationship between the PNR and the surrounding cubic lattice was presented by Hirota *et al.*[8] Based on neutron time-of-flight measurements of the diffuse scattering in PMN at 300 K performed by Vakhrushev *et al.*,[9] Hirota *et al.* noticed that the corresponding ionic displacements could be decomposed into a scalar shift (displacement) common to all atoms, and a pattern of shifts that preserves the unit cell center-of-mass. It was further shown that the center-of-mass conserving shifts are consistent with neutron inelastic measurements of the soft TO phonon intensity in PMN above T_d,[10] thus providing compelling evidence that the polar nanoregions result from the condensation of a soft mode at the Burns temperature.[11]

Subsequent measurements on PZN-8%PT using neutron diffraction techniques by Ohwada *et al.* suggest that the zero-field cooled structure at low temperature is not rhombohedral, as had been previously believed.[12] Instead, surprising evidence of a new phase, termed phase X, was found that exhibits an average cubic unit cell structure. These findings motivated the high-energy x-ray study by Xu *et al.* on pure PZN,[13] and the high-resolution neutron study by Gehring *et al.* on PMN-10%PT.[14] Both of these studies revealed a low-temperature bulk phase that is not rhombohedral, but rather consistent with the phase X observed by Ohwada *et al.* in PZN-8%PT. It has been suggested that the phase-shifted model of the PNR could provide a plausible explanation for the presence of phase X at low temperatures, as a uniform shift of the PNR would present a natural energy barrier against the formation of a uniform polar (e.g., rhombohedral) state.

To shed more light on this idea, we have performed a study of the PNR in PZN-8%PT by measuring the response of the neutron diffuse scattering to external electric fields **E** applied along the [001] direction. As is well known, a classic ferroelectric system will break into domains in zero field when cooled below T_c. The subsequent application of an electric field can produce a nearly uniform polar state (no diffuse scattering) by aligning all of the domains via domain wall motion. In the case of the relaxor ferroelectric PZN-8%PT, we have examined the diffuse scattering below the cubic-to-tetragonal phase transition temperature $T_c\sim$470 K near the two orthogonal reflections (300) and (003) for which the diffuse scattering is known to be strong. Our data show that the diffuse scattering near (003), which measures the projections of ionic displacements along [001], decreases under an external [001] field as expected. By contrast, the diffuse scattering near the orthogonal (300) reflection is unaffected, even for field strengths up to 10 kV/cm. Thus a uniform polar state is not achieved. The model of phase-shifted PNR provides one possible explanation for this unusual behavior if one assumes that an electric field applied along [001] decreases or removes the PNR shifts along [001] while preserving those along [100]. The diffuse scattering would then decrease anisotropically, as is observed.

II. EXPERIMENTAL DETAILS

The neutron scattering data presented here were obtained on the BT9 triple-axis spectrometer located at the NIST Cen-

ter for Neutron Research. The diffuse scattering near the two orthogonal reciprocal lattice points (300) and (003) was measured at a fixed neutron energy $E_i = E_f = 14.7$ meV ($\lambda = 2.36$ Å) using the (002) reflection of highly-oriented pyrolytic graphite (HOPG) crystals as monochromator and analyzer. Horizontal beam collimations were 40′-47′-S-40′-80′ (S = sample).

The high-quality single crystal of PZN-8%PT used in this study was grown by the flux solution method[15] at the Pennsylvania State University. It is a sister crystal to the one used by Ohwada *et al.* in an earlier study,[12] some results from which are presented in this paper, and grown using the same technique. The crystal weighs 1.1 *g* (0.15 cm^3), and is a rectangular block with {100} faces and dimensions 7.2 $\times 6.9 \times 3.0$ mm^3. Gold electrodes were plated onto the two largest surfaces of the crystal to which thin gauge copper wires were attached using a fired-on silver conductive adhesive epoxy cured at 100 °C for 2 h. In this geometry the field is always applied along a cubic [001] axis. These wires were twisted and soldered onto leads connected to a high voltage power supply. A voltmeter was used to measure the voltage difference across the two gold-plated surfaces of the crystal directly. This test was performed both before and after the experiment to verify that the voltage set by the power supply appeared across the sample, and that the wires had not become detached from the sample during the measurements. The difference between the set and measured voltage drop was always less than 1%.

The crystal was mounted onto an electrically insulating boron nitride post using boron nitride paste to provide a strain-free environment for the sample. The crystal [010] axis was oriented vertically, giving access to reflections of the form (*h*0*l*). The sample holder assembly was then mounted inside the vacuum space of a high-temperature closed-cycle ^{3}He refrigerator, which was subsequently positioned and fixed onto the goniometer of the BT9 spectrometer. The sample has a cubic lattice spacing of 4.04 Å at 500 K, so 1 rlu (reciprocal lattice unit) equals 1.56 $Å^{-1}$.

III. DIFFUSE SCATTERING

The PZN-8%PT phase *E*-*T* diagram has been mapped out by Ohwada *et al.*, and is shown in Fig. 1.[12] The data presented in the top panel were taken while cooling in a constant electric field applied along [001], whereas those shown in the bottom panel were taken with increasing field (also along [001]) at a fixed temperature after first cooling in zero field. The electric field acts to stabilize the tetragonal phase as can be seen from the slopes of the tetragonal (T) to cubic (C) and monoclinic (M) phase boundaries shown in Fig. 1(a), where the T-C (M-T) transition temperature increases (decreases) with field. The transition temperatures, represented by the circles in Fig. 1, were determined from measurements of the lattice constants. While this relaxor compound clearly exhibits a tetragonally-distorted structure, the precise nature of the polar order is still unknown.

Important information can be obtained about the polar order in the tetragonal phase of PZN-8%PT through measurements of the neutron diffuse scattering. Figure 2 shows

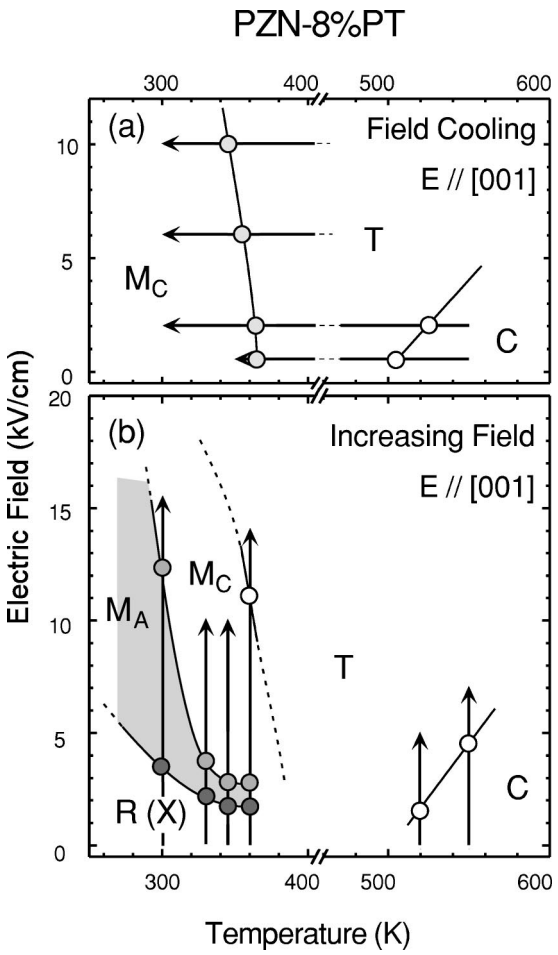

FIG. 1. The *E*-*T* phase diagram of PZN-8%PT as determined by Ohwada *et al.* (Ref. 12). The notations C, T, M, and R refer to cubic, tetragonal, monoclinic, and rhombohedral phases, respectively. The arrows point in the scan direction, while the length of the arrows correspond to the scan range. The circles denote the transition temperatures determined from each scan.

neutron scattering measurements made by Ohwada *et al.* on a sister PZN-8%PT single crystal near the (003) reciprocal lattice position, for which the diffuse scattering structure factor is known to be strong.[12] The diffuse scattering intensity measured at the scattering vector $\mathbf{Q} = (0.04, 0, 3)$ is shown as a function of temperature at $E = 0$ kV/cm (closed circles) and 3 kV/cm (open circles). The 3 kV/cm data were taken while cooling from high temperature, with the field applied along the [001] direction. In the cubic phase ($T \geqslant 520$ K) the diffuse scattering intensities are equal, indicating no field dependence. However at lower temperature, in the tetragonal phase, the diffuse scattering intensity is strongly suppressed by the field while the zero-field diffuse scattering intensity remains strong and even increases with cooling. For purposes of comparison, the integrated Bragg peak intensity measured at (002) in zero-field is shown (note the scale on the right-hand side of Fig. 2). The Bragg intensity increases sharply below ~500 K, which is consistent with the phase diagram in Fig. 1.

The data in Fig. 2 were taken at a fixed scattering vector **Q** at two different field values. Information about the geom-

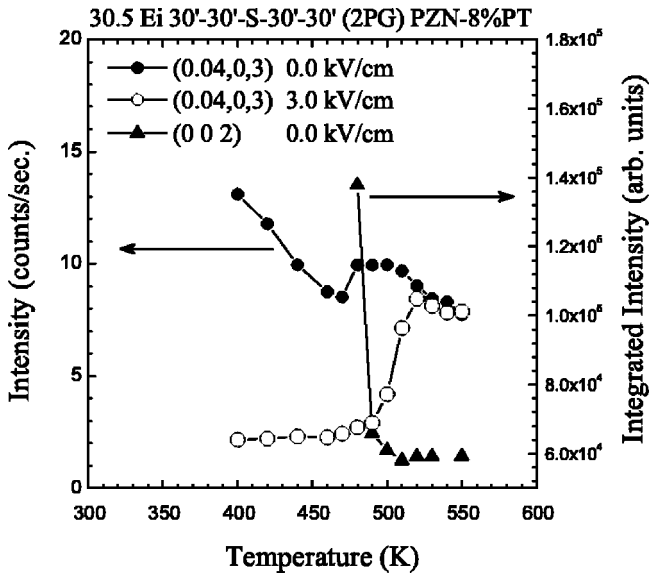

FIG. 2. Temperature dependence of the neutron diffuse scattering at $\mathbf{Q}=(0.04,0,3)$ in zero field (closed circles) and $E=3$ kV/cm // [001] (open circles). The zero-field Bragg intensity measured at (002) is shown as a function of temperature by the closed triangles. These data were taken by Ohwada *et al.* on a sister crystal of PZN-8%PT.

etry of the diffuse scattering is presented in Fig. 3, which compares the diffuse scattering intensity measured at two pairs of orthogonal reciprocal lattice points at a fixed field strength of 2 kV/cm oriented along the [001] axis. These measurements were also made while field cooling from temperatures well above T_c. In addition, waiting times between successive data points ranged from 30 min to 1 h, depending on the temperature step size (1 h for a step size of 100 K) to ensure proper thermal equilibrium was attained. The diffuse intensities measured near (003) (open circles) reflect the size of the ionic displacements **u** projected along

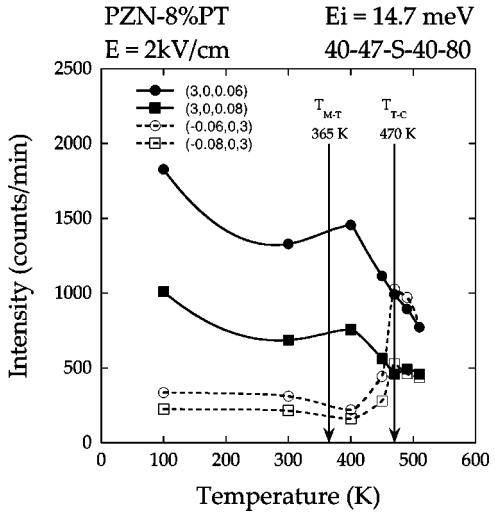

FIG. 3. Comparison of the diffuse scattering intensities measured near the orthogonal reciprocal lattice vectors (300) (closed symbols) and (003) (open symbols) as a function of temperature in a field of 2 kV/cm applied along [001].

[001] through the diffuse scattering cross section dependence on $|\mathbf{Q}\cdot\mathbf{u}|^2$, and decrease upon cooling in field in agreement with the data of Fig. 2. However the striking behavior revealed in this figure is that the diffuse intensities measured around (300), for which **Q** is orthogonal to the external field, do *not* decrease with cooling, but instead increase, much like the zero-field data shown in Fig. 2. The vertical arrows in this figure indicate the phase transition temperatures $T_{\mathrm{M-T}}$ and $T_{\mathrm{T-C}}$ between the monoclinic and tetragonal, and tetragonal and cubic phases, respectively.

To clarify this behavior wide scans were made of the scattered neutron intensity as a function of the reduced momentum transfer q transverse to both the (300) and (003) Bragg positions as a function of field and temperature. The resulting data are plotted on a log-intensity scale in Fig. 4. The top two panels displays transverse q-scans in zero field, and the bottom two panels show the same scans taken after cooling the sample in a 2 kV/cm field. In the cubic phase at 500 K (upper right panel) we observe diffuse scattering of roughly equal intensity in zero field along directions transverse to both $\mathbf{Q}=(300)$ and (003). This scattering does not change when an external electric field of 2 kV/cm is applied along the [001] direction at the same temperature (lower right panel). In the tetragonal phase at 400 K (upper left panel) the zero-field diffuse scattering changes slightly, becoming a little stronger around (003) compared to (300). When the sample is field cooled, the diffuse scattering transverse to (003) decreases substantially (lower left panel), as expected from the data shown in Fig. 2 and Fig. 3. What is remarkable, however, is that the diffuse scattering transverse to (300) (orthogonal to the field direction) is unaffected. These data reveal the very unexpected result that the application of an external 2 kV/cm field is insufficient to produce a uniform polarization in the tetragonal phase of the relaxor PZN-8%PT. The dotted line in the lower left panel of Fig. 4 indicates the measured instrumental (Gaussian) transverse q-resolution. Although data are not shown, we observed the same behavior in the monoclinic phase of PZN-8%PT at 300 K as in the tetragonal phase at 400 K.

An effort was made to determine the field strength E_c at which the diffuse scattering intensity near (300) begins to decrease. Figure 5 shows the diffuse scattering intensity measured at $\mathbf{Q}=(3,0,-0.06)$ at 450 K, still in the tetragonal phase, from zero to 10 kV/cm. All of these data were taken as a function of increasing electric field strength after first field cooling from 520 K in a field of 2 kV/cm, except for the zero field data point, which was obtained after zero-field cooling. The total time for this measurement was slightly more than 1 h. The closed and open circles are successive measurements at the same temperature and Q. The closed triangles show the corresponding diffuse scattering intensities measured at $\mathbf{Q}=(0.06,0,3)$, which clearly decrease with increasing field. These data demonstrate the inability of even a strong external electric field to diminish the diffuse scattering orthogonal to the field direction. Hence the underlying mechanism responsible for the diffuse scattering in PZN-8%PT must have an energy barrier that is sufficiently large to stabilize it against external fields of at least 10 kV/cm.

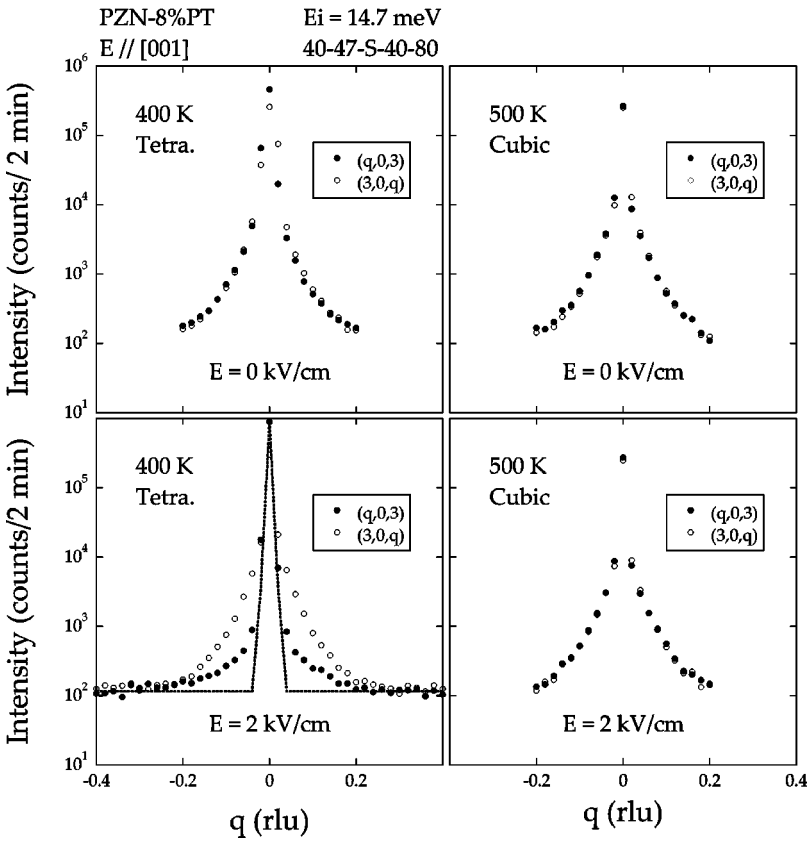

FIG. 4. A log-scale comparison of the diffuse scattering intensities measured transverse to the (300) (open circles) and (003) (closed circles) reciprocal lattice positions at 400 K (tetragonal phase) and 500 K (cubic phase).The top panels show data in zero field, and the bottom panels show data in an electric field of 2 kV/cm applied along [001]. The dashed line in the lower left panel represents the instrumental transverse q-resolution.

IV. DISCUSSION

The results on PZN-8%PT presented here are significant not because the diffuse scattering transverse to (003) is suppressed by an external electric field, which is expected, but rather because the diffuse scattering measured transverse to (300) is *not*. Independent of any model, our data provide unambiguous evidence that the polar state in this important relaxor material is not uniform, even in the presence of electric fields as strong as 10 kV/cm. This finding would appear to contradict those of Fujishiro *et al.*, who have reported the establishment of a homogeneous polar phase in PMN (and PMN-10%PT) by application of an electric field of 1.73 kV/cm along [111].[16] However this study was based on measurements of the optical birefrigence using light with a wavelength $\lambda = 6,330$ Å, which is insensitive to disorder on the nanometer scale such as that observed here in PZN-8%PT using neutron techniques ($\lambda = 2.36$ Å). As shown by Xu *et al.*, the correlation length associated with the PNR in PMN is of order 60 Å at low temperature.[17] The persistence of this nanoscale disorder against electric field must therefore be explained by any model that purports to address the fundamental properties of these lead-oxide relaxor compounds. We note further that two recent neutron diffuse scattering studies of PZN-8%PT (Ref. 18) and PMN (Ref. 17) demonstrate that the diffuse scattering in these relaxors is predominantly elastic in nature below T_c. Thus the reduction in diffuse scattering that we observe by applying an electric field does not simply result from a change in phonon linewidths.

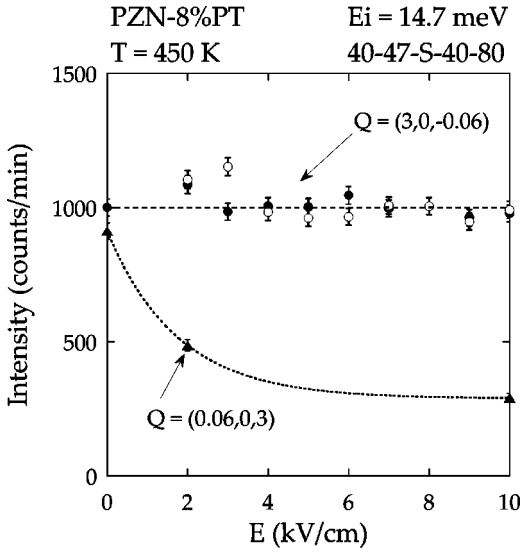

FIG. 5. Plot of the diffuse scattering intensity measured in the tetragonal phase at (3,0,-0.06) at 450 K as a function of increasing field strength applied along the [001] direction. The open and closed circles represent independent measurements. The closed triangles correspond to the diffuse scattering intensity measured at (0.06,0,3) for comparison. The lines are guides to the eye.

While not unique, we believe that the concept of the phase-shifted polar nanoregions can provide a natural explanation for the field and **Q**-dependence of the diffuse scattering we observe in PZN-8%PT. This is illustrated by the three-panel schematic diagram shown in Fig. 6. In the top panel, the system is shown in the cubic phase, but below the Burns temperature. The white squares represent non-polar

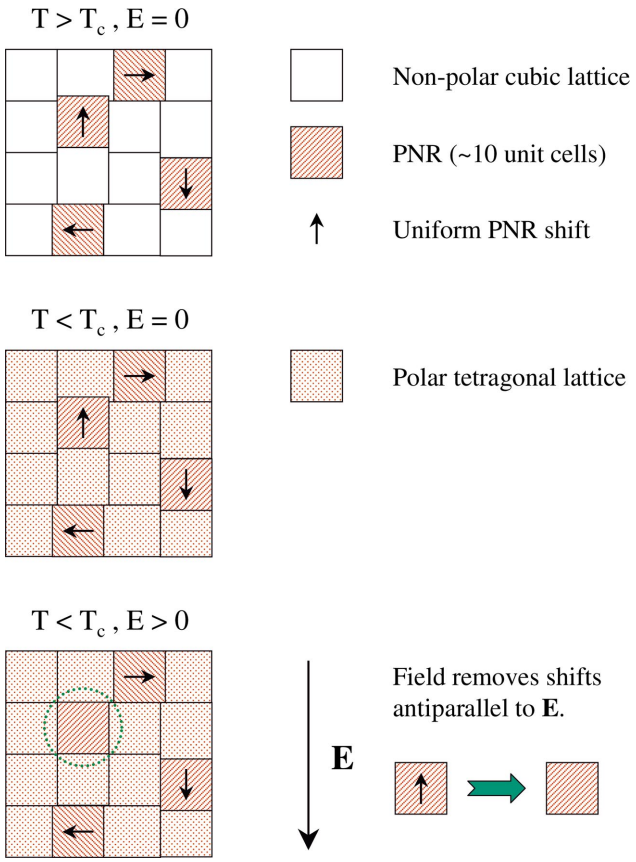

FIG. 6. (Color) Top panel: Phase-shifted PNR embedded in a non-polar cubic lattice for $T_d > T > T_c$. Middle panel: Below T_c the lattice achieves a polarization of its own, but the phase shift remains. Bottom panel: An applied electric field removes shifts along **E**, while preserving those that are orthogonal.

regions of the lattice (note that these are not individual unit cells), while the PNR are shown as hatched red regions corresponding to something of the order of 10 unit cells, and are slightly displaced in different directions relative to the cubic lattice. The arrows represent the direction and size of the uniform shift, which occurs in the direction of the PNR polarization. In the tetragonal phase $T < T_c$ the lattice develops its own polarization, which is indicated by the dotted red shading, while the uniform shift of the PNR remains intact (see the upper left panel of Fig. 4). In fact, a very recent study of the domain structure of PMN-20%PT using piezoresponse force microscopy by Shvartsman and Kholkin strongly supports such a picture of PNR embedded in micron-sized ferroelectric domains.[19] Then, under an external electric field we speculate that PNR shifts antiparallel to **E** are removed (or reduced), thereby reducing the local disorder, and in turn suppressing the diffuse scattering. At the same time, PNR shifts orthogonal to **E** are unaffected, and hence the corresponding diffuse scattering is unchanged (see lower left panel of Fig. 4).

It is difficult to quantify precisely how much of the diffuse scattering near the (300) reciprocal lattice position remains. Thus we can only speculate that shifts parallel to **E** are affected less (if at all) than those antiparallel to **E**. This would seem a reasonable idea in that it should be harder to increase the shift than it is to remove it. In this context, it is interesting to note that recent NMR work by Blinc *et al.* shows that ~50% of the PMN crystal they studied remained in the "glassy matrix state" in the presence of an applied field $E = 3$ kV/cm $> E_c = 1.7$ kV/cm below $T_c = 210$ K.[20] This result is consistent with our findings on PZN-8%PT, but in direct contradiction with those of Fujishiro *et al.*

The lower right panel of Fig. 4 indicates that the diffuse scattering near (003) is unaffected by an external field at 500 K. This is because there is no energetic incentive for the PNR to move in the cubic phase, at least not for moderate field strengths, which can be understood if one assumes that the PNR are strongly pinned to the underlying chemical short-range order. It has been argued that specific local cation configurations generate local fields, h_{loc}, that make the Pb ions they surround unstable with respect to a specific displacement. In such regions h_{loc} tends to be small and homogeneous. In a disordered matrix h_{loc} varies more from Pb site to Pb site, interfering with correlated Pb-displacements.[21] Below T_c this situation changes because the polar tetragonal lattice produces an extremely large internal dipole field that can affect the PNR, making them more susceptible to the influence of an external field.

Two high q-resolution studies in zero field have since been performed by Gehring *et al.* on PMN-10%PT, and Xu *et al.* on PMN-20%PT and PMN-27%PT.[14,22] These studies have examined the low-temperature phase in the PMN-xPT system, and document the existence of phase X up to $PbTiO_3$ concentrations as high as 20%, whereas the 27% sample finally exhibits the expected rhombohedral phase. These results are noteworthy because the stability of this new phase X against the formation of a global rhombohedral polar phase at temperatures below T_c can also be understood in terms of the phase-shifted PNR model. The latter study by Xu *et al.* in particular demonstrates that phase X is both undistorted and rhombohedrally polarized.

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