

# Persistence and memory of polar nanoregions in a ferroelectric relaxor under an electric field

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The response of polar nanoregions (PNR) in the ferroelectric relaxor  $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}]_3\text{O}_3$  subject to a [111]-oriented electric field has been studied by neutron diffuse scattering. Contrary to classical expectations, the diffuse scattering associated with the PNR persists, and is even partially enhanced, after field cooling. The effect of the external electric field is retained by the PNR after the field is removed. The “memory” of the applied field reappears even after heating the system above the Curie temperature  $T_C$  and cooling in zero field.

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Relaxor and ferroelectric relaxor materials have garnered enormous attention in the materials science and condensed matter physics communities due to their record-setting dielectric and piezoelectric properties.<sup>1</sup> They have supplanted lead zirconate (PZT) ceramics as the basis of state-of-the-art piezoelectric sensors and actuators that convert between mechanical and electrical forms of energy<sup>2</sup> and show potential as ferroelectric nonvolatile memories.<sup>3</sup> Compared to classic ferroelectrics, a unique property of these materials is the appearance of nanometer-sized regions having a local, randomly oriented polarization at the Burns temperature  $T_d$ ,<sup>4</sup> which is a few hundred degrees above  $T_m$ , the temperature where the dielectric permittivity reaches a maximum. These polar nanoregions (PNR) act like precursors of the spontaneous polarization in the low-temperature phase and are believed to play a key role in the unusual relaxor behavior.<sup>5</sup> Several theoretical models based on random fields in a dipole glass<sup>6,7</sup> have been proposed to explain the properties of the PNR. The PNR have been imaged directly with high-resolution piezoresponse force microscopy,<sup>8,9</sup> while extensive studies have been performed using both neutron<sup>10–15</sup> and x-ray<sup>16,17</sup> diffuse scattering techniques. These scattering measurements probe intensities in reciprocal space, which are Fourier transforms of real space structures, and provide valuable information about the magnitudes and orientations of the polarizations of the PNR, their dynamic properties, and the sizes and shapes of the PNR.

There are many unsolved fundamental questions concerning the PNR. Do they facilitate the ferroelectric phase transition of the system or do they impede it? Are the PNR contributing to the high piezoelectric response? In studies of ferroelectrics, an external field is often applied to monitor how the system responds. Yet few studies have examined the PNR response to an external field. Previous studies<sup>18,19</sup> have shown that the neutron diffuse scattering measured in directions transverse to the scattering vector can be partially suppressed in relaxor systems by an electric field. In particular, the anisotropic response of the diffuse scattering described in Ref. 19 suggests that those PNR having “properly oriented” polarizations could be forced to “melt” into the surrounding polar environment with the assistance of an external field, thereby producing a more “microscopically uniform” polar state.

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_3\text{O}_3$  (PZN) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_3\text{O}_3$  (PMN)

are prototypical lead perovskite relaxors with very similar dynamic and structural properties.<sup>20</sup> When mixed with  $\text{PbTiO}_3$  (PT) to form solid solutions, the relaxor properties of PZN and PMN are gradually suppressed, and a low-temperature ferroelectric phase is stabilized. Yet at low PT doping, PZN- $x$ PT and PMN- $x$ PT still exhibit frequency-dependent broad dielectric responses indicative of relaxor behavior in these systems. In addition, the reciprocal-space geometries of the diffuse scattering observed in zero-field-cooled (ZFC) PZN- $x$ PT and PMN- $x$ PT samples, for (small)  $x$  on the rhombohedral side of the PT phase diagram,<sup>21</sup> are almost identical,<sup>12,16,22</sup> and display similar temperature dependences<sup>20,22,23</sup> when scaled to the Curie temperature  $T_C$ . PT doping is especially important for applications of these materials because it enhances the piezoelectric property, which reaches maximum at the morphotropic phase boundary (MPB)<sup>21</sup> ( $x \approx 8\%$  for PZN- $x$ PT). We have therefore chosen PZN-8%PT to study how the PNR react to an external electric field. In zero field, PZN-8%PT transforms from cubic to tetragonal then rhombohedral<sup>24</sup> phases upon cooling. Because of the  $\langle 111 \rangle$  type polarizations associated with the rhombohedral ground state at low temperatures, we chose to investigate the effect of an electric field applied along the [111] direction. The lattice parameter in the cubic phase is  $a = 4.045 \text{ \AA}$ . Our experimental measurements are then described in terms of reciprocal lattice units (rlu) where  $1 \text{ rlu} = a^* = 2\pi/a = 1.553 \text{ \AA}^{-1}$ . Contrary to classical expectations, we find that the diffuse scattering does not diminish with the application of an external electric field. Instead, after field cooling, only a part of the diffuse scattering is suppressed in reciprocal space, while another part is markedly enhanced. We also observed interesting “memory” behavior in which the effects of an external field remain after the removal of the field, vanish above  $T_C \sim 450 \text{ K}$ , and then reappear after zero-field cooling below  $T_C$ .

The PZN-8%PT single crystal used in this study was provided by TRS ceramics.<sup>25</sup> The crystal is rectangular in shape, having dimensions  $5 \times 5 \times 3 \text{ mm}^3$  with (111),  $(\bar{2}11)$ , and  $(0\bar{1}1)$  surfaces. The Cr/Au electrodes were sputtered onto the top and bottom (111) crystal surfaces. The neutron diffuse scattering measurements were performed with the BT9 triple-axis spectrometer located at the NIST center for Neutron Research. The measurements were made using a fixed

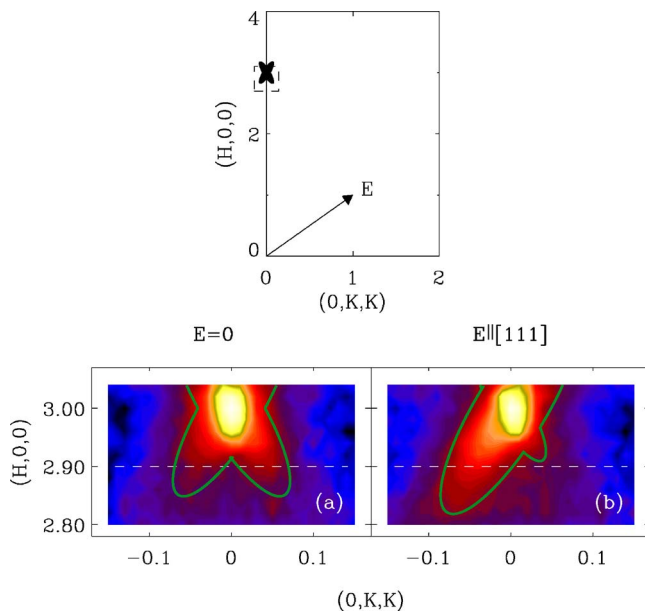


FIG. 1. (Color online) The top frame is a schematic of the (HKK) reciprocal scattering plane, in which neutron diffuse scattering measurements were performed close to the (300) Bragg peak. The electric field was oriented along [111] as shown by the arrow. The bottom frames show data measured at  $T=300$  K after the sample was (a) zero-field cooled (ZFC), and (b) field cooled (FC) with  $E=2$  kV/cm along [111] through  $T_C$ . The dashed lines indicate the location of the cuts at  $(2.9, K, K)$ , shown later in Fig. 2. The solid green (gray) lines are guides to the eye to help emphasize the symmetric (a) and asymmetric (b) “butterfly” shapes of the diffuse scattering.

incident neutron energy  $E_i$  of 14.7 meV, obtained from the (002) reflection of a highly oriented pyrolytic graphitic (HOPG) monochromator, horizontal beam collimations of  $40' - 40' - 40' - 80'$ , and the (002) reflection of an HOPG analyzer to fix the energy of the scattered neutron beam. The sample was oriented with the  $(0\bar{1}1)$  surface facing vertically. The scattering plane is therefore the (HKK) plane, which is defined by the two primary vectors [100] and [011]. The [111] electric field direction lies in the horizontal scattering plane.

Ideally, diffuse scattering intensities should be measured around different  $\{111\}$  peaks to gauge the net effect of a [111]-oriented electric field. However, the neutron diffuse scattering is very weak near  $\{111\}$  Bragg peaks due to a small neutron-scattering structure factor.<sup>13</sup> Instead, our measurements were performed near the (300) Bragg peak, where the diffuse scattering is strong, and the Bragg peak intensity is weak (see Fig. 1). Because of limitations on the maximum achievable scattering angle, we were only able to measure the lower half ( $H \leq 3$ ) of the butterfly pattern. The data obtained at  $T=300$  K ( $< T_C \approx 440$  K in zero field) are shown in the bottom frame of Fig. 1. When the crystal is zero-field cooled (ZFC), the diffuse scattering pattern is symmetric about the [100] axis, and forms the butterfly shape with “wings” of equal intensity on each side shown in Fig. 1(a). This pattern is consistent with the three-dimensional diffuse scattering distribution consisting of  $\langle 110 \rangle$  rod-type intensities

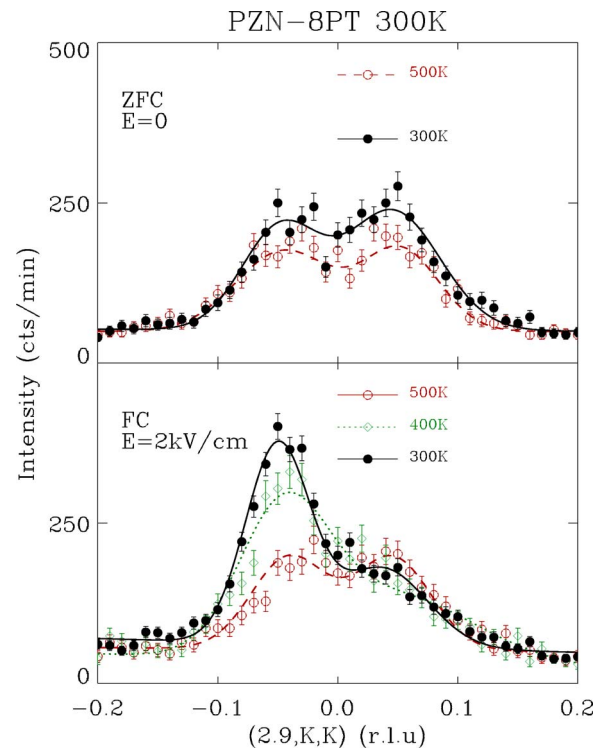


FIG. 2. (Color online) Linear scans performed at  $(2.9, K, K)$ , for the ZFC state (top panel), and the FC state (bottom panel), measured at different temperatures. The solid lines are fits to a sum of two Gaussian peaks.

reported in Ref. 22, where PNR with different polarizations contribute to different  $\langle 110 \rangle$  diffuse rods. Because of the non-zero out-of-plane wave vector resolution of our measurements, the tails of the  $\langle 110 \rangle$  rods are picked up when scanning away from the center of the Bragg peak in the (HKK) plane. This results in the butterfly-shaped pattern, which (neglecting the  $Q^2$  factor in the diffuse intensity) is symmetric about the wave vector  $\mathbf{Q}=(3, 0, 0)$ , as required by the crystal symmetry.

After zero-field cooling to  $T=300$  K (below  $T_C$ ) we applied a moderate electric field  $E=2$  kV/cm along the [111] direction. No change in the diffuse scattering was observed, suggesting that the PNR are robust against an external field in the ferroelectric phase. The sample was then heated to  $T=500$  K, and an electric field of  $E=2$  kV/cm along [111] was reapplied. No changes in the diffuse scattering were evident at 500 K as a result of the field. However, after field cooling through  $T_C$  ( $\approx 460$  K for  $E=2$  kV/cm) back to  $T=300$  K, the diffuse scattering developed a strong asymmetry about the [100] direction [Fig. 1(b)]. The left wing is clearly enhanced while the right one is suppressed. A more detailed look at the temperature dependence of the diffuse scattering is provided in Fig. 2. Here linear cuts through the diffuse scattering along  $(2.9, K, K)$  (dashed line in Fig. 1) are plotted. In the ZFC state, the symmetric double-peaked profiles indicate that the intensities from both wings increase equally with cooling. In the FC state, for which the [111]-oriented  $E$  field was initially applied at  $T=500$  K in the cubic paraelectric phase, it is only after cooling below  $T_C$  that the intensity of the left wing begins to increase, whereas the

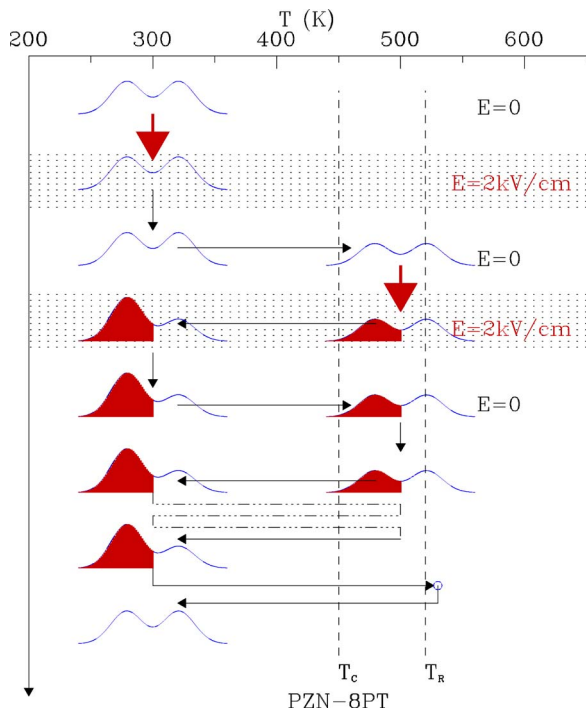


FIG. 3. (Color online) A schematic diagram showing the chronological change of the diffuse scattering, characterized by the two-peak profile of scans along  $(2.9, K, K)$ . The shaded peaks denote states where the PNR retains a “memory” of the electric field. The vertical dashed line at  $T_R$  indicates the temperature above which this field memory is lost. Red (thick) arrows and the dotted-shaded regions are used to denote when the external electric field was applied.

right wing intensity remains almost constant. At  $T=300$  K, the left wing intensity is clearly much higher than that measured in the ZFC state. Upon removal of the electric field at  $T=300$  K, the asymmetric diffuse pattern still remains, indicating that the PNR are “frozen” the FC state. This behavior is quite similar to that of a spin-glass system<sup>26</sup> where cooling through  $T_C$  in zero and nonzero magnetic fields leads to different final states, for which the difference is only observable below  $T_C$ .

Additional measurements reveal an extremely interesting memory effect. After field cooling below  $T_C$  and then removing the field (for which the leads across the sample were shorted), the sample was heated above  $T_C$  to  $T=500$  K and kept there for  $\geq 2$  h. Measurements around several lattice Bragg peaks confirmed that the system had been brought into the paraelectric cubic phase. At  $T > T_C$ , the diffuse scattering cuts along  $(2.9, K, K)$  consist of two symmetric peaks. However, the asymmetric line shape reappears after cooling back to  $T=300$  K. The effect of the previous electric field is still “remembered” after extensive thermal cycling through  $T_C$ . A schematic representation of the diffuse intensity line shapes measured at  $(2.9, K, K)$  is shown in Fig. 3 in chronological order. This memory effect is lost when the crystal is heated up to  $T=525$  K and then cooled in zero field. The highest temperature at which the compound can still retain the memory of a  $[111]$ -oriented electric field thus lies between 500 and 525 K, roughly 50 K greater than  $T_C$ , and is denoted

as  $T_R$ , the “repoling” temperature, in Fig. 3. Similar repoling effects have also been observed in other relaxor systems such as PLZT<sup>27</sup> and SBN.<sup>28</sup>

The persistence of the diffuse scattering in this relaxor compound in the presence of an external field is truly remarkable. Previous diffuse scattering measurements on PZN- $x$ PT systems<sup>14,22,29,30</sup> have implied the existence of PNR into the low-temperature ferroelectric phase upon zero-field cooling, while a similar persistence effect of the PNR under zero field was also observed with Raman measurements<sup>31–33</sup> in another relaxor system based on  $\text{KTaO}_3$  doped with Li or Nb. However, the nature of PNR in a external electric field-induced ferroelectric phase was still not clear. In a conventional ferroelectric compound, an external electric field promotes the establishment of a macroscopic ferroelectric phase via domain rotation. It was similarly expected that an external electric field would be able to affect the PNR such that they would tend to align with the field and merge into the surrounding ferroelectric polar lattice, resulting in a decrease of the diffuse scattering intensity. Our results clearly indicate otherwise. The enhancement of diffuse scattering demonstrates that a more uniform polar state has not been achieved. The low-temperature phase of PZN-8%PT consists of PNR embedded within a ferroelectric polar environment. This is a very interesting situation in which stable short-range polar order (the PNR) persists through a phase transition and coexists with long-range polar order. The application of an external electric field does not suppress the short-range polar order. Instead, the short-range polar order develops inside the long-range polar order and can even be “enhanced” by the field.

There have been theoretical arguments<sup>7</sup> based on random-field models suggesting that the low-temperature glassy phase of the relaxor may not be able to switch to the normal behavior of ferroelectrics through poling. Our results provide unambiguous confirmation of this thesis in that, even after cooling under a moderate external electric field, the relaxor PZN-8%PT still exhibits the strong neutron diffuse scattering characteristic of embedded PNR and thus does not transform into a uniform ferroelectric phase below  $T_C$ . Contrary to the naive belief that ferroelectric domains develop from the PNR, these unusual local polar nanoregions appear to be displaced, or “out-of-phase” with respect to the surrounding lattice. In addition to the already well-known “uniform-phase-shift” concept,<sup>11</sup> the PNR also have  $\langle 110 \rangle$  type polarizations<sup>22</sup> that are different from that of the surrounding  $\langle 111 \rangle$  type polar environment. Having polarizations different from the environment is probably one of the reasons they prevent the PNR from merging into the surrounding polar lattice. Neither the internal field due to the ordered polar lattice nor a moderate external field can dissolve the PNR. This polar nanostructure clearly distinguishes PZN-8%PT from classic ferroelectrics.

An interesting speculation that can be made from our results is that the diffuse scattering intensity is redistributed, or shifted from one wing of the butterfly to the other. This may suggest a redistribution of PNR with different polar orientations. With the formation of an ordered polar environment in PZN-8%PT below  $T_C$ , the internal electric field is already significant compared to the moderate field of 2 kV/cm ap-



plied, whereas the PNR are always robust, and persist and grow with cooling. It is therefore reasonable to conjecture that a moderate external electric field only affects the alignment of the ferroelectric domains in which the PNR are embedded, but not the PNR themselves directly. A field along the [111] direction helps the formation of ferroelectric domains along the field direction<sup>25</sup> and reduces the ambiguity of multiple  $\langle 111 \rangle$  domains, thus revealing the natural configuration of PNR in a [111] polarized environment at a macroscopic level. This model is purely speculative, and more data are required to confirm or refute it. However, its simplicity can be appreciated as a starting point for developing an understanding of PNR behavior.

After removal of the field, the effect on the crystal remains and so does the configuration of the PNR. However, we do not currently understand the reason for the memory effect, where heating to  $T_C < T < T_R$  does not “depole” the system. The memory of the electric field is only hidden and reappears again when zero-field cooled below  $T_C$ . Reference 28 proposes a model in which residue charges may be the key behind the repoling effect. In the residue charge model, PNR are one of the main sources that can help to stabilize these residue charges, when real ferroelectric domains do not exist above  $T_C$ . Therefore, it is very important to further understand the memory effect on the PNR. Considering magnetic systems with random fields, the effect of an external magnetic field can lead to very different behaviors, even a change of  $T_C$ , between FC and ZFC.<sup>34</sup> In those cases, non-equilibrium effects play an essential role. In relaxor systems, similar random-field models for a dipole glass can be con-

sidered. Based on our measurements of the structural changes,<sup>25</sup>  $T_C \sim 460$  K for  $E=2$  kV/cm was only slightly higher than  $T_C \sim 440$  K for  $E=0$  kV/cm. However, the electric field may also have effects on some other hidden degrees of freedom that do not fully dissolve at  $T_C$  and, therefore, are not directly observable in structural measurements. For example, one such possibility is that the effect of the electric field may be “remembered” by the lattice dynamics, i. e., atomic motions associated with the PNR. Even when the whole system goes into a paraelectric phase above  $T_C$ , the memory of the previous configuration could be embedded within the atomic motions in a metastable phase at  $T_C < T < T_R$ . The system may not be able to equilibrate over experimentally accessible time scales. These hidden effects could resurface again upon cooling and produce the spontaneous repoling. The results we have reported here also have significant implications in device applications, such as ferroelectric memories. An electric field can be used to embed information in the relaxor system. After removing the field, the information will only surface for  $T < T_C$ , but cannot be erased unless heating the system up to  $T > T_R$ , making the device useful for temperatures in the neighborhood of  $T_C$ , where the various relaxor properties are optimal.

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- <sup>1</sup>S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).  
<sup>2</sup>K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer, Dordrecht, 1996).  
<sup>3</sup>B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature* (London) **401**, 682 (1999).  
<sup>4</sup>G. Burns and F. H. Dacol, *Phys. Rev. B* **28**, 2527 (1983).  
<sup>5</sup>L. E. Cross, *Ferroelectrics* **76**, 241 (1987).  
<sup>6</sup>R. Pirc and R. Blinc, *Phys. Rev. B* **60**, 13470 (1999).  
<sup>7</sup>R. Fisch, *Phys. Rev. B* **67**, 094110 (2003).  
<sup>8</sup>P. Lehnen, W. Kleemann, T. Woike, and R. Pankrath, *Phys. Rev. B* **64**, 224109 (2001).  
<sup>9</sup>V. V. Shvartsman and A. L. Kholkin, *Phys. Rev. B* **69**, 014102 (2004).  
<sup>10</sup>S. B. Vakhruhev, A. A. Naberezhnov, N. M. Okuneva, and B. N. Savenko, *Phys. Solid State* **37**, 1993 (1995).  
<sup>11</sup>K. Hirota, Z.-G. Ye, S. Wakimoto, P. M. Gehring, and G. Shirane, *Phys. Rev. B* **65**, 104105 (2002).  
<sup>12</sup>G. Xu, G. Shirane, J. R. D. Copley, and P. M. Gehring, *Phys. Rev. B* **69**, 064112 (2004).  
<sup>13</sup>H. Hiraka, S.-H. Lee, P. M. Gehring, G. Xu, and G. Shirane, *Phys. Rev. B* **70**, 184105 (2004).  
<sup>14</sup>J. Hlinka, S. Kamba, J. Petzelt, J. Kulda, C. A. Randall, and S. J. Zhang, *J. Phys.: Condens. Matter* **15**, 4249 (2003).  
<sup>15</sup>S. N. Gvasaliya, S. G. Lushnikov, and B. Roessli, *Phys. Rev. B* **69**, 092105 (2004).  
<sup>16</sup>H. You and Q. M. Zhang, *Phys. Rev. Lett.* **79**, 3950 (1997).  
<sup>17</sup>N. Takesue, Y. Fujii, and H. You, *Phys. Rev. B* **64**, 184112 (2001).  
<sup>18</sup>S. B. Vakhruhev, A. A. Naberezhnov, N. M. Okuneva, and B. N. Savenko, *Phys. Solid State* **40**, 1728 (1998).  
<sup>19</sup>P. M. Gehring, K. Ohwada, and G. Shirane, *Phys. Rev. B* **70**, 014110 (2004).  
<sup>20</sup>C. Stock, R. J. Birgeneau, S. Wakimoto, J. S. Gardner, W. Chen, Z.-G. Ye, and G. Shirane, *Phys. Rev. B* **69**, 094104 (2004).  
<sup>21</sup>J. Kuwata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).  
<sup>22</sup>G. Xu, Z. Zhong, H. Hiraka, and G. Shirane, *Phys. Rev. B* **70**, 174109 (2004).  
<sup>23</sup>T. Y. Koo, P. M. Gehring, G. Shirane, V. Kiryukhin, S.-G. Lee, and S.-W. Cheong, *Phys. Rev. B* **65**, 144113 (2002).  
<sup>24</sup>B. Noheda, D. E. Cox, and G. Shirane, *Ferroelectrics* **267**, 147 (2002).  
<sup>25</sup>For this particular sample, the structural phase transitions were determined by monitoring the intensity and splitting of the (200), (022), and (111) Bragg peaks during the cooling (ZFC and FC) processes in our diffuse measurements. In zero field,  $T_C \approx 440$  K for the transition from cubic to tetragonal symmetry, and  $T_{C2} \approx 340$  K for the transition from tetragonal to rhombohedral symmetry. For  $E=2$  kV/cm oriented along the [111] direction,  $T_C \approx 460$  K.  $T_{C2} \approx 340$  K does not change much under

- field. The Bragg profile of the field-cooled (111) Bragg peak is also dominated by the intensity from domains polarized along the field.
- <sup>26</sup>K. H. Fisher and J. A. Hertz, *Spin Glasses* (Cambridge University Press, Cambridge, England, 1991).
- <sup>27</sup>F. Cordero, F. Craciun, A. Franco, D. Piazza, and C. Galassi, *Phys. Rev. Lett.* **93**, 097601 (2004).
- <sup>28</sup>T. Granzow, T. Woike, M. Wöhlecke, M. Imlau, and W. Kleemann, *Phys. Rev. Lett.* **89**, 127601 (2002).
- <sup>29</sup>D. La-Orautapong, J. Toulouse, J. L. Robertson, and Z.-G. Ye, *Phys. Rev. B* **64**, 212101 (2001).
- <sup>30</sup>D. La-Orautapong, J. Toulouse, Z.-G. Ye, W. Chen, R. Erwin, and J. L. Robertson, *Phys. Rev. B* **67**, 134110 (2003).
- <sup>31</sup>J. Toulouse, P. DiAntonio, B. E. Vugmeister, X. M. Wang, and L. A. Knauss, *Phys. Rev. Lett.* **68**, 232 (1992).
- <sup>32</sup>B. E. Vugmeister, P. DiAntonio, and J. Toulouse, *Phys. Rev. Lett.* **75**, 1646 (1995).
- <sup>33</sup>P. DiAntonio, B. E. Vugmeister, J. Toulouse, and L. A. Boatner, *Phys. Rev. B* **47**, 5629 (1993).
- <sup>34</sup>R. J. Birgeneau, *J. Magn. Magn. Mater.* **177**, 1 (1998).