Probing local polar structures in PZN-xPT and PMN-xPT relaxor ferroelectrics with neutron and x-ray scattering

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Abstract.
“Polar nano-regions” (PNR) are nanometer sized local polar structures found in relaxor ferroelectric materials. They play key roles in understanding many relaxor properties. Here I will discuss some of our recent work using neutron scattering and x-ray diffraction to probe the properties of the PNR in two prototypical lead based perovskite relaxor systems Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN), Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), and their solid solutions with PbTiO$_3$ (PT). The local atomic structures in the PNR are rather complicated, consisting of polarizations/atomic shifts along both $h110i$ and $h100i$ directions. These different (components of) local polarizations respond differently to external electric fields along $[001]$ or $[111]$ directions; and are associated with phonons of different polarizations (T1 and T2 phonon modes). Our work also indicates that the PNR are dynamic at high temperatures well above the Curie temperature $T_C$, and gradually freeze with cooling. A significant portion of the PNR has already become static before a long-range polar order can be established in the bulk. The short-range polar order in the PNR is quite robust, and persists when the system is cooled (with or without external electric field) into the ferroelectric phase. Because of the frustration between charge neutrality and lattice strain in relaxor systems, the low temperature phase of these relaxor materials usually does not have perfect long-range order, but rather a phase where both short-range and long-range polar orders coexist and compete.

1. Introduction
Relaxor ferroelectrics differ from conventional ferroelectrics by having highly frequency dependent dielectric response ($\varepsilon$) with a broad maximum in temperature. In recent years, lead based perovskite relaxors taking the form of Pb(B’B”)O$_3$ have attracted a lot of attention because of their unusual dielectric and piezoelectric response and great potential for industrial applications [1, 2, 3]. Although the origin of many relaxor properties are still not entirely understood, it is widely believed that the composition disorder on the B-site plays key role in determining the bulk response [4, 5]. Here the B-site is normally occupied by two cations with different valencies. For example, in the two prototypical lead based perovskite relaxors Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN) and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), Zn$^{2+}$/Mg$^{2+}$ and Nb$^{5+}$ take a 1 : 2 ratio on B-site to achieve an average valence of 4+ for charge conservation. Charge neutrality would naturally lead to chemical order on the B-site, while this 1 : 2 type order is not favored by lattice strain. The frustration between the two makes these systems unique in
ferroelectric materials [6], and the resulting local charge imbalance due to the randomness of B-site occupancy creates local random fields, which is the key in understanding many relaxor properties [7, 8, 9, 10, 11].

In addition to the chemical disorder/short-range order, short-range polar order is also present in relaxor systems. The concept of “polar nano-regions” (PNR) was initially proposed by Burns and Dacol [12], to explain the deviation from linear behavior in their optical measurements from a series of relaxor systems including PZN and PMN. It was suggested that while the majority of the lattice still remain unpolarized, local polar clusters start to form at a temperature $T_d$, called the “Burns temperature”, which is typically a few hundred degrees above the Curie temperature $T_C$. The PNR are believed to be several nanometers in size, grow with cooling, and contribute to many important relaxor properties. For example, the large frequency dependency of the dielectric response can be naturally explained with the relaxation process of the PNR [4].

Diffuse scattering measurements probes how local atomic positions differ from the average crystal structures, and are therefore very sensitive to local inhomogeneities and short-range orders in solid materials. The PNR in lead based relaxors have been extensively studied by both x-ray [13, 14, 15] and neutron [16, 17, 18, 19, 20, 21, 22, 23, 24] diffuse scattering measurements, as well as other bulk probes including Raman and dielectric measurements [25, 26], and high resolution piezoelectric force microscopy [27, 28]. It has been shown that the PNR not only compete with, but also can coexist with long-range polar orders in relaxor compounds [29, 30]. They do respond to external electric fields [31, 32, 29, 33], but cannot be fully suppressed. The low temperature phase of these relaxor ferroelectric materials is actually a very special phase where long-range (the bulk) and short-range (the PNR) polar orders coexist [30], and accompanied by large lattice strains induced by the PNR [18, 34, 30].

In this paper, I will review our work on the polar nanoregions in PMN, PZN, and their solid solutions with PbTiO$_3$ (PT) with neutron and x-ray scattering over the last decade. The local atomic structures in the polar nano-regions are complicated, consisting of polarizations both along the $\langle100\rangle$ and $\langle110\rangle$ directions [35]. They respond differently to external electric fields along different directions. The PNR also start with being partially dynamic at high temperature and gradually freeze with cooling - the process can be probed with neutron spin-echo measurements which has a much better energy resolution than conventional neutron scattering techniques [36, 35]. Finally, I will discuss how the PNR interact with the bulk through their coupling to phonon modes, and its implications on various bulk properties.

2. Structures, polarizations of the PNR and their electric field response

2.1. $\langle110\rangle$ polarizations and the “pancake model”

With small PT doping, the solid solutions of PMN-xPT and PZN-xPT still exhibit relaxor properties [37, 38], and diffuse scattering from these systems are very similar in general [15, 39]. The diffuse scattering intensities appear above $T_C$, and increase monotonically with cooling. In order to obtain information on the structure, shape, and polarizations of the PNR, one needs to measure the distribution of diffuse scattering intensities in the reciprocal space. An example of these measurements is shown in Fig. 1. Here a mesh scan from neutron diffuse scattering measurements taken at 200 K from a single crystal PMN, around the $\langle100\rangle$ Bragg peak in the (HOL) plane is plotted. The intensity is highly anisotropic in the reciprocal space, taking a “butterfly” shape in the (HOL) plane. A more detailed mapping of the three-dimensional distribution of diffuse scattering intensities from single crystals of PZN-xPT for x=0, 4.5% and 8% has been performed with high energy x-ray diffraction [15]. It was found that the diffuse scattering is dominated by rod type intensities along various $\langle110\rangle$ directions. Although there are totally six different $\langle110\rangle$ rods, they do not always show up with the same intensity across different Bragg peaks. A sketch of the intensity distribution in the 3-D reciprocal space is plotted in Fig. 2.
Since rod type intensities in reciprocal space correspond to planar type correlations/structures in real space, a model (the “pancake” model) is proposed that PNR must take a planar shape in real space [15]. In this model, there are six possible orientations/polarizations of PNR, with \{110\} type polarizations, correlated in \{110\} planes, that give rise to \{110\} diffuse rods (see Fig. 3). The in-plane and out-of-plane correlation lengths (or, the diameter and thickness of the “pancake” PNR, respectively) can be estimated from the line widths of diffuse scattering perpendicular and along the intensity rod directions. A rough estimate will give a in-plane correlation length of 10 to 20 nm (20 to 40 lattice spacings) while the out-of-plane correlation length is about four times smaller [24, 15].

More x-ray and neutron diffuse scattering measurements have confirmed that the “butter-fly”-shaped diffuse scattering is dominant in most PMN-xPT and PZN-xPT samples [13, 15, 39, 40] for small \(x\). The “butter-fly” diffuse are results of (short-range) ordered \{110\} type polarizations, extending in the perpendicular \{110\} directions in reciprocal space - similar to T2 phonon modes in these perovskite systems, which are the transverse phonon modes with \{110\} polarizations propagating along the perpendicular \{110\} directions. We therefore also refer to the “butter-fly” diffuse as the “T2-diuse”. In fact, later in the paper, I will show that the “butter-fly” diffuse scattering can interact strongly with the T2 phonon modes in relaxors.

When more PbTiO\(_3\) is added into the solid solution, the relaxor properties gradually disappear and the system becomes more of a conventional ferroelectric. Diffuse scattering studies for systems on the ferroelectric side of the PT-doping phase diagram have shown that the “butter-fly” diffuse completely disappears [41, 39], indicating that no PNR exists in the ferroelectric side of the phase diagram. There are, however, arguments suggesting that the “butter-fly” diffuse scatterings from relaxors are in fact Huang-scattering due to defects and strains in the system. If the “butter-fly” diffuse scattering intensities were only strain related, their intensities should scale with \(Q^2 |F(G)|^2\) where \(Q\) is the measurement wave-vector and \(|F(G)|^2\) is the lattice structure factor that gives the Bragg peak intensity at the reflection \(G\) near \(Q\). This is clearly not the
Figure 3. (Color online) PNR in the real space and their contributions to the diffuse scattering in the reciprocal space. A “pancake” shaped PNR in real space corresponds to rod type diffuse scattering in reciprocal space. From (a) to (f), we show PNR with in-plane polarizations along the [011], [101], [110], [011], [101], and [110] directions, correlated in the (011), (101), (110), (011), (101), and (110) planes, and contributing to the diffuse rods along [011], [101], [110], [011], [101], and [110] directions, respectively (see Ref.[15]).

case, shown by measurements on the relative diffuse scattering intensities across various Bragg peaks [18, 20, 30]. In fact, the atomic shifts in the PNR that contribute to the “butter-fly” diffuse scattering intensities can always be decomposed into two components, one is a relative shift of various atoms in the unit cell without movement of the center-of-mass – this is optic type component and contribute to local polar moments; another is a “uniform phase shift” which is the movement of all atoms in the unit cell together, corresponding to the acoustic type component that contribute to strain [18, 30].

The “butter-fly” diffuse scattering from the PNR also respond to external electric fields in a very unusual manner. An external electric field along the [001] direction applied to single crystal PMN-xPT [42] and PZN-xPT [35] samples has been shown to have virtually no effect on the “butter-fly” diffuse scattering pattern. On the other hand, an external field along the [111] direction can induce dramatic changes on the diffuse pattern. Naively one would expect an external field along [111] direction to stabilize the long-range polar order in the low temperature rhombohedral (R) phase, and suppress the diffuse scattering intensity from the PNR. Our neutron [29] and x-ray [33] diffuse scattering measurements indicate otherwise. In PZN-xPT single crystal samples, the “butter-fly” diffuse scattering does not simply disappear with field cooling (E along [111]). Instead, a “redistribution” of diffuse scattering intensities across different ⟨110⟩ rods has been observed [29, 33] (see Fig. 4). The portion of diffuse scattering coming from
PNR with polarizations perpendicular to the external [111] field has been enhanced, while the part from PNR with polarizations not perpendicular to the external field has been partially suppressed. The overall diffuse scattering intensity appears to be conserved (compared to that measured under the zero-field-cooled condition).

Figure 4. (Color online) Sketch of the three-dimensional diffuse scattering distribution from single crystal PZN. They are plotted in the 3-D reciprocal space around (100), (110), (111), (010), and (001) reciprocal lattice points for (a) E=0, and (b) E along [111]. In (b), the diffuse rods along the [110], [101], and [011] directions are enhanced, while the diffuse rods along the [110], [101], and [011] are suppressed (see Ref. [33]).

Figure 5. (Color online) A schematic showing the PNR configurations in a relaxor system in (a) the paraelectric phase, (b) ZFC into the ferroelectric phase, and (c) FC into the ferroelectric phase. The large arrows indicate the polarization of the ferroelectric domains separated by domain walls (solid lines). The small squares represent the PNR (see Ref. [30]).

These results can be understood in a simple picture. In the paraelectric high temperature phase, there is no long-range ferroelectric domains, and PNR with different (110) polarizations are equivalent under the cubic symmetry. When the system enters the low temperature phase, long-range polar order is established and ferroelectric domains with (111) polarizations are formed. Within these domains, the symmetry is lowered to R, and the different (110) directions are not equivalent any more. If within a certain ferroelectric domain, the PNR would prefer to exist in a configuration where their polarizations are perpendicular to that of the domain, all our previous results can be explained easily. As shown in Fig. 5 (b), under ZFC, after multi-domain averaging, in the crystal there is no macroscopic preferred (110) polarization of the PNR, resulting in the symmetric “butterfly” diffuse scattering shown in Figs. 1, 2. However, with FC, the volume of the ferroelectric domain polarized along the field [111] direction is greatly enhanced [see Fig. 5 (c)], and our measurements thus provide direct information on how the PNR reside in a [111] polarized ferroelectric lattice - they tend to have polarizations perpendicular to that of their surrounding lattice.

The case for pure PMN is an exception. Once an external electric field along [111] direction is applied, in addition to the redistribution of diffuse scattering intensities between different (110) directions, there is also an overall suppression of the diffuse scattering by the field [43]. In the mean time, Bragg peak intensities increase, indicating an enhancement of long-range order in the system. Note that in pure PMN, no long-range polar order is established without external field and therefore no macroscopic ferroelectric domains exist at low temperature. However,
there could be polar-orders developing in the system at low temperature in the mesoscopic range (e.g. \( \sim 1 \mu m \)) that provides local \((111)\) polarized lattice environment for the PNR. With an external electric field, the re-arrangements of these mesoscopic polar lattice can give rise to the redistribution of PNR and therefore diffuse scattering. On the other hand, not having a long-range ferroelectric order seems to also make the short-range polar order in the PNR less stable and more sensitive to external fields.

This situation where the two competing orders can co-exist, and having the long-range order helps stabilizing the short-range polar order, is quite unusual. In addition, as the temperature decreases, both orders will develop (with the exception of pure PMN) - the long-range polar order develops as evidenced by the increase of rhombohedral distortion with cooling; and the short-range order develops shown by the increase of diffuse scattering intensities. The robustness of these local polar orders within the long-range polarized lattice is yet another indication of charge-lattice frustration in relaxor systems.

2.2. \((001)\) polarizations and the “T1” diffuse

As mentioned previously in the article, the “butter-fly” diffuse scattering is barely affected by an external field along the \([001]\) direction. However, there is evidence suggesting possible diffuse scattering components away from the \((110)\) rods in the “butter-fly” diffuse. For instance, neutron diffuse scattering experiments [32] on a single crystal of PZN-8\%PT show that the diffuse scattering measured along \((H03)\) is strongly suppressed by an external \([001]\) field, whereas that measured along \((30L)\) remains unaffected. This effect has been confirmed later in our measurements on PZN-4.5\%PT [35] [see panels (c) and (d) of Fig. 6] and cannot be explained by a simple redistribution of the T2-diffuse scattering.

From Fig. 6, we notice that this extra component of diffuse scattering that can respond to an external field along \([001]\) direction is measured at \(q\) along \([001]\) or \([100]\) away from the Bragg peak. Detailed analysis [35] indicates that the local atomic shifts contributing to this extra component are also along the \((001)\) directions perpendicular to \(q\). Considering its similarities to the T1 phonon modes, where transverse phonons with \((001)\) type polarizations propagate along the perpendicular \((001)\) directions, we therefore refer to this component of diffuse scattering as the “T1” diffuse. The “T1” component of the diffuse scattering follows similar temperature trend as the “butterfly” diffuse, but is considerably weaker in intensity, and can only be clearly identified by examining the change of diffuse scattering intensity when an external field along \([001]\) direction is applied. The structure factors for the T1-diffuse also differ from those of the “butterfly” diffuse, yet one can still decompose the atomic shifts (along \((001)\) directions) that contribute to the T1-diffuse into an acoustic strain component plus an optic polar component [35].

Neutron pair-density-function (PDF) measurements on PMN [45] suggest that the average local Pb displacements are along the \((111)\) directions. There is no inconsistency between the PDF measurements and the diffuse scattering measurements. The PDF measurements probes the average atomic positions, while the diffuse scattering measurements probe the (short-range) order of various atomic displacements. An local environment with Pb shifted along \((111)\) directions but only the \((001)\) and \((110)\) components of the shifts are short-range ordered (with different correlations), will be able to explain the experimental data from different techniques.

Overall, the local structure in these relaxor compounds are complicated. Our diffuse scattering measurements have found clear contributions from at least two type of (short-range ordered) local atomic displacements. They have similar temperature dependence, and both have strain/polar components; while they respond quite differently to external electric fields.
Figure 6. (Color online) (a) Schematic diagram of the neutron scattering measurements made in the (HOL) scattering plane with an electric field applied along [111]. The large (red) and small (blue) ellipses reflect how the “butter-fly” diffuse scattering intensity is redistributed after the sample is field cooled (FC). (b) Measurements of the diffuse scattering intensity near (002) along the dashed arrow shown in panel (a) at 200 K (from Ref. [44]). Scans were made along (H,0,2.1) because they intercept both wings of the butter-fly sufficiently far from (002) that significant contamination from unwanted Bragg peak scattering can be avoided, thus making it possible to monitor how intensities of the two wings change with field and temperature. Open circles represent zero-field cooled (ZFC) data and closed circles represent FC data. (c) Same schematic diagram as in panel (a) except with the electric field applied along [001]. Dashed lines denote linear q-scans performed across Bragg peak positions. (d) Linear q-scans at 200 K along [100] measured across (003) [see scan (i) in panel (c)]. Error bars in (b) and (d) represent the square root of the number of counts. The figure is taken from Ref. [35].

3. Dynamic PNR and interaction with phonons

3.1. Dynamic PNR

One important question on the PNR is whether they have a static or dynamic origin. Most of our previous work has only been focused on the static structures of the PNR using elastic diffuse scattering, or, at least, “quasi-elastic”. Nevertheless, our neutron diffuse scattering measurements are limited by the energy resolution of the instruments, which could range between
0.1 meV to ~ 1 meV depending on the instrument set-up and the type of instrument used. The x-ray diffuse scattering measurements, on the other hand, cannot really distinguish between the static and dynamic nature of the diffuse scattering because of its very coarse energy resolution.

![Figure 7](image-url) (Color online) Neutron spin-echo data from PMN for different temperatures (see Ref. [36]).

![Figure 8](image-url) (Color online) Neutron spin-echo data from PZN-4.5%PT for different temperatures and electric field effect (see Ref. [35]).

The neutron spin-echo (NSE) spectroscopy is ideal for this purpose [46]. In principle, NSE measurements probe how a certain mode decays with time. In our case, we can use NSE to probe how long-lived the diffuse scattering from the PNR is. Figs. 7 and 8 show NSE measurements on single crystals of PMN and PZN-4.5%PT at \( Q = (0.95, -0.05, 0) \) [36] and \( (0.05, 0, 1) \) [35], respectively. The measurements at \( Q = (0.95, -0.05, 0) \) probe mostly the T2-diuse (butterfly-diuse), while those at \( (0.05, 0, 1) \) have a larger contribution from the T1-diuse. Clearly, these results suggest that both the T1 and T2 diffuse scattering intensities have a significant dynamic portion at high temperatures. The lifetime of the dynamic portion can also be extracted from the data. For example, in PZN-4.5%PT, at high temperature (550 K), the lifetime of the dynamic portion of the PNR is about 0.004 ns, corresponding to an energy width (half width at half maximum HWHM) of 0.16 meV. With cooling, not only the dynamic/static ratio decreases, but also the lifetime of the dynamic portion increases. At 200 K in PZN-4.5%PT, the lifetime of the dynamic portion increases to about 0.01 ns with an energy width HWHM ~ 0.007 meV [35]. The situation is very similar in PMN [36]. These results indicate that the PNR gradually freezes with cooling, and become mostly static at low enough temperatures.

### 3.2. PNR interacting with phonons

There have long been suggestions that the diffuse scattering from PNR can couple to the transverse optic (TO) [47, 48] and transverse acoustic (TA) [49, 21, 50] phonon modes in relaxor ferroelectrics. Our neutron scattering measurements show that this coupling is strongest for PNR and phonons with the same polarizations. For instance, the “butterfly” diffuse (T2-diuse) couples strongly to the TA phonon mode with the same \((110)\) polarizations (T2 mode) [44], while the T1-diuse couples to the T1 phonon mode [51].
The implications of the interaction between the PNR and phonons in the bulk goes beyond the coupling itself. Here we find that the PNR are related to the softening of a particular phonon mode \[44\]. A soft phonon mode is usually associated with a phase instability, which is necessary for a system to have a high piezoelectric response \[52, 53, 54, 55, 56\]. Our results suggest that there might be some connections between the local polar structures (PNR) and the extraordinary bulk response in relaxor compounds.

4. Summary
Our neutron and x-ray scattering studies on PZN-xPT and PMN-xPT relaxor compounds have shown that these materials have complex local structures due to lattice-charge frustration. The local structures have both polar and strain characteristics. They are partially dynamic at high temperatures, gradually freeze with cooling, and can coexist with the long-range polar phase at low temperature. These local structures can also interact with the bulk through their coupling to phonons in the bulk material, which may be a key in understanding the extraordinary piezoelectric and electromechanical properties of these lead based perovskite relaxor systems.

5. acknowledgements
The work discussed in this article has been carried out with many collaborators. I would first like to give my special acknowledgment to Dr. Gen Shirane, who started our work on relaxor systems in the late 1990’s. I would also like to thank all other collaborators including: F. Bai, Y. Bing, H. Cao, W. Chen, K. H. Conlon, J. R. D. Copley, J. S. Gardner, P. M. Gehring, M. J. Gutmann, H. Hiraka, K. Hirota, S.-H. Lee, J.-F. Li, H. Luo, M. Matsuura, K. Ohwada, C. Stock, I. Swainson, D. Viehland, S. Wakimoto, T. R. Welberry, J. Wen, H. Woo, Z.-G. Ye, Z. Xu, X. Zhao, and Z. Zhong. Financial support from the U.S. Department of Energy under contract No. DE-AC02-98CH10886 is also gratefully acknowledged.

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