Diffuse scattering from the lead-based relaxor ferroelectric $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$

Antonio Cervellino,^{a,b,*} S. N. Gvasaliya,^{c,b} O. Zaharko,^b B. Roessli,^b G. M. Rotaru,^b R. A. Cowley,^d S. G. Lushnikov,^e T. A. Shaplygina^e and M. T. Fernandez-Diaz^f

^aSwiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland, ^bLaboratory for Neutron Scattering, PSI, CH-5232 Villigen, Switzerland, ^cLaboratory for Solid State Physics, ETH Hönggerberg, 8093 Zurich, Switzerland, ^dClarendon Laboratory, Department of Physics, Oxford University, Parks Road, Oxford OX1 3PU, England, ^eIoffe Physical Technical Institute, 194021 St Petersburg, Russia, and ^fInstitut Laue–Langevin, 156X, 38042 Grenoble Cedex, France. Correspondence e-mail: antonio.cervellino@psi.ch

The relaxor ferroelectric $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ was studied by single-crystal neutron and synchrotron X-ray diffraction, and its detailed atomic structure modelled in terms of static Pb displacements that lead to the formation of polar nanoregions. Similar to the other members of the Pb-based relaxor family like $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ or $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ the diffuse scattering in the $[H00]/[0K0]$ scattering plane has a butterfly shape around the $h00$ Bragg reflections and is orthogonal to the scattering vector for $hh0$ peaks. In the $[HH0]/[00L]$ plane the diffuse scattering is elongated along the $\langle 112 \rangle$ directions and is orthogonal to the scattering vector for hhh reflections. It is found that a model consisting of correlated Pb displacements along the $\langle 111 \rangle$ directions reproduces adequately the main features of the diffuse scattering in $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ when the correlation lengths between the Pb-ion displacement vectors are longest along the $\langle 111 \rangle$ and shortest along the $\langle 11\bar{2} \rangle$ and $\langle 1\bar{1}0 \rangle$ directions.

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1. Introduction

Cubic perovskites $AB'_x B''_{1-x}\text{O}_3$ with a random occupation of the B site form a special class of ferroelectrics. In these materials the dielectric permittivity has a maximum around T_{max} that is not associated with any structural phase transition. Because the maximum of the dielectric constant is broad in temperature and also depends on the frequency, these materials are called 'relaxor ferroelectrics'. $\text{Pb}B'_{1/3}B''_{2/3}\text{O}_3$ ($B' = \text{Zn}, \text{Mg}; B'' = \text{Nb}, \text{Ta}$) are typical relaxor ferroelectrics. To explain the broad maximum in the dielectric permittivity it was proposed by Smolenskii & Agranovskaya (1959) that fluctuations in the distribution of $B':B''$ ions lead to a coexistence of polar and nonpolar regions in these materials as the temperature is reduced. Later, Burns & Scott (1973) used the same approach to explain the temperature dependence of the refractive index, namely that polar regions of nanometre size form below a characteristic temperature, which for $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) is $T_d \simeq 620$ K.

Extensive studies of the phonons in relaxor ferroelectrics by inelastic neutron scattering were unable to identify the soft mode that together with the Lyddane–Sachs–Teller relationship would explain the temperature dependence of the dielectric permittivity. Recently, however, it was shown that a quasi-elastic mode appears below the Burns temperature in PMN, whose intensity increases with decreasing temperature and reaches a maximum at $T \simeq 380$ K (Gvasaliya, Lushnikov

et al., 2004; Hiraka *et al.*, 2004). The slow fluctuations associated with this scattering correspond to atomic motions correlated over a few unit cells only. In addition there is strictly elastic diffuse intensity in PMN which appears at $T \simeq 420$ K and indicates that static domains develop below that temperature (Gvasaliya *et al.*, 2005). The intensity of the diffuse scattering increases with decreasing temperature and saturates below $T \simeq 100$ K. These findings are in accord with a model of slowly fluctuating polar nanoregions (commonly named PNR) in relaxor ferroelectrics that freeze with decreasing temperature but do not undergo a phase transition to a long-range ferroelectric state owing to the random fields (Cowley *et al.*, 2009).

Because the size of the polar nanoregions does not exceed a few hundred ångströms, they give rise to the presence of diffuse scattering in both the X-ray and neutron spectra. The distribution of the diffuse scattering in reciprocal space has been investigated by many groups. Vakhrushev *et al.* (1995) found that the diffuse scattering in PMN is predominantly orthogonal to the scattering vector $\mathbf{Q}$ and that the intensity is weak near Bragg peaks with even parity ($2h\ 2k\ 2l$). Xu *et al.* (2004) investigated the distribution of diffuse scattering from $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ [(1-x)PZN-xPT] using X-ray scattering techniques and found that in the $(hk0)$ plane the diffuse intensity either consists of elongated streaks perpendicular to the scattering vector $\mathbf{Q}$ (e.g. around 110) or has the shape of a 'butterfly' (e.g. around 100). Although there

is still no complete understanding of all components of diffuse scattering in $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT), as discussed later, it has been recognized that its strongest component below the Burns temperature originates from correlated Pb-ion displacements (Welberry *et al.*, 2006). Correlated Pb displacements also constitute the polar nanoregions. However, neither the shape and size of the PNR in relaxor ferroelectrics nor the direction of the Pb displacements are fully understood. The displacement magnitude instead was obtained from powder diffraction measurements. For example, early powder neutron diffraction measurements from PMN by Bonneau *et al.* (1991) showed that Pb ions are displaced from the (0, 0, 0) position below $T \simeq 800$ K and that the magnitude of these displacements increases with decreasing temperature. At $T = 5$ K the Pb ions are displaced by ~ 0.36 Å along the $\langle 111 \rangle$ directions. The probability density function of Pb in PMN was determined (Chernyshev *et al.*, 1994; Vakhrushev & Okuneva, 2002) and it was found that, while at room temperature Pb is isotropically displaced, the Pb potential has a double-well shape at low temperature. Values of such magnitude can explain the strength of the main diffuse scattering component.

PMT is a typical relaxor ferroelectric. As for PMN the average crystal structure is cubic at all temperatures. The real part of the dielectric permittivity has a maximum at $T \simeq 170$ K at a frequency of $\nu = 10$ kHz. Powder neutron diffraction (Gvasaliya, Roessli *et al.*, 2004) has shown that the magnitude of the Pb displacements grows rapidly below the Burns temperature, which is ~ 570 K for PMT (Korshunov *et al.*, 1992). The Pb displacements give rise to neutron diffuse scattering, the temperature dependence of which correlates well with that of the atomic displacements. Because of the similarities existing between the physical properties of PMT and those of PMN and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PZN), we decided to investigate the detailed atomic structure by neutron and synchrotron X-ray scattering. The diffuse scattering of PMT in the $[H00]/[0K0]$ plane is orthogonal to the scattering vector for the $hh0$ Bragg reflections and has a butterfly shape near the $h00$ peaks. In the $[HH0]/[00L]$ plane the diffuse scattering of $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ is elongated along the $\langle 112 \rangle$ directions, which indicates that the motion of the Pb ions has a short correlation length along that direction.

In the following, $\mathbf{Q}$ is the momentum transfer vector and $Q = |\mathbf{Q}| = 4\pi \sin(\theta)/\lambda$, with 2θ the scattering angle and λ the incident wavelength. The reciprocal-lattice vectors are denoted by $\boldsymbol{\tau}$, and the relative momentum transfer vector by $\mathbf{q} = \mathbf{Q} - \boldsymbol{\tau}$.

2. Experimental results

2.1. Single-crystal neutron diffraction

We performed a high-resolution neutron single-crystal experiment on a PMT sample on D9 at ILL. The diffractometer is located on the hot source and allows access to Bragg reflections at large Q values. The short neutron wavelength of 0.513 Å, combined with the small crystal size ($1.6 \times 1.1 \times 0.8$ mm), also helped to minimize extinction problems. Bragg

intensities were collected at $T = 20$ and 300 K. At room temperature 632 reflections were measured up to $Q = 15.82$ Å⁻¹ and 612 ($Q \leq 19.45$ Å⁻¹) at $T = 20$ K, with the maximum Miller index 11. A symmetry test showed that the crystal symmetry is cubic at both temperatures, $R_{\text{eq}} = 3.35\%$ for the 300 K data set and $R_{\text{eq}} = 5.92\%$ at 20 K.

The cubic symmetry describes the average periodic structure only. Atomic displacements break this symmetry locally; however the global symmetry is retained through the formation of domains, so PMT must be described as a perturbed periodic structure. Whereas the aim of this paper is to clarify the nature of the perturbation, the diffraction data contain information about the size of the displacements that will be used as a constraint for the analysis of the diffuse scattering patterns. To analyse the atomic displacements we used the Patterson function $P(\mathbf{d})$, which is calculated through the Fourier transform of the observed Bragg intensities:

$$P(\mathbf{d}) = \sum_{\boldsymbol{\tau}} I_{\boldsymbol{\tau}} \cos(\boldsymbol{\tau} \cdot \mathbf{d}) = \frac{1}{v} \int d^3\mathbf{r} \rho(\mathbf{r}) \rho(\mathbf{d} + \mathbf{r}), \quad (1)$$

where $\boldsymbol{\tau}$ are the Bragg reflections, $I_{\boldsymbol{\tau}}$ their observed intensities, $\rho(\mathbf{r})$ the scattering density and v the unit-cell volume. In order to properly set the zero of $P(\mathbf{d})$ the value of I_{000} is needed; this value could be calculated after the structure refinement described below and then added to the list of the observed intensities. Equation (1) shows that the Patterson function is the self-convolution of the scattering density, so the position of the peaks in $P(\mathbf{d})$ gives direct access to the interatomic distances $\mathbf{d}$ (Giacovazzo *et al.*, 1992). Cuts through the Patterson maps across the main interatomic peaks are shown in Fig. 1. The most pronounced characteristic in the cut through the Patterson map shown in Fig. 1 is visible in the Pb–B interatomic peaks. At room temperature the Pb–B average length is ~ 2.5 Å with a distribution of ~ 0.3 Å. At low temperature the Pb–B length shows a maximum away from the distance in the cubic perovskite structure. As the B–O peaks do not show anything similar, we must attribute this to the displacements of the Pb atoms from their average position. At room temperature the Pb atoms lie in a spherical region about their nominal positions, while for $T = 20$ K the Pb

Figure 1
Linear cuts through the Patterson maps at 20 K (continuous line) and 300 K (dotted line) along the $\langle 011 \rangle$ (left) and $\langle 100 \rangle$ (right) directions. Endpoints in crystal coordinates are shown for clarity, together with the atom pairs corresponding to the relevant Patterson map peaks.

Table 1Atomic parameters obtained for PMT at $T = 20$ and 300 K.

The atomic displacements are modelled with three split positions for the Pb ions (Pb_x denotes Pb displacements along $\langle 100 \rangle$, Pb_{xx} along $\langle 110 \rangle$ and Pb_{xxx} along $\langle 111 \rangle$). G is the number of ions in the unit cell; $B_{22} = B_{11}$, B_{33} denote anisotropic and B_{iso} isotropic displacement parameters in $\text{\AA}^2$.

Atom	G	x	y	z	B_{11}	B_{33}	B_{iso}
20 K							
Pb_x	1/3	0.090 (4)	0	0			0.88 (7)
Pb_{xx}	1/3	0.056 (4)	x	0			0.88 (7)
Pb_{xxx}	1/3	0.045 (3)	x	x			0.88 (7)
O	3	1/2	1/2	0	1.86 (4)	0.960 (4)	
Ta/Mg	1	1/2	1/2	1/2	0.586 (8)	B_{11}	
300 K							
Pb_x	1/3	0.076 (9)	0	0			1.2 (2)
Pb_{xx}	1/3	0.05 (1)	x	0			1.2 (2)
Pb_{xxx}	1/3	0.04 6(8)	x	x			1.2 (2)
O	3	1/2	1/2	0	1.96 (7)	0.85 (7)	
Ta/Mg	1	1/2	1/2	1/2	0.62 (2)	B_{11}	

displacements are better defined in magnitude and Pb atoms lie on an isotropic spherical shell.

Moreover, a least-square fit to the diffraction data was performed using the program *JANA2000* (Petricek *et al.*, 2005). The refined atomic parameters are summarized in Table 1. In agreement with the analysis of Vakhrushev & Okuneva (2002) for PMN, the structural refinement at $T = 20$ K indicates equiprobable displacements of the Pb ions along all directions by 0.34 (2) $\text{\AA}$. The displacements of the O ions were modelled by anisotropic displacement parameters.

Figure 2

(a) False-colour image of diffuse scattering intensities from PMT (reconstructed experimental data) in the $[H00]/[0K0]$ scattering plane. The direction of streaks of diffuse intensity is shown by a solid line and they extend along the $\langle 110 \rangle$ -type directions. (b) False-colour image of diffuse scattering intensities from PMT (reconstructed experimental data) in the $[HH0]/[00L]$ scattering plane. The direction of streaks of diffuse intensity is shown by a solid line and they extend along the $\langle 112 \rangle$ -type directions. The intensity spots visible at the $1/2(hhl)$ positions are due to partial order in the B sublattice. The data were taken at $T = 175$ K. The inset to Fig. 2(b) shows the distribution of the diffuse scattering around the 220 Bragg peak. The distance from the centre of the inset to the boundaries along the $\langle HH0 \rangle$ and $\langle 00L \rangle$ directions is $0.78 \text{ \AA}^{-1}$. Note that the diffuse scattering is elongated along the $\langle 112 \rangle$ direction. Note also the presence of a few reconstruction artefacts and powder rings from the sample support – the strongest near the origin, weaker ones also farther in the plane; one of these at first sight can be confused with apparent additional streaks across the 020 and 200 peaks.

The result of the refinement shows that the O thermal ellipsoids have a larger component in the $\langle 110 \rangle$ plane. We also observe that the oxygen-related Patterson peaks increase and get sharper with increasing temperature, which is direct evidence for the anomalous decrease of the thermal displacement parameters of the oxygen atoms observed in a previous powder diffraction experiment (Gvasaliya, Roessli *et al.*, 2004). While we cannot disregard the possibility that O displacements are correlated with Pb ones, this is not a dominant feature. We could not obtain from the diffraction results evidence about the anisotropy of the displacements, although the spatial resolution would in principle be sufficient for this purpose. We attribute this limitation either to the averaging over many symmetry-equivalent polar nanoregion domains or to a large fraction of thick domain walls [or nonpolar regions (Smolenskii & Agranovskaya, 1959)] between the PNR that are not ordered. Furthermore, even if the PNR are ordered the displacements are only partly collinear. However, the results obtained from the diffraction data allow us to restrict the analysis of the diffuse scattering to Pb displacements only.

2.2. X-ray diffuse scattering

The diffuse scattering was measured in a single crystal of PMT at the Swiss–Norwegian Beam Line (SNBL) at the ESRF. The measurements were performed in transmission geometry with the wavelength $\lambda = 0.71076 \text{ \AA}$. Diffuse scattering is present in a broad temperature range between $T = 100$ and 450 K (Gvasaliya *et al.*, 2003). We chose to collect data at $T = 175$ K, where the diffuse scattering is strongest. Systematic maps of scattered intensity were collected by a Mar-345 imaging-plate detector with the single crystal being rotated in steps of 0.5° around the vertical axis. From these data the distribution of the diffuse intensity in the $[H00]/[0K0]$ and $[HH0]/[00L]$ scattering planes could be reconstructed, using the program *CrysAlis* produced by Oxford Diffraction (Abingdon, Oxfordshire, UK), to merge the measured maps.

Fig. 2 shows the reconstruction of the scattered intensity distribution in the $[H00]/[0K0]$ and $[HH0]/[00L]$ scattering planes at $T = 175$ K. As known from previous neutron scattering measurements, diffuse scattering is particularly strong at this temperature. The diffuse scattering in PMT has a ‘butterfly’-shaped distribution similar to that found in PMN around the 200 Bragg reflection and within the $[H00]/[0K0]$ scattering plane as shown in Fig. 2(a). It can be observed that the diffuse scattering is

elongated along the four equivalent $\langle 110 \rangle$ directions around these zone centres, while the diffuse scattering is essentially orthogonal to the scattering vector $\mathbf{Q}$ around the 220 Bragg peak. Comparing these measurements with the diffuse scattering obtained when the single crystal is aligned in the $[HH0]/[00L]$ plane shows firstly that the diffuse scattering is extended along the $\langle 112 \rangle$ directions around the 200 Bragg peak. Secondly, it can be observed in Fig. 2(b) that the diffuse scattering around the 220 Bragg peak has four wings of intensity that extend along the $\langle 112 \rangle$ directions and no diffuse intensity is visible along the $\langle 110 \rangle$ directions. This last observation shows that the intensity of the diffuse scattering depends on the direction of the atomic displacements relative to the orientation of the scattering vector $\mathbf{Q}$.

The same effect was observed in $(1-x)\text{PZN}-x\text{PT}$ (Xu *et al.*, 2004; You & Zhang, 1997), where the diffuse scattering was modelled by introducing a polarization factor of the form $(\mathbf{Q} \cdot \mathbf{u})^2$. This polarization factor is due to the atoms having collinear displacements from their average position in the unit cell. The diffuse intensity varies as $(\mathbf{Q} \cdot \mathbf{u})^2$, with $\mathbf{u}$ the direction of the atomic displacements (Krivoglaz, 1969). It is this polarization factor that causes the absence of diffuse intensity when the displacement disorder is perpendicular to the scattering vector $\mathbf{Q}$ as we observe for PMT in the vicinity of the 110 Bragg peak. The diffuse scattering in PMT at low temperatures was found to be truly elastic from neutron diffraction measurements (Gvasaliya *et al.*, 2003), and must originate from static displacements rather than from the freezing of a transverse optic phonon mode.

3. Model of the diffuse scattering in PMT

To analyse the diffuse scattering in PMT we introduce a model that takes into account the shape of the polar nanoregions as well as the direction and magnitude of the displacements. We define therefore a shape function $S(\mathbf{r})$ for a polar nanoregion. The autocorrelation function $G(\mathbf{r})$ of $S(\mathbf{r})$ is

$$G(\mathbf{r}) = \int d^3\mathbf{r}' S(\mathbf{r}') S(\mathbf{r} - \mathbf{r}') \quad (2)$$

and its Fourier transform

$$\tilde{G}(\mathbf{Q}) = \int d^3\mathbf{r} G(\mathbf{r}) \exp(-i\mathbf{Q} \cdot \mathbf{r}). \quad (3)$$

For the case of a periodic crystal with limited dimensions described by $S(\mathbf{r})$, the diffracted intensity is given by

$$I(\mathbf{Q}) = |F(\mathbf{Q})|^2 \sum_{\tau} \tilde{G}(\mathbf{Q} - \tau), \quad (4)$$

where $F(\mathbf{Q}) = \sum_j \rho_j(\mathbf{r}) \exp(-i\mathbf{Q} \cdot \mathbf{r}_j)$ is the structure amplitude of one unit cell and $\rho_j(\mathbf{r})$ the scattering density of atom j ; τ is a reciprocal-lattice vector.

For a disordered crystal the scattering density $\rho(\mathbf{r})$ ¹ can be decomposed into an average atomic density $\rho_a(\mathbf{r}) \propto \delta(\mathbf{r} - \mathbf{r}_j)$ and a random density $\rho_b(\mathbf{r}) \propto \delta(\mathbf{r} - \mathbf{r}_j - \mathbf{u}_j) - \delta(\mathbf{r} - \mathbf{r}_j)$, $\mathbf{u}_j$ being displacement vectors, so that the atomic distribution in the crystal is described by $\rho(\mathbf{r}) = \rho_a(\mathbf{r}) + \rho_b(\mathbf{r})$. The average

atomic structure contributes to the Bragg reflections and its scattered intensity is vanishingly small away from the reciprocal-lattice vectors. In that case it is justified to neglect interference effects and to make the assumption that $|F(\mathbf{Q})|^2 \simeq |F_a(\mathbf{Q})|^2 + |F_b(\mathbf{Q})|^2$. In this approximation the total scattered intensity consists of the superposition of Bragg peaks with broad diffuse components centred around the reciprocal-lattice vectors.

3.1. The form factor

The diffuse scattering measured in PMT was modelled by assuming that only the Pb ion is displaced from its average position $[\mathbf{r}_{\text{Pb}} = (0, 0, 0)]$ in the $Pm\bar{3}m$ space group. If we suppose that the Pb atom is displaced by a vector $\mathbf{u}$, we obtain for the random density

$$F_b(\mathbf{Q}) = b_{\text{Pb}} \{ \exp[-i\mathbf{Q} \cdot (\mathbf{r}_{\text{Pb}} + \mathbf{u})] - \exp(-i\mathbf{Q} \cdot \mathbf{r}_{\text{Pb}}) \}, \quad (5)$$

where b_{Pb} is the form factor (including Debye–Waller factor) of the Pb ion in the unit cell. Since for our simplified model the cubic unit cell of PMT contains only one ion (Pb) that is displaced from its average site, the form factor for the diffuse intensity reduces to

$$|F_b(\mathbf{Q})|^2 = 2b_{\text{Pb}}^2 [1 - \cos(\mathbf{Q} \cdot \mathbf{u})] = 4b_{\text{Pb}}^2 \sin^2(\mathbf{Q} \cdot \mathbf{u}/2). \quad (6)$$

For small values of $\mathbf{Q} \cdot \mathbf{u}$ equation (6) is proportional to $(\mathbf{Q} \cdot \mathbf{u})^2$, which is the form used by Xu *et al.* (2004) and You & Zhang (1997).

It is instructive to present here the $\mathbf{Q}$ dependence of the diffuse scattering of the Pb ions of the *average* structure which are located on a spherical shell of radius u , *i.e.*

$$\rho_a(\mathbf{r}) = b_{\text{Pb}} \frac{\delta(|\mathbf{r} - \mathbf{r}_{\text{Pb}}| - u)}{4\pi u^2}, \quad (7)$$

as suggested by neutron diffraction in both PMN (Bonneau *et al.*, 1991; Vakhrušev & Okuneva, 2002) and PMT (*cf.* §2.2 and Gvasaliya, Roessli *et al.*, 2004). In that case, we obtain

$$F_b(\mathbf{Q}) = b_{\text{Pb}} \exp(i\mathbf{Q} \cdot \mathbf{r}_{\text{Pb}}) \left[\exp(i\mathbf{Q} \cdot \mathbf{u}) - \frac{\sin(Qu)}{Qu} \right], \quad (8)$$

and the scattered diffuse intensity is modulated by a structure factor

$$|F_b(\mathbf{Q})|^2 = b_{\text{Pb}}^2 \left\{ 1 + \left[\frac{\sin(Qu)}{Qu} \right]^2 - 2 \frac{\sin(Qu)}{Qu} \cos(\mathbf{Q} \cdot \mathbf{u}) \right\}, \quad (9)$$

whose first nonzero term in the small- $\mathbf{Q} \cdot \mathbf{u}$ expansion is still proportional to $(\mathbf{Q} \cdot \mathbf{u})^2$.

This scattering differs from Huang scattering that arises for small concentrations of defects, although apparently this can lead in some cases to similar diffuse scattering shapes (Barabash & Krivoglaz, 1979). However, we found that it cannot reproduce simultaneously all diffuse scattering around all Bragg peaks. The reason is briefly explained. In the case of Huang scattering, assuming perfect isotropy of defect and matrix, the displacements have spherical symmetry around each defect and the scattering is proportional to $I_{\text{Huang}} \propto [Q \cos(\varphi)]^2/q^2$, where φ is the angle between $\mathbf{Q}$ and

¹ We neglect here atomic form factors and Debye–Waller factors.

the wavevector $\mathbf{q}$. Huang scattering is present around all Bragg reflections and its intensity is enhanced along the scattering vector $\mathbf{Q}$ while the diffuse intensity vanishes when $\mathbf{Q} \perp \mathbf{q}$. Inspection of the diffuse scattering measured in PMT at $T = 175$ K shows that the planes of zero intensity are not always perpendicular to $\mathbf{Q}$. For example, Fig. 2 shows that the diffuse scattering measured in PMT around the 110 Bragg position with the crystal oriented with the [001] axis vertical is elongated in the direction transverse to the scattering vector and is zero along $\mathbf{Q}$. These results are contrary to those expected for Huang scattering. A more complex treatment (Krivoglaz, 1969) is generally needed for Huang scattering in real solids that never satisfy perfect isotropy. However, this is not enough to invalidate this argument.

We note that it was found that weak diffuse scattering is still present in PMN above the Burns temperature, with, however, a different distribution of intensity in reciprocal space. At high temperature this residual diffuse scattering could mainly arise from Huang scattering, the chemical disorder on the B site and the related size effect. On the other hand, correlated atomic displacements, which give rise to the dominant diffuse scattering in PMT, disappear above the Burns temperature (Gvasaliya, Roessli *et al.*, 2004; Gehring *et al.*, 2009).

3.2. The choice of the line shape

The line shape of the diffuse scattering depends upon the shape function $S(\mathbf{r})$ which describes the form and size of the PNR. If the Pb displacements were to be perfectly aligned within any sharply defined geometric region, there would be characteristic intensity modulations, which have not been observed. Moreover, Monte Carlo simulations of the diffuse scattering in PMN have shown that the domain wall structure of the polar nanoregions is complicated (Paściak *et al.*, 2007) which makes it difficult to describe the shape function with a simple analytical function. However, the autocorrelation of the shape $G(\mathbf{r})$ can be described by an analytical function and in this case the shape is defined in a stochastic way.

Our model describes $G(\mathbf{r})$ by decaying exponentials with an anisotropic decay length. This leads to power-law decay of the diffuse scattering. In fact, it has been demonstrated in PMN that the line shape of the diffuse scattering generally follows a $q^{-\alpha}$ dependence, with $\alpha > 2$ and weakly depending on the temperature, becoming higher at room temperature (You, 2000). Others (Chetverikov *et al.*, 2002) found that α varies between 1.5 and 2.6 as a function of temperature. The 'pancake' model of Xu *et al.* (2004) assumes that PNR have cylindrical symmetry, which yields an exponent $\alpha = 2$ along the axis, $\alpha = 3$ in the orthogonal plane, and higher values along general directions.² In the following we will assume a more general (ellipsoidal) anisotropy for the autocorrelation function (following Ciccariello *et al.*, 2002, appendix), keeping its exponential character:

² If the autocorrelation function has cylindrical symmetry $G(\mathbf{r}) = \exp[-|\mathbf{w}_1 \cdot \mathbf{r}|/L_1] \exp[-(r_\perp/L_r)]$ with L_1 along the cylinder axis and L_r perpendicular to it, the Fourier transform is $\tilde{G}(\mathbf{Q}) = 2\pi L_1^2 L_r / [1 + 2\pi L_1(\mathbf{w}_1 \cdot \mathbf{Q})^2] / [1 + (2\pi L_r Q_\perp)^2]^{1.5}$.

$$G(\mathbf{r}) = \exp(-\xi),$$

$$\xi \equiv \frac{r^2}{[L_1^2(\mathbf{w}_1 \cdot \mathbf{r})^2 + L_2^2(\mathbf{w}_2 \cdot \mathbf{r})^2 + L_3^2(\mathbf{w}_3 \cdot \mathbf{r})^2]^{1/2}}; \quad (10)$$

$$\tilde{G}(\mathbf{Q}) = C[1/(1 + Q^2 \Xi^2)^2],$$

$$\Xi \equiv (1/Q)[L_1^2(\mathbf{w}_1 \cdot \mathbf{Q})^2 + L_2^2(\mathbf{w}_2 \cdot \mathbf{Q})^2 + L_3^2(\mathbf{w}_3 \cdot \mathbf{Q})^2]^{1/2}. \quad (11)$$

L_1, L_2, L_3 correspond to the average dimensions of the PNR along the mutually orthogonal directions defined by the unit vectors $\mathbf{w}_i$ ($i = 1, 2, 3$); C is an inessential constant. This is consistent with a power-law decay dependent on the symmetry of the scattering and the magnitude of the wavevector Q .

4. Interpretation of the diffuse scattering in PMT

In order to model the diffuse scattering in PMT, the direction of the static displacements has to be known. There is however no consensus about the direction of the Pb displacement in the literature. In the analysis by Xu *et al.* (2004) of the diffuse scattering in $(1-x)\text{PZN}-x\text{PT}$, the polarization (displacement) direction is parallel to $\langle 1\bar{1}0 \rangle$. In contrast, using neutron scattering and a pair distribution function analysis, Jeong *et al.* (2005) found direct evidence that displacements in PMN have rhombohedral symmetry, which suggests that the Pb atoms are displaced along the $\langle 111 \rangle$ direction. Initially we assumed that ionic displacements $\mathbf{u}$ were along the directions equivalent to $\langle 1\bar{1}0 \rangle$ under the O_h cubic point group, and chose the unit vectors that define the dimensions of the PNR as $\mathbf{w}_1 = [110]/2^{1/2}$, $\mathbf{w}_2 = [1\bar{1}0]/2^{1/2}$ and $\mathbf{w}_3 = [001]$. In this model, there are six domains which correspond to the symmetrically equivalent $\langle 110 \rangle$ directions in the cubic structure. When $L_1 \ll L_2 = L_3$, the model is equivalent to the 'pancake' model of the PNR of Xu *et al.* (2004). This model accounts properly for the distribution of the diffuse scattering in PMT in the $h00$ Brillouin zones with $\langle 001 \rangle$ perpendicular to the scattering plane when $L_1 \simeq 5a$ (20 Å) (a being PMT's lattice parameter) and $L_2 = L_3 \simeq 25a$. In the $[HH0]/[00L]$ scattering plane, the diffuse scattering has the shape of a 'butterfly' with wings along the $\langle 111 \rangle$ directions that is reproduced by these calculations. We find, however, that this model cannot reproduce the distribution of diffuse scattering intensities in the $[HH0]/[00L]$ plane. Inspection of the diffuse intensity map in PMT reveals that the most intense streaks of diffuse scattering around the $00l$ and $hh0$ Bragg peaks are extended along the $\pm(11 \mp 2)$ directions. These streaks are inconsistent with the pancake model, which predicts streaks along the $\pm(11 \mp 1)$ directions. Also the shape of the diffuse scattering measured around the 222 Bragg peak is less isotropic than that calculated for the pancake model and the measurements show that the diffuse scattering is mainly normal to the scattering vector $\mathbf{Q}$, as shown in Fig. 2(b). For these reasons we searched for an alternative model to describe the distribution of the diffuse scattering in PMT. One possibility is that in the $[HH0]/[00L]$ scattering plane the most intense streaks extend along $\pm(11 \mp 2)$ and the length of the PNR is short along these

directions. The simplest way of building PNR with *e.g.* a short $\langle 11\bar{2} \rangle$ extension is to choose $\mathbf{w}_1 = 1/(2)^{1/2}[\bar{1}\bar{1}0]$, $\mathbf{w}_2 = 1/(3)^{1/2}[111]$ and $\mathbf{w}_3 = 1/(6)^{1/2}[11\bar{2}]$. In this case there are 12 possible polar nanoregion domains that will contribute to the patterns of diffuse intensity. The diffuse scattering was calculated for displacements $\mathbf{u}$ along these directions and the best agreement between the observed and calculated diffuse intensity patterns was obtained by choosing $\mathbf{u}$ along the $\langle 111 \rangle$ direction. For the other directions of atomic displacements the distribution of intensity wings around some of the Bragg peaks was incorrect.

From the previous section we suggest that for PMT a model with the Pb displaced along $\langle 111 \rangle$ and PNR with the longest dimension along $\langle 110 \rangle$ can describe the data. The dimension of the PNR could be estimated from the width of the diffuse intensity away from the Bragg peaks and for $T = 175$ K a good optical match with the data was obtained with $L_1 \simeq L_3 \simeq 7a$ and $L_2 \simeq 20a$. Calculated diffuse scattering maps are shown in Figs. 3(a) and 3(b) and can be compared with the experimental data presented in Fig. 2.

5. Discussion and conclusions

Our main results can be summarized as follows:

(i) Patterson analysis provides direct evidence that the potential at the Pb sites develops a double-well structure at low temperature causing the Pb ions to be distributed on a shell with radius ~ 0.3 Å. The observed absence of some diffuse streaks is in agreement with the form of the structure factor given by equations (6) and (9). In addition, it should be possible to measure the change in the Pb potential with temperature by computing the diffuse scattering intensities as a function of scattering vector $\mathbf{Q}$. As the displacements are important ($u \simeq 0.2 \dots 0.3$ Å), this would require recording the

distribution of the diffuse scattering intensity at large scattering vectors. Having Pb ions displaced along the $\langle 111 \rangle$ direction is consistent with the analysis of the local structure of relaxor ferroelectrics by pair distribution function (Jeong *et al.*, 2005) and with the observations of a rhombohedral phase transition that can be induced by application of an electric field (Calvarin *et al.*, 1995). Also recent dielectric measurements in PMN doped with PbTiO_3 in an applied electric field have shown that the spontaneous polarization in the PNR is along the $\langle 1, 1, 1 \rangle$ direction (Li *et al.*, 2008).

(ii) Describing the structure of the PNR in terms of Pb displacements only might be too simple a model. From single-crystal data, we have only indirect evidence for displacements of cations at B and O sites. These ions then probably play a less important role in the formation of the diffuse scattering. However, we note that a qualitative understanding of the X-ray diffuse scattering could be obtained by considering only the Pb displacements. This might be due to the smaller X-ray cross section of the O ions compared with the metal cations. Neutron diffuse scattering could then probably shed more light on the O ions' behaviour if the diffuse scattering was measured with better resolution than is possible now.

(iii) The main structural feature causing the characteristic butterfly diffuse scattering in PMT is the formation of PNR where Pb atoms are displaced along one $\langle 111 \rangle$ direction; the PNR have large correlation lengths only along the $\langle 111 \rangle$ direction parallel to the Pb displacement direction.

In conclusion, we have analysed the distribution of displacements in PMT by single-crystal neutron diffraction and synchrotron radiation. The diffuse scattering and especially its structural origin have been understood qualitatively.

Another interesting topic is the relationship between coherent Pb $\langle 111 \rangle$ displacements in PNR and the well known B-site partial ordering (Akbas & Davies, 1997, 2000; Montgomery & Akbas, 1999). This consists of the B-site cations ordering as an NaCl-type superlattice, with Na-type sites containing one Ta atom and Cl-type sites containing in 1/3 of cases a Ta atom and in the remaining 2/3 of cases one Mg atom. Of course, every admixture of such order with the fully disordered cases is possible; moreover, antiphase domains are very likely to form within the NaCl superlattice. This superstructure results in $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ broad satellites (see Fig. 2b), with intensity dependent on the degree of superlattice ordering and broadening due to antiphase domains. We could not measure this superstructure quantitatively, because the Mg/Ta contrast is too weak for neutrons while the X-ray Bragg peak intensities, owing to the limited dynamic range of the detector used, were saturated. A comprehensive and detailed microstructural study of all

Figure 3

False-colour images of calculated diffuse scattering intensities from PMT (a) in the $[H00]/[0K0]$ and (b) in the $[HH0]/[00L]$ scattering planes. The intensities are given on a logarithmic scale, approximately the same as used in Fig. 2. The $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ satellites due to B-site partial ordering are not included here, neither are the main Bragg peaks (saturated in Fig. 2) or the experimental background.

systematic atomic displacements and their relationship with the *B*-site superstructure order is necessary to understand this relationship and to bridge the gap between structure and macroscopic properties of relaxor ferroelectrics.

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