We have studied the diffuse scattering in the relaxor Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) using triple-axis neutron scattering techniques. The diffuse scattering first appears around the Burns temperature $T_d \approx 620$ K, indicating that its origin lies within the polar nanoregions (PNR). While the relative intensities of the diffuse scattering around (101), (200), and (300) are consistent with those previously reported by Vakhrushev et al., they are, surprisingly, entirely different from those of the lowest-energy transverse optic (TO) phonon. This observation led Naberezhnov et al. to claim that this TO mode could not be the ferroelectric soft mode. However, a recent neutron study by Gehring et al. has unambiguously shown that the lowest-energy TO mode does soften on cooling, and that the relative intensities are similar to those of PbTiO$_3$. If the diffuse scattering in PMN originates from the condensation of a soft TO mode, then the atomic displacements of the PNR must satisfy the center of mass condition. But, the atomic displacements determined from diffuse scattering intensities do not fulfill this condition. To resolve this contradiction, we propose a simple model in which this unexpected high-temperature deviation arises from small, randomly oriented, very local regions of non-reversible polarization (the PNR) that begin to appear within the otherwise non-polar crystal structure below $T_d$, which is often called the Burns temperature. Recent neutron inelastic scattering studies on PZN and PZN doped with 8% PbTiO$_3$ (PZN-8%PT) in their respective cubic phases at 500 K have shown that the lowest-energy transverse optic (TO) phonon modes are overdamped for reduced wave vectors $q$ less than a characteristic wave vector $q_{\text{ef}} \sim 0.2$ Å$^{-1}$, but underdamped otherwise. It is now believed that this damping is caused by the PNR because they couple strongly to the polar nature of the TO modes.

Vakhrushev et al. carried out neutron diffraction studies on PMN and observed strong diffuse scattering which remains even at 500 K. They found that the $q$-width of the diffuse peak, which is inversely proportional to the correlation length, is temperature dependent, and that both the Bragg and diffuse peaks exhibit history dependent effects in the field-cooled (FC) and zero field-cooled (ZFC) regimes, similar to that of a typical spin glass. The transition to this glass-like state occurs around 230 K, which is slightly below $T_{\text{max}}$. The diffuse scattering in PMN was subsequently measured around 16 reciprocal lattice points, from which the directions and relative magnitudes of the ionic displacements were determined. The observed diffuse scattering is broader along the direction transverse to the scattering vector $Q \perp Q$ than...
it is along the longitudinal direction \( \mathbf{Q}_\parallel \), a feature that is consistent with scattering from ferroelectric fluctuations. Bonneau et al.\(^7\) measured both x-ray and neutron powder diffraction from PMN and reported that additional diffuse scattering appears in the tails of the Bragg peaks below about 600 K. Neutron powder diffraction data taken by Zhao et al.\(^8\) show a marked break in the linear temperature dependence of the cubic unit cell volume, also around 600 K, and is shown in Fig. 1(a). More recently, Naberezhnov et al.\(^6\) have confirmed that the diffuse scattering indeed becomes visible below 650 K, as shown in Fig. 1(b). These results strongly imply that the diffuse scattering in PMN results from the formation of the PNR at \( T_d \).

Naberezhnov et al.\(^6\) have also studied the lattice dynamics of PMN using neutron inelastic scattering methods between 300 and 900 K. They calculated dynamical structure factors using the room temperature diffuse scattering results of Vakhruhev et al.\(^8\), and concluded that (221) was the best zone in which to look for the ferroelectric soft mode phonon. However, they observed no underdamped soft TO phonon in the vicinity of (221) even at 900 K. Instead, they observed well-shaped peaks from the transverse acoustic (TA) and the lowest-lying TO modes near (220), although nearly no diffuse scattering was observed around (220). They therefore concluded that the observed lowest-lying TO mode could not be identified with the ferroelectric soft mode because it exhibited a structure factor that was absolutely inconsistent with that expected from the ferroelectric diffuse scattering peak intensities. However, a recent neutron inelastic scattering study by Gehring et al.\(^7\) has unambiguously shown that the lowest-energy zone center TO mode does soften significantly on cooling from 1100 K to \( T_d \), below which it becomes overdamped, and that the relative phonon intensities measured in different zones are very similar to those found in PbTiO\(_3\), a prototypical (displacive) ferroelectric system.

It is thus clear that an important discrepancy exists between the relative intensities of the soft TO mode and those of the diffuse scattering in PMN. Since each is related to either dynamic or static atomic displacements toward the same ferroelectric state, the relative intensities should be consistent. The aim of this paper is to determine how the diffuse scattering in PMN connects to the soft TO mode, and thereby resolve this discrepancy. To study the diffuse scattering in PMN in detail, we have carried out neutron diffraction measurements from 200 to 700 K. We have concentrated on the diffuse scattering around the three Bragg reflections (101), (200), and (300), and measured the \( q \)-profiles and the temperature dependence. These results, as well as the experimental conditions, are summarized in Section II. In Section III we describe our phonon structure factor calculations using the atomic displacements determined from the diffuse scattering intensities, which helps to clarify the inconsistency between the relative intensities of the soft TO mode and of the diffuse scattering. We believe this discrepancy can only be resolved if one assumes the simple model in which the PNR are shifted along their polar direction relative to the surrounding cubic matrix. Finally, we compare our experimental results with those from previous neutron and x-ray scattering studies, and discuss one possible origin of this new concept, which we call a “phase-shifted condensed soft mode,” in Section IV.

II. DIFFUSE SCATTERING

The neutron diffuse scattering data presented here were obtained on the BT9 triple-axis spectrometer located at the NIST Center for Neutron Research. The data were taken with fixed incident neutron energy \( E_i = 14.7 \text{ meV} (\lambda = 2.36 \text{ Å}) \), and with horizontal beam collimations 40'-46'-S-40'-80' or 40'-10'-S-10'-80' (°S° = sample). Single crystals of PMN were grown by a top-seeded solution growth technique using PbO as flux. The growth conditions were determined based on the pseudo-binary phase diagram established from PMN and PbO. An as-grown single crystal with a nearly half-cubic morphology, having a volume of 0.4 cm\(^3\) and a weight of 3.25 g, was used for the diffuse scattering measurements. The crystal exhibits three naturally grown \{1 0 0\}\(_{\text{cubic}}\) facets,
and was mounted on a boron nitride post using tantalum wire with one of the facets facing vertically, and then attached to the cold-head of a high-temperature closed-cycle helium refrigerator. This orientation gave access to reflections of the form $(h0l)$ in the scattering plane. The lattice constant of PMN is $a = 4.04$ Å at room temperature, thus 1 rlu (reciprocal lattice unit) corresponds to $2\pi/a = 1.553$ Å$^{-1}$.

Figure 2(a) shows peak profiles of the transverse diffuse scattering in the vicinity of (101). Note that the $y$-axis is displayed on a logarithmic scale. At 690 K, there is no diffuse scattering. The peak profile is well-described by a Gaussian function with a full-width at half-maximum (FWHM) corresponding to that of the instrumental $q$-resolution at the (101) Bragg peak. With decreasing temperature, a weak signal starts to emerge out of the (101) Bragg peak, growing more rapidly as the temperature is lowered. The observed diffuse scattering can be nicely fit with a Lorentzian function as shown in Fig. 2(a). The temperature dependence of the diffuse scattering is more clearly presented in Fig. 2(b). The diffuse scattering appears below about 600–650 K, consistent with the Burns temperature $T_d \sim 620$ K for PMN, and increases almost exponentially with decreasing temperature.

The diffuse scattering peak profiles were more closely examined by employing a tighter collimation of $40'-10'-S-10'-80'$. Figure 3 depicts the transverse diffuse scattering profiles at (101), (200), and (300) at $T = 300$ and 370 K. Although the difference in the diffuse scattering intensity between these two temperatures is not very large, as is apparent from Fig. 3, it is nevertheless discernable...
FIG. 4: Intensity contours of the diffuse scattering around (101) at (a) 270 K and (b) 370 K. (c) Difference between (a) and (b).

at (101). A significantly larger difference is observed at (300), which indicates that the diffuse scattering is stronger at (300) than at (101). No difference in intensity at finite $q$ near (200) was found, which suggests the diffuse scattering is very weak at (200). We speculate that the tail-like feature near $q = 0$ for (200) is due to contamination from the TA phonon, which is quite strong near (200), as some TA mode scattering will inevitably spill into the elastic profile because of the imperfect instrumental energy resolution. The relative intensities of the (101), (200), and (300) diffuse scattering peaks are consistent with those reported in the previous neutron diffraction measurement by Vakhrushev et al. We have also carried out a detailed survey of the (101) diffuse scattering, the results of which are shown in Fig. 4. The diffuse scattering is highly elongated along the direction transverse to the scattering vector, which is also consistent with the previous report. Similar neutron diffuse scattering results at (101) and (200) were recently observed by Koo et al. in a single crystal sample of PMN doped with 20% PbTiO$_3$.

FIG. 5: Energy spectra of the transverse acoustic and optic phonons at 690 K, i.e., above the Burns temperature $T_d$, around (a) (200) and (b) (300).

III. FERROELECTRIC PHONON

Gehring et al. have recently reported that the lowest-energy zone center TO mode in PMN softens on cooling from 1100 K to $T_d$, and that the relative intensities measured in different zones are very similar to those found in PbTiO$_3$. This result sharply contradicts the fact that the relative intensities of the diffuse scattering in different zones are entirely different from those of the lowest-energy transverse optic (TO) phonons, an observation which led Naberezhnov et al. to claim that the lowest-energy TO mode could not be the ferroelectric soft mode. To understand how PMN undergoes the diffuse transition through the formation of the PNR, this contradiction must be resolved. In this section, we revisit the soft mode of PMN and introduce a new concept, the “phase-shifted condensed soft mode,” as a microscopic description of PNR formation.

As shown in the previous section, we observe no diffuse scattering around (200), consistent with previous reports. However, TO phonons are clearly observed around both (200) and (300) as shown in Fig. 5, which shows two constant-$Q$ scans at 690 K (i.e., above the Burns temperature $T_d$) at (2, 0, −0.2) and (3, 0, −0.2). The solid curves are fits to two Lorentzian functions of $E$, the neutron energy transfer, convolved with the proper instrumental resolution function. From the fitting results, the ratio of the two TO phonon intensities is

$$\frac{|F_{obs}(200)|^2}{|F_{obs}(300)|^2} = 1.24 \pm 0.20.$$  \hspace{1cm} (1)

According to the pioneering work by Harada et al.
which describes the determination of the normal mode vibrational displacements in perovskites from measured phonon intensities, the relative intensities of phonons are determined mostly by the ratio of two dominant modes, i.e., the Slater mode and the Last mode. In the Slater mode, the oxygen and Mg/Nb (MN) atoms vibrate in opposition while the Pb atoms remain stationary. The Last mode corresponds to opposing motions of the (Mg/Nb)O₆ octahedra and the Pb atoms. In both modes, the three oxygen atoms in the unit cell move as a rigid unit. We define the ratio of the two modes as $S = S_2/S_1$, where $S_1$ and $S_2$ represent the contribution from the Slater mode ($S_1$) and Last mode ($S_2$), respectively.

Let us first determine the ratio $S$. Figure 6(a) shows the inelastic structure factors $|F_{inel}|^2$ at (101), (200) and (300) as a function of $S$, which are calculated using the formula given by Harada et al. If we assume that the atomic displacements $s_1$ and $s_2$ are parallel to the [100] direction for the sake of simplicity. Combining Eqs.(1) and (5) of Ref. 11, we have obtained $|F_{inel}|^2$ for the lowest branch at the zone center ($q = 0$) using constant-$Q$ scans as follows:

$$|F_{inel}|^2 = \sum_{\kappa} |Q \cdot \xi_{\kappa}| b_\kappa \exp (-W_{\kappa}) \exp (iG \cdot R_{\kappa}),$$  

where the scattering vector $(Q)$ is the sum of the reciprocal lattice vector $(G)$ and the phonon wave number $(q = 0)$, and the normalized displacement vector for the $\kappa$-th atom, $\xi_{\kappa}$, in our condition is

$$\xi_{\kappa} = s_{\kappa 1} + S s_{\kappa 2}.$$  

From Table 1 of Ref. 11, the atomic displacements along the [100] direction are

$$\xi_{Pb} = -Sk',$$

$$\xi_{MN} = -k + S,$$

$$\xi_{O} = 1 + S,$$

where the center of mass condition requires $k = 3M(O)/M(MN) = 0.686$ and $k' = [M(MN) + 3M(O)]/M(Pb) = 0.596$. The calculated values are normalized by the sum of $|F_{inel}|^2$ over all reflections that can be reached with an incident neutron energy $E_i = 14.7$ meV: (100), (110), (200), (210), (220), (300), (310) and their equivalent. Debye-Waller factors, $\exp (-W_{\kappa})$, are calculated using $B_{Pb} = 0.915$ and $B_{NM} = 0.483$ and $B_{O} = 1.02$.

Figure 6(a) indicates that the experimentally observed intensity ratio of $|F_{obs}(200)|^2/|F_{obs}(300)|^2 = 1.24$ obtained in Eq. (3) is realized between $S = 1.0$ and 1.5.

If the diffuse scattering of PMN originates from the condensation of the soft TO mode, then the above formula should be also applicable to the diffuse scattering intensities and that the atomic displacements determined from the diffuse scattering intensities must also satisfy the center of mass condition:

$$\sum_{\kappa} \delta(\kappa)M(\kappa) = 0,$$

where $\delta(\kappa)$ and $M(\kappa)$ are the displacement and the atomic mass of the $\kappa$-th atom, respectively. However, the values $\delta(\kappa)$ determined from the diffuse scattering intensities by Vakhrushev et al. do not satisfy the center of mass condition. This contradiction is a natural corollary to the observed inconsistency between the relative intensities of the diffuse and the soft TO mode scattering.

To resolve this discrepancy, we propose a simple model in which the atomic displacements consist of two components, $\delta(\kappa) = \delta_{CM}(\kappa) + \delta_{shift}$. In this model, $\delta_{CM}$ is induced by the condensation of the soft mode, and thus satisfies the center of mass condition. On the other hand, $\delta_{shift}$ shifts the PNR along their polar directions relative to the surrounding cubic matrix, which is, in other words, a phase shift. By applying this model, the $\delta(\kappa)$ values listed in Eq. (3) can be separated into two parts:

$$\delta_{CM}(Pb) = 0.42,$$

$$\delta_{CM}(MN) = -0.40,$$

$$\delta_{CM}(O) = -1.22.$$
Note that the $\delta_{CM}$ values are uniquely determined from the center of mass condition and can be further decomposed into contributions from the Slater mode and the Last mode. The corresponding ratio $S$ between the Slater mode and Last mode contributions is 1.5, which is consistent with the value obtained in Fig. 6(a). Note that the phase shift $\delta_{shift}$ becomes effective only when the PNR condense out from the soft TO mode. Hence the phonon intensities are determined only by the $\delta_{CM}$ values.

Now that we have confirmed that the $\delta_{CM}$ values derived from the diffuse scattering intensities are consistent with the inelastic scattering intensities of the soft TO mode, we can calculate how the diffuse scattering intensities depend on the phase factor $\delta_{shift}$ with the constraint $S = 1.5$ using the $\delta_{CM}$ values listed in Eq. (7). The results are shown in Fig. 6(b). Note that the values at $\delta_{shift} = 0$ are identical to those at $S = 1.5$ in Fig. 6(a) as expected. At $\delta_{shift} = 0.58$, which was derived above to satisfy the center of mass condition, the diffuse intensity around (200) approaches zero, in agreement with experiment. Thus, our “phase-shifted condensed soft mode” model consistently explains both the diffuse scattering and the soft mode intensities from the same atomic displacements.

Lastly, we consider the phase shift from the crystal lattice point of view. Figure 7 depicts the atomic displacements schematically with three different phase shift values. Figure 7(a) shows the displacements of Eq. (7) without the phase shift, which satisfies the center of mass condition and gives the same relative intensities for both the diffuse scattering and the soft TO mode. However, once all the atoms undergo an additional shift along the same direction by the same amount $\delta_{shift} = +0.6$, the center of mass condition is no longer satisfied, resulting in the accidental disappearance of the (200) diffuse neutron scattering intensity. Figure 7(c), which depicts a uniform shift of $\delta_{shift} = -0.6$, is shown just for comparison.

**IV. DISCUSSION**

In the preceding sections we have demonstrated how the inconsistency between the diffuse scattering and the soft TO mode intensities is explained naturally within the framework of a “phase-shifted condensed soft mode.” Our data on the diffuse scattering cross-sections in three different Brillouin zones along with our measurements of the soft TO mode phonons in two different zones serve as a confirmation of the detailed measurements already published by other groups. However, while our data are in agreement, our interpretations differ entirely. The simplicity of our model argues in its favor. Other than the standard picture of condensed local ferroelectric fluctuations created by a soft phonon, there is only one added feature, that being a uniform phase shift of the PNR relative to the surrounding cubic matrix. We believe the simpler solution is the correct one.

The process of separating the observed atomic displacements into optic mode displacements $\delta_{CM}$ and a single phase shift parameter $\delta_{shift}$ is straightforward and unique, and requires no adjustable parameters. We realized this fact a long time ago. We did not recognize, however, the significance of the derived center of mass structure. Only recently, when the true soft mode of PMN was observed directly by neutron scattering at high temperature, did we recognize the identity of the diffuse structure as a condensed soft mode. Then the idea of the phase shift followed naturally. But one important question still remains: what is the microscopic origin of this phase shift? It should be emphasized that the direction of the phase shift is not arbitrary as is clear from Fig. 7. Our model requires that the phase shift be parallel, not antiparallel, to the polarization resulting from the atomic displacement. Under zero external electric field, as is the case here, the polarization direction of a single PNR can be parallel to any symmetric direction of (111), i.e., [111], [111], ···, [111]. Therefore, the phase-shifted directions of the PNR are microscopically aligned to their polarizations, although they appear macroscopically random. Then, why is the phase shift of the PNR parallel to their
polarization?

We speculate that microscopic inhomogeneities in the site-occupancy of the Mg$^{2+}$ and Nb$^{5+}$ cations produce a local electric field gradient that determines the direction of polarization of the PNR. In other words, a nanoregion exposed to a local field gradient becomes a polar nanoregion with a polarization parallel to the gradient. Once a PNR is formed, its polarization starts to interact with the local field gradient, and may result in shifting the PNR in order to compensate for the Coulomb interaction with the lattice distortion due to the phase shift. The phase shift in this case is parallel to the local field gradient, and thus to the polarization of the PNR. Since the microscopic inhomogeneities associated with the spatial distribution of the Mg$^{2+}$ and Nb$^{5+}$ cations cause random charged domains, the local field gradient is random. Therefore, the polarizations of the PNR should also be random. However, as explained above, the phase shift of a particular PNR is always parallel to its polarization. These descriptions are still qualitative, and need to be tested experimentally. It is particularly important to study the microscopic properties of the PNR, such as their correlation lengths and textures as a function of temperature as well as electric field. We also need to understand the chemical inhomogeneity of Mg$^{2+}$ and Nb$^{5+}$ microscopically.

Finally, our model should help to resolve some of the conflicting x-ray diffuse scattering interpretations. The diffuse intensity around (200) is only accidentally zero when measured with neutrons, but it should be non-zero when measured with x-rays because of the differences between the neutron nuclear scattering lengths and the x-ray atomic scattering factors.

In summary, we have studied the diffuse scattering of the relaxor Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ over a wide temperature range with neutron scattering techniques. We have confirmed that the relative intensities are consistent with previous reports and that the diffuse intensity starts increasing below the Burns temperature $T_B$. We have revisited the soft transverse-optic mode, the existence of which has been recently confirmed, and examined the inconsistency between the soft phonon and the diffuse intensities. We have proposed a new concept, the “phase-shifted condensed soft mode,” which naturally explains the inconsistency as well as the microscopic origin of the formation of the polar nanoregions.

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