Soft Phonon Anomalies in the Relaxor Ferroelectric $Pb(Zn_{1/3}Nb_{2/3})_{0.92}Ti_{0.08}O_3$

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Neutron inelastic scattering measurements of the polar transverse optic phonon mode dispersion in the cubic relaxor $Pb(Zn_{1/3}Nb_{2/3})_{0.92}Ti_{0.08}O_3$ at 500 K reveal anomalous behavior in which the optic branch appears to drop precipitously into the acoustic branch at a finite value of the momentum transfer $q = 0.2$ Å^{-1} measured from the zone center. We speculate that this behavior is the result of nanometer-sized polar regions in the crystal.

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The discovery by Kuwata *et al.* in 1982 that it was possible to produce single crystals of the relaxor-ferroelectric material $Pb(Zn_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PZN-xPT) represented an important achievement in the field of ferroelectrics [1]. Because the parent compounds $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $PbTiO_3$ (PT) form a solid solution, it was possible to tune the stoichiometry of the material to lie near the morphotropic phase boundary (MPB) that separates the rhombohedral and tetragonal regions of the phase diagram [1–3]. Such MPB compositions in $Pb(Zn_{1-x}Ti_x)O_3$ (PZT), the material of choice for the fabrication of high-performance electromechanical actuators, exhibit exceptional piezoelectric properties, and have generated much scientific study [4]. However, in contrast to PZN-xPT, all attempts to date to grow large single crystals of PZT near the MPB have failed, and this has impeded progress in fully characterizing the PZT system.

The dielectric and piezoelectric properties of single crystals of both PZN-xPT and PMN-xPT (M = Mg) have since been examined by Park *et al.* who measured the strain as a function of applied electric field [2,3]. These materials were found to exhibit remarkably large piezoelectric coefficients $d_{33} > 2500$ pC/N and strain levels $S \sim 1.7\%$ for rhombohedral crystals oriented along the pseudocubic [001] direction. This level of strain represents an order of magnitude increase over that presently achievable by conventional piezoelectric and electrostrictive ceramics including PZT. That these ultrahigh strain levels can be achieved with nearly no dielectric loss ($<1\%$) due to hysteresis suggests that both PMN-xPT and PZN-xPT hold promise in establishing the next generation of solid state transducers [5]. A very recent theoretical advance in our understanding of these materials occurred when it was shown, using first principles calculations, that the *intrinsic* piezoelectric coefficient e_{33} of MPB PMN-40%PT was dramatically enhanced relative to that for PZT by a factor of 2.7 [6]. Motivated by these experimental and theoretical results, we have studied the dynamics of the soft polar optic phonon mode in a high quality single crystal of PZN-8%PT, for which the measured value of d_{33} is a maximum, using neutron inelastic scattering methods.

In prototypical ferroelectric systems such as $PbTiO_3$ it is well known that the condensation or softening of a zone-center transverse optic (TO) phonon is responsible for the transformation from a cubic paraelectric phase to a tetragonal ferroelectric phase. This is readily seen in neutron inelastic scattering measurements made at several temperatures above the Curie temperature. In the top panel of Fig. 1 we show the dispersion of the lowest-energy TO branch in $PbTiO_3$ where at 20 K above T_c the zone center ($\zeta = 0$) energy has fallen to 3 meV [7].

In relaxor compounds, however, there is a built-in disorder that produces a diffuse phase transition in which the dielectric permittivity ϵ exhibits a broad maximum as a function of temperature at $T_{\max}$. In the case of PMN and PZN, both of which have the simple ABO_3 perovskite structure, the disorder results from the B site being occupied by ions of differing valence (either Mg^{2+} or Zn^{2+}, and Nb^{5+}). This breaks the translational symmetry of the crystal. Despite years of intensive research, the physics of the observed diffuse phase transition is still not well understood [8–10]. Moreover, it is interesting to note that no definitive evidence for a soft mode has been found in these systems. The bottom panel of Fig. 1 shows neutron scattering data taken by Naberezhnov *et al.* on PMN [11] exactly analogous to that shown in the top panel for $PbTiO_3$, except that the temperature is $\sim$570 K higher than $T_{\max}$.

A seminal model for the disorder inherent to relaxors was first proposed by Burns and Dacol in 1983 [12]. By using measurements of the optic index of refraction on both ceramic samples of $(Pb_{1-3x/2}La_x)(Zr_yTi_{1-y})O_3$ (PLZT) and single crystals of PMN and PZN [12], they demonstrated that a randomly oriented local polarization P_d develops at a well-defined temperature T_d, frequently referred to as the Burns temperature, several hundred degrees above the apparent transition temperature $T_{\max}$. Subsequent studies have provided additional evidence of the existence of T_d [13–15]. The spatial extent of these locally polarized regions was conjectured to be of the order of several unit cells just below T_d, and has given rise to the term "polar micro-regions," or PMR [16]. For PZN-8%PT, the formation of PMR occurs at $T_d \sim 700$ K, well above the

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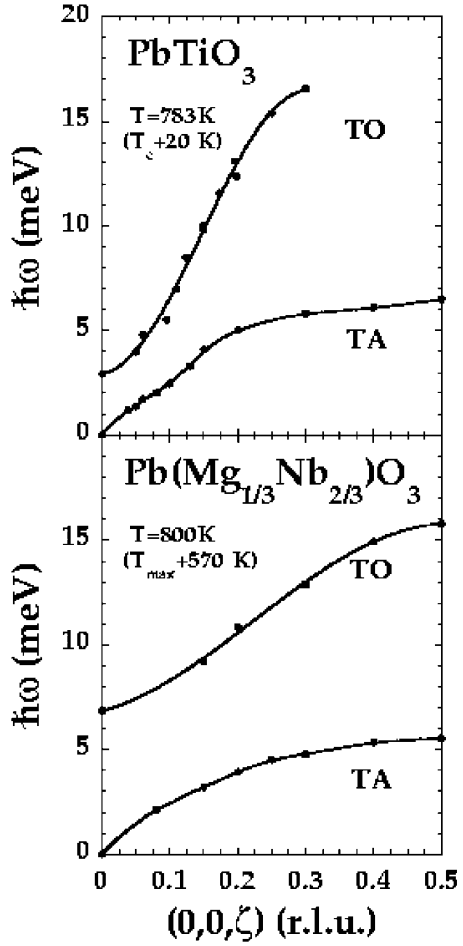

FIG. 1. Top: dispersion of the lowest-energy TO mode and the TA mode in $PbTiO_3$, measured just above T_c (from Ref. 7). Bottom: dispersion curves of the equivalent modes in PMN measured far above $T_{\max}$ (from Ref. 11).

cubic-to-tetragonal phase transition at $T_c \sim 450$ K. We find striking anomalies in the TO phonon branch (the same branch that goes soft at the zone center at T_c in $PbTiO_3$) that we speculate are directly caused by these PMR.

All of the neutron scattering experiments were performed on the BT2 and BT9 triple-axis spectrometers located at the NIST Center for Neutron Research. The (002) reflection of highly oriented pyrolytic graphite (HOPG) was used to monochromate and analyze the incident and scattered neutron beams. An HOPG transmission filter was used to eliminate higher-order neutron wavelengths. The majority of our data were taken by holding the final neutron energy E_f fixed at 14.7 meV ($\lambda_f = 2.36$ Å) while varying the incident neutron energy E_i, and using horizontal beam collimations 60′-40′-S-40′-40′. The single crystal of PZN-8%PT used in this study weighs 2.8 g and was grown using the high-temperature flux technique described elsewhere [3]. The crystal was mounted onto an aluminum holder and oriented with either the cubic $[\bar{1}10]$ or [001] axis vertical. It was then placed inside a vacuum furnace capable of reaching temperatures up to 670 K.

Two types of scans were used to collect data. Constant-energy scans were performed by keeping the energy transfer $\hbar\omega = \Delta E = E_i - E_f$ fixed while varying the momentum transfer $\vec{Q}$. Constant-$\vec{Q}$ scans were performed by holding the momentum transfer $\vec{Q} = \vec{k}_i - \vec{k}_f$ ($k = 2\pi/\lambda$) fixed while varying the energy transfer ΔE. Using these scans, the dispersions of both the transverse acoustic (TA) and the lowest-energy transverse optic phonon modes were mapped out at a temperature of 500 K (still in the cubic phase, but well below the Burns temperature of ~700 K). In Fig. 2 we plot where the peak in the scattered neutron intensity occurs as a function of $\hbar\omega$ and $\vec{q}$, where $\vec{q} = \vec{Q} - \vec{G}$ is the momentum transfer measured relative to the $\vec{G} = (2, 2, 0)$ and $(4, 0, 0)$ Bragg reflections along the symmetry directions [001] and [110], respectively. The horizontal scales of the left and right halves of the figure have been adjusted so that each corresponds to the same q (Å^{-1}) per unit length. The sizes of the vertical and horizontal bars represent the phonon FWHM (full width at half maximum) linewidths in $\hbar\omega$ (meV) and q (Å^{-1}), respectively, and were derived from Gaussian least-squares fits to the constant-$\vec{Q}$ and constant-E scans. The lowest energy

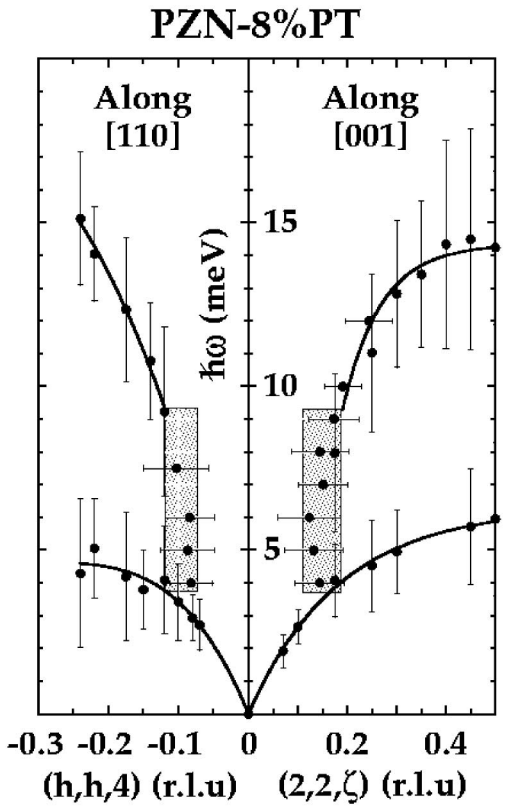

FIG. 2. Solid dots represent positions of peak scattered neutron intensity taken from constant-$\vec{Q}$ and constant-E scans at 500 K along both [110] and [001] symmetry directions. Vertical (horizontal) bars represent phonon FWHM linewidths in $\hbar\omega$ (q). Solid lines are guides to the eye indicating the TA and TO phonon dispersions.

data points trace out the TA phonon branch along [110] and [001]. Solid lines have been drawn through these points as a guide to the eye, and are nearly identical to that shown for PMN in Fig. 1.

By far the most striking feature in Fig. 2 is the unexpected collapse of the TO mode near the zone center where the polar optic branch appears to drop precipitously, like a waterfall, into the acoustic branch. This anomalous behavior, shown by the shaded regions in Fig. 2, stands in stark contrast to that of PMN at high temperature where the same phonon branch intercepts the $\hbar\omega$ axis at a finite energy (see bottom panel of Fig. 1). The strange drop in the TO phonon energy occurs for $q \sim 0.13$ r.l.u. (reciprocal-lattice units) measured along [001], and for $q \sim 0.08$ r.l.u. measured along [110] (1 r.l.u. along $[110] = \sqrt{2}$ r.l.u. along $[001] = \sqrt{2}(2\pi/a) = 2.18$ Å^{-1}). It is quite intriguing to note that these q values are both approximately equal to 0.2 Å^{-1}.

To clarify the nature of this unusual observation, we show an extended constant-E scan taken at $\Delta E = 6$ meV in Fig. 3 along with a constant-$\vec{Q}$ scan in the inset. Both scans were taken at the same temperature of 500 K, near the (2,2,0) Bragg peak, and along the [001] direction. The small horizontal bar shown under the left peak of the constant-E scan represents the instrumental FWHM q resolution, and is clearly far smaller than the experimentally observed peak linewidth. We see immediately that the constant-$\vec{Q}$ scan shows no evidence of any well-defined phonon peak, most likely because the phonons near the zone center are overdamped. However, the constant-E scan indicates the presence of a ridge of scattering intensity at $\zeta = q = 0.13$ r.l.u., or about 0.2 Å^{-1}, that sits atop the scattering associated with the overdamped phonons. Thus the sharp drop in the TO branch that appears to take place in Fig. 2 does not correspond to a real dispersion curve as such. Rather, it simply indicates a region of $(\hbar\omega, q)$ space in which the phonon scattering cross section is enhanced. The origin of this enhancement is unknown; however, we speculate that it is a direct result of the PMR described by Burns and Dacol [12]. If the length scale associated with this enhancement is of order $2\pi/q$, this corresponds to ~31 Å, or about 7 to 8 unit cells, consistent with Burns and Dacol's conjecture.

Limited data were also taken as a function of temperature to determine the effect on this anomalous ridge of scattering. In Fig. 4 we show two constant-E scans, both measured at an energy transfer $\Delta E = 5$ meV along the [010] direction, with one taken at 450 K and the other at 600 K. The solid and dashed lines are fits to simple Gaussian functions of q. As is clearly seen, the ridge of scattering shifts to smaller q, i.e., *towards* the zone center, with

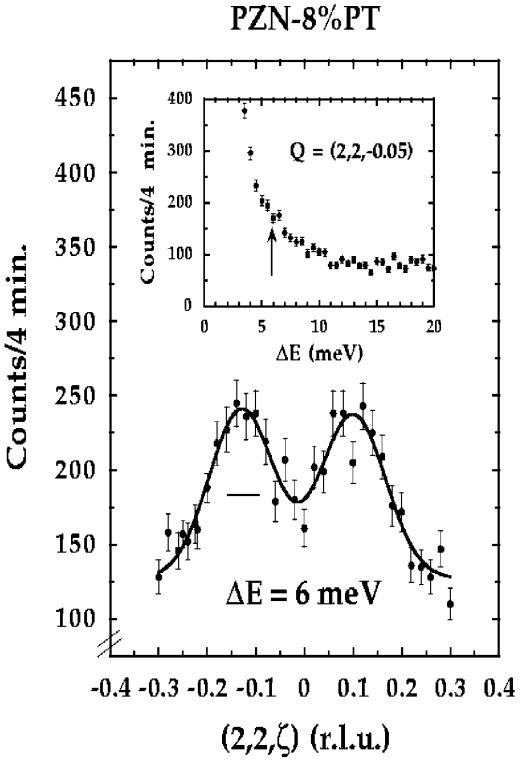

FIG. 3. Single constant-E scan measured along [001] at 6 meV at 500 K near the $(2, 2, 0)$ Bragg peak. The solid line is a fit to a double Gaussian function of ζ. The inset shows no peak in the scattered intensity measured along the energy axis. The arrow indicates the position of the constant-E scan.

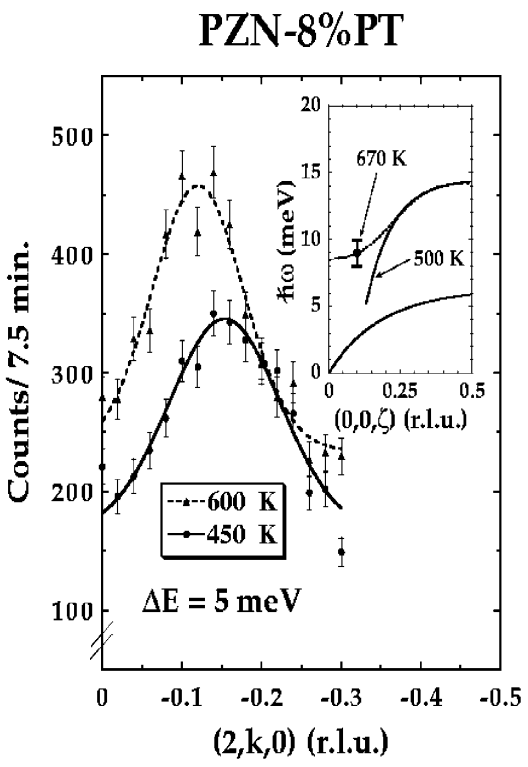

FIG. 4. Two constant-E scans measured along [010] at 5 meV at different temperatures. The peak shifts towards the zone center with increasing temperature. The inset suggests schematically how the TO branch dispersion recovers at higher temperatures.

increasing temperature. These data strongly suggest a picture, shown schematically in the inset of Fig. 4, in which the ridge of scattering evolves into the expected classic TO phonon branch behavior at higher temperature. A single data point, obtained briefly at 670 K to avoid damaging the crystal, is plotted in the inset of Fig. 4, and tentatively corroborates this picture.

We have discovered an anomalous enhancement of the polar TO phonon scattering cross section that occurs at a specific value of $q = 0.2$ Å^{-1}, independent of whether we measure along the [001] or [110] direction. We believe this to be direct microscopic evidence of the PMR proposed by Burns and Dacol [12]. The presence of such small polarized regions of the crystal above T_c should effectively prevent the propagation of long-wavelength ($q \rightarrow 0$) soft mode phonons. A similar conclusion was reached by Tsurumi *et al.* based on dielectric measurements of PMN [16]. The observation that the phonon scattering cross section is enhanced 0.2 Å^{-1} from the zone center gives a measure of the size of the PMR consistent with the estimates of Burns and Dacol. If true, then this unusual behavior should be observed in other related relaxor systems. Indeed, tentative evidence for this has already been observed at room temperature in neutron scattering measurements on PMN [17]. This enhancement should also be reflected in x-ray diffuse scattering intensities ([18,19]), although it may be masked by the superposition of strong acoustic modes.

Our picture is not yet complete. Whereas Fig. 3 demonstrates that these anomalies appear as ridges on top of a broad overdamped cross section, the complete nature of this cross section can only be revealed by an extensive contour map of the Brillouin zone, for which we lack sufficient data. Another important aspect which requires further study is exactly how the "waterfall" evolves, at much higher temperatures, into the standard optic mode dispersion as shown in Fig. 1 for PMN. We have not yet carried out this experiment because of the concern of possible crystal deterioration at these high temperatures under vacuum [3]. We intend to do so only after all other key experiments have been completed [20].

Our current picture suggests that the TO phonon dispersion should change if one alters the state of the PMR. It is known that a macro-ferroelectric phase can be created in these relaxor crystals by cooling the crystal in a field, or by application, at room temperature, of a sufficiently strong field. We are now planning neutron inelastic measurements on such a crystal, as well as on PZN.

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