Soft Mode Anomalies in the Perovskite Relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$

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Abstract. Room temperature neutron inelastic scattering measurements of the polar transverse optic (TO) phonon mode in the cubic relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) reveal anomalous behavior, similar to that recently observed in $Pb(Zn_{1/3}Nb_{2/3})_{0.92}Ti_{0.08}O_3$, in which the optic branch *appears* to drop precipitously into the acoustic branch at a finite value of the momentum transfer $q = 0.23$ Å^{-1}, measured from the zone center. By contrast, a recent neutron study indicates that PMN exhibits a normal TO phonon branch at much higher temperature (800 K). We thus speculate that this unusual feature is common to all relaxor materials at low temperatures, and is the result of the presence of nanometer-scale polarized domains in the crystal that form below a temperature T_d, which effectively prevent the propagation of long wavelength ($q = 0$) phonons.

INTRODUCTION

In the past year two neutron inelastic scattering studies have been published on single crystal specimens of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})_{0.92}Ti_{0.08}O_3$ (PZN-8%PT), which have the complex perovskite structures $A(B'B'')O_3$ and $A(B'B''B''')O_3$, respectively, in an attempt to elucidate the nature of the lattice dynamics in these relaxor-based systems [1,2]. Of particular interest to both studies was the soft phonon mode that is ubiquitous in ferroelectric and perovskite systems. The displacive structural phase transition in classical ferroelectric systems such as $PbTiO_3$, which has the simple ABO_3 perovskite structure, is driven by the condensation or softening of a zone-center transverse optic (TO) phonon, i. e. a "soft mode," that transforms the system from a cubic paraelectric phase to a tetragonal ferroelectric phase. Direct evidence of this soft mode behavior is easily obtained from neutron inelastic scattering measurements made at different temperatures above the Curie temperature T_c. The top panel of Fig. 1 shows, for example, the phonon dispersion of the lowest-energy TO branch in $PbTiO_3$ (PT) measured 20 K above T_c. Here one can see that the zone-center phonon ($\zeta = 0$ in Fig. 1), or soft mode energy has already dropped to a very low value of 3 meV [3]. As $T \rightarrow T_c$, the soft mode energy $\hbar\omega_o \propto (T - T_c)^{1/2} \rightarrow 0$.

In contrast to well-ordered perovskite systems such as $PbTiO_3$, the so-called "relaxor" systems possess a built-in disorder that stifles the ferroelectric transition. Instead of a sharp transition at T_c, PMN undergoes a "diffuse" phase transition in which the dielectric permittivity ϵ exhibits a broad maximum as a function of

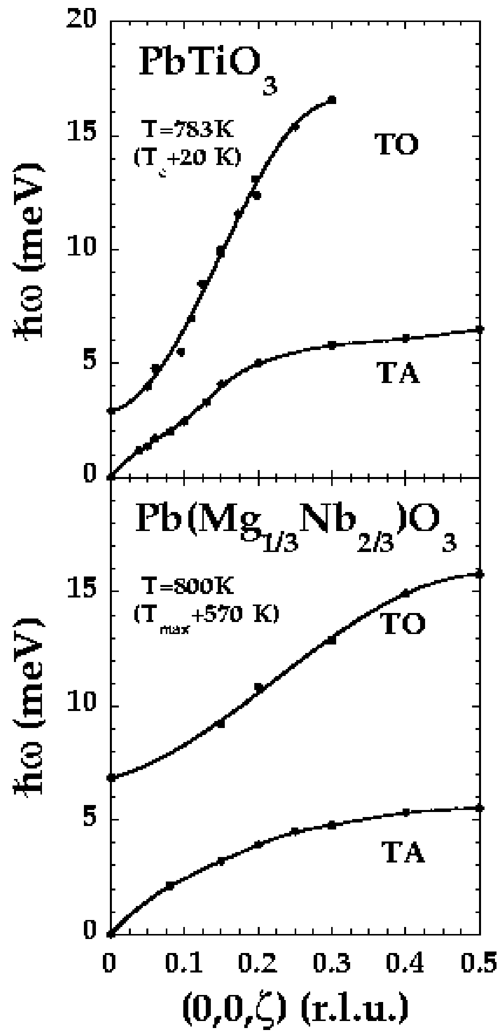

FIGURE 1. Top - Dispersions of the lowest-energy TO mode and the TA mode in $PbTiO_3$, measured just above T_c (from [3]). Bottom - Dispersions of the equivalent modes in PMN measured far above T_{max} (from [1]).

temperature at $T_{max} = 230$ K. The disorder in relaxors can be either compositional or frustrated in nature [4]. In the case of PMN and PZN (Z = Zn), the disorder is compositional and results from the B-site being occupied by ions of differing valence (either Mg^{2+} or Zn^{2+}, and Nb^{5+}). Hence the randomness of the B-site cation breaks the local translational symmetry of the crystal. Yet despite years of intensive research, the physics of the observed diffuse phase transition is still not well understood [5–7]. Moreover, it is interesting to note that no definitive evidence of a soft mode has been found in these systems.

In a series of papers published in 1983, Burns and Dacol proposed an elegant model to describe the disorder intrinsic to relaxor systems [8]. 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) as well as microscopically homogeneous single crystals of PMN and PZN [8], they demonstrated that a randomly-oriented local polarization P_d develops at a well-defined temperature T_d, often referred to as the Burns temperature, several hundred degrees above the apparent ferroelectric transition temperature T_c. The spatial extent of these locally polarized regions in the vicinity of T_d was conjectured to be $\sim$ several unit cells, and has given rise to the term "polar micro-regions," or PMR [9]. For PMN, the formation of the PMR occurs at $\sim$ 617 K [8], well above the temperature $T_{max} = 230$ K where the dielectric permittivity reaches a maximum [1]. Recently, using neutron inelastic scattering techniques, we have found striking anomalies in the lowest-energy 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 same nanometer-sized PMR.

SEARCH FOR A SOFT MODE IN PMN

Our phonon measurements on relaxor systems began with PMN at the NIST Center for Neutron Research (NCNR) in 1997. At that time many diffuse scattering studies of PMN using x-rays and neutrons had already been published [10,11]. However, there were no published neutron inelastic scattering measurements on PMN until the 1999 phonon study by Naberezhnov *et al* [1]. The bottom panel of Fig. 1 shows neutron scattering data taken by Naberezhnov *et al.* on PMN exactly analogous to those shown in the top panel for $PbTiO_3$, except that the PMN data were taken at 800 K, a temperature that is much higher relative to the transition temperature of PMN, i. e. $\sim$ 570 K above T_{max}.

The neutron scattering measurements presented here were performed at the NCNR using both the BT2 and BT9 triple-axis spectrometers. The (002) reflections of highly-oriented pyrolytic graphite (HOPG) crystals were used to monochromate and analyze the incident and scattered neutron beams. An HOPG transmission filter was used to eliminate higher-order neutron wavelengths. Inelastic measurements were made 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. Typical horizontal beam collimations used were $60'$-$40'$-$40'$-$80'$ and $40'$-$48'$-$48'$-$80'$. The single crystal of PMN used in this study measures 0.5 cm^3 in volume, and was the identical crystal used by Naberezhnov *et al* [1]. It was grown using the Chochralsky technique described elsewhere [1]. The crystal was mounted onto an aluminum holder and oriented in air with either the cubic $[\bar{1}10]$ or [001] axis vertical.

We used two types of scans to collect data. Constant energy (constant-E) 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 (TO) phonon modes were mapped out at room temperature (still in the cubic phase, but well below the Burns temperature $T_d \sim 617$ K).

In Fig. 2 we plot the positions of the peak in the scattered neutron intensity

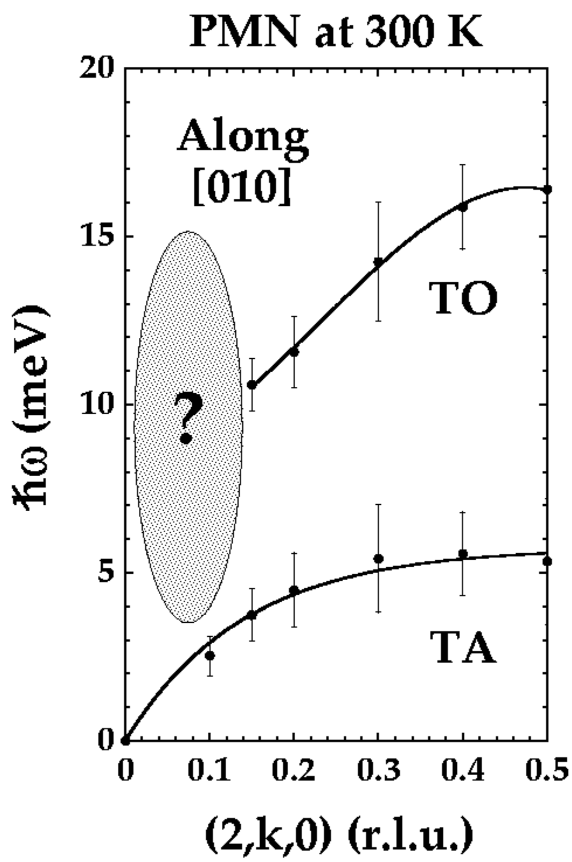

FIGURE 2. Solid dots represent positions of peak scattered neutron intensity taken from constant-$\vec{Q}$ scans at 300 K along the [010] symmetry direction. Vertical bars represent phonon FWHM linewidths in meV. Solid lines are guides to the eye indicating the TA and TO dispersion curves. Shaded area represents region of Brillouin zone where constant-$\vec{Q}$ scans showed no well-defined peaks.

taken from constant-$\vec{Q}$ scans at 300 K as a function of $\hbar\omega$ and $|\vec{q}| = k$. Here $\vec{q} = \vec{Q} - \vec{G}$ is the momentum transfer measured relative to the $\vec{G} = (2, 0, 0)$ Bragg reflection along the [010] symmetry direction. Limited data were also taken near $(3, 0, 0)$. The lengths of the vertical bars represent the measured phonon peak FWHM linewidths (full-width at half-maximum) in $\hbar\omega$ (meV), and were derived from Gaussian least-squares fits to the constant-$\vec{Q}$ scans. The lowest-energy data points trace out the TA phonon branch along [010], and solid lines have been drawn through these points as a guide to the eye. We see that the TA dispersion curve is essentially the same as that shown for PMN at 800 K in the bottom panel of Fig. 1.

It is also clear from the dispersion diagram presented in Fig. 2 that our room

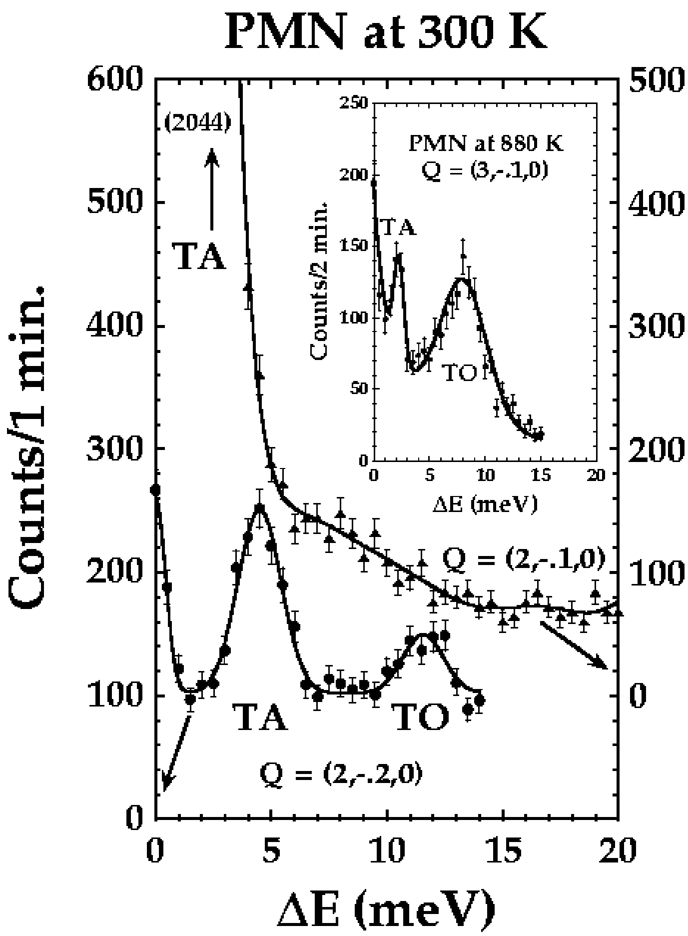

FIGURE 3. Data from constant-$\vec{Q}$ scans taken near (2,0,0) at 300 K. Lines are guides to the eye. The scan at $q = -0.2$ r.l.u. shows well-defined TA and TO modes. But at $q = -0.1$ r.l.u., only the TA peak is well-defined. The TO mode is strongly overdamped. The inset, however, shows data taken on the same crystal at the same q at 880 K in which the TO mode is clearly well-defined (from [12]).

temperature data show the same TO modes at high q as those reported at 800K by Naberezhnov *et al.* However the scattering intensities for this mode for $q \leq$ 0.15 r.l.u. (reciprocal lattice units) were scarcely above background at $(2, q, 0)$ as well as at $(3, q, 0)$. This is evident in Fig. 3 where two constant-$\vec{Q}$ scans, taken near (2,0,0) at 300 K, are shown. For q = -0.2 r.l.u. (1 r.l.u. = 2π/a = 1.553 Å^{-1}), we observe two well-defined peaks corresponding to scattering from the TA and TO modes. But for q = -0.1 r.l.u. only the TA mode is well-defined. The TO mode scattering is weak and broadly distributed in q. By contrast, the inset of Fig. 3 shows a very prominent peak in the scattering from the TO mode at the same q (-0.1 r.l.u.) taken on the same crystal (data from [12]), the only difference being that these data were taken at much higher temperature, i. e. 880 K. The differences between these two sets of data (880 K versus 300 K) remained a puzzle as we could not locate where the TO phonon scattering intensity had gone at room temperature, and so we were forced to abandon our search for the soft mode for the time being.

THE MORPHOTROPIC PHASE BOUNDARY AND PZN-8%PT

Our phonon studies of relaxor single crystals were subsequently resumed two years later from a very different perspective. The nearly vertical morphotropic phase boundary (MPB) in $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), plotted as temperature T against Ti concentration x, which separates the rhombohedral and tetragonal regions of the PZT phase diagram near a Ti concentration of 50%, had recently been reinvestigated by Noheda *et al* [13,14]. There they found a previously unknown monoclinic phase above 300 K that separates the tetragonal and rhombohedral phases. This was an exceedingly important discovery, and was extensively discussed in this conference [15], because the monoclinic phase forms a natural bridge between the tetragonal and rhombohedral phases, and sheds new light on possible explanations for the enhanced piezoelectric properties observed in PZT ceramics for compositions that lie close to the MPB.

Motivated by this result, Gehring, Park and Shirane realized that a very similar MPB boundary exists in $(1-x)$PZN-xPT around $x = 0.08$ [2]. These are solid solutions which exhibit even greater piezoelectric properties than are observed in PZT ceramics. Moreover, unlike the case of PZT, they can be grown into large high quality single crystals, ideal for neutron inelastic scattering studies. The soft phonons in $PbTiO_3$ (PT) had already been thoroughly characterized by Shirane *et al* [3]. Hence their idea was to study the phonons in $(1-x)$PZN-xPT at higher x, say 20% PT, and then trace the evolution of the transverse optic modes to 8% PT and PZN as a function of x. In this way it was hoped that the scattering associated with the missing optic branch at small q for PMN (at room temperature) could be located.

The neutron inelastic measurements on PZN-8%PT were performed at 500 K. By employing a combination of both constant-$\vec{Q}$ and constant-E scans, an anomalous enhancement of the scattering cross section was discovered between 0.10 r.l.u. $< |\vec{q}| <$ 0.15 r.l.u. [2]. This enhancement was located at a fixed q relative to the zone center over a large range of energy transfer extending from 4 meV to 9 meV. When plotted in the form of a standard "dispersion" diagram, the TO branch appears to fall precipitously into the acoustic branch. For this reason, this feature was referred to as a "waterfall", and is shown as the shaded region in the inset to Fig. 4.

It was conjectured that these waterfalls are caused by the polarized micro-regions first demonstrated by Burns and Dacol [8]. The existence of such polarized regions, which are of finite spatial extent, should effectively inhibit the propagation of the ferroelectric TO mode. Moreover, the size of these regions can be estimated as $2\pi/q$, which at 500 K corresponds to about 31 Å, or roughly 7 to 8 unit cells. This

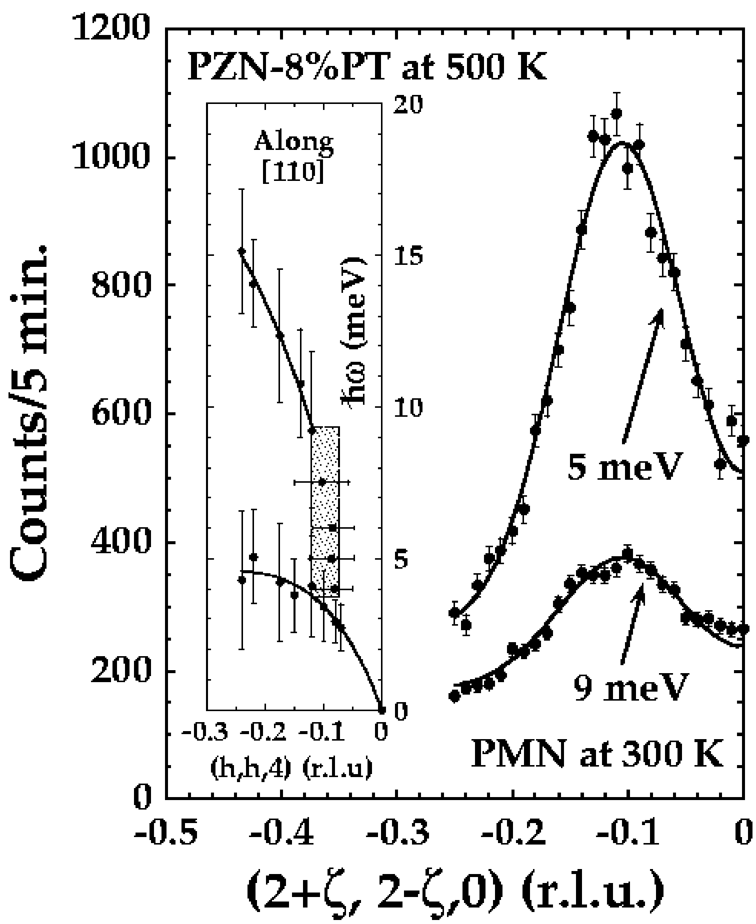

FIGURE 4. Two constant-E scans measured along [110] at 5 meV and 9 meV at 300 K. These scans demonstrate the presence of the same anomalous scattering that was observed in PZN-8%PT (shown in the inset, from [2]).

value is consistent with that put forth in the picture of Burns and Dacol.

At this point it was natural to ask whether or not the same anomalous "waterfall" was present in PMN below 800 K, as this would provide a natural explanation for the missing low-q portion of the optic branch in PMN at 300 K. Upon re-examining our old PMN data taken at room temperature, we found two constant-E scans at 5 and 9 meV which we had taken along the [110] direction near (2,2,0). These data, shown in the right hand portion of Fig. 4, clearly indicate the presence of an anomalous enhancement of the scattering intensity *at a fixed* q ($\zeta = -0.105$ r.l.u.), just as had been observed in the neutron scattering study of PZN-8%PT. Hence we conclude that the waterfall is also present in PMN. This can be seen simply by plotting the peak positions from these two constant-E scans in Fig. 2, using $k = \sqrt{2} \times |-0.105|$ r.l.u. $= 0.15$ r.l.u. to account for the fact that these data were taken along the [110] direction.

DISCUSSION AND INTERPRETATION

Naberezhnov *et al.* identified the normal-looking optic phonon branch at 800 K shown in Fig. 1 as a hard TO1 mode, and not as the ferroelectric soft mode, because the $\vec{Q}$-dependence of the associated dynamic structure factor was inconsistent with that expected for ferroelectric fluctuations, i. e. nearly no critical scattering was observed near the (2,2,0) Bragg peak in the vicinity of T_{max} [1]. On the other hand, the absence of critical fluctuations at (2,2,0) may simply mean that the eigenvectors for PMN are different from those of $PbTiO_3$. The lowest polar optic mode is still clearly present and well-defined at 880 K. At lower temperatures, using the same PMN single crystal, we observe an overdamped phonon scattering cross section in addition to this new anomalous scattering at small q below T_d, i. e. the waterfall. So the proper question to ask is whether or not this TO1 branch is the lowest-energy polar optic mode in PMN.

Before this point can be settled uniquely, more neutron measurements will be needed at temperatures both above and below T_d to show precisely how the anomalous scattering changes with temperature, that is, whether or not the waterfall evolves into the TO1 branch measured by Naberezhnov *et al.* at 880 K. For this purpose, constant-E scans will be of particular importance since, as we learned in 1997, the waterfall is not readily visible without them.

At present, our picture of PMN is that at high temperatures $T > T_d$ the system behaves like all other simple perovskites. When the polarized micro-regions are formed below the Burns temperature, the crystal behaves as a two-phase mixture from a lattice dynamical point of view. The PMR exhibit the anomalous waterfall as found in PZN-8%PT, whereas the non-PMR regions show a gradual change from the regular TO branch to one which is overdamped. These are shown very nicely in the constant-$\vec{Q}$ data of Vakhrushev *et al.* at $(3, q, 0)$ between 880 K and 450 K [12]. Consequently we believe that the study of Naberezhnov *et al.* properly characterized the coupled modes of PMN at small q, whereas the study of Gehring, Park and Shirane characterized the modes at intermediate q in which the highly unusual waterfall was discovered.

Future measurements are being planned to determine whether or not an applied electric field can influence the shape of the waterfall.

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