

# SOFT PHONON ANOMALIES IN RELAXOR FERROELECTRICS

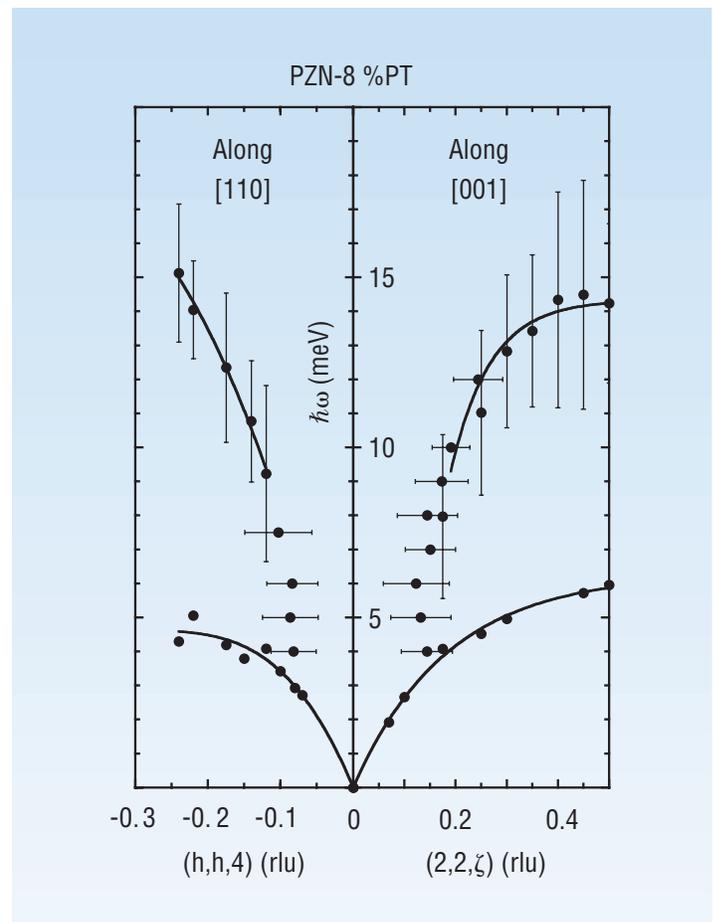
Our current phonon studies of ferroelectrics at the NCNR are part of a systematic investigation of  $ABO_3$  perovskite oxides that exhibit exceptionally high piezoelectric responses. Two solid solutions,  $(Pb[Zn_{1/3}Nb_{2/3}]O_3)_{1-x}(PbTiO_3)_x$  (PZN- $x$ PT) and  $(PbZrO_3)_{1-x}PbTiO_3$  (PZT) have been extensively investigated in recent years. A common feature of these two systems is the morphotropic phase boundary (MPB), which separates the tetragonal and rhombohedral regions of the  $T$ - $x$  phase diagram. The maximum piezoelectric activity is located on the rhombohedral side of the MPB for both systems. PZN- $x$ PT, however, can sustain ultrahigh strain levels, with  $< 1\%$  hysteretic loss, fully one order of magnitude larger than those attainable with conventional PZT-based piezoelectric ceramics. These two remarkable properties suggest that PZN- $x$ PT holds great promise for the next generation of solid-state transducers.

The compositions of the perovskite B-sites of PZN- $x$ PT and PZT differ in a key respect. Whereas an isovalent mixture of  $Zr^{4+}$  and  $Ti^{4+}$  ions occupies the PZT B-site, a more disparate group of heterovalent  $Zn^{2+}$ ,  $Ti^{4+}$ , and  $Nb^{5+}$  ions shares the PZN- $x$ PT B-site. This creates intense quenched random electric fields that are thought to produce the so-called relaxor phase, which is characterized by a diffuse phase transition and a broad and strongly dispersive peak in the dielectric susceptibility. Despite years of research, the physics of this diffuse phase transition is still not well understood. In prototypical ferroelectric systems such as  $PbTiO_3$ , it is well known that the softening of a zone-center transverse optic (TO) phonon drives the transition from a cubic paraelectric phase to a tetragonal ferroelectric phase. In relaxor compounds such as pure PZN, however, the mixed-valence character of the B-site sharply breaks the translational symmetry, resulting in much more complex lattice dynamics. In fact, no definitive evidence for a soft mode has been found in these relaxor systems.

Motivated by these results, we have examined the lattice dynamics of the polar TO phonon mode in a high quality single crystal of PZN-8 %PT, for which the measured value of the piezoelectric coefficient  $d_{33}$  is a maximum. Figure 1 shows neutron scattering data taken on PZN-8 %PT in its cubic phase at 500 K ( $\approx 50$  K above  $T_c$ ) [1]. The maximum scattered neutron intensity has been plotted as a function of energy transfer  $\hbar\omega$  and momentum

transfer  $q$  along the symmetry directions  $[110]$  and  $[001]$ . The lowest-energy data points trace out a normal TA phonon branch along both  $[110]$  and  $[001]$ . What is striking, however, is that Fig. 1 shows no evidence of a zone center TO mode at all. Instead, the data suggest a precipitous drop of the TO branch into the TA branch, somewhat resembling a waterfall. This anomalous feature is highlighted by the shaded regions in Fig. 1, and stands in marked contrast to the behavior of  $PbTiO_3$  where the same TO phonon branch intercepts the  $\hbar\omega$ -axis at a finite energy.

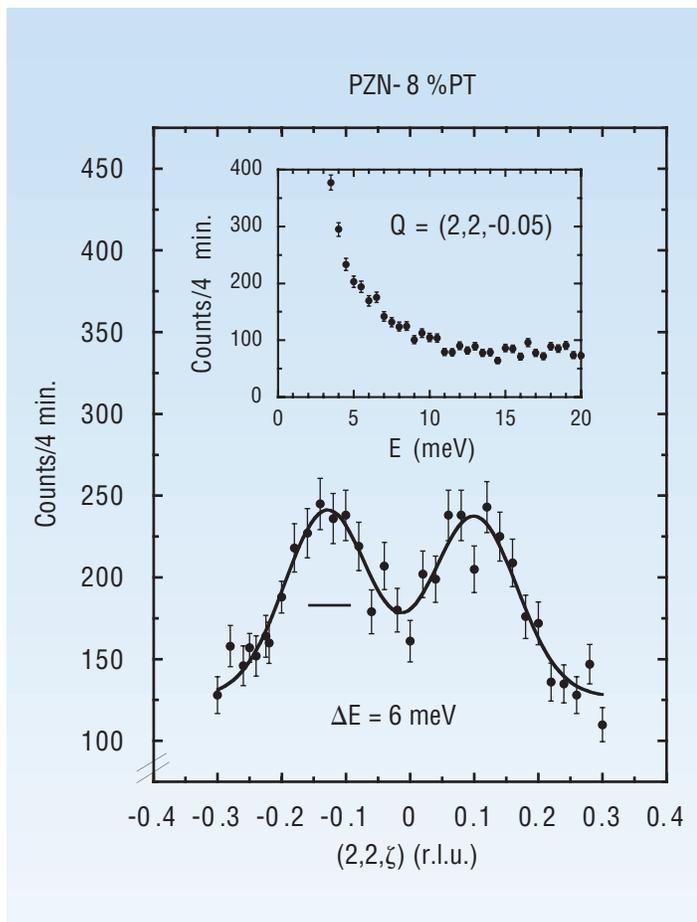
To clarify the nature of this unusual observation, we show a constant- $E$  scan at  $\hbar\omega = 6$  meV in Fig. 2 along with a constant- $Q$  scan in the insert [1]. Both scans were taken at 500 K near the (220) Bragg peak, and along the  $[001]$  direction. The small horizontal



**FIGURE 1.** Solid dots represent positions of peak scattered neutron intensity taken from constant- $Q$  and constant- $E$  scans at 500 K. Vertical (horizontal) bars represent phonon FWHM linewidths. Solid lines indicate TA and TO phonon dispersions.

bar shown under the left peak of the constant- $E$  scan represents the instrumental FWHM  $q$ -resolution. We see immediately that the constant- $Q$  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  $\zeta = 0.13$  r.l.u., or about  $0.2 \text{ \AA}^{-1}$ . Thus, the sharp drop in TO branch that appears to take place in Fig. 1 does not correspond to a real dispersion. Rather, it simply indicates a region of  $(\hbar\omega, q)$ -space in which the phonon scattering cross section is enhanced. The question remains why does this happen?

In 1983 Burns and Dacol proposed a seminal model for the disorder intrinsic to relaxor ferroelectrics [3]. Using measurements



**FIGURE 2.** Constant- $E$  scan measured along  $[001]$  at  $6 \text{ meV}$  at  $500 \text{ K}$  near the  $(220)$  Bragg peak. Solid line is a fit to a double Gaussian function of  $\zeta$ . No peak is discernible in the constant- $Q$  scan shown in the insert.

of the optic index of refraction on a variety of samples, including single crystals of PZN, they demonstrated that a randomly oriented local polarization  $P_d$  develops at a well-defined temperature  $T_d$  several hundred degrees *above* the transition temperature  $T_c$ . The origin of this local polarization, not present in normal ferroelectrics above  $T_c$ , was conjectured to arise from the formation of polarized micro-regions (PMR) of the crystal that are richer in  $\text{Nb}^{5+}$  than the average chemical formula.

The presence of such randomly oriented PMR above  $T_c$  in PZN-8 %PT should effectively impede the propagation of polar phonon modes whose wavelength exceeds the size of the PMR. The observation that the phonon scattering cross section is dramatically affected  $\approx 0.2 \text{ \AA}^{-1}$  from the zone center gives a measure of the dynamic size of these polarized domains. If the length scale associated with the anomalous “waterfall” is of order  $2\pi/q$ , this would correspond to  $31 \text{ \AA}$ , or about 7 to 8 unit cells, a size that is consistent with Burns and Dacol’s conjecture. We have recently been able to model this behavior quite well for PZN using a simple coupled-mode that assumes a highly  $q$ -dependent linewidth  $\Gamma(q)$  that increases sharply for  $q < 0.2 \text{ \AA}^{-1}$  [2]. Hence we speculate that the striking anomalies in the TO phonon branch shown in Fig. 1 (the same branch that goes soft at the zone center at  $T_c$  in  $\text{PbTiO}_3$ ) for  $q < 0.2 \text{ \AA}^{-1}$  are directly caused by these PMR which serve to dampen the zone center TO phonon modes. If true, then this unusual behavior should be observed in other related relaxor systems. Direct evidence for this has already been observed at room temperature in neutron scattering measurements on PMN ( $M = \text{Mg}$ ) [4].

## REFERENCES

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