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Soft Phonon Anomalies in Relaxor Ferroelectrics

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A review is given of the phonon anomalies, which have been termed "waterfalls," that were recently discovered through a series of neutron inelastic scattering measurements on the lead-oxide relaxor systems PZN-xPT, PMN, and PZN. We discuss a simple coupled-mode model that has been used successfully to describe the basic features of the waterfall, and which relates this unusual feature to the presence of polar micro-regions.

KEYWORDS: relaxor, ferroelectric, soft mode, neutron scattering, PMN, PZN, PZN-xPT, polar micro-regions

§1. Introduction

Our current phonon studies of relaxor ferroelectrics are part of a systematic investigation of perovskite oxides that have exceptionally high piezo responses. Two solid solutions, the phase diagrams for which are shown in Fig. 1, 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 ferroelectric phases. This boundary, particularly for $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), is nearly vertical against the concentration parameter x. In both cases the maximum piezo activity is located on the rhombohedral side of the MPB. A key difference between these two systems is the relaxor behavior of $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ (PZN-xPT), for which the B-site of the end member PZN is occupied by the heterovalent ions Zn^{2+} and Nb^{5+}. The mixed-valence character of the B-site produces unique relaxor properties such as dielectric relaxation, and the appearance of nanometer-sized polar domains in the cubic phase. Extensive x-ray scattering experiments have already been carried out to investigate the nature of the phase transitions near the MPB. Here we will review the current activity of neutron scattering studies of soft phonons in relaxor ferroelectrics.

The recent discovery of a monoclinic phase by Noheda *et al.* that intervenes between the rhombohedral and tetragonal phases (shown as the hatched region in Fig. 1) has suggested a new interpretation of the origin of the high piezoelectricity in PZT.[1)] This result lead to the further experimental study of poled ceramics by Guo *et al.*[2)] A subsequent first-principles calculation has given theoretical backing for the high piezo effect in the monoclinic phase which permits additional freedom for the polar ions that is not otherwise allowed in the other phases.[3)] The next stage of this investigation was to have been a dynamical study of this material, namely phonons. Unfortunately, however, large single crystals of PZT with compositions near the MPB are not available for phonon studies. Indeed, most work to date on this system has been limited to ceramic samples.

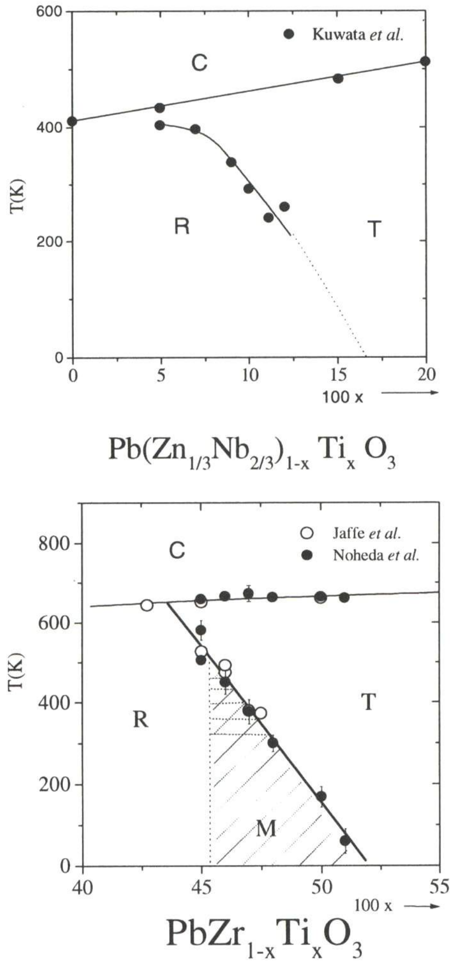

Fig. 1. Phase diagrams for the PZN-PT and PZT systems. The MPB is represented by the solid line between the rhombohedral and tetragonal phases. An intervening monoclinic phase has been discovered in PZT,[1)] and is speculated for PZN-PT.

On the other hand, Kuwata *et al.* produced, in 1982, large single crystals of the relaxor ferroelectric PZN-xPT.[4)] Neutron inelastic scattering studies on similar single crystals has resulted in the observation of a unique and unexpected phonon anomaly, the so-called "waterfall," by Gehring *et al.* for $x = 0.08$ (PZN-8%PT) which is shown in Fig. 2.[5] In this case, the polar transverse optic (TO) phonons appear to drop precipitously into the acoustic branch at a finite value of the reduced momentum transfer $q = 0.2$ Å^{-1}, measured from the zone center, thereby resembling a waterfall when plotted as a standard dispersion diagram. It was speculated that this behavior is the result of the nanometer-sized polar regions, also known as polar micro-regions (PMR),[6] that develop at temperatures far above T_c, a phenomenon first proposed by Burns and Dacol.[7]

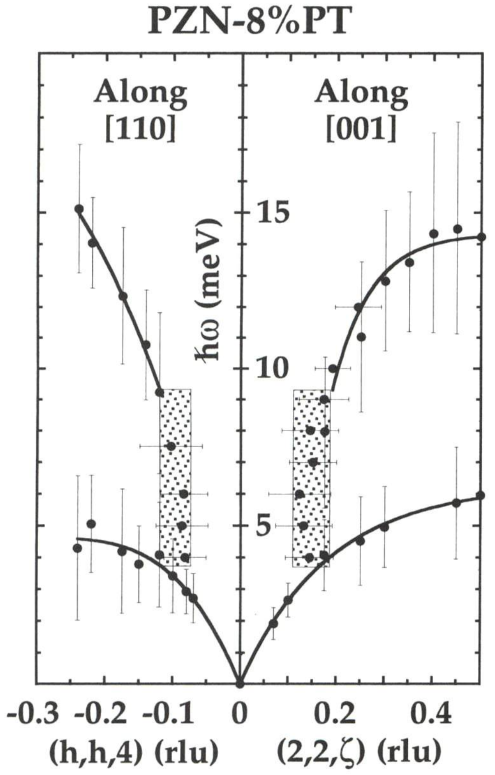

Fig. 2. Solid dots represent positions of peak scattered neutron intensity taken from constant-$\vec{Q}$ and constant-E scans at 500 K along both [110] and [001] symmetry directions. Vertical (horizontal) bars represent phonon FWHM linewidths in $\hbar\omega$ (q). Solid lines are guides to the eye indicating the TA and TO phonon dispersions. (From ref. 5.)

In this review article, we compare previous phonon measurements in PMN ($Pb(Mg_{1/3}Nb_{2/3})O_3$)[8,9] and PZN-8%PT,[5] as well as current work on pure PZN.[10] Very recently, a simple coupled-mode model was proposed to relate the waterfall to the PMR.[10] We begin with a survey of the relaxor properties of PMN, perhaps the most typical and well-studied of the relaxor ferroelectrics.

§2. PMN - $Pb(Mg_{1/3}Nb_{2/3})O_3$

PMN is considered the prototypical relaxor compound, and has been studied using a wide variety of different experimental techniques. The real part of the dielectric susceptibility ϵ' exhibits a broad peak at a temperature $T_{max} = 230$ K that shifts to higher temperature with increasing frequency. The crystal structure remains cubic down to 10 K;[11] it exhibits a polar ferroelectric phase around 212 K only when cooled under electric field.[12] In this respect PMN is very different from PZN which undergoes a cubic – rhombohedral phase transition around 410 K, as shown in Fig. 1. In 1983 Burns and Dacol proposed a seminal model of the disorder intrinsic to relaxors.[7] Using measurements of the optic index of refraction, they demonstrated that a randomly-oriented local polarization P_d develops in the form of polar micro-regions (PMR), at a well defined temperature T_d. This temperature, often referred to as the Burns temperature, is about 610 K for PMN,[7] and is much higher than T_{max} = 230 K.

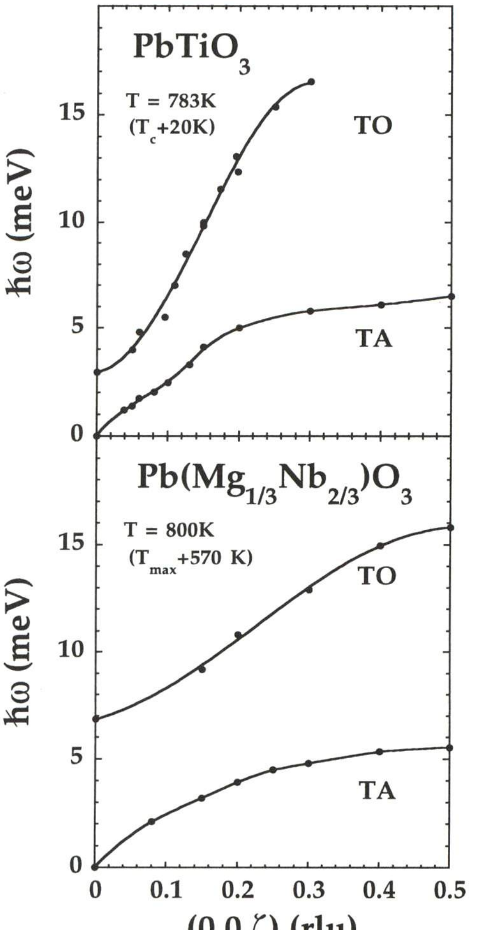

Fig. 3. Top - Dispersion of the lowest energy TO mode and the TA mode in $PbTiO_3$, measured just above T_c (from ref. 13). Bottom - Dispersion curves of the equivalent modes in PMN measured far above T_{max} (from ref. 8).

An extensive study of the low-frequency (< 16 meV) phonons in PMN was first reported by Naberezhnov *et al.*[8] They covered a wide temperature range from 500 K to 900 K, thereby spanning both sides of the Burns temperature T_d = 610 K. Data were collected for small q where the optic mode is overdamped, and the analysis was done assuming a coupled-mode description. Their phonon dispersion curves measured at 800 K are shown in Fig. 3 together with analogous data for $PbTiO_3$.[13] The transverse optic mode TO (referred to as TO1) appears to be the expected soft mode branch common to all other ferroelectric oxides. However, the assumption was made for PMN that the TO1 branch could not be the same soft mode branch because the Q-dependence of the structure factor was inconsistent with that expected for the ferroelectric fluctuations. This assumption does not appear to be justified as we will demonstrate later. (Naberezhnov *et al.* introduced a fictitious QO branch that was derived solely from the overdamped mode in the context of their mode-coupling analysis.) The series of neutron measurements summarized in this review demonstrate that the normal TO phonon branch of PMN, shown in Fig. 3, actually transforms into the waterfall below the Burns temperature.

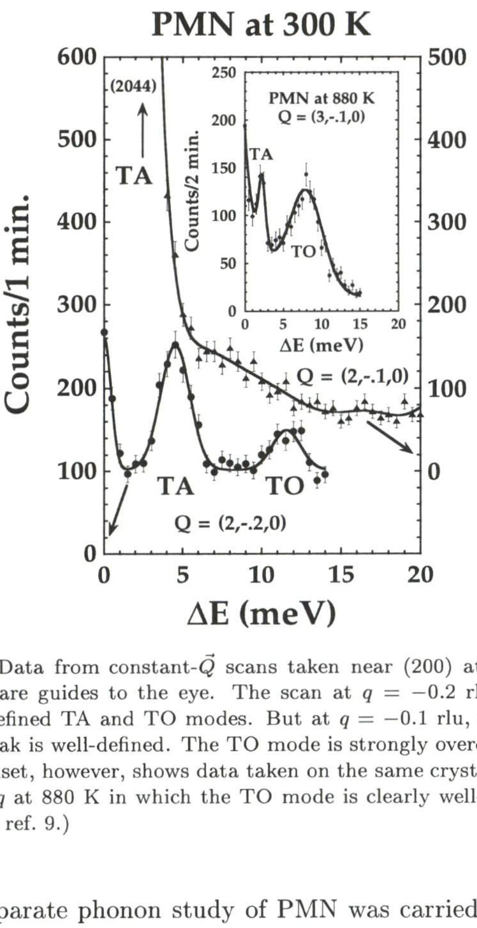

Fig. 4. Data from constant-$\vec{Q}$ scans taken near (200) at 300 K. Lines are guides to the eye. The scan at $q = -0.2$ rlu shows well-defined TA and TO modes. But at $q = -0.1$ rlu, only the TA peak is well-defined. The TO mode is strongly overdamped. The inset, however, shows data taken on the same crystal at the same q at 880 K in which the TO mode is clearly well-defined. (From ref. 9.)

A separate phonon study of PMN was carried out at room temperature at the NIST Center for Neutron Research in 1997, and some of the results are shown in Fig. 4.[9] These data were collected prior to the discovery of the waterfall in PZN−8%PT shown in Fig. 2. In marked contrast to the normal constant-$\vec{Q}$ scan in PMN observed by Naberezhnov *et al.* at 880 K, shown in the inset to Fig. 4, for which well-defined peaks are clearly visible for both the TA and TO modes, the TO phonon cross section for $q = -0.10$ rlu is mysteriously absent at 300 K. Only after the discovery of the waterfall in PZN−8%PT was it realized that the same anomaly was present in PMN as well, and was the cause of the missing TO branch at low q and low temperature. PMN, it should be mentioned, possesses the advantage of having a relatively low Burns temperature compared to that of other relaxors. Hence the optic modes in PMN can be studied above T_d, in the absence of any PMR. The PZN system, on the other hand, decomposes near its (higher) Burns temperature.

§3. Model Description of the Waterfall

Phonon measurements on relaxors have since been extended to pure PZN, the x=0 end member compound shown in the PZN-xPT phase diagram in Fig. 1. During the course of these experiments, a simple but effective model for the anomalous waterfall was developed. We will describe this model now before we present the new results from the detailed study of the phonon cross sections in PZN.[10] In the case of neutron energy loss, the scattering intensity distribution I for two interacting modes with frequencies Ω_1 and Ω_2, and widths Γ_1 and Γ_2, is given by the expression[15]

$$I \sim [n(\omega)+1]\frac{\omega}{A^2+\omega^2B^2}\times \\ ([(\Omega_2^2-\omega^2)B-\Gamma_2A]F_1^2+2\lambda BF_1F_2+ \\ [(\Omega_1^2-\omega^2)B-\Gamma_1A]F_2^2), \tag{3.1}$$

where A and B are given by

$$A=(\Omega_1^2-\omega^2)(\Omega_2^2-\omega^2)-\omega^2\Gamma_1\Gamma_2, \\ B=\Gamma_1(\Omega_2^2-\omega^2)+\Gamma_2(\Omega_1^2-\omega^2), \tag{3.2}$$

and $n(\omega)$ is simply the Bose factor $[e^{(\omega/k_BT)}-1]^{-1}$. The quantities $F_{1,2}$ are the structure factors of modes 1 and 2, and λ is the coupling strength between the two modes. This equation has been shown to decribe the behavior of coupled-phonon cross sections quite well.[10,14,15]

The essential physics behind the mode-coupled description of the low-frequency dynamics of relaxor ferroelectrics is built into the linewidth of the optic mode Γ_1, which is assumed to become sharply q-dependent when the polar micro-regions are formed at the Burn's temperature T_d. If we suppose that the PMR have an average diameter given by $2\pi/q_{wf}$, where q_{wf} represents the reciprocal space position of the waterfall, then those optic phonons having $q < q_{wf}$ will not be able to propagate easily because their wavelength exceeds the average size of the PMR. These polar lattice vibrations are effectively impeded by the boundary of the PMR. The simplest way to simulate this situation is to assume a sudden and steep increase in Γ_1 at q_{wf}. Fig. 5 shows several model constant-$\vec{Q}$ simulations based on this assumption using the value $q_{wf} = 0.15$ rlu.[10,16] For simplicity, the dispersions of both optic and acoustic modes were ignored by holding the parameters $\Omega_{1,2}$ fixed at 10 and 5 meV, respectively, over the entire Brillouin zone.

For $q > q_{wf}$ one observes two broad peaks, as expected. At momentum transfers q below q_{wf}, however, the optic mode becomes highly overdamped and its profile extends in energy below that of the acoustic mode.

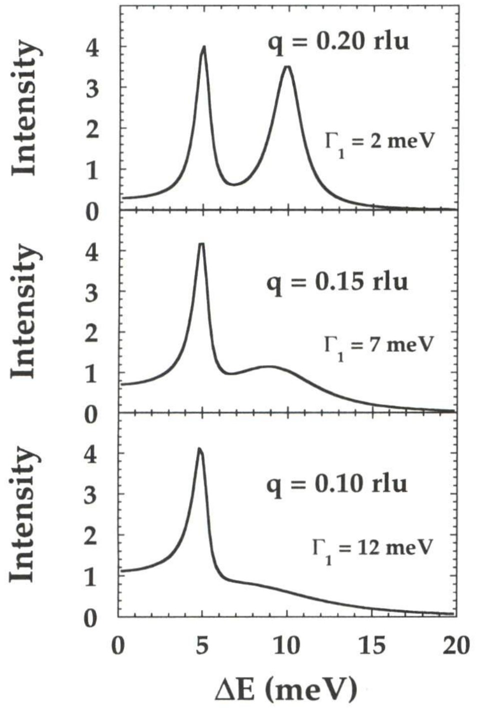

Fig. 5. Model simulations assuming a coupled-mode intensity distribution and a strongly q-dependent TO phonon linewidth Γ_1. Three constant-$\vec{Q}$ scans are shown corresponding to $q = 0.20$, 0.15, and 0.10 rlu, with $q = 0.15$ rlu representing the reciprocal space position of the anomalous waterfall feature.[10,16]

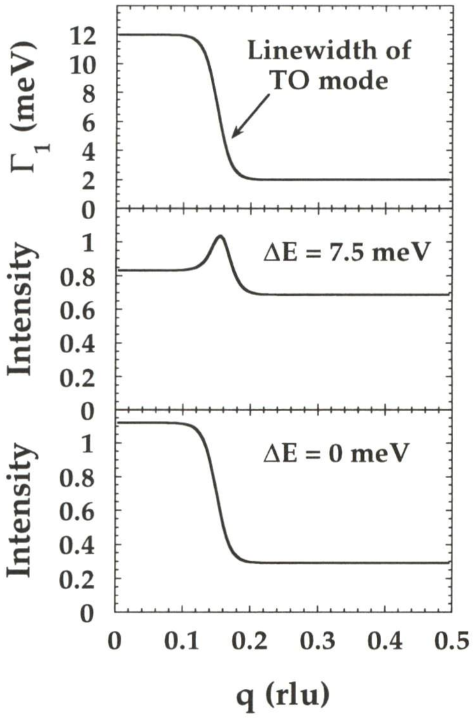

Fig. 6. Model simulations of two constant-E scans at 0 and 7.5 meV. The q-dependence of the TO linewidth Γ_1 is shown in the top panel for ease of comparison.[10,16]

Alongside each constant-$\vec{Q}$ scan is shown the corresponding value of Γ_1 used in the simulation. The waterfall thus represents the crossover between a high-q regime, in which one observes two well-defined peaks corresponding to two propagating modes, and a low-q regime, in which one observes an overdamped optic mode plus an acoustic peak. This simple model cross section describes all of the experimental observations very well. Indeed, one can favorably compare the simulated scan at $q = 0.10$ rlu in Fig. 5 with the corresponding experimental scan shown in Fig. 4. One can see now that the waterfall is not actually an enhancement of the phonon scattering cross section. Instead, it is simply a redistribution of the optic mode profile that is caused by the polar microregions which induce a sudden change in the optic mode linewidth at a specific q that is related to the average size of the PMR. In order to illustrate the basic characteristics of the coupled-mode model scattering cross section, the q-dependence of the optic mode linewidth Γ_1 is shown in Fig. 6 along with two simulated constant-E scans at 0 and 7.5 meV. It is apparent that the sharp increase in Γ_1 has a pronounced effect on both cross sections in the vicinity of $q_{\rm wf}$.

§4. PZN - $Pb(Zn_{1/3}Nb_{2/3})O_3$

Extensive surveys of the phonon profiles in pure PZN have now been completed. Two large, high quality single crystals, weighing 4.4 and 2.3 grams, were examined and gave identical results. These crystals were mounted in the ($hk0$) zone, and the data were taken on the BT2 triple-axis spectrometer located at the NIST Center for Neutron Research. At low temperatures a neutron energy loss configuration was used with a fixed final energy of 14.7 meV, whereas a neutron energy gain configuration with a fixed incident energy of 14.7 meV was employed at high temperatures. PZN has a cubic-to-rhombohedral phase transition around 410 K, so data were collected at 500 K, well above the ferroelectric transition. Fig. 7 shows several typical constant-E scans at 500 K for the 4.4 gram PZN crystal. Both the −6 and −8 meV (negative for neutron energy gain) scans are centered at the same q, namely $q_{\rm wf}$, indicating the presence of the waterfall anomaly in PZN. These two scans are to be compared to the 7.5 meV scan shown in Fig. 6. At a higher energy transfer of −12 meV, the scattering has shifted to higher $q > q_{\rm wf}$, and one recovers a normal propagating TO mode.

In order to produce a detailed contour map of the scattering intensity in the cubic phase, constant-$\vec{Q}$ scans were taken in 0.04 rlu steps across the entire Brillouin zone near (200). The results are shown in Fig. 8. A constant background has been subtracted from the data, and the resulting intensities placed on a logarithmic color scale. Both the TO and TA phonon branches are clearly visible above $q_{\rm wf} \sim 0.14$ rlu. At $q_{\rm wf}$, however, the waterfall is readily visible as the broad vertical red feature that appears to drop into the TA phonon branch. The TA mode appears saturated (yellow color) below 5 meV only because the intensities displayed in Fig. 8 were limited in their range to better show the waterfall.

An attempt to measure the high-temperature ($T > T_{\rm d}$) limiting behavior of phonons for $q < q_{\rm wf}$ was made using PZN−8%PT.[5] Unfortunately, due to the high Burns temperature for PZN, it was not possible to reach

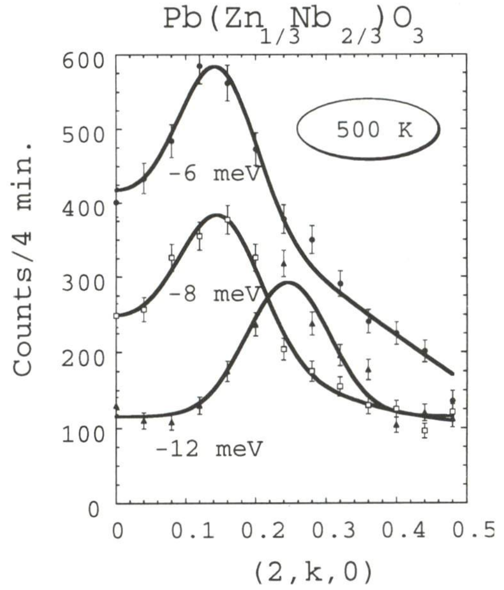

Fig. 7. Three constant-E scans taken on PZN at 500 K using neutron energy gain. The scans at −6 and −8 meV are centered at the same q, indicating the presence of the waterfall. The −12 meV scan is shifted to higher q and lies outside the waterfall region.

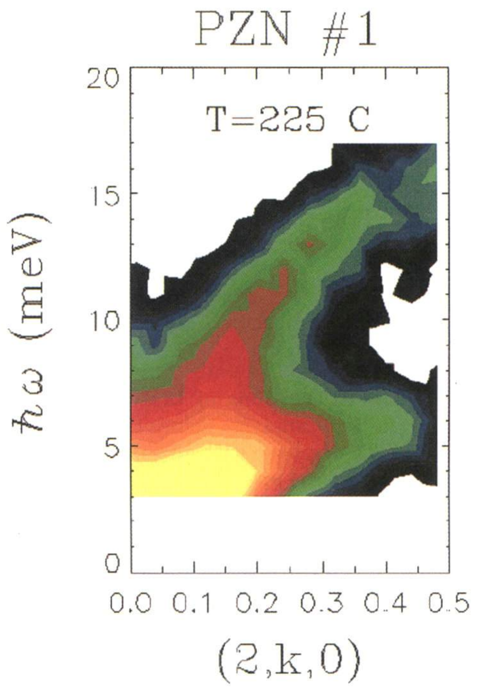

Fig. 8. Contour map of the background subtracted scattering intensity from PZN at 500 K measured near (200). The intensity is indicated by a logarithmic color scale that is limited to a narrow range in order to better show the waterfall. Yellow is the most intense.

sufficiently high temperatures to recover a normal TO phonon dispersion; at present PMN appears to offer the best chance to study this aspect of the waterfall problem. In the case of PZN, the evolution of the phonons through the phase transition at 410 K and to lower temperatures have been investigated.[10] The intensity of the anomalous waterfall decreases gradually through the phase transition and almost disappears at 150 K. At the same time a normal optic mode near q=0 is recovered at 11 meV. At present this result is interpreted to mean that the polar micro-regions have become sufficiently large at low temperatures to permit the propagation of long-wavelength optic modes.

Our current experimental results give a good estimate of the linewidth of the optical branch as a function of q. The simplest model identifies the q for the waterfall with the average size of the PMR. A more sophisticated theoretical model is clearly needed to relate the distribution of sizes of the PMR to the observed phonon profiles. Currently we are examing the effects of an applied electric-field on the waterfall and low-q phonons to determine the effect of the field on the PMR.

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