Recent neutron scattering measurements performed on the relaxor ferroelectric Pb[(Zn$_{1/3}$Nb$_{2/3}$)$_{0.92}$Ti$_{0.08}$]O$_3$ (PZN-8% PT) in its cubic phase at 500 K, have revealed an anomalous ridge of inelastic scattering centered $\sim$ 0.2 Å$^{-1}$ from the zone center (Gehring et al., Phys. Rev. Lett. 84, 5216 (2000)). This ridge of scattering resembles a waterfall when plotted as a phonon dispersion diagram, and extends vertically from the transverse acoustic (TA) branch near 4 meV to the transverse optic (TO) branch near 9 meV. No zone center optic mode was found. We report new results from an extensive neutron scattering study of pure PZN that exhibits the same waterfall feature. We are able to model the dynamics of the waterfall using a simple coupled-mode model that assumes a strongly q-dependent optic mode linewidth $\Gamma(q)$ that increases sharply near 0.2 Å$^{-1}$ as one approaches the zone center. This model was motivated by the results of Burns and Dacol in 1983, who observed the formation of a randomly-oriented local polarization in PZN at temperatures far above its ferroelectric phase transition temperature. The dramatic increase in $\Gamma_1$ is believed to occur when the wavelength of the optic mode becomes comparable to the size of the small polarized micro-regions (PMR) associated with this randomly-oriented local polarization, with the consequence that longer wavelength optic modes cannot propagate and become overdamped. Below $T_c = 410$ K, the intensity of the waterfall diminishes. At lowest temperatures ($\sim 30$ K) the waterfall is absent, and we observe the recovery of a zone center transverse optic mode near 10.5 meV.

I. INTRODUCTION

Scientific research in the field of relaxor ferroelectrics has surged markedly over the past several years. Perhaps the primary driving force behind the rapidly increasing number of publications in this area has been the observation of an exceptionally large piezoelectric response in single crystals of the two complex perovskite systems Pb[(M$_{2/3}$Nb$_{1/3}$)$_{1-x}$Ti$_x$]O$_3$ (PMN-xPT) and Pb[(Zn$_{1/3}$Nb$_{2/3}$)$_{1-x}$Ti$_x$]O$_3$ (PZN-xPT) for compositions $x$ that lie near the morphotropic phase boundary (MPB), which separates the rhombohedral and tetragonal regions of the phase diagram. These systems differ from the classic and well-studied simple perovskite $ABO_3$ compounds by virtue of the mixed-valence character of the B-site cation. In the case of PMN and PZN ($x=0$), the B-site is occupied by either Mg$^{2+}$ or Zn$^{2+}$, and Nb$^{5+}$ ions with a stoichiometry of 1/3 and 2/3, respectively, which is required to preserve charge neutrality. This built-in disorder sharply breaks the translational symmetry of the lattice and produces a so-called “diffuse” phase transition in which the dielectric permittivity $\epsilon$ exhibits a very large and broad peak at a characteristic temperature $T_{\text{max}}$ that is also strongly frequency-dependent. In contrast to the normal ferroelectric parent compound PbTiO$_3$ (PT), in which the condensation of a transverse optic (TO) zone center phonon leads to a transition from a cubic paraelectric phase to a tetragonal long-range ordered state with a non-vanishing spontaneous polarization below a critical temperature $T_c = 763$ K, the prototype relaxor compound PMN exhibits a diffuse transition at $T_{\text{max}} = 230$ K and no spontaneous polarization at any temperature studied.

Stimulated by the unusual properties of these complex systems, we performed a recent neutron inelastic scattering study to examine the lattice dynamics of a high-quality single crystal of PZN-8%PT, the composition for which the piezoelectric response is largest in the PZN-xPT system. The PZN-xPT phase diagram as a function of PT concentration $x$ is shown in Fig. 1. The maximum piezoelectric activity occurs on the rhombohedral side of the MPB, which is indicated by the steep dashed line. Our measurements of the phonon dispersion of the polar TO mode in the cubic phase at 500 K revealed an unexpected ridge of scattering centered at a momentum transfer $q = 0.2$ Å$^{-1}$, measured from the zone center. The ridge extends in energy from $\sim$ 4 meV to 9 meV such that, when plotted as a standard phonon dispersion diagram, it resembles a waterfall in which the TO branch appears to drop precipitously into the transverse acoustic (TA) branch. This anomalous feature, hereafter referred to as the waterfall, was observed in both of the two Brik-louin zones we surveyed (2,2,l) and (h,h,4), which cover the two different symmetry directions [001] and [110]. Similar data taken on a large single crystal of pure PMN at room temperature also showed the presence of a waterfall, suggesting that this feature may be common to all relaxor systems.\[\]
Further evidence in support of our picture correlating the waterfall with the appearance of the PMR comes from the neutron inelastic scattering data of Naberezhnov et al. As shown in Fig. 2, they observed a normal TO and TA phonon dispersion in the closely related relaxor ferroelectric compound PMN at 800 K > T_d = 617 K, where no polar regions remain. Their data were obtained on the same crystal we studied at room temperature where the waterfall was observed. For PZN-8%PT, the formation of the PMR is estimated to occur at T_d ~ 790 K, which is well above the cubic-to-tetragonal phase transition at T_c ~ 450 K, and also beyond the temperature at which the crystal begins to decompose.

In this paper we present a more complete lattice dynamical study of pure PZN, in which we also observe an anomalous ridge of scattering that closely resembles the waterfall seen in PZN-8%PT and PMN. PZN differs from PMN in that it exhibits an explicit structural phase transformation at 410 K from cubic to tetragonal symmetry. The value of T_max for PZN is just slightly above T_c = 410 K, and thus much higher than T_max = 230 K for PMN. We further present a simple mode-coupling model that clearly relates this unusual feature of the TO phonon branch (the same branch that goes soft at the zone center at T_c in PbTiO_3) to the PMR. Our current study does not, however, cover the critical scattering at
small \( q \) below 0.075 Å\(^{-1}\). Extensive studies in this area have already been carried out using neutron and x-ray scattering techniques. As we will show, this is the portion of the Brillouin zone where the TO mode is over-damped because of the PMR.

II. EXPERIMENTAL

Two single crystals of PZN were used in this study, the first, labelled PZN#1, weighs 4.2 grams and the second, labelled PZN#2, weighs 2.3 grams. Both crystals were grown using the high-temperature flux technique described elsewhere. Each crystal was mounted onto an aluminum holder and oriented with the cubic [001] axis vertical, thereby giving access to the \((H0K0)\) scattering zone. They were then placed inside a vacuum furnace capable of reaching temperatures of up to 900 K. For temperatures below room temperature, a specially designed closed-cycle helium refrigerator was used to cover the range from 25 K to 670 K.

All of the neutron scattering data presented here were obtained on the BT2 triple-axis spectrometer 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 holding the incident neutron energy \( E_i \) fixed at 14.7 meV \((\lambda_i = 2.36 \text{ Å})\) while varying the final neutron energy \( E_f \), and using horizontal beam collimations of 60’-40’-S-40’-40’ and 60’-40’-S-40’-open.

Two basic types of inelastic scans were used to collect data on each sample. Constant-\( E \) scans were performed by holding 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 \( \Delta E \). Using a combination of these scans, the dispersions of both the TA and the lowest-energy TO phonon modes were mapped out at a temperature of 500 K (still in the cubic phase, but well below the Burns temperature for PZN of \( T_d \sim 750 \) K).

It is worthwhile to note that the high temperature data were taken using neutron energy gain, i.e. by scanning \( E_f \) such that the energy transfer \( \hbar \omega < 0 \). This process is known as phonon annihilation. At high temperatures, and not too large energies, the phonon thermal population factor makes this mode of operation feasible. More importantly, the instrumental energy resolution function contains the factor \( \cot 2\theta_a \), where \( 2\theta_a \) is the analyzer (HOPG) scattering angle. Hence the energy resolution increases with increasing energy because \( 2\theta_a \) decreases. The net result is an increased neutron count rate at the expense of a broader linewidth, thereby making the relatively weaker transverse optic mode easier to see.

III. INELASTIC SCATTERING DATA FROM PZN NEAR \( Q = (2,0,0) \)

The waterfall, previously reported in PZN-8\%PT, is shown for PZN#1 at 500 K in Fig. 3. The data points represent the peak scattered neutron intensity plotted as a function of \( \hbar \omega \) and \( \vec{q} \), where \( \vec{q} = \vec{Q} - \vec{G} \) is the momentum transfer relative to the \( \vec{G} = (2,0,0) \) Bragg reflection, measured along the cubic [010] symmetry direction. The solid dots represent data from constant-\( \vec{Q} \) scans whereas the two open circles are data derived from constant-\( E \) scans. These latter two data points signal the onset of the waterfall regime in which the TO phonon branch appears to dive into the TA branch, and are thus connected by a dashed line. The lowest-energy data points trace out the TA phonon branch along [010]. Solid lines are drawn through these points as a guide to the eye, and are nearly identical to those shown for PMN in Fig. 1.

![Figure 3](image-url)
values correspond to phonon annihilation as described above). We note that both of the -6 and -8 meV scans are peaked at the same value of \( k = q \), thereby indicating the presence of the waterfall. Remarkably, the 0 meV cross section exhibits an enormous change in the vicinity of the waterfall \( q \)-vector. This demonstrates that the effects of the PMR extend in energy all the way from the TO branch through the TA branch and into the elastic channel. The -12 meV scan, by contrast, peaks at a larger momentum transfer \( q \sim 0.24 \text{ rlu} \) that lies outside the waterfall regime, and instead represents a genuinely propagating TO phonon mode.

To illustrate this behavior as clearly as possible, a series of constant-\( \vec{Q} \) scans were collected in steps of 0.04 rlu along \((2, k, 0)\) that spanned the entire Brillouin zone. After subtraction of a constant background, the data have been plotted as a contour plot in Fig. 6. For ease of comparison, the contour plot has been drawn with the same vertical and horizontal scales used in Fig.'s 2 and 3. The intensity data are represented on a logarithmic color scale with yellow representing the highest intensity, and black the lowest. At large \( q \) near the zone boundary, the TO and TA phonon branches are readily apparent as broad green features. Near the waterfall regime, the TO branch appears to drop almost vertically into the TA branch with a corresponding increase in intensity. Below \( q \sim 0.14 \text{ rlu} \), the intensity contours show no peak (scanning vertically) that could correspond to a propagating mode. The acoustic mode looks to be flat below 4 meV only because the color scale covers a limited intensity range above which all data are colored yellow. The intensity range was limited on purpose to make the waterfall feature more visible. Even so, one can notice a very rapid increase in the TA phonon intensity in the vicinity of the waterfall, suggesting that a transfer of intensity might be occurring between the TO and TA modes. To examine this possibility, we performed model calculations using a simple mode-coupling scheme to attempt to simulate the anomalous features reported here in the PZN compound.

![Fig. 4. Constant-\( E \) scans at 0, -6, -8, and -12 meV (phonon annihilation) measured at 500 K on PZN crystal #1.](image)

![Fig. 5. Constant-\( \vec{Q} \) scans at 0.00, 0.24, 0.28, and 0.48 rlu measured at 500 K on PZN crystal #1.](image)
IV. MODE-COUPLING MODEL

During the course of our experiments on relaxor ferroelectrics, a simple but effective model describing the anomalous low-frequency lattice dynamics was developed assuming a coupling between the TO and TA phonon modes. For the case of neutron energy loss, the scattering intensity distribution $I$ for two interacting modes with frequencies $\Omega_1$ and $\Omega_2$, and widths $\Gamma_1$ and $\Gamma_2$, is given by the expression

$$I \sim \left[ n(\omega) \right] \frac{\omega}{A^2 + \omega^2 B^2} \times \left( [(\Omega_2^2 - \omega^2) - \Gamma_2 A] F_2^2 + 2\lambda B F_1 F_2 + [(\Omega_1^2 - \omega^2) - \Gamma_1 A] F_1^2 \right),$$

(1)

where $A$ and $B$ are given by

$$A = (\Omega_1^2 - \omega^2)(\Omega_2^2 - \omega^2) - \omega^2 \Gamma_1 \Gamma_2,$$

$$B = \Gamma_1 (\Omega_2^2 - \omega^2) + \Gamma_2 (\Omega_1^2 - \omega^2),$$

(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 $\lambda$ is the coupling strength between the two modes. Extensive model calculations based on this equation, which has been shown to describe the behavior of coupled-phonon cross sections quite well, have been performed in collaboration with K. Ohwada at the Institute of Solid State Physics, University of Tokyo.

Fig. 6. 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.

Fig. 7. Model simulations assuming a coupled-mode intensity distribution and a strongly $q$-dependent TO phonon linewidth $\Gamma_1$. Three constant-$Q$ scans are shown corresponding to $q = 0.20$, 0.15, and 0.10 rlu, with $q = 0.15$ rlu taken to be the reciprocal space position of the anomalous waterfall feature.

The essential physics behind the mode-coupled model description of the waterfall is built into the linewidth of the TO mode $\Gamma_1$, which is assumed to become sharply $q$-dependent as the polar micro-regions begin to form 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. This idea has also been discussed by Tsurumi et al. The simplest way to simulate this situation is to assume a sudden and steep increase in $\Gamma_1(q)$ at $q_{wf}$. For this purpose, a Fermi-distribution function of $q$ works extremely well. Fig. 7 shows several model constant-$Q$ simulations based on this assumption, using the values $q_{wf} = 0.15$ rlu, $\lambda = 10$, $F_1 = 1$, $F_2 = 4$, and $\Gamma_2 = 1$. For
simplicity and purposes of illustration, 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. Similarly, instrumental resolution effects were not included.

For $q > q_{\text{wf}}$ one observes two broad peaks, as expected. At momentum transfers $q < q_{\text{wf}}$, however, the optic mode becomes highly overdamped and its profile extends in energy below that of the acoustic mode. Alongside each constant-$\vec{Q}$ scan is shown the corresponding value of $\Gamma_1$ 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 $q = 0.15$ rlu in Fig. 7 with the experimental scan for $\vec{Q} = (2,0.16,0)$ shown in Fig. 5. One can see now that the waterfall is not a TO phonon dispersion at all. Instead, it is simply a redistribution of the optic mode profile that is caused by the PMR which force a sudden change in the optic mode linewidth at a specific $q$ related to the average size of the PMR.

V. TEMPERATURE DEPENDENCE

Our data on the temperature dependence of the waterfall in PZN are limited by the fact that PZN decomposes at a temperature less than the Burns temperature. This prevents us from performing measurements above $T_d$ which are of interest because we wish to monitor the recovery of zone center and low-$q$ TO phonons at temperatures where the polarized micro-regions no longer exist. PMN, by contrast, has a lower $T_d$. Hence Naberezhnov et al. were able to measure the TO phonon dispersion at 800 K $> T_d$ where they observed a normal TO phonon branch.\footnote{Selected phonons were briefly studied at 860 K in PZN-8\%PT.} There the scattering intensity associated with the waterfall increased (as expected from the Bose temperature factor) beyond that measured at 500 K, and the peak position of the waterfall, measured using constant-$E$ scans, shifted in towards the zone center, i.e. from $(2,0.14,0)$ to $(2,0.10,0)$. Constant-$Q$ data at $(2,0.10,0)$ show a broad peak around 10 meV. These data suggest that around 860 K the PMR have already begun to form inside of a “uniform,” or unpolarized crystal. A complete understanding of the behavior in this temperature range must await the further study of PMN.

Below the PZN tetragonal-to-rhombohedral phase transition at 410 K the scattering intensity associated with the waterfall decreases gradually, and is almost completely gone at 100 K. This behavior is summarized in the inset to Fig. 9 where the raw intensity (no background subtraction) at $\vec{Q} = (2,-.12,0)$ and $\hbar\omega = 7$ meV is plotted versus temperature. Figure 9 itself shows a constant-$\vec{Q}$ scan at $(2,0,0)$ and 25 K which clearly shows the presence of a zone center TO mode.

In order to illustrate the basic characteristics of the scattering cross section within the coupled-mode model, the $q$-dependence of the optic mode linewidth $\Gamma_1$ is shown in Fig. 8 along with two simulated constant-$E$ scans at 0 and 7.5 meV. It is apparent that the sharp increase in $\Gamma_1$ has a corresponding and pronounced effect on both cross sections in the vicinity of $q_{\text{wf}}$. The jump in the elastic cross section occurs because of the sum rule for the scattering. Hence the extreme broadening of the TO mode that occurs near $q_{\text{wf}}$ extends underneath the TA branch and into the elastic channel. We emphasize that despite the fact that no resolution effects, Bragg or background terms were included in these calculations, the agreement with experiment is surprisingly good. Indeed, the cross section calculated for 0 meV is striking in its similarity to the experimentally measured elastic cross section shown in the top panel of Fig. 4, and thus lends strong credence to the coupled-mode model.
decreasing $q$ in the crystal which serve to damp the polar TO modes. In this way we are able to relate the waterfall directly to data by postulating a sharply decreasing linewidth $\Gamma_1$ that exhibits a large step-like increase with decreasing $q$ upon reaching the waterfall wavevector $q_{wf}$. In this way we are able to relate the waterfall wavevector directly to the presence of nanometer-sized polarized micro-regions in the crystal which serve to damp the polar TO modes at low $q$. A brief review of the waterfall and related neutron inelastic scattering measurements on various relaxor systems has recently been submitted for publication. It is hoped that our results with stimulate theoretical calculations of the precise $q$-dependence of $\Gamma_1$ to allow for comparison with experiment. It would be very interesting to investigate the effects of an applied electric field $E$ on the waterfall, and we have already begun measurements to this end.

VI. DISCUSSION

We have discovered an anomalous ridge of scattering positioned roughly 0.2 Å⁻¹ from the zone center in the relaxor systems PZN-8%PT, PZN, and also PMN in their respective cubic phases. This scattering was observed in various different Brillouin zones including (220) and (004) in PZN-8%PT, and (200), (300), and (220) in PZN. The ridge of scattering is extended in energy in such a way as to make the lowest-lying TO phonon branch appear to drop precipitously into the TA phonon branch at a specific value of $q$, thereby resembling a waterfall. Equally remarkable is the manifestation of a huge elastic cross section near the same value of $q$. An unusual feature has also been observed by Lushnikov et al. for pure PMN using Raman and neutron inelastic scattering techniques at 77 K over an extended energy range from 5.2 meV to 6.8 meV, which nearly coincides with that of the waterfall feature reported here. This was interpreted as evidence of a fracton, i.e. an excitation on a fractal lattice. We have shown that a simple coupled-mode model can be used effectively to describe our neutron inelastic data by postulating a sharply $q$-dependent TO phonon linewidth $\Gamma_1$ that exhibits a large step-like increase with decreasing $q$. In this way we are able to relate the waterfall directly to the presence of nanometer-sized polarized micro-regions in the crystal which serve to damp the polar TO modes.

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