Dynamical Effects of Polar Nanoregions in Relaxor Ferroelectrics

Relaxor ferroelectrics exhibit exceptional piezoelectric properties. Single crystals of some of these materials can achieve ultrahigh strains under applied electric fields that are fully one order of magnitude larger than those attainable in conventional lead-zirconate-titanate (PZT) ceramics, which are widely used in solid-state actuators that convert electrical energy into mechanical energy. The additional properties of large electromechanical coupling and low dielectric loss suggest that industrial use of relaxors may revolutionize the areas of medical imaging, naval sonar, and other acoustic applications. Relaxors are further characterized by a markedly frequency-dependent dielectric susceptibility that is very broad in temperature. The recent neutron scattering studies briefly described here provide new insight on the behavior of these systems.

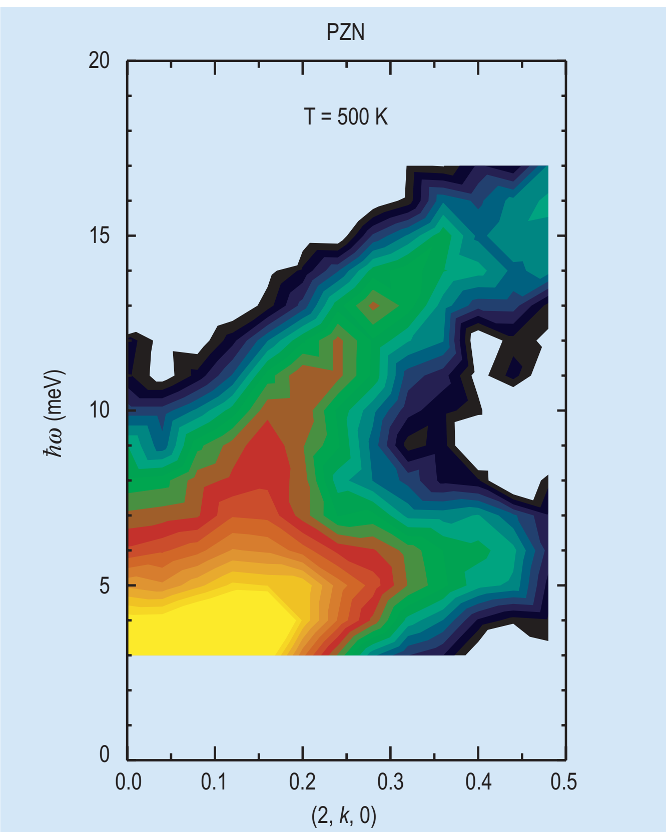

Fig. 1. Contour plot of the neutron inelastic scattering intensity measured in PZN in its cubic phase in the (200) Brillouin zone. The color scale varies logarithmically with intensity, and is limited in range to make the weaker features more visible.

A key feature that appears to be common to all of the relaxor compounds, and which is believed to play a fundamental role in producing the enhanced piezoelectricity, is the formation at high temperature of tiny regions of local and randomly-oriented electric polarization just several unit cells in size, also known as polar nanoregions (PNR). The existence of these PNR was inferred from the observation that the optical index of refraction in a variety of disordered ferroelectric systems deviates from a linear temperature dependence at a temperature T_d far above T_c [2].

$Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) are two of the most studied compounds as their piezoelectric responses rank among the highest [1]. These compounds crystallize in the complex perovskite structure $Pb(B'B'')O_3$, where the B' and B" atoms are generally heterovalent. Thus the relaxor compounds possess not only chemical disorder, but usually a mixed-valence character as well.

Our studies of PZN and PMN have focused on understanding the mechanism underlying the formation of the PNR, as well as their effect on the lattice dynamics. The latter are clearly manifest in neutron scattering measurements. The long-wavelength transverse optic (TO) phonons are heavily damped in energy below T_d in PZN, which gives rise to the anomalous "waterfall" feature shown in Fig. 1 [3]. This damping is strongly wavevector dependent, and becomes significant when the wavelength of the lattice vibration becomes comparable to the average size of the PNR, which is estimated to be of the order of 30 Å to 40 Å.

Subsequent experiments were performed above T_d = 620 K in PMN to look for a soft mode, given the obvious similarities to the classic soft-mode ferroelectric $PbTiO_3$. Surprisingly, the phonon damping persists well above T_d, as shown in Fig. 2 [4]. This implies that the PNR exist as dynamic entities above T_d, but are still effective at inhibiting the propagation of long wavelength phonon modes. Even more interesting is how the zone-center TO mode softens and broadens in energy as the temperature approaches T_d from above, and that only the zone-center TO mode becomes overdamped (no peak at non-zero energy) at T_d. Modes at higher wavevector q become overdamped too, but only below T_d. This behav-

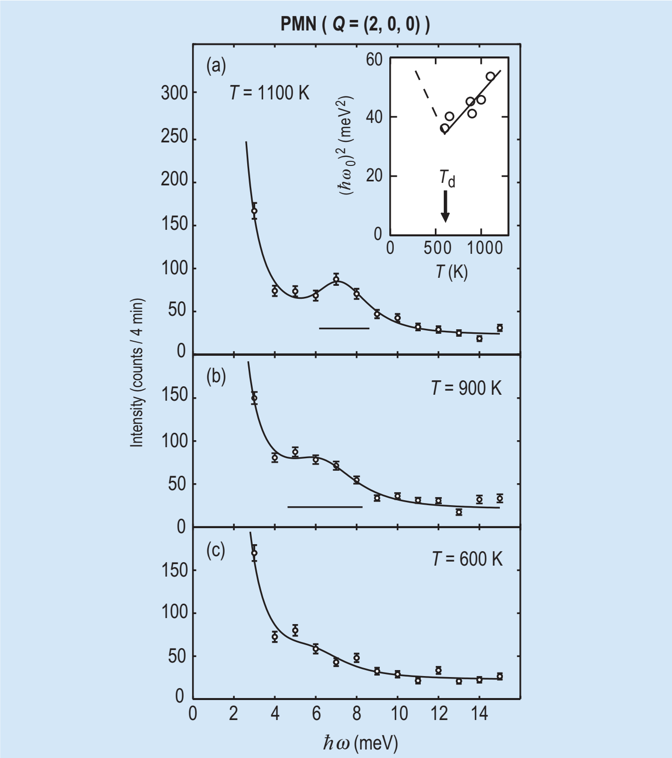

Fig. 2. Temperature dependence of the zone-center TO phonon in PMN measured at (200).

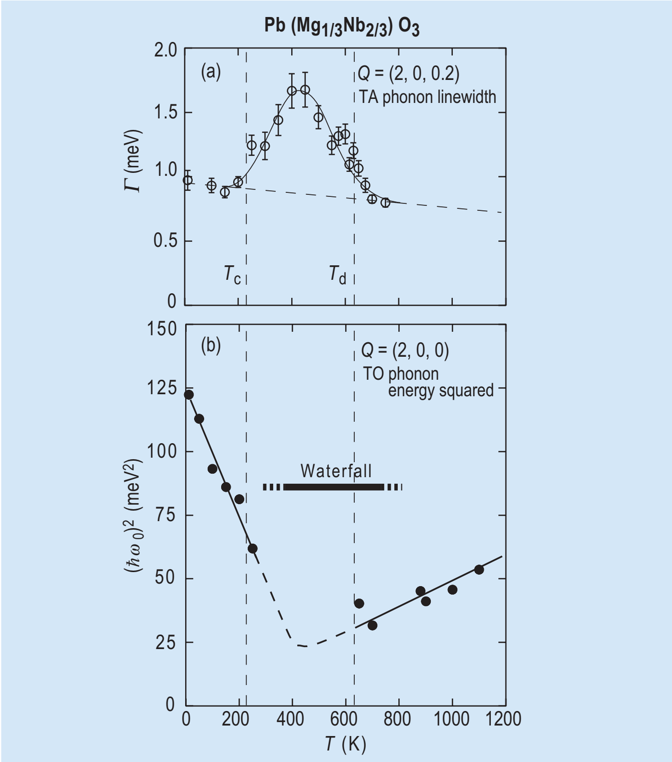

Fig. 3. Summary of the TA and soft mode dynamics in PMN between 10 K and 1100 K.

ior suggests that the zone-center TO mode condenses at T_d, thereby giving rise to the PNR. Consistent with this picture is the observation that the square of the zone-center TO mode energy varies linearly with temperature, as happens in normal soft-mode ferroelectrics. This is shown in Fig. 3, which summarizes the soft TO mode dynamics in PMN between 10 K and 1100 K [5].

An anomalous broadening of the acoustic modes, shown in the upper panel of Fig. 3, also occurs at T_d, as does the onset of diffuse scattering associated with the PNR. The diffuse scattering structure factors can be reconciled with those of the TO phonons in different Brillouin zones by postulating a uniform shift of the PNR along their polarization direction [6]. Furthermore, a model that couples the TA and TO modes is able to describe all of the observed phonon lineshapes extremely well [7]. This then suggests a novel idea in which PMN exhibits the condensation of a *coupled* soft TO mode at T_d. Such a coupled-mode would carry an acoustic component, and thus provide a natural explanation of the uniform shift of the PNR. If true, this would complete an elegant description for the dynamical formation of the PNR in PMN, and most likely other relaxors as well.

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