Tilt Modes in the Relaxor $PbMg_{1/3}Nb_{2/3}O_3$

C. Stock[1] and I.P. Swainson[1]

[1] ISIS, RAL, Didcot, United Kingdom 0X11 0QX

[2] Canadian Neutron Beam Centre, National Research Council Canada, Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0

The lead-based relaxor ferroelectrics are chemically disordered perovskites that have remarkable structural, dynamical, and electromechanical properties. $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) displays the broad, frequency-dependent peak in the dielectric response as a function of temperature that is characteristic of relaxors. Even though PMN posseses an unusually large dielectric susceptibility $\varepsilon \sim 25\ 000$, it does not exhibit a well-defined structural transition, and thus no ferroelectricity, in zero-electric field.

An anomalous temperature- and wave vector-dependent damping produces a false, dispersion-like feature known as the "waterfall," has been observed in PMN. At wave vectors away from the zone centre. To date, however, almost no interest had been taken in the zone boundary dynamics of the relaxors, since ferroelectricity is a Γ-point property. The structure of PMN and cubic-P Brillouin zone are shown in Fig 1. We decided to measure the dynamics along the *M-T-R* zone edge and began measurements on C5 and N5.

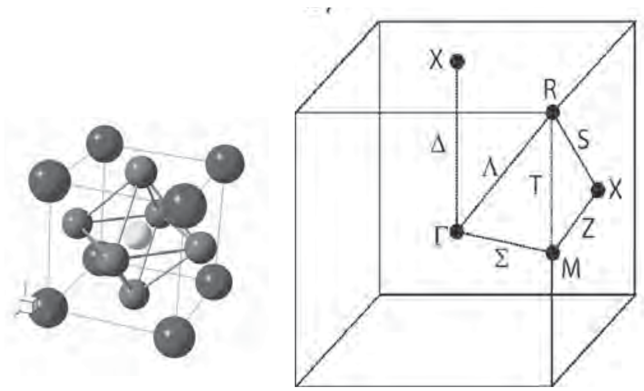

Fig 1. Left: Perovskite structure: O: face centres; Pb: corners; Nb/Mg: center. Right: P-cubic Brillouin zone, also showing the *M-T-R* zone edge.

Our initial hypothesis was that classical tilt instabilities of the perovskites may couple indirectly to the ferroelectric activity, and a line of such modes is known to exist along M-T-R. We found considerable low-frequency activity at the zone boundary, including columns of scattering that descend from the phonon at M and R from the C5 and N5 data. (Such columns have been rarely seen in insulators, although another example that was discovered at CRL was that of calcite by MT Dove and coworkers. A famous non-insulator example is beneath the dip in the dispersion of β-Ti and Zr, related to ω-phase formation in these metals.) Clearly such modes are not normal modes, since a phonon can have only one frequency per wavevector. Later we extended these measurements on SPINS and DCS at NIST (Fig. 2), from which the effect can be more clearly seen in terms of a contour plot (Fig. 3).

The columns soften at 400 K, with a corresponding maximum in their intensity (Fig. 4), similar to the onset of the zone-centre diffuse scattering, indicating a coupling between the ferroelectric and the zone boundary activity. As the modes run along *M-T-R* and taking into account the observed splitting of the degeneracies at R, our initial idea was that these modes

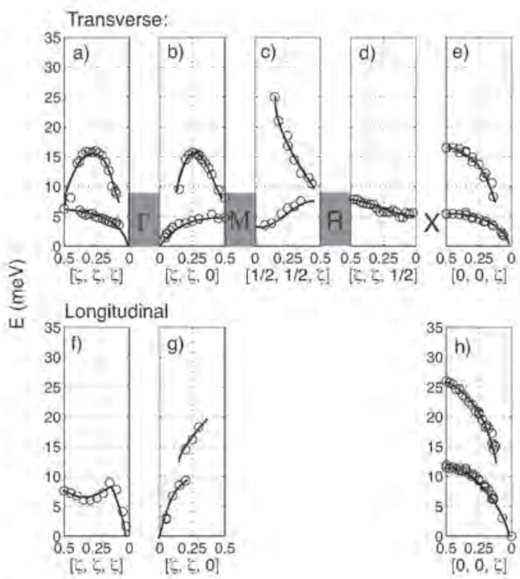

Fig 2. Summary of all disperision curves measured from PMN at 300 K, along various directions of the Brillouin zone: from C5/N5/Spins/DCS.

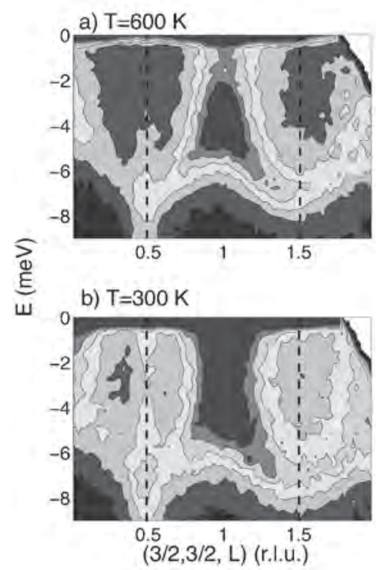

Fig 3. Originally in colour (Ref 1). The *x*-axis is the wave vector along the T-edge, Q_T = (3/2 3/2, *L*), so that *L* = 1 corresponds to an M-point, and *L* = *x*/2 corresponds to an R-point. The negative-energy transfer on the y-axis corresponds to energy-gain of the neutron. The low-frequency optic mode runs from M-R between 6 to 8 meV in frequency. The strong, dark band at *L* = 1 is the column at M. A smaller column descends from R points, and is very clear at 300 K, L=0.5. (DCS data – NIST)

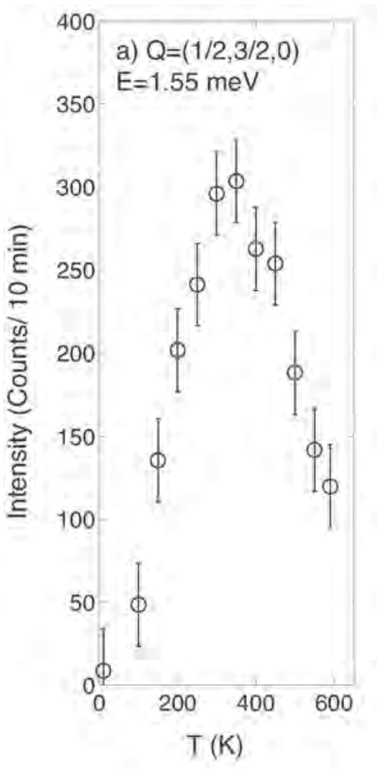

Fig 4. *C5 data showing the intensity of the M-point column as a function of temperature, showing a maximum near 400 K.*

were the tilt modes, since they are commonly active in perovksites. However, for the zone in which the first measurements were made, the structure factors for the tilt modes are zero. Therefore, tilt modes cannot be responsible for this activity. From a study of the published dispersion curves of many perovskites, and from direct structure factor calculations of modes in many zones, we concluded that the *M-T-R* branch is a set of soft antiferroelectric modes R_4^--T_1-M_3^-. R_4^- involves Pb and O motion (Fig. 5), whereas M_3^- consists only of Pb motions. This result could be explained in terms of coupling of antiferromagnetic modes to a primary ferroelectric order parameter. However, from comparison to other systems in which columns are known to exist (e.g. calcite), the antiferroelectric modes are more likely to be order parameters that compete with the ferroelectric ordering.

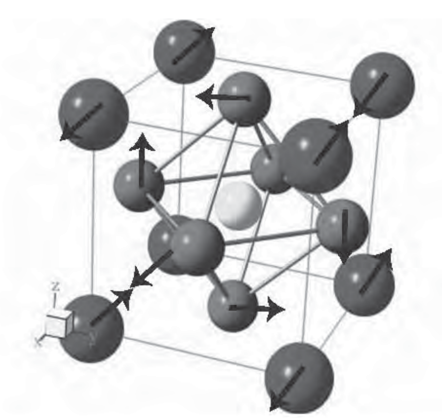

Fig 5. *Eigenvectors of the low-frequency mode at R.*

References

[1] Soft phonon columns on the edge of the Brillouin zone in the relaxor $PbMg_{1/3}Nb_{2/3}O_3$ Physical Review B 79, 224301 (2009). I. P. Swainson, C. Stock, P. M. Gehring, Guangyong Xu, K. Hirota, Y. Qiu, H. Luo, X. Zhao, J.-F. Li, and D. Viehland. DOI: 10.1103/PhysRevB.79.224301