IXS for ferroic transitions: archetypal antipolar soft mode in francisite $Cu_3Bi(SeO_3)_2O_2Cl$

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Inelastic scattering techniques at large have been for decades instrumental in investigations of ferroic transitions and their structural instabilities. When it comes to instabilities at the zone boundary, inelastic x-ray (IXS) or neutron scattering are typically required. Here, we apply IXS to studies of antiferroelectricity.

Antiferroelectric materials (AFE) undergo a structural phase transition from a high-symmetry to a low-symmetry phase where antiparallel arrays of electric dipoles emerge or order [1, 2]. In a direct analogy with antiferrodistortive transitions, one might in principle conceive an ideal AFE phase transition as being driven by an "antipolar" soft-mode, i.e. a soft phonon mode at the zone boundary involving antiparallel ion displacements and connected via the phonon branch to a polar mode at the zone center with parallel displacements of the same ions. However, in practice, this simple scenario has never been demonstrated. Instead, known AFE transitions are dominantly of the order-disorder type or display complex behaviours where antiparallel cation displacements are only part of the story, as in the model $PbZrO_3$.

Here, we investigate the orthorhombic francisite $Cu_3Bi(SeO_3)_2O_2Cl$. At 115 K this compound undergoes a structural phase transition characterized by antiparallel displacements of the Cl and Cu atoms along the *a* axis, leading to a doubling of the unit cell along the *c* axis [3]. The small but clear dielectric anomaly and the nearly degenerate energies of the non-polar and polar polymorphs [4] tend to confirm the AFE character of the transition, even though the switching under electric field has not been reported yet.

We found evidence for a soft mode both below and above T_c by means of, respectively, Raman spectroscopy and a combination of Inelastic X-ray scattering (IXS) and thermal diffuse scattering (TDS). In both cases, the soft-mode could be fitted with a damped harmonic oscillator and its energy squared was found to follow a linear behaviour as a function of temperature in a large temperature range around T_c (Fig. 1). Altogether, this confirms the scenario of a simple displacive antipolar transition [5].

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