Lead zirconate: antiferroelectricity as a missed incommensurate state

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Antiferroelectricity in lead zirconate $PbZrO_3$ (PZ) manifesting itself by the appearance of anomalous hysteresis loops was discovered 60 years ago[1]. Since that time its properties have been extensively studied. PZ undergoes antiferroelectric phase transition from Pm3m to Pbam space group at T_c ≈508 K, demonstrating sharp nearly divergent growth of ε on cooling from above 508 K with strong peak around this temperature ($\varepsilon \approx 4700$). The structure of the low-temperature phase is described by combination of the order parameters corresponding to R (q=$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) and Σ (q=$\frac{1}{4}$ $\frac{1}{4}$ 0) points. In the paper[2] it was demonstrated that phase transition in PZ can be considered a sequence of the transitions related to the condensation of R-component first and then and of Σ-component (q=$\frac{1}{4}$ $\frac{1}{4}$ 0) appearing at lower temperature. In Ref.3 it was shown that the dielectric response in PZ is dominated by the central mode (CM) with low-frequency part of the phonon spectrum giving around Tc contribution of the order of 300 only. CM was attributed to the lead ions rattling motion. No neutron or X-ray inelastic scattering experiments were ever performed on PZ crystals to check the critical dynamics details and to confirm or disprove the results of Ref.3.

Lattice dynamics of $PbZrO_3$ crystal was studied using Inelastic X-ray scattering (IXS) technique. Experiment was done at BL35XU high resolution inelastic X-ray scattering beamline of the SPring8 Synchrotron radiation source. Si(111) monochromator (E= 21.748 keV) was used, providing 1.5 meV resolution. X-rays scattered by the sample were analyzed by 12 analyzers, providing information for 12 values of the scattering vector $\vec{q}$. Experimentally observed spectra were extremely anisotropic and depended on the polarization vectors as well. In the case of the excitations propagating in (110) direction and polarized in $(1\bar{1}0)$ direction (in-plane polarization) extremely low-lying TA phonon resonances were observed accompanied by the broad (broader than resolution) central peak and weak phonon TO phonon resonances (Figure 1a). Central peal can be identified with the central mode reported by Ostapchuk et al.

In the Figure 2 dispersion surface for the lowest TA

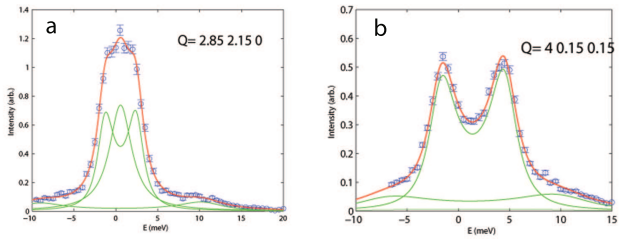

FIG. 1: Experimentally measured IXS curves for q=(0.15 0.15 0); a – in-plane polarized (along $(1\bar{1}0)$) and b – out-of-plane polarized (along (001))

phonons propagating in (hk0) plane and the dispersion curve for the in-plane polarized TA phonons in (110) direction are shown. The most remarkable feature of these results is the fact that the phonon dispersion curve of the TA phonons softens on approaching T_c in toto, without any singularity in Σ point. The softening of the TA mode can be explained in terms of mode coupling and forming some mixed TA-TO mode with real softening of the TO mode that push down the TA one (see e.g. Ref.4).

We also carefully checked phonon resonances in R-point and have found no softening of any phonon mode. At the moment we cannot make final conclusion about intrinsic instability at R-point, because R-type order parameter in PZ is related to the oxygen octahedra tilts and the sensitivity of the x-rays for the displacements of oxygen in the lead-containing compound is obviously low.

For additional information about the critical phenomena in the paraelectric phase of PZ we have carried out X-ray diffuse scattering (DS) experiment. Measurements were performed at Swiss-Norwegian beamline of ESRF. Observed pattern of the diffuse scattering was practically identical to that typically observed in the relaxor ferroelectrics[5]. We did not find neither specific features at Σ-point nor the temperature dependent contribution at R-point. Similar to the IXS experiments we only found critical increase of the DS intensity in the vicinities of the Γ-points. We have simulated the shape of the

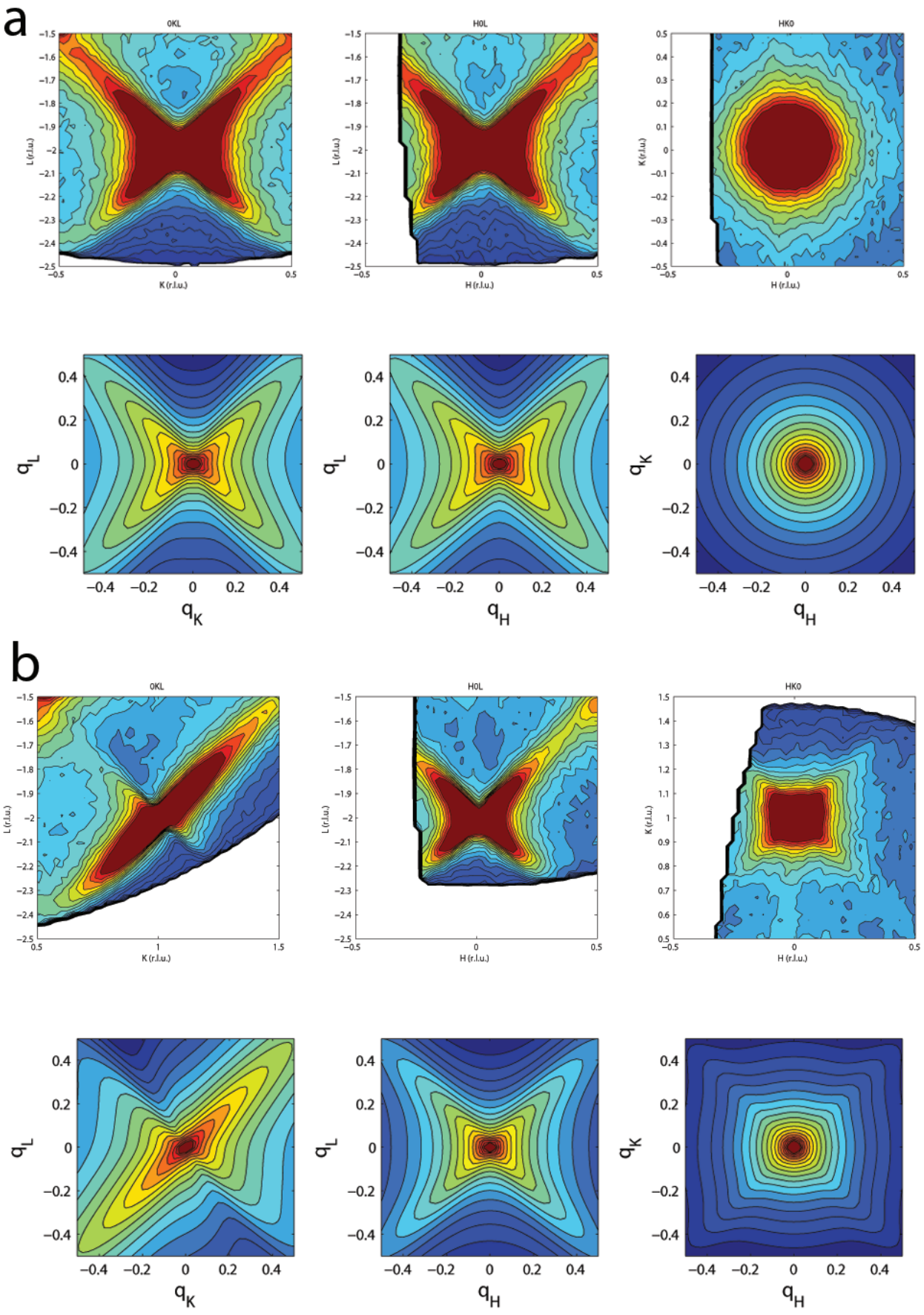

FIG. 4. Experimental (rows 1 and 3) and simulated (rows 2 and 4) 2-D intensity maps in the vicinities of (a) $(0\ 0\ \overline{2})$ and (b)$(0\ 1\ \overline{2})$ reciprocal lattice points. Taking into account the flexoelectric coupling in these simulations enables a good qualitative description of the peculiar shapes of these maps.

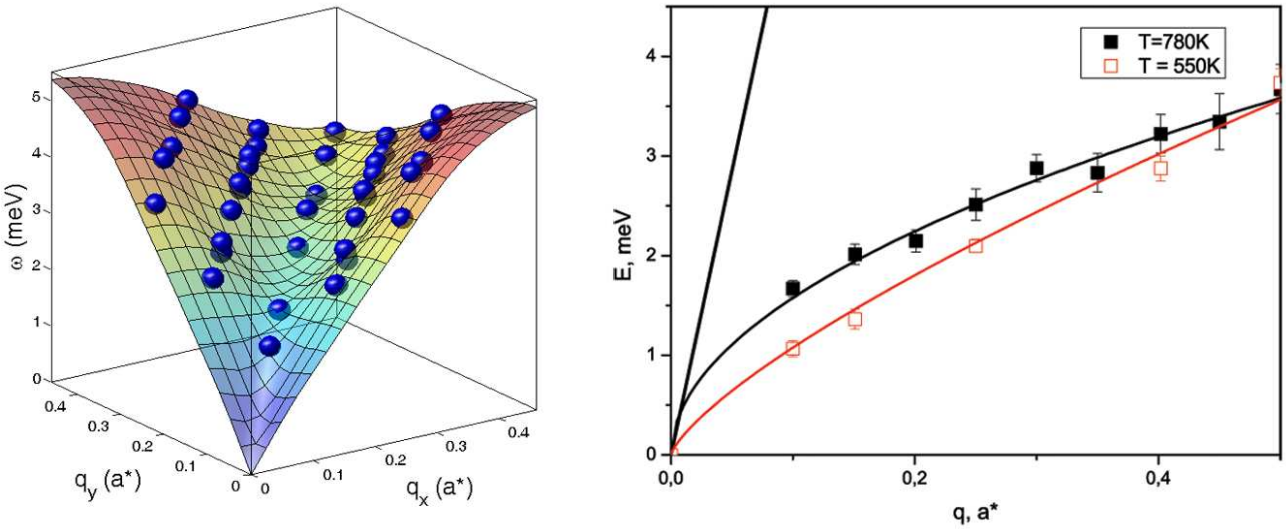

FIG. 2: a – Dispersion surface for the lowest TA phonons propagating in (hk0) plane. b – phonon dispersion curve for the in-plane polarized phonons in (110) direction at 780 and 550 K, thick solid line - sound velocity, calculated from the elastic constants

q-dependence of the diffuse scattering intensity in the vicinities of several reciprocal lattice points using simplified 5-mode model[6,7]. In the frames of this model we assumed that the DS originates from the low-lying phonons and have simulated the dynamical properties by the lattice vibrations of the effective diatomic crystal. In this case for each value of the reduced wavevector q we have only 6 phonon modes and we took into consideration only 5 lowest: 2*TA+LA+2*TO. LO mode was ignored because its frequency is much higher. We have described q-dependence of the intensity as:

$$I(\mathbf{Q}) \propto T \sum_{i=1}^{5} \frac{1}{\omega_i(\mathbf{q})} |\mathbf{Q} \cdot u_i(q)|^2$$

Here $\omega_i(\mathbf{q})$ and $\mathbf{u}_i(q)$ are frequencies and eigenvectors of the phonon modes calculated using the simplified 5-mode dynamical matrix[6,7]. Presented expression is similar to the usual one[8], but there are no phase factors $\exp i\mathbf{Q} \cdot r_j$. So this formula gives correct description of the shape of the DS around any reciprocal lattice point, but cannot be used for the comparison of the intensity around different Bragg peaks.

Performed simulation provided good agreement with the experimental data and so confirmed that all observed DS is related to the only intrinsic instability at γ-point. Theoretical analysis of the phase transformation in PZ including the results described above is discussed in the report of Tagantsev et al. at this conference[9]. The authors would like to thank the Russian Foundation for Basic Research (grant 11-02-00687-), Russian Ministry of Education and Science (grant 2012-1.9-519-003-078) and Swiss National Science Foundation (FNSNF) for funding this project. They also thank the facilities at SPring-8 and the ESRF for their kind hospitality during the experiments.

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