The origin of antiferroelectricity in $PbZrO_3$

Lead zirconate, $PbZrO_3$ (PZ) is an intriguing antiferroelectric material, and has been extensively studied [1]. The properties of this crystal are determined by the strong competition between ferroelectric and antiferroelectric ordering. The structure of the low-temperature phase is described by a combination of the order parameters that correspond to R (½ ½ ½) and Σ (¼ ¼ 0) points. In Ref. 2, it was demonstrated that phase transition in PZ can be considered as a sequence of the transitions related first to the condensation of R-component and then to that of the Σ-component. Structural analysis demonstrated that antiferroelectricity in PZ is described by antiparallel shifts of lead ions accompanied by oxygen octahedral tilts, suggesting condensation of three soft modes at the same time. However, such a situation is very unlikely, and is inconsistent with the idea of a single irreducible representation describing the structural change.

Using beamline **BL35XU**, we investigated the dispersion of the low-frequency phonon modes to gain understanding of this phase transition. Previous phonon work [3] had only looked at phonons at q=0. Combining our phonon dispersion measurements with diffuse scattering maps, we were able to propose a model of the phase transition in this material that is driven by flexoelectric coupling [4].

The phonon spectra are extremely anisotropic. In the case of the excitations propagating in the [1 1 0] direction and polarized in the [1 $\bar{1}$ 0] direction (in-plane polarization), extremely low-lying transverse acoustical (TA) phonon resonances were observed together with a broad central peak and weak transverse optical (TO) phonon resonances (Fig. 1). The central peak can be identified with the central mode reported by Ostapchuk *et al.* [3]. The excitations propagating in the [1 1 0] direction and polarized in the [0 0 1] direction (out-of-plane polarization), are well resolved (Fig. 1(d)). Below the transition temperature, the frequency of the TA mode jumped up and the central peak practically disappeared (Fig. 1(b)).

Figure 2(a) shows the phonon dispersion surface for the TA phonons propagating and polarized in the (1 1 0) plane. A deep valley for q along the (1 1 0) direction is observed. Phonon dispersion curves along this direction demonstrate anomalously low frequencies and pronounced softening upon approaching the transition temperature. We found no features of the phonon frequencies or damping constant around the Σ-point, as confirmed by the diffuse scattering measurements [4]. In Fig. 3, the surface plot of the central peak intensity is presented. No singularity is observed around q=(¼ ¼ 0). We also carefully measured R-point spectra, which also consisted of broadened, temperature-independent phonon resonances and a central peak demonstrating traceable temperature dependence with critical temperature of about 100 K. Thus, the R-point phonon mode or central peak cannot be considered as the relevant excitation for the phase transition at around 500 K.

We were able to describe the phonon dispersion using a model that includes flexoelectric coupling of the acoustic and the TO modes [4]. Only three adjustable parameters are needed: the isotropic and anisotropic slopes of the TO branch, and isotropic flexoelectric constant. The results of the model calculations are shown in Fig. 2(b): the TA mode frequency is strongly lowered and the temperature evolution of the TA dispersion is completely governed by the softening of the TO mode. At a certain soft mode frequency, the TA mode may lose its stability at some arbitrary q_i and transform to an incommensurate phase. Our calculations demonstrate that $PbZrO_3$ is indeed close to such a stability limit, and that the softening of the

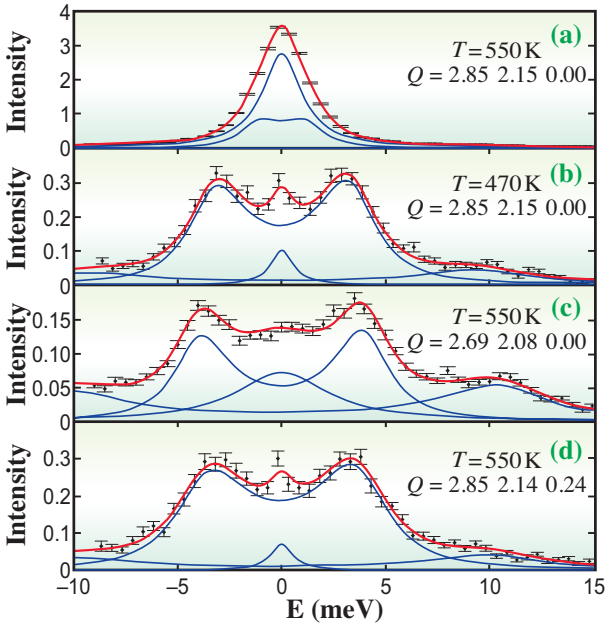

Fig. 1. Phonon resonances for Q in the (320) Brillouin zone: **(a)** q along (110) in-plane polarized above T_c; **(b)** q along (110) in-plane polarized below T_c; **(c)** in-plane polarized q tilted from (110); **(d)** q along (110) out-of-plane polarized above T_c.

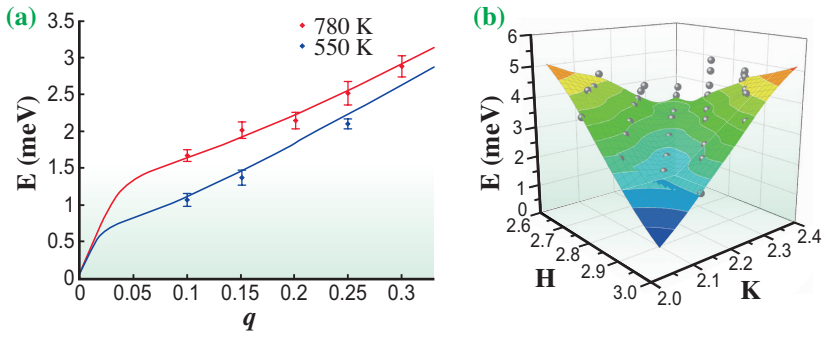

Fig. 2. **(a)** Phonon dispersion curves for in-plane polarized TA phonon branch at T=780 K and 550 K (dots: experimental data; solid lines: calculation results). **(b)** Experimental phonon dispersion surface for in-plane polarized TA phonons; gray spheres are experimental points.

TO mode is responsible for both the critical growth of the dielectric susceptibility in the paraelectric phase and the loss of the stability (softening) of the whole TA branch.

The antiferroelectric phase transition can then be considered as an incomplete incommensurate phase transition resulting from the flexoelectric coupling between the TA and TO modes. Fixing the wave vector at the commensurate Σ-point is the result of the *umklapp* term in the free energy. Formation of the R-type order parameter is triggered by the appearance of the Σ-type one and can be described in terms of the Holakovsky-type instability [5], resulting from biquadratic coupling between these two parameters [4].

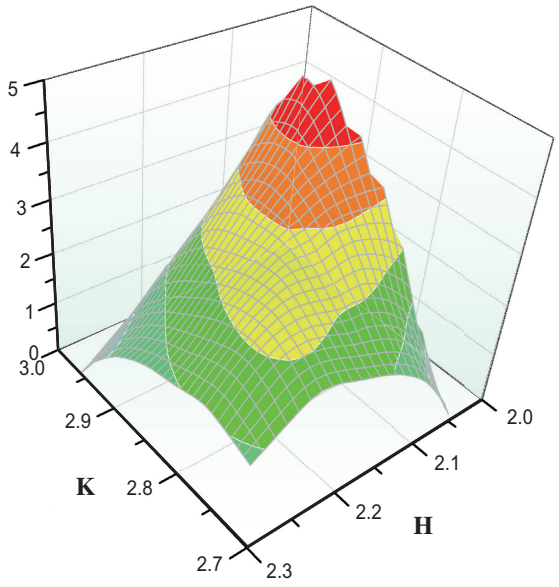

Fig. 3. Surface plot of the central peak intensity at 550 K.

Sergey Vakhrushev[a,b,*], R. Burkovsky[a,b,c] and Alfred Q. Baron[d]

[a] Ioffe Physico-Technical Institute, Russia
[b] St. Petersburg State Polytekhnical University, Russia
[c] European Synchrotron Radiation Facility, France
[d] SPring-8/RIKEN·JASRI

*E-mail: s.vakhrushev@mail.ioffe.ru

References

[1] H. Maniwa *et al.*: Phys. Rev. **83** (1951) 1078.
[2] H. Fujishita and S. Hoshino: J. Phys. Soc. Jpn. **53** (1984) 226.
[3] T. Ostapchuk *et al.*: J. Phys.: Cond Matter **13** (2001) 2677.
[4] *A.K. Tagantsev, K. Vaideeswaran, S.B. Vakhrushev, A.V. Filimonov, R.G. Burkovsky, A. Shaganov, D. Andronikova, A.I. Rudskoy, A.Q.R. Baron, H. Uchiyama, D. Chernyshov, A. Bosak, Z. Ujma, K. Roleder, A. Majchrowski, J.-H. Ko and N. Setter: Nat. Commun.* ***4*** *(2013) 2229.*
[5] J. Holakovsky: Phys. Status Solidi **56** (1973) 615.