Multiple Soft-Mode Vibrations of Lead Zirconate

J. Hlinka, T. Ostapchuk, E. Buixaderas, C. Kadlec, P. Kuzel, I. Gregora, J. Kroupa, M. Savinov, A. Klic, and J. Drahokoupil

Institute of Physics, Academy of Sciences of the Czech Republic Na Slovance 2, 182 21 Prague 8, Czech Republic

I. Etxebarria
Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, P.K. 644, 48080 Bilbao, Spain

J. Dec
Institute of Materials Science, University of Silesia, Bankowa 12, PL-40-007 Katowice, Poland

(Published 12 May 2014)

Reexamination of the antiferroelectricity in PbZrO$_3$ [1–4] resulted in the renunciation of the original simple two-sublattice Kittel model [5], at least in the case of this canonical antiferroelectric (AFE) oxide. Most recent studies suggest that the AFE state in lead zirconate is induced by a single lattice mode—the ferroelectric (FE) soft mode—through its flexoelectric [6–10] interaction with antiphase lead displacements [4]. The oxygen octahedra tilt displacements are triggered [11] by a biquadratic interaction to the antiphase lead displacements [4]. This novel approach to the antiferroelectricity in PbZrO$_3$ raises many questions not only with respect to this single compound and its widespread derivatives [12–16], but also with respect to interfacial engineering [17,18], design strategy of new antiferroelectrics, and their new application perspectives as well [1,2,19].

Here we describe a detailed polarized IR and Raman spectroscopic study of single domain specimens of AFE PbZrO$_3$. The obtained results demonstrate the existence of multiple soft modes of different symmetry. From their analysis an alternative model has emerged, in which (i) the whole phonon branch related to lead vibrations is intrinsically soft, and (ii) the AFE state is directly stabilized by a trilinear term to another two oxygen octahedra tilt modes.

The paraelectric (PE) phase of PbZrO$_3$ is a simple cubic perovskite with a 5-atom unit cell (Pm$3m$, $Z = 1$). Below the AFE phase transition ($T_C \sim 500$ K), it goes over to an orthorhombic $Pbam$ ($Z = 8$) structure [20,21]. The space-group symmetry change can be well understood [2] as a result of the condensation of 2 order parameters [2,4,17,21–23]: a polarization wave of a propagation vector $Q_S = (0.25, 0.25, 0)$$_{pc}$ and a $Q_R = (0.5, 0.5, 0.5)$$_{pc}$ oxygen octahedra tilt mode (here pc stands for pseudocubic lattice, see Figs. 1 and 2). Superpositions of $Q_S$, $Q_R$ include also $\Gamma, X, M$, and $Q_S = (0.25, 0.25, 0.5)$$_{pc}$ cubic-phase Brillouin zone points. All of these points become Brillouin zone centers in the $Pbam$ phase [see Fig. 2(a)] and the corresponding lattice modes give rise to $16A_g + 16B_{1g} + 14B_{2g} + 14B_{3g} + 12A_u + 11B_{1u} + 17B_{2u} + 17B_{3u}$ optic modes of the $Pbam$ structure. In the AFE phase, the optical spectroscopy thus effectively allows probing phonon modes from the $\Sigma$ and $S$ lines.

Density functional theory calculations demonstrated that the cubic structure of PbZrO$_3$ is instable at low temperatures with respect to the Pb ion off centering as well as concerted oxygen octahedra tilts [3,23,25–27,31]. The corresponding finite-temperature phonon frequencies can be estimated from the inelastic neutron and x-ray scattering studies PbTiO$_3$-PbZrO$_3$ solid solutions (PZT) in their common cubic phase. For example, the frequencies of the $M_5', M_3', X_5', X_3'$, and $R_{15}$ Pb-dominated modes can be extrapolated from the measurements of the PbTiO$_3$ [28–30] and the PZT single crystals [32]. The acoustic mode dispersion can be estimated from PbZrO$_3$ measurements of Refs. [4,33,34], and the zone-center mode frequency can be estimated from the dielectric measurements [4,35,36]. The lowest frequency phonon dispersion curves of the cubic PbZrO$_3$ obtained in this way (near the phase transition point) are traced in Fig. 2(b).

In the limit of vanishing structural distortion (small order parameters), $\Gamma$-point modes of the $Pbam$ orthorhombic
Table I. Correlation between \textit{D}_2h irreducible representations of \textit{Pbam} Pb-ion zone-center vibrations (top row of the table) and their counterparts in the parent cubic phase. \(\Sigma_i\) and \(S_i\) stands for modes associated with \(Q_{\Sigma}\) and \(Q_{S}\) wave vectors, respectively. Other labels are as those of Ref. [31].

\[
\begin{array}{cccccccc}
A_g & B_{1g}(xy) & B_{2g}(xz) & B_{3g}(yz) & A_u & B_{1u}(z) & B_{2u}(y) & B_{3u}(x) \\
\hline
\Gamma & \Gamma_{15} & \Gamma_{15} & \Gamma_{15} \\
X & X_2' & X_5' & X_5' \\
M_{5} & M_{5}' & M_{5}' & M_{2}' \\
R_{15} & R_{15} & R_{15} & R_{15} \\
\Sigma_{3} & \Sigma_{3} & \Sigma_{4} & \Sigma_{4} \\
S_{3} & S_{1} & S_{4} & S_{4} \\
\end{array}
\]
Actually, present results even suggest that both frequency of all For example, we have verified that the overall IR plasma due to the mode mixing. In particular, modes listed within the spectra of IR reflectivity and time-domain THz spectroscopy, Porto notation. Panel (c) shows the real part of the low-frequency at 80 K. The scattering geometry is indicated using standard

\[ \Omega \]

is close to the IR plasma frequency of the Last soft mode –47. Moreover, among the modes of the same irreducible branches are temperature dependent here.

Obviously, among the modes of the same reducible representation, the temperature dependence can be shared due to the mode mixing. In particular, modes listed within the same column in Table I are coupled in the AFE phase. For example, we have verified that the overall IR plasma frequency [48] of all \( B_{3g} \) modes observed below 100 cm\(^{-1} \) is close to the IR plasma frequency of the Last soft mode \( \Omega_{\text{Last}} = 618 \text{ cm}^{-1} \) determined from the analysis of the cubic phase spectra [48]. Since the bare \( X'_3, \Sigma_1, \) and \( S_1 \) modes have the \( B_{3g} \) symmetry but no intrinsic IR strength, the relative integral intensities of the \( B_{3g} \) modes observed in the conductivity spectrum below 100 cm\(^{-1} \) [Fig. 3(c)] can be directly interpreted as a measure of their eigenvector exchange with the pure Last mode [48]. This mixing is quite considerable.

Are the observed temperature variations of phonon frequencies large or small? Within the Landau theory of the second-order structural phase transition, the squared soft-phonon frequency shows a linear temperature dependence (Cochran law). A stronger, nonlinear temperature dependence is expected below a first-order phase transition [44–47]. Actually, present results even suggest that both \( \Sigma_3 \) and \( S_3 \) branches are temperature dependent here.

Let us stress that the \( \Sigma_3 \) mode components resulting squared bare Last mode frequency \( \omega^2_{\text{Last}} \), and traced the resulting squared bare Last mode frequency \( \omega^2_{\text{Last}} = \Omega^2_{\text{Last}}/\epsilon(0), \) and \( \omega^2_{\text{Last}} \) is determined from the analysis of the cubic phase spectra [48]. Since the bare \( X'_3, \Sigma_1, \) and \( S_1 \) modes have the \( B_{3g} \) symmetry but no intrinsic IR strength, the relative integral intensities of the \( B_{3g} \) modes observed in the conductivity spectrum below 100 cm\(^{-1} \) [Fig. 3(c)] can be directly interpreted as a measure of their eigenvector exchange with the pure Last mode [48]. This mixing is quite considerable.

Are the observed temperature variations of phonon frequencies large or small? Within the Landau theory of the second-order structural phase transition, the squared soft-phonon frequency shows a linear temperature dependence (Cochran law). A stronger, nonlinear temperature dependence is expected below a first-order phase transition [44–47]. Actually, present results even suggest that both \( \Sigma_3 \) and \( S_3 \) branches are temperature dependent here.

Let us stress that the \( \Sigma_3 \) mode components resulting squared bare Last mode frequency \( \omega^2_{\text{Last}} = \Omega^2_{\text{Last}}/\epsilon(0), \) and \( \omega^2_{\text{Last}} \) is determined from the analysis of the cubic phase spectra [48]. Since the bare \( X'_3, \Sigma_1, \) and \( S_1 \) modes have the \( B_{3g} \) symmetry but no intrinsic IR strength, the relative integral intensities of the \( B_{3g} \) modes observed in the conductivity spectrum below 100 cm\(^{-1} \) [Fig. 3(c)] can be directly interpreted as a measure of their eigenvector exchange with the pure Last mode [48]. This mixing is quite considerable.

Are the observed temperature variations of phonon frequencies large or small? Within the Landau theory of the second-order structural phase transition, the squared soft-phonon frequency shows a linear temperature dependence (Cochran law). A stronger, nonlinear temperature dependence is expected below a first-order phase transition [44–47]. Actually, present results even suggest that both \( \Sigma_3 \) and \( S_3 \) branches are temperature dependent here.

Let us stress that the \( \Sigma_3 \) mode components resulting squared bare Last mode frequency \( \omega^2_{\text{Last}} = \Omega^2_{\text{Last}}/\epsilon(0), \) and \( \omega^2_{\text{Last}} \) is determined from the analysis of the cubic phase spectra [48]. Since the bare \( X'_3, \Sigma_1, \) and \( S_1 \) modes have the \( B_{3g} \) symmetry but no intrinsic IR strength, the relative integral intensities of the \( B_{3g} \) modes observed in the conductivity spectrum below 100 cm\(^{-1} \) [Fig. 3(c)] can be directly interpreted as a measure of their eigenvector exchange with the pure Last mode [48]. This mixing is quite considerable.
material, one should be also able to switch the staggered polarization configuration to the FE one by an electric field. This suggests that AFE materials should have both the zone-center and zone-boundary soft mode. It is most naturally realized when the whole polarization branch is soft [Fig. 5(c)]. This often results in an incommensurate instability [45–47]. A combination of the present experimental results and those of Ref. [4] implies that PbZrO$_3$ does exhibit a flat soft polarization branch, still without any trace of a local minimum near the AFE wave vector [Fig. 5(d)]. Therefore, an additional ingredient responsible for the antiferroelectricity is needed beyond the quasiharmonic approximation, i.e., a nonlinear coupling term. The existence of the second family of soft modes (range 100–150 cm$^{-1}$) suggests that this term involves the oxygen octahedra tilts.

To illustrate this idea, we consider a 1D chain of alternating lead and oxygen ions in the direction of the AFE wave vector, e.g., all ions located on the line connecting (1) and (3) Pb ions shown in Fig. 1. A simple soft branch potential related to $x$ displacement of $n$th lead ion $p_n$ reads

$$\sum \left[ \frac{\alpha}{2} p_n^2 + \frac{\beta}{4} p_n^4 + \frac{J}{2} (p_{n+1} - p_n)^2 \right],$$

with $\alpha = \alpha(T - T_0)$, $\alpha, \beta, J > 0$. Note that the usual Landau term $\alpha/2 \sum p_n^2$ for the soft macroscopic polarization is replaced with an effective-Hamiltonian-like [23,25] $\alpha/2 \sum p_n^2$ expression describing the soft microscopic polarization. Therefore, this term directly controls the stability of both AFE and FE modes. The second ingredient is a potential associated with $x$ and $y$ displacements of the $n$th oxygen ion $x_n, y_n$ and a coupling term to adjacent Pb ions that favors their AFE arrangement, such as

$$\sum \left[ \frac{A}{2} (x_n^2 + y_n^2) + \frac{B}{4} (x_n^4 + y_n^4) + \frac{K}{2} (p_{n+1} - p_n)x_ny_n \right],$$

with $A, B > 0$. The phase diagram of this model is sketched in Fig. 5(e). The direct paraelectric ($p_n = 0$) to AFE ($p_n = p(\pm 1)^n$) phase transition occurs if $|K| > K_0 \approx 0.9425$. For a smaller magnitude of $K$, the AFE transition is preceded by the FE one ($p_n = p$), as in the Zr-rich side of the temperature-concentration phase diagram of the PZT system. Similar phase diagrams can be expected to hold for a more realistic, 3D lattice model with all the trilinear coupling terms allowed by symmetry, such as that involving the product of the $\Sigma_3$ polarization wave with $R_{25}$ and $S_3$ octahedra rotation modes [49]. In this sense the AFE phase transition of PbZrO$_3$ is analogous to the avalanche [50–52] and “hybrid-improper-like” [53] transitions.

In summary, this polarized Raman, IR, and THz spectroscopic study of AFE PbZrO$_3$ single crystals has established that there are several low frequency modes with anomalously temperature dependent phonon frequencies distributed among seven active irreducible representations. We conclude that the modes around 130 cm$^{-1}$ are associated with oxygen octahedra tilt vibrations, while those below about 100 cm$^{-1}$ are due to the Pb ion fluctuations. Softening of the latter can be understood as a consequence of a soft and flat phonon branch, without having to recall specific biquadratic couplings for each such mode separately. It is emphasized that, in general, flat soft polarization branches ensure a simultaneous instability with respect to both the homogeneous and the staggered polarization, that seems to be the essential prerequisite of an AFE material [54,55]. Switching is actually easier when the AFE instability is weaker than the FE one. However, this situation requires an additional element stabilizing the staggered polarization, such as the above proposed trilinear term for PbZrO$_3$. We hope that this piece of understanding can help to discover new useful antiferroelectrics as well as to model the finite-temperature properties of the current PbZrO$_3$-based materials.

The authors are indebted to J. Petzelt for a critical reading of the manuscript. The work was supported by the Czech Science Foundation (Project No. GACR 13-15110S).

---

References:

[1] H. Liu and B. Dkhil, Z. Kristallogr. 226, 163 (2011).
[2] K. M. Rabe, in Functional Metal Oxides: New Science and Novel Applications, edited by Satish Ogale and V. Venkateshan (Wiley, Hoboken, NJ, 2013).
[3] S. E. Reyes-Lillo and K. M. Rabe, Phys. Rev. B 88, 180102 (2013).
[4] A. K. Tagantsev, K. Vaideeswaran, S. B. Vakhrushev, A. V. Filimonov, R. G. Bukovskiy, A. Shaganov, D. Andronikova, A. I. Rudskoy, A. Q. R. Baron, H. Uchiyama, D. Chernyshov, A. I. Rudskoy, A. Q. R. Baron, H. Uchiyama, D. Chernyshov, A. I. Rudskoy, A. Q. R. Baron, H. Uchiyama, D. Chernyshov.
