Effect of pressure on the zone-center phonons of $PbTiO_3$ and on the ferroelectric-paraelectric phase transition

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The first-order Raman spectrum of single-crystalline $PbTiO_3$ in the teatragonal ferroelectric phase was studied at room temperature as a function of hydrostatic pressure up to 80 kbar. Mode Grüneisen parameters, as well as higher-order coefficients in the expansion of phonon frequency vs pressure are reported for all zone-center TO phonons. The pressure P_1 at which the ferroelectric-paraelectric (FE $\rightarrow$ PE) phase transition would occur continously can be obtained by fitting the pressure dependence of the lowest E(TO) "soft" mode frequency with a Curie-Weiss-type law. This criterion yields $P_1 = 90 \pm 4$ kbar. Limits for the first derivative of the transition temperature with pressure are similarly obtained and yield $5.2 < -dT_C/dP < 5.9$ K/kbar. The information on the FE $\rightarrow$ PE phase transition obtained here is in good agreement with previously reported data obtained by measuring the pressure dependence of the dielectric constant in the PE phase.

I. INTRODUCTION

Lead titanate is one of the perovskite-type ferroelectrics[1] with a Curie temperature $T_C = 765$ K.[2] The general characteristics of this crystal are similar to those of the prototype of the family, $BaTiO_3$. The structure of the ferroelectric (FE) phase[3] involves a larger tetragonal distortion (space group C_{4v}-$p4mm$) than in $BaTiO_3$; thus the parameters associated with the polar phase, such as spontaneous polarization and ionic shifts, are considerably larger. Also, $PbTiO_3$ offers a wide temperature range at which the tetragonal phase is stable with noticeable change in the pertinent parameters and is the first member of this family in which well-defined soft modes were observed in the paraelectric (PE) as well as in the FE phases.[4]

Measurements of the dielectric constant ϵ in the PE phase show a temperature dependence[2,5]

$$\epsilon = C/(T - T_0) , \tag{1}$$

where C is a constant and $T_0 = 722$ K$< T_C$. The difference between T_C (temperature at which the transition occurs) and T_0 (temperature at which ϵ^{-1} extrapolates to zero) signifies the degree of first-order character in the transition.[5]

The phonon spectrum of $PbTiO_3$ was studied with neutron scattering,[4] infrared absorption,[6] and Raman scattering.[7,8] Dielectric-constant[2] and neutron-scattering measurements[4] establish the existence of a long-wavelength ($q = 0$) transverse-optic (TO) soft mode in the PE phase, the frequency of which has a temperature dependence

$$\omega_f^2 = K/\epsilon = A_f (T - T_0), \tag{2}$$

where both K and A_f are constants. These studies reveal the existence of a well-defined soft mode in the FE phase as well, whose atomic motions correspond to the tetragonal distortion.[4] The PE $\rightarrow$ FE transition is thus caused by instability of the lattice against this soft mode owing to cancellation of the short-range forces by the long-range Coulomb forces. The short-range forces increase much more rapidly with decreasing interatomic distance than do the Coulomb forces. Since ω_f is determined by a balance of these two forces, a small change in volume can produce large relative changes in ω_f and hence a large mode Grüneisen parameter (MGP) γ_f. Knowledge of γ_f is necessary in treating many of the properties of these materials. This is especially true in the case of theoretical treatments of ultrasonic attenuation and velocities where γ_f enters as one of the principal parameters.[9] To our knowledge, no direct measurement (Raman, infrared, or neutron scattering) of this volume dependence has been reported.

Samara[2] measured the pressure dependence of ϵ in the PE phase at different temperatures, in the region 0–24 kbar, and obtained indirectly values of γ_f from the relationship $\omega_f^2 \alpha \epsilon^{-1}$ [see Eq. (2)]. The dielectric constant was found to have a pressure dependence given by

$$\epsilon = C^*/(P - P_0) . \tag{3}$$

Here C^* and P_0 are constants at any given temperature corresponding to the quantities C and T_0 in Eq. (1), respectively. A pressure $P_c > P_0$ (analogous to T_C) at which the phase transition occurs at a given temperature can also be defined.[2,10] In this and other ferroelectric materials a decrease in T_C with increasing pressure was observed.[2,10] This can be understood in the following

way: The tetragonal cell of the FE phase has a larger volume than the cubic cell of the PE phase[3]; hence application of pressure has the effect of stabilizing the latter phase, thus reducing T_C. Therefore, the FE → PE transition could be observed in $PbTiO_3$ at room temperature with the application of sufficiently high pressures. From Samara's measurements at 620 K ($P_0 = 16.5$ kbar) and 640 K ($P_0 = 12.8$ kbar) a linear extrapolation would yield $P_0 = 76$ kbar at room temperature. This gives a lower bound for the pressure (P_c) at which the transition should occur at room temperature (since $P_c > P_0$).

It is clear from the previous discussion that measurements of the $q \simeq 0$ optic-mode frequencies and in particular the soft mode as a function of very high pressures in this family of materials are of great interest. We report here the first measurement of the first-order Raman spectrum of $PbTiO_3$ with hydrostatic pressures of up to 80 kbar. The measurements were performed at room temperature on a single-crystal sample in the FE phase. All TO modes were observed, and from their pressure dependence linear (MGP's) and higher-order coefficients in the expansion of phonon frequency versus pressure are obtained. Our experiment suggests that a Curie-Weiss-type law,

$$\omega_j^2 = C^{*\prime}(P_1 - P), \tag{4}$$

holds for the soft E (TO1) mode. Since we are approaching the transition from the FE side, the inequality

$$P_0 < P_c < P_1 \tag{5}$$

must hold. From the behavior of this mode a value $P_1 \simeq 90$ kbars is obtained. The crossing points of A_1 and E modes which are degenerate (Γ_{15}) in the cubic phase are obtained by extrapolation of our pressure data. There are two such pairs labeled[8] A_1(TO2), E(TO2) and A_1(TO3), E(TO4) for which crossing points of 88 and 95 kbars, respectively, are obtained. These crossing points are in remarkable mutual coincidence and occur also in the neighborhood of the value for P_1 obtained from the soft-mode behavior. While this agreement may be fortuitous, we feel its occurrence may be interpreted as a self-consistency check.

II. THE EXPERIMENT

Single-crystalline samples of $PbTiO_3$ (grown by the Remeika[5] flux method) of approximate dimensions $0.2 \times 0.2 \times 0.1$ mm were used. High pressures up to 80 kbars were generated by placing the sample inside a 0.4-mm hole in a 0.3-mm-thick gasket made of copper-beryllium alloy. The pressure transmitting fluid is a 4:1 mixture of methanol-ethanol which ensures a hydrostatic environment up to 96 kbar. The gasket was pressed between two anvils, one of which is made of sapphire to serve as optical window as well. The pressure was monitored by measuring the position of two fluorescence lines from a splinter of ruby placed next to the sample.[11,12] Details of the pressure system and its use in light-scattering measurements are given elsewhere.[12,13]

The measurements were performed in the backscattering configuration with incident and scattered beams propagating perpendicular to the tetragonal c axis. The scattered light was analyzed with a 0.5-m Spex double monochromator with photon-counting detection. As a source of excitation the 5145-Å line of a 4-w argon-ion laser was used.

III. RESULTS AND DISCUSSION

The first-order Raman spectrum of tetragonal (C_{4v}) $PbTiO_3$ was reported by Burns and Scott.[8] It was found by these authors that this material exhibits well-behaved single-crystal Raman spectra which obey the proper selection rules, in contrast to the other ferroelectric perovskites such as $BaTiO_3$.[14-16]

There are twelve optic modes in the cubic PE phase: three triply degenerate T_{1u} (Γ_{15})—infrared active, Raman inactive—and one triply degenerate T_{2u} mode (Γ_{25})—infrared and Raman inactive. These modes split according to

$$T_{1u} \rightarrow A_1 + E, \quad T_{2u} \rightarrow E + B_1$$

in the tetragonal phase. All modes are Raman active and all but the B_1 are also infrared active. Hence all A_1 and E modes are also split into TO and LO components by long-range Coulomb forces when propagating along symmetry axes. All modes were observed and identified in Ref. 8, whose labeling system is used throughout the present work. Figure 1 shows representative spectra taken at two different pressures. In the geometry of the present work (see Sec. II) all TO modes are allowed and all were also observed, whereas the LO modes are forbidden and none were observed. The mode labeled A_1(TO1), however, only appears weakly in the high-pressure spectra and is absent from spectra taken outside the cell. Also, this mode could not be isolated from the E (LO1) (occurring at the same energy) in previous Raman measurements[8] and was observed as a quasimode. Therefore the labeling used in the present work can only be considered as *tentative*. It could also correspond to a quasimode induced by slight tilting of the sample within the pressure cell [or residual

E (LO1)].

The complete spectrum was recorded for several pressures up to 66.3 kbar. At 80 kbar, the Raman spectrum was still present, although peak positions could not be determined due to breaking of the sapphire window during the run. This is a common occurrence since the limit of our pressure apparatus is around 80 kbar, and the limiting factor is breakage of the sapphire window. Three facts are worthy of note. (i) The Raman spectrum was still present at 80 kbar, which gives a lower limit for P_c, i.e., $P_c > 80$ kbar. (ii) The over-all intensity of the Raman spectrum decreases continuously as pressure increases and the FE → PE transition approaches. (iii) The soft-mode line-width was not found to diverge as the transition approached, in contrast to the temperature measurements of Burns and Scott.[8] However, quantitative line-width measurements at low frequencies are made difficult by the large amount of diffuse scattered light inherent to the pressure technique (see Sec. II).

In Fig. 2 we plot peak position versus pressure for all observed structures. The experimental points were subjected to a least-squares fit with polynomials containing terms up to third order in pressure. The modes labeled E(TO1), A_1(TO1), E(TO3) + B_1, and E(TO4) are best fitted by straight lines, while the E(TO2) and A_1(TO2) modes require terms quadratic in the pressure and the A_1(TO3) mode is best fitted with a polynomial containing both quadratic and cubic terms in P. The solid line of Fig. 2 represents the result of these fits and the fit parameters are listed in Table I. Also listed in Table I are MGP's, γ_j, taken from the linear term of the fit. These parameters are defined as

$$\gamma_j = -\left(\frac{d\ln\omega_j}{d\ln V}\right)_{P=0} = \frac{B_T}{\omega_j}\left(\frac{d\omega_j}{dP}\right)_{P=0}, \quad T = \text{const} \tag{6}$$

where ω_j is the frequency of the jth mode, B_T = 857 kbar[17] is the isothermal bulk modulus, V the crystal volume, and P the applied pressure. From this figure we see that the pair of modes A_1(TO3), E(TO4) and A_1(TO2), E(TO2) get considerably closer to each other as pressure increases. This identifies them as members of the anisotropy-split triplets T_{1u} (Γ_{15}) (in the cubic phase), whereas the mode labeled E(TO3) + B_1 corresponds to the cubic T_{2u} mode, which is apparently not split by the tetragonal distortion. From the least-square fits to these pairs of modes, the pressure at which they cross can be extrapolated. The estimated

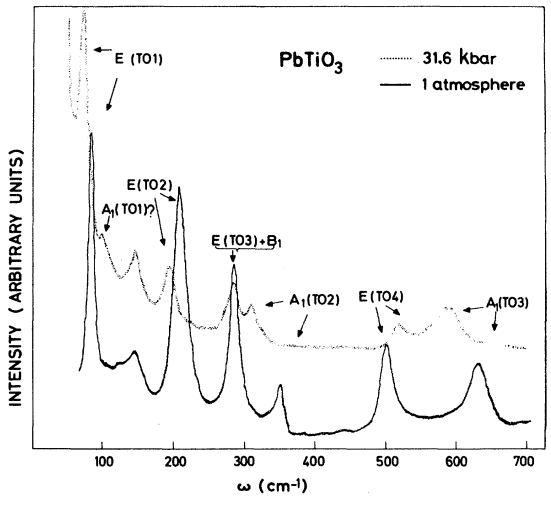

FIG. 1. Representative spectra of $PbTiO_3$ at atmospheric pressure and at P = 31.6 kbar. The spectra were taken at room temperature, in backscattering configuration, with both incident and scattered light propagating perpendicular to the tetragonal c axis.

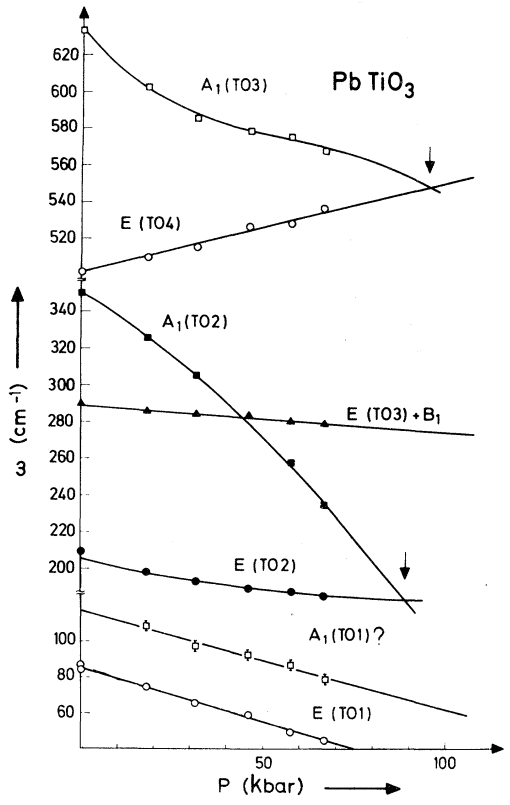

FIG. 2. Pressure dependence of the frequencies of the different modes. The dots correspond to measured values while the solid lines represent least-squares fits to the data using polynomials with up to cubic terms in P. The arrows indicate extrapolated crossing points.

TABLE I. Parameters obtained from a least-squares fit of the pressure dependence of the phonon frequencies for the different observed modes.

Mode	$\omega(P=0)$ (cm^{-1})	$d\omega/dP$ (cm^{-1}/kbar)	$10^2(d^2\omega/dP^2)$ (cm^{-1}/kbar^{-2})	$10^3(d^3\omega/dP^3)$ (cm^{-1}/kbar^{-3})	γ
E(TO1)	85.0±0.3	−0.60±0.02	···	···	−6.0±0.2
A_1(TO1)?	117±3	−0.55±0.05	···	···	−4.0±0.5
E(TO2)	205±3	−0.43±0.10	−0.4±0.2	···	−1.8±0.4
E(TO3)+B_1	289±0.5	−0.15±0.03	···	···	−0.44±0.09
A_1(TO2)	350±1	−1.15±0.08	−1.7±0.3	···	−2.8±0.2
E(TO4)	501.5±0.6	0.49±0.05	···	···	0.84±0.08
A_1(TO3)	634±1.5	−2.4±0.2	7±2	1.2±0.6	−3.2±0.3

crossing points are listed in Table II. Observe that modes which exhibit the greater nonlinearities in their pressure dependence also show the strongest nonlinear behavior as a function of temperature.[8] An estimate of P_1 can be obtained by examining more closely the pressure dependence of the soft E(TO1) mode. On the basis of the behavior of the soft-mode frequency in the cubic PE phase, inferred by pressure measurements of the dielectric constant[2] [Eq. (3)], one might expect a similar dependence for the soft E(TO1) mode in the FE phase, such as given in Eq. (4). This equation could be rewritten as

$$\omega^2_{E(\mathrm{TO1})}=\omega_0^2(1-P/P_1), \tag{7}$$

where ω_0 is the frequency of the E(TO1) mode at zero pressure. In Fig. 3 we plot $\omega^2_{E(\mathrm{TO1})}$ versus pressure. The experimental points (circles) were fitted by least squares to the linear dependence of Eq. (7) (solid line). The fit is extremely good and the parameters obtained from it ($\omega_0=84.3\pm0.5$ cm^{-1}, $P_1=90\pm4$ kbar) are listed in Table II. We observe that the estimate of P_1 obtained by this method is in close agreement with the crossing point of the anisotropy-split Γ_{15} triplets. This coincidence could be fortuitous, but its occurrence is suggestive evidence in favor of the internal consistency of the previous analysis.

The fact that $\omega_{E(\mathrm{TO1})}$ can be equally well fitted by a linear dependence in pressure (see Fig. 2) can be explained if we notice that the last measured point (66.3 kbar) is still far from the extrapolated value of P_1 and therefore the nonlinear terms arising from Eq. (7) are not yet strongly noticeable. From Eq. (7) a slightly different value for the MGP of this mode is obtained:

$$\gamma_{E(\mathrm{TO1})}=+\frac{B_T}{\omega_0}\frac{d\omega_{E(\mathrm{TO1})}}{dP}=-\frac{B_T}{2P_1}=-4.8\pm0.2, \tag{8}$$

20% smaller than the one listed in Table I.

Keeping inequality (5) in mind, it seems safe to set the following limits to the transition pressure P_c:

$$80<P_c<90\pm4 \text{ kbar}. \tag{9}$$

The lower limit can be compared to the value of

TABLE II. Critical pressure P_1 for the ferroelectric phase transition of $PbTiO_3$ and crossing points (extrapolated) of pairs of phonons which are degenerate in the cubic phase.

Criteria	P (kbar)
Crossing point of A_1(TO2) and E(TO2) modes	88±12
Crossing of A_1(TO3) and E(TO4) modes	95±13
P_1 extrapolated from Eq. (6) and data for $\omega^2_{E(\mathrm{TO1})}$	90±4

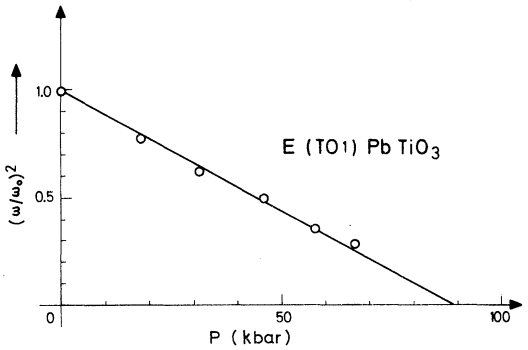

FIG. 3. Frequency squared vs pressure for the soft E(TO1) mode.

P_0 [see inequality (5)] extrapolated linearly from Samara's dielectric measurements,[2] $P_0 = 76$ kbar. The close agreement between this value and our experimental findings implies that the P-vs-T relationship for this phase transition does not deviate strongly from a simple linear relation in the range from 0 to 80 kbar (or alternatively from 300 to 640 K). It is then of value to give limits for the quantity dT_C/dP. The inequality (9) suggests

$$5.2 < -\frac{dT_C}{dP} < 5.9 \text{ K/kbar} . \tag{10}$$

Finally, a tentative comparison can be made between soft-mode MGP's obtained in the present work for the tetragonal FE phase and those inferred by Samara[2] (in the PE phase) from dielectric-constant measurements. In Ref. 2 the relationship

$$\gamma_f(P, T) = B_T \epsilon / 2C^* \tag{11}$$

is proposed to obtain the MGP of the soft mode in the cubic PE phase. Using Eq. (3) this reduces to

$$\gamma_f(0, T) = -B_T(T)/2P_0(T) . \tag{12}$$

In order to compare the MGP's from our experiments with those obtained by use of Eq. (12), values of B_T and P_0 for $T = 300$ K are required. B_T is given at room temperature by Kabalkina *et al.*[17]; hence some form of extrapolation is needed to predict P_0 at room temperature from Samara's high-temperature P_0's. Using the same linear extrapolation as before, the values $P_0 = 76$ kbar and $\gamma_f = -5.9$ are obtained, in very close agreement with our measured values for $\gamma_{E(\mathrm{TO1})}$. The agreement obtained with a linear extrapolation of P_0 gives added support to the thesis that the P-vs-T relationship in this transition remains linear (or very closely linear) from 640 to 300 K.

In conclusion, we obtained linear (MGP's) and higher-order coefficients in the expansion of phonon frequency versus pressure for all TO modes in $PbTiO_3$. These coefficients are useful for the determination of anharmonic parameters in the interionic potential. Used in conjunction with measurements of phonon frequencies as a function of temperature[7,8] and thermal-expansion data,[1] the frequency change with temperature at constant volume can be obtained. Lattice dynamical models for this crystal should profit from this experimental knowledge. Also, from the present work information about the FE – PE phase transition was obtained which shows substantial agreement with dielectric-constant measurements.

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