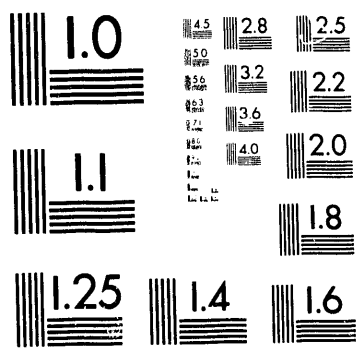
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The Multicomponent Lineshape of the Anharmonic A_1(TO) Phonon in $PbTiO_3$*

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THE MULTICOMPONENT LINESHAPE OF THE ANHARMONIC A_1(TO) PHONON IN $PbTiO_3$*

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ABSTRACT Detailed Raman studies of the optical phonons in single-crystal $PbTiO_3$ indicate that the frequencies and symmetry assignments in the literature must be revised. In this study, all $\vec{k} \cong 0$ optical phonon modes are directly observed and are shown to rigorously obey Raman selection rules. The angular dependence of the phonon frequencies indicates that the energy of the lowest frequency A_1(TO) mode, which exhibits an anomalous anharmonisity-induced lineshape, is higher than the energy of the lowest frequency E(LO) mode at 300°K.

INTRODUCTION

The phonon structure of $PbTiO_3$ has been studied by a variety of techniques [1-6]. These results classify the ferroelectric phase transition in $PbTiO_3$ as a prototypical "soft-mode" displacive type, with soft modes observed in both the paraelectric (PE) and ferroelectric (FE) phases [1]. The first detailed Raman scattering experiments of $PbTiO_3$, carried out by Burns et al. [3], who observed the softening of the intense, lowest-frequency E(TO) mode. The softening of the lowest-frequency A1(TO) phonon was not be directly observed, but was inferred by fitting the angular dependence of the oblique phonon spectra using Merten's relation [7]. Based on the Raman selection rules a more recent study [5] has called into question the frequencies and symmetry assignments of Burns et al. [3]. However, no explanation was given for the anomalous line shape of the peak associated with the A_1(TO) phonon in Ref. 5. In this paper, we report detailed Raman studies of the optical phonons of high-quality single-crystal $PbTiO_3$. In contrast to all earlier studies, we observed directly all $\vec{k} \cong 0$ optical phonon modes and map the full angular dependence of the oblique (i.e. off-axis) phonons, which demonstrates that the phonons rigorously obey the Raman selection rules. Our results, in agreement with those of Ref. 6, indicate that revisions are needed in the frequency and symmetry assignments established in the literature [3,4,6]. We also observe that the A_1(TO) mode exhibits an anomalous, highly-anisotropic lineshape which we attribute to the anharmonic nature of the effective interatomic potential associated with this phonon.

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EXPERIMENTAL

The growth [8], preparation, [8,9] and detwinning [10] of our $PbTiO_3$ single crystals has been reported previously. Unlike previous studies[3], the DC resistivity of the as-grown multi-domain crystals was very high (~3.2 x 10^{10} Ω-cm). Typically, only U^{+3} compensated crystals exhibit such high DC resistivities [11]. After preparation, the resulting single crystals were transparent, yellowish in color and consisted of a single FE domain with final dimensions of 2.5 x 2.5 x 1.5 mm. The Raman instrumentation has been previously reported [12]. Raman scattering data (~0.5 cm^{-1} resolution) were obtained at 487.9 nm @ 100 mW using 180° backscattering, 90° scattering and platelet [13] scattering geometries.

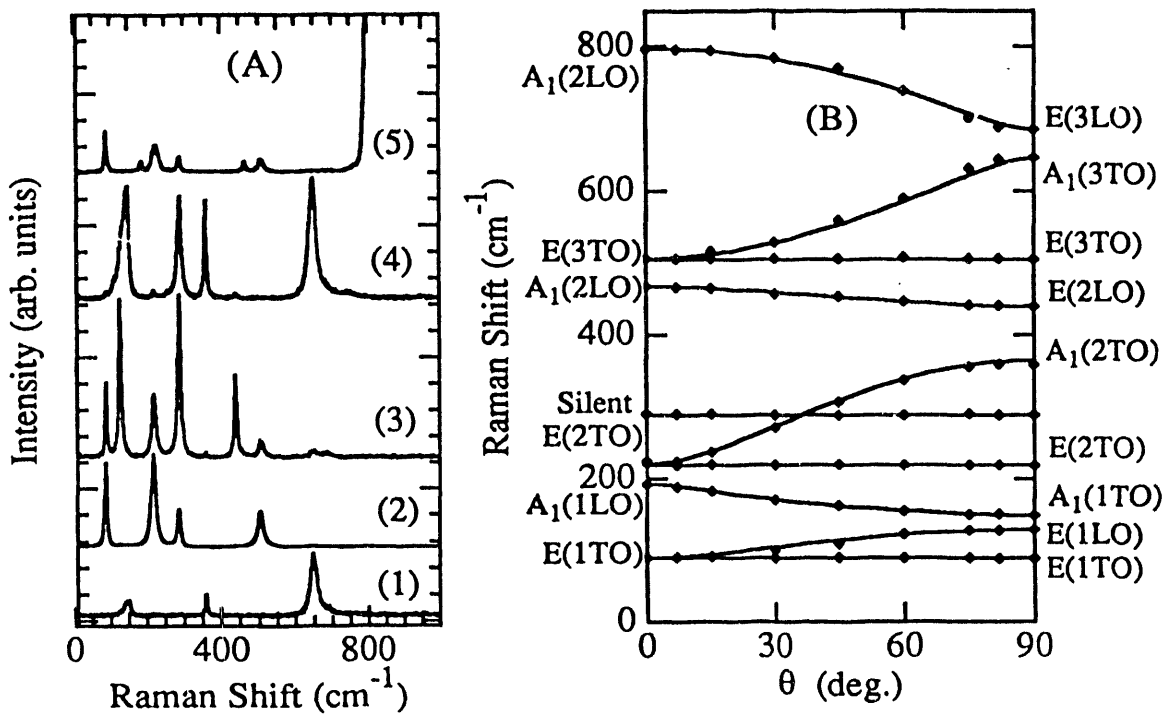

FIGURE 1. (A) Raman spectra of single-domain single-crystal $PbTiO_3$ at 300°K. (B) Frequencies of the oblique phonons (◆) in $PbTiO_3$ plotted as a function of θ, the angle between the $\vec{c}$ axis and the phonon wavevector $\vec{k}$. The solid lines are the predicted angular dispersion derived from Merten's equation, Eq. (1).

PHONON SYMMETRY AND THE ANGULAR DEPENDENCE OF THE OBLIQUE MODES

The expected symmetries of the phonon modes in $PbTiO_3$ are well understood. In the FE phase [$T<T_c$; C_{4v}^1 (P4mm) space group], each of the three PE phase [$T>T_c$; O_h^1 (Fm3m) space group] T_{1u} modes and one T_{2u} mode split into pairs of modes transforming as A_1+E, and B_1+E, respectively, which are both Raman and infrared active. Long range electrostatic forces split the $T_{1u} \Rightarrow A_1+E$ modes into TO and LO components. Splitting

of the $T_{2u} \Rightarrow B_1 + E$ modes (designated as "silent") is also allowed, but not observed[3-6]. In this paper, we will follow the labeling scheme used by Burns et al.[3]: modes that arise from the $3T_{1u}$ modes are labeled in sequence 1, 2, and 3 from low to high frequency, (e. g., the three E(TO) modes will be called E(1TO), E(2TO), and E(3TO)).

Fig. 1A shows typical Raman spectra of $PbTiO_3$. Spectra (1), (3), and (4) were taken in platelet geometry with $\vec{q} // \vec{a}$ and polarized (zz), (zx)+(zy), (xx)+(yy)+(xy), respectively, while spectrum (2) was taken in x(zy)x geometry ($\vec{q} // \vec{a}$). Spectrum (5) was taken in unpolarized platelet geometry with $\vec{q} // \vec{c}$. From the selection rules, the three peaks observed spectrum (1) should correspond to the $3A_1$(TO) modes. Burns et al. [3] observed a similar spectrum [3] [x(zz)y] and assigned the two higher energy peaks at 359.5 and 647.0 cm^{-1} to the A_1(2TO) and A_1(3TO) modes, respectively. However, because of lineshape asymmetry, the 148.5 cm^{-1} peak was not assigned to the A_1(1TO) phonon, but was interpreted as an "extraneous" line. We assume this to mean that this mode arise from some higher order scattering process; however, no detailed explanation of its origin was proposed. In the more recent study [5], the 148.5 cm^{-1} peak was assigned to the A_1(1TO) phonon based solely on its polarization.

The selection rules allow only E(TO) modes in spectrum (2) and both E(TO) and E(LO) modes in spectrum (3). Therefore, in agreement with Ref. 3, we assign the peaks at 87.5, 218.5 and 505.0 cm^{-1} to the E(1TO), E(2TO), and E(3TO) phonons, respectively, and the peaks at 128.0, and 440.5 cm^{-1} to the E(1LO), and E(2LO) phonons, respectively. The E(3LO) was not observed by Burns et al., [3] but was fit to a value ≈36 cm^{-1} lower than our measured result of 687.0 cm^{-1}. The peak at 289 cm^{-1} is assigned to the E-symmetry component of the "silent" mode [3,6]. Only the $3A_1$(TO) modes and the B_1-symmetry component of the "silent" mode are allowed in spectrum (4); clearly the peak at 289 cm^{-1} corresponds B_1 "silent" mode. In spectrum (5), the allowed symmetries are E(TO) and A_1(1LO), and we observe the A_1(1LO), A_1(2LO), and A_1(3LO) modes at 194.0, 465.0 and 795.0 cm^{-1}, respectively. Burns et al. [3] reported the frequency of the A_1(2LO) mode at 440.5 cm^{-1}; 24.5 cm^{-1} lower than our observed value. Burns et al. [3] did not directly measure the frequency of the A_1(1LO) mode; by fitting to Merten's relation, it was determined to be 215 cm^{-1}; 21.0 cm^{-1} higher than measured.

From selection rules, it is tempting to assign the 148.5 cm^{-1} peak to the A_1(1TO) mode. However, the high resolution of our data (0.5 cm^{-1}) shows that this peak exhibits an anomalous lineshape unexpected for a single phonon. In the previous low resolution studies [3-5] (≥4.0 cm^{-1}), the lineshape only showed a slight asymmetry. In our data, this feature clearly consists of several peaks. However, this peak does not correspond to the weak second-order Raman spectrum of $PbTiO_3$ [5]. To demonstrate that this feature is indeed the A_1(1TO) phonon, we consider the angular dispersion of the phonon mode frequencies. For uniaxial crystals, the phonon mode frequencies disperse as a function of the angle θ between $\vec{k}$ and the $\vec{c}$ axis (i.e., the FE spontaneous polarization direction).

Phonons observed for $\theta = 0,\pi/2$ correspond to the pure LO and TO modes, while at intermediate values of θ, the modes are termed oblique phonons or "quasimodes". The frequency dispersion of the oblique phonons is given by the zeros of general form of Merten's equation [7],

$$\begin{aligned}&\varepsilon_c(\infty)\cos^2\theta\prod_i(\omega_c(iLO)-\omega^2)\prod_i(\omega_a(iTO)-\omega^2)+\\&\varepsilon_a(\infty)\sin^2\theta\prod_i(\omega_a(iLO)-\omega^2)\prod_i(\omega_c(iTO)-\omega^2)=0.\end{aligned} \tag{1}$$

which is derived from the generalized form of the LST relation [3,12], where $\varepsilon_c(\infty)$ and $\varepsilon_a(\infty)$ are the dielectric constants derived from the ordinary and extraordinary optical refractive indexes. If the frequencies of all the $3n-3$ principal axes phonons are known, then the frequencies of the oblique modes at any angle θ are given by the $3n-3$ values of ω which satisfy Eq. (1). It is important to note that no specification of the symmetry of the modes for $\theta = 0,\pi/2$ is implied by Eq. 1. The actual symmetries will depend on whether the elastic anisotropy is larger or smaller than the electrostatic splitting [7].

In Fig. 1B, the frequencies (▲) of the oblique phonon modes in $PbTiO_3$ are plotted versus θ, and the symmetry assignments established from selection rules are labeled along the principal axes. The angular dependence of the quasimodes associated with the 148.5 cm^{-1} peak connects this peak to the A_1(1LO) mode at 194.0 cm^{-1} ($\vec{k} \parallel \vec{c}$). Therefore, the 148.5 cm^{-1} peak is the fundamental A_1(1TO) phonon which exhibits an anomalous lineshape. This symmetry assignment is natural since this satisfies the Raman selection rules and since this is the only remaining unassigned phonon. To summarize, the frequencies (in cm^{-1}) of the principal axis phonons are: B_1+E 289.0; E(TO) 87.5, 218.5, 505.0; E(LO) 128.0, 440.5, 687.0; A_1(TO) 148.5, 359.5, 647.0; and A_1(LO) 194.0, 465.0, 795.0. These frequencies, together with the literature values [14] of ε_a and ε_c were used to calculate the solutions to Merten's relation, Eq. (1), shown as the solid lines in Fig. 1B; note that this is not a fit. The largest discrepancy from the measured values is ≈8 cm^{-1}, which further supports our assignment for the A_1(1TO) mode.

We note that at T=300°K, the frequency of the A_1(1TO) mode, which is expected to exhibit soft-mode behavior, is higher than the frequency of the E(1LO) mode which should be relatively insensitive to temperature. Therefore, at some elevated temperature, the energies of the E(1LO) and A_1(1TO) $\vec{k}\cong 0$ modes must cross. The mode softening reported in Ref. 6, indicates that most of the softening occurs within ~50°K of T_c. It is possible that the E(1LO)–A_1(1TO) mode crossing could occur in the vicinity of T_c and play a role in the dynamics of the phase transition. This is currently under investigation.

A_1(1TO) LINESHAPE AND ANHARMONISITY

In Fig. 2, we show the temperature dependence of the lineshape of the A_1(1TO) mode; the solid lines represent the experimental data. Note that the line shape appears to be a superposition of subpeaks. At T=400°K, four distinct peaks are clearly visible which we label 1 to 4 (1 is the highest energy). The shoulder at ~87.5 cm^{-1} results from leakage of the strong E(1TO) mode. As the temperature is lowered, the intensity of peaks 2-4 decrease, and the individual peaks become more difficult to resolve. In order to obtain the temperature dependence of the relative intensities of the subpeaks that comprise the lineshape of the A_1(1TO) mode, we fit the spectra to a sum of lorentzian functions [6]. The dotted line is the resultant fit and the dashed lines are the individual lorentzian components.

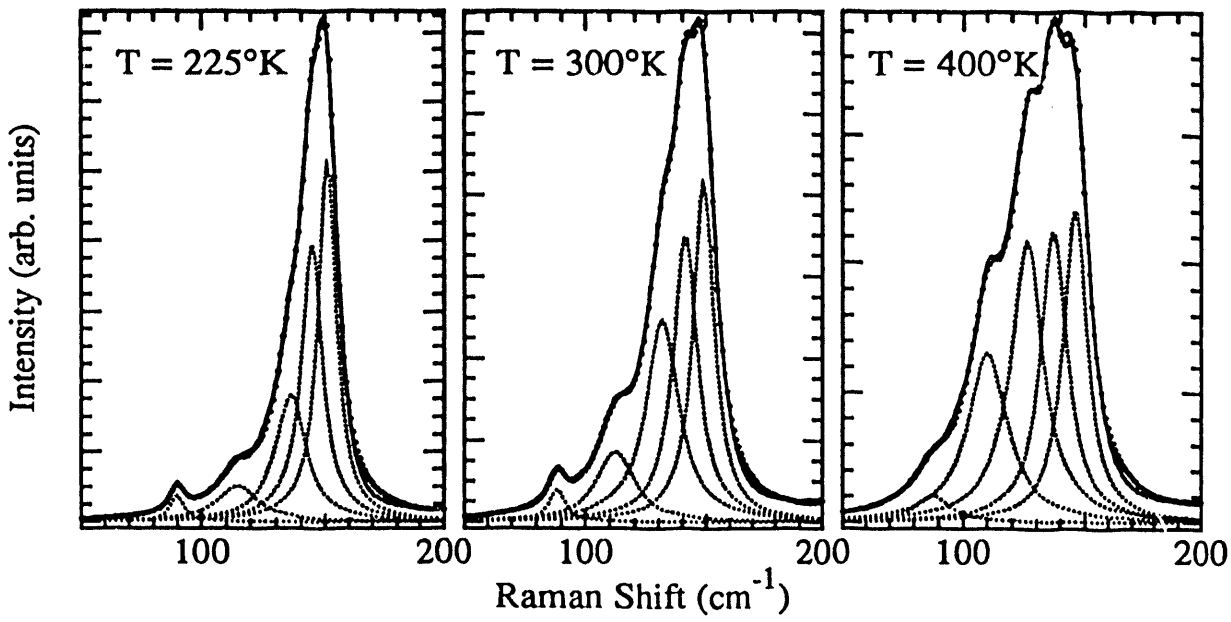

FIGURE 2: Temperature dependence of the lineshape of the A_1(1TO) phonon obtained in 180° backscattering. The solid line is the experimental data and the dotted line is the result of a fit to a sum of lorentzian functions and the dashed lines are the individual lorentzian components.

From normal mode calculations [15], the calculated $\vec{k}\cong 0$ ionic motions of the A_1(1TO) phonon are a relatively rigid displacement of the O_6 octahedra relative to the Ti and pseudo-cubic Pb cage. The line shapes of the peaks in Fig. 1B can be qualitatively understood assuming a double-well potential for the A_1(1TO) phonon. The two equivalent minima of this highly anharmonic potential have been used to describe the two equivalent states of dielectric polarization in ferroelectric materials such as $PbTiO_3$ [16]. It is known [17] that the anharmonic contributions to the lattice potential energy are large and cannot be treated in perturbation theory. The explanation we propose is that the low frequency shoulders of the A_1(TO) mode are due to transitions between the excited phonon states in this potential well. We suggest that Peak 1 would correspond to a

transition from the first excited state to the ground state (Stokes scattering), while peaks 2-4 would correspond to transitions from higher excited states to adjacent lower energy excited states. It should be emphasized that this is not a two phonon process since it only involves a single quantum. The energy differences between these transitions arises as a direct result of the removal of the degeneracy in the harmonic approximation. We have reported a more rigorous phenomenological description of this model[18].

CONCLUSION

We have reported detailed Raman studies of the optical phonons of high-quality single-crystal $PbTiO_3$. All $\vec{k} \cong 0$ optical phonon modes are directly observed and are shown to rigorously obey Raman selection rules indicating that the mode energies and symmetry assignments in the literature [3] must be revised. The angular dependence of the oblique phonon frequencies was shown to compare well with the predicted dispersion from Merten's relation. We have proposed a model in which we attribute the anomalous lineshape of the A_1(TO) mode to the anharmonic nature of the lattice.

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