

## Raman Line Shapes of Anharmonic Phonons

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Anharmonic effects in crystals typically result in the symmetric broadening of the single-phonon Lorentzian line shape. However, a simple model, based on consideration of a highly anharmonic potential, shows that anharmonicity can lead not only to asymmetric line shapes but also to line shapes composed of multiple subpeaks. Experimental Raman data on the soft  $A_1(\text{TO})$  phonon in ferroelectric  $\text{PbTiO}_3$  indicates that this mode does indeed consist of a series of subpeaks whose intensities are accurately predicted (with no fitting parameters) by our model.

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One of the powerful tools available to experimental condensed matter physics is Raman scattering. It is the inelastic scattering of light from elementary excitations of matter [1], and it has been used with enormous success in studying a great variety of problems involving vibrational, magnetic, and electronic properties of solids, liquids, and gases. In first-order Raman scattering process, i.e., involving the creation or destruction of a single quantum, the measured frequency shift of the peak relative to the incident radiation is equal to the energy of the excitation and the Lorentzian line shape of the peak is related to the lifetime of the state in question. Previously, non-Lorentzian line shapes have typically been traced to second or higher order scattering processes [2] (i.e., involving more than one quantum), Fano-type line shapes [3] resulting from the interaction of a single state with a continuum background of states, or disorder induced breakdown of wave vector conservation. In this Letter, we wish to show that very asymmetric line shapes, indeed even line shapes with structure, can be understood in terms of a "single excitation" picture.

The Raman scattering results we shall present are for single-crystal  $\text{PbTiO}_3$ , which is considered as the prototypical displacive ferroelectric material [4]. While there have been a number of Raman scattering investigations in this material concentrating on various aspects of the ferroelectric transition [5–8], of interest to the present work is the existing ambiguity in the literature regarding the identification of the lowest-frequency  $A_1(\text{TO})$  phonon [5,7]. The softening of this mode, together with that of the lowest-frequency  $E(\text{TO})$  phonon, is believed to be indicative of the displacive nature of the phase transition at around  $\sim 769$  K. Burns and Scott [5] dismissed assigning the intense peak at  $148\text{ cm}^{-1}$  observed in  $x(\text{zz})y$  geometry (i.e., with propagation vector,  $\mathbf{q}$ , in the basal plane) as the  $A_1(\text{TO})$  phonon because the line shape of this peak was clearly non-Lorentzian; they labeled it as "spurious" and concluded that the real peak corresponding to the phonon was buried beneath it. On the other hand, Fontana *et al.* [7] assigned this peak to the  $A_1(\text{TO})$  phonon as a result of its polarization characteristics; however, they did not give an explanation for the asymmetry

of its line shape. We have recently undertaken a detailed study of single-crystal  $\text{PbTiO}_3$  and, from measurement of the angular dispersion of the phonons, positively conclude that the intense peak at  $148\text{ cm}^{-1}$  for  $\mathbf{q}$  in the basal plane is the  $A_1(\text{TO})$  phonon. The complete result of this investigation will be presented elsewhere [9]: Here we wish only to concentrate on the explanation of the multicomponent line shape since this aspect is of potential interest to a considerably broader audience.

High resolution ( $0.5\text{ cm}^{-1}$ ) Raman spectra of the  $A_1(\text{TO})$  phonon are shown in Fig. 1 as a function of temperature (400, 300, 225 K). Except for the feature at  $\approx 87\text{ cm}^{-1}$ , which is leakage from the lowest  $E(\text{TO})$  mode, all the other structure is associated with the  $A_1(\text{TO})$  mode. An important point to note is that the line shape is not a smooth function but appears to be a superposition of subpeaks. At  $T=400$  K, the line shape clearly shows four distinct peaks at 148.5, 137.5, 126.5, and  $110.5\text{ cm}^{-1}$ , which we will label the peaks as 1, 2, 3, and 4, respectively. The spectra have been fitted as the sum of five Lorentzians; the individual peaks obtained from the fit are shown by the dotted lines, the full line is the sum of these peaks and is almost indistinguishable from the experimental data. At lower temperatures the fitting procedure was not reliable because the subpeaks are weaker and not well resolved.

The line shapes of the experimental peaks in Fig. 1 can be qualitatively understood assuming a double-well potential for the phonon as shown in Fig. 2. This type of potential is eminently reasonable for tetragonal ferroelectric materials such as  $\text{PbTiO}_3$  [10], and it describes the two equivalent minima corresponding to the two equivalent states of dielectric polarization (i.e.,  $+z$  and  $-z$ ); it is known [11] that the anharmonic contributions to the lattice potential energy are so large that they cannot be treated in perturbation theory. The explanation we propose is that the low-frequency shoulders of the  $A_1(\text{TO})$  mode are due to transitions between the excited phonon states in the potential well. We illustrate these transitions in Fig. 2, where the energy levels shown in one side of the double well depict the possible phonon states associated with the  $A_1(\text{TO})$  mode. Peak 1 of this phonon

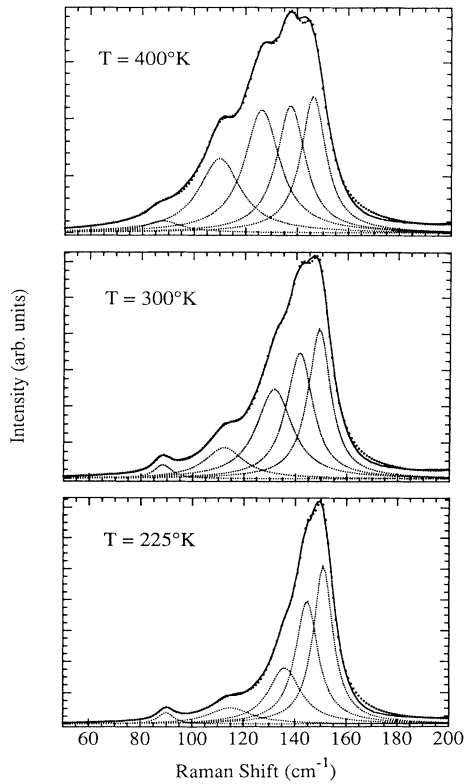


FIG. 1. Temperature dependence of the line shape of the  $A_1(1TO)$  phonon obtained in  $180^\circ$  backscattering. The solid line is the experimental data, the dotted line is the result of a fit to a sum of Lorentzian functions, and the dashed lines are the individual Lorentzian components.

(highest energy) would correspond to a transition from the first excited state to the ground state (Stokes scattering). Peaks 2–4 would correspond to transitions from higher energy 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. This distinction of transitions between the different levels of the potential arises as a direct result of lifting the degeneracy of the transitions in the harmonic approximation.

The arguments of the preceding paragraph can be made more rigorous in the following way: Consider the potential energy,  $\Phi(Q)$ , for the normal mode coordinate,  $Q$ , of the form [11]

$$\Phi(Q) = \frac{\tilde{k}_s}{2} Q^2 + \frac{\xi}{4} Q^4 + \frac{\zeta}{6} Q^6. \quad (1)$$

This potential, schematically shown in Fig. 2(a), can be envisioned either in the extended mode representation (phonon picture) or as a local normal coordinate [12,13]. In this latter case it qualitatively corresponds to the atomic motion depicted in Fig. 2(b). By applying perturbation theory to one of the anharmonic minima of the

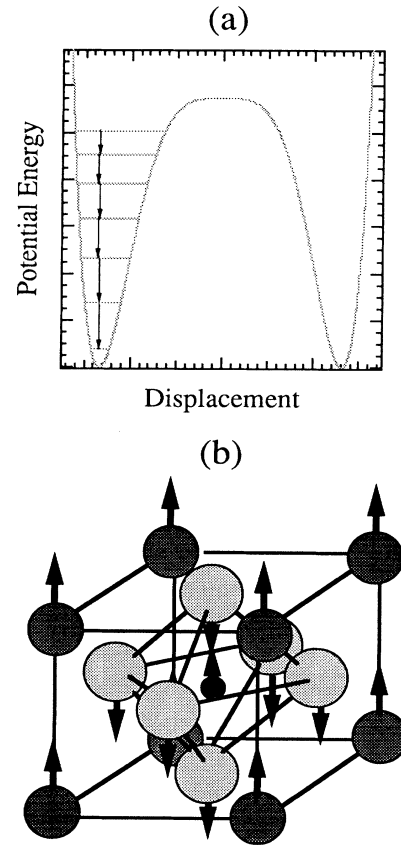


FIG. 2. (a) Schematic representation of the double-well potential along the  $c$  axis in the ferroelectric phase of  $PbTiO_3$  illustrating the anharmonic nature of the potential of the  $A_1(1TO)$  phonon. We attribute the complex nature of the line shape of this mode to transitions between the excited phonon states in the well. (b) An illustration of the atomic displacements associated with the  $A_1(1TO)$  phonon for  $\mathbf{k} \approx 0$ .

double well potential, the calculation of the energy levels can be performed in either representation. In the extended picture the result has the same form as the partial anharmonic contribution to the free energy [14]. In the local picture one can directly use the more familiar equations for anharmonic corrections from Ref. [15]. Both approaches lead to energy differences between levels  $E_{n+1} - E_n$  of the form

$$\Delta E = E_{n+1} - E_n = \hbar \omega_0 - f(\tilde{k}_s, \xi, \zeta, n), \quad (2)$$

where  $\hbar \omega_0$  is the solution to the harmonic part of Eq. (1) and  $f$  is a function which depends on the parameters  $\tilde{k}_s$ ,  $\xi$ ,  $\zeta$ , and  $n$ . To lowest order, the correction term  $f$  in Eq. (2) is linear in  $n$  [15] leading to an expected splitting between our measured subpeaks which is independent of  $n$ . From our 400 K data, we find that the spacings between subpeaks are 11, 12, and 15  $\text{cm}^{-1}$ ; that these spacings are not equal is attributed to higher order perturbation corrections.

TABLE I. Theoretical and experimental intensity ratios of the peaks associated with the  $A_1(\text{ITO})$  phonon line shape.

Temperature	225 K	300 K	400 K
Theory			
0 to 1	1.00	1.00	1.00
1 to 2	0.78	0.98	1.17
2 to 3	0.45	0.73	1.03
3 to 4	0.23	0.48	0.81
Experiment			
0 to 1	1.00	1.00	1.00
1 to 2	0.88	0.98	1.22
2 to 3	0.55	0.87	1.04
3 to 4	0.21	0.35	0.87

Since the intensity of a given transition is proportional to the population of the initial state which is determined from the Gibbs distribution [15] and, in the harmonic approximation, the matrix element is proportional to  $\sqrt{n+1}$  [16], the relative intensity  $R$  of the transition (Stokes) from level  $n+1$  to  $n$  to that of the 1 to 0 transition is given by

$$R = (n+1) \exp\left(-\frac{n\hbar\omega}{k_B T}\right), \quad (3)$$

where for the phonon in question  $\hbar\omega$  is  $148 \text{ cm}^{-1} = 213 \text{ K}$  and  $k_B$  is Boltzmann's constant. In Table I, we list the intensity ratio values determined from Eq. (3) at various temperatures and compare them with the integrated intensities of the  $A_1(\text{ITO})$ -phonon peaks 1 through 4 estimated from the fit of the Raman data to Lorentzians. The agreement is well within the experimental errors.

An additional consequence of our interpretation is that the high lying phonon states in the well should also have shorter lifetimes so that we expect the peak linewidths to gradually broaden as the energies of the levels increase. This is also qualitatively observed in the line shapes in Fig. 1.

Recently, Raman line shapes composed of multiple peaks have been reported in the coherent anti-Stokes Raman scattering (CARS) vibron spectrum of shock compressed  $\text{N}_2$  [17] (i.e.,  $T > 2500 \text{ K}$  and pressure  $> 10 \text{ GPa}$ ). In this Letter, the nature of the line shape was associated with the anharmonic component of the molecular potential in the molecular crystal. To our knowledge, the current Letter is the first report of anharmonicity-associated multiple-peak Raman line shapes in the phonon spectrum of a solid under conditions of temperature and pressure near ambient.

In conclusion, we have presented a model to account for multicomponent line shapes of "single phonon" Raman lines in cases where the lattice anharmonicity is substantial. With this approach, the structure of the line shape becomes a probe which should provide detailed in-

formation about the interatomic potentials associated with a given mode. Recent data [7,18] suggests that the nature of the ferroelectric phase transition in  $\text{PbTiO}_3$  has an order-disorder component as opposed to the purely displacive character originally inferred from the phonon mode softening [4-6]. We anticipate that our ongoing investigations of the Raman spectrum of  $\text{PbTiO}_3$  at high temperatures (close to the ferroelectric phase transition) will contribute to a clearer understanding of this phenomena.

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