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Phonon self-energy in $LiTaO_3$ and $LiNbO_3$

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Infrared reflection spectra (extraordinary ray) of lithium niobate and lithium tantalate in the temperature range 300–1300 K exhibit a feature which cannot be described correctly with an additional classical oscillator and which is understood as a phonon self-energy effect. Comparison is made with room-temperature Raman data where two additional peaks in the same spectral region have been assigned to a fundamental polar phonon mode activated by a distortion of the structure.

In a recent work, Penna and co-workers[1] reported the observation of a number of peaks in the A_1-type Raman spectrum of lithium tantalate at room temperature and this number is greater than expected from a group-theory analysis based on recent determination of the crystal structure, viz., four A_1 modes. Since their total number of modes is consistent with that predicted by an analysis involving the group C_3, Penna *et al.*[1] assigned the nine peaks to fundamental phonons and asserted that the structure of $LiTaO_3$ is slightly distorted so that the symmetry group would be C_3 instead of C_{3v}. Among the five additional modes, three are found above 300 cm^{-1} near 460, 660, and 750 cm^{-1}. A_1-type modes in $LiTaO_3$ are polar, hence infrared active. The present paper reports the analysis of the extraordinary reflectivity spectrum in the range 275–1000 cm^{-1} which also exhibits features—but not necessarily "peaks," as will be emphasized—at two of these three frequencies, viz., ~450 and 660 cm^{-1}. Results at high temperature in $LiTaO_3$ and the isomorphous compound $LiNbO_3$ indicate the occurrence of same effect and will be also reported. Due to the fortuitous sensitivity of the reflectivity technique to the dispersion found near 460 cm^{-1}, we will concentrate on this point. Penna *et al.* report the existence of a polar phonon mode the TO and LO frequencies of which are 458 and 465 cm^{-1}, respectively, with a damping of 13 cm^{-1}.

The reflectivity spectrum of $LiTaO_3$ at room temperature is shown in Fig. 1. Our results agree well with those of Barker *et al.*[2] in the range 400–1000 cm^{-1}. Concerning the band 200–400 cm^{-1}, the reflectivity found at the top is a few percent higher than that reported in Ref. 2. Results at higher temperature, but still in the ferroelectric phase, are shown in Figs. 2 and 3 for $LiTaO_3$ and $LiNbO_3$. Barker and co-workers[2] were able to fit their room-temperature reflection spectrum with the usual dielectric function model expressed as a sum of classical oscillator contributions

$$\epsilon = \epsilon_\infty + \sum_j \Delta\epsilon_j \frac{\Omega_{j\mathrm{TO}}^2}{\Omega_{j\mathrm{TO}}^2 - \omega^2 + i\gamma_{j\mathrm{TO}}\omega} . \qquad (1)$$

We reported recently[3] that attempts to fit $LiNbO_3$ A_1 spectra with the model equation (1) are worse and worse with the increase of the temperature at which the spectrum was recorded, while the fit is rather correct at room temperature as shown previously by Barker and Loudon.[4] The fact that

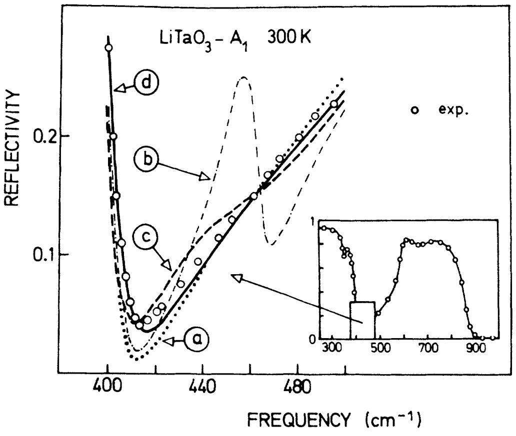

FIG. 1. Comparison of experimental reflectivity data with curves calculated with (a) the four-parameter model equation (2), (b) the same model with the additional oscillator reported by Penna *et al*. (Ref. 1), (c) with a strongly damped polar mode at 460 cm^{-1} (TO-LO splitting higher than that of Penna *et al*. (Ref. 1) with a damping ~ 100 cm^{-1}), (d) with phonon self-energy terms of the form shown in Fig. 4 acting on the TO mode near 600 cm^{-1} [Eq. (4)]. All calculated curves are merged apart from the region of the minimum and fit the experimental data satisfactorily as shown in the inset.

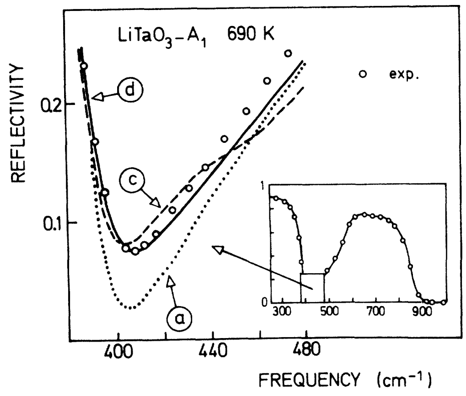

FIG. 2. Same as legend to Fig. 1.

not only dampings are considered as constant but also same damping for TO and LO modes is implicitly assumed in the case of a single reflection band as emphasized in Ref. 5, constitutes a weakness of the classical dispersion theory equation (1). Same TO and LO dampings may be a good approximation when the reflection band is narrow and then when nearly same phonon decays are expected but there is no reason for an identity between γ_{TO} and γ_{LO} when the LO energy is far above the TO one, that is when the reflection band is wide. Both infrared and Raman results[4,6,7] indicate differences between TO and LO dampings of adjacent modes in these compounds. For these reasons, we tried to fit reflectivity data with the aid of the factorized form of the dielectric function[5,8]

$$\epsilon = \epsilon_\infty \prod_j \frac{\Omega_{j\mathrm{LO}}^2 - \omega^2 + i\gamma_{j\mathrm{LO}}\omega}{\Omega_{j\mathrm{TO}}^2 - \omega^2 + i\gamma_{j\mathrm{TO}}\omega} . \qquad (2)$$

This model has several advantages which have been the subject of recent papers,[5,9] which we will merely outline. The TO and LO frequencies are approximately positioned at the highest-slope points of the low- and high-frequency edges of a reflection band, respectively. A preliminary dressing to the data fit is thus readily achieved as soon as TO and LO frequencies are positioned. Dampings γ_{TO} and γ_{LO} impose the slopes at these edges, respectively. The number of runs used to obtain agreement with the data turns out to be much less than that when Eq. (1) is used. In addition, fits are generally better near LO frequencies without inclusion of additional secondary oscillators which often palliate the weakness of the classical dielectric function. Fits of the model equation (2) to the LiTaO$_3$ and LiNbO$_3$ data are satisfactory at any frequency and temperature apart from the reflectivity minimum near 420 cm^{-1} where the data are higher than the calculated curve. Since the width near the minimum reaches at least 30 cm^{-1}, a lack of resolution cannot be invoked to explain the discrepancy. The situation is reversed with respect to that reported by Barker and Hopfield[10] concerning BaTiO$_3$, SrTiO$_3$, and KTaO$_3$ where the experimental data are below the curve calculated with Eq. (1), at a similar reflectivity minimum. As a result, any attempt to couple modes according to their theory yields worse fits.[3] Actually the failure of both models equations (1) and (2) is not surprising because a Kramers-Kronig analysis reveals an asymmetrical line shape for both TO near 600-cm^{-1} and LO near 400-cm^{-1} phonon modes. This asymmetry is more or less pronounced, depending on compound and temperature (results for LiNbO$_3$ in Ref. 3). Equations (1) and (2), which imply constant dampings, are thus not expected to correctly describe asymmetrical phonon lines that may reflect frequency-dependent damping functions.

We have calculated the frequency-dependent real $\Delta\omega(\omega)$ and imaginary $\Gamma(\omega)$ parts of the phonon self-energy of the TO mode near 600 cm^{-1}. A Kramers-Kronig analysis has been combined with Eq. (2), and constant TO and LO frequencies and dampings which yield a good description of the reflection spectrum outside the range of the minimum at 420 cm^{-1}. The result is shown as dots in Fig. 4 for LiNbO$_3$ at 1175 K, for example. A peak is clearly visible in the γ function at ~460 cm^{-1}. Based on Green's-function approach, Maradudin and Fein[11] have established the form of the lowest-order phonon self-energy. Let us rewrite their result in the form

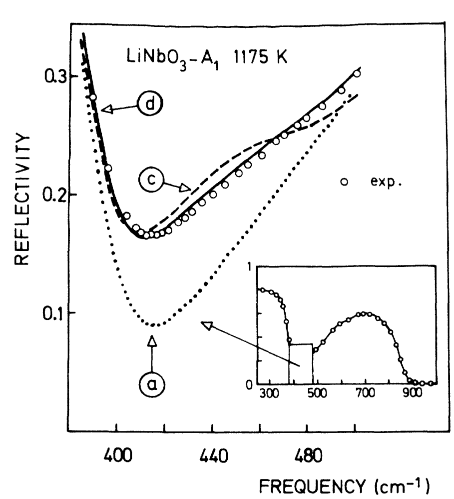

FIG. 3. Same as legend to Fig. 1.

$$\Delta\omega_j(\omega)+i\Gamma_j(\omega)=\frac{18}{\hbar^2}\sum_{\vec{k}_1 j_1 j_2}|V^{(3)}(\vec{0}j,\vec{k}_1 j_1,-\vec{k}_1 j_2)|^2 \times\left(\frac{n_1+n_2+1}{\omega-\omega_1-\omega_2-i\Gamma}+\frac{2(n_1-n_2)}{\omega+\omega_1-\omega_2-i\Gamma}\right), \qquad (3)$$

where symbols have their standard meaning and where a finite linewidth Γ has been conferred to the original δ functions. If an intense two-phonon peak exists at the frequency $\omega_{2\mathrm{ph}}=\omega_2\pm\omega_1$, and if the phonon self-energy functions are assumed to be flat up to the limits of influence of the mode $\vec{0}j$ apart from this peak, an oversimplification of Eq. (3) yields

$$\Delta\omega(\omega)+\tfrac{1}{2}i\gamma(\omega)=\Delta\omega_0+\tfrac{1}{2}i\gamma_0+g^2/(\omega-\omega_{2\mathrm{ph}}-i\Gamma), \qquad (4)$$

where g has the dimension of a frequency. Equation (4) is fully consistent with the experimental result shown in Fig. 4.

First we have attempted to explain the high level of reflectivity in the minimum at 420 cm^{-1} as an effect of the additional phonon reported by Penna *et al.*[1] ($\Omega_{\mathrm{TO}}=458$, $\Omega_{\mathrm{LO}}=465$ cm^{-1}) although no sequence "hump and hole" is visible in the reflection spectrum at 460 cm^{-1}. The result is shown in Fig. 1. The conclusion is that such a polar phonon mode with a splitting of 7 cm^{-1} and a damping of 13 cm^{-1} as reported by Penna should be clearly observed in the reflection spectrum, contrary to experiment. If this oscillator is considerably damped then the reflectivity level fall again below the data. If one increases the TO-LO splitting up to ~13 cm^{-1} and if one keeps a high damping (typically 100 cm^{-1}), the correct reflectivity level is then reached but one "sees" a dip in the calculated reflectivity which is not observed experimentally and thus one does not fit the data correctly. This situation is found more or less marked in both lithium niobate and tantalate at any temperature. Conversely, a fit with the factorized form of the dielectric function Eq. (2) where the phonon self-energy of the TO mode near 600 cm^{-1} alone is described with the model Eq. (4) whereas all other TO- and LO-phonon modes are described with constant parameters, allows the best agreement with experimental data as shown in Figs. 1–3. The form of the $\Delta\omega(\omega)$ and $\gamma(\omega)$ functions used is shown in Fig. 4, for example. The structure of both calculated curves is clearly consistent with the result deduced from the experiment. Minor discrepancies are due to inaccuracies of the Kramers-Kronig analysis in the present conditions together with the simplifications inherent to both models Eqs. (2) and (4).

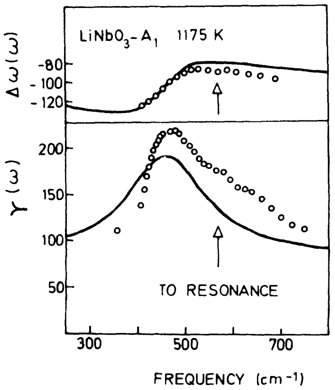

FIG. 4. Experimental phonon self-energy terms (dots) of the 572-cm^{-1} TO mode. Full curves are self-energy functions calculated with the model Eq. (4) which are found to fit the experimental reflection spectrum as shown in Fig. 3.

We would like to emphasize that the actual position of the TO phonons whose frequencies are below 275 cm^{-1} and which are not observed presently (that is essentially the most polar TO mode near 200 cm^{-1}) is found to play a negligible role in the calculation of the spectrum. This is an additional advantage of the model Eq. (2). The reflectivity indeed appears essentially determined by the Ω_{TO} and γ_{TO} parameters in the low-frequency half of a band, while it is the LO parameters that play the essential part in the high-frequency half, hence the usefulness of the four-parameter model is derived. Concerning the lowest-frequency TO mode, any downshift of the frequency is accompanied by an increase of the oscillator strength as long as LO frequencies are fixed. Both effects approximately counterbalance each other so that the contribution of this TO mode to the dielectric function remains nearly a constant at frequencies above 300 cm^{-1}. Johnston and Kaminow[12] reported that the 200-cm^{-1} TO mode softens with increasing temperature down to the transition temperature at ~890 K. Penna and co-workers[13] claimed that they did not observe any softening of this mode although their own measurements show a considerable decrease of the asymptote of the lowest-frequency A_1 polariton from 200 cm^{-1} down to 45 cm^{-1} where it seems to saturate. The softening (although perhaps not down to zero) of the asymptote of the polariton, which is the position of the A_1 TO phonon itself, is confirmed by other authors.[14] But independent of this controversy, it appears that some confidence can be attached to the parameters obtained in the present analysis according to the arguments above. To reinforce this assertion, let us note that the frequencies determined presently agree

TABLE I. Comparison of Raman data of Ref. 1 with the TO and LO frequencies associated with the main infrared bands observed presently at room temperature in $LiTaO_3$.

	LO	TO	LO
Penna *et al*. (Ref. 1)	401	594	866
This work	403	594	863

within 0.5% with those given by Penna *et al.*[1] as shown in Table I.

It should be pointed out that the consideration of frequency-dependent parameters for the 594-cm^{-1} TO phonon, thus accounting for its asymmetrical line shape, also confers a reverse asymmetrical shape to the adjacent 403 cm^{-1} LO phonon, consistent with the experiment.[3] This is readily understood by inspection of Eq. (11) in Ref. 5. γ_{TO} and γ_{LO} dampings indeed are nothing more than the damping function evaluated at the Ω_{TO} and Ω_{LO} frequencies, notwithstanding the values that both $\Delta\omega(\omega)$ and $\gamma(\omega)$ functions take between both frequencies, especially in the vicinity of a peak in the two-phonon density of states in the present case.

Several tries have shown that the dip near 660 cm^{-1} may be described indifferently either with an additional oscillator as done by Barker *et al.*[2] or by the model equation (4). But if the first description is choosen, then a TO-LO splitting of at least 5 cm^{-1} associated with a damping of ~60 cm^{-1} is necessary to account for the dip in the reflectivity. Raman data indicate no TO-LO splitting higher than 1 cm^{-1} if any, and the same peak appears in both A_1 and E spectra (the same dip is observed in the E infrared spectrum as well). Consequently, it seems to us that a description of the dip based on the phonon self-energy mechanism also should be preferred.

Our results in the range 400–600 cm^{-1} seem to have several important consequences. First, no dip assignable to a polar mode is found in the reflectivity near 460 cm^{-1}, whereas the data are consistent with a peak in the two-phonon density of states which contributes to the reflectivity via an anharmonic mechanism involving the frequency-dependent phonon self-energy of the neighbor TO mode and which consequently creates asymmetric phonon lines. This situation prevails in both $LiTaO_3$ and $LiNbO_3$ compounds at any temperature in the range 300–1300 K. The dependence of the phonon self-energy on temperature, especially in the vicinity of the phase transition will be presented in a subsequent paper. Thus rather large anharmonicities are found in both crystals. One may then wonder whether the additional structure observed in the Raman spectrum[1] actually could be two-phonon peaks instead of fundamental phonons activated by a lowering of symmetry.

The second point concerns infrared reflectivity spectroscopy. It is not physically clear, especially in the transparent regime,[15] whether a hump in the several-phonon density of states is observed in the infrared absorption as a polar nth-order mode with a finite oscillator strength or via phonon self-energy terms of the fundamental modes. An example where the reflectivity technique is sensitive enough to conclude in favor of the second mechanism is presently found. *Ab initio* calculations limited to single-polar-mode crystals also support the physics of the phonon self-energy by comparison with experimental infrared spectra.[16]

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