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Analysis of quasielastic light scattering in $LiTaO_3$ near T_C

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We have reexamined the Raman spectra of lithium tantalate from 294 to 1059 K with special emphasis upon the quasielastic scattering from 0–200 cm^{-1}. We show that the complete A_1-symmetry spectrum at each temperature, including both the lowest-energy optical phonon and the quasielastic scattering, can be fitted to the response function for a system with a relaxing self-energy $\chi^{-1}(\omega,T)=\omega_0^2(T)-\omega^2-i\omega\gamma(T)-\delta^2(T)/[1-i\omega\tau(T)]$ and that the fitting parameters vary monotonically with temperature. In agreement with recent analysis of $LiNbO_3$ [Okamoto, Wang, and Scott, Phys. Rev. B 32, 6787 (1985)] we find that the linewidth γ for the lowest energy A_1 phonon increases rapidly with temperature, from 27 cm^{-1} at 294 K to 382 cm^{-1} very near T_C; τ exhibits a critical slowing down from 0.50 ps far from T_C to 2.6 ps at T_C and continues to increase above T_C (5.3 ps at 1059 K); the lowest-energy optical phonon "softens" only slightly, from ω_0 of 202 cm^{-1} at 294 K to 178 cm^{-1} at $T_C=881$ K (determined from the dielectric constant), and that the coupling constant $\delta^2(T)$ increases supralinearly with temperature, as in $LiNbO_3$.

INTRODUCTION

Lithium niobate and lithium tantalate have undergone a large number of spectroscopic studies over the last two decades.[1–8] Despite their isomorphic structures, they appear to differ considerably in their dynamic properties near their Curie temperatures. This has led to an ongoing controversy concerning such qualitative and basic matters as the nature of their ferroelectric phase transitions—in particular, whether they are better described as displacive or order disorder, two points of view argued most effectively by Johnston and Kaminow[1] and by Penna *et al.*,[6–8] respectively.

In a very recent publication[9] Okamoto, Wang, and Scott attempted to reconcile early work and to show that the complete $LiNbO_3$ spectrum for trace α_{jj} polarizability scattering is compatible with what has become the standard model[10–12] for systems with relaxing self energies:

$$\chi^{-1}(\omega,T)=\omega_0^2(T)-\omega^2-i\omega\gamma(T)-\frac{\delta^2(T)}{1-i\omega\tau(T)} \quad (1)$$

describes a system with a damped harmonic oscillator representing the lowest-energy optical phonon of long wavelength and totally symmetric character in the ferroelectric phase; this phonon is coupled to a Debye relaxation of characteristic time $\tau(T)$. This analysis showed that the optical phonon in question was only moderately "soft"—that the decrease toward zero frequency as T approached T_C from below arises primarily from the nonlinear divergence in its linewidth rather than from an intrinsic decrease in the quasiharmonic frequency $\omega_0(T)$. In this sense our results fall somewhat midway between the displacive interpretation of Kaminow and Johnston[1] and the order-disorder view of Penna *et al.*[6–8] In addition to this information about soft-mode frequency and damping, we were able to extract unambiguous numerical values for the relaxation time $\tau(T)$ of the unspecified mode into which the lowest-energy transverse optical phonon is coupled, and the strength of the coupling constant $\delta^2(T)$.

The present paper extends these studies to lithium tantalate. We would like to see if the same formalism [Eq. (1) above] is capable of describing high temperature spectra in $LiTaO_3$, and how the parameters of the theory compare between $LiNbO_3$ and $LiTaO_3$. We emphasize at the outset that Penna *et al.*[6–8] should be credited with first pointing out the existence of a Debye relaxation spectrum in $LiTaO_3$ characterized by a temperature-dependent relaxation time $\tau(T)$. They in fact argued for the applicability of Eq. (1) to this material. However, they did not fit the parameters [other than relaxation time $\tau(T)$] appearing in Eq. (1) to their observed spectra.

EXPERIMENT

The data to be presented here were obtained from a large crystal of lithium tantalate grown from congruent melt in Nanjing, China. It was a rectangular parallelepiped, x-ray oriented, poled, and free of twins. The Raman spectra were obtained with an Ar laser emitting approximately 500 mW at 514.5 nm. Spectral slit widths were typically ≈ 3 cm^{-1} over the temperature range from 294 to 1059 K. Since the quasielastic scattering to be analyzed here lies in the region extending beyond 50 cm^{-1}, it was not particularly useful to employ an iodine filter and single-moded laser.

Representative data are shown in Fig. 1 for several temperatures. It can be seen from this figure that the primary spectral change is in the relative intensity of the quasielastic scattering from approximately 0 to 50 cm^{-1}, with respect to the intensity of the lowest-energy A_1(TO) phonon at about 200 cm^{-1}. There is also a noticeable increase in the linewidth of the latter mode.

Fitting data like those shown in Fig. 1 to $kT/\hbar\omega$ times the imaginary part of the response function whose inverse is given in Eq. (1) yielded five parameters at each temperature: The quasiharmonic phonon frequency $\omega_0(T)$,

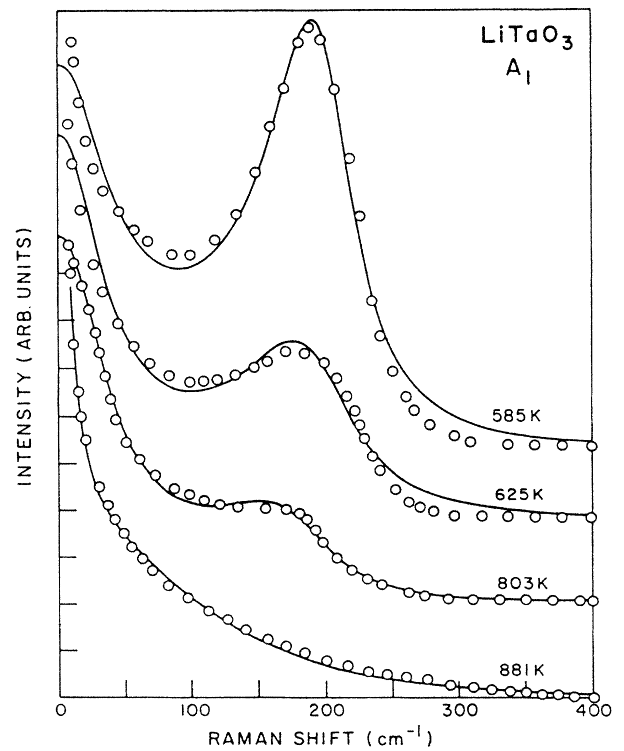

FIG. 1. Typical Raman data for *zz*-polarizability tensor component in $LiTaO_3$ at temperatures from 585 K to $T_C = 881$ K. Solid curves are least-squares fit to a population factor (kT/ω) times the imaginary part of the response function whose inverse is given in Eq. (1).

the phonon damping constant $\gamma(T)$, the Debye relaxation time $\tau(T)$, the coupling constant $\delta^2(T)$ describing interaction between the A_1(TO) phonon and the Debye relaxation, and an overall intensity factor. These data are summarized at 13 temperatures in Table I. Their values are discussed in the following section.

Correlation matrices were examined for these parameters at each temperature. As discussed in our work[9] on $LiNbO_3$, these were not excessively correlated. Therefore, we think that the parameters listed in Table I are numerically meaningful. The most serious problem arises for $\delta^2(T)$ and $\tau(T)$; when the imaginary part of the susceptibility described in Eq. (1) is taken, the *effective* coupling parameter becomes $\delta^2(T)\tau(T)$, rather than $\delta^2(T)$. This may be readily seen by multiplying $\delta^2(T)/(1-i\omega\tau)$ by $(1+i\omega\tau)$ and separating the real and imaginary parts. As a result, in this kind of analysis, both in Ref. 9 and the present work, the product $\delta^2(T)\tau(T)$ is more reliably obtained than is $\delta^2(T)$ alone.

ANALYSIS

The frequency data for the quasiharmonic frequency of the lowest-energy A_1(TO) phonon show a total decrease of 12% between room temperature and T_C. This compares with approximately 18% in $LiNbO_3$ and shows that $LiTaO_3$ is slightly less displacive than $LiNbO_3$. Of greater interest is the temperature dependence of soft-mode linewidth. If the data are fitted in Fig. 2 using a formula

$$\gamma(T) = A + BT + \frac{CT_C^*}{T_C^* - T} , \qquad (2)$$

where T_C^* is an adjustable parameter not equal to the Curie temperature, the best fit yields $A = 1.5 \pm 5.5$ cm^{-1}, $B = 0.075 \pm 0.01$ cm^{-1}/K, $C = 5.5 \pm 0.3$ cm^{-1}, and $T_C^* = 890 \pm 2$ K. This is the form suggested by our recent work on linewidth divergences in uniaxial ferroelectrics.[13]

Analyzing the values of $\delta^2(T)$ and $\tau(T)$ from Table I is somewhat more complicated. For reasons discussed in the preceding section, the products $\delta^2(T)\tau(T)$ are the most reliable parameters. It is quite interesting to note in Fig. 3 that these products are also about the same for $LiNbO_3$

TABLE I. Lithium tantalate phonon parameters.

Temperature (K)	Soft-mode frequency ω_0 (cm^{-1})	Soft-mode linewidth γ (cm^{-1})	$\delta^2(T)\tau(T)$ (cm^{-1})	Inverse Debye relaxation time (cm^{-1})	Coupling constant $\delta^2(T)$ (cm^{-2})
294±1	202±2	27±2	uncertain	uncertain	uncertain
323	201±1	29±1	uncertain	uncertain	uncertain
389	198±1	41±1	uncertain	uncertain	uncertain
467	196±2	49±1	133±28	uncertain	uncertain
505	195±1	56±2	151±14	uncertain	uncertain
563	195±1	67±4	166±9	uncertain	uncertain
585	195±2	71±5	176±7	54±6	9500±40
625	194±3	78±12	182±9	66±7	12010±60
690	187±3	90±13	192±18	66±8	12670±60
803	183±3	107±8	261±13	54±7	14090±90
838	184±2	156±6	281±7	30±2	8370±80
850	178±3	178±3	288±11	24±1	7000±70
865	179±5[a]	270±9[a]	352±8[a]	17±2[a]	5910±50[a]
$881 = T_C$	178±5[a]	382±12[a]	419±20[a]	13±2[a]	5450±40[a]
958				8±2	
1059				6±2	

[a] Denotes a measurement in the temperature region in which the mode is overdamped; this value is less reliable than others in its column.

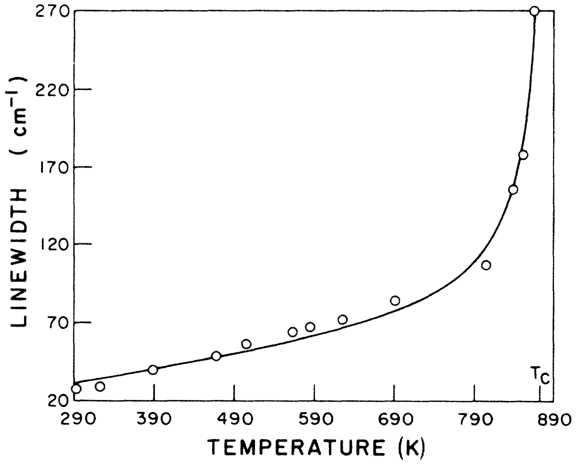

FIG. 2. Linewidth $\gamma(T)$ for lowest-energy A_1(TO) phonon in $LiTaO_3$. Solid curve is a fit to Eq. (2) with parameters given in the text.

and $LiTaO_3$ at the same absolute temperatures, despite the differences in their transition temperatures. And it is both curious and unexplained that the linewidths and coupling term $\delta^2\tau$ appear to scale together with absolute temperature, if data very near T_C [where the last term in Eq. (2) is important] are ignored.

Our interpretation of these data is that both soft-mode linewidths and coupling constants are controlled by the same microscopic extrinsic process. This probably involves charged defects, which could be oxygen vacancies. In the paragraph that follows we discuss evidence that these defects are characterized by relaxation times that continue to grow longer above T_C; they are therefore not intimately related to the transition itself (which favors oxygen vacancies in comparison with off-center Li ions).

The data for relaxation time $\tau(T)$ are unreliable below approximately 570 K. The reason is that at low temperatures the quasielastic scattering is weak in intensity. This makes the results sensitive to the assumptions made for the background subtraction procedure. From 585 K to within 50 K of T_C the relaxation time is constant, within experimental uncertainty; the reciprocal relaxation time τ^{-1} is equal to 60 ± 6 cm^{-1}. This compares with 18 cm^{-1} in $LiNbO_3$. However, within 50 K of T_C critical slowing down of $\tau(T)$ is manifest, as shown in Fig. 4. It is notable that the quasielastic scattering in $LiTaO_3$ continues to narrow as one continues to heat the sample well above T_C. This is not expected for critical quasielastic scattering, and among other things, it rules out Brillouin scattering as a significant source of intensity. We find the width of quasielastic scattering to decrease from approximately 60 cm^{-1} just below T_C to 13 cm^{-1} at T_C, then to 8 cm^{-1} at 958 K and 6 cm^{-1} at 1059 K. These values are still outside our experimental resolution of 3 cm^{-1}. The implication is that there is an extrinsic scattering mechanism that continues to display a slowing down with increasing temperature well above T_C. It is possible that this relates to the "glassy" ferroelectric behavior observed by Burns in other materials.[14] The final comparison we can make from Table I is that of coupling constants δ^2. In our previous paper we found that these diverged approximately as $t^{-1.4}$ for a congruent specimen, where t is reduced temperature $(T_C-T)/T_C$, but were nonmonotonic for a stoichiometric sample, with a decrease near T_C. In the present study of $LiTaO_3$ we find only a 50% increase in $\delta^2(T)$ as temperature is increased from 585 to 803 K. A conspicuous error in our last paper was the claim that the divergence in $\delta^2(T)$ agreed with the theory of Halperin and Varma. In fact Halperin and Varma predict[15] that above T_C, a linear dependence of $\delta^2(T)$ on $1/T$ with a dip at T_C whereas our data (as well as those[15] on $RbCaF_3$) display an approximately linear dependence on reduced temperature. The experimental results therefore did not

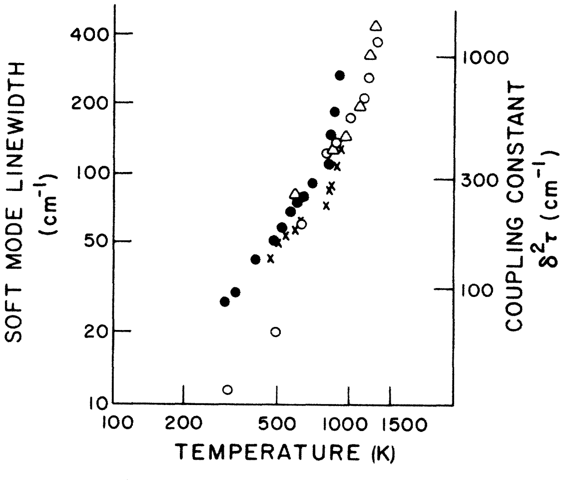

FIG. 3. Optical parameters relating to the phase transitions in $LiTaO_3$ and $LiNbO_3$. Open circles are soft-mode linewidths in $LiNbO_3$; solid circles are soft-mode linewidths in $LiTaO_3$; crosses are coupling constants $\delta^2\tau$ in $LiTaO_3$; triangles are coupling constants $\delta^2\tau$ in congruent $LiNbO_3$. The fact that all these data fall along more or less the same curve suggests to us that the soft-mode linewidth dependence arises from coupling with defects, probably oxygen vacancies, since the coupling constant δ^2 must have such an origin.

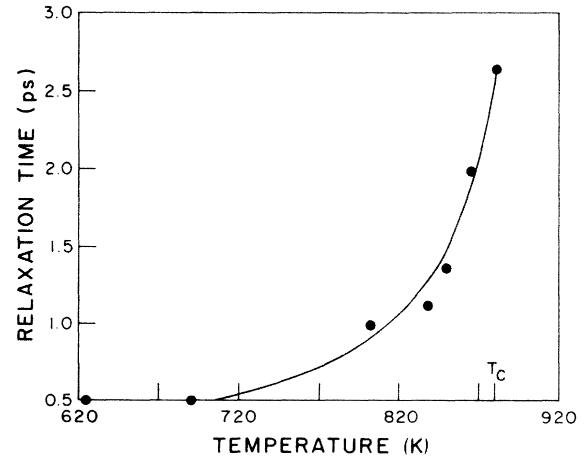

FIG. 4. Relaxation time $\tau(T)$ in $LiTaO_3$. Solid curve is a fit to Eq. (3) with $T_C^*=923$ K and $\tau_0=0.12$ ps. Note that this T_C^* is greater than that of 890 K from the linewidth data in Fig. 2.

agree with the theory at all. A similar disagreement is observed for $\delta^2(T)$ in the present work.

If we compare values of δ in $LiNbO_3$ and $LiTaO_3$ we find δ varies from 97 cm^{-1} at 585 K to 119 cm^{-1} at 803 K in $LiTaO_3$; whereas δ varies from 85 cm^{-1} at 848 K to 155 cm^{-1} at 1224 K in $LiNbO_3$. Expressed in terms of reduced temperature, that is $\delta=97$ cm^{-1} at $t=0.66$ in $LiTaO_3$, $\delta=91$ cm^{-1} at $t=0.66$ in congruent $LiNbO_3$, $\delta=99$ cm^{-1} in stoichiometric $LiNbO_3$. Thus, the absolute value of the coupling constant seems to scale with reduced temperature in the isomorphic materials. At larger values of t we find slightly less close agreement. At $t=0.8$, $\delta=113$ cm^{-1} in $LiTaO_3$, 155 cm^{-1} in congruent $LiNbO_3$, and 121 cm^{-1} in stoichiometric $LiNbO_3$. In general, it appears that δ scales nearly as reduced temperature in these materials.

It is useful to point out that the central mode intensity compared with the intensity of the soft optical phonon is predicted[10–12] to vary as $\delta^2(T)/\omega_0^2(T)$. If we examine that prediction by reference to Fig. 1, we see that at 585 K (top trace) the prediction is for intensity ratio of 1:4. Using the fitted linewidths and a factor of 2 which enters (there is one central mode and two—Stokes and anti-Stokes—TO phonons; or alternatively, one must consider only positive frequencies—half of the central mode), this predicts a ratio of peak heights of 71:108, in reasonable accord with observations (the fit of 585 K data gives an experimental peak height ratio of 88:100).

In Fig. 4 we plot relaxation time $\tau(T)$ versus temperature. The solid curve is a fit to

$$\tau(T)=\tau_0[T_C^*/(T_C^*-T)]=t^{-1}\tau_0$$

with $T_C^*=923$ K and $\tau_0=0.12$ ps. This t^{-1} dependence is the "classical" van Hove value; the equivalent terminology is that the product of critical exponents $z\nu=1.0$.

SUMMARY

The Raman data in $LiTaO_3$ have been fitted to a model of a damped harmonic oscillator which has a relaxing self-energy. It is found that such a description describes the data well from ambient temperatures to T_C. The coupling constant is found to scale with reduced temperature t in $LiNbO_3$ and $LiTaO_3$ and is of order 10^2 cm^{-1} at $t=0.7$. The relaxation time in $LiTaO_3$ is approximately 0.55 ps far from T_C and exhibits a t^{-1} divergence near T_C. In both $LiNbO_3$ and $LiTaO_3$, the linewidths for the lowest-energy totally symmetric transverse optical phonon increase supralinearly with temperature; their values near T_C are more than an order of magnitude greater than ambient. Over a 50-K range of temperature near T_C these can be best fitted to divergences of form t^{-1}. Over a wider range of T, far from T_C, there is a strong increase in γ which is approximately a power law in *absolute* temperature. Although the microscopic origin of the latter increase in linewidth is not understood, a clue is provided in the present work from the fact that the coupling constant $\delta^2(T)$ has the same dependence. Since $\delta^2(T)$ explicitly comes from coupling between the TO phonon and defects having Debye relaxations, it follows that these are probably also the cause of the anomalous soft optic mode damping. In $LiTaO_3$ it is known[16] independently that there are typically 0.6% oxygen vacancies; these are the likely causes.

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