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Measurement of Anharmonic Renormalization of Phonon Frequencies*

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The shift and broadening of several phonon modes in KCl and RbCl have been measured as a function of temperature from 10 to 400 °K by means of first-order Raman spectra induced by Tl^+ impurities. Mode Grüneisen parameters are computed for the major phonon frequencies which contribute to the Raman spectra. These dominant phonons lie near the zone boundary.

In some recent papers,[1,2] it has been shown that impurity ions induce first-order Raman scattering in alkali halides. In the present paper we report the use of this technique to study anharmonic effects in the phonon spectra of thallium-doped KCl and RbCl at temperatures between 10 and 400 °K.

In these crystals, the Tl^+ occupies the cation site, which has O_h point symmetry, and the induced Raman scattering is from the even-parity A_{1g}, E_g, and T_{2g} vibrations in which the Tl^+ is at rest. In Refs. 1 and 2 it was found that the Tl^+ acts as an isotopic defect; i.e., force-constant changes relative to Rb^+ or K^+ are $0 \pm 10\%$. Hence, the induced Raman spectra constitute a direct probe of the vibrational spectra for the pure host lattices. Variations of these Raman spectra with temperature give information on the anharmonic interactions which cause both a shift and broadening of the phonon frequencies. Theories of this anharmonic renormalization have been described by many authors.[3-5]

The shifts and broadenings have been measured directly by neutron scattering.[6] Both Raman scattering[7] and infrared absorption and reflectance measurements[8] have also been used in pure crystals, but are restricted to the $\vec{q} = 0$ optic-phonon modes.

However, in the case of impurity-induced Raman scattering, the impurities break the translational symmetry of the lattice and relax the $\vec{q} \approx 0$ selection rule which holds for pure crystals. Thus, in our Raman experiments we are able to observe phonons at many points in the Brillouin zone. This leads to continuous rather than discrete spectra which are first order, being allowed because the impurity also breaks the inversion symmetry for its neighbors.

The Tl^+-induced spectra at 15 °K for E_g and T_{2g} phonons in KCl : Tl^+ and for E_g phonons in RbCl : Tl^+ are shown in Fig. 1. They were recorded in the same manner as described in Ref. 1 except that, in order to improve the signal to noise and to work with higher resolution, the spectra were repeatedly swept and the signal accumulated in a multichannel memory unit (Enhancetron 1024). The KCl spectra in Fig. 1 are the result of 15 sweeps, while the RbCl spectrum was obtained with 26 sweeps. The instrumental resolutions for the spectra are indicated in Fig. 1. While the absolute peak positions are uncertain by ± 2 cm^{-1}, owing to possible spectrometer errors, the relative positions are accurate to less than 1 cm^{-1}. The concentrations of Tl^+ in the samples were 8.9×10^{19} cm^{-3} for KCl and $\sim 1 \times 10^{19}$ cm^{-3} for RbCl.

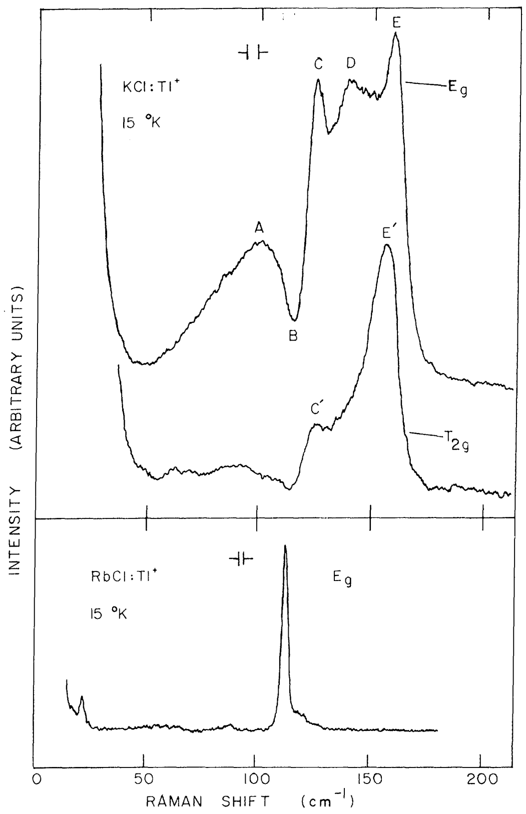

FIG. 1. Stokes spectra at 15 °K for top, KCl : Tl^+ E_g and T_{2g} modes taken at equal gain (features A – E′ are discussed in the text); bottom, RbCl : Tl^+ E_g mode. The background due to second-order scattering from the pure crystals is negligible at this temperature and energy. The small peak near 20 cm^{-1} in the RbCl : Tl^+ spectrum is a spectrometer ghost.

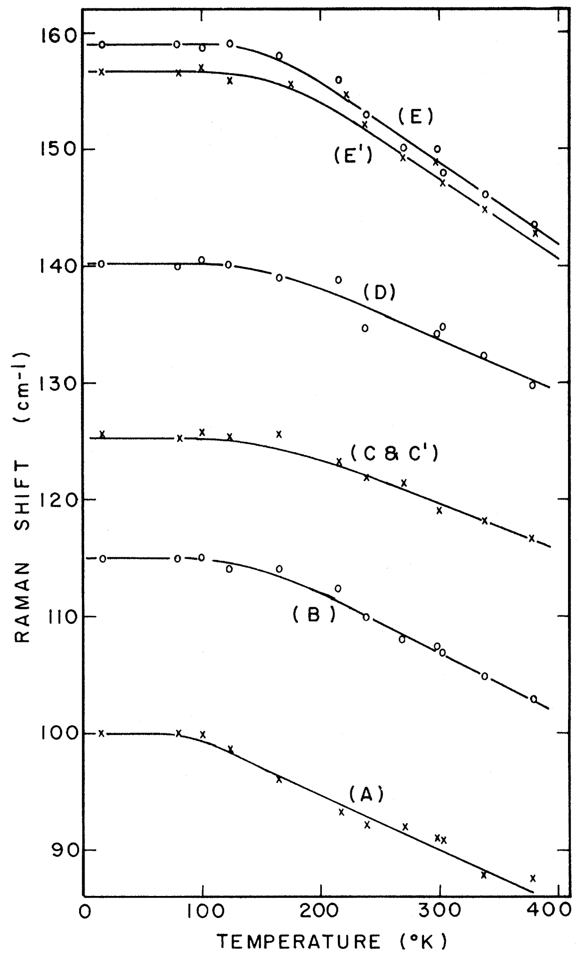

FIG. 2. Temperature dependence of the position of the features A through E in the KCl: Tl$^+$ spectra of Fig. 1.

As discussed in Refs. 1 and 2, one can explain these spectra quite adequately in terms of a model involving only the motions of the nearest neighbors of the impurity. Thus, the peaks in Fig. 1 are interpreted as arising from those phonons for which the projection of the density of states onto the n-n displacements of appropriate point symmetry is large.

The main features of the KCl E_g spectrum are labeled A through E and of the KCl T_{2g} spectrum C′ and E′. The temperature dependence of the positions of these features is shown in Fig. 2. The frequencies vary linearly with temperature at high temperatures, and are temperature independent in the liquid-helium region.

The inelastic neutron data of Copley, Macpherson, and Timusk,[9] and of Raunio and Almqvist[10] can be used to identify some of the phonons responsible for these features. A arises from acoustic phonons over a broad region of the Brillouin zone, and does not correspond to a particular zone-boundary symmetry point. The dip B is coincident with the frequency for the TO mode at L in the Brillouin zone. C and C′ (identical in frequency) are coincident with the minimum in the TO branch at W, while D does not correspond to any zone-boundary symmetry point. E and E′ are seen in Figs. 1 and 2 to differ slightly in frequency. Even though the difference is less than the resolution it is repeatable from run to run and sample to sample. The frequencies of E and E′ lie near a peak in the density of states, obtained from a shell-model fit to the neutron data and attributed to a saddle point in the LO branch.[9]

The temperature dependences for these features of the KCl spectra (Fig. 2) lie on reasonably smooth curves, except for A and D. D can be seen in Fig. 1 to be a broad band and the determination of its center was uncertain. A is also a broad band and, in addition, appears to shift to lower energy as the temperature is increased because the low-frequency part of the spectrum is enhanced as a result of the temperature-dependent factors in the scattering efficiency.[11] At 367 °K, for example, the peak at A is shifted upward by 4 cm^{-1} when the data are divided by the one phonon temperature factor. Figure 2 shows the corrected peak positions.

We have not made detailed measurements on the widths of the peaks for KCl since it was not clear how these should be defined, and in any case, the weakness of the scattering made it necessary to work with rather coarse resolution.

For RbCl, the sharpness of the E_g line at 113 cm^{-1} (Fig. 1) suggests that it is due to phonons at a single critical point in the Brillouin zone. However, complete inelastic neutron measurements have not been made, and an unambiguous identification is impossible. The rigid-ion model calculation by Karo,[12] the neutron measurements and analysis of the second-order Raman spectra of pure RbCl by Raunio and Rolandson,[13, 14] and the breathing-shell-model calculation[2] made using room-temperature parameters suggest that this phonon lies near the LA and TO cutoffs at L and the TO cutoff at Γ. Of these modes only the TO at L has a projection onto the E_g symmetry vibrations of the Tl$^+$ nearest neighbors so that this is the most probable. An exact identification must await measurement of the dispersion curves.

The temperature dependence of the position of this E_g phonon for RbCl is shown in Fig. 3. The temperature dependence of the full width at half-height is also shown. In determining the width, the resolution ranged from 0.8 cm^{-1} at low temperature to 3 cm^{-1} at high temperatures. There are two sources of uncertainty in the width. First, at high temperatures, determination of the base line becomes uncertain because the other very small E_g peaks seen in Fig. 1 become larger and the entire spectrum is superimposed on a second-order background.

Second, since the exact line shape is not known, one cannot correct for the instrumental resolution by the usual convolution techniques. We have used the approximate method of subtracting the square of the instrumental width from the square of the measured width to obtain the "true" width.

As can be seen in Fig. 3, the frequency and the width of the RbCl phonon have rather different temperature dependences. Within the experimental uncertainty, the width increases continuously as a linear function of temperature. The position, on the other hand, is temperature independent at low temperatures, varies linearly at intermediate temperatures, and begins to flatten out again above room temperature. The difference between the measured high-temperature positions and the extrapolated linear dependence is greater than the experimental uncertainties.

At present, we have not made a detailed application of the theories[3-5] for anharmonic renormalization to our data. However, the KCl temperature dependences agree qualitatively with theoretical results using third- and fourth-order anharmonic terms in the phonon self-energy.[3, 5] Our data are also in good numerical agreement with the neutron results of Raunio and Almqvist taken at 80 and 300 °K, and similar behavior has been observed in KBr and NaI by inelastic neutron scattering[6] and for the TO mode at $q \approx 0$ for RbI and AgBr by infrared absorption.[8]

We can compare our data with measurements of bulk thermal properties as follows. If the frequency ν_i of a normal mode of the crystal is solely a function of the volume, then the Grüneisen parameter for the mode is given by

$$\gamma_i \equiv -\frac{\partial \ln \nu_i}{\partial \ln V} = -\frac{1}{3\alpha\nu_i}\left(\frac{\partial \nu_i}{\partial T}\right)_p ,$$

where α is the linear thermal-expansion coefficient. For KCl at low temperatures, α goes to zero as T^3, whereas at high temperatures ($T \gtrsim$ Debye temperature) α is constant.[15] Our data are not accurate enough at low temperatures to give reliable values of γ_i, since both $(\partial \nu_i / \partial T)_p$ and α approach zero as $T \to 0$. However, at 300 °K we obtain $\gamma_i = 4.1$, 2.9, 2.9, 2.9, 4.0, and 3.9 for features A, C, C′, D, E, and E′ of Fig. 1, respectively.

From the combination of thermal-expansion, compressibility, and specific-heat data, the weighted average Grüneisen parameter for KCl at 300 °K is 1.45.[15] The contribution from acoustic modes near $q = 0$ to this average, obtained from the pressure dependence of elastic constants, is 1.06.[15] Thus higher values of γ_i, such as we have observed for optic and acoustic modes well away from $q = 0$, are to be expected, since modes with greater γ_i than the average must be present to

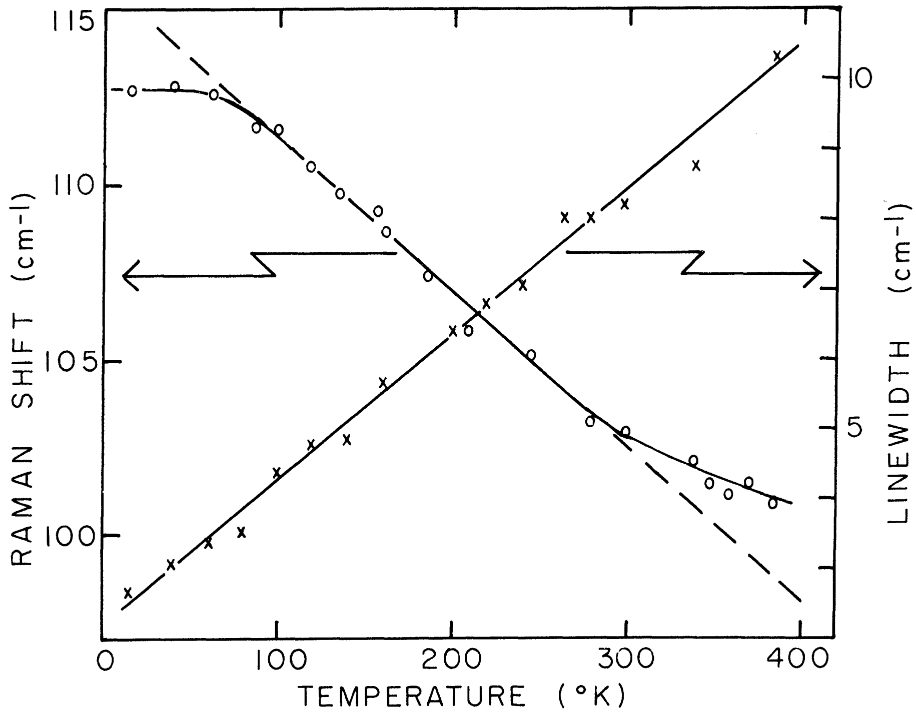

FIG. 3. Temperature dependence of the position and full width at half-height of the peak in RbCl : Tl$^+$ spectrum of Fig. 1.

compensate for the $q \approx 0$ acoustic modes.

RbCl is more complicated. The frequency shift and width clearly involve different combinations of anharmonic processes, since the width is changing rapidly at low temperatures in a region where the frequency is constant. This is similar to the behavior of the TO mode at $q = 0$ in AgBr.[8] However, the flattening out at high temperatures of the peak position is unusual and suggests a partial cancellation between competing anharmonic processes. It would be very interesting to see if this effect is observed by neutron scattering.

In conclusion, it appears that impurity-induced Raman scattering can be used to study anharmonic interactions in solids, and gives results in at least qualitative agreement with results obtained by more conventional techniques. The removal of translational symmetry allows the observation of phonons away from the zone center which can, otherwise, only be studied by the rather more cumbersome method of neutron scattering.

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Impurity Raman Scattering from CaF_2:Ce

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We have investigated the scattering from CaF_2:Ce crystals in which part of the trivalent Ce impurities have been reduced to the divalent state. Although the Ce^{2+} concentration was extremely low (~10 ppm) we observe electronic Raman scattering. In addition, we have observed a defect-induced spectrum closely approximating the unperturbed one-phonon density of states. The latter scattering is due to phonon modulation of the impurity Rayleigh scattering.

I. INTRODUCTION

Crystalline materials containing a divalent cerium impurity have attracted considerable interest lately, partly because of the potentially useful photochromic properties of such substances.[1] An unusual feature of Ce^{2+} is the fact that in most solids the ground state appears to be a member of the $5d^1 4f^1$ manifold.[2] Very little is known about the low-lying states of Ce^{2+} in solid matrices since at the low concentrations available (< 0.01%), infrared absorption techniques lack sufficient sensitivity and EPR is masked by the large Ce^{3+} background from several sites. We therefore decided to study the electronic Raman scattering[3,4] from divalent Ce^{2+} in CaF_2 crystals. This method is often more sensitive than infrared methods,[4,5] and with the near resonance conditions (laser energy near the