Raman Detection of One-Phonon–Two-Phonon Interactions in CuCl

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A large q-direction dependence of the broad band close to the TO peak is observed and explained qualitatively and quantitatively. The TO peak is found to be repelled out of a two-phonon band by a strong third-order anharmonic interaction.

In a crystal having the zinc-blende structure, the first-order Raman scattering allows detection of either the TO($q \sim 0$) phonon or the LO($q \sim 0$) phonon, according to the selected direction $\hat{q}$ of the transferred momentum. We have measured at 40 K the scattered intensities of a CuCl single crystal for various $\hat{q}$ directions (Fig. 1). Because all the spectra were recorded with the same spectral slit width (2 cm^{-1}), the heights (eventually above the continuum) of the sharp lines at 171 and 208 cm^{-1} could be taken to fix a common intensity scale for the drawings of Fig. 1 by making use of the fact that the chosen geometries impose $I_B = 0.5(I_A + I_C)$.

The unusual features in CuCl are the broad and strong band of the TO spectrum[1-3] (curve A) in the 140–170 cm^{-1} range, reaching a very sharp line at 171 cm^{-1} with a maximum at 151 cm^{-1}, and its replacement by a weak and featureless continuum in the LO spectrum (curve C). This observation of $\hat{q}$-dependent, first-order-like spectra obviously differs from the recent results of Shand *et al.*[3] and excludes the assignment of the broad band to a pure second-order Raman scattering.

We propose to explain these features by the existence of strong anharmonic interactions between one of the $q \sim 0$ optical phonons and a two-phonon continuum limited on the high-frequency side by a P_3 type of singularity[4] due to a Brillouin zone critical point. The resulting scattered intensity is given by an expression of the form[5]

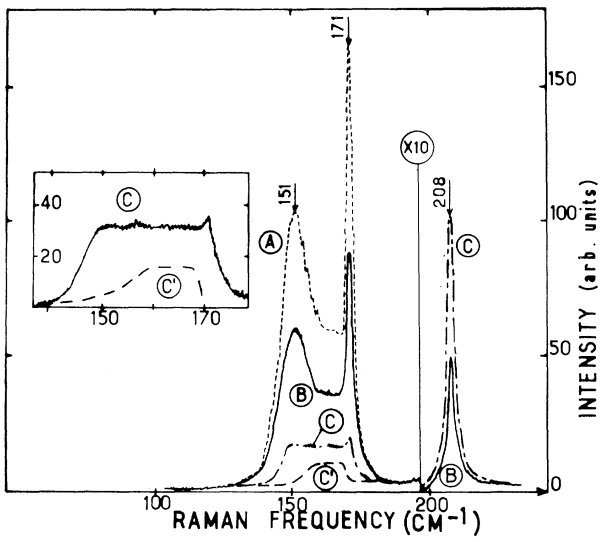

FIG. 1. Scattered intensities recorded for CuCl at 40 K. Curve A, TO experiment in a transverse geometry $y(x,y)x$; curve B, (0.5TO + 0.5LO) experiment in a transverse geometry $z(x,y)x$; curve C, LO experiment of backward scattering $z(x,y)\bar{z}$. x, y, and z are the crystallographic cubic axes. Curve C', corrected LO experiment (see text). The unit of ordinate near 208 cm^{-1} is 10 times larger than that at low frequencies.

$$I_i(\omega) \sim (R_i^{xy})^2 (V_3^{\,i})^2 \Gamma(\omega) / \{[\omega - \omega_i - (V_3^{\,i})^2 \Delta(\omega)]^2 + (V_3^{\,i})^4 [\Gamma(\omega)]^2\}, \quad (1)$$

where i labels the TO *or* LO phonon with frequency ω_i, R_i^{xy} is the usual first-order Raman tensor element, the anharmonic third-order interaction being given by the usual formula[5]:

$$(V_3^{\,i})^2 [\Delta(\omega) + i\Gamma(\omega)] \simeq \sum_{\substack{\vec{q}_1, j_1, j_2, \\ \vec{q}_3, j_3, j_4}} v(\vec{0}i, \vec{q}_1 j_1, -\vec{q}_1 j_2) G(\omega, \vec{q}_1 j_1, -\vec{q}_1 j_2, \vec{q}_3 j_3, -\vec{q}_3 j_4) v(\vec{0}i, \vec{q}_3 j_3, -\vec{q}_3 j_4). \quad (2)$$

The summation in Eq. (2) is practically limited to only that combination of branches which has the proper symmetry and a P_3-type singularity at the frequency ω_s, and for which the third-order interaction v is large. At zero temperature and in the vicinity of the band edge ω_s one can write

$$\omega < \omega_s: \ \Gamma(\omega) = D(\omega_s - \omega)^{1/2},$$
$$\Delta(\omega) = \Delta_s + B(\omega - \omega_s),$$
$$\omega > \omega_s: \ \Gamma(\omega) = C, \quad \Delta(\omega) = \Delta_s - D(\omega - \omega_s)^{1/2},$$

showing the existence of a maximum for $\Delta(\omega)$ at $\omega = \omega_s$. As a consequence, if ω_{TO} is not too far below ω_s and if $(V_3^{TO})^2\Delta_s$ (which reflects the strength of the anharmonic interaction) is large enough, the term

$$\omega - \omega_{TO} - (V_3^{TO})^2\Delta(\omega) \tag{3}$$

appearing in the denominator of Eq. (1) vanishes at least at a frequency $\omega_0 > \omega_s$ giving rise to a δ line. This is a case of Fermi resonance where the line corresponding to the optical phonon is repelled out of the broad band by the interaction. Note that the integrated intensity of the δ line depends on the slope of $\Delta(\omega)$ so that it is a very rapidly increasing function of $\omega_0 - \omega_s$.

Actually in the case of CuCl, $\Gamma(\omega)$, as a function of decreasing frequency, first increases and then decreases again to vanish well above 100 cm^{-1}.[6] This results, through Kramers-Kronig relations, in a minimum for $\Delta(\omega)$, so that Eq. (3) passes again through zero for $\omega = \omega_1$ and $\omega = \omega_2$ [see Fig. 2(a)] with $\omega_2 < \omega_{TO} < \omega_1 < \omega_s < \omega_0$. The maxima of $I_{TO}(\omega)$ [Eq. (1)] related to the vanishing of one term [Eq. (3)] of its denominator, are or are not apparent, depending on both the magnitude and the ω dependence of the other term. It turns out that the ω_2 maximum is a well-pronounced one, while that related to ω_1 is undetected.

In order to get a quantitative fit related to the above given ideas, we built up $\Delta(\omega)$ and $\Gamma(\omega)$ in the following way. We started by assuming an arbitrary two-phonon density of states of the form

$$\gamma(\omega) = D\{1 - [(\omega - \omega_c)/a]^2\}^{1/2},$$

which has a P_3 singularity at $\omega_s = \omega_c + a$, and for which we suppose a constant interaction with the TO phonon. We further assumed an interaction inside the phonon continuum through a fourth-order anharmonic interaction V_4 and followed Ruvalds-Zawadowski simplification of the problem.[7] The sign of V_4 was selected to enhance the high-frequency side of both $\Gamma(\omega)$ and $\Delta(\omega)$. A typical result for $\Delta(\omega)$, $\Gamma(\omega)$, and the comparison between Eq. (1) and the experimental spectrum are given in Figs. 2(a) and 2(b). The present fit was obtained with the following parameters: $a = 16.3$ cm^{-1}; $\omega_0 - \omega_s = 0.55$ cm^{-1}; $V_4D = 0.49$; $(V_3^{TO})^2D = 10.6$ cm^{-1}; $R_{TO}^{xy} = 28$ (cm^{-1} × intensity unit)$^{1/2}$. This fit is rather convincing and suggests the following comments:

(a) As Eq. (1) depends only on $(V_3^{TO})^2[\Delta(\omega) + i\Gamma(\omega)]$, only this function can be determined: Neither the existence of a Ruvalds-Zawadowski type of interaction, nor the strictly elliptic shape of the band should be inferred from the present calculation. For the same reason (and also because of experimental inaccuracies among the above-determined parameters), only the effective bandwidth $2a$ has a physical meaning while, e.g., a 10% variation of V_4D leads to a quite undiscernable result, provided $\omega_0 - \omega_s$ is simultaneously corrected by as much as 100%. We therefore think that the only important feature revealed by the TO spectrum is the existence of three zeros for Eq. (3).

(b) We find $\omega_{TO} = 158$ cm^{-1}. From the Lyddane-

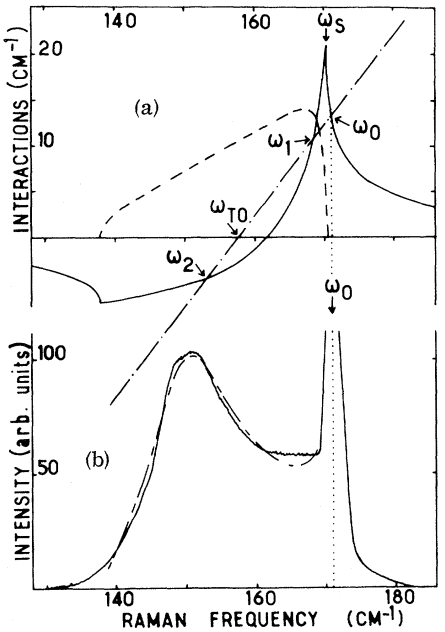

FIG. 2. (a) Continuous line, $(V_3^{TO})^2\Delta(\omega)$; dashed line, $(V_3^{TO})^2\Gamma(\omega)$; dot-dashed straight line, $\omega - \omega_{TO}$. (b) Continuous line, experimental TO spectrum (enlargement of curve A, Fig. 1); dot-dashed line, calculated spectrum.

Sachs-Teller relation, $\omega_{LO} = 208$ cm^{-1} and $\epsilon_\infty = 3.61$,[8] we get $\epsilon_0 = 6.25$ in good agreement with a recent determination at 40 K.[1]

(c) The calculated ω_1 frequency is so close to ω_0 that an extemely high resolution (~ 0.1 cm^{-1}) would be required to observe a dip near 171 cm^{-1}.

(d) Because of the high value of $(V_3^{TO})^2 d[\Delta(\omega_0)]/d\omega = \alpha$, the calculated integrated intensity of the δ peak at ω_0 is reduced by a factor $1-\alpha = 4.9$ with respect to the value it would have if $\alpha = 0$, and agrees exactly with our measured integrated intensity at 171 cm^{-1}. At higher temperature, the broadening of the individual phonon states blurs the sharpness of the P_3 singularity at ω_s and consequently reduces α. As a consequence, the intensity of the ω_0 line will increase and the line will broaden. The intensity ratio between this line and the continuum is thus a nontrivial function of the temperature and will increase less rapidly than a usual two-phonon/one-phonon ratio. This is, in fact, what has been previously measured by Potts *et al.*[1] who could not explain their result.

Concerning the LO spectrum, ω_{LO} is far from the continuum so that $\Delta(\omega)$ and $\Gamma(\omega)$ may be neglected in the denominator of Eq. (1) which gives a δ peak at $\omega_{LO} = 208$ cm^{-1} and a broad but weak band in the 140–170 cm^{-1} range.

A discussion of the "purity" of the C experiment of Fig. 1 is in order here. Since the crystal is not perfectly homogeneous, a small amount of the light is elastically scattered, giving rise, even in backscattering geometry, to a small fraction f of transverse spectrum. This fraction is obtained by assuming that, in curve C, the 171 cm^{-1} peak is entirely due to this parasitic light. The corrected curve C' is then constructed from the following relation:

$$I_{C'} = I_C - fI_A .$$

In agreement with the last above approximation, the curve C' (Fig. 1) is more or less shaped as $\Gamma(\omega)$ [Fig. 2(a)]. This enables us to give a rough experimental estimation of $(V_3^{TO})^2/(V_3^{LO})^2 \sim 1.2$. This slightly higher than unity ratio may be because of a difference in the anharmonic coefficients and/or because of the superposition of a very weak pure second-order Raman scattering.

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Distinction between Lattice and Cluster Models of the Jahn-Teller Effect in an Orbital Doublet

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Acoustic-paramagnetic-resonance and electric-field–induced thermally detected EPR measurements have been made in crystals of Al_2O_3:Ni^{3+}. To reconcile theory with experiment, dynamic Jahn-Teller effects must be present, and, in addition, $2q-p$ is shown to be less than unity. This is the first reported example of an orbital doublet for which the multimode rather than the cluster model is needed.

The importance of the vibronic coupling of an E-type ion with its surroundings is often revealed by values of factors p and q which appear in the effective Hamiltonian.[1] In two recent articles, Halperin and Englman[2] and Gauthier and Walker[3] show theoretically that when the coupling is to a