PHYSICAL REVIEW B VOLUME 14, NUMBER 10 15 NOVEMBER 1976

Experimental and theoretical study of the anomalous Raman spectrum in the transverse optic phonon region of CuCl†

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(Received 24 May 1976)

Raman spectra were obtained at 40 K as a function of hydrostatic pressure up to 7 kbar for the anomalous-TO-phonon region in CuCl. Two prominent peaks, previously labeled as β and γ, and a weaker peak, labeled here as β', were observed. The β and γ peaks showed a weak linear pressure shift, while the ratio of the integrated intensity of the γ peak to the height of the β peak showed a strong linear pressure dependence. A theory was employed which invoked a cubic anharmonic coupling of the harmonic TO phonon to a two-phonon background characterized by a Van Hove P_3 singularity at its high-frequency end. In this theory the "TO" is the entire β-γ region. Fits of the theory to the data showed that the two most important parameters, ω_c, the frequency of the singularity, and ω_{TO}, the harmonic-TO-phonon frequency, showed linear pressure dependences. The TO frequency, lower than ω_c, varied more rapidly with pressure than did ω_c, leading quantitatively to the observed ratio of γ area to β peak height. It was also predicted that above a pressure of 16.6 kbar, ω_{TO} would exceed ω_c and the spectrum would assume a qualitatively different form.

I. INTRODUCTION

The lattice dynamics of copper chloride have been the subject of many studies, and the results of these studies have not always been in agreement. In this paper we examine the particular problem of the nature of the anomalous transverse-optic phonon at the center of the Brillouin zone.

CuCl crystallizes in the zinc-blende structure and one therefore expects to observe a single TO phonon and single LO phonon at the zone center. Iwasa and Burstein[1] in 1965 reported room-temperature Raman measurements showing a single TO mode at 153 cm^{-1} and an LO mode at 201 cm^{-1}. In 1966 Iwasa did infrared reflectivity experiments on single crystals of CuCl and found a basically featureless reflectivity maximum which could be fit very well by assuming TO and LO frequencies of 177 and 214 cm^{-1}, respectively, at helium temperature.[2] His normal incidence and oblique incidence transmission experiments on thin film confirmed these results.

Plendl *et al.*[3] also reported their infrared transmission and reflectivity results in 1966. Their transmission measurements at helium temperature showed that the band in the TO vicinity was a doublet with components at 159 and 181 cm^{-1}. Reflectivity measurements on pressed pellets at hydrogen temperatures showed a broad maximum, analyzed to give $\omega_{TO} = 181$ cm^{-1} and $\omega_{LO} = 217$ cm^{-1}, and secondary maxima at 159 and 169 cm^{-1}. Thus, in 1966 there was already evidence for structure in the infrared spectrum in the vicinity of the TO. Because they are in accord with recent measurements we shall designate the modes at 159, 181, and 217 cm^{-1} by the Kaminow and Turner[4] notation as the β, γ, and δ bands. We shall designate the mode at 169 cm^{-1} as the β' band (the band labeled α by Kaminow and Turner, observed by many workers, is a second-order difference band and of no interest in the present discussion). We shall put all other literature references into this language of β, β', γ, and δ; what we call γ was identified by many authors to be the TO.

The nature of the structure in what one presumes is the TO region was not clarified by subsequent infrared,[5-7] Raman[8] or inelastic neutron scattering[9] results. One can see a compilation of the various data in Table I, where it is evident that there was disagreement among the early infrared results but substantial agreement among the Raman measurements. The neutron results showed TO peak and a single LO peak, with frequencies substantially different from any of the frequencies determined optically. It was later argued by Prevot and Sieskind[14] that the neutron data had to be corrected in order to fit their second-order Raman spectra. The presence of only two peaks in the neutron results led various investigators to identify the β band as a two-phonon difference band.

A very complete Raman study was published in 1972 by Kaminow and Turner,[4] who examined several single crystals at several temperatures between 105 and 295 K. From polarization selection rules they identified δ as the LO mode, and concluded that both β and γ obeyed the selection rules for a TO phonon. However, their data showed that the β peak had the temperature dependence expected for a single phonon while the γ peak did not. They argued that this double peak was probably

TABLE I. β, β', γ, and δ frequencies for CuCl; all entries in cm^{-1}.

		β	β'	γ	δ
Infrared	Nitrogen temperatures	149[b]		174[a] 179[b]	210[a] 220[b]
	Helium temperatures	159[c] 159[d] 160[b] 156[e]	169[c] 168[e]	181[c] 181[d] 185[b] 173.5[e] 177[a]	214[a] 217[c] 220[b]
Raman	Room temperature	120.5[g] 122[h] 123[i] 123[j] 123[k]		158.5[g] 161[h] 153[f] 162[i] 163[j] 162[k]	198[g] 199[h] 196[i] 199[j] 199[k] 201[f]
	Nitrogen temperatures	146[g] 146[l] 143[m,i] 147[j] 146.5[k] 146[n]		172[g] 172[l] 172[n] 172[m,i] 174[j] 172[k]	210[g] 210[l] 211[m,i] 210[j] 211[k]
	Helium temperatures	156[j] 151[o,p]	168[j]	175[j] 171[o,p]	209[j] 208[o,p]
Neutron	Room temperature			182[b]	218[b]

[a] Reference 2.
[b] Reference 7.
[c] Reference 3.
[d] Reference 5.
[e] Reference 12.
[f] Reference 1.
[g] Reference 8.
[h] Reference 11.
[i] Reference 4.
[j] Reference 13.
[k] Reference 14.
[l] Reference 10.
[m] Measured at 105 K.
[n] Reference 15.
[o] Measured at 40 K.
[p] Reference 16.

due to lattice anharmonicity and that an unambiguous assignment of either β or γ as the TO could not be made.

Ikezawa[12] reported his 2-K infrared transmission measurements in 1973, and concluded that γ was the TO while β was a two-phonon difference band. He also observed the small peak between β and γ, seen earlier by Plendl *et al*,[3] which we here designate as β'.

Raman measurements down to helium temperatures were reported in 1974 by Potts *et al.*[13] who found the same polarization properties as Kaminow and Turner. They confirmed Kaminow and Turner's results that β had the temperature dependence of a single phonon while γ did not display the behavior of either a one-phonon or a two-phonon mode. They noted that γ became very sharp at 7 K while β remained broad, and also observed the β' band at 7 K. After reviewing several unsuccessful attempts to explain their data using various phenomenological ideas, they concluded that neither β nor γ could be identified as the TO.

In an attempt to clarify the problem Shand, Ching, and Burstein[15] did forward and backward scattering experiments at nitrogen temperatures. The back scattering geometry which they used allowed scattering by LO phonons but not by TO phonons. Both the β and γ peaks appeared in the back scattering spectrum and they thus rejected both as being the TO phonon. By fitting their polariton data (forward scattering) the authors deduced a value of 174 cm^{-1} for the TO mode at nitrogen temperatures.

At about the same time, Krauzman *et al.*[16] published their experimental (40 K) and theoretical results. They observed that the β-γ region was very weak in the back scattering spectrum and used this fact as a criterion to assign the *entire* β-γ region as the "TO" spectrum, in contrast to the results of Shand *et al.* Krauzman *et al.* viewed the entire β-γ spectrum as arising from an anharmonic coupling between the harmonic TO and a two-phonon continuum. This continuum was assumed to terminate on its high frequency side with a P_3-type Van Hove singularity which determined the details of the β-γ spectrum.

As it was obvious that anharmonic interactions played an important role in CuCl we decided to perform Raman measurements at low temperatures as a function of hydrostatic pressure. We anticipated that the results would help us unravel some of the confusion about the TO region. At the same time we recognized that our experiments could be used as a test of the theoretical ideas of Krauzman *et al.*, as we would be probing the anharmonic interactions on which their model rests.

In Sec. II of this paper we shall discuss our experimental techniques and results, and detail the conclusions which can be drawn directly from experiment. Section III will be devoted to a rather complete discussion of the theory of Krauzman *et al.* In Sec. IV we will compare experiment and theory and the paper will be summarized in Sec. V.

II. EXPERIMENT

A. Experimental details

The Raman scattering apparatus consisted of the standard double monochromator with photon counting electronics, and an argon-ion laser as the light source. The laser was operated on the 514.5-nm line at the reduced power of 300 mW in order to keep sample heating to a minimum. (CuCl is slightly absorptive at 514.5 nm.) The laser power was kept at the same level for all runs and the sample alignment was unchanged during changes of pressure so that intensity measurements could be compared.

Some of the pressure-induced changes in the Raman spectra were small, and as such were beyond the mechanical calibrations of the spectrometer. Therefore a small neon lamp was placed at the entrance slit of the monochromator and two neon lines were recorded in each spectrum. All spectral features were thus measured relative to the neon lines.

Pressures were generated by a system which employed helium gas as the transmitting medium. The sample cell contained three sapphire windows. Two windows allowed the laser beam to enter the cell, traverse the sample, and leave the cell. The other window allowed the usual 90° scattering geometry to be employed. This system allows routine runs at helium temperature; each run has a better than 90% chance of success. Details of the apparatus will be published separately.[17]

The pressure cell was mounted on a cold finger in a conventional liquid-helium optical cryostat. The temperature was monitored outside the cell. As the Raman spectrum for copper chloride is temperature dependent care was taken to have all runs occur at the same temperature. The exact temperature at the sample is not known but was estimated to be 40 K.

Helium gas solidifies at temperatures well above 40 K for the highest pressures employed here, and in order to change the pressure it was necessary to warm the pressure cell above nitrogen temperature, adjust to the new pressure value, and recool to 40 K. The helium line, made of $\frac{1}{16}$-in.-o.d. and 0.01-in.-i.d. type 316 stainless steel, entered the pressure cell opposite the cold finger of the cryostat. This ensured that the helium froze from the side opposite the source of pressure, thereby freezing at constant pressure rather than at constant volume, greatly simplifying determination of the pressure inside the cell. Freezing at constant pressure was verified by monitoring the pressure in the room-temperature portion of the helium line.

All results reported here were obtained by raising the system to its highest pressure, recording the spectrum, then lowering the pressure by 500 bars, recording the spectrum, etc. This procedure eliminated any problems with hysteresis effects. In order to avoid catastrophic failures of the pressure apparatus no measurements were taken above about 7 kbars, even though the system has been tested at 10 kbars. Data were not obtained for cell pressures below 2 kbars because the cell did not seal in this range.

Symmetries for all features in the Raman spectra were known from other experiments.[13,16] so that polarized light was not necessary. Therefore we did not place polarizers inside the pressure cell, a procedure which is normally required because sapphire windows under pressure depolarize the light. The CuCl crystals were cut and oriented so that the incident light propagated along [110] and the scattered light along [001]. This means that the scattered spectra contain the TO spectrum with a weight of 2 and the LO spectrum with a weight of 1.

B. Experimental results

Representative 40-K Raman spectra are shown in Fig. 1 for low (1 bar), medium (3.52 kbars), and high pressures (6.80 kbars). These are unpolarized spectra and show β and γ. One should note first the differences between these spectra and those obtained earlier[13,16] at one bar and lower temperatures. First, as can be seen by comparing the γ peaks in Fig. 1 with the same peak in Ref. 13 and 16, the peak at 40 K is broader than the peak at 7 K. Second, the small peak between the β and γ peaks, seen at lowest temperatures in Ref. 13 and 16, is not well defined at low pressures at 40 K. The δ peak (i.e., the LO mode), not shown in Fig. 1, will be discussed separately with the results for the other copper halides.[17]

We now examine Fig. 1 for the effects of pressure at 40 K. First, the small peak between β and γ, seen at zero pressure at 7 K is again seen at high pressures at 40 K. This is somewhat contrary to one's expectations. CuCl is known[18] to have a negative coefficient of thermal expansion below about 100 K. Therefore, an increase of temperature, which causes this small peak to disappear at zero pressure, results in a decrease in unit cell volume. However, an increase of pressure, which causes the peak to appear at 40 K, also results in a decrease in unit cell volume.

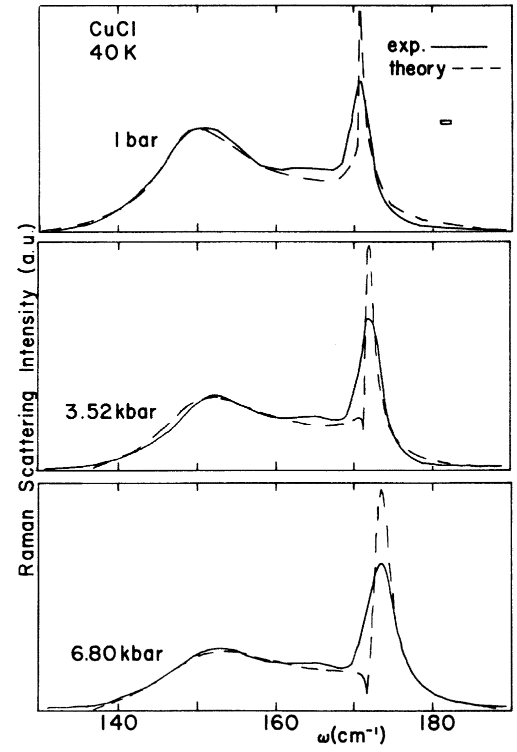

FIG. 1. Experimental (solid curve) and theoretical (dashed curve) Raman spectra in the region of the TO phonon of CuCl at 1 bar, 3.52 kbar, and 6.80 kbar. The box to the right of the 1-bar spectra corresponds to experimental noise (vertical) and instrumental resolution (horizontal).

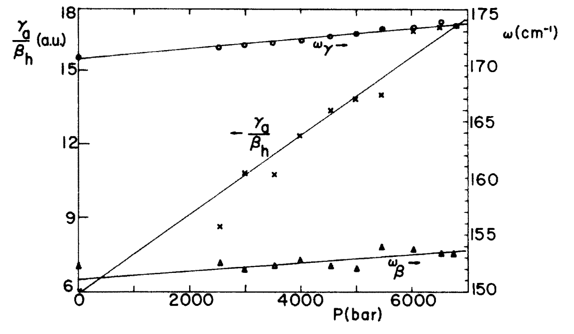

FIG. 2. Ratio of the area of the γ peak to the height of the β band (left scale) and the frequencies of the γ peak and β band (right scale) for the 11 spectra.

These results seem contradictory. This small peak is not explained by the theory to be described below. It is a small effect when compared with β and γ, but it is at present one of the unresolved problems in CuCl.

The second pressure effect is the small shift of the β and γ peaks with pressure as seen in Fig. 2. Between 1 bar and 6.8 kbars the β peak is observed to shift only 2.2 cm^{-1} (or 0.2% per kbar) and the γ peak only 3.0 cm^{-1} (0.3% per kbar). That this shift is small can perhaps be seen better by translating into the language of mode Grüneisen parameters, which have the values of 0.9 and 1.3 for β and γ, respectively, at 40 K.

The third effect of pressure is strong relative changes in the peak intensities. One can see clearly in Fig. 1 that the β and γ peak heights have different pressure dependences. The γ peak is also seen to be narrow; it is narrow enough that spectrometer slit effects, for which corrections are difficult, are important. (The instrumental resolution is shown in the figure.) In general we ran with the slits open wide enough to pass sufficient light for a good signal-to-noise ratio. The intensity of the overall spectrum, therefore, depends on the slit width. But in addition a narrow peak such as γ, when scanned by a slit of comparable or greater width, will appear to be lower and broader than it actually is, even though its integrated area is insensitive to the slits (except for the overall spectral intensity discussed above). Therefore, we have numerically measured the integrated area of the γ peak. As the exact shape of the low-frequency side of the peak is influenced by the β peak, we have defined the γ area as being the area of the high-frequency half of the peak multiplied by 2. On the other hand the β peak is so broad that slit corrections are unimportant. Furthermore its "width," which is difficult to determine, can be seen from Fig. 1 to be relatively independent of pressure. Therefore, we have taken the ratio of the area of the γ peak to the height of the β peak, which is independent of slit corrections, as measuring the relative intensities of these two spectral features.

Figure 2 shows the observed pressure dependence of the ratio. It shows a strong pressure dependence of 28% per kbar.

These contrasting results of a small pressure dependence of the peak frequencies and a large pressure dependence of relative peak intensities gives us a clue as to the kind of theory which one must investigate. Peak positions are determined by the positions of the poles in the phonon self-energy and peak shapes are determined by the magnitude of the imaginary part of the phonon self-energy and the slope of the real part.

In order for the intensity to show a strong pressure dependence while the peak positions show a weak pressure dependence, one requires that the phonon self-energy have a rapidly varying frequency dependence in the frequency range of interest. This suggests, in turn, that the self-energy be characterized by a singularity in the frequency range of interest. These points will be made more precise in the next section.

III. THEORY

A. Qualitative remarks

The theory given here was originally outlined in Ref. 14; we give a more complete treatment now. Let us assume a system of phonons which interact anharmonically. The anharmonic interactions will in general manifest themselves in two ways. The phonon frequencies will be shifted from their harmonic values and the phonons will have finite rather than infinite lifetimes. One way to express this is to write the phonon self-energy in the form

$$S(\omega,\vec{q})=\Delta(\omega,\vec{q})+i\Gamma(\omega,\vec{q}), \tag{1}$$

where ω is the phonon frequency and $\vec{q}$ is its wave vector. $\Delta(\omega,\vec{q})$ and $\Gamma(\omega,\vec{q})$, the real and imaginary parts of the self-energy, are related by a Kramers-Kronig transform. Once the phonon self-energy is known one can calculate the Raman intensity by an expression of the form

$$I(\omega)=R\Gamma(\omega,\vec{q})/\{[\omega-\omega_i-\Delta(\omega,\vec{q})]^2+\Gamma^2(\omega,\vec{q})\}, \tag{2}$$

where ω_i is the frequency of the Raman active phonon and R is the one-phonon Raman scattering cross section. The demoninator becomes small, and hence the Raman intensity becomes large, at ω equal to $\omega_i+\Delta(\omega,\vec{q})$.

We examine Eq. (2) under two extremes. (i) $\Gamma(\omega,\vec{q})$ is small. In this case $I(\omega)$ is small everywhere except for $\omega\simeq\omega_i+\Delta(\omega,\vec{q})$ where the band is very strong. One expects a narrow but intense band. (ii) $\Gamma(\omega,\vec{q})$ is large. In this case structure in $\Gamma(\omega,\vec{q})$ cannot be ignored and the Raman line will have a shape determined largely by the shape of $\Gamma(\omega,\vec{q})$.

We can now compare Eq. (2) to experiment and deduce some properties of the self-energy. The experimental γ band is narrow and intense. Therefore one expects $\Gamma(\omega,\vec{q})$ to be small in this frequency range. The experimental β band is broad and one accordingly expects $\Gamma(\omega,\vec{q})$ to be appreciable in this frequency range. The β and γ bands adjoin each other. This implies that $\Gamma(\omega,\vec{q})$ must change from being appreciable to being small in a very small frequency interval. We shall assume that $\Gamma(\omega,\vec{q})$ has a singularity on its high-frequency side ω_c.

$\Gamma(\omega,\vec{q})$ and $\Delta(\omega,\vec{q})$ are not independent; they are related by a Kramers-Kronig transform. Therefore, a singularity in $\Gamma(\omega,\vec{q})$ implies a singularity in $\Delta(\omega,\vec{q})$. That is, where $\Gamma(\omega,\vec{q})$ is rapidly varying, one expects $\Delta(\omega,\vec{q})$ to be rapidly varying. In addition, above the singularity, where Γ is small, $\omega\approx\omega_i+\Delta$ will produce a sharp peak which has an intensity determined by the integral of Eq. (2) over this frequency region. Approximating $\Delta(\omega)$ by $S_0+\omega S_1$ within the integral leads to the conclusion that the slope of $\Delta(\omega)$ determines the integrated intensity of the sharp peak [area $\sim 1/(1+|S_1|)$]. Thus, if ω_i moves relative to ω_c as a function of pressure, the intensity of a Raman peak above ω_c will be strongly pressure dependent because of the changing slope of $\Delta(\omega)$ where $\omega\approx\omega_i+\Delta(\omega)$.

These remarks can be seen illustratively in Fig. 3, where we have plotted Γ as a function of frequency. We have selected a structureless form for Γ and have made it rapidly varying near its singularity at ω_c. We have also drawn Δ as a function of frequency, where Δ is the Kramers-Kronig transform of Γ. The singularity is also seen in Δ. We consider three cases for the self-energy of a TO phonon:

(i) In Fig. 3(a) we show the situation for Γ and Δ small. We note that the denominator in Eq. (2) is small when $\omega\approx\omega_{\mathrm{TO}}+\Delta$. This is illustrated graphically by drawing the line $\omega-\omega_{\mathrm{TO}}$ and looking for its intercepts with Δ. In Fig. 3(a), $\omega_{\mathrm{TO}}<\omega_c$ and we see that there is but one intercept, at a frequency less than ω_{TO}. Therefore, there would be only one Raman active band and it would occur for a frequency less than the harmonic frequency ω_{TO}.

(ii) In Fig. 3(b) we show the situation for Γ and Δ large and $\omega_{\mathrm{TO}}<\omega_c$. There are now three intersections with Δ, two near ω_c, and one below the harmonic frequency ω_{TO}. The lowest- and highest-frequency intersections should produce peaks in the Raman spectrum but the middle intersection could produce a peak or a dip in the spectrum depending on the relative slopes of Δ and Γ.

(iii) For ω_i large enough, as seen in Fig. 3(c), there is only one intersection and therefore a single peak in the Raman spectrum occurring at a frequency greater than ω_{TO} and a smaller band below ω_c where Γ is significant. The exact position of the peak depends on the magnitude of Δ. We note that $\Delta(\omega)$, $\Gamma(\omega)$, and the value of ω_{TO} shown in Fig. 3(b) are those which reproduce our experimental spectrum at 3.52 kbars, shown in Fig. 1.

B. Calculation of the Raman intensity

We now turn to the calculation of $\Delta(\omega,\vec{q})$ and $\Gamma(\omega,\vec{q})$. We know that we are dealing with one-phonon Raman scattering and from symmetry there are but one TO phonon and one LO phonon at the zone center. One-phonon Raman scattering is restricted to the center of the Brillouin zone, and therefore there are no single phonons to which we

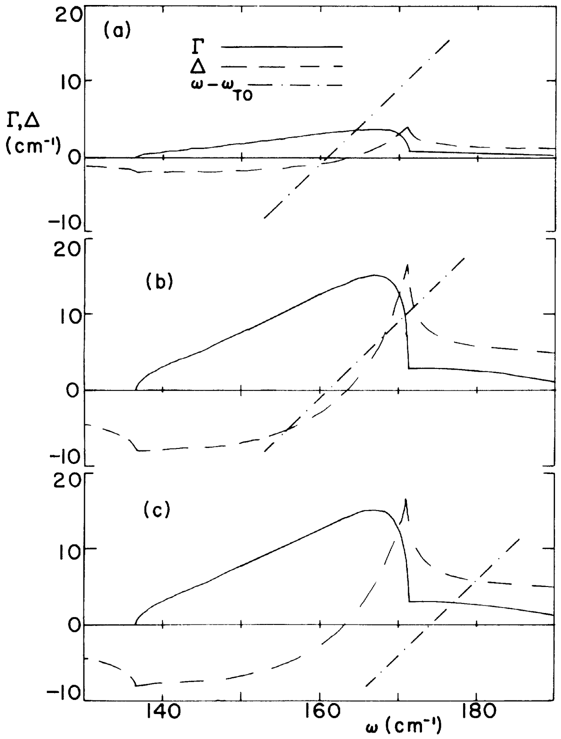

FIG. 3. Real part Δ (dashed curve), and imaginary part Γ (solid curve) of the TO phonon self-energy. The dotted and dashed line is ω-ω_{TO}. Part (b) corresponds to the theoretical Raman spectra at 3.52 kbars shown in Fig. 1.

can couple the TO. The simplest possibility we can consider then, is a cubic anharmonic coupling of the TO phonon to two phonons. These two phonons must have equal and opposite wave vectors in order to insure $\vec{q}_{TOTAL} = 0$. There are undoubtedly many different frequencies which give such combinations, and therefore we assume that the TO is coupled to a two-phonon continuum having a Van Hove singularity of the type designated as P_3. That is, the two-phonon density of states, and hence $\Gamma(\omega, \vec{q})$, varies as $(\omega-\omega_c)^{1/2}$ for $\omega < \omega_c$, and $\Gamma(\omega, \vec{q}) = \text{constant}$ for $\omega > \omega_c$. Such a singularity arises from regions of the two-phonon dispersion curves which are maximal in three directions.

The available inelastic neutron data are not sufficiently accurate to allow us to extract a two-phonon density of states. Even if they were reliable, however, it is not clear which parts of the two-phonon density of states ought to be taken to couple to the TO. All we know is that we want phonon pairs in the frequency range 150–180 cm⁻¹, and we expect a singularity near $\omega_c = 180$ cm⁻¹. For these reasons we simply construct our own density of states.

We start with an elliptically shaped density of states $\gamma(\omega) = D\gamma_0(\omega)$, where

$$\gamma_0(\omega) = \left| 1 - \left(\frac{\omega - \omega_c + a}{a} \right)^2 \right|^{1/2} \quad \text{for } \omega_c - 2a < \omega < \omega_c , \tag{3}$$

and $\gamma(\omega) = 0$, otherwise. This is merely the upper-half of an ellipse reaching from $\omega_c - 2a$ to ω_c, with semi-axes D and a. Equation (3) clearly has the desired singularity at ω_c, but it also has one at $\omega_c - 2a$. This latter singularity turns out to be unimportant as it is so far from ω_{TO}.

With $\gamma(\omega)$ taken as the imaginary part of the phonon self-energy then the real part, $\delta(\omega)$, is computed from the Kramers-Kronig transform to be

$$\delta(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\gamma(\omega')}{(\omega - \omega')} d\omega' , \quad \text{giving } \delta(\omega) = D\delta_0(\omega) ,$$

$$\delta_0(\omega) = \begin{cases} x + (x^2 - 1)^{1/2}, & x < -1 , \\ x , & |x| \leq 1 , \\ x - (x^2 - 1)^{1/2}, & x > 1 , \end{cases} \tag{4}$$

where $x = (\omega - \omega_c + a)/a$.

We designate the coupling of one phonon to two phonons by V_3. We must also consider that there can be an anharmonic fourth-order interaction between pairs of phonons in the two-phonon density of states. This interaction will be designated by V_4. Both the cubic and quartic anharmonicity will contribute to the self energy. If one follows the method of Ruvalds and Zawadowski[19] then one obtains for the real and imaginary parts of the phonon self energy, respectively,

$$\Delta(\omega) = \frac{V_3^2 D \{\delta_0(\omega)[1 - V_4 D \delta_0(\omega)] - V_4 D \gamma_0^2(\omega)\}}{[1 - V_4 D \delta_0(\omega)]^2 + V_4^2 D^2 \gamma_0^2(\omega)} ,$$

$$\Gamma(\omega) = \frac{V_3^2 D \gamma_0(\omega)}{[1 - V_4 D \delta_0(\omega)]^2 + V_4^2 D^2 \gamma_0^2(\omega)} . \tag{5}$$

As can be seen, the effect of a positive V_4 is to skew the density of states to the high-frequency end, and produce a result illustrated by $\Gamma(\omega)$ in Fig. 3.

The Raman intensity is now computed by substituting Eq. (5) into Eq. (2) and solving numerically. One notes that the theory contains the following parameters. The density of states, Eq. (3), contains the position of the singularity ω_c, and the frequency range of the density of states a. The phonon self-energy, Eq. (5), contains the cubic and quartic anharmonicity parameters V_3^2D and V_4D. Lastly, the Raman intensity, Eq. (2), contains the absolute one-phonon Raman cross section R and the TO frequency ω_{TO}.

IV. COMPARISON OF EXPERIMENT AND THEORY

A. Curve fitting

There were 11 sets of data, corresponding to runs at ten pressures in the pressure cell and zero pressure with the sample outside the pressure cell. Digital data were taken for the computer by reading the scattered intensity at 2 cm^{-1} intervals in the β-γ region. (The instrumental resolution was 2 cm^{-1}.) This procedure gave about 30 data points for each spectrum. These data, for all 11 spectra, were entered into the computer along with a routine for doing a least-squares fit of the theory to the experiment. As discussed above the experiments were done at 40 K resulting in broadening of the peaks. This was accounted for by adding to $\Gamma(\omega)$ a smooth function

$$g(\omega)=A\left|\frac{(\omega-\omega_c)^2}{B^2}-1\right|^2, \quad \omega_c-B<\omega<\omega_c+B \tag{6}$$

and $g(\omega)=0$ otherwise. B was selected to be 30 cm^{-1} and A was kept as a parameter. This function $g(\omega)$ merely represents an additional piece of the imaginary part of the phonon self-energy, and is essentially constant over the important frequency range near ω_c. The effect of $g(\omega)$ is, as one might expect, merely to broaden the peaks.

As was discussed in Ref. 14 and verified here some of the parameters can be varied over wide ranges without affecting the quality of the fit, and some of the parameters are more critical than others. Therefore, it was decided to hold V_4D/a within 1% for all pressures. This is equivalent to stating that it is only the behavior of the density of states near the singularity which is important. The computer was therefore required to fit all 11 spectra simultaneously with constrained V_4D/a.

B. Results and discussion

Figure 1 shows the experimental spectra and theoretical fit for three pressures—0, 3.52, and 6.80 kbar, covering the range of our measurements. As can be seen the fit is equally good for all three pressures. These results are typical of our experience for all 11 spectra.

One notes several features in Fig. 1. First, the small peak between the β and γ peaks is not reproduced by the theory for those pressures at which it occurs. Second, the theoretical γ peak is narrower and more intense than the experimental peak. However, if the theoretical spectrum were to be convoluted with our 2-cm^{-1} instrumental resolution then the γ peak would be broadened and diminished in height, bringing it close to the experimental peak. The integrated area under the γ peak was required by the fitting routine to be the same as observed experimentally, and the computer was then allowed to fit the β band as best it could. As can be seen the β peak is reproduced very well. Third, a small dip in the spectrum at the low-frequency foot of the γ peak is noted in the theoretical spectra. This possibility was discussed in the previous section. This dip is clearly too narrow to be resolved by our instrumentation, which would merely smooth it out.

With the fits in hand one can now turn to a detailed examination of the results in order to see whether the theory has in fact been tested by the experiments. There are several points to be made.

1. Pressure dependence of the parameters V_3^2D, V_4D, R, A, and a

Values for these parameters for all 11 spectra are listed in Table II. As noted above it was demonstrated previously[16] that some of the parameters are correlated. Accordingly, we constrained the ratio V_4D/a to vary only within a range of ±1%. While both V_4D and a are listed in Table II (columns 4 and 5, respectively) V_4D is determined from a and the ratio V_4D/a, listed in column 6.

The physical significance of this ratio is of interest. Imagine two rather different elliptical two-phonon density of states curves, designated by rather different widths, measured by a. One can use two different values of the skewing parameter V_4D and generate two skewed density of states curves which differ substantially at their low frequency ends but are basically the same near ω_c. It is only the ratio V_4D/a which matters in the curve fitting. This is equivalent to the statement that it is only the behavior of the two-phonon density of states near the singularity which is important in determining the Raman spectrum. This result was to some extent anticipated, but it is comforting to see it happen as it obviates the need for a detailed justification for a particular assumed shape for the density of states. Further, one needs no pressure dependence of V_4D/a to explain the pressure dependence of our data, and hence all of the pressure dependence is contained in the other parameters.

It can be seen in Table II that the one-phonon Raman scattering cross section is basically independent of pressure. Except for the zero pressure value (whose spectrum was obtained under different conditions than the other ten) one sees only a random variation of R within ±10% of its average value of 15.1. The significance of this result is unclear except that one might note that in terms of significant alterations of polarizability derivatives or effective charges we have covered only a small pressure range.

TABLE II. Values of the fitting parameters.

Pressure (kbar)	V_3^2D (cm^{-1})	A (cm^{-1})	R (a.u.)	V_4D (cm^{-1})	a (cm^{-1})	V_4D/a (no dim.)
0	8.34	3.73	11.9	0.516	20.3	0.0254
2.54	8.42	3.00	15.1	0.488	19.4	0.0251
2.97	9.90	3.12	15.5	0.448	17.8	0.0252
3.52	9.83	3.04	15.0	0.435	17.3	0.0252
3.99	10.7	3.22	15.2	0.441	17.5	0.0252
4.53	11.0	3.25	15.8	0.430	17.4	0.0248
4.99	11.1	3.35	15.5	0.468	18.6	0.0252
5.45	10.1	2.98	14.4	0.454	18.0	0.0252
6.03	11.4	3.13	16.5	0.427	17.0	0.0251
6.52	11.4	3.26	16.2	0.424	17.0	0.0249
6.80	11.4	3.11	15.1	0.434	17.5	0.0248

There are two comments to make about the parameter V_3^2D. First, it is large. Its value of about 10 cm^{-1} is to be compared with "normal" half-widths at half-maximum of 1 or 2 cm^{-1} measured for "normal" Raman lines at low temperatures. The large size of V_3^2D agrees with the basic idea of the entire theory, which is a strong cubic anharmonic coupling. Second, V_3^2D is mildly pressure dependent, increasing about 5% per kilobar. As CuCl is known to be strongly anharmonic, one would expect the anharmonic coupling to depend on the lattice parameter and therefore to be pressure dependent.

A, the height of the "constant background" [Eq. (6)] which simulates the effect of doing the experiment at 40 K, is seen from Table II to be pressure independent. This parameter therefore accounts for the broadening of the γ peak because the sample is at 40 K. It is interesting that a width defined experimentally by (γ area)/(γ height) is strongly pressure dependent. The theory therefore seems to be capable of distinguishing between A (an added constant density of states) and the slope of $\Delta(\omega)$. As previously discussed this slope determines the area of the γ peak, and hence the pressure dependence of (γ area)/(β height).

In sum, the five parameters discussed here are either independent of pressure or are only slightly pressure dependent. These parameters are not responsible for the strong pressure dependence of (γ area)/(β height). One must look to the pressure dependence of the remaining two parameters, ω_c and ω_{TO}, for an explanation.

2. Pressure dependence of ω_c and ω_{TO}

These parameters are crucial to the theory as it is their interplay which most heavily determines the relative intensities of the β and γ peaks. Figure 4 shows the values of these parameters at the various pressures; it can be seen that both vary smoothly with pressure, increasing in both cases with increasing pressure. Also shown in Fig. 4 as a reference is the pressure dependence of ω_γ. The fluctuations in ω_c and ω_{TO} are significantly smaller than the fluctuations for the other fitting parameters discussed above.

ω_{TO} is especially interesting as it is the frequency of the "harmonic" TO phonon. One can use its pressure dependence to compute a mode Grüneisen parameter, and the result is 2.4. This is to be compared to the mode Grüneisen parameters of 2.4 and 2.2 for the TO mode in CuBr and CuI, respectively.[17] In those two systems, of course, the TO phonon frequency is observed directly in Raman scattering and anharmonic effects are presumably small, while in the present case of CuCl ω_{TO} is inferred by fitting a theory to the data. Agreement of the mode Grüneisen parameters does not constitute a proof for the theory employed here, but it is gratifying nonetheless.

As seen in Fig. 4, ω_c and ω_{TO} increase with pressure at different rates. Extrapolation of the linear fits upward in frequency shows that they

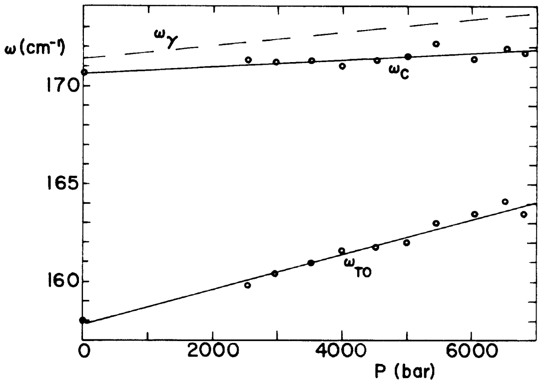

FIG. 4. Theoretical values of the frequencies of the singularity ω_c, and the TO phonon ω_{TO}, at 11 pressures.

will intersect at a pressure of 16.6 kbars, where ω_{TO} and ω_c will have the value of 173 cm^{-1}. Therefore, in terms of the present theory, in the range of 15–20 kbars the TO spectrum ought to go over to a single TO peak at a frequency somewhat above $\omega_c = \omega_{\mathrm{TO}} = 173\ \mathrm{cm}^{-1}$, and a weak peak below ω_c [cf. Fig. 3(c)], analogous to the LO spectrum observed at all temperatures and pressures here. The transition to this situation would not, of course, be abrupt but would occur gradually.

3. Pressure dependence of the β and γ frequencies and intensities

We now turn to an explanation of the strong pressure dependence of (γ area)/(β height). The crux of the explanation can be seen by considering jointly Figs. 3(b) and 4. From Fig. 3(b) one sees that the frequency of the β and γ peaks is determined by the lowest- and highest-frequency intercepts of $\Delta(\omega)$ and the line determined by $\omega - \omega_{\mathrm{TO}}$. If ω_{TO} moves upward in frequency with pressure faster than ω_c moves with pressure, then both ω_β and ω_γ should increase with increasing pressure. Figure 4 shows that ω_{TO} does increase faster with pressure than does ω_c, and Fig. 2 shows that experimentally both ω_β and ω_γ increase with increasing pressure. Further, from Fig. 1 one sees that the theory fits both ω_β and ω_γ. Therefore, the theory accounts qualitatively and quantitatively for the pressure dependence of ω_β and ω_γ.

Also, from Fig. 3(b), one sees that if $\omega_c - \omega_{\mathrm{TO}}$ decreases with increasing pressure then the intercepts of $\Delta(\omega)$ with $\omega - \omega_{\mathrm{TO}}$ will occur at successively lower values for the *slope* of $\Delta(\omega)$, S_1. As shown above the intensity of the γ peak is proportional to $(1+|S_1|)^{-1}$. From Fig. 4 one sees that $\omega_c - \omega_{\mathrm{TO}}$ does, in fact, decrease with increasing pressure and therefore the intensity of the γ peak ought to be strongly pressure dependent as the slope of $\Delta(\omega)$ varies rapidly with frequency near ω_c.

On the other hand, at the lowest frequency intercept of $\omega - \omega_{\mathrm{TO}}$ and $\Delta(\omega)$ in Fig. 3(b) we see that $\Gamma(\omega)$ is large and thus determines the height of the β peak. Therefore, the intensity of the β peak is expected to be less sensitive to pressure and determined largely by the two-phonon density of states. One thus expects from the theory that (γ area)/(β height) will be strongly pressure dependent, and this is what one observes experimentally. This behavior is rooted in the fact that small changes in $\omega_c - \omega_{\mathrm{TO}}$ give large changes in the slope of $\Delta(\omega)$ at the highest frequency intercept point.

We see, then, that the theory explains all of our experimental results qualitatively and quantitatively in an internally self-consistent way. Within this context we feel that we have tested the theory and that the theory unifies all of our data. It would be desirable to see the theory applied to other experimental results as, for example, polariton experiments or high-resolution inelastic neutron experiments in the TO region at $q=0$. It would also be of significant interest to see Raman experiments done under hydrostatic pressure of 15–20 kbars at low temperatures, to see whether the TO spectrum goes over to the behavior seen for the LO spectrum.

V. SUMMARY

An experimental and theoretical study has been made of the anomalous TO region in CuCl, with the following results.

(i) Raman spectra were obtained as a function of hydrostatic pressures up to 7 kbars at 40 K, and the behavior of the peaks labeled β, β', and γ was studied.

(ii) While both the β and γ peaks shifted upward in frequency with pressure the shifts were small, corresponding to mode Grüneisen parameters of 0.9 and 1.3, respectively.

(iii) The ratio of the integrated area of the γ peak to the intensity of the β peak was observed to depend strongly on pressure, varying by 28% per kbar.

(iv) A theory was employed which explained both the β and γ peaks as jointly being the TO phonon in CuCl. This arises because the harmonic TO is coupled by cubic anharmonicity to a two-phonon density of states characterized by a Van Hove P_3 singularity on its high-frequency end.

(v) Fits of the theory to the data showed that the parameters in the theory designated as V_3^2D, V_4D, R, A, and a had sensible pressure dependences (frequently quite small).

(vi) The two most critical parameters of the theory, ω_c and ω_{TO}, were seen to have different linear dependences on pressure. These dependences resulted in a quantitative explanation for the observed pressure dependence of the ratio of the area of the γ peak to height of β peak.

(vii) The pressure dependences of ω_c and ω_{TO} also led to the prediction that at 40 K a pressure of 16.6 kbars ought to produce a qualitatively different Raman spectrum.

[†] Supported by NSF Grant No. DMR75-10414 and No. DMR74-17918, and by the Deutscheforschungsgemeinschaft.

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