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Temperature dependence of the Raman scattering from CuCl[†]

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Temperature dependence of the Raman scattering from CuCl has been measured from room temperature down to 7 °K. The LO-mode frequency shows a slight decrease at low temperatures, apparently mirroring the low-temperature negative thermal expansion. An unambiguous observation of the TO-mode scattering is not made because of the curious β-γ double peak anomaly described by Kaminow and Turner. Discrepancies in the Lyddane-Sachs-Teller relation may be accounted for by using for ω_{TO} a weighted average of the β- and γ-mode frequencies; measurements of ϵ_0 have been extended down to 7 °K to verify this assumption. Attempts to fit the observed spectrum in the region of the β and γ peaks using available uncoupled- and coupled-mode theories are described.

INTRODUCTION

We report here our measurements down to liquid-helium temperatures of the temperature dependence of the Raman scattering from the zinc-blende semiconductor cuprous chloride. In an earlier paper[1] we reported on similar studies on cuprous bromide and cuprous iodide. A great deal of interest has centered on the intermediate nature of the interatomic bonding in these materials: while forming covalent bonds in a tethahedral coordination their ionicities are very near the Phillips criterion[2] for the onset of the rocksalt structure. Previous experimental studies of the lattice dynamics of CuCl include neutron measurements of the (300 °K) phonon dispersion curves,[3] infrared spectroscopic measurements,[4,5] and Raman scattering.[6-9] These Raman studies were either performed at room temperature using unoriented crystals,[6] or at a few temperatures between 300 °K and liquid-nitrogen temperature.[7-9] The temperature region below 90 °K is of interest because of the anomalous thermal expansion of CuCl, the lattice parameter increases with decreasing temperature below about 90 °K [10] and should affect the frequencies of the Raman-active zone-center optic-phonon modes.

Samples were grown using the travelling solvent technique.[11] Spectra were excited using 100 mW from an argon-ion laser oscillating at 5145 Å, and were observed at 90° using the conventional techniques. Spectral resolution varied from 2 cm^{-1} at 300 K to less than 1 cm^{-1} for the narrowest features at 7 °K. For the zinc-blende structure of CuCl, both the LO and TO zone-center phonon modes corresponding to the irreducible representation Γ_{25} should be observable in a 90 ° Raman-scattering experiment. For the geometry $x'(zx')z$ {using the notation $\vec{k}_i(\hat{e}_i, \hat{e}_s)\vec{k}_s$, with $z=[001]$, $x'=[110]$}, both the LO and TO modes should be excited, while the $x'(zy')z$ geometry should yield scattering from the TO mode only.

RESULTS

In Fig. 1 we show the Raman Stokes spectra recorded at room temperature. In Fig. 1(a), where we should observe scattering from the LO and TO zone-center phonons, we can distinguish four peaks which we label α, β, γ and δ to conform to the notation of Kaminow and Turner.[9] Our measured frequencies for these room-temperature features agree well with those given by previous authors.[6-9] For the geometry shown in Fig. 1(b) scattering from the TO mode only should be observed; we see the α, β,

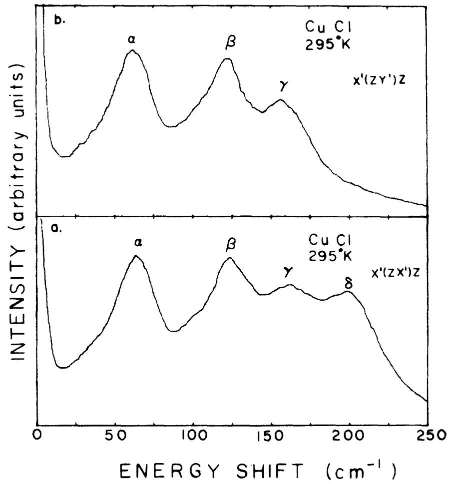

FIG. 1. Raman Stokes spectra of CuCl recorded at 295 °K for the scattering geometries (a) $x'(zx')z$ and (b) $x'(zy')z$.

and γ peaks appearing again with the same relative intensities, but the δ peak has disappeared. The peak δ, then, has a behavior characteristic of scattering from the LO phonon. It should be noted, however, that the room-temperature value for this peak in the Raman spectrum is 199 ± 2 cm^{-1},while neutron-diffraction measurements[3] show an energy of 216 cm^{-1} for the LO phonon at Γ. The origin of this discrepancy may lie in the relatively large uncertainty in the neutron measurements.

The peak α (64 cm^{-1} at 295 °K) has been attributed by Prevot *et al.*[8] to a two-phonon band involving either the combinations 2TA(X) (64 cm^{-1}) or LA − TA(L) (67 cm^{-1}). We observe the α band to vanish exponentially at low temperatures (cf. Fig. 2), so it must be a difference band. Its frequency of 64 cm^{-1} would lead us to accept the LA − TA(L) difference band assignment rather than the conclusions of Nusimovici and Meskaoui,[7] who assigned this peak to scattering from the two-phonon combination LO − LA (X) (73 cm^{-1} at 295 °K). However, the errors in the neutron data (5–8%) leave us with the clear conclusion that this choice is not definitive

The polarization properties of the α band can also be invoked to clarify the choice between LO − LA (X) and LA − TA(L). Were the band due to LO − LA(X) then it should appear in Γ_{15} only; if it were due to LA − TA(L) then it should appear both in Γ_{12} and Γ_{15}. The α band does appear both in Γ_{12} and Γ_{15} but is only about $\frac{1}{5}$ as strong in Γ_{12} as in Γ_{15} (the Γ_{12} spectrum is not shown here as it is not the main point of our paper). However, the entire Γ_{12} spectrum is only about $\frac{1}{5}$ as strong as the entire Γ_{15} spectrum; thus the α band has significant strength within the Γ_{12} spectrum. One is tempted to conclude that the α-band appearance in the Γ_{12} and Γ_{15} makes its identification as LA − TA(L) credible. But the smallness and quality of the sample used for the Γ_{12} experiment provide the possibility of depolarization within the sample, and hence the choice between LO − LA(X) and LA − TA(L) is not as clear as one would like.

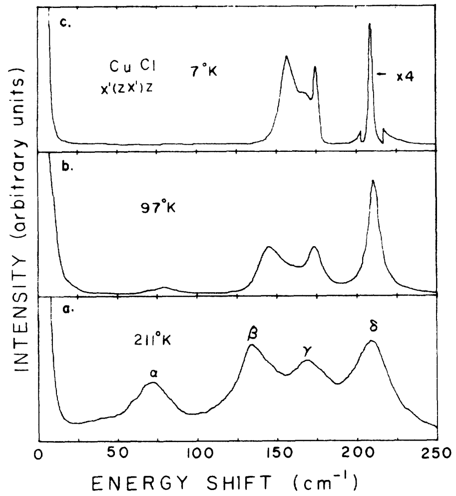

FIG. 2. Raman Stokes spectra of CuCl recorded in the geometry $x'(zx')z$ at temperatures (a) 211 °K, (b) 97 °K, (c) 7 °K. In (c) the vertical scale has been reduced by a factor of 4 in the vicinity of the δ peak.

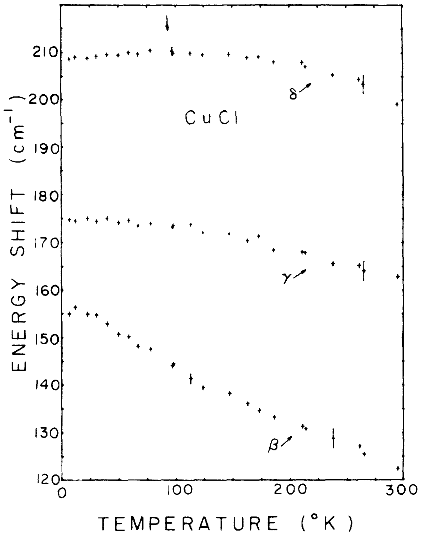

FIG. 3. Temperature dependence of Raman scattering peaks β, γ, and δ in CuCl. Experimental uncertainties range from ± 2 cm^{-1} at 295 °K to less than ± 1 cm^{-1} at 7 °K. The arrow at the top of the figure indicates the temperature at which the lattice parameter assumes a minimum in this system.

The most interesting features of the spectrum are the β and γ bands. The neutron-determined energy for the TO(Γ) phonon at room temperature is 183 cm^{-1}, while β and γ have energies 123 and 163 cm^{-1}, respectively, at this temperature. Several authors[6–8] have suggested that γ be associated with the TO mode, while β would be a two-phonon combination band. The persistence of significant intensity in the β band at lower temperatures shows this explanation to be inadequate. We will return to this point later.

In Fig. 2 we show the LO + TO spectrum at successively lower temperatures. The δ peak narrows considerably while its peak intensity increases; the vertical scale has been decreased by a factor of 4 in the vicinity of δ on the 7 °K trace in order to bring out the features of the β and γ bands. The β peak shifts rapidly to higher frequencies with decreasing temperature, while its width does not decrease too noticeably over this temperature range. γ shows a slower shift to higher frequencies with decreasing temperature. At 100 °K, the integrated intensities of β and γ are comparable, but at the lowest temperature γ has clearly decreased relative to β. This situation is to be contrasted to that in the infrared absorption spectrum[4] where a similar double-peak anomaly occurs. The two peaks in that experiment have comparable intensities at 100 °K, but at 5 °K about 75% of the absorption strength lies in the higher-energy band—that which we call γ.

In Fig. 3 we display the temperature dependence of the features β, γ, and δ. δ exhibits a slow increase from 199 to 211 cm^{-1} at about 100 °K, thereupon decreasing to a value 208.5 cm^{-1} at 7 °K. Below 100 °K, the position of δ can be determined to within an uncertainty of less than 1 cm^{-1}. The arrow in Fig. 3 indicates the position of minimum lattice parameter.[10] This softening of the LO frequency in the low-temperature region of negative thermal expansion is similar to that observed in CuBr.[1] In both these systems, the LO-mode frequency appears to follow the unit cell volume in this low temperature range. We can discern no similar behavior in the temperature dependence of the β- and γ-mode frequencies. β shows an almost constant increase down to the lowest temperatures. γ increases at a much more moderate rate down to about 125 °K and shows no further increase from thereon. Similarly, in CuBr the TO frequency showed no influence of the negative thermal expansion.

In Table I we show values of the Lyddane-Sachs-Teller (LST) ratios, $\epsilon_0/\epsilon_\infty = (\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})^2$, obtained from various room-temperature measurements. The squared ratios of the LO and TO zone-center frequencies determined from neutron scattering and infrared transmission are seen to be in good agreement despite the discrepancies in the mode frequencies. Taking δ to be the LO phonon in our Raman measurements and choosing β or γ to be the TO, we obtain LST ratios 2.62 or 1.49, respectively. As was pointed out by Kaminow and Turner,[9] taking the mean of the β and γ frequencies to be the TO frequency gives good agreement with the $\epsilon_0/\epsilon_\infty$ ratio. It should be emphasized that since β and γ are both infrared active they will both contribute to ϵ_0, so using their mean frequency in the LST relation is not an unreasonable assumption. Support for this point of view is to be found in the fact that ϵ_0 is known[9] to decrease rather rapidly with decreasing temperature down to 90 °K, the lowest temperature reached before, reflecting the decrease in the difference between the δ and the average $\beta\gamma$-mode frequencies.

TABLE I. Comparison of the Lyddane-Sachs-Teller (LST) ratios in CuCl as determined by various measurements.

Measurement		LST Ratio
Dielectric constants	$\epsilon_0 = 7.9$[a] $\epsilon_\infty = 3.61$[b]	$\epsilon_0/\epsilon_\infty = 2.19$
Neutron diffraction[c]	$\omega_{\mathrm{TO}} = 183\ \mathrm{cm}^{-1}$ $\omega_{\mathrm{LO}} = 216\ \mathrm{cm}^{-1}$	$(\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})^2 = 1.39$
Infrared[d]	$\omega_{\mathrm{TO}} = 155\ \mathrm{cm}^{-1}$ $\omega_{\mathrm{LO}} = 195\ \mathrm{cm}^{-1}$	$(\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})^2 = 1.58$
Raman[e]	$\omega_\beta = 123\ \mathrm{cm}^{-1}$ $\omega_\gamma = 163\ \mathrm{cm}^{-1}$ $\omega_\delta = 199\ \mathrm{cm}^{-1}$	$(\omega_\delta/\omega_\beta)^2 = 2.62$ $(\omega_\delta/\omega_\gamma)^2 = 1.49$

[a] Reference 12.

[b] A. Feldman and D. Horowitz, J. Opt. Soc. Am. 59, 1406 (1969).

[c] Reference 3.

[d] From oblique incidence infrared transmission measurements on a thin CuCl slab by S. Iwasa thesis (University of Pennsylvania, 1965) (unpublished).

[e] Present work.

We have measured the temperature dependence of of the dielectric constant, ϵ_0, over the entire range from 295 to 7 °K. Measurements were made using a cavity perturbation technique in a TM_{010} mode cavity at 9 GHz.[13] In order to avoid the difficulties normally incurred in obtaining absolute values of the dielectric constant using this method, we have chosen to normalize our data to the published room-temperature value of 7.9 [12] (our measured value was 7.4 at 295 °K). This adjustment should have no effect on the temperature dependence of the dielectric constant which is our concern here. The results of these measurements are shown in Fig. 4. Experimental uncertainties in the determination of the normalized value of ϵ_0 are estimated to be less than 0.04. Between room temperature and liquid-nitrogen temperature the decrease in $\epsilon_0(T)$ is approximately linear, with a slope $8.03 \times 10^{-3}\ {}^\circ\mathrm{K}^{-1}$ which is somewhat larger than that reported by Kaminow and Turner[9] for this temperature range (approximately $5.6 \times 10^{-3}\ {}^\circ\mathrm{K}^{-1}$). Below 85 °K, ϵ_0 shows a less rapid decrease and appears to be approaching a constant value of about 5.95. We also plot in Fig. 4 the values for ϵ_0 obtained using $\epsilon_0 = (\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})^2 \epsilon_\infty$, where ω_{LO} was taken to be the frequency of the δ peak, $\epsilon_\infty = 3.61$, and ω_{TO}^2 was found by taking the weighted average of the squares of the β- and γ-peak frequencies. The weighting factor was the experimentally observed *Raman intensity*; i.e.,

$$\omega_{\mathrm{TO}}^2 = \frac{I_\beta \omega_\beta^2 + I_\gamma \omega_\gamma^2}{I_\beta + I_\gamma} . \qquad (1)$$

This method appears to give values of ϵ_0 which are in reasonable agreement with those determined by our direct measurements. Such agreement is not seen if we weight the β and γ peaks by their *infrared* strengths. So the discrepancy in the LST relation may be accounted for by including the β and γ peaks in the analysis. However, the identification of β

and γ remains to be made.

In Fig. 5 we compare the integrated intensities of the β, γ, and δ bands. In Fig. 5(a) the δ-mode intensity is plotted as a function of temperature; the dashed line represents $[\bar{n}(\omega, T)+1]$ where $\bar{n}(\omega, T)$ is the Bose-Einstein population factor evaluated at the δ-peak frequency. Clearly, the δ intensity appears to have a temperature dependence characteristic of a first-order Raman line. Having established this, we choose to plot in Fig. 5(b) the ratio of the β intensity to that of δ, and in Fig. 5(c) the ratio of the γ intensity to that of δ. In making the calculations for Figs. 5(b) and 5(c) we have not deconvoluted the combined β-γ band as was correctly done by Kaminow and Turner. At temperatures below about 80 °K the β and γ bands are clearly enough separated that a simple graphical reduction of the combined band into its β and γ components seems adequate. We have included in Figs. 5(b) and 5(c) the results of Kaminow and Turner and have also included our own graphical reduction up to 125 °K, beyond where we feel it to be valid, in order to show that the results from the two methods join on to each other in the overlap region and agree reasonably well within their joint uncertainties. (Error bars are included for our points; Kaminow and Turner's uncertainties can be seen from the scatter of their points to be about the same as ours.)

The dashed line in Fig. 5(b) represents the ratio $[\bar{n}(\omega_\beta, T)+1]/[\bar{n}(\omega_\delta, T)+1]$, where the population factors are evaluated at the experimentally observed frequencies. *In spite of considerable scatter, it appears that β might also exhibit a temperature dependence corresponding to a first-order Raman line.* In Fig. 5(c), however, we note a quite anomalous behavior for the γ-mode intensity. The dashed line again represents the behavior to be expected if γ were a simple one-phonon band. This clearly does not fit the data. Kaminow and Turner reported the γ intensity to increase with decreasing temperature down to 100 °K, whereas we observe an obvious decrease in this intensity on going from 100 to 7 °K. In the discussion to follow we shall discuss various attempts to account for this anamalous behavior of the scattering intensity.

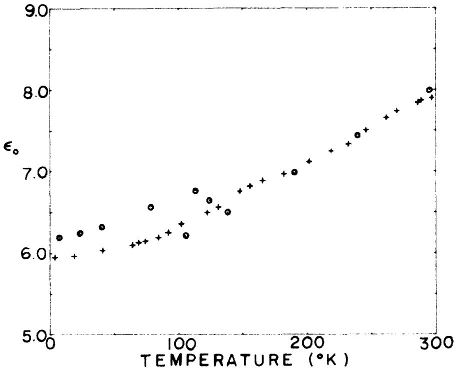

FIG. 4. Temperature dependence of the low-frequency dielectric constant of CuCl. The crosses represent measurements made at 9 GHz , normalized to the value 7.9 at 295 °K. The circles represent values obtained from the LST relation, using for ω_{TO}^2 the average ω_β^2 and ω_γ^2 weighted according to their Raman scattering intensities as described in the text.

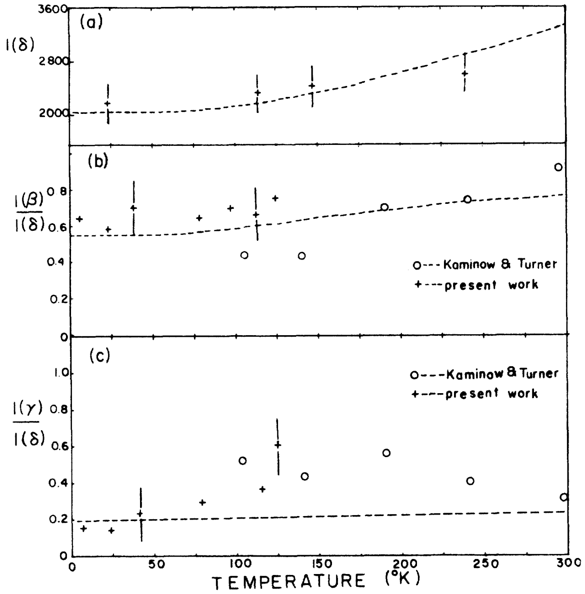

FIG. 5. (a) Integral intensity of the δ peak as a function of temperature. The dashed line represents the temperature dependence predicted for a first-order Raman line at the δ-peak frequency. (b) and (c) Observed ratios of β- and γ-peak intensities to δ-peak intensity as functions of temperature. The dashed lines represent the behaviors to be expected for first-order Raman lines.

DISCUSSION

As was mentioned above, several previous authors have assigned γ to be the TO mode while β would be some two phonon combination [e.g., the LA + TA (L) combination suggested by Prevot *et al.*[8]]. Such an explanation is equivalent to representing the frequency-dependent dielectric constant of the crystal by the form[14]

$$\epsilon(\omega)=\epsilon_\infty+\sum_{i=0}^{n}\frac{S_i}{1-(\omega/\omega_1)^2+i(\omega/\omega_i^2)\gamma_i}\ , \qquad (2)$$

where the sum is taken over n independent Lorentzian oscillators of strength S_i, width γ_i, and frequency ω_i. We shall use this simple model by letting S_0 represent the peak height of the TO lattice resonance (assumed to be γ), while S_1 (and any additional term) would represent a two-phonon combination band (i.e., β). Let the integrated intensities of β and γ be represented by $I(\omega_i)$ and $I(\omega_0)$, respectively. Then, using the experimental results of Kaminow and Turner that $I(\omega_i) \approx 3I(\omega_0)$ at 295 °K, we should expect to observe $I(\omega_i) \approx \frac{3}{8}I(\omega_0)$ at 7 °K. In making this estimate we have used the thermal population factors $[\bar{n}(\omega_\gamma, T)+1]$ for a first-order line and $[\bar{n}(\omega_\beta/2, T)+1]^2$ as an approximation for a second-order summation band. Were the identity of β as a specific second-order feature known, then the correct temperature dependence for this feature could be computed using the known frequencies of the two phonons involved. Our 7 °K results show $I(\omega_i) \approx 5I(\omega_0)$. Similar results follow from taking β to be the TO resonance, and γ to be a second-order band, though we view this second possibility to be even less likely in view of the extremely small width of the low-temperature γ peak. Clearly, the assumption of uncoupled oscillators is inadequate to account for the temperature dependence of the β- and γ-mode intensities shown in Fig. 5.

Our observed temperature dependence might be accounted for if, as has been suggested,[9] we consider β and γ to represent hybrid modes resulting from the coupling of a one-phonon line to a two-phonon background. Various types of coupled phonon interactions have been observed previously in Raman studies. These may be described briefly as follows[15]: (a) In $SrTiO_3$, two phonons interact directly as the energy of one is swept toward that of the second by the application of an external electric field. (b) In $BaTiO_3$, optic phonons interact indirectly through anharmonic terms which couple each to a two-phonon acoustic background. (c) In diamond, a bound state in the two-phonon system is split off slightly from the high energy end of the two phonon continuum. (d) In α-quartz, a temperature-dependent one-phonon state interacts with a two-phonon state as it is swept through the latter.

Cases (a) and (b) do not apply to the present study since, in the case of CuCl with two atoms per unit cell, we have only one Raman-active TO mode. Similarly, case (c) results only in a slight shift of a two-phonon combination and has no bearing on the problem under consideration here. Case (d) warrants further attention. In the case of α-quartz (and $AlPO_4$ as well[15]), a soft optic-phonon mode moves rapidly with increasing temperature toward a temperature-independent two-phonon band. In the overlap region, an "anticrossing" characteristic of two coupled oscillators was observed.[15] We note that no such anticrossing behavior is observed in CuCl. Even at low temperatures, where the β and γ frequencies are approaching each other, we see no evidence for the level repulsion observed in α-quartz and $AlPO_4$.

Similar to case (d) is the asymmetry observed by Raman scattering on the low-energy side of the TO resonance in GaP by Barker.[16] He was able to account for this asymmetry by using a dielectric function for coupled oscillators:

$$\epsilon(\omega) = \epsilon_\infty + S_0\left(1-\sum S_i\right)\Big/\left[1-\left(\frac{\omega}{\omega_0}\right)^2 + i\frac{\omega}{\omega_0^2}\gamma_0 - \sum_{i=1}^{n}\frac{S_i}{1-(\omega/\omega_i)^2 + i(\omega/\omega_i^2)\gamma_i}\right]. \tag{3}$$

The sum in the denominator represents subsidiary oscillators (probably two-phonon bands) having frequencies near ω_0. The effects of this sum will be to cause the main peak to appear at a frequency other than ω_0 and to cause the shape of the observed peak to reflect the frequency dependence of the damping function. It must be noted that the resultant asymmetry in the case of GaP[16] was comparatively slight and the rapid decrease with temperature of the intensities of the participating two-phonon bands caused this distortion to disappear at 100 °K. For CuCl, however, the "asymmetry" is quite pronounced even at the lowest temperatures and a small "third peak" is seen between β and γ at 7 °K.

We have attempted, unsuccessfully, to fit the Raman spectrum of CuCl in the vicinity of the β and γ bands using Eq. (3). We assumed γ to be a one phonon band with ω_0 *less* than the neutron-determined TO resonance and let β result from the sum of one or two Lorentzians in the frequency-dependent damping constant and were able to reproduce the room-temperature spectrum. Assuming β to be a second-order band, we varied the ratios S_0/S_i by one and two-phonon population factors and varied ω_0 and ω_i with temperature so the coupled modes would have the observed temperature dependence of the β and γ peaks. This did not reproduce the low-temperature spectra. Neither could we reproduce the low-temperature spectra by letting both β and γ be one phonon peaks. Under any assumptions, it does not appear possible to maintain a large intensity in the β band without broadening the γ peak well beyond the experimentally observed linewidth, nor can we reproduce the "third peak" between β and γ seen at 7 °K. Attempts were made to describe β using more asymmetric line shapes but the number of adjustable parameters became even more unwieldy and the results did not appear to be approaching a better description of the situation. Similar attempts taking β to be the TO resonance and γ to be a two-phonon band were equally unsuccessful.

In summary, it does not appear that the β-γ double-peak anomaly observed by Raman scattering in CuCl can be accounted for by any of the mechanisms previously invoked to describe coupled mode systems.

CONCLUSION

We have extended the Raman measurements of the CuCl spectrum down to liquid-helium temperatures. Below 90 °K we have observed a softening of the LO mode frequency reflecting the negative thermal expansion of this crystal in a manner similar to that previously observed in CuBr. We have been able to confirm the assignment of a prominent second-order feature (64-cm^{-1} peak at 295 °K) as being due to scattering from phonons near the combination LA – TA(L). Finally, we have traced the temperature dependence of the frequencies and intensities of the curious double peaks (123 and 163 cm^{-1} at 295 °K) down to the lowest temperatures and described our attempts to fit this region of the spectrum using available independent- and coupled-mode theories. We feel that this problem is of sufficient interest to warrant an extended theoretical treatment. Work is currently under way in our laboratory to attempt an unambiguous determination of the TO mode experimentally, i.e., we are looking for polariton scattering from CuCl. In such an experiment, the TO mode should be identifiable by a decrease in its frequency as the scattering angle decreases toward zero.

ACKNOWLEDGMENTS

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[1] J. E. Potts, R. C. Hanson, C. T. Walker, and C. Schwab, Solid State Commun. 13, 389 (1973).

[2] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[3] C. Carabatos, B. Hennion, K. Kunc, F. Moussa, and C. Scwab, Phys. Rev. Lett. 26, 770 (1971).

[4] J. N. Plendl, A. Hadni, J. Claudel, Y. Henninger, G. Morlot, P. Strimer, and L. C. Mansur, Appl. Opt. 5, 397 (1966); J. N. Plendl and L. C. Mansur, Appl. Opt. 11, 1194 (1972).

[5] A. Hadni, F. Brehat, J. Claudel, and P. Strimer, J. Chem. Phys. 49, 471 (1968).

[6] S. Iwasa and E. Burstein, J. Phys. (Paris) 26, 614 (1965); M. Krauzman, *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1969), p. 109.

[7] M. A. Nusimovici and A. Meskaoui, Phys. Status Solidi B 62, K69 (1972).

[8] B. Prevot, C. Carabatos, and M. Leroy, C. R. Acad. Sci. Paris 274, 707 (1972).

[9] I. P. Kaminow and E. H. Turner, Phys. Rev. B 5, 1564 (1972).

[10] H. F. Schaake, Air Force Cambridge Research Laboratories, Report No. AFCRL-69-0538, 1969 (unpublished).

[11] C. Schwab, Ph.D. thesis (University of Strasbourg, 1970) (unpublished).

[12] Obtained by infrared reflectivity measurements at 320 and 144 μm by R. H. Stolen (unpublished); quoted in Ref. 9.

[13] B. J. Slagsvold and C. F. Schwerdfeger, Rev. Sci. Instrum. 43, 154 (1972).

[14] In the simple picture we are considering, the Raman line shape is just the dielectric response function for the mode multiplied by a thermal population factor; see A. S. Barker and R. Loudon, Rev. Mod. Phys. 44, 18 (1972).

[15] For references and a more complete discussion, see J. F. Scott, Phys. Rev. Lett. 24, 1107 (1970).

[16] A. S. Barker, Phys. Rev. 165, 917 (1968).