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# The Origin of the Anomalous TO-Doublet in Cubic CuCl Studied by Light Scattering

By

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Light scattering experiments are performed concerning polaritons associated with the anomalous TO-doublet in CuCl. A quantitative description of the dispersion behaviour, recorded at liquid $N_2$ temperature, may be obtained by taking into account coupling of the fundamental zone centered TO-phonon with second order modes due to two van Hove singularities. This description is in good agreement with recent calculations of the two-phonon density of states in CuCl.

Es werden Lichtstreuexperimente an Polaritonen, die mit dem anomalen TO-Dublett in CuCl verknüpft sind, durchgeführt. Eine quantitative Beschreibung des Dispersionsverhaltens, das bei der Temperatur des flüssigen Stickstoffs aufgenommen wurde, wird unter Berücksichtigung der Kopplung des fundamentalen TO-Phonons im Zonenzentrum mit Moden zweiter Ordnung infolge von zwei van Hove-Singularitäten erhalten. Diese Beschreibung ist in guter Übereinstimmung mit kürzlichen Berechnungen der Zwei-Phononenzustandsdichte in CuCl.

## 1. Introduction

Since CuCl is two atomic and exhibits a simple zincblende structure ($F\bar{4}3m$ for $t < 680$ K) the fundamental optical phonon spectrum near the $\Gamma$-point of the first Brillouin zone is expected to consist only of one TO- and one LO-phonon. It is well known, however, since several years ago that the situation is not as simple as this. CuCl clearly shows a single LO-phonon at 211 $cm^{-1}$ which can be assigned unambiguously by means of light scattering selection rules. The TO-mode correspondingly assigned, however, consists of a characteristic double peak with maxima at 141 and 172 $cm^{-1}$. The origin of this doublet has been subject to much discussion within the last few years [1 to 10]. The component at 141 $cm^{-1}$ has been assigned as a pure second-order mode by [2, 4, 9]. On the contrary [3, 6, 10] conclude that the double peak is essentially caused by lattice anharmonicity and that the second, additional peak cannot be assigned to an individual fundamental or a two-phonon process. The structure of the phonon spectrum is supposed to be caused by strong anharmonic coupling between the TO($\Gamma$) phonon and density of states modes for the combination of two branch frequencies at symmetrical points in the Brillouin zone by [3, 7, 10]. Numerical calculations of the phonon dispersion curves for the whole first BZ of CuCl have been carried out by [8, 11, 12]. The models used were a rigid ion model [12], a deformable bond approximation method [11], and a double shell model [8]. Calculations following the latter model applied to CuCl allowed the best quantitative fit of neutron scattering data [12] that have been obtained so far. Our following interpretation of the TO-double peak closely follows the two-phonon density of states calculations by [13].

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## 2. Experimental

The experiments in the present work were carried out on an oriented CuCl single crystal with dimensions $11 \times 7 \times 7$ mm$^3$. A $Kr^+$ laser with an average output of $\approx 500$ mW at 647.1 nm was used to excite the spectra. A Jarrel Ash double monochromator and a photon counting system were used to process the Raman scattering. Right angle and near forward scattering geometries allowed recording of phonon and polariton spectra [14]. The experimental forward scattering technique necessarily had to be refined in order to suppress stray light which appeared strongly in the low frequency polariton region of the material (130 to $\approx 170$ cm$^{-1}$). All spectra were recorded at liquid nitrogen temperature.

## 3. Results and Discussion

Fig. 1 shows the typical first-order phonon spectrum of CuCl: an LO-phonon at 211 cm$^{-1}$ and the TO-double peak at 172 and 141 cm$^{-1}$. The lines have been symmetrized by Lorentzian curves (dashed curves), the measured halfwidths of which are given for the $TO_1$ and $LO_1$-components. Symmetrization of the complete double peak including the $TO_2$-component clearly indicates that the structure contains another component between $TO_1$ and $TO_2$. This observation is strongly supported by the experimental results obtained by Krauzman et al. [7]. These authors present Raman scattering measurements concerning the CuCl phonons at 40 K. Further

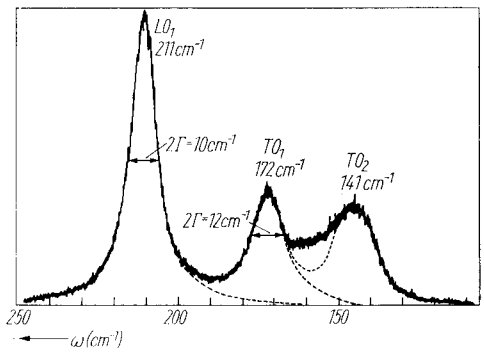


Fig. 1. First-order phonon spectrum of CuCl. Laser data: 647.1 nm, $\approx 500$ mW. Spectral slit width: 4 cm$^{-1}$, time constant: 1 s, scan: 10 cm$^{-1}$/min, scattering geometry $z(y'y')x'$. Dashed curves show the Lorentzian-shape symmetrized lines

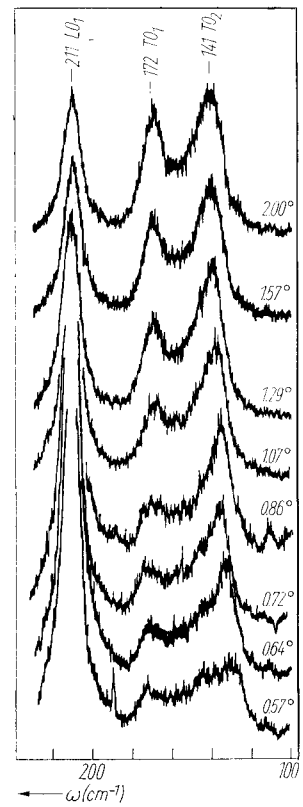


Fig. 2. Polariton spectra of the TO-double component in CuCl. Laser data: 647.1 nm, $\approx 500$ mW, spectral slit width: 5 cm$^{-1}$, time constant: 2 s, scan: 5 cm$^{-1}$/min, scattering geometry $z(xy)z$ corresponds to $\varphi = 0°$. The angles to the right in the figure are internal scattering angles

improved experiments by Potts et al. [5] at 7 K show a real separate third peak between the $TO_1$ and $TO_2$-components.

In Fig. 2 a representative spectra series of the polaritons as recorded in our present work is reproduced. The numbers to the right denote the internal scattering angles between the laser beam and the direction of the recorded stray light. The acceptance angle of the latter was restricted to $< 0.2°$ by an aperture. A quantitative evaluation of the spectra shows that both peaks move towards lower wave numbers for decreasing scattering angles. Earlier polariton scattering experiments by Shand et al. [6] were analyzed only qualitatively. The result that also the $TO_1$-phonon shows dispersion remained undetected hitherto.

In order to check the different interpretations of the double peak we have to calculate the observed polariton dispersion behaviour from corresponding theoretical models.

In a first step we examine the question whether the double peak is caused by polariton Fermi resonance of a fundamental mode with one second-order mode due to a density of states maximum [15]. The dispersion curves $\omega = \omega(k)$ can be calculated from

$$k = \left[\frac{\omega^2}{c^2}\left(\varepsilon_\infty + \frac{S_{\mathrm{TO}}\,\omega_{\mathrm{TO}}^2}{\omega_{\mathrm{TO}}^2 - \omega^2} + \frac{S_*\,\omega_*}{\omega_*^2 - \omega^2}\right)\right]^{1/2}. \tag{1}$$

The fundamental mode frequency $\omega_{\mathrm{TO}}$, the second-order phonon frequency $\omega_*$ and its mode strength $S_*$ have been varied as free parameters within reasonable limits. Before inserting the wave numbers expressed in $\mathrm{cm}^{-1}$ in (1) they have to be expressed as frequencies $\omega = 2\pi c(1/\lambda)$. The best fit of our experimental data was obtained for $\omega_{\mathrm{TO}} = 172\ \mathrm{cm}^{-1}$, $\omega_* = 143\ \mathrm{cm}^{-1}$, and $S_* = 0.6 \pm 0.1$. The values $\omega_{\mathrm{LO}} = 211\ \mathrm{cm}^{-1}$ and $\varepsilon_\infty = 3.61$ [16] in general remained fixed although some variation of $\varepsilon_\infty$, see e.g. [17], was examined too. This "best fit" of the dispersion curves still was unsatisfactory because the deviation of the calculated dispersion branches from the experimental data points was clearly outside the experimental error in the resonance region. Fig. 3 shows the result. Better fitting of the upper data points enlarges the disagreement on the lower branch and vice versa.

In a second step two second-order phonons near the fundamental mode were introduced both interacting with the polaritons associated with the zone centered TO-phonon. The generalization of (1) becomes

$$k = \left[\frac{\omega^2}{c^2}\left(\varepsilon_\infty + \sum_{j=1}^{3}\frac{S_j\omega_{\mathrm{T}j}^2}{\omega_{\mathrm{T}j}^2 - \omega^2}\right)\right]^{1/2}. \tag{2}$$

The oscillator strengths $S_1$, $S_2$, and $S_3$ herein are determined by the equations

$$\left.\begin{aligned}
S_1 &= (\omega_{\mathrm{L}1}^2 - \omega_{\mathrm{T}1}^2)\,\frac{\varepsilon_\infty}{\omega_{\mathrm{T}1}^2}\,\frac{(\omega_{\mathrm{L}2}^2 - \omega_{\mathrm{T}1}^2)\,(\omega_{\mathrm{L}3}^2 - \omega_{\mathrm{T}1}^2)}{(\omega_{\mathrm{T}2}^2 - \omega_{\mathrm{T}1}^2)\,(\omega_{\mathrm{T}3}^2 - \omega_{\mathrm{T}1}^2)},\\
S_2 &= (\omega_{\mathrm{L}2}^2 - \omega_{\mathrm{T}2}^2)\,\frac{\varepsilon_\infty}{\omega_{\mathrm{T}2}^2}\,\frac{(\omega_{\mathrm{L}1}^2 - \omega_{\mathrm{T}2}^2)\,(\omega_{\mathrm{L}3}^2 - \omega_{\mathrm{T}2}^2)}{(\omega_{\mathrm{T}1}^2 - \omega_{\mathrm{T}2}^2)\,(\omega_{\mathrm{T}3}^2 - \omega_{\mathrm{T}2}^2)},\\
S_3 &= (\omega_{\mathrm{L}3}^2 - \omega_{\mathrm{T}3}^2)\,\frac{\varepsilon_\infty}{\omega_{\mathrm{T}3}^2}\,\frac{(\omega_{\mathrm{L}1}^2 - \omega_{\mathrm{T}3}^2)\,(\omega_{\mathrm{L}2}^2 - \omega_{\mathrm{T}3}^2)}{(\omega_{\mathrm{T}1}^2 - \omega_{\mathrm{T}3}^2)\,(\omega_{\mathrm{T}2}^2 - \omega_{\mathrm{T}3}^2)},
\end{aligned}\right\} \tag{3}$$

see [14]. The $S_\alpha$ are proportional essentially to the TO–LO splittings of the corresponding modes (see first factors!). $S_1$ with $\omega_{\mathrm{T}1} = 172\ \mathrm{cm}^{-1}$ and $\omega_{\mathrm{L}1} = 211\ \mathrm{cm}^{-1}$ therefore dominates the two others. An almost perfect fit of the recorded polariton frequencies

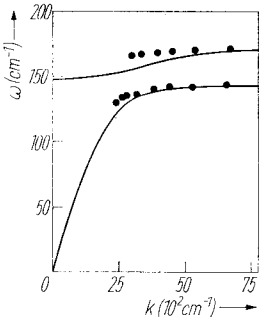


Fig. 3

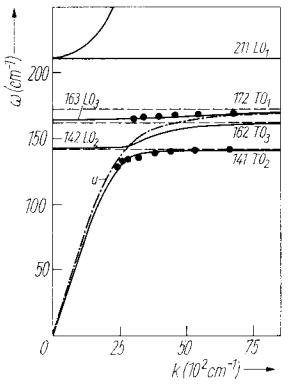


Fig. 4

Fig. 3. Best theoretical fit of the experimentally observed CuCl polariton dispersion data by a two-oscillator model, see text. No satisfactory agreement was obtained

Fig. 4. Theoretical fit of the polariton frequency data using a three-oscillator model, see text. The dash-dotted curve "u" corresponds to an undisturbed polariton dispersion branch associated with a fundamental phonon frequency $\omega_{TO_1} = 172$ cm$^{-1}$

could be obtained by introducing $\omega_{T2} = 141$ cm$^{-1}$, $\omega_{L2} = 142$ cm$^{-1}$, $\omega_{T3} = 162$ cm$^{-1}$, and $\omega_{L3} = 163$ cm$^{-1}$. $S_2$ and $S_3$ obviously have to be chosen very small compared with $S_1$. The introduction of these two disturbing second-order modes is strongly supported by recent two-phonon density of states calculations by Prevot et al. [13]. The authors obtain a maximum at 144 cm$^{-1}$ originating essentially from TA(L) + + LA(L) and another one at 168 cm$^{-1}$ originating from TA(X) + LA(X). Both second-order modes are expected to be simultaneous Raman- and IR-active which is a necessary condition for our above interpretation. An interpretation of the double peak as a more general "peculiar damping phenomenon" of the fundamental mode which has not much to do with anharmonic coupling to well defined second-order or other lattice modes seems not very realistic to us: The recorded polariton dispersion behaviour clearly shows that both peaks separate for decreasing $k$, the lower one moving towards $\omega = 0$ and the upper one towards $\omega = 163$ cm$^{-1}$, see Fig. 4. Furthermore the low frequency "damping feature" increases in intensity compared with the higher frequency peak, see Fig. 2. For $k < 1500$ cm$^{-1}$ the fundamental mode and its "damping structure" would be separated by more than 100 cm$^{-1}$! The lower frequency peak therefore seems to originate from a rather well defined lattice mode. Phonon spectra recorded at 4.2 K by Fukumoto et al. [9] indicate that the situation hardly will be qualitatively different at very low temperatures unless the low frequency peak loses its IR-activity which would imply a phase transition.

We now examine the weak intermediate polariton branch decreasing in frequency from $\omega_{T3} = 162$ cm$^{-1}$ to $\omega_{L2} = 142$ cm$^{-1}$ for decreasing $k$, see Fig. 4. As already pointed out before Raman scattering experiments at He temperatures [5, 7] clearly indicated the existence of a third mode between the two well-known TO-peaks of CuCl, see also Fig. 1. This third mode should exist in the spectra of Fig. 2, too, however, they give no positive arguments. We therefore calculate the relative polariton scattering intensities which are essentially proportional to the element $\chi_{xy}$ of the suscepti-

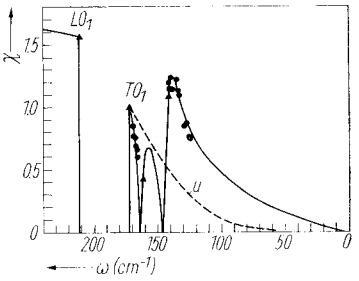


Fig. 5. The numerically calculated function of the susceptibility tensor element $\chi_{xy}(\omega)$ and experimental data points for CuCl in the polariton region. Triangles are data points obtained for large wave vectors ($k \approx 10^5$ cm$^{-1}$) by right angle scattering

bility tensor:

$$I \sim |\chi_{xy}(\omega)|^2 . \tag{4}$$

Using a method which has been proposed by Burstein et al. [18] and somewhat modified by the authors [19] the susceptibility tensor element $\chi_{xy}$ as a function of frequency can be calculated numerically as follows:

$$\chi_{xy}(\omega) = \frac{\sum_{j=1}^{3} \frac{a_{xy}^{(j)} \sqrt{\varrho_j}\, \omega_{\mathrm{T}j}}{\omega_{\mathrm{T}j}^2 - \omega^2} + b_{xy}}{\left(1 + \sum_{j=1}^{3} \frac{4\pi \varrho_j\, \omega_{\mathrm{T}j}^4}{\varepsilon_\infty (\omega_{\mathrm{T}j}^2 - \omega^2)^2}\right)^{1/2}} \sqrt{\frac{4\pi}{\varepsilon_\infty}}\, \omega E . \tag{5}$$

The mode strengths herein have been written as $S_j = 4\pi\varrho_j$. $a_{xy}$ and $b_{xy}$ are the atomic displacement and the electro-optic tensor elements, see [14]. $E$ is a normalization factor which remains constant in the polariton region [19]. By using the measured integrated TO-phonon intensities derived from Fig. 1 as input data (determination of $E$!) the LO-phonon intensity and the frequency dependent polariton scattering intensities can be evaluated from equations (4) and (5). The function $\chi(\omega)$ and the corresponding experimental data points are compared in Fig. 5. The agreement between theory and the recorded intensity data is very good. In particular the scattering intensities of the third intermediate polariton branch under discussion remains small compared with those of the well-known $TO_1$ and $TO_2$-components. Fig. 5 therefore again supports the interpretation of the TO-mode structure in CuCl given above. The dashed curve indicated by "u" in Fig. 5 describes $\chi_{xy}$ as a function of frequency in the absence of disturbing second-order phonons.

We finally note that although the frequency shift of the $TO_1$-component in the polariton spectra of Fig. 2 is only a few wave numbers above the experimental error its observed scattering intensity for larger $k$-vectors clearly increases in perfect agreement with the curve in Fig. 5. At the same time the $TO_2$-component is expected to decrease which also happens. When comparing the inverted intensity ratio of the two strong TO-components in Fig. 1 and the $\varphi = 2.00°$ spectrum in Fig. 2 this can be verified easily. Our present calculation of the CuCl Raman spectra does not include damping effects explicitly. The introduction of $-i\gamma\omega$ terms in the resonance denominators is adequate to describe the lineshapes in detail. However, the peak frequencies and integrated intensities quantitatively analyzed in this work hardly are touched by reasonable (constant) damping terms corresponding to the (almost constant) recorded linewidths. The deviations showed to be of the same magnitude as the experimental errors.

We summarize: The experimentally observed TO-double-peak structure of CuCl can be described in a satisfactory way by polariton Fermi resonances of the fundamental TO($\Gamma$)-mode with a phonon frequency at $\omega_{\mathrm{T1}} = 172$ cm$^{-1}$ and two second-

order density of states modes at $\omega_{T3} = 162\ \mathrm{cm}^{-1}$ and $\omega_{T2} = 141\ \mathrm{cm}^{-1}$. This interpretation is in good agreement with the recently calculated two-phonon density of states for the whole first BZ and with calculated polariton dispersion curves and scattering intensities around the centre of the first BZ. We assume that some coupling of the $k = 0$ TO-phonon with the two second-order modes takes place also for large wave vectors ($k \approx 10^5\ \mathrm{cm}^{-1}$) in the pure phonon region. This would explain why the selection rules hold so perfectly for the entire double-peak structure. A situation similar to that in CuCl has been observed recently also in CdS [20].

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