

## Pressure-Induced Disappearance of the Raman Anomaly in CuCl

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(Received 23 September 1998)

Raman spectra of CuCl were measured at  $T = 5$  K under hydrostatic pressures up to 3.3 GPa. The anomalous line shape of the transverse-optic (TO) scattering, which consists of a broad structure with several maxima, undergoes a drastic change under pressure. The anomaly disappears completely at 3 GPa. These pressure effects are well reproduced by a model calculation of the anharmonic coupling of the TO mode to acoustic two-phonon states (Fermi resonance). The results demonstrate that the ambient pressure TO anomaly does not arise from local vibrational modes of Cu atoms in off-center positions. [S0031-9007(98)08185-X]

PACS numbers: 63.20.Kr, 62.50.+p, 78.30.-j

Copper chloride is a highly ionic I-VII semiconductor crystallizing in the zinc-blende (ZB) structure. It exhibits several unusual properties, e.g., a large negative thermal expansion at low temperatures, a decrease of the elastic shear constants with increasing pressure, large mean square displacements of Cu atoms even at low temperature, and a high value of the ionic conductivity at high temperatures [1]. Another highly unusual feature, which has attracted recent interest [2–5], is the anomalous first-order Raman spectrum [5–8]. Instead of narrow Raman lines corresponding to the characteristic transverse optical (TO) and longitudinal optical (LO) modes of ZB-type crystals, CuCl shows, in the region of the TO mode frequency, a broad structure consisting of three maxima with TO-like polarization characteristics [6].

Two different explanations have been proposed for the anomalous TO structure. The Fermi resonance model (FRM) assumes an anharmonic coupling of the TO phonon to resonant acoustic two-phonon states [6,9]. The anharmonic interactions result in a shift and broadening of the TO mode and a transfer of oscillator strength to the two-phonon scattering. In the off-center model (OCM) a sizable fraction of the Cu ions is assumed to occupy off-center positions in the [111] antibonding directions [10,11], resulting in a contribution of local vibrations to the Raman response. Recent *ab initio* calculations by Wei *et al.* [2] predict metastable off-center minima along [111] and therefore support this model. According to the first-principles calculations of Park and Chadi [3] various off-center defects should even be *stable*, including  $\text{Cu}_4$  groups formed by displacing four neighboring Cu ions towards each other. On the other hand, the effects of isotope substitution were recently found to be consistent with the FRM [5]. Thus, the question of FRM versus OCM interpretation of the Raman anomaly in CuCl has remained a matter of ongoing debate [4].

Raman spectroscopy at high hydrostatic pressures and sufficiently low temperature is a means to discriminate between the two different explanations for the Raman anomaly. Off-center positions are predicted to become energetically more favorable under pressure [3], a fact

which should lead to an intensity gain of local vibrational modes. Within the FRM, a major change is expected in the TO-like Raman response because of a detuning of the resonance due to different pressure coefficients of optical and two-phonon acoustic branches.

In this Letter we report Raman spectra of CuCl samples measured at  $T = 5$  K under hydrostatic pressures up to 3.3 GPa, which corresponds to the stability range of ZB-type CuCl at low temperature [12]. The experiments reveal substantial reversible changes in the Raman response. These are well reproduced by a FRM-type calculation of the pressure-dependent Raman spectrum. No indication is seen for any defect-related effects.

The results of earlier pressure Raman studies of CuCl up to 0.7 GPa were explained in terms of the FRM [7]. However, it was also argued that later experimental results up to 3.2 GPa [8] are not conclusive with respect to ruling out the local vibrational mode picture [11]. The ambiguity in the interpretation of the previous pressure Raman data partly results from the fact that the experiments were performed at relatively high temperatures (40–77 K) where the Raman features of CuCl are strongly broadened already.

The crystals (thickness 20  $\mu\text{m}$ , [111] orientation) used in this study were grown by vapor transport from isotopically pure (99.9%)  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  [13]. Pressures were generated in a diamond anvil cell (DAC) and measured by the ruby luminescence method [14]. Helium served as pressure medium in order to avoid chemical reactions and ensure fully hydrostatic conditions. The pressure was always changed at 275 K. Raman scattering experiments were performed in backscattering geometry at a temperature of 5 K using the 647.1 nm line of a  $\text{Kr}^+$  laser at a low power density of less than 400  $\text{W}/\text{cm}^2$ . The scattered light was analyzed by a triple-grating spectrometer combined with a charge-coupled device detector.

Figure 1 shows Raman spectra of CuCl measured at different pressures ( $T = 5$  K). The most prominent effect is the drastic change in the line shape of the TO-like structure, which extends from 140 to 175  $\text{cm}^{-1}$  at zero pressure. The intensity of the  $\gamma$  peak increases strongly

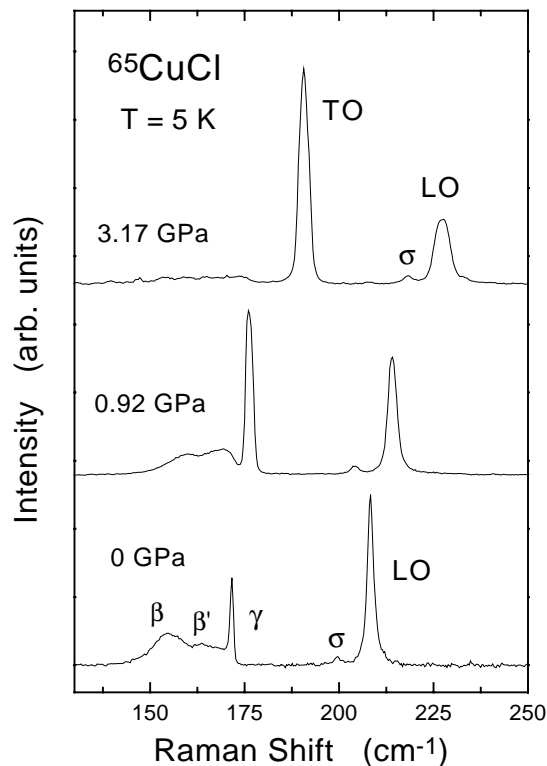


FIG. 1. Low-temperature Raman spectra of  $^{65}\text{CuCl}$  measured at different pressures. The spectra are normalized with respect to the area under the LO peak.

relative to the LO peak height, while the intensities of the peaks  $\beta$  and  $\beta'$  decrease with increasing pressure and are barely resolved at 3 GPa. In Raman spectra measured inside the DAC we observe a peak  $\sigma$  at a frequency about  $10\text{ cm}^{-1}$  below that of the LO mode. This feature is attributed to a Fuchs-Kliewer surface mode [15] excited under the particular optical configuration *inside* the DAC. The mode was not observed for samples outside of the DAC. This rules out a defect-related mode.

Figure 2 shows the frequencies of Raman peak maxima as a function of pressure. Fitted pressure coefficients are given in Table I. The shifts of the peak positions of the TO-like structure differ from those expected for optical modes in ZB-type semiconductors [16,17]. The features  $\beta$  and  $\beta'$  exhibit a pronounced sublinear frequency shift. The dominant TO-like peak  $\gamma$  shifts to higher frequencies at an overall rate similar to that of the LO mode, but the shift is weakly *superlinear*. This effect becomes more evident in Fig. 3(a) which shows the frequency difference between LO and  $\gamma$  peak. The splitting increases first and at pressures above  $\sim 1.5$  GPa it begins to decrease. A decrease corresponds to the normal behavior of a LO-TO splitting in a polar semiconductor, where it reflects a change in the Born effective charge [16,17].

Obviously, the Raman spectrum of CuCl develops, with increasing pressure, into that typical for ZB-type semiconductors; i.e., near 3 GPa it exhibits sharp TO and

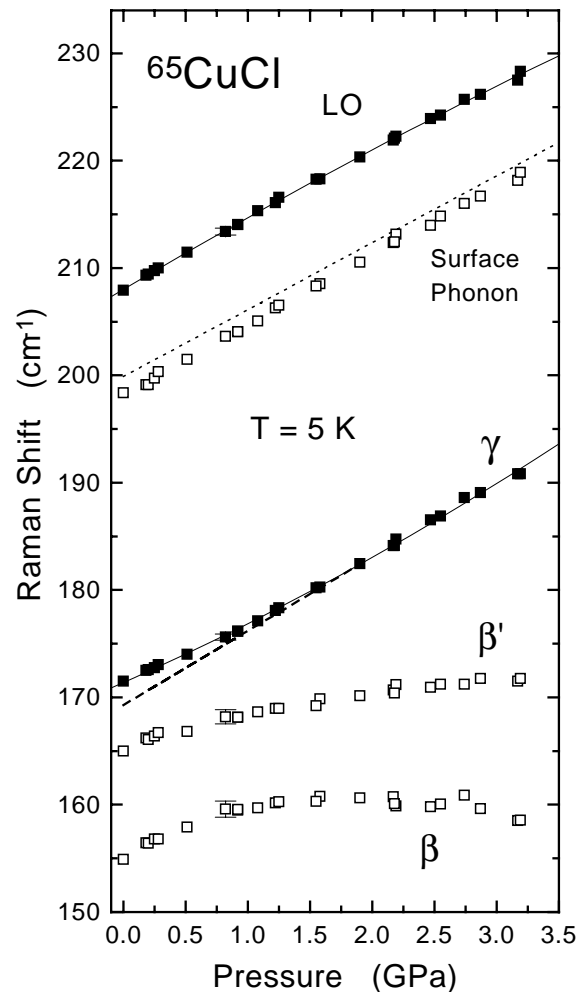


FIG. 2. Frequencies of Raman peak maxima for  $^{65}\text{CuCl}$  as a function of pressure. Solid lines through the data points for the  $\gamma$  and LO peak represent fitted curves. The dashed line represents the linear slope of the  $\gamma$  mode data above 1.7 GPa. The dotted line indicates the calculated frequency of the surface phonon mode.

LO peaks with an intensity ratio of about 2:1, a decreasing tendency for the LO-TO splitting, and only weak acoustic two-phonon scattering. In other words, the TO anomaly

TABLE I. Pressure derivatives of Raman peak frequencies of  $^{65}\text{CuCl}$  at zero pressure as obtained from quadratic fits to the data. The mode Grüneisen parameters  $\gamma_G = (B_0/\omega_0)\partial\omega/\partial P$  were calculated using a bulk modulus  $B_0 = 45.9$  GPa.

Peak	$\omega_0$ ( $\text{cm}^{-1}$ )	$\frac{d\omega}{dP}$ ( $\frac{\text{cm}^{-1}}{\text{GPa}}$ )	$\frac{1}{2} \frac{d^2\omega}{dP^2}$ ( $\frac{\text{cm}^{-1}}{\text{GPa}^2}$ )	$\gamma_G$
$\gamma$	171.5(1)	5.15(19)	0.34(06)	
TO <sup>a</sup>	169.3(4)	6.9(2)		1.9(1)
$\sigma$	198.4(4)	6.85(19)	-0.12(06)	1.6(1)
LO	207.92(05)	6.87(13)	-0.19(04)	1.52(7)

<sup>a</sup>From backward extrapolation of the data above 1.7 GPa; see dashed line in Fig. 2.

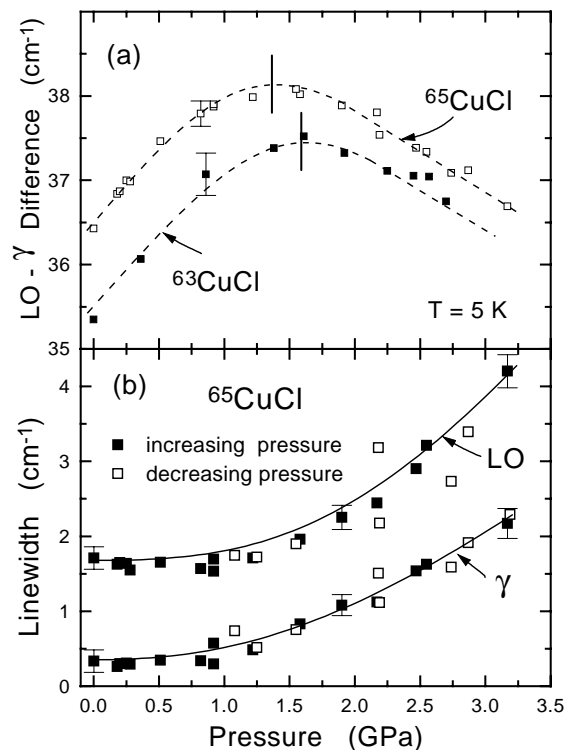


FIG. 3. (a) Difference between LO and  $\gamma$  peak frequencies for <sup>65</sup>CuCl and <sup>63</sup>CuCl and (b) linewidths (FWHM) of the LO and  $\gamma$  peaks in <sup>65</sup>CuCl as a function of pressure. Lines represent guides to the eye.

has disappeared near 3 GPa. All observed pressure effects are fully reversible. This applies to frequency shifts *and* to the widths of spectral features. Figure 3(b) shows the linewidths (FWHM, full width at half maximum) of the  $\gamma$  and LO peak for increasing and decreasing pressure. The widths were determined by fitting Lorentzian profiles to experimental spectra, which were first deconvoluted by a Gaussian with a FWHM of  $0.8 \text{ cm}^{-1}$  corresponding to the spectrometer resolution.

According to the calculations of Park and Chadi [3] the concentration of Cu ions in off-center positions should increase under pressure. This applies to the correlated displacements of groups of four Cu ions ( $\text{Cu}_4$  defects) as well as other cation displacements [3]. Therefore, the Raman intensity of the peaks  $\beta$  and  $\beta'$ , which have been attributed to local vibrational modes, should also increase with pressure. The opposite trend is observed in the present experiment (see Fig. 1). We conclude that the unusual TO-like structure in the zero-pressure Raman spectrum cannot be taken as evidence for a sizable concentration of Cu ions in off-center positions. Also, from the evolution of the Raman spectra with pressure there is no indication for an increase in the defect concentration.

We show now that the observed pressure effects are consistent with a detuning of a Fermi resonance. The strength of the anharmonic coupling of a TO phonon (wave

vector  $\vec{q} = \vec{0}$ ) to acoustic two-phonon states of total wave vector  $\vec{q} = \vec{0}$  is determined by Fourier coefficients of the third derivatives of the lattice potential with respect to the atomic displacements. For a weak coupling and assuming that the coupling matrix elements ( $V_3$ ) are the same for all three-phonon combinations involved, the imaginary part  $\Gamma(\omega)$  of the low-temperature phonon self-energy is proportional to the sum  $\rho_2(\omega)$  over those two-phonon states which fulfill energy and momentum conservation [18,19]

$$\Gamma(\omega) = |V_3|^2 \rho_2(\omega). \quad (1)$$

The Raman line shape can be expressed as [18,19]

$$I(\omega) \propto \frac{\Gamma(\omega)}{[\omega - \omega_b - \Delta(\omega)]^2 + \Gamma^2(\omega)}, \quad (2)$$

where  $\omega_b$  is the bare TO phonon frequency and  $\Delta(\omega)$  is the real part of the self-energy obtained by a Kramers-Kronig transformation of  $\Gamma(\omega)$ . Given the phonon dispersion relations,  $\rho_2(\omega)$  is obtained by integration over the Brillouin zone. It was recently shown that, based on a realistic shell model for the phonon dispersion of CuCl [20], one obtains good agreement between model calculation and experimental zero-pressure Raman spectrum, if a coupling constant of  $|V_3|^2 = 70 \text{ cm}^{-2}$  is assumed [5]. Figure 4 shows the resulting real and imaginary parts to the phonon self-energy as well as the calculated Raman profile and the experimental spectrum [21]. At zero pressure the TO frequency  $\omega_b$  falls into a region of high values of  $\Gamma(\omega)$  arising from combinations of LA and TA branches at the  $L$ ,  $X$ , and  $K$  points of the Brillouin zone.

In ZB-type semiconductors the LA phonons shift to higher frequencies under pressure, while the TA phonons at the Brillouin zone boundary usually have negative pressure coefficients [16,17]. The positive and negative shifts approximately compensate each other. Thus the pronounced LA + TA structure in  $\rho_2(\omega)$  is expected to remain almost unshifted under pressure. In order to simulate the effect of pressure we furthermore assume that the anharmonic coupling constant  $|V_3|^2$  remains constant, so that the phonon self-energy is independent of pressure. The only pressure-dependent parameter then is the shift of the TO mode to higher frequencies at a rate given by the experimental data for pressures above 1.7 GPa. Figure 4(a) shows Raman spectra calculated in this way for pressures of 1 and 3 GPa. The changes in the line shape of the TO structure reproduce well the experimentally observed changes in the Raman spectra (compare Fig. 1). The reason for the drastic change in Raman line shape is that the bare TO frequency shifts out of the range of the strong LA + TA structure in  $\Gamma(\omega)$ , as indicated by the vertical lines in Fig. 4(b). Consequently, the Raman spectrum develops into that typical for a ZB-type crystal. The comparison of experimental results with the numerical simulation provides convincing evidence that the dominant effect causing the anomalous TO line

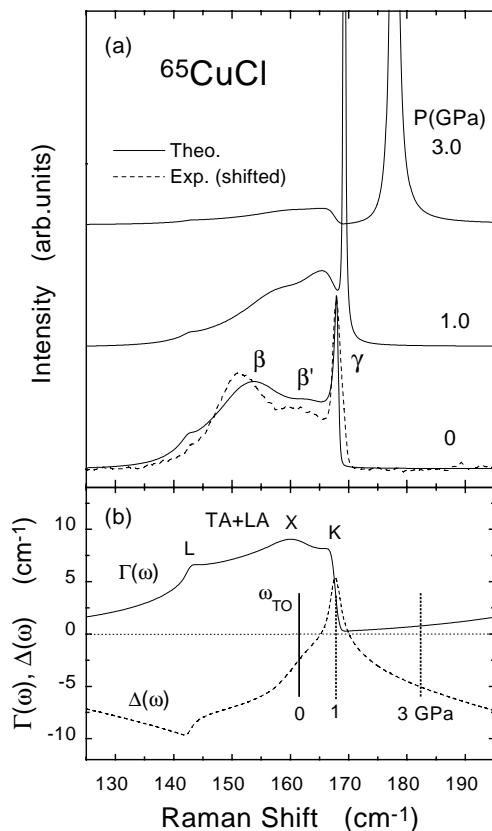


FIG. 4. (a) Raman spectra of  $^{65}\text{CuCl}$  calculated for different pressures ( $T = 0$  K). The dashed line represents the zero-pressure experimental spectrum [21]. (b) Calculated real and imaginary parts of the phonon self-energy. The vertical bars mark the frequencies of the bare TO mode used for the calculation of spectra shown in (a).

shape of CuCl at ambient pressure is the anharmonic coupling between phonons.

The increase in linewidths at pressures above  $\sim 1.5$  GPa [see Fig. 3(b)] is also attributed to the anharmonic coupling. The pressure dependence of the linewidths as well as the larger width of the LO mode compared to the TO mode is consistent with the positive slope of  $\Gamma(\omega)$  at frequencies above  $170\text{ cm}^{-1}$  [compare Fig. 4(b)]. It implies that the lifetimes of the optical phonons decrease as they shift to higher frequency. The isotope effect on the pressure where the LO- $\gamma$  splitting shows a maximum [see Fig. 3(a)] is consistent with the interpretation of zero-pressure Raman data [5].

In conclusion, we have measured the pressure dependence of the Raman spectrum of CuCl up to 3.3 GPa at 5 K. The broad anomalous TO structure transforms into a narrow TO line under pressure, becoming well separated from the pronounced LA + TA structure in the two-phonon density of states. A simulation of the Raman spectrum shows that anharmonic coupling of the TO phonon with the two-phonon density of states (a Fermi

resonance) accounts well for the spectral changes induced by pressure. The off-center models seem to explain other anomalous properties of CuCl, but they cannot draw any justification from the Raman anomaly.

We thank T. Ruf for helpful discussions and U. Oelke, W. Dieterich, and U. Engelhardt for technical assistance.

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