Effect of Pressure on the Anomalous Raman Spectrum of CuBr

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Raman spectra of isotopically pure zinc-blende CuBr (^{63}Cu^{81}Br) were measured at $T = 10$ K under hydrostatic pressures up to 4 GPa. The ambient-pressure spectrum consists of a transverse-optic (TO) phonon line and an anomalous broad band located at frequencies near the expected first-order longitudinal-optic (LO) scattering. Application of hydrostatic pressure leads to an increase of the linewidth of the TO mode and to a significant change of the LO scattering band which above 3 GPa develops into a single LO phonon peak of narrow linewidth. The disappearance of the LO Raman anomaly as well as the broadening of the TO mode with pressure are explained by pressure-dependent third-order anharmonic interactions of zone-center optical phonons with $\mathbf{q} = 0$ two-phonon states.

Introduction The copper halides are highly ionic tetrahedral semiconductors with zinc-blende structure at ambient conditions. They exhibit several unusual physical properties, among them pronounced anomalies in their low-temperature first-order Raman spectra [1–9]. CuCl, for instance, shows a narrow longitudinal-optic (LO) Raman mode but the Raman scattering with transverse-optic (TO) polarization characteristics consists of a broad multi-peak band [1, 5, 7]. Regarding CuBr, anomalies in the first-order Raman spectrum of the zincblende phase at liquid helium temperatures were first discussed by Vardeny and Brafman [6]. Recent Raman measurements of zinc-blende CuBr as a function of isotopic composition [10] have revealed that in this case the scattering with LO polarization characteristics is clearly anomalous, consisting of a broad band with three components whose frequencies depend on the isotopic composition. The effects of isotopic composition [8] and hydrostatic pressure [9] on the low-temperature Raman spectra of CuCl have been explained in terms of a Fermi resonance (FR) [1, 11, 12], i.e. by third-order anharmonic interaction between the TO mode and two-phonon states. Arguments in favor of this interpretation, as compared to models considering static or dynamic off-center displacements of Cu ions [5, 7, 13–15], have been emphasized in a recent debate [16, 17]. Other examples where an analysis based on a FR model has been successfully applied to explain Raman anomalies and their dependence on isotopic composition are the LO and TO Raman scattering of CuBr [10] and GaP [18], respectively.

We report here results of low-temperature Raman measurements of single crystals of CuBr (isotopic composition ^{63}Cu^{81}Br) measured under hydrostatic pressures up to

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4 GPa, i.e. well beyond the range (0–0.7 GPa) probed in earlier experiments [2]. The motivation for our study arises from the fact that lattice dynamical properties can be tuned by pressure over a much wider range as compared to that accessible by a variation of the isotopic composition. This also applies to the anharmonic coupling between phonons [19–23]. Of particular interest here is the effect of pressure on the anomalous LO Raman scattering of CuBr. Using isotopically pure samples has the advantage that effects of isotopic mixtures (i.e., mass fluctuations) on the Raman spectra [10] are avoided. It has been argued that off-center movements of Cu ions, producing static structural disorder, should be less important in CuBr compared to CuCl [6]. Similarly, dynamical disorder, which according to molecular dynamics simulations may occur in CuCl even at 20 K [15], has been suggested to become important in CuBr only above 100 K [5]. Thus, our low-temperature ($T = 10$ K) Raman study of CuBr under pressure is expected to probe changes in anharmonic effects only.

Experimental   Crystals of $^{63}Cu^{81}Br$ were grown by the vapor transport method [24] from isotopically pure (99%) ^{63}Cu and ^{81}Br. The samples were platelets having [111] orientation and a thickness less than 30 μm. They were cut into pieces of about 100×100 μm in size and fitted into the gasket hole of a diamond anvil cell. Helium was used as a pressure transmitting medium. In order to keep non-hydrostatic stresses as low as possible, all pressure changes were made at temperatures above the melting point of helium, followed by slow cooling to 10 K. The pressure was determined by the ruby luminescence method [25], taking into account temperature effects on the ruby R1 line energy [26]. Raman experiments were performed in backscattering geometry using the 647.1 nm line of a Kr+-ion laser at an intensity of less than 100 W/cm^2 on the sample. The scattered light was analyzed by a Jobin-Yvon T64000 triple spectrometer in combination with a multichannel detector.

Results and Discussion   Figure 1 shows the low-temperature Raman spectra of $^{63}Cu^{81}Br$ measured at different pressures up to 4 GPa. Two major features appear in the spectra, corresponding to the TO and LO scattering. At zero pressure ($P = 0$) the LO scattering consists of a broad band, extending from 155 to 177 cm^{-1}. This band consists of a central component (β) and two shoulders shifted to lower (η) and higher (γ) frequencies with respect to the β peak. With increasing pressure the β and η components decrease in intensity whereas the γ component becomes the most pronounced LO feature. Above 3 GPa, the LO scattering consists of a single narrow peak with only a weak band at its low-energy side. Regarding the TO mode, the width increases by a factor of about four between 0 and 4 GPa. Near the highest pressure of 4 GPa a tail develops at its high frequency side. All frequency shifts and changes in linewidths of spectral features observed under pressure are fully reversible.

For a quantitative characterization of the frequency changes we have fitted the experimental spectrum at each pressure with a superposition of Voigt profiles. These are Lorentzians convoluted with a Gaussian where the Gaussian full width at half maximum (FWHM) is the spectrometer resolution of 1.4 cm^{-1}. The LO feature has been modeled by three peaks. Figure 2 shows the obtained Raman peak frequencies of the TO and LO(γ) features as a function of pressure. The linear pressure coefficients, obtained by fitting second-order polynomials to the experimental data of Fig. 2, are 8.0(3) and 4.4(2) cm^{-1}/GPa for the TO and LO(γ) features, respectively.
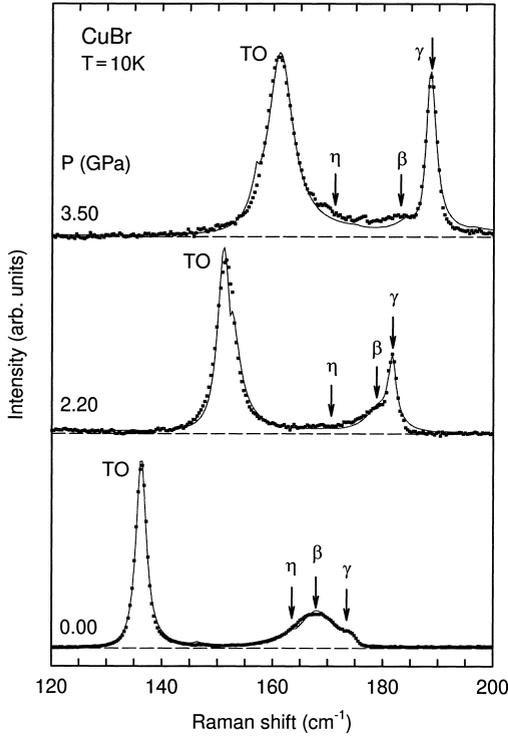
Fig. 1. Low-temperature ($T = 10$ K) Raman spectra of the zinc-blende phase of $^{63}Cu^{81}Br$ measured at different pressures (symbols). The spectra are normalized with respect to the height of the TO mode. Solid lines refer to the results of fitting a Fermi resonance model to the experimental spectra

Raman lineshapes similar to those observed for CuCl and CuBr at $P = 0$ were obtained in early calculations of the anharmonic interaction of $\mathbf{q} = 0$ optical phonons with acoustic $\mathbf{q} = 0$ two-phonon states [11]. The changes of the $P = 0$ Raman spectra of CuCl [8] and CuBr [10] as a function of isotopic composition and the effect of pressure on the anomalous TO Raman scattering in CuCl [9] could be well reproduced by a FR model. We show here that a FR model, based on a realistic two-phonon density of states (TP-DOS) for $\mathbf{q} = 0$ combinations, can account for the changes in both the TO and LO Raman features of CuBr as a function of pressure.

The Raman spectrum $I(\omega)$ as a function of frequency ω can be expressed as [19, 27]

$$I(\omega) = R \, \frac{\Gamma(\omega)}{[\omega - \omega_b - \Delta(\omega)]^2 + \Gamma^2(\omega)} \; . \tag{1}$$

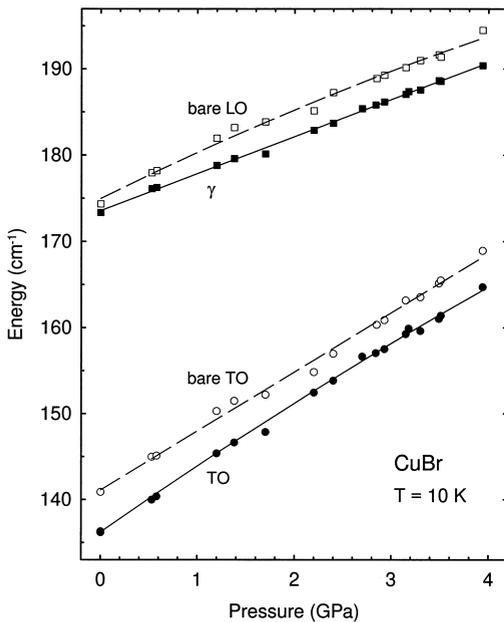Here ω_b is the bare (uncoupled) phonon frequency, $\Gamma(\omega)$ and $\Delta(\omega)$ are the

Fig. 2. Frequencies of Raman peak maxima for $^{63}Cu^{81}Br$ as a function of pressure (closed symbols). Open symbols represent the bare TO and LO phonon frequencies obtained by fitting a Fermi resonance model to the experimental spectra. Solid and dashed lines represent fitted quadratic relations

imaginary and real parts of the low-temperature phonon self-energy, and R is an intensity scaling factor. $\Gamma(\omega)$ is proportional to the TP-DOS $\rho(\omega)$ and can be expressed as

$$\Gamma(\omega) \propto |V_3|^2 \, \rho(\omega - \delta) \,. \tag{2}$$

The squared third-order matrix element $|V_3|^2$ is a measure of the coupling strength between zone-center optical phonons and $\mathbf{q} = 0$ two-phonon combinations. We have assumed that $|V_3|^2$ is independent of frequency. $\Delta(\omega)$ is obtained by a Hilbert transformation of $\Gamma(\omega)$. The quantity δ represents a small rigid shift of the TP-DOS as explained below.

In the simulation of the Raman spectrum at $P = 0$ we have tested three spectral forms of the TP-DOS. They were calculated using shell and rigid ion models which fit the experimental phonon dispersion relations of CuBr [28, 29]. The calculated $P = 0$ Raman spectrum is highly sensitive to the exact frequencies of singularities in the TP-DOS. Thus, in the simulation we have allowed for a small rigid frequency shift δ of the TP-DOS (see Eq. (2)). To fit the LO-like features we have used Eqs. (1) and (2) with four free parameters: the bare LO phonon frequency ω_b, the squared matrix element ($|V_3|^2$), the shift δ, and the Raman intensity factor R. The TO feature was fitted in a similar way, except that the value of the TP-DOS shift δ (less well determined in this case) was fixed to that obtained for the LO mode at the same pressure. The best overall agreement with the experimental Raman spectrum at $P = 0$ was obtained when using the TP-DOS of the shell model with parameter set I [28], shifted in frequency by $\delta = 5$ cm^{-1}. Figure 3 shows the corresponding TP-DOS of CuBr for the relevant frequency range. Also indicated are the fitted bare phonon frequencies of the TO and LO modes at $P = 0$. The corresponding calculated Raman spectrum almost fully reproduces the experimental data (see the lower panel of Fig. 1).

The shell model I was also used for the simulation of the high-pressure Raman spectra. We have made the simplifying assumption that the effect of pressure on the TP-DOS can be described by a pressure-dependent rigid frequency shift δ. The agreement between the experimental data and the fitted Raman spectra (see Fig. 1) is also good at high pressures; small differences between data and fitted curves are not unexpected because we have forced all $\mathbf{q} = 0$ two-phonon combinations to shift at the same rate with pressure. The values of the fitted bare TO and LO phonon frequencies as a func-
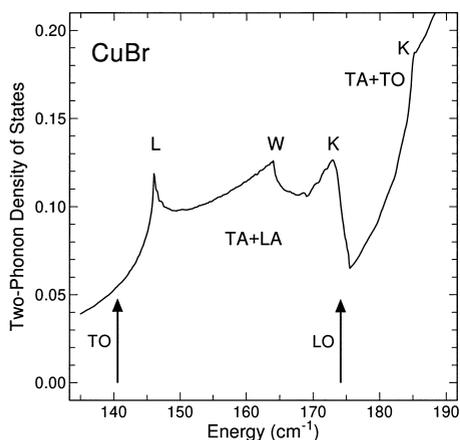

Fig. 3. Two-phonon density of states (TP-DOS) at zero pressure as calculated with the shell model (parameter set I [28]). The assignment of the TP-DOS singularities to the corresponding points in the Brillouin zone and the frequencies of the bare TO and LO phonons at $P = 0$ are also indicated

tion of pressure are displayed in Fig. 2. The linear pressure coefficients for the bare TO and LO frequencies are 8.0 and 6.1 cm^{-1}/GPa, respectively. Using a bulk modulus value of $B_0 = 36.6(8)$ GPa [30] the corresponding Grüneisen parameters are 2.14(6) and 1.31(16). For comparison, values of 2.4 and 1.9 are given in Ref. [2]. The decrease of the LO–TO splitting under pressure indicates a decrease of Born's transverse effective charge [31].

By referring to Fig. 3 we offer a qualitative interpretation of the experimental results and the above analysis based on a FR model. At zero pressure the bare LO phonon would be located in the region of the falling edge following the maximum due to the TA(K)+LA(K) acoustic phonon combinations. The anharmonic coupling between the LO phonon and the two-phonon TA(W)+LA(W) and TA(K)+LA(K) states causes the large broadening of the LO feature and introduces additional structure in the LO scattering. As pressure increases, the bare LO phonon frequency increases faster than that of the falling edge in the TP-DOS, thus moving into a range of smaller TP-DOS. This leads to a reduction of the anharmonic coupling effects and therefore explains that the LO(γ) structure develops into a narrow peak. However, at pressures above about 2 GPa the LO phonon moves into the region of larger TA(K)+TO(K) TP-DOS. This explains the small increase of the LO(γ) width with increasing pressure observed above 2 GPa. At $P = 0$ the bare TO phonon is located in the lower tail of the TA(L)+LA(L) maximum in the TP-DOS. As pressure increases the TO mode moves into a region of larger density of TA(L)+LA(L) states, leading to an enhanced anharmonic coupling between the TO mode and TA(L)+LA(L) combinations which causes a broadening of the TO mode.

In summary, we have measured low-temperature Raman spectra of isotopically pure CuBr (^{63}Cu^{81}Br) under hydrostatic pressures up to 4 GPa, which is the limit of stability of the zinc-blende phase. The anomalous broad structure of the longitudinal-optic (LO) scattering in the zinc-blende phase exhibits a major change under pressure and develops into a rather narrow spectral feature. On the other hand, a significant broadening of the TO mode of CuBr is observed with increasing pressure. Both these effects are attributed to changes in the third-order anharmonic coupling of the zone-center optical phonons to phonons at lower energy. We have demonstrated that all observed spectral changes can be fully accounted for by a Fermi resonance model in combination with a realistic model of the experimental phonon dispersion curves. A more detailed account of the present work and results of a low-temperature Raman study of high-pressure phases of CuBr will be given elsewhere [32].

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