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Raman-scattering study of pressure-induced phase transitions in CuI

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The pressure-induced phase transitions: zinc-blende (ZB) → rhombohedral → tetragonal in CuI were studied by Raman scattering. The rhombohedral primitive cell is presented as a slightly distorted ZB unit cell that is twice as long as the primitive cell in the [111] direction. By folding back the ZB Brillouin zone, an approximation to the phonon dispersion curves of the rhombohedral structure in the [111] direction can be obtained. A comparison can then be made between the rhombohedral Raman frequencies and those obtained by neutron scattering at the ZB zone boundary at L. The agreement was found to be satisfactory. A similar analysis is made of the tetragonal phase; it can be related to the zinc-blende structure by means of a doubled primitive cell which involves a slight distortion of the iodine sublattice but a large rearrangement of the copper sublattice. The Brillouin zone must be folded along one cubic axis. The mode Grüneisen parameters were calculated for the rhombohedral phase and all of them were found to be positive including that of the E mode that corresponds to TA(L) of the ZB structure.

INTRODUCTION

Cuprous iodide exhibits a zinc-blende structure with one molecule per primitive unit cell at standard temperature and pressure. When hydrostatic pressure is applied CuI is known to undergo a number of phase transitions.[1-3] At about 14 kbar (room temperature), the structure transforms into a rhombohedral one with two molecules per unit cell[3] (space group C_{3v}^5). At about 41 kbar the structure changes into a tetragonal D_{4h}^7 structure, again with two molecules per unit cell.[3] Moore *et al.*[2] pointed out that both high-pressure structures are superstructures of the zinc-blende structure, although a detailed structural analysis was first given in Ref. 3.

The situation concerning additional phase transitions is not as clear. Two phase transitions were reported at 4 and 5 kbar by Van Valkenburg[4] but could not be confirmed by others[1-3] including the present work. The other phase known at room temperature is that of the halite structure which seems to become stable only well above 100 kbar at room temperature.[3]

Raman-scattering measurements of zinc-blende (ZB) CuI were reported by several authors.[5-7] The first-order Raman lines of the Raman spectra have recently been reported as a function of pressure at several temperatures including room temperature[7]; these measurements were restricted to 7 kbar, namely, to the ZB phase only.

Here we report the study of Raman scattering as a function of pressure in the ZB, rhombohedral, and tetragonal phases. The results are analyzed making use of the superstructure relationship of these structures to the zinc-blende structure and the strong polarizability of the I^- ions.

EXPERIMENTAL AND RESULTS

The optical pressure cell used has been described by Hawke *et al.*[8] The pressure has been measured using the frequency shift of the ruby luminescence line, a method that enables the pressure determination to within 1 kbar.

The Raman system was standard, with a triple Spex monochromator (spectral slit width 1 cm^{-1}), the incident radiation being a 6764-Å Kr$^+$ line (100 mW). A backscattering configuration was used. Because of the sapphire window of the pressure cell no attempt was made to use different polarization configurations and therefore polycrystalline materials were studied. The use of a single crystal does not necessarily promise that after it undergoes a phase transition to a uniaxial (rhombohedral or tetragonal) structure a unidirectional orientation is reached; the creation of domains should then be anticipated. Three different samples were used yielding almost identical results in terms of frequencies, halfwidths, and relative intensities as a function of pressure.

Figure 1 shows three Raman spectra, each in a different phase. At 6.3 kbar with two atoms per unit cell of the ZB structure one can see [Fig. 1(a)] the relatively strong TO line at 131 cm^{-1} and a weak LO line at 144 cm^{-1} that appears as a shoulder on the intense TO line. At 84 cm^{-1} a very broad two-phonon band is seen. In fact, by measuring a single crystal in a low-pressure cell (reaching 10 kbar) this structure was resolved into two lines. The frequency of the upper one shifted up with pressure and that of the lower one shifted down; from 80 and 93 cm^{-1} at 1 bar to 75 and 96 cm^{-1}, respectively, at 8.9 kbar. In Fig. 1(b) the Raman spectra of the rhombohedral phase (at

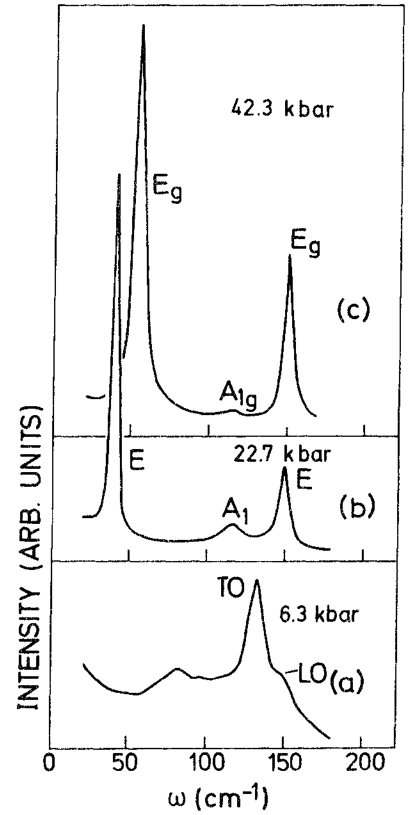

FIG. 1. Raman spectra of CuI in the ZB phase at 6.3 kbar (a), in the rhombohedral phase at 22.7 kbar (b), and in the tetragonal phase at 42.3 kbar (c).

22.7 kbar) is shown, the main features being an extremely intense line at 39 cm^{-1} and an additional well-defined line at 116 cm^{-1}. In Fig. 1(c) the Raman spectrum of the tetragonal phase (at 42.3 kbar) is shown. It looks rather similar to Fig. 1(b) though the frequencies, the halfwidths and the relative intensities of the Raman lines did change. The halfwidth of the most intense line of the rhombohedral phase is 4 cm^{-1}, independent of pressure in that phase. The halfwidth of the most intense line in the tetragonal phase is 8 cm^{-1}. The high-frequency line halfwidth is 8 cm^{-1} in the rhombohedral phase and 7 cm^{-1} in the tetragonal one. The weakest of the rhombohedral lines becomes weaker in the tetragonal structure and is broad (15 cm^{-1}) in both phases. Of course, these are different structures and a correspondence between the lines has *a priori* no basis in spite of the general remarkable resemblance of the two spectra.

Figure 2 shows the shifts of the frequencies versus pressure for the various Raman lines. It demonstrates the jumps in the frequencies of the different Raman lines at the two phase transitions. In fact, for each phase transition there is a small pressure range for which the two sets of lines coexist, although the new set is then relatively weak. It should be emphasized that the pressure was completely hydrostatic as judged from the fact that the crystals were free to move when the cell was rotated. The first phase transition started at 14 kbar and was completed at 15 kbar. The second phase transition started at 39 kbar and was completed at 41 kbar.

DISCUSSION

The rhombohedral phase can be described as a distortion of the ZB structure in the [111] direction. In order to clarify this kind of distortion, the rhombohedral unit cell is shown in Fig. 3 within the frame of the hexagonal unit cells for both the ZB (thin line) and the rhombohedral structure (heavy line). This figure represents atoms of one kind only (I), the copper atoms have a fixed spacing from the corresponding iodine atoms. The primitive cell of the rhombohedral phase has nearly the same angle between unit vectors ($\alpha_h = 33.54°$ at 16 kbar)[3] as for *the same* unit cell in the cubic modification ($\alpha_h = 33.56°$). Thus the $c_{\text{hex}}/a_{\text{hex}}$ ratio of hexagonal lattice constants in the

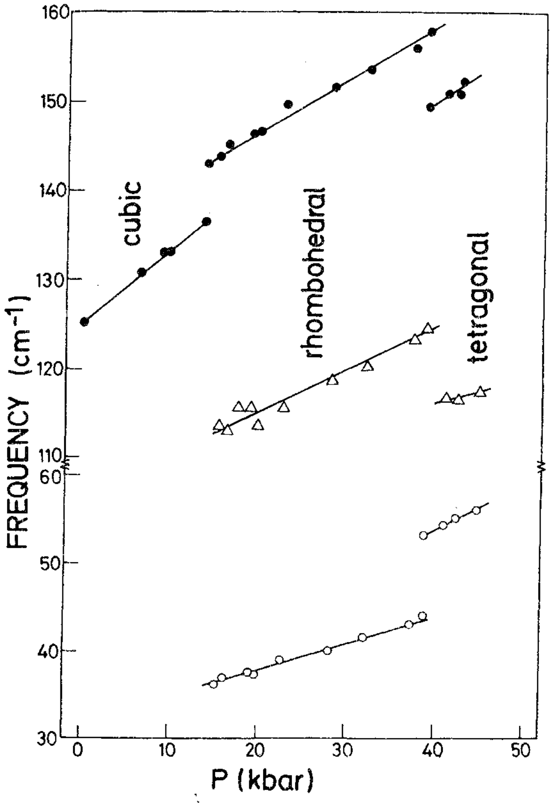

FIG. 2. Frequencies of Raman lines of CuI as function of pressure.

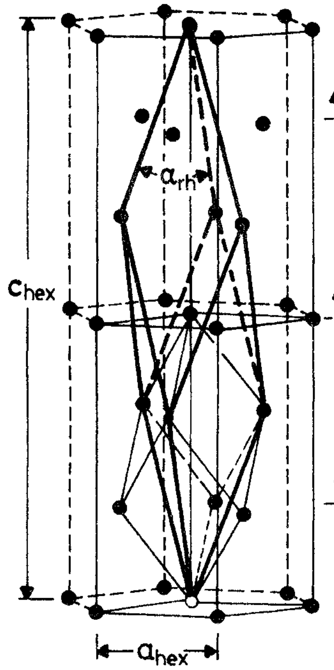

FIG. 3. Rhombohedral primitive cell of the C_{3v}^5 modification of CuI in a hexagonal coordinates frame (heavy line). The original ZB primitive cell is shown (thin line) and the sense of shifts of the atomic planes is indicated by arrows.

rhombohedral modification (4.90 at 16 kbar)[3] must also be nearly the same as in the cubic crystal (4.89): the unit cell deforms uniformly in all directions through the cubic-rhombohedral phase transition. However, in spite of this uniform deformation the cubic symmetry is broken by the displacement of the atoms within the unit cell shown in Fig. 3. The two iodine atoms in the rhombohedral cell are at (0, 0, 0) and $c(0, 0, 0.535)$, while the copper atoms are at $c(0, 0, 0.14)$ and $c(0, 0, 0.675)$. The corresponding positions in the cubic lattice are

$$\mathrm{I}\begin{cases}(0,0,0)\,,\\ c(0,0,0.5)\,,\end{cases}\qquad \mathrm{Cu}\begin{cases}c(0,0,0.125)\,,\\ c(0,0,0.625)\,.\end{cases}$$

The new rhombohedral cell contains twice as many atoms as the ZB primitive cell; its length in the [111] direction is double that of the ZB cell in the same direction. The point-group symmetry is changed from T_d to C_{3v} through the rearrangement of the atoms described above. The space group becomes C_{3v}^5. With four atoms per unit cell nine optic phonons are expected $(3E+3A_1)$ all of them Raman and infrared active. The doubling of the unit cell along the [111] direction implies the existence of a large zone (that of the ZB structure) that can be folded back along the L direction in a manner that the L zone boundary phonons of ZB will now be at $\vec{k}\approx 0$ for the rhombohedral phase. Figure 4 shows the ZB phonon branches in the L and X directions determined from neutron scattering (triangles) and calculated (lines) by Henion *et al.*[9] The LO(Γ) frequency is at 160 cm^{-1} instead of 140 cm^{-1} measured by Raman scattering. The circles in Fig. 4 show the phonons that should be Raman active in the rhombohedral phase; those which are double circled were actually measured.

The pressure dependence of the LO-TO splitting in the cubic phase suggests a nearly zero splitting at the phase transition. Since this means that the dynamical charge is zero, we conjecture that the electrostatic splitting will also be zero in the rhombohedral phase: nothing which could be interpreted as an LO-TO splitting has been observed in Fig. 1(b). Also, the flat nature of the LO and TO bands of Fig. 4 and their close proximity suggests that the peak near 150 cm^{-1} in Fig. 1(b) is due to a superposition of two L_3 and two L_1 modes corresponding to the LO, TO, L_1, and L_3 modes of Fig. 4. The peak, however, should be dominated in a polycrystalline sample by the doubly degenerate L_3 modes (TO-L_3 flat branch of Fig. 4). No evidence of a crystal-field splitting is seen for this line. The weak line at 115 cm^{-1} in Fig. 1 can be safely attributed to the folded L_1 acoustic mode (A_1 symmetry) while the strong line at 38 cm^{-1} must be due to the folded L_3 acoustic mode (E symmetry). Because of its low frequency the eigenvectors of this mode must mainly correspond to a motion of the iodine ions. The strong polarizabil-

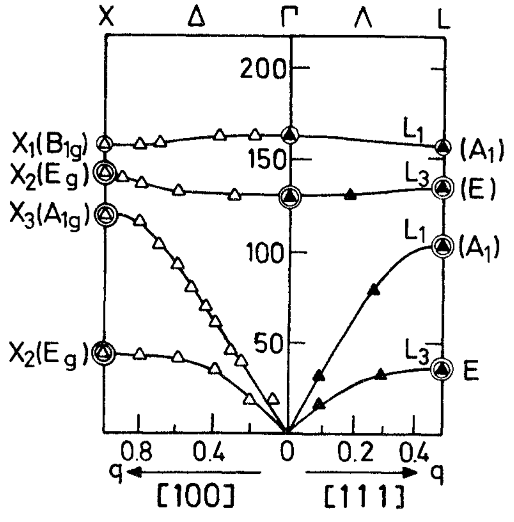

FIG. 4. Dispersion curves of ZB CuI in the [111] direction: the lines are the results of a calculation, the triangles neutron scattering data (Ref. 9). Raman active frequencies indicated by circles (except that the modes are forbidden in the tetragonal modification), the observed ones by double circles.

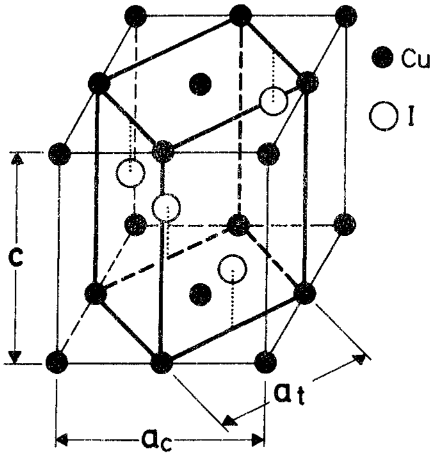

FIG. 5. Tetragonal primitive cell of the D_{4h}^{7} modification of CuI (heavy line) shown inside the cubic unit cell of ZB.

ity of these ions[10] explains the strength of the 38-cm^{-1} mode. Strong 2TA(L) structure is found in the spectrum of the isoelectronic material ZnTe while the 2TO(L) structure cannot be observed,[11] a result also of the strong polarizability of the anion.

The frequencies of the new modes [TA(L), LA(L)] can be compared to the neutron scattering data bearing in mind two facts: (i) because of the volume contraction of 4% at the cubic to rhombohedral phase transition[3] there might have occurred a frequency jump of the two acoustic phonons. Although these phonons were not active in the ZB phase it can be assumed that this jump is small in view of the small jump of the TO frequency at the 14-kbar transition; (ii) one does not know with certainty the slope of the frequency shift with pressure of these modes in the ZB phase, although it can be assumed the same as in the rhombohedral modes. When the linear plots of the frequency shift versus pressure in the rhombohedral phase (Fig. 2) are extrapolated to zero pressure one obtains 32 and 106 cm^{-1} as compared to 35 and 102 cm^{-1} obtained for TA(L) and LA(L), respectively, by neutron scattering.

The primitive cell of the tetragonal modification of CuI, as reported in Ref. 3, is shown in Fig. 5 inscribed into the cubic cell of ZB. The c_t/a_t ratio, 1.42 at 65 kbar,[3] is also in this case within error the same as for the corresponding *tetragonal* unit cell in the cubic crystal ($\sqrt{2}$). The iodine sublattice is only slightly distorted with respect to the cubic modification: the cubic coordinates of the two ions per unit cell are (0.25, 0.25, 0.28) and (0.75, 0.25, 0.72) instead of (0.25, 0.25, 0.25) and (0.75, 0.25, 0.75). These two iodine ions have been shifted vertically by $\pm 0.03c$, respectively, a small distortion indeed. The copper ions, located at the center of the side faces of the cubic cell, however, have been dropped to the basal plane as shown in Fig. 5. This hardly represents a small distortion; it is not possible to track in a continuous way the evolution of the phonons of ZB as the copper ions are dropped to the basal plane. In spite of this large perturbation, the Brillouin zone is still that of ZB folded along the [001] direction. While it is not rigorously possible to assign the phonons of the tetragonal structure to specific Γ and X phonons of ZB, the fact that only $\frac{1}{2}$ of the atoms of one of the two subcells is being strongly perturbed may still permit an approximate assignment. A comparison of Fig. 1(c) with Fig. 1(b) supports this conjecture.

In the D_{4h} point group of the tetragonal phase the A_{1g}, B_{1g}, B_{2g}, and E_g representations are Raman active. The structure of the tetragonal phase of CuI (D_{4h}) is similar to that of PbO with anion and cation interchanged. For the nine optical phonons at $\vec{k}=0$, one obtains the following representations in the corresponding D_{4h} space group[12]:

$$\begin{aligned} &A_{2u},\ E_u\text{: infrared active},\\ &A_{1g},\ B_{1g},\ E_g,\ E_g\text{: Raman active}. \end{aligned} \tag{1}$$

We should therefore expect four lines and only three appear in Fig. 1(c). We now proceed to discuss the eigenvectors associated with these represenations.

The A_{1g} phonons are vibrations along c of the two iodine sublattices solely. They thus correspond to LA phonons at X in the ZB lattice. The B_{1g} phonons are similar vibrations of the copper sublattices and correspond to the LO modes of ZB. The 2E_g modes are mixed Cu-I modes but because of the heavy I ions the lower E_g, corresponding to TA(X), should mainly be a vibration of the I sublattices. The other E_g is mainly a vibration of the copper lattice and corresponds to TO(X). The infrared-allowed A_{2u} and E_u modes correspond to the optical phonons of ZB at Γ. Under these conditions we believe that it is reasonable to assign the three peaks of Fig. 1(c) in the following way. The peak at 53 cm^{-1} corresponds to the E_g or TA(X) mode, mainly iodine-like and thus strong, the peak at 115 cm^{-1} is A_{1g} or LA(X), while the peak at 148 cm^{-1} has E_g or equivalently TO(X) symmetry. The Cu-like B_{1g} LO(X) mode, which should be weak, may be hidden under E_g as it was in the rhombohedral case. The only puzzle left in this picture is why the iodine-like A_{1g} peak is so weak. In view of this anomaly and of the difficulties in the determination of crystal structures at high pressures an additional investigation of the tetragonal phase would be desirable.

From the data of frequencies as a function of pressure presented in Fig. 2 the mode Grüneisen parameters can be calculated either with

$$\gamma_i(k) \equiv \frac{1}{\chi_T\,\omega_i(k)}\left(\frac{\partial(\omega_i(k))}{\partial P}\right)_T , \qquad (2)$$

when the isothermal compressibility χ_T is known or from the equivalent relation

$$\gamma_i(k) \equiv -d\ln\omega_i(k)/d\ln V , \qquad (3)$$

when P-V data are available. For the ZB phase one can use T at 1 bar determined from elastic constants measurements.[13] This should give a fairly good approximation of γ_i for pressures up to 14 kbar. For the rhombohedral phase information on elastic constants is not available. On the other hand P-V data are given by Bridgman[14] for the two phases (up to 40 kbar).

χ_T at 1 bar (2.76×10^{-3} cm^2/kbar)[13] along with the data of Fig. 2 yield $\gamma[\mathrm{TO}(\Gamma)] = 2.46$ compared with the value of 2.4 reported by Hochheimer *et al.*[7] at room temperature. From Eq. (3) with Bridgman's[13] P-V data we find $\gamma[\mathrm{TO}(\Gamma)] = 2.65$. We note that an extrapolation of the Grüneisen parameters of the group-IV, -III-V, and -II-VI compounds[15] yields for the I-VII compounds $\gamma_i(\mathrm{TO}) = 2.2$ and $\gamma_i(\mathrm{LO}) = 1.1$, in reasonable agreement with the values reported here for $\gamma_i(\mathrm{TO})$.

Using P-V data of the rhombohedral phase the following mode Grüneisen parameters are obtained (ZB notation): $\gamma[\mathrm{TO}(\Gamma, L)] = 1.47$, $\gamma[\mathrm{LA}(L)] = 1.64$, and $\gamma[\mathrm{TA}(L)] = 3.24$. Unlike other ZB materials in which $\gamma_i[\mathrm{TA}(L)]$ and $\gamma_i[\mathrm{TA}(X)]$ are negative[15] the equivalent γ_i here are found to be positive and relatively large.

The question now arises as to whether the $\gamma_i(\mathrm{TA})$ for the high-pressure phases can be taken as a measure of the Grüneisen parameter of the corresponding Raman-forbidden modes in the ZB modification. The behavior of the wurtzite-type II-VI semiconductors,[16] also folded-zone analogs of ZB, induces us to answer this question in an affirmative way. In this case CuI would have positive $\gamma_i(\mathrm{TA})$ at the zone edge, a behavior radically different from that found in many other ZB-type semiconductors.[15] In support of this conclusion one can adduce the fact that the expansion coefficient of CuI does not become negative at low temperatures.[17] The expansion coefficient of CuBr and CuCl does, however, become negative at low temperatures in a way which suggests negative $\gamma_i(\mathrm{TA})$.[17,15] We should also point out that negative γ_i have been measured for the TA phonons near Γ in CuCl.[18] We cannot find an explanation for this drastic difference in the behavior of $\gamma_i(\mathrm{TA})$ between CuI on the one hand and CuBr and CuCl on the other. More direct measurements of $\gamma_i(\mathrm{TA})$ for these materials would be highly desirable.

We cannot determine the γ_i of the tetragonal phase for both the lack of P-V data and sufficient ω-P data. One conclusion can, however, be drawn from Fig. 2, namely, that all γ_i of the observed modes are positive.

CONCLUSIONS

The phase transitions of CuI under pressure induce changes in the Raman spectra. Frequency discontinuities are observed at the phase transitions, new lines appear and changes in halfwidths and relative intensities do occur.

The rhombohedral phase has a primitive cell double in length compared to the ZB primitive cell in the [111] direction. By folding back the ZB Brillouin zone in this direction the rhombohedral dispersion curves are obtained, and new Raman active lines (at $k = 0$) are observed. Because of the pressure effects on the frequencies only an approximation to the ZB L critical points is obtained that is in close agreement with the neutron scattering data. A similar analysis was conducted for the tetragonal structure on the basis of the D_{4h}^7 space group.

The mode-Grüneisen parameters in the rhombohedral phase were calculated and it was found that for all of them including TA(L), $\gamma_i > 0$. This is an unexpected result in view of the fact that $\gamma[\mathrm{TA}(L)] < 0$ for several ZB materials.

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