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Pressure dependence of the Raman A_1 mode and pressure-induced phase transition in $CuInSe_2$

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The pressure dependence of the Raman A_1 mode of $CuInSe_2$ has been studied up to 6.9 GPa in a gasketed diamond-anvil cell and the Grüneisen parameter of the optical phonon A_1 has been measured. From changes in the Raman spectra of the samples under pressure, a first-order phase transition, from the chalcopyrite to the disordered rocksalt structure, was observed at 7.1 GPa. In the downstroke the high-pressure NaCl-type phase of $CuInSe_2$ reverts to a polycrystalline chalcopyrite structure at 4.2 GPa. After the phase transition, the Raman studies performed on the pressure-quenched samples show that the sample is disordered and microcrystalline.

I. INTRODUCTION

The ternary compound $CuInSe_2$ is a direct-energy-gap semiconductor ($E_g \sim 1$ eV at 300 K) that crystallizes in the tetragonal chalcopyrite ($I\bar{4}2d$) structure. Recently it has received considerable attention because of its potential application in solar-energy conversion.[1-3] In fact, it has been reported[4] that a dual solar-cell structure, consisting of a thick layer of GaAs mounted on a $CuInSe_2$ thin film cell, yields a one-sun efficiency of 22.6%.

Although the literature abounds with data on the electrical,[5,6] optical,[7-9] and lattice-vibration properties[10-12] at normal pressure, only a limited number of high-pressure studies have been performed on this compound.[13,14] An earlier *in situ* high-pressure x-ray diffraction study[13] on $CuInSe_2$ has indicated that the chalcopyrite structure becomes unstable under pressure and transforms to the NaCl-type structure at 6.0 GPa.

In our recent optical absorption study[14] carried out on single-crystal samples of $CuInSe_2$ as a function of pressure, evidence of a pressure-induced phase transformation was seen at 7.1 GPa under hydrostatic conditions. Hence, in the present work, the Raman scattering spectra of $CuInSe_2$ single crystals as a function of pressure up to 14 GPa have been measured in order to get additional information on the phase transition of this material. The results lead to a revision of some of the previous assignments of the Raman frequencies for $CuInSe_2$. From the data, the pressure dependence of the A_1 mode, the mode-Grüneisen parameter γ_{A_1}, and the transition pressure were obtained. After the pressure cycle was completed, the Raman scattering measurements performed on the retrieved samples gave some information about the size of the crystallites created by the phase transition.

II. EXPERIMENTAL METHODS

The single-crystal samples of $CuInSe_2$ used in the present study were obtained from the same ingot, grown by the vertical Bridgman technique as described in Ref. 8 and also used in the aforementioned high-pressure optical absorption study. The samples were 30 μm thick with transverse dimension of about 150 μm. They were prepared by mechanically lapping and polishing on both sides of the platelets and later were broken into small pieces for the required dimensions of the pressure chamber.

Nonpolarized Raman scattering measurements were performed in a membrane diamond-anvil cell[15] (MDAC) where the pressure can be varied by pneumatic bellows. The pressure transmitting fluid was a 4:1 mixture of methanol-ethanol. This mixture retains fluidity up to 10 GPa.[16] The pressure was calibrated to within ±0.1 GPa by using the power five ruby luminescence scale with the pressure in GPa related to the wavelength λ by[17]

$$P = 380.8[(\lambda/\lambda_0)^5 - 1] \ . \tag{1}$$

The ruby samples were ~4.000 ppm Cr^{3+} doped and 5–15 μm in average dimensions. The spectrometer was a XY1000 Dilor System, used in the double monochromator OMA mode, in the backscattering geometry and the resolution was better than 1 cm^{-1}. The 514.5 nm ($h\nu = 2.409$ eV) line of an argon laser was used at powers of 5 mW with the sample outside the cell. The laser spot was 20 μm in diameter. In the cell, because of the high absorption coefficient of the sample ($\alpha \sim 10^5$ cm^{-1} at 2.409 eV), a power of 50 mW incident on the diamonds proved to be low enough not to cause any heating of the sample in the pressurizing medium. This was verified by varying the incident power and observing that neither the Stokes to anti-Stokes intensity ratio, nor the frequency of the A_1 mode, varied within the experimental precision. The location of the laser spot on the sample on the Dilor spectrometer mount could be monitored and reliably reproduced within 5 micrometers and with the MDAC, the pressure was pneumatically varied without any misalignment. Thus the Raman results given here actually are a set of measurements made on various well-localized regions of the sample.

III. RESULTS AND DISCUSSION

A. Vibrational modes at $P = 0$

The $A^{I}B^{III}C_2^{VI}$ chalcopyrite-structure materials are ternary analogs of the II-VI compounds which have the cubic zinc-blende structure.

The unit-cell volume of the chalcopyrite structure is twice the volume of the cubic one, with the Brillouin zone being four times smaller than that of the corresponding zinc-blende structure. As a result, the symmetry points Γ, X, and W of the zinc-blende Brillouin zone transform into Γ in the chalcopyrite structure.[18] As the primitive cell of the tetragonal samples contains two formula units, the number of vibrational modes, determined from the degrees of freedom, is 24.[18] The acoustic ones are classified according to the irreducible representation

$$\Gamma_{\text{ac}}=B_2+E$$

and, the optical ones, to

$$\Gamma_{\text{opt}}=A_1(R)+2A_2+3B_1(R)+3B_2(IR,R)+6E(IR,R)\ .$$

It has been shown that the A_1 mode is the dominant feature in the Raman spectrum of $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ chalcopyrite-structure semiconductors,[19] and is due to a pure anion motion in the sense that cations are at rest and each anion vibrates along the a or b directions. According to a simplified version of the valence-force-field model of the Keating theory, an analytical expression for the frequency of the A_1 mode is given by[20]

$$\omega^2(A_1)=\frac{2(\alpha_A+\alpha_B)}{m_C}\ , \tag{2}$$

where α_A and α_B are the two central (bond-stretching) force constants describing the interaction between nearest neighbors and m_C is the mass of the anion C.

Figure 3(a) shows a typical spectrum obtained by the backscattering geometry from CuInSe_2 single crystals at $P=0$ and 300 K. The nonpolarized Raman scattering from the totally symmetric A_1 mode is the strongest one and can easily be identified[21,22] at 172 cm^{-1}. Under the present experimental conditions the other optical modes cannot be distinguished. Using the expression (2) and the values of α_A and α_B of 25.8 and 44.7 nm^{-1}, respectively,[23] and the Se mass $m_c=78.96$ amu, the theoretical value of the A_1 mode is 174 cm^{-1}, which is very close to the experimental one. The frequency for the A_1 mode has been determined by Gan *et al.*[10] from polarized Raman scattering spectra at 186 cm^{-1}. However, looking at the existing literature data, Neumann[23] suggested that the frequencies of the A_1, B_2, and E modes given in Ref. 10 are surprisingly closer to those for CuGaSe_2, reported by Bodnar *et al.*,[24] than the values for CuInSe_2. Further evidence for this supposition comes from recent Raman scattering studies under pressure made on CuGaSe_2 single crystals,[25] where a value of 183 cm^{-1} at $P=0$ has been obtained for the A_1 mode. Further polarized Raman scattering, and also neutron scattering measurements, are in progress to determine reliable values for the frequencies of the high-energy zone-center optical phonons in CuInSe_2.

B. Upstroke

The room-temperature first-order Raman A_1 peaks recorded at 0.1, 2.7, and 5.4 GPa for CuInSe_2 are shown in Fig. 1. It can be seen that the peak shifts to higher frequencies as the pressure is increased, and the observed width of about 8.3 cm^{-1} is a combination of instrumental resolution and intrinsic broadening. The A_1 mode is symmetric and there is no appreciable change in its line shape with applied pressure.

The resulting pressure dependence of the A_1 phonons is sublinear and is shown in Fig. 2 up to 6.9 GPa. A similar effect was observed for Si, GaP,[26] GaAs,[27] CuGaS_2, and AgGaS_2.[28] We have fitted the experimental data to a quadratic expression:

$$\omega(A_1)=172.8+5.13P-0.19P^2\ , \tag{3}$$

with P in GPa and ω in cm^{-1}. The effect of pressure on the phonon dispersion curve can be described in terms of the mode-Grüneisen parameters γ_i defined by

$$\gamma_i=-\frac{\partial\ln\omega_i}{\partial\ln V}=\frac{1}{K_T\omega_i}\frac{\partial\omega_i}{\partial P}\ , \tag{4}$$

where ω_i is a phonon frequency, K_T is the isothermal compressibility, V is the crystal volume, and P is the pressure. Using the bulk modulus of $B_0=49$ GPa reported by Fernández and Wasim[29] and the linear coefficient of Eq. (3), we get for the $\gamma_{A_1}=1.46$. This value is in agreement with the values observed for the optical phonons in the III-V and II-VI compounds.[27]

Upon further compression (at 6.9 GPa the Raman in-

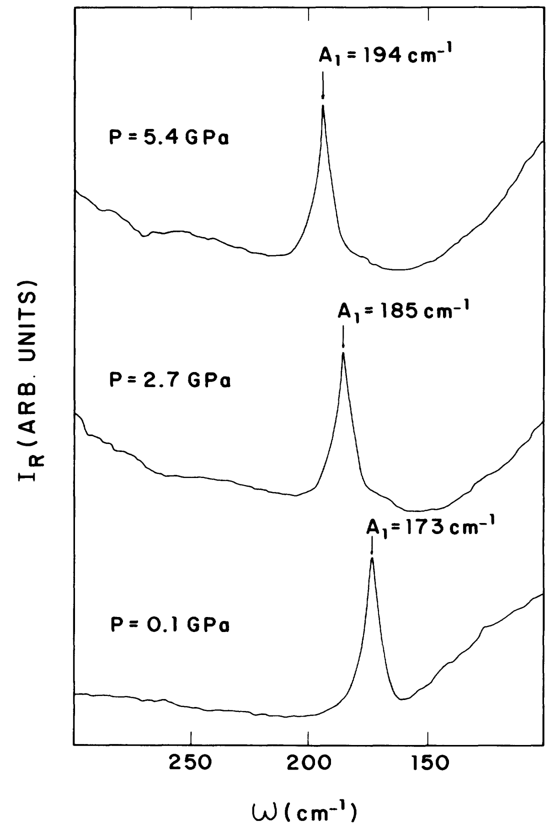

FIG. 1. Room-temperature first-order Raman spectrum of CuInSe_2 for pressures of 0.1, 2.7 and 5.4 GPa.

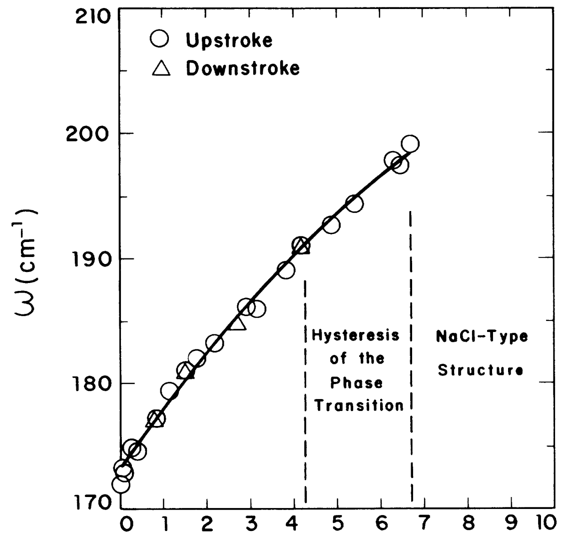

FIG. 2. The pressure dependence of the A_1 mode of $CuInSe_2$ up to 6.9 GPa. Solid line: quadratic fit to the experimental data.

tensity decreased sharply) no Raman peaks were observed. This behavior could be due to a phase transition from chalcopyrite structure to a modification of $CuInSe_2$ with a highly opaque form. This result is consistent with previous optical absorption experiments made at high pressures[14]: Between 7.1 and 8.0 GPa, the $CuInSe_2$ became suddenly opaque. We presume that a first-order phase transformation to an NaCl-type structure, identical to that reported by x-ray measurement under high pressure,[13] had occurred.

Further, the absence of any Raman peaks in this high-pressure phase is consistent with the formation of an NaCl-type phase, since first-order Raman activity in the later would be prohibited by symmetry.[28] Thus the Raman behavior is consistent with the phase transition at 7.1 GPa to the NaCl-type phase [$CuInSe_2$(II)].

C. Downstroke

In the completely transformed samples ($P_{\max} \sim 13.5$ GPa), no Raman modes were observed between the maximum pressure and ~4.2 GPa. Below this pressure the A_1 mode reappears and the frequency shift with decreasing pressure follows the general trend of Eq. (3) (Fig. 2). This result seems to indicate that, when the pressure is decreased, the high-pressure phase of $CuInSe_2$ [$CuInSe_2$(II)] reverts to the chalcopyrite structure [$CuInSe_2$(I)] at 4.2 GPa. The hysteresis of this transformation is 2.9 GPa, as defined by the difference between the full transformation to $CuInSe_2$(II) (7.1 GPa) and completion of the reverse one (4.2 GPa).

This behavior is to be expected since the chalcopyrite-to-NaCl-type-structure transition involves a drastic change in the primary coordination as well as the bonding characteristics and would therefore be a very sluggish phase transition at room temperature. If one were to take the classical rule for locating phase transitions, that is at the midpoint of the hysteresis cycle, we would find $P_t = 5.6$ GPa at 300 K.

After undergoing the I→II→I transitions the samples are retrieved with their approximate original shape. On occasion, slight geometrical distortions are observable by microscopic examination, probably due to the severe pressure gradient which occurs in the sample when it undergoes the volume change (~16%) at the transition.[13] The retrieved crystals were studied as a function of the maximum pressure ($P_{\max}$), at ambient pressure outside the MDAC [Figs. 3(b) and 3(c)]. We also observe in Fig. 3(a) the shape of the original single-crystal A_1 mode. On the retrieved $CuInSe_2$ material the A_1 modes are broadened and shifted. This fact has been used in several papers[30–32] to evaluate the average size of crystallites, by noting that the correlation length L of the optical phonons will be limited by crystallite size and thus selection rules will be lifted over a wave vector interval $\Delta k \sim 1/L$. When this is a sizable fraction (a few percent) of the Brillouin zone, the downward curvature of the $\omega(k)$ optical-phonon branch will cause the A_1 phonon peak to be broadened and shifted to lower frequencies. In the case of fully transformed GaAs samples with $P_{\max} > 18$ GPa,[32] for instance, it is found a LO frequency shift of -3.3 cm^{-1}, and a full width at half maximum (FWHM) in-

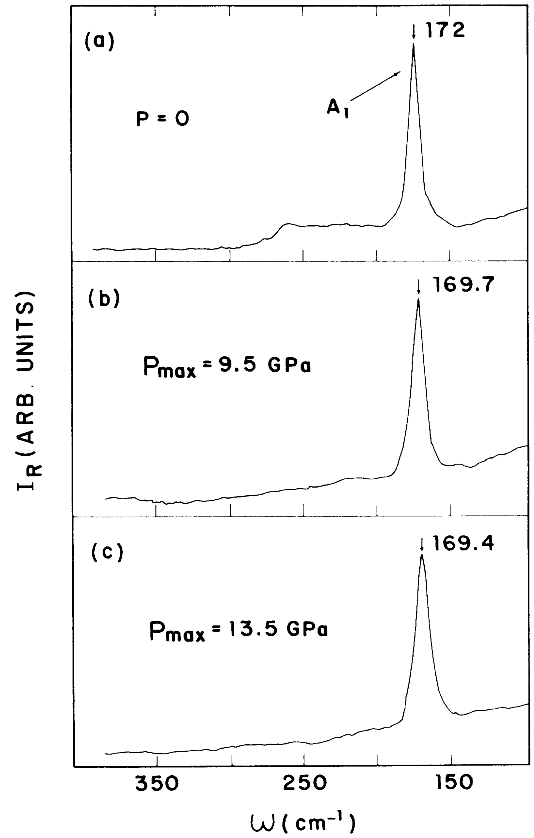

FIG. 3. Raman spectrum of pressurized $CuInSe_2$ samples at 300 K. (a) Initial spectrum of the original slab before pressurization. (b) Ambient pressure spectrum after pressurization to 9.5 GPa. (c) Ambient pressure spectrum after pressurization to 13.5 GPa.

crease of 5.5 cm^{-1}, which correspond to crystallite sizes of about 5–6 nm. In the present case with $P_{\text{max}}=13.5$ GPa we find that the A_1 mode shift of -2.6 cm^{-1}, and the FWHM increases by 2.4 cm^{-1} as a consequence of the decrease of the optical-phonon lifetime in the disordered material. As no measurements of the phonon dispersion curves of CuInSe_2 mode with neutron scattering are available in the literature, it is not possible to determine quantitatively the crystallite sizes of the retrieved CuInSe_2 sample. However, the observed shift and FWHM broadening indicate that the recovered sample of CuInSe_2, after the I→II→I phase transitions, is disordered and microcrystalline.

IV. CONCLUSIONS

The following conclusions have been reached as a result of this paper.

(1) The upstroke pressure dependence of the A_1 optical mode of CuInSe_2 shows the expected positive value of the Grüneisen parameter, similar to the value found in other tetrahedral semiconductors.

(2) When the pressure increases, the changes in the Raman A_1 mode clearly establish a phase transition near 7.1 GPa in CuInSe_2, possibly to the rocksalt structure. The absence of Raman peaks in the high-pressure phase is consistent with this. On the downstroke run, the high-pressure phase of CuInSe_2 reverts to the chalcopyrite structure at 4.2 GPa. It is to be noted that the observed hysteresis may be closely related to the drastic change in bonding when the high-pressure NaCl phase transforms to the tetrahedrally coordinated chalcopyrite structure.

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