PHYSICAL REVIEW B, VOLUME 63, 125202

Pressure dependence of local vibrational modes in InP

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(Received 21 August 2000; published 7 March 2001)

Using infrared spectroscopy and a diamond-anvil cell, we have observed carbon and carbon-hydrogen local vibrational modes (LVM's) in InP at hydrostatic pressures as high as 5.5 GPa at liquid-helium temperatures. For pressures beyond 4.5 GPa, the carbon-hydrogen mode was not observed, perhaps as a result of a transformation of the complex into a different configuration. The LVM arising from carbon substitutional impurities varies linearly with pressure, whereas the shift of the carbon-hydrogen mode has a positive curvature. Both of these observations are in qualitative agreement with the pressure dependence of LVM's in GaAs. While the substitutional carbon impurities show very similar pressure shifts in the two materials, the linear pressure coefficient of the carbon-hydrogen stretch mode in InP is nearly three times that in GaAs. For all the measured modes, the Grüneisen parameters increase with pressure.

DOI: 10.1103/PhysRevB.63.125202 PACS number(s): 63.20.Pw, 62.50.+p, 61.72.−y

Local vibrational mode (LVM) spectroscopy is a useful technique for determining the microscopic structure of impurities and defects in semiconductors.[1–3] LVM's of impurities are localized in real and frequency space,[4] giving rise to sharp infrared (IR) absorption peaks at liquid-helium temperatures.[3] Hydrogen, for example, typically has LVM frequencies 5–10 times the maximum phonon frequency and has narrow IR absorption peaks.[5–7] After the discoveries that hydrogen passivates donors[8] and acceptors[9] in GaAs, numerous hydrogen-related complexes have been observed in compound semiconductors.[5,10] In this paper, we report measurements of the dependence of carbon and carbon-hydrogen LVM's in InP under large hydrostatic pressures. The observations are compared to previous studies in GaAs.[11]

The effect of pressure on LVM's in semiconductors has only recently been studied and has shown interesting results. Pressure has been applied, in conjunction with LVM spectroscopy, to probe *DX* centers in GaAs,[12] resonant interactions in AlSb,[13] hydrogen-related complexes in GaAs,[11] and interstitial oxygen in silicon.[14] The results of this paper suggest that hydrostatic pressure may be used to differentiate between different hydrogen configurations that have the same symmetry (e.g., bond-centered vs antibonding).

To generate pressure up to 5.5 GPa, we used a piston-cylinder diamond-anvil cell.[15] Type I diamonds with a culet diameter of 700 μm were used. InP samples were polished to a thickness of 25 μm, and square pieces approximately 200 μm on a side were used. After a 250 μm thick stainless-steel gasket was indented to a thickness of 100 μm, a 340-μm hole was drilled in the center of the indentation. Nitrogen was used as a pressure medium and was loaded into the gasket hole, along with the sample, by liquid immersion.[16] To determine the pressure at liquid-helium temperatures, we measured the IR absorption peak of the v_3 vibrational mode of CO_2 impurities in the solid N_2 matrix. The v_3 mode frequency is sensitive to hydrostatic pressure[17] and provides a precise *in situ* pressure calibration.

Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform spectrometer with a KBr beamsplitter. The samples were kept at a temperature of 9 K in a Janis STVP continuous-flow liquid-helium cryostat with wedged ZnSe windows. The spectral range was 500 to 5000 cm^{-1} and the instrumental resolution was 1 cm^{-1}. An off-axis parabolic mirror and light-concentrating cone focused the light through the first diamond and onto the sample. The light then passed through the second diamond and onto a Ge:Cu photoconductor detector.

An InP:C epilayer (sample MR949) was grown by metal-organic chemical vapor deposition to a thickness of 8 μm on semi-insulating (100) InP:Fe substrates.[18] Carbon doping ($[C]=1\times10^{19}\,cm^{-3}$) was provided by carbon tetrachloride with hydrogen as a carrier gas. The high doping concentration was required to achieve a sufficient signal-to-noise ratio. The InP:C epilayers were semi-insulating as grown. It has been shown[18] that approximately half of the carbon impurities are paired with hydrogen (C_P-H) while the other half are substitutional carbon acceptors (C_P) that are compensated by donors. At liquid-helium temperatures, the C_P-H stretch mode and C_P mode have frequencies of 2703 and 547 cm^{-1}, respectively. It was proposed[18] that the hydrogen attaches directly to the carbon acceptor, in a [111] bond-centered orientation, adjacent to a host indium atom (Fig. 1 inset). This bond-centered model is believed to apply for all known C_v-H pairs in group III-V semiconductors.[19]

IR spectra for several different pressures are shown in Fig. 1. In this figure, the spectra were taken during a decrease in pressure. The pressure was increased and decreased several times, and no evidence of hysteresis was observed. Both

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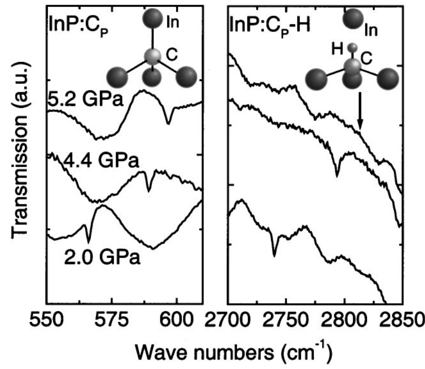

FIG. 1. IR spectra of InP:C,H for three different pressures, at a temperature of 9 K. The arrow indicates where the $^{12}C_P$-H peak should be at 5.2 GPa, by extrapolation from the lower pressure data.

the C_P and C_P-H peak frequencies increase with increasing pressure. For pressures beyond approximately 4.5 GPa, the C_P-H peak was not observed. The arrow in Fig. 1 indicates where the peak should be, by extrapolation from the lower pressure data. The disappearance of this peak may be due to nonhydrostatic stresses that cause significant line broadening. It is not clear, however, why the carbon LVM would not be affected to the same degree. A second possibility is that the C_P-H complex transforms into a different configuration at high pressures, since there is no associated change in the C_P LVM. For example, the bond-centered configuration could convert to an antibonding structure. However, the dipole moment of the latter center would have to be smaller than that of the former center, since no new peak is observed.

The C_P LVM frequency is plotted as a function of pressure in Fig. 2. This plot combines data taken from two separate measurements that verified the reproducibility of the results. Two different InP pieces, from the same sample, were used. In addition to LVM's, the pressure-dependent shifts of InP two-phonon modes were also measured. The two-phonon modes have been identified previously as 2 TO and LO+TO modes.[20] In the range of pressures studied, the frequencies of the phonon modes and C_P LVM vary linearly with pressure. Least-squares linear fits yield the following expressions:

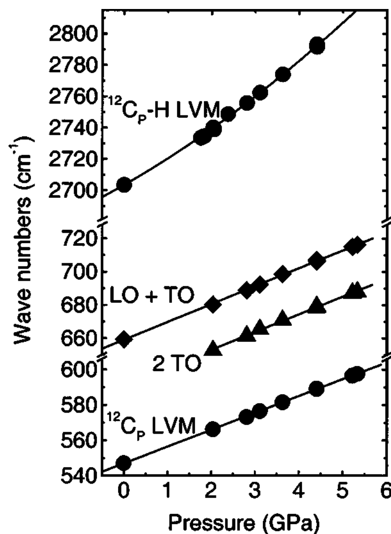

FIG. 2. InP:$^{12}C_P$ LVM, two-phonon frequencies, and InP:$^{12}C_P$-H stretch-mode frequency as a function of pressure. The solid lines are linear fits to the data [Eqs. (1)–(3), (5)].

$$\upsilon(\mathrm{InP}{:}^{12}\mathrm{C_P}) = 546.9 + 9.5P, \tag{1}$$

$$\upsilon(\mathrm{InP},2TO) = 631.6 + 10.7P, \tag{2}$$

$$\upsilon(\mathrm{InP},LO+TO) = 659.0 + 10.8P, \tag{3}$$

where the frequencies υ are in cm^{-1} and pressures P are in GPa. The similarity between the phonon and LVM shifts is consistent with a mass-defect model, in which the properties of the bonds are not affected by the substitution of an impurity. The pressure dependence of the carbon LVM is similar to that in GaAs:[11]

$$\upsilon(\mathrm{GaAs}{:}^{12}\mathrm{C_{As}}) = 582.7 + 9.3P. \tag{4}$$

The C_P-H stretch-mode frequency is plotted as a function of pressure in Fig. 2. The plot shows a slight positive curvature. A least-squares quadratic fit yields

$$\upsilon(\mathrm{InP}{:}^{12}\mathrm{C_P\text{-}H}) = 2703.4 + 16.4P + 0.9P^2. \tag{5}$$

A positive curvature was also observed in GaAs:C,H stretch modes:[11]

$$\upsilon(\mathrm{GaAs}{:}^{12}\mathrm{C_{As}\text{-}H}) = 2635.2 + 6.0P + 1.1P^2. \tag{6}$$

While the quadratic terms are similar, the linear term for InP:C_P-H is nearly three times that for GaAs:C_{AS}H. The reason for this significant difference is not obvious. One contributing factor may be the weaker C_P-In bond compared with the C_{As}-Ga bond.[21,22] The weaker bond would allow for a larger displacement of the C_P-H pair toward the plane of the three neighboring In atoms, allowing us to speculate that this could lead to a larger rate of change of the LVM frequency with increasing pressure.

To quantitatively compare the results in InP and GaAs, the data are plotted as a function of lattice compression $-\Delta V/V_0$, where ΔV is the change in crystal volume and V_0 is the volume at zero pressure. The pressure and compression are related by the Murnaghan equation of state.[23]

$$-\frac{\Delta V}{V_0} = 1 - \left(\frac{B}{B + B'P}\right)^{1/B'}, \tag{7}$$

where B is the bulk modulus at zero pressure and B' is its pressure derivative. For InP, $B = 72.5$ GPa and $B' = 4.67$.[24] For GaAs, $B = 75.0$ GPa and $B' = 4.5$.[25] Using these values, the ^{12}C and ^{12}C-H LVM frequencies are plotted for InP and GaAs in Fig. 3. The solid lines are least-squares fits to the following polynomial:

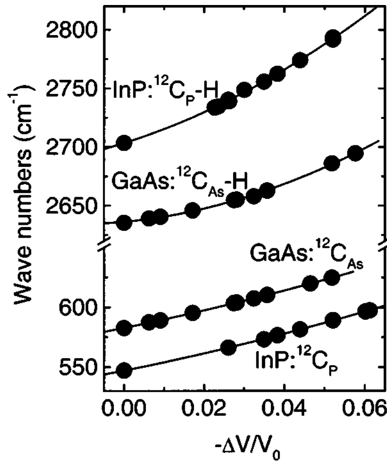

FIG. 3. [12]C and ^{12}C-H LVM frequencies as a function of lattice compression $(-\Delta V/V_0)$, for GaAs (Ref. 11) and InP (this paper). The solid lines are polynomial least-squares fits to Eq. (8).

$$v=a+b(-\Delta V/V_0)+c(\Delta V/V_0)^2. \tag{8}$$

The coefficients a, b, and c are listed in Table I. When plotted in this way, it is apparent that all the plots of frequency versus pressure have a positive curvature.

The Grüneisen parameter for a given vibrational mode is defined as

$$\gamma=-\frac{V}{v}\frac{dv}{dV}. \tag{9}$$

Although Grüneisen parameters are usually defined in the limit as pressure approaches zero, in this analysis we are looking at the variation of γ with pressure. Inserting Eq. (8) into Eq. (9) yields

$$\gamma=\frac{(1+\Delta V/V_0)(b-2c\Delta V/V_0)}{a-b\Delta V/V_0+c(\Delta V/V_0)^2}. \tag{10}$$

The Grüneisen parameters for LVM's in GaAs and InP are plotted in Fig. 4. It is clear that all the Grüneisen parameters increase with pressure. The GaAs:$^{12}C_{As}$, InP:$^{12}C_P$, and InP $LO+TO$ modes have very similar Grüneisen parameters.

Although the C-H modes in GaAs and InP have much different pressure dependencies, the shifts of their Grüneisen parameters are quite similar. The C_P and C_P-H modes have

TABLE I. Coefficients for Eq. (8), which describes the frequencies of vibrational modes as a function of lattice compression.

Mode	a (cm^{-1})	b (cm^{-1} GPa^{-1})	c (cm^{-1} GPa^{-2})
InP:$^{12}C_P$	547.1±0.2	664±15	2680±220
GaAs:$^{12}C_{As}$	582.8±0.1	688±12	2340±230
InP:$^{12}C_P$-H	2703.4±1.0	1074±65	12190±1090
GaAs:$^{12}C_{As}$-H	2636.2±0.6	324±46	12000±770
InP($LO+TO$)	659.2±0.4	743±26	3120±390

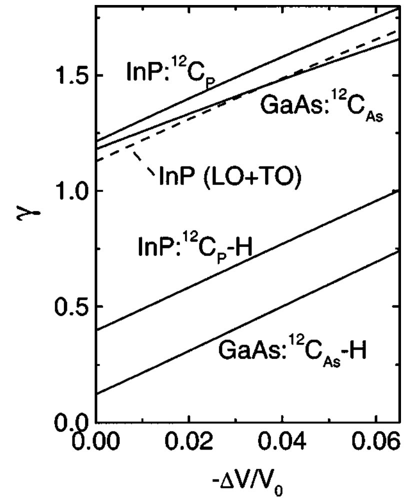

FIG. 4. Grüneisen parameters (γ) as a function of lattice compression $(-\Delta V/V_0)$, for GaAs[11] and InP (this paper). The lines are plots of Eq. (10), using the parameters listed in Table I. LVM's are shown by the solid lines and the InP LO+TO phonon mode is shown by the dashed line.

Grüneisen derivatives of $-d\gamma/d(\Delta V/V_0)=9\pm0.5$. Therefore, the different pressure behavior (linear vs supralinear) results solely from the fact that the bulk modulus increases with pressure. These experimental observations are consistent with *ab initio* calculations of phonon frequencies in semiconductors under pressure.[26] In the case of diamond, for example, the calculated plot of Raman frequency versus *pressure* shows a negative curvature, whereas the plot of frequency versus *volume* shows a positive curvature.[27]

In summary, we have measured the pressure dependence of LVM frequencies in InP. As in the case of AlSb:^{12}C[17], GaAs:^{28}Si[12], GaAs:^{12}C, and GaAs:^{13}C[11], we find that the InP:$^{12}C_P$ LVM frequency varies linearly with pressure. The pressure-dependent shift of the InP:$^{12}C_P$-H stretch mode has a positive curvature, as in the case of GaAs. This result supports the hypothesis that bond-centered hydrogen complexes generally exhibit positive curvatures in their frequency vs pressure plots. In contrast, GaAs:S,H complexes show a negative curvature.[11] If these trends are general, then hydrostatic pressure may prove to be a useful technique for differentiating between bond-centered and antibonding configurations. Although Grüneisen parameters for the various modes are different, they exhibit remarkably similar pressure dependencies. Further experimental and theoretical investigations will be required to determine whether this is a general phenomenon.

The authors wish to acknowledge E. E. Haller and J. Beeman (Lawrence Berkeley National Laboratory) for providing the Ge:Cu detector and S. Watson (Washington State University) for construction of the diamond-anvil cells. This work was supported by the U.S. National Science Foundation through Grant No. DMR-9901625 and the EPSERC, U.K. on Grant No. GR/K 96977. Support was also provided by WSU's Institute for Shock Physics through the D.O.E., Grant No. DE-FG03-97SF21388.

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