

## Acceptor–hydrogen complexes in semiconductors under pressure

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### Abstract

The structure of acceptor–hydrogen complexes is a subject of fundamental and technological interest. To probe the interactions between hydrogen, the acceptor, and the surrounding host atoms, hydrostatic pressure may be applied over a wide range. Using infrared spectroscopy at liquid-helium temperatures, we have observed carbon and carbon–hydrogen local vibrational mode (LVMs) in InP at hydrostatic pressures as high as 5.5 GPa. 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 LVMs 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. © 2001 Elsevier Science B.V. All rights reserved.

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Hydrostatic pressure is an important experimental parameter that can be tuned over a wide range in order to obtain insight into the properties of solids [1]. The development of high-pressure diamond anvil cells (DACs) has led to extensive experimental research on the properties of high-density molecular solids [2] and semiconductors [3]. In a DAC, a sample is placed in a pressure-transmitting ambient, such as liquid nitrogen or alcohol mixtures. Pressures up to several hundred GPa (1 GPa = 10 kbar =  $10^{-2}$  Mbar = 9870 atm) have been achieved.

DACs are well suited to infrared (IR) spectroscopy. Diamonds are transparent over a wide spectral range, although type I diamonds contain nitrogen impurities that strongly absorb from 1000 to 1500  $\text{cm}^{-1}$ . Type II-A diamonds does not contain this absorption band. In addition, all diamonds contain a two-photon absorption band around 2100  $\text{cm}^{-1}$ .  $\text{N}_2$ , Ar, or He are typically used

as the ambient, since, unlike alcohol mixtures, they are transparent to IR light. In  $\text{N}_2$ , a vibrational mode of  $\text{CO}_2$  impurities is sensitive to pressure and is used as a precise in situ pressure calibration for IR absorption experiments [4]. This calibration has been established up to a pressure of 7 GPa.

To measure the IR spectra of semiconductors under pressure, a custom diamond anvil cell has been designed and fabricated (Fig. 1). In this cell, force is applied by six Allen screws, which squeeze together a piston and cylinder [5]. The diamonds are supported by flat and hemispherical backing plates made from tungsten carbide. An off-axis parabolic mirror efficiently focuses the collimated IR beam onto the sample. A photoconductive Ge:Cu detector is placed in close proximity to the sample, so that a large fraction of the transmitted IR light is collected. The entire assembly is placed in a Janis STVP-100 liquid-helium cryostat and kept at a temperature of 6–12 K. The low temperatures are advantageous for two reasons. First, the local vibrational mode (LVM) lines sharpen with decreasing

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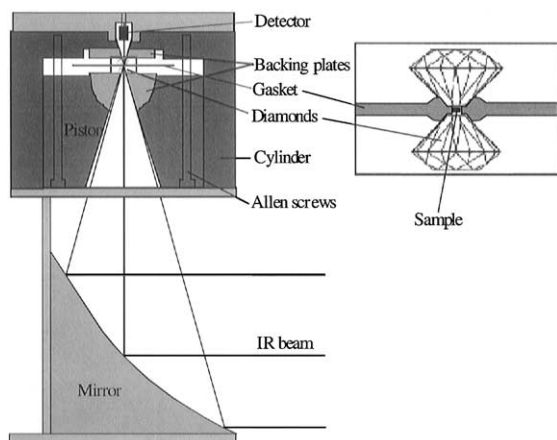


Fig. 1. Cross section of DACs used for IR spectroscopy. The diamonds, gasket, and sample are shown in the inset.

temperature. Second, the sensitive, low-noise Ge:Cu detector operates at liquid-helium temperatures.

LVM spectroscopy is a useful technique for determining the microscopic structure of impurities and defects in semiconductors [6–8]. LVMs of impurities are localized in real and frequency space [9], giving rise to sharp IR absorption peaks at liquid-helium temperatures [8]. Hydrogen, for example, typically has LVM frequencies 5–10 times the maximum phonon frequency and has narrow IR absorption peaks [10–12]. After the discoveries that hydrogen passivates donors [13] and acceptors [14] in GaAs, numerous hydrogen-related complexes have been observed in compound semiconductors [10,15]. In this paper, we review measurements of the dependence of carbon and carbon–hydrogen LVMs in GaAs and InP under large hydrostatic pressures.

The effect of pressure on LVMs 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 [16], resonant interactions in AlSb [17], hydrogen-related complexes in GaAs [18] and InP [19] and interstitial oxygen in silicon [20]. It is hoped that hydrostatic pressure may be used to differentiate between different hydrogen configurations that have the same symmetry (e.g., bond-centered vs. antibonding).

Samples discussed in this paper were carbon-doped and grown by metalorganic chemical vapor deposition on semi-insulating substrates. For the case of InP:C, it has been shown [21] 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  $\text{cm}^{-1}$ , respectively. It was proposed [21] that the hydrogen attaches directly to the

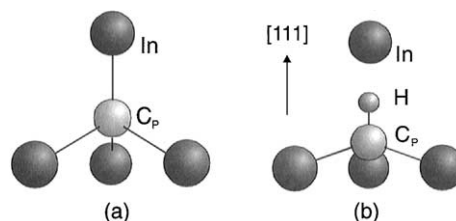


Fig. 2. Schematic diagrams of (a) substitutional carbon acceptor ( $C_P$ ) and (b) carbon–hydrogen pair ( $C_P-H$ ), in InP.

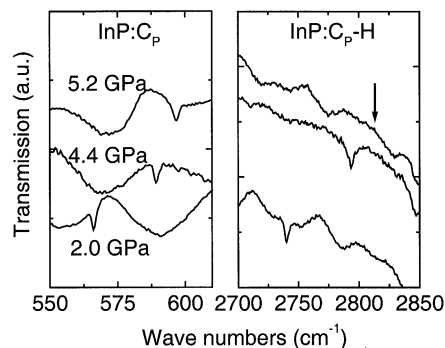


Fig. 3. IR spectra of InP:C, H for three different pressures, at a temperature of 9 K. The arrow indicates where the  $^{12}C_P-H$  peak should be at 5.2 GPa, by extrapolation from the lower pressure data.

carbon acceptor, in a [1 1 1] bond-centered orientation, adjacent to a host indium atom (Fig. 2). This bond-centered model is believed to apply for all known  $C_V-H$  pairs in III–V semiconductors [22].

IR spectra for several different pressures are shown in Fig. 3. 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 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. 3 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. However, no new peak is observed, so that the location of the “missing hydrogen” is currently an unsolved mystery.

The pressure-dependent shifts of InP two-phonon modes and  $C_P$  LVM were measured. The two-phonon modes have been identified previously as 2 TO and LO+TO modes [23]. In the range of pressures studied,

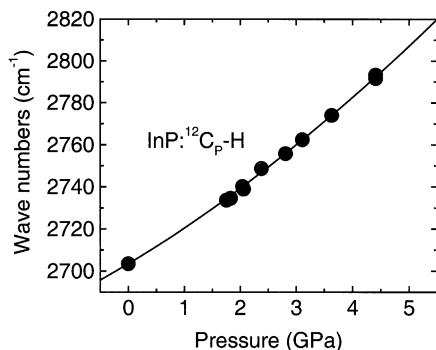


Fig. 4. InP:  $^{12}\text{C}_\text{P}$ -H stretch-mode frequency as a function of pressure. The solid line is a polynomial least-squares fit to the data [Eq. (5)].

the frequencies of the phonon modes and  $\text{C}_\text{P}$  LVM vary linearly with pressure. Least-squares linear fits yield the following expressions:

$$\nu(\text{InP} : ^{12}\text{C}_\text{P}) = 546.9 + 9.5P, \quad (1)$$

$$\nu(\text{InP}, 2\text{TO}) = 631.6 + 10.7P, \quad (2)$$

$$\nu(\text{InP}, \text{LO} + \text{TO}) = 659.0 + 10.8P, \quad (3)$$

where the frequencies  $\nu$  are in  $\text{cm}^{-1}$  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 (Ref. [18]):

$$\nu(\text{GaAs} : ^{12}\text{C}_\text{As}) = 582.7 + 9.3P. \quad (4)$$

The  $\text{C}_\text{P}$ -H stretch-mode frequency is plotted as a function of pressure in Fig. 4. The plot shows a slight positive curvature. A least-squares quadratic fit yields

$$\nu(\text{InP} : ^{12}\text{C}_\text{P}-\text{H}) = 2703.4 + 16.4P + 0.9P^2. \quad (5)$$

A positive curvature was also observed in GaAs: C, H stretch modes [18]:

$$\nu(\text{GaAs} : ^{12}\text{C}_\text{As}-\text{H}) = 2635.2 + 6.0P + 1.1P^2. \quad (6)$$

While the quadratic terms are similar, the linear term for InP:  $\text{C}_\text{P}$ -H is nearly three times that for GaAs:  $\text{C}_\text{As}$ -H. The reason for this significant difference is not obvious. One contributing factor may be the weaker  $\text{C}_\text{P}$ -In bond compared with the  $\text{C}_\text{As}$ -Ga bond [24,25]. The weaker bond would allow for a larger displacement of the  $\text{C}_\text{P}$ -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.

In summary, we have measured the pressure dependence of LVM frequencies in InP. As in the case of AlSb:  $^{12}\text{C}$  [4], GaAs:  $^{28}\text{Si}$  [16], GaAs:  $^{12}\text{C}$ , and GaAs:  $^{13}\text{C}$  [18], we find that the InP:  $^{12}\text{C}_\text{P}$  LVM

frequency varies linearly with pressure. The pressure-dependent shift of the InP:  $^{12}\text{C}_\text{P}$ -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 the future, hydrostatic pressure may prove to be a useful technique for differentiating between bond-centered and antibonding configurations. For instance, the different theoretical models proposed for Mg-H complexes in GaN should predict different pressure-dependent LVM shifts, allowing us to test the models experimentally.

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