

## HYDROGEN LOCAL VIBRATIONAL MODES IN COMPOUND SEMICONDUCTORS

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### ABSTRACT

Local vibrational mode (LVM) spectroscopy of hydrogen and deuterium in GaP, AlSb, ZnSe, and GaN has provided important information about the structures of dopant-hydrogen complexes and their interaction with the host lattice. In GaN:Mg, for example, hydrogen binds to a host nitrogen which is adjacent to the magnesium acceptor. In GaP and ZnSe, it has been demonstrated that the temperature dependent shifts of LVM's are proportional to the lattice thermal energy, a consequence of the anharmonic coupling of the local mode to acoustical phonons.

Large hydrostatic pressures have been applied to semiconductors to probe the vibrational properties of hydrogen-related complexes. In GaAs, the pressure dependent shifts of the  $^{12}\text{C-H}$  and  $^{13}\text{C-H}$  stretch modes have positive curvatures, while the shift of the S-H stretch mode has a negative curvature. This may be related to the fact that in the bond-centered C-H complex, the hydrogen is compressed between the carbon acceptor and one gallium host atom, whereas in the S-H complex, the hydrogen occupies an interstitial position and is not crowded by neighboring atoms. If these trends are general, then hydrostatic pressure may be a powerful tool in determining the position of the hydrogen atom(s) in a complex.

In AlSb, pressure was utilized to resolve a mystery as to why the Se-D complex gives rise to one stretch mode peak while the Se-H stretch mode splits into three peaks. This anomalous splitting is explained in terms of a new resonant interaction between the stretch mode and combination modes involving a wag mode harmonic and extended lattice phonons. The interaction gives rise to vibrational modes with both localized and extended components. When the temperature or hydrostatic pressure is varied, the modes exhibit anti-crossing behavior.

### INTRODUCTION

Since the discovery of hydrogen passivation of acceptors [1] and donors [2] in GaAs, a great deal of research has been performed on hydrogen in compound semiconductors. In this paper, I describe recent results of local vibrational mode (LVM) spectroscopy of hydrogen-related complexes in compound semiconductors. LVM spectroscopy is a useful technique for determining the microscopic structure of impurities

and defects in semiconductors [3,4]. Hydrogen LVM's can be unambiguously identified through the substitution of deuterium, which reduces the LVM frequency by a factor of approximately  $\sqrt{2}$ . The LVM frequencies and the isotopic frequency ratio  $r = \nu_H/\nu_D$  provide information about the bonding and position of the hydrogen [5].

To date, a large number of hydrogen-related complexes have been discovered in III-V semiconductors. C-H complexes in GaAs have been intensively studied, both theoretically [6] and experimentally [7], over the past five years. The four isotope combinations of these complexes ( $^{12}\text{C-H}$ ,  $^{13}\text{C-H}$ ,  $^{12}\text{C-D}$ ,  $^{13}\text{C-D}$ ) each have four modes - one stretch ( $A_1$ ), one longitudinal ( $A_1$ ), and two transverse ( $E^-$  and  $E^+$ ) - resulting in sixteen LVM's, all of which have been observed experimentally. In addition, the  $\text{C}_{\text{As}}\text{-C}_{\text{As}}$  split interstitial pair can be passivated, resulting in the formation of  $(\text{C}_{\text{As}})_2\text{H}$  and  $(\text{C}_{\text{As}})_2\text{H}_2$  complexes [8,9]. C-H complexes have also been discovered in AlAs [10] and GaP [11].

Group VI donor - hydrogen complexes in GaAs give rise to sharp infrared absorption peaks due to hydrogen and deuterium stretch and wag modes [12,13]. In these complexes, hydrogen is believed to reside in an antibonding orientation. Pajot and Song [14] have observed numerous infrared absorption peaks between 2940 and 3500  $\text{cm}^{-1}$  in oxygen-doped GaAs which are attributed to N-H and O-H stretch modes. Although hydrogen has long been suspected to form interstitial  $\text{H}_2$  molecules in semiconductors, they have only recently been observed in GaAs by Raman spectroscopy [15].

For group II acceptor - hydrogen complexes in GaAs [2], InP [16], and GaP [17], results from LVM spectroscopy show conclusively that hydrogen binds to the host anion in a bond-centered orientation, along a [111] direction, adjacent to the acceptor (Fig. 2). By measuring overtones of hydrogen LVM's in InP, Darwich *et al.* [16] have determined the anharmonicity of the hydrogen potentials. As the atomic number of the group II acceptor increases from Be to Cd, the stretch mode frequency and isotopic frequency ratio  $r = \nu_H/\nu_D$  increase.

In this paper, acceptor-hydrogen complexes in the wide band-gap semiconductors ZnSe and GaN are described. In addition, recent discoveries involving hydrogen LVM's under pressure are reviewed.

## EXPERIMENTAL DETAILS

Mid-infrared absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform spectrometer with a KBr or  $\text{CaF}_2$  beamsplitter. The samples were kept at a temperature of 9 K in a Janis liquid-helium cryostat with ZnSe windows. The instrumental resolution was varied from 0.5 to 2  $\text{cm}^{-1}$ , such that all peaks were fully resolved. Unless stated otherwise, spectroscopic data were obtained at or near liquid-helium temperatures (4-15 K).

To generate pressures up to 7 GPa, we used a modified Merrill-Bassett diamond-anvil cell [18,19]. Samples were cut into disks 300  $\mu\text{m}$  in diameter and polished to a thickness of 50-200  $\mu\text{m}$ . Liquid nitrogen was used as a pressure medium and was loaded into the cell, along with the sample, using the liquid-immersion technique [20]. A light concentrating cone focused the light through the diamonds, the sample, and onto a Ge:Cu photoconductor mounted directly behind the sample. To determine the pressure at liquid

helium temperatures, we measured the infrared absorption peak of the  $\nu_3$  vibrational mode of  $\text{CO}_2$  impurities in the  $\text{N}_2$  matrix. The  $\nu_3$  mode varies linearly with pressure [21] and provides a precise *in situ* calibration of the pressure.

## HYDROGEN IN ZnSe:As

### Introduction

ZnSe showed early promise as a material for blue laser diodes, with nitrogen as the preferred *p*-type dopant [22,23]. LVM spectroscopy of MOCVD-grown ZnSe:N revealed the presence of N-H complexes [24,25]. Arsenic, which replaces a host selenium atom, has also been investigated as a possible shallow acceptor [26]. The incorporation of hydrogen in arsenic- and MOCVD-grown ZnSe has been studied by secondary ion mass spectrometry (SIMS) [27]. The hydrogen incorporation in ZnSe:As increases strongly when hydrogen is used as a carrier gas instead of nitrogen, as discussed below.

### Experiment

A ZnSe:As sample that was grown with hydrogen as a carrier gas has an infrared absorption peak at  $2165.6 \text{ cm}^{-1}$  at a sample temperature of 7 K (Fig. 1) [28]. When nitrogen is used as a carrier gas, the same peak is present, but its area is reduced by a factor of 14, in good agreement with SIMS measurements [27]. In the case of the nitrogen carrier gas, the hydrogen most likely originates from the metalorganic precursors. The sample that was grown with deuterium as a carrier gas has an absorption peak at  $1557.1 \text{ cm}^{-1}$ , along with the hydrogen-related peak at  $2165.6 \text{ cm}^{-1}$  (Fig. 1). The isotopic ratio is  $r = \nu_{\text{H}}/\nu_{\text{D}} = 1.3908$ . The area of the hydrogen-related peak is approximately 3 times that of the deuterium-related peak. Previous SIMS measurements of the samples show  $[\text{H}] = 6 \times 10^{18} \text{ cm}^{-3}$  and  $[\text{D}] = 1 \times 10^{18} \text{ cm}^{-3}$  [27]. These results suggest that most of the hydrogen incorporation does not come directly from the carrier gas, but rather from the metalorganic molecules.

### Bond-centered model

Since the frequency of the ZnSe:As,H mode is similar to that of the  $\text{AsH}_3$  bond-stretching mode frequency ( $2116 \text{ cm}^{-1}$ ) [29], we propose that the hydrogen binds directly to the arsenic acceptor. In several respects, the As-H complex in ZnSe is remarkably similar to the Zn-H complex in GaAs [2]. In GaAs, zinc is an acceptor which occupies a substitutional gallium site. Hydrogen passivates zinc by attaching to a *host* arsenic atom, in a bond-centered orientation, adjacent to the zinc *acceptor*. In ZnSe:As the hydrogen attaches to the arsenic *acceptor*, in a bond-centered orientation, adjacent to the *host* zinc atom (Fig. 2). The stretch mode frequency of the GaAs:Zn,H complex is  $2146.0 \text{ cm}^{-1}$  at a temperature of 6 K, and the isotopic frequency ratio is  $r = 1.3860$ . The fact that the r-

values and LVM frequencies of the two complexes are very similar lends further support to the bond-centered model.

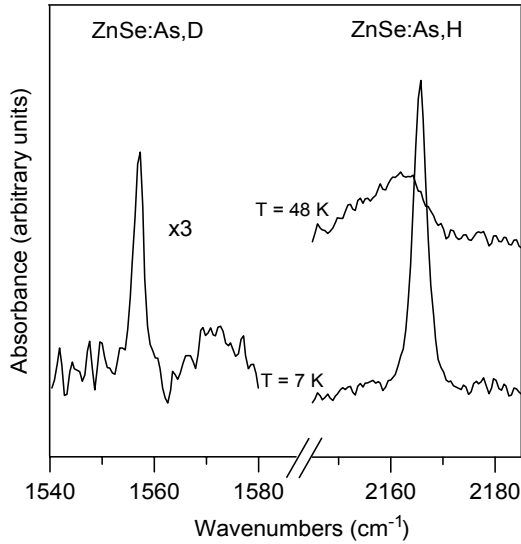


Figure 1. Infrared absorption peaks of As-D and As-H complexes in ZnSe.

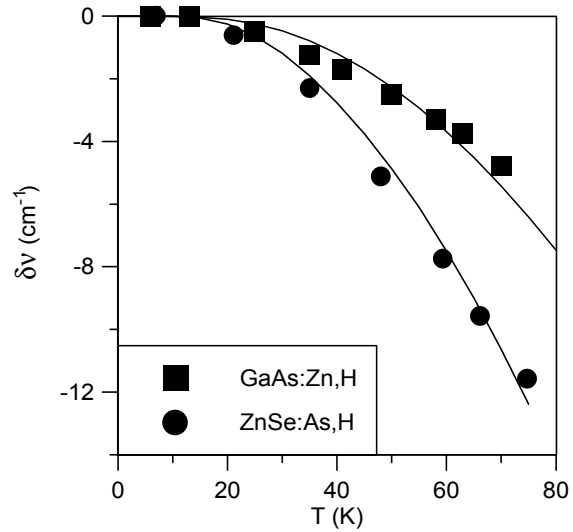


Figure 2. Temperature dependent shifts of LVM frequencies of GaAs:Zn,H and ZnSe:As,H.

### Temperature Dependence

The temperature dependent behavior of the ZnSe:As,H LVM is shown in Fig. 3. As explained in Refs. [17] and [30], the LVM shift is proportional to the thermal lattice energy  $U(T)$ :

$$\delta(\hbar\omega) = \beta U(T), \quad (1)$$

where  $U(T)$  is given in units of energy per atom,  $N_A$  is Avagadro's number, and  $\beta$  is a dimensionless constant. Roughly speaking,  $\beta$  is the fraction of thermal energy that is transferred to the hydrogen's vibrational motion from its neighboring atoms.

The values of  $U(T)$  are obtained by numerically integrating the experimental values of the specific heat  $C_V(T)$  reported by Irwin and LaCombe [31], neglecting the zero temperature energy. The data can be approximated by a linear least-squares fit to Eq. (1), with  $\beta = -0.34$ . The temperature dependent shift and the fit are shown in Fig. 42. At 77 K, the shift of the ZnSe:As,H mode is approximately twice that of the GaAs:Zn,H mode.

The ZnSe:As,H mode has a slightly higher frequency, higher  $r$ -factor, and stronger temperature dependence than the GaAs:Zn,H mode [32]. For the GaAs:Zn,H mode,  $\beta = -0.24$ . These observations suggest that the coupling between the zinc and the hydrogen is somewhat weaker in GaAs than in ZnSe. The effect of the zinc can be modeled as a repulsive potential which confines the hydrogen atom. The potential increases the frequency and the  $r$ -factor, the latter because hydrogen has a larger amplitude than deuterium and overlaps the potential more. The temperature dependent shift of the frequency is caused primarily by coupling between the hydrogen and the neighboring zinc atom, which undergoes random thermal motion. Greater coupling leads to an LVM with

a more pronounced temperature dependence. The exact cause of this greater coupling, however, is not currently understood.

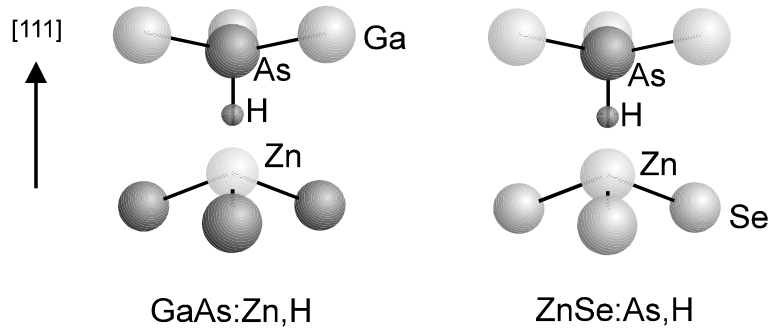


Figure 3. Bond-centered models for GaAs:Zn,H and ZnSe:As,H complexes.

## HYDROGEN IN GaN:Mg

### Introduction

The development of blue light-emitting diodes (LED's) [33] and laser diodes [34] has focused a great deal of research activity on GaN-based III-V nitrides. The band gaps of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys cover a wide spectral range, from red (InN) to UV (GaN), making this alloy system ideal for numerous optoelectronic applications [35].

MOCVD is the dominant growth technique for III-V nitride devices, with Mg the most common *p*-type dopant. As a result of hydrogen passivation during growth, as-grown GaN:Mg is semi-insulating. It was shown empirically that low energy electron beam irradiation (LEEBI) [36] or thermal annealing at temperatures above 600°C in an  $\text{N}_2$  ambient [37] were required to activate the Mg acceptors. Since thermal annealing had been shown to dissociate acceptor-hydrogen complexes in numerous other semiconductors [1,2], it was assumed that Mg-H complexes were formed in GaN as well. It required infrared spectroscopy, however, to positively identify the Mg-H complexes [38]. In GaN grown by MBE, the lack of hydrogen enables one to grow *p*-type GaN:Mg without LEEBI or thermal annealing [39].

### N-H Model

Theoretical calculations predict that hydrogen attaches to a nitrogen atom in an antibonding orientation (Fig. 4) in the Mg-H complex [40], in stark contrast to acceptor-hydrogen complexes in non-nitride semiconductors. This difference can be attributed to the ionicity of the Ga-N bond, in which there is no local maximum of the charge density at the bond center. In the strongly covalent Ga-As and Si-Si bonds, on the other hand, there is a maximum in the charge density which attracts the proton to the bond centered location.

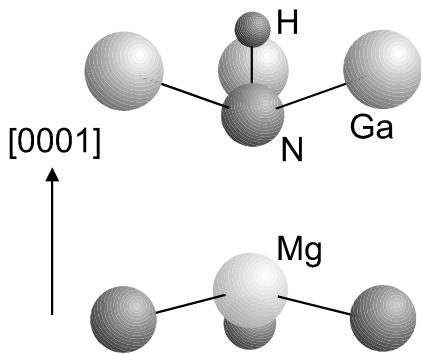


Figure 4. Antibonding model for Mg-H complex in GaN.

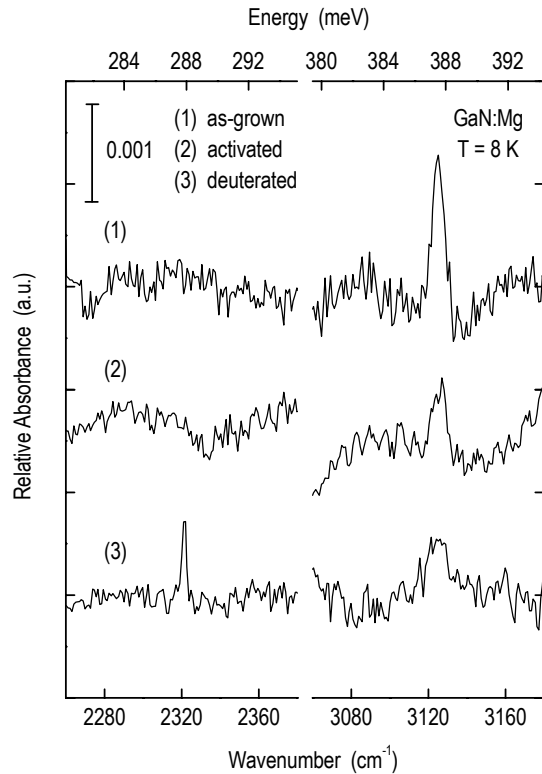


Figure 5. Infrared absorption peaks for as-grown, activated, and deuterated GaN:Mg.

The predicted stretch mode frequency of hydrogen in the Mg-H complex is  $3360 \text{ cm}^{-1}$  [40], which is similar to that of  $\text{NH}_3$  ( $3444 \text{ cm}^{-1}$ ). The stretch mode frequency was experimentally observed at  $3125 \text{ cm}^{-1}$  in  $4 \mu\text{m}$  thick epilayers of MOCVD-grown GaN:Mg [38]. This frequency agrees quite well with the theoretical prediction of  $3360 \text{ cm}^{-1}$  and is similar to the stretch mode frequencies of N-H complexes in GaAs [14] and ZnSe [24,25]. Upon annealing, the peak at  $3125 \text{ cm}^{-1}$  decreases by a factor of two (Fig. 5) and is correlated with an increase in the conductivity. Annealed samples that are exposed to a remote deuterium plasma show a deuterium stretch mode peak at  $2321 \text{ cm}^{-1}$ . The isotopic frequency ratio is  $r = \nu_{\text{H}}/\nu_{\text{D}} = 1.346$ , which is very similar to that of  $\text{NH}_3$  ( $r = 1.342$ ), lending further support to the N-H model. Whether the hydrogen resides in an antibonding or bond-centered position, however, has not yet been determined experimentally.

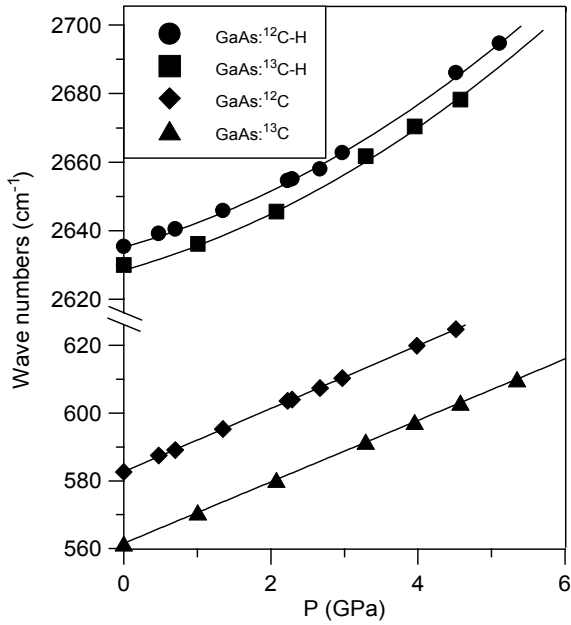


Figure 6. GaAs:C,H and GaAs:C LVM's as a function of pressure.

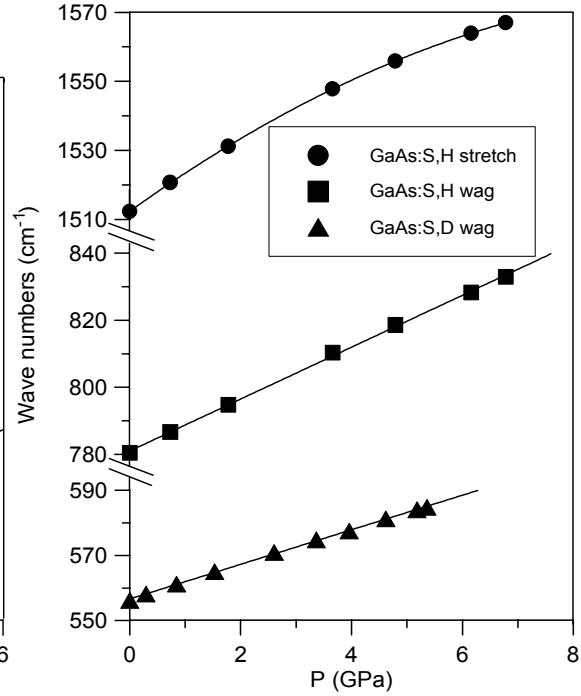


Figure 7. GaAs:S,H and GaAs:S,D LVM's as a function of pressure.

## GaAs LVM's UNDER PRESSURE

The application of hydrostatic pressure is an excellent tool for probing the electronic and vibrational properties of defects in semiconductors [41-43]. Only recently has this experimental probe been utilized to investigate hydrogen-related complexes.

### GaAs:C,H

In the GaAs:C,H complex, the hydrogen attaches directly to the carbon acceptor, in a [111] bond-centered orientation, adjacent to a host gallium atom [6,7]. At atmospheric pressure and liquid-helium temperatures, the  $^{12}\text{C-H}$  and  $^{13}\text{C-H}$  stretch modes have frequencies of 2635.2 and 2628.5  $\text{cm}^{-1}$ , respectively [7].

The peak positions of the  $^{12}\text{C-H}$ ,  $^{13}\text{C-H}$ ,  $^{12}\text{C}$ , and  $^{13}\text{C}$  modes are plotted as a function of pressure in Fig. 6. The substitutional carbon LVM's vary linearly with pressure, with least square fits given by

$$\nu(^{12}\text{C}_{\text{As}}) = 582.7 + 9.31 P \quad (2)$$

$$\nu(^{13}\text{C}_{\text{As}}) = 561.5 + 9.08 P, \quad (3)$$

where  $\nu(^{12}\text{C}_{\text{As}})$  and  $\nu(^{13}\text{C}_{\text{As}})$  are the LVM frequencies in  $\text{cm}^{-1}$  and  $P$  is in GPa. The plots of the hydrogen stretch modes as a function of pressure are nonlinear, with a positive curvature. Least square quadratic fits yield

$$\nu(^{12}\text{C}_{\text{As-H}}) = 2635.2 + 6.0 P + 1.1 P^2 \quad (4)$$

$$\nu(^{13}\text{C}_{\text{As-H}}) = 2628.5 + 6.0 P + 1.1 P^2, \quad (5)$$

where the shifts of the two carbon isotopes are constrained to be equal. Since the  $^{12}\text{C}_{\text{As-H}}$  and  $^{13}\text{C}_{\text{As-H}}$  stretch mode frequencies only differ by 0.3%, the difference in pressure dependence cannot be resolved experimentally.

### GaAs:S,H

In group VI donor - hydrogen complexes, the hydrogen is believed to bond with a host gallium in a [111] antibonding orientation [15]. Since the hydrogen is isolated from the donor, its LVM frequency is very insensitive to the donor species, only varying  $\sim 10 \text{ cm}^{-1}$  from S to Te. We measured the pressure dependence of the S-H stretch and wag modes and the S-D wag mode. The S-D stretch mode was too weak to be detected in the diamond anvil cell sample. The frequencies of the stretch and wag modes are plotted as a function of pressure in Fig. 7. The S-H and S-D modes vary linearly with pressure, with least square fits given by

$$\nu(\text{S-H wag}) = 781.0 + 7.7 P \quad (6)$$

$$\nu(\text{S-D wag}) = 556.6 + 5.3 P. \quad (7)$$

The plot of the hydrogen stretch mode as a function of pressure is nonlinear, with a negative curvature. A least square quadratic fit yields

$$\nu(\text{S-H stretch}) = 1512.3 + 11.6 P - 0.52 P^2. \quad (8)$$

### Summary

In summary, we have measured the pressure dependence of several LVM frequencies in GaAs [44]. As in the case of AlSb:  $^{12}\text{C}$  [21] and GaAs:  $^{28}\text{Si}$  [43], we find that the  $^{12}\text{C}$  and  $^{13}\text{C}$  LVM frequencies vary linearly with pressure. The pressure dependent shifts of the  $^{12}\text{C-H}$  and  $^{13}\text{C-H}$  stretch modes have positive curvatures, while the shift of the S-H stretch mode has a negative curvature. This may be related to the fact that in the bond-centered C-H complex, the hydrogen is compressed between the carbon acceptor and one gallium host atom, whereas in the S-H complex, the hydrogen occupies an interstitial position and is not crowded by neighboring atoms.

### AlSb:Se,H UNDER PRESSURE

At liquid-helium temperatures, hydrogenated AlSb:Se has stretch mode peaks at  $1608.6$  and  $1615.7 \text{ cm}^{-1}$ , whereas the Se-D mode has only one stretch mode peak at  $1173.4 \text{ cm}^{-1}$  [45]. In addition, there is a small Se-H peak at  $1606.3 \text{ cm}^{-1}$ . Hydrogenated and deuterated AlSb:Te have only one stretch mode peak each, at  $1599.0$  and  $1164.4 \text{ cm}^{-1}$  respectively. The anomalous splitting of the Se-H peak may be explained in terms of a resonance between the stretch mode and combination modes involving extended lattice phonons and a wag mode harmonic [46].

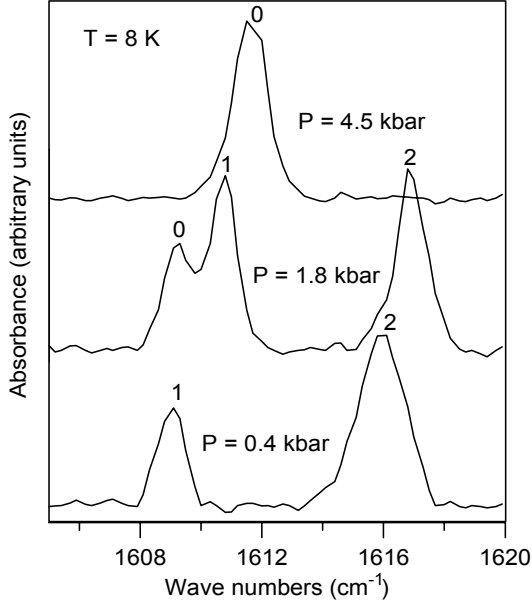


Figure 8. Se-H peaks in AlSb.

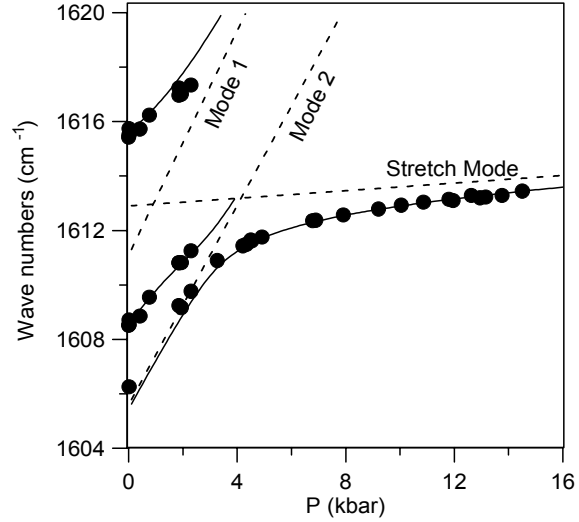


Figure 9. Se-H peaks in AlSb as a function of pressure.

Hydrostatic pressure was utilized to change the resonance conditions between local and extended modes. Varying the pressure has an advantage over varying the temperature in that the lines do not broaden, so all three peaks are resolved. We find that the strength of peak 0, which is negligibly small at ambient pressure, increases rapidly at the expense of peaks 1 and 2 (Fig. 8). At pressures above 4.5 kbar, only peak 0 can be detected. The integrated absorption for all the peaks remains constant to within experimental error. The peak positions are plotted in Fig. 9.

To explain the existence of three peaks, it is proposed that the stretch mode  $\omega_s$  interacts with two “unknown” modes  $\omega_1$  and  $\omega_2$ . It is noteworthy that the calculated AlSb optical phonon density of states has a sharp peak at  $\omega_p = 290 \text{ cm}^{-1}$  [47]. The experimentally measured frequency of the  $N = 3$  and  $N = 4$  wag mode harmonics ( $\Gamma_1$ ) are  $\omega_{wag,3} = 1032 \text{ cm}^{-1}$  and  $\omega_{wag,4} = 1316 \text{ cm}^{-1}$ , respectively [45]. The combination modes may therefore be given by

$$\omega_1 = 2 \omega_p + \omega_{wag,3} \sim 1612 \text{ cm}^{-1} \quad (11)$$

$$\omega_2 = \omega_p + \omega_{wag,4} \sim 1606 \text{ cm}^{-1}. \quad (12)$$

The pressure dependence of the peaks can be understood qualitatively as follows: the stretch mode interacts primarily with combination mode 1 and splits into two branches. The low-frequency branch then interacts with mode 2, with a smaller coupling energy. The anti-crossing between the three modes yields three infrared active peaks at pressures of  $\sim 2$  kbar. For higher pressures, only the lowest branch, peak 0, is “LVM-like.”

To estimate the pressure dependence of the phonon-wag combination modes, the pressure dependence of the second harmonic ( $N=0 \rightarrow 2$ ) wag mode was measured. At liquid-helium temperatures and atmospheric pressure, this mode has a frequency of 665.5

cm<sup>-1</sup> [45]. As in the case of wag modes in GaAs, the pressure dependence of the frequency is linear, with a least-squares fit given by

$$\omega_{wag,2} = 665.5 + 0.64 P, \quad (13)$$

where  $P$  is the pressure in kbar and  $\omega_{wag,2}$  is in units of cm<sup>-1</sup>. The second harmonic wag mode peak was measured at the same time as the stretch mode peaks. The fact that the stretch mode splits whereas the wag mode does not split supports the claim that the splitting of the stretch mode is due to a resonant interaction, as opposed to a second configuration of the complex.

The measured pressure dependence of optical phonons in AlSb is given by  $d\omega/dP \sim 0.55$  cm<sup>-1</sup>/kbar [48]. Using this value with Eq. (13), we estimate the pressure dependence of the combination modes:

$$\omega_1 = 1611.1 + 2.06 P \quad (14)$$

$$\omega_2 = 1605.6 + 1.83 P, \quad (15)$$

where  $P$  is the pressure in kbar and the frequencies are in units of cm<sup>-1</sup>. The pressure dependence of the stretch mode is determined by measuring peak 0 at high pressures:

$$\omega_s = 1612.9 + 0.07 P. \quad (16)$$

Note that the zero pressure values are the same as those given in the variable temperature analysis.

The three-level Hamiltonian is given by

$$H = \begin{bmatrix} \omega_s & A & B \\ A & \omega_1 & 0 \\ B & 0 & \omega_2 \end{bmatrix}, \quad (17)$$

where  $A = \langle N_s = 1 | H_{\text{int}} | N_p = 2, N_w = 3 \rangle$ ,  $B = \langle N_s = 1 | H_{\text{int}} | N_p = 1, N_w = 4 \rangle$ , and for simplicity the interaction between the combination modes is neglected. We use values of  $A = 3.45$  cm<sup>-1</sup>, as before, and  $B = 0.9$  cm<sup>-1</sup>. The eigenvalues of the Hamiltonian [Eq. (17)] are calculated numerically. We obtain very good agreement between the model and experiment (Fig. 9).

## CONCLUSIONS

Hydrogen in semiconductors continues to be an important topic, both from a scientific and technological viewpoint. Recent measurements have utilized temperature and hydrostatic pressure as experimental probes of hydrogen LVM's. From the shifts of the LVM frequencies, information can be obtained about the interaction between hydrogen and impurity/host atoms. In the future, these techniques may be used to provide clues about the location of hydrogen atoms within complexes as well as the nature of LVM-phonon interactions.

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