

# Local Vibrational Mode Spectroscopy of Hydrogen in Compound Semiconductors

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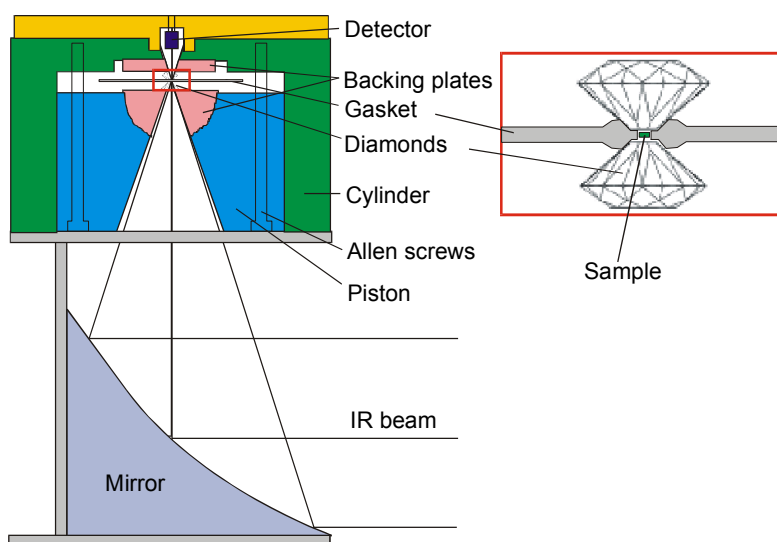
**Abstract.** Infrared (IR) and Raman spectroscopy are useful techniques for characterizing hydrogen-related defects in semiconductors. This paper will focus on hydrogen in compound semiconductors such as AlSb, GaAs, GaN, InP, and ZnO. In most compound semiconductors studied to date, hydrogen forms neutral complexes with donors or acceptors. In GaN:Mg grown by metalorganic chemical vapor deposition, for example, hydrogen forms pairs with Mg acceptors so that the semiconductors is semi-insulating as grown. In ZnO, however, theoretical and experimental work has shown that hydrogen is a shallow donor. We have observed hydrogen local vibrational modes in ZnO annealed in hydrogen gas, allowing us to speculate as to the structure of the hydrogen complex. The use of high pressures in conjunction with IR spectroscopy may provide a means for distinguishing between similar configurations. In GaN:Mg,H, the local vibrational mode exhibits a small shift with pressure. By comparing this shift with the predictions of *ab initio* calculations, we can rule out the bond-centered (BC) configuration.

## INTRODUCTION

The addition of impurities to a semiconductor, whether intentional or accidental, affects the electrical properties by introducing energy levels into the band gap. In addition to altering the electronic characteristics of semiconductors, impurities also affect the vibrational properties. When an impurity is introduced into an otherwise perfect crystal, the translational symmetry is broken and one or more new vibrational modes may appear. If a mass defect replaces a heavier host atom, for example, its vibrational frequency will lie above the lattice phonon frequency range [1]. Unlike a lattice phonon, the vibrational mode of the defect is localized in real space and frequency space, and is referred to as a *local vibrational mode* (LVM). The study of LVMs in semiconductors contributes to a fundamental understanding of vibrational dynamics and impurity-host interactions. This area of research is of practical benefit, providing spectroscopic “fingerprints” as well as detailed information about the microscopic structure of technologically relevant defect centers. Reviews of LVMs in semiconductors are given by Newman [2], Barker and Sievers [1], Stavola [3], and McCluskey [4]. Reviews of hydrogen in semiconductors include Clerjaud [5]; Pankove and Johnson [6]; Estreicher [7]; Pearton, Corbett, and Stavola [8]; Haller [9]; and Nickel [10].

## EXPERIMENT: HIGH PRESSURE SPECTROSCOPY

A low-temperature, high-pressure IR diamond-anvil cell was designed and tested in our laboratory (Fig. 1). In this cell, force is applied by six Allen screws, which squeeze together a piston and cylinder [11]. The diamonds are supported by flat and hemispherical backing plates made from tungsten carbide. An off-axis parabolic mirror efficiently focuses a collimated IR beam onto the sample. A photoconducting 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 4-12 K. The advantages of low temperatures are twofold. First, the vibrational modes that are observed do not exhibit thermal broadening. Second, the Ge detectors [12] are extremely sensitive, with very little electrical noise, at cryogenic temperatures. The diamond-anvil cell has been used up to 7 GPa and has shown excellent performance.



**FIGURE 1.** Cross section of DAC assembly designed for FTIR spectroscopy. Diamond anvils, gasket, and sample are shown in the inset.

## CARBON-HYDROGEN COMPLEXES UNDER PRESSURE

Using the IR diamond-anvil cell, we observed carbon and carbon-hydrogen local vibrational modes (LVMs) in InP [13] and GaAs [14] at hydrostatic pressures as high as 5.5 GPa at liquid-helium temperatures. Both the C and C-H LVM frequencies increase with increasing pressure. For pressures beyond approximately 4.5 GPa, the C<sub>P</sub>-H peak was not observed. This is in contrast to GaAs, in which the C<sub>As</sub>-H peak does not disappear, for the same pressure range. Currently, this is an “unsolved mystery!”

For all the measured modes, the Grüneisen parameters increase with pressure. Although the C-H modes in GaAs and InP have much different pressure dependencies, the shifts of their Grüneisen parameters [ $\gamma=(d\omega/\omega)/(dV/V)$ ] are quite similar. The  $C_P$  and  $C_P$ -H modes have Grüneisen derivatives of  $-d\gamma/d(\Delta V/V_0) = 9\pm 0.5$ . Therefore, the different pressure behavior (linear vs. supralinear) results solely from the fact that the bulk modulus increases with pressure.

## RESONANT VIBRATIONAL INTERACTIONS

In AlSb, hydrogen (or deuterium) passivates Se donors to form electrically neutral complexes. At liquid-helium temperatures, hydrogenated AlSb:Se has stretch-mode peaks at 1609 and 1616  $\text{cm}^{-1}$ , respectively, whereas deuterated AlSb:Se has only one peak at 1173.4  $\text{cm}^{-1}$  [15]. The anomalous splitting of the hydrogen mode has been attributed to a resonant interaction between the stretch mode and a “combination” mode. It has been proposed that the combination mode involves both localized and extended-lattice phonons [16]. Since such a mode would involve five vibrational quanta, it is practically IR inactive. By varying the temperature or pressure, an anti-crossing between the peaks was observed.

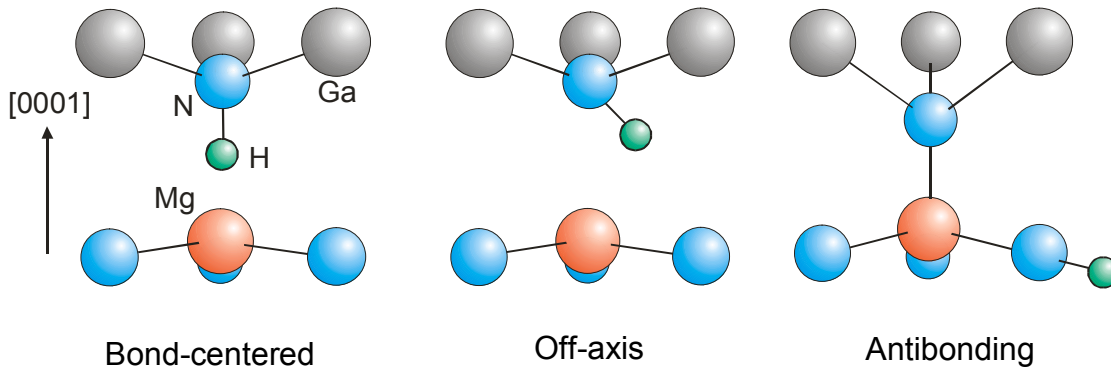
### Proposed pump-probe experiments

It is proposed that time-resolved IR spectroscopy will be performed at Jefferson Lab, to measure the quantum “beating” between the two weakly interacting vibrational modes. Pump-probe experiments will be performed to observe the oscillation between the two modes. The wavelength of light will be 6.2  $\mu\text{m}$  (1612  $\text{cm}^{-1}$ ) and the pulse duration will be 1-2 ps. When the pulse is absorbed by the Se-H complex, the vibrational system is put into a purely “stretch mode” state. Single-color pump-probe experiments will be performed, to determine the vibrational lifetime of the Se-H LVM (transient bleaching spectroscopy). From the linewidths of the two peaks, it can be inferred that the lifetime of the combination mode is longer than that of the stretch mode. In that case, the exponential decay of the mode should be modulated by an oscillation with a period of approximately 4 ps. Two-color pump-probe experiments, combined with the single-color experiments, would yield a detailed picture of the vibrational dynamics. These experiments will provide an important test of the resonant-interaction model.

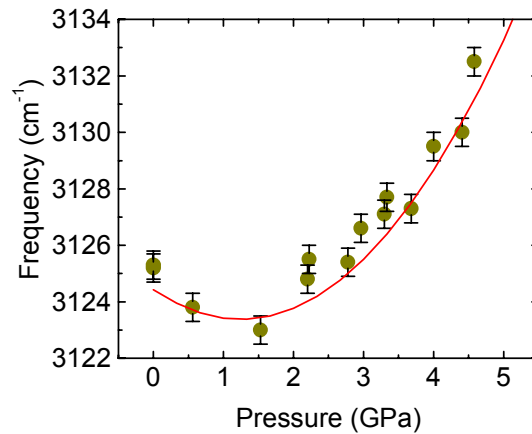
## MAGNESIUM-HYDROGEN COMPLEX IN GALLIUM NITRIDE

A technologically important example of hydrogen in semiconductors is the Mg-H complex in GaN [17]. Mg is the preferred acceptor dopant in GaN-based blue lasers [18]. However, the presence of hydrogen suppresses the electrical activity of Mg. Three models for this complex [19,20,21,22] are shown in Fig. 2. We have used high-pressure vibrational spectroscopy to discriminate between competing models for the structure of the Mg-H complex. Toward that end, the N-H vibrational mode was

measured as a function of pressure (Fig. 3). The experimental pressure shift was compared with predictions from first-principles calculations [23]. For the bond-centered configuration, the calculated frequency shift was  $15 \text{ cm}^{-1}/\text{GPa}$ , much larger than the experimentally observed shift. Hence, the bond-centered model can be excluded. For the off-axis and antibonding configurations, the calculated shifts were  $-0.3$  and  $1.5 \text{ cm}^{-1}$ , respectively. Within the uncertainty of the calculations, both of these results are consistent with experiment. Future work will attempt to explain the *nonlinear* behavior of the Mg-H mode, which may help determine which structure is correct.



**FIGURE 2.** Three models for the Mg-H complex in GaN



**FIGURE 3.** Mg-H LVM frequency in GaN as a function of pressure.

## HYDROGEN IN ZINC OXIDE

Zinc oxide (ZnO) is a wide-bandgap semiconductor that has generated intense interest for a range of optical, electronic, and mechanical applications. First-principles calculations by Van de Walle [24] predicted that hydrogen impurities in ZnO are shallow donors. Recent results on muonium in ZnO [25] and electron nuclear double resonance measurements on n-type ZnO [26] have provided experimental evidence that hydrogen is a shallow donor. In order to determine the microscopic structure of hydrogen donors, we used infrared (IR) spectroscopy to measure LVMs in ZnO annealed in hydrogen gas at 700°C [27]. An oxygen-hydrogen stretch mode was observed at 3326.3 cm<sup>-1</sup> at liquid-helium temperatures, in good agreement with the theoretical predictions for hydrogen in an antibonding configuration. The low-temperature IR spectrum of ZnO annealed in deuterium showed a weak peak at 2470.3 cm<sup>-1</sup>, which we attribute to O-D complexes. The isotopic frequency ratio between the O-H and O-D modes is  $r = 1.3465$ , in very good agreement with the value for O-H complexes in GaP ( $r = 1.3464$ ) [28].

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