PHYSICAL REVIEW B **77**, 085213 (2008)

Vibrational properties of the H-N-H complex in dilute III-N-V alloys: Infrared spectroscopy and density functional theory

S. Kleekajai, F. Jiang,* K. Colon,† M. Stavola,‡ W. B. Fowler, and K. R. Martin§
Department of Physics and Sherman Fairchild Laboratory, Lehigh University, Bethlehem, Pennsylvania 18015, USA

A. Polimeni and M. Capizzi
CNISM and Dipartimento di Fisica, Sapienza Universitá di Roma, I-00185 Roma, Italy

Y. G. Hong, H. P. Xin, and C. W. Tu
Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093, USA

G. Bais, S. Rubini, and F. Martelli
Laboratorio Nazionale TASC-INFM-CNR, Area Science Park, Strada Statale 14, Km. 163.5, I-34012 Trieste, Italy

(Received 14 November 2007; revised manuscript received 28 December 2007; published 28 February 2008)

The nitrogen and hydrogen vibrational modes of hydrogenated $GaAs_{1-y}N_y$ and $GaP_{1-y}N_y$ have been studied by infrared absorption spectroscopy and density functional theory. Data for the stretching modes observed for samples containing both hydrogen and deuterium show that the dominant defect complex contains two weakly coupled N-H stretching modes. Theory predicts an H-N-H complex with C_{1h} symmetry whose vibrational properties are in excellent agreement with experiment. Additional results provide further support for the defect model that has been proposed. Uniaxial stress results confirm that the symmetry of the H-N-H complex must be lower than trigonal. The vibrational properties predicted by theory for the H-N-H complex also lead to an assignment of the wagging modes that are observed. Experimental and theoretical results for $GaAs_{1-y}N_y$ and $GaP_{1-y}N_y$ are remarkably similar, showing that the same H-N-H defect complex is responsible for the properties of H in these fascinating materials.

DOI: 10.1103/PhysRevB.77.085213 PACS number(s): 78.30.Fs, 61.72.Bb, 63.20.Pw

I. INTRODUCTION

The addition of a few percent of nitrogen to GaAs or GaP causes a large reduction in the band gap.[1–4] The subsequent addition of hydrogen eliminates the effect of nitrogen and causes the band gap to increase to nearly the value of the nitrogen-free host.[5–8] This modification of the band gap caused by hydrogenation is a surprising and unusual behavior for hydrogen in semiconductors[9] and has attracted much recent attention. Theoretical calculations by several groups led to the suggestion that hydrogen forms a dimer in the III-N-V alloys known as H_2^* that is stabilized by the presence of a substitutional nitrogen atom, and that $H_2^*(N)$ is the cause of the unusual behavior of hydrogen in these materials.[10–15] Two possible $H_2^*(N)$ configurations were predicted, each of which has one hydrogen atom at a bond-center site and a second hydrogen atom at an antibonding site along a $\langle 111 \rangle$ axis. For each of these configurations, one hydrogen atom is bonded to a nitrogen atom and the second hydrogen atom is bonded to a gallium atom.

Vibrational spectroscopy[16] provides a direct, structure-sensitive probe of the defects that are formed in the hydrogenated III-N-V alloys because the vibrational modes associated with both the nitrogen and the hydrogen atoms can be studied. An IR absorption study of $GaAs_{1-y}N_y$ found that the principal defect produced by hydrogenation is inconsistent with the properties of the $H_2^*(N)$ defects predicted by theory.[17] An analysis of the IR spectra observed for samples that contained both hydrogen and deuterium showed that the principal defect observed in vibrational spectroscopy contains *two* weakly coupled N-H stretching modes and *no* Ga-H modes. This conclusion is inconsistent with the $H_2^*(N)$ complexes proposed by theory which would contain only a single N-H stretching mode.[10–15]

Recent calculations have suggested an alternative configuration for an H-N-H complex that has C_{1h} symmetry (Fig. 1) and vibrational properties that are consistent with experiment.[18,19] Furthermore, the results of a recent study of the x-ray absorption near-edge structure (XANES) for $GaAs_{1-y}N_y$:H that combined experiment and theory found results consistent with a C_{2v} or "asymmetric C_{2v}" N-H_2 defect structure and gave no evidence for the presence of $H_2^*(N)$.[20]

The dilute $GaP_{1-y}N_y$ alloys show behavior similar to that of $GaAs_{1-y}N_y$. The band gap of $GaP_{1-y}N_y$ is also decreased by the addition of nitrogen and then is increased by the subsequent addition of hydrogen.[7,8] In the present paper IR absorption experiments are reported for hydrogenated $GaP_{1-y}N_y$ to determine whether the H-N-H centers that had been seen by IR spectroscopy for $GaAs_{1-y}N_y$:H are also common to $GaP_{1-y}N_y$:H. Theoretical calculations are carried out on this system and the results are used as a framework to analyze the experimental results. Uniaxial stress experiments are also reported which confirm that the H-N-H centers in $GaAs_{1-y}N_y$:H have symmetry lower than trigonal.

The wagginglike modes seen previously in the range 1000–1500 cm^{-1} for $GaAs_{1-y}N_y$:H have remained relatively unexplored.[17] Not all lines showed both hydrogen and deuterium counterparts, making their assignments questionable. Moreover, the possibility remained that some of the previ-

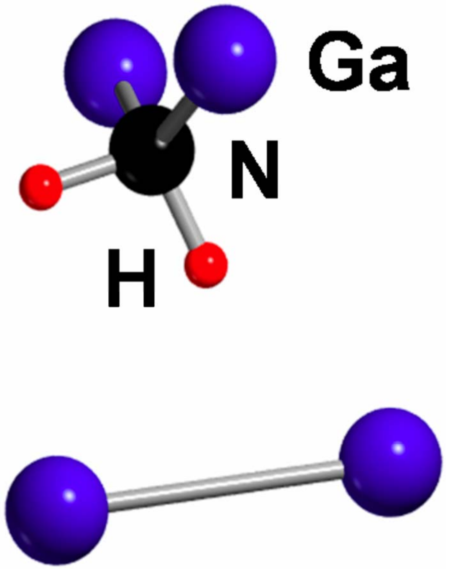

FIG. 1. (Color online) The relaxed H-N-H defect in $GaAs_{1-y}N_y$ as computed using CRYSTAL 2003 (Ref. 37).

ously unassigned lines might be associated with the elusive $H_2^*(N)$ center favored by theory, or other recently proposed defect structures. Results in the present paper for the wagging modes observed for both $GaAs_{1-y}N_y$:H and $GaP_{1-y}N_y$:H and their interpretation shed light on the assignments of the wagging modes of the H-N-H centers seen in the dilute III-N-V alloys and provide further evidence for an H-N-H defect structure containing two inequivalent hydrogen atoms.

In spite of this progress, the identification of the defects that are formed in the hydrogenated III-N-V alloys remains controversial. An $H_2^*(N)$ structure is predicted theoretically to be more stable than the H-N-H structure that explains the observed vibrational properties.[4–8,19] Du *et al.* suggested[19] that the observed H-N-H defect may arise from the neutralization of a stable $(H\text{-}N\text{-}H)^{2+}$ defect, but other kinetic scenarios also warrant consideration. Recent experiments suggest that more than two hydrogen atoms per nitrogen atom are required to produce the band gap shifts in the dilute III-N-V alloys caused by hydrogenation.[21] Moreover, theory suggests that up to four hydrogen atoms can be bound in the vicinity of a single nitrogen atom.[22] Other experimental studies suggest that additional hydrogen atoms, possibly as H_2 molecules, are stabilized by the presence of nitrogen.[23] Finally, a recent optical and structural investigation found that two H atoms are responsible for the passivation of N in $GaAs_{1-y}N_y$, and a third, less tightly bound, H atom gives a compressive lattice strain observed in as-hydrogenated samples that can be eliminated by annealing for 13 h near 250 °C.[24]

Studies of the vibrational properties of the hydrogenated III-N-V alloys provide an excellent strategy for probing the microscopic properties of the important nitrogen- and hydrogen-containing defects in these fascinating materials. A comparison of the vibrational modes of H and D in $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ and the elucidation of their assignments is the primary goal of the present paper.

II. EXPERIMENTAL AND THEORETICAL PROCEDURES

A. Experiment

The $GaP_{1-y}N_y$ samples used for our experiments were grown by gas-source molecular beam epitaxy (MBE) on undoped (001) GaP substrates. The $GaP_{1-y}N_y$ epilayers were grown on a 300 nm GaP buffer layer and were 800 nm thick. We examined $GaP_{1-y}N_y$ samples with $y=0.7\%$, 1%, 2.3%, and 3.5%. The $GaAs_{1-y}N_y$ samples used for most of the experiments reported here were grown by plasma-assisted, solid-source MBE on an undoped (001) GaAs substrate. A 350 nm thick $GaAs_{1-y}N_y$ layer with $y=0.87\%$ was grown on a 1 μm thick GaAs buffer layer and was capped with a 5 nm thick layer of GaAs. The substrate for the $GaAs_{1-y}N_y$ epitaxial layer was 2 mm thick so that samples suitable for uniaxial stress measurements could be prepared. Hydrogenation or deuteration of samples was performed with a Kaufman ion source with the samples held at 300 °C. The ion energy was 100 eV, and current densities of $\sim 10\ \mu A/cm^2$ were used. Anneals were performed in a tube furnace in a He ambient.

Photoluminescence measurements for $GaP_{1-y}N_y$ samples were performed with a grating monochromator, an Ar^+ laser, and a cooled photomultiplier with a GaAs cathode; for $GaAs_{1-y}N_y$ samples, a frequency-doubled vanadate:Nd laser and a liquid N_2-cooled InGaAs linear array were used. IR absorption spectra were measured over the range $350-4000\ cm^{-1}$ with a Bomem DA.3 Fourier transform spectrometer equipped with a KBr beam splitter and HgCdTe, InSb, and Si-bolometer detectors. For absorption measurements made in the absence of stress, samples were cooled in a variable-temperature, cold-finger cryostat.

Uniaxial stress experiments were performed with a push rod apparatus that was cooled in an Oxford CF 1204 cryostat using He contact gas. For spectra measured with polarized light, a wire grid polarizer was placed in the IR beam path after the cryostat. $GaAs_{1-y}N_y$ samples for uniaxial stress experiments were prepared with dimensions $2\times3\times10\ mm^3$. Stresses were applied along the long axes of samples that had been oriented along either the [100] or [110] directions. The probing light was incident along the [001] direction.

B. Theory

The computations reported here were carried out with the CRYSTAL2006 code[25] using density functional theory with a gradient-corrected approximation to the exchange-correlation functional (Becke exchange[26] with 20% Hartree-Fock, Lee-Yang-Parr correlation,[27] 90% nonlocal exchange, 81% nonlocal correlation; potential B3LYP). The calculations were carried out in a periodic supercell approach with two hydrogen impurities in face-centered cubic supercells containing 32 other atoms. Computed lattice constants of 5.77 and 5.65 Å were used for GaAs and GaP, respectively. A $4\times4\times4$ k-point mesh of Monkhorst-Pack[28] type was used. The self-consistent field energy convergence criterion was 10^{-7} hartree.

Gaussian basis functions[29] were of the type $s(3)s(1)s(1)sp(1)$ for hydrogen and $s(7)sp(3)sp(1)sp(1)$ for nitrogen. For gallium, arsenic, and phosphorus, most of the

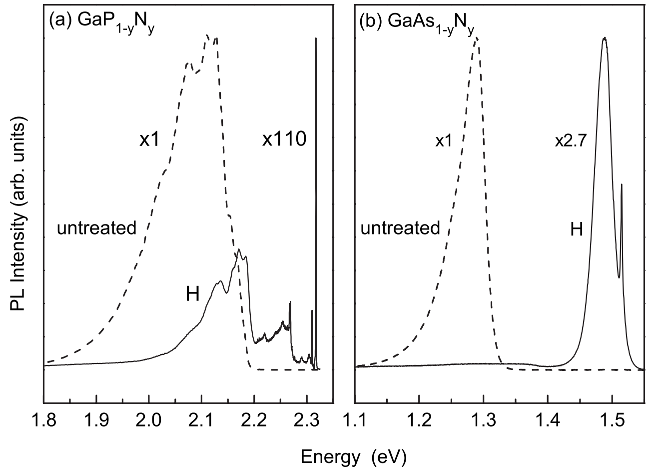

FIG. 2. Photoluminescence spectra measured at 10 K (a) for a $GaP_{0.993}N_{0.007}$ sample hydrogenated with a dose of 1.5×10^{19} ions/cm^2 (laser excitation $\lambda = 458$ nm and power 20 mW), and (b) for a $GaAs_{0.9913}N_{0.0087}$ sample hydrogenated with a dose of 3.0×10^{18} ions/cm^2 (laser excitation $\lambda = 532$ nm and power 10 mW). The spectra shown with dashed lines are for the as-grown samples and the spectra shown with solid lines were measured following hydrogenation.

calculations utilized Barthelat-Durand[30] pseudopotentials, with corresponding basis functions.

III. EXPERIMENTAL AND THEORETICAL RESULTS AND ANALYSES

Photoluminescence spectra were measured for our $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ samples to confirm the shift in the band gap energy caused by hydrogenation or deuteration. The effect of hydrogenation on the N modes of $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ was also examined. The annealing behaviors of the band gap shifts and of the N modes are used in the following sections as benchmarks to support the assignments of the H (and D) vibrational lines observed in hydrogenated (and deuterated) $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ to the centers that are responsible for the shifts of the band gap.

Selected photoluminescence spectra are shown in Figs. 2(a) and 2(b). The band gap energies (0 K) of GaAs and GaP are 1.519 and 2.350 eV, respectively. Untreated samples show band gap energies that have been shifted to lower energy by the presence of N. The spectra shown in Fig. 2 confirm that hydrogenation has caused the band gap energies to increase in our samples to near the values obtained for N-free GaP and GaAs, similar to results that have been reported previously.[7,31,32] In $GaP_{1-y}N_y$, a number of bound exciton features are revealed by hydrogenation or deuteration. Annealing at temperatures between 400 and 500 °C has been shown to completely eliminate the effect of hydrogenation or deuteration, causing the reduced band gap energies that are characteristic of the dilute III-N-V alloys to be recovered.[7]

Previous studies of $GaAs_{1-y}N_y$ identified a vibrational line at 471 cm^{-1} that was assigned to an isolated ^{14}N atom substituting on an As site.[33,34] A vibrational line at 458 cm^{-1} due to ^{15}N was also observed, supporting this assignment.[34] A recent study of $GaP_{1-y}N_y$ by Raman spectroscopy revealed a similar N mode at 496.5 cm^{-1} (room temperature) that was assigned to a N atom substituting on a P site.[8] Figure 3 shows IR spectra (4.2 K) for $GaP_{1-y}N_y$ samples with several N concentrations. The 496 cm^{-1} line increases in intensity as the N concentration is increased, consistent with its assignment to a N mode.

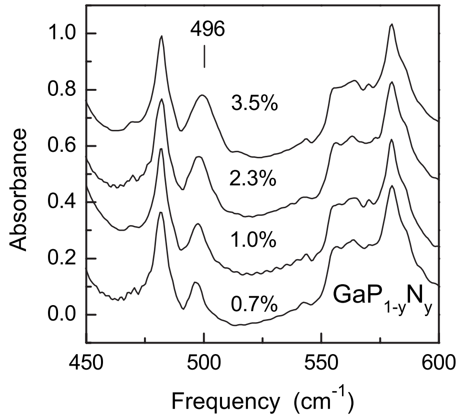

FIG. 3. Absorbance spectra measured near 4.2 K with a resolution of 2 cm^{-1} for $GaP_{1-y}N_y$ epitaxial layers with different N concentrations grown on GaP substrates. For these spectra, the empty sample holder was used for the reference. The base line corrected spectra are displaced vertically for clarity.

The N mode in $GaAs_{1-y}N_y$ was found previously to be eliminated by hydrogenation or deuteration.[17,32] Similarly, the intensity of the N mode in $GaP_{1-y}N_y$ is also reduced by hydrogenation. Difference spectra are shown in Figs. 4(a) and 4(b) for deuterated samples of $GaP_{0.993}N_{0.007}$ and $GaAs_{0.992}N_{0.008}$ that were subsequently annealed at the temperatures shown. A sample without H or D was used for reference, so the N mode, whose intensity is reduced by deuteration, is seen as a negative peak in these spectra. Upon annealing near 400 °C, the reduction in the N-mode intensity caused by deuteration is eliminated for both the $GaP_{0.993}N_{0.007}$ and $GaAs_{0.992}N_{0.008}$ samples, further supporting the assignment of the 496.5 cm^{-1} line seen in $GaP_{1-y}N_y$ to isolated N_P, similar to the 471 cm^{-1} line assigned to N_{As} in $GaAs_{1-y}N_y$. This annealing behavior for the recovery of the N mode that is common to both $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ agrees with the recovery of the band gap energies of $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ that has been studied previously by photoluminescence measurements for hydrogenated or deuterated samples.[7,31,32]

A. Stretching modes: Experiment

The hydrogenation of $GaAs_{1-y}N_y$ was found previously to introduce two N-H stretching modes.[17] The hydrogenation of $GaP_{1-y}N_y$ produces a similar N-H mode spectrum (Fig. 5). The $GaP_{1-y}N_y$ sample with $y = 0.7\%$ showed the sharpest N-H (and N-D) lines, so the IR results for this sample have been the focus of most of our work. The deuteration of $GaP_{1-y}N_y$ produces a spectrum that shows the corresponding

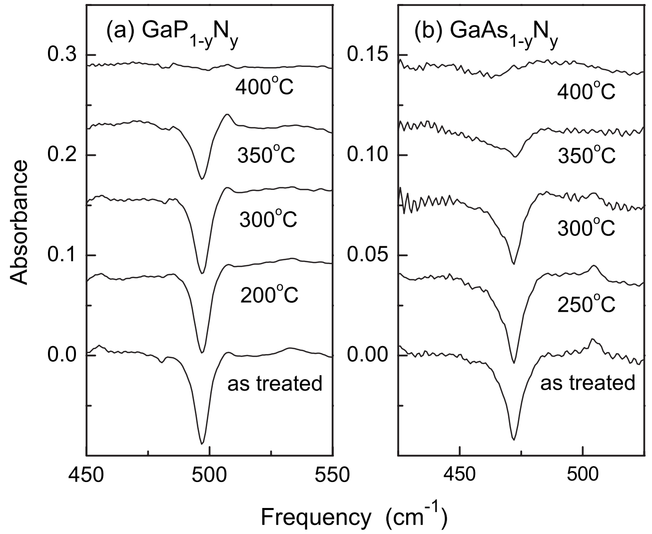

FIG. 4. Absorbance spectra measured near 4.2 K with a resolution of 2 cm^{-1} for (a) a deuterated $\text{GaP}_{0.993}\text{N}_{0.007}$ sample (with dose 1×10^{19} ions/cm^2) and (b) a deuterated $\text{GaAs}_{0.992}\text{N}_{0.008}$ sample (with dose 2×10^{18} ions/cm^2) that were subsequently annealed (30 min) at the temperatures shown. Samples that did not contain D were used for reference, so the N mode whose intensity is reduced by deuteration is seen as a downward peak in the spectrum.

N-D mode [Fig. 6(a)] that is remarkably similar to that seen for deuterated $\text{GaAs}_{1-y}\text{N}_y$ [Fig. 6(b)]. Upon annealing, the N-D stretching modes disappear together near 400 °C (Fig. 7) and at the same annealing temperature where the N mode and band gap energy of $\text{GaP}_{1-y}\text{N}_y$ are recovered. These annealing results support the assignment of the N-H (and N-D) vibrational lines to the defect responsible for the shift of the band gap energy caused by hydrogenation. Frequencies of the N-H and N-D stretching modes of hydrogenated and deuterated $\text{GaP}_{1-y}\text{N}_y$ and $\text{GaAs}_{1-y}\text{N}_y$ are given in Tables I and II.

Typical stretching frequencies for N-H and Ga-H modes in semiconductors are approximately 3000 and 1800 cm^{-1}, respectively. The frequencies of the IR lines seen near 3200 and 2970 cm^{-1} for both $\text{GaP}_{1-y}\text{N}_y$:H and $\text{GaAs}_{1-y}\text{N}_y$:H are consistent with H bonded to a light atom such as N. There is no evidence for any vibrational lines that might be due to a Ga-H stretching mode. The frequency ratio $r = \omega_\text{H}/\omega_\text{D}$ is also sensitive to the atom to which the H (or D) atom is attached. For H or D attached to an infinitely massive atom, a value of $r = (\text{m}_\text{D}/\text{m}_\text{H})^{1/2} = 1.414$ would be expected. For H bonded to a light atom such as O or N, a typical value for r is 1.34, and for H bonded to a heavier atom such as Ga, a typical value for r is 1.39. For all of the vibrational lines observed for

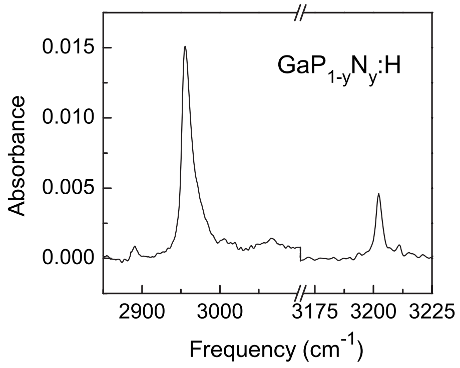

FIG. 5. Absorbance spectrum measured near 4.2 K with a resolution of 1 cm^{-1} showing the H-stretching modes for a $\text{GaP}_{0.993}\text{N}_{0.007}$ sample that had been hydrogenated with a dose of 1.5×10^{19} ions/cm^2.

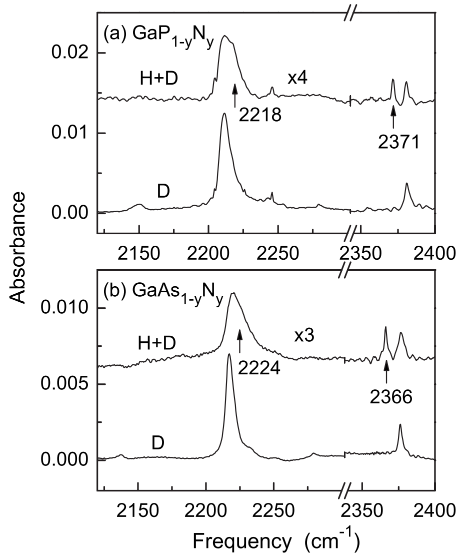

FIG. 6. Absorbance spectra measured near 4.2 K with a resolution of 1 cm^{-1} showing the D-stretching modes for (a) $\text{GaP}_{0.993}\text{N}_{0.007}$ and (b) $\text{GaAs}_{0.9913}\text{N}_{0.0087}$ samples. In panel (a) the lower spectrum was measured for a sample that had been deuterated with a dose 1×10^{19} ions/cm^2 and the upper spectrum was measured for a sample treated with both H and D with a dose 2.4×10^{19} ions/cm^2. In panel (b) the lower spectrum was measured for a sample that had been deuterated with a dose 3×10^{18} ions/cm^2 and the upper spectrum was measured for a sample treated with both H and D with a dose 3×10^{18} ions/cm^2.

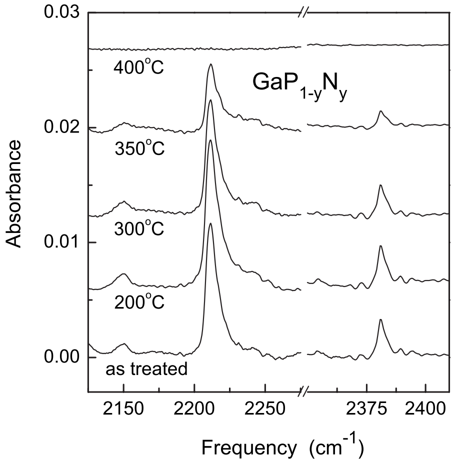

FIG. 7. Absorbance spectra measured near 4.2 K with a resolution of 1 cm^{-1} showing the D-stretching modes for a deuterated $\text{GaP}_{0.993}\text{N}_{0.007}$ sample (with dose 1×10^{19} ions/cm^2) that was subsequently annealed (30 min) at the temperatures shown.

TABLE I. Experimental vibrational frequencies (in units cm^{-1}) for the H and D modes seen in hydrogenated and deuterated $GaP_{0.993}N_{0.007}$. The frequency ratio $r=\omega_H/\omega_D$ is also given. Weak lines are indicated by a (w).

Assignments	ω_H	ω_D	r
Stretch	3202	2381	1.345
Stretch	2955	2211	1.336
Second harmonic	2891(w)	2150(w)	1.345
In-plane wag	1458	1082	1.348
Out-of-plane wag	1069		

hydrogenated $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$, a typical value for r is 1.345, consistent with their assignments to N-H vibrational modes.

Two possible $H_2^*(N)$ configurations were predicted by theory,[10–15] raising the question of whether the two N-H modes that have been observed are due to just one defect that contains two inequivalent N-H oscillators or to two different defects, each of which contains a single N-H oscillator. This question is answered by IR spectra that are measured for III-N-V samples that contain both H and D. We focus on the D-stretching spectra observed for $GaAs_{1-y}N_y$ that are shown in Fig. 6(b). For a deuterated sample, there are two D-stretching lines observed at 2376 and 2217 cm^{-1}. For a sample that contained H and D, two additional D-stretching lines appear at a reduced separation compared to the lines in the sample containing only D. One line is fully resolved and appears at a frequency of 2366 cm^{-1}. A second line appears as a poorly resolved shoulder that broadens the 2217 cm^{-1} line. A subtraction of the D spectrum from the H+D spectrum yields a value of 2224 cm^{-1} for the frequency of the line giving rise to the shoulder. The appearance of two new lines with reduced separation upon the introduction of H and D establishes that the D-stretching lines at 2376 and 2217 cm^{-1} are due to a single defect that contains two coupled D atoms. For the corresponding defects that contain both H and D (that is, the H-N-D and D-N-H complexes), the stretching modes are dynamically decoupled to produce the pair of new D-stretching lines shown in Fig. 6(b).[35]

Very similar vibrational spectra are observed for $GaP_{1-y}N_y$ into which H and D had been introduced [Fig. 6(a)]. For a deuterated sample, D-stretching lines are observed at 2381 and 2211 cm^{-1}. For a sample treated with both H and D, dynamically decoupled lines are observed at 2371 and 2218 cm^{-1}. These results show that the vibrational properties seen previously for $GaAs_{1-y}N_y$ (Ref. 17) are also common to $GaP_{1-y}N_y$. The observation that the dominant defect in hydrogenated $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ contains two inequivalent, weakly coupled, N-H oscillators and no Ga-H bonds rules out $H_2^*(N)$ structures for both of these dilute III-N-V alloys.

TABLE II. Experimental vibrational frequencies (in units cm^{-1}) for the H and D modes seen in hydrogenated and deuterated $GaAs_{0.9913}N_{0.0087}$. The frequency ratio $r=\omega_H/\omega_D$ is also given. Weak lines are indicated by a (w).

Assignments	ω_H	ω_D	r
Stretch	3195	2376	1.345
Stretch	2967	2217	1.338
Second harmonic	2868(w)	2137(w)	1.342
In-plane wag	1447	1076	1.345
Out-of-plane wag	1068	798	1.338
Out-of-plane wag	1057		

It is ironic that the vibrational properties that have been observed for H in the dilute III-N-V alloys are remarkably similar to what had been seen previously for H_2^* in Si (Ref. 36), a defect that consists of H_{BC} and H_{AB} atoms lying along the same trigonal axis, and that these same vibrational properties rule out the presence of $H_2^*(N)$ in III-N-V materials. In the Si case, there are two coupled Si-H stretch modes. The coimplantation of H and D into Si was shown to produce an HD^* complex that gives rise to dynamically decoupled Si-H and Si-D modes. H_2^* in Si and the H-N-H centers seen in the III-N-V alloys show similar spectroscopic characteristics because the H_2^* structure in Si contains two Si-H oscillators and the H-N-H structure in III-N-V materials contains two weakly coupled N-H oscillators. However, the H-N-H structure does not contain a Ga-H bond that would be characteristic of $H_2^*(N)$.

B. Stretching modes: Theory

A defect structure (Fig. 1) that is consistent with the vibrational properties of the H-N-H complex seen in both $GaAs_{1-y}N_y$:H and $GaP_{1-y}N_y$:H has been predicted by theory.[18,19] This defect consists of two inequivalent H atoms bonded to the same N atom. A related structure with both H atoms near bond centers was proposed by Bonapasta *et al.*[15] However, the apparent C_{2v} symmetry of their structure is inconsistent with the requirement imposed by experiment that the two H atoms be inequivalent. Fowler *et al.*[18] and Du *et al.*[19] independently proposed the canted structure with C_{1h} symmetry for the H-N-H defect in $GaAs_{1-y}N_y$:H shown in Fig. 1 and have calculated vibrational properties that are in very good agreement with experiment. Ciatto *et al.*[20] found that such a structure is also consistent with the results of XANES experiments. Du *et al.* also investigated the electronic structure of the H-N-H defect shown in Fig. 1 and determined that the termination of the two nitrogen bonds with hydrogen atoms and the formation of the Ga-Ga bond clear the $GaAs_{1-y}N_y$ band gap of states.[19]

In Ref. 18 we had used[37] CRYSTAL2003 to carry out detailed calculations on H-N-H in $GaAs_{1-y}N_y$. By minimizing the energy and then carrying out point-by-point calculations, we obtained anharmonic vibrational frequencies for both stretch and bend modes. Details of these calculations are given in Ref. 18. The use of CRYSTAL2006 for H-N-H in both $GaAs_{1-y}N_y$ and $GaP_{1-y}N_y$ in the present case allows both energy minimization and "automatic" calculation of harmonic frequencies.

We find that the H-N-H defect in $GaP_{1-y}N_y$ is predicted to have harmonic vibrational properties so similar to those in

TABLE III. Harmonic vibrational frequencies (in units cm^{-1}) calculated for the hydrogen and deuterium vibrational modes of the H-N-H, H-N-D, D-N-H, and D-N-D centers in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ and $\mathrm{GaP}_{1-y}\mathrm{N}_y$. Because of the absence of anharmonic corrections, these results should not be compared directly to experiment. Rather, their value is in comparison within and between the two systems.

System	Type	GaP	GaAs
H-N-H	Stretch	3171	3298
		3003	3084
	In-plane wag	1718	1674
		682	765
	Out of plane	1217	1271
		1142	1156
H-N-D	Stretch	3021	3085
		2300	2403
	In-plane wag	1521	1485
		573	649
	Out of plane	1217	1269
		828	845
D-N-H	Stretch	3158	3297
		2201	2247
	In-plane wag	1501	1477
		580	643
	Out of plane	1142	1163
		874	923
D-N-D	Stretch	2311	2409
		2184	2241
	In-plane wag	1242	1221
		518	581
	Out of plane	878	942
		823	828

$\mathrm{GaAs}_{1-y}\mathrm{N}_y$ (Table III) that we have not repeated the extensive anharmonic analyses reported for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ in Ref. 18. Again, a defect with C_{1h} symmetry is predicted, looking remarkably identical to that found in Ref. 18: the H-N-H angle differs from that of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ by less than 0.2° and the "canting" angle differs by 1°. (In this context it should be noted that in Ref. 18, the bond-centered and interstitial hydrogens in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$, H_B and H_I, were inadvertently mislabeled in the discussion in Sec. II D. In particular, the N-H_B stretching force constant is predicted to be smaller than that for N-H_I. A similar result is found for the H-N-H defect in $\mathrm{GaP}_{1-y}\mathrm{N}_y$.) As seen in Table III, the harmonic frequencies for H-N-H in $\mathrm{GaP}_{1-y}\mathrm{N}_y$ are predicted to equal those in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ with an average difference of less than 5%. While these frequencies by themselves should not be compared in detail with experiment, the similarity of results in the two systems means that for the purposes of detailed experimental analysis, it is appropriate to utilize the results of the anharmonic analyses of Ref. 18.

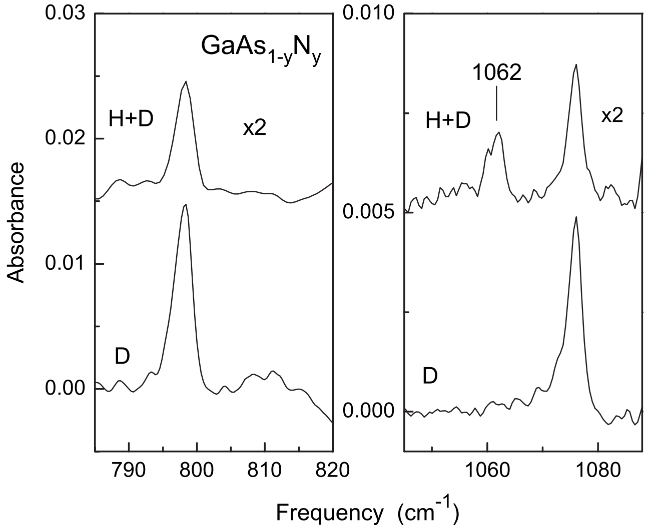

FIG. 8. Absorbance spectra measured near 4.2 K with a resolution of 1 cm^{-1} showing the D-wagging modes for a $\mathrm{GaAs}_{0.9913}\mathrm{N}_{0.0087}$ sample. The lower spectrum was measured for a sample that had been deuterated with a dose 3×10^{18} ions/cm^2 and the upper spectrum was measured for a sample treated with both H and D with a dose 3×10^{18} ions/cm^2.

C. Wagging modes: Theory

The assignments of the wagging modes seen previously for hydrogenated $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ have been incomplete.[17] Theory for the H-N-H center shown in Fig. 1 predicted four wagging modes, two in-plane wags and two out-of-plane wags. Of these, the highest and lowest frequencies arise from the in-plane wags.[18] This result helps us to clarify the assignments of the wagging modes seen in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ and $\mathrm{GaP}_{1-y}\mathrm{N}_y$ treated with H or D.

Calculations[18] including anharmonic corrections predicted the presence of two in-plane wagging modes with frequencies in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H at 1333 and 606 cm^{-1} and two out-of-plane wagging modes at 1086 and 1046 cm^{-1}. The corresponding *harmonic* frequencies for these modes are given in Table III. Because the calculated harmonic frequencies for these modes in both $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H and $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H are so similar, it should be fruitful to use comparative results from both systems to deduce assignments of experimental frequencies.

D. Wagging modes: Experiment

An H vibrational line at 1447 cm^{-1} and its D counterpart at 1076 cm^{-1} were previously assigned to N-H and N-D wagging. An additional line was seen at 798 cm^{-1} in deuterated samples, but no H counterpart was found, making the assignment of this line to a D-wagging mode uncertain. Spectra of the 1076 and 798 cm^{-1} lines that were observed for a deuterated $\mathrm{GaAs}_{0.9913}\mathrm{N}_{0.0087}$ sample are shown in Fig. 8.

Spectra for $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ samples that had been treated with H or D are shown in Fig. 9. For the hydrogenated $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ sample, there are two lines at 1458 and

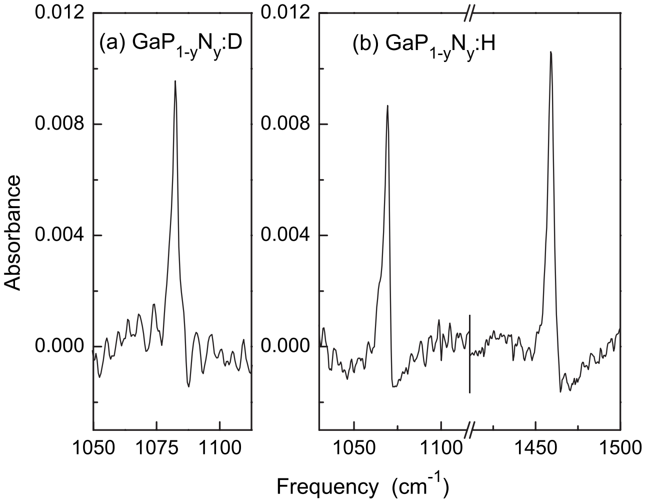

FIG. 9. Absorbance spectra measured near 4.2 K with a resolution of 1 cm^{-1} showing (a) the D wagging mode for a deuterated $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ sample (with dose 1×10^{19} ions/cm^2) and (b) the H-wagging modes for a hydrogenated $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ sample (with dose 1.5×10^{19} ions/cm^2).

1069 cm^{-1}. For the deuterated sample, there is a line at 1082 cm^{-1} that is the D counterpart of the 1458 cm^{-1} line. These IR lines are eliminated by an anneal at 400 °C, similar to the behavior of both the N mode at 496 cm^{-1} (Fig. 4) and the H-stretching lines (Fig. 7), providing support for their assignment to the same H-N-H defect that is responsible for the shift in band gap energy for $\mathrm{GaP}_{1-y}\mathrm{N}_y$. The frequencies of the lines seen for $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ are given in Table I. A comparison with the predictions of theory suggests the assignment of the 1458 cm^{-1} line seen for hydrogenated $\mathrm{GaP}_{0.993}\mathrm{N}_{0.007}$ to the high-frequency, in-plane, N-H wagging mode, and a similar assignment for the 1447 cm^{-1} line seen for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$. The D counterparts of both of these lines are assigned to the corresponding in-plane, N-D wagging modes.

The vibrational spectrum seen for $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H complements the results seen for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H. The 1069 cm^{-1} line seen for hydrogenated $\mathrm{GaP}_{1-y}\mathrm{N}_y$ is a candidate for an additional N-H wagging mode. The D-wagging counterpart of the 1069 cm^{-1} line has not been observed in deuterated $\mathrm{GaP}_{1-y}\mathrm{N}_y$ because of interference with phonon-related absorption. However, the unassigned line at 798 cm^{-1} seen for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:D is near the frequency that would be expected for the N-D wagging counterpart of the 1069 cm^{-1} N-H wagging line. Therefore, it seems reasonable to assign the 1069 cm^{-1} line seen in $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H to one of the out-of-plane, N-H wagging modes predicted by theory for the H-N-H complex and the 798 cm^{-1} line seen in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:D to an out-of-plane N-D wagging mode for the D-N-D complex.

The appearance of an N-H wagging line at 1069 cm^{-1} in $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H with no corresponding feature in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H prompted a closer examination of the vibrational spectrum of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H because the IR spectra of these materials are, otherwise, so similar. Spectra measured for the N-H wagging region of $\mathrm{GaAs}_{0.9913}\mathrm{N}_{0.0087}$:H are shown in Fig. 10. A strong N-H wagging line is seen at 1447 cm^{-1} and is eliminated by annealing near 400 °C, similar to other lines of the H-N-H centers seen in $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H and $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H. Two additional lines are seen at 1068 and 1057 cm^{-1}. Their correspondence to the 1069 cm^{-1} line in $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H and to predictions of theory[18] suggests their assignment to the two out-of-plane wag modes. These lines are approximately seven times weaker than the 1447 cm^{-1} line, explaining why they had not been seen in previous experiments. They are also eliminated by an anneal at 400 °C, supporting their assignment to the same H-N-H complex.

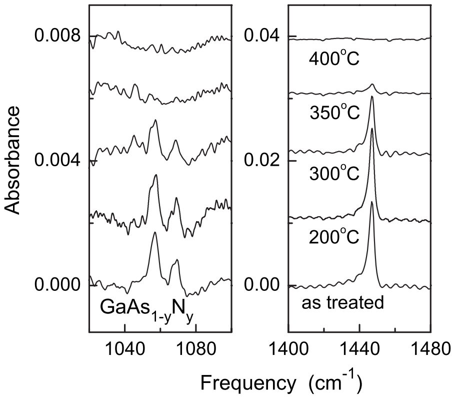

FIG. 10. Absorbance spectra measured near 4.2 K with a resolution of 1 cm^{-1} showing the H-wagging modes for a hydrogenated $\mathrm{GaAs}_{0.9913}\mathrm{N}_{0.0087}$ sample (with a dose 3×10^{18} ions/cm^2) that was subsequently annealed (30 min) at the temperatures shown.

Why are not the same wagging lines seen in both $\mathrm{GaP}_{1-y}\mathrm{N}_y$:H and $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H? One possibility is that in $\mathrm{GaP}_{1-y}\mathrm{N}_y$, one of the out-of-plane wag modes is considerably more intense than the second which, therefore, has not been observed. If the two out-of-plane wagging modes were to be accidentally close in frequency, they could be coupled by anharmonic interactions and share their intensity. Such an accidental coupling of the out-of-plane wagging modes would explain why two lines are seen only in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$:H and also why each of these individual lines is weaker than the other lines assigned to wagging-mode vibrations in both $\mathrm{GaP}_{1-y}\mathrm{N}_y$ and $\mathrm{GaAs}_{1-y}\mathrm{N}_y$.

We have also attempted to observe the wagging-mode spectrum for the $\mathrm{GaAs}_{0.9913}\mathrm{N}_{0.0087}$ sample treated with H and D. Only the in-plane D-wagging mode at 1076 cm^{-1} gave rise to a new, dynamically decoupled line at 1062 cm^{-1} (Fig. 8). This result shows that the wagging modes are also vibrationally coupled. There is no additional line seen in the same sample associated with the out-of-plane wagging mode at 798 cm^{-1}, suggesting that the 1076 cm^{-1} D-wagging mode is coupled to the other in-plane wagging mode that is predicted to lie at much lower frequency.

A Fermi resonance interaction[38] of the second harmonic of the in-plane wagging mode and an N-H stretching mode confirms that both modes are associated with the same H-N-H defect. For example, Fig. 5 shows a weak line at 2891 cm^{-1} for a hydrogenated $\mathrm{GaP}_{1-y}\mathrm{N}_y$ sample [with Fig. 6(a) showing its counterpart at 2150 cm^{-1} for a deuterated sample]. This weak line is assigned to the second harmonic of the 1458 cm^{-1} line whose intensity is strengthened by

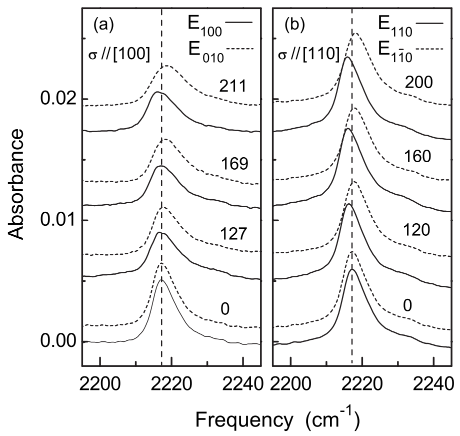

FIG. 11. Effect of stress applied along the (a) [100] and (b) [110] directions for the 2217 cm^{-1} line of the D-N-D defect in $GaAs_{0.9913}N_{0.0087}$. Spectra were measured with polarized light (for a viewing direction along [001]) near 5 K with a resolution of 1 cm^{-1}. The magnitude of the applied stress is given in units MPa and the polarization directions are shown.

Fermi resonance,[38] i.e., by an anharmonic interaction with the 2955 cm^{-1} N-H stretching mode. The situation is similar to $GaAs_{1-y}N_y$ where the line at 2868 cm^{-1} (Table II) was assigned to the second harmonic of the wagging mode at 1447 cm^{-1} whose intensity is strengthened by Fermi resonance with the 2967 cm^{-1} stretching mode.[17]

E. Uniaxial stress

The vibrational lines of the D-N-D center were measured as a function of applied uniaxial stress for stresses up to ~200 MPa for the [100] and [110] stress directions for oriented $GaAs_{0.993}N_{0.007}$ samples that were grown on a 2 mm thick GaAs substrate. Only the 2217 cm^{-1} line showed appreciable shifts under stress compared to the IR linewidths of roughly 3–9 cm^{-1}. Spectra for the 2217 cm^{-1} line measured as a function of stress are shown in Fig. 11. The 2217 cm^{-1} line is split into two components with different polarization dependences for both the [100] and [110] stress directions. These results are inconsistent with a trigonal defect such as H_2^* which would not show a splitting of the spectral line for a nondegenerate vibrational mode for a [100] applied stress. The data in Fig. 11 reveal a symmetry for the D-N-D complex that must be C_{2v} or lower.[39] Unfortunately, the widths of the lines do not permit the resolution of the additional splittings that would be characteristic of a defect with C_{1h} symmetry required by our analysis of the vibrational spectra.

IV. CONCLUSION

In conclusion, both the experimental and theoretical results for hydrogenated $GaP_{1-y}N_y$ are remarkably similar to previous results[17,18] for $GaAs_{1-y}N_y$. The vibrational spectrum observed for hydrogenated $GaP_{1-y}N_y$ shows two N-H stretching lines at 3202 and 2955 cm^{-1}. Spectra measured for samples that contain both H and D show that these N-H lines are due to a defect with two weakly coupled N-H modes. Density functional theory predicts a canted H-N-H defect structure with C_{1h} symmetry and vibrational properties that are in good agreement with experiment. Corresponding N-D lines are also observed and are explained similarly.

The wagging-mode spectra seen for $GaP_{1-y}N_y$ complement previous results[17] for $GaAs_{1-y}N_y$. In addition to a hydrogen-wagging mode at 1458 cm^{-1}, there is a second wagging mode at 1069 cm^{-1} in hydrogenated $GaP_{1-y}N_y$ that had not been seen previously for $GaAs_{1-y}N_y$. Theory suggests the assignment of the 1458 and 1069 cm^{-1} lines to in-plane and out-of-plane wagging modes, respectively.

A closer examination of hydrogenated $GaAs_{1-y}N_y$ revealed two weak lines at 1068 and 1057 cm^{-1} in addition to the in-plane wagging mode at 1447 cm^{-1} reported previously.[17] The 1068 and 1057 cm^{-1} lines are assigned to out-of-plane N-H wagging modes. The assignment of the wagging modes for both $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ provides further support for an H-N-H center with C_{1h} symmetry. The formation of an H-N-H center and the absence of H_2^*(N) in both $GaP_{1-y}N_y$ and $GaAs_{1-y}N_y$ show that the experimental results found previously[17] for $GaAs_{1-y}N_y$ by vibrational spectroscopy are not anomalous but, instead, are general to hydrogenated III-N-V materials.

In spite of the progress that has been made toward understanding the dominant nitrogen- and hydrogen-containing defects in the hydrogenated III-N-V alloys, open questions remain. Defect structures containing more than two hydrogen atoms per nitrogen atom have been predicted[22] and recent experimental results[21,23,24] also suggest that additional hydrogen can be added to the basic H-N-H structure that is required to explain the band gap shift caused by hydrogen. The experimental results reported here for samples hydrogenated at 300 °C can be explained by an H-N-H complex. If additional H atoms are present, their vibrational coupling to the H-N-H core must be weak. Experiments are planned to investigate whether these additional H atoms will be present when hydrogenation treatments are carried out at lower temperatures. Moreover, calculations of possible structures and their vibrational properties are in progress. We anticipate that complementary studies by vibrational spectroscopy and theory will continue to play an important role in answering these questions.

ACKNOWLEDGMENTS

We thank George D. Watkins for helpful discussions. Work performed at L. U. was supported by NSF Grant No. 0403641 and an NSF REU site grant.

[*] Permanent address: Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA.

[†] Permanent address: Department of Astronomy, University of Florida, Gainesville, FL 32611, USA.

[‡] Author to whom correspondence should be addressed; michael.stavola@lehigh.edu

[§] Permanent address: Department of Physics, University of Pittsburgh at Johnstown, Johnstown, PA 15904, USA.

[1] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).

[2] W. G. Bi and C. W. Tu, Appl. Phys. Lett. **70**, 1608 (1997).

[3] *Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, Amsterdam, 2005).

[4] *Physics and Applications of Dilute Nitrides*, edited by I. A. Buyanova and W. M. Chen (Taylor & Francis, New York, 2004).

[5] A. Polimeni, G. Baldassarri H. v., H. M. Bissiri, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 201304(R) (2001).

[6] A. Polimeni and M. Capizzi, in *Physics and Applications of Dilute Nitrides* (Ref. 4), Chap. 6.

[7] A. Polimeni, M. Bissiri, M. Felici, M. Capizzi, I. A. Buyanova, W. M. Chen, H. P. Xin, and C. W. Tu, Phys. Rev. B **67**, 201303(R) (2003).

[8] I. A. Buyanova, M. Izadifard, I. G. Ivanov, J. Birch, W. M. Chen, M. Felici, A. Polimeni, M. Capizzi, Y. G. Hong, H. P. Xin, and C. W. Tu, Phys. Rev. B **70**, 245215 (2004).

[9] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992).

[10] P. Dixon, D. Richardson, R. Jones, C. D. Latham, S. Öberg, V. J. B. Torres, and P. Briddon, Phys. Status Solidi B **210**, 321 (1998).

[11] A. Janotti, S. B. Zhang, and S.-H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).

[12] Y.-S. Kim and K. J. Chang, Phys. Rev. B **66**, 073313 (2002).

[13] A. Janotti, S. B. Zhang, S.-H. Wei, and C. G. Van de Walle, Phys. Rev. Lett. **89**, 086403 (2002).

[14] A. Amore Bonapasta, F. Filippone, P. Giannozzi, M. Capizzi, and A. Polimeni, Phys. Rev. Lett. **89**, 216401 (2002).

[15] A. Amore Bonapasta, F. Filippone, and P. Giannozzi, Phys. Rev. B **68**, 115202 (2003).

[16] M. Stavola, in *Identification of Defects in Semiconductors*, edited by M. Stavola (Academic, San Diego, CA, 1999), Chap. 3, p. 153.

[17] F. Jiang, M. Stavola, M. Capizzi, A. Polimeni, A. Amore Bonapasta, and F. Filippone, Phys. Rev. B **69**, 041309(R) (2004).

[18] W. B. Fowler, K. R. Martin, K. Washer, and M. Stavola, Phys. Rev. B **72**, 035208 (2005).

[19] M.-H. Du, S. Limpijumnong, and S. B. Zhang, Phys. Rev. B **72**, 073202 (2005).

[20] G. Ciatto, F. Boscherini, A. A. Bonapasta, F. Filippone, A. Polimeni, and M. Capizzi, Phys. Rev. B **71**, 201301(R) (2005).

[21] I. A. Buyanova, W. M. Chen, M. Izadifard, S. J. Pearton, G. Bihler, M. S. Brandt, Y. G. Hong, and C. W. Tu, Appl. Phys. Lett. **90**, 021920 (2007).

[22] A. Amore Bonapasta, F. Filippone, and G. Mattioli, Phys. Rev. Lett. **98**, 206403 (2007).

[23] G. Bisognin, D. De Salvador, A. V. Drigo, E. Napolitani, A. Sambo, M. Berti, A. Polimeni, M. Felici, M. Capizzi, M. Güngerich, P. J. Klar, G. Bais, F. Jabeen, M. Piccin, S. Rubini, F. Martelli, and A. Franciosi, Appl. Phys. Lett. **89**, 061904 (2006).

[24] M. Berti, G. Bisognin, D. De Salvador, E. Napolitani, S. Vangelista, A. Polimeni, M. Capizzi, F. Boscherini, G. Ciatto, S. Rubini, F. Martelli, and A. Franciosi, Phys. Rev. B **76**, 205323 (2007).

[25] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, Ph. D'Arco, and M. Llunell, *Crystal06 User's Manual* (University of Torino, Torino, 2006).

[26] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[27] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[28] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[29] Basis functions were obtained from the web site of M. D. Towler, http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html

[30] P. Durand and J. C. Barthelat, Theor. Chim. Acta **38**, 283 (1975); J. C. Barthelat and P. Durand, Gazz. Chim. Ital. **108**, 225 (1978).

[31] G. Baldassarri H. v. H., M. Bissiri, A. Polimeni, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, Appl. Phys. Lett. **78**, 3472 (2001).

[32] A. Polimeni, G. Ciatto, L. Ortega, F. Jiang, F. Boscherini, F. Filippone, A. A. Bonapasta, M. Stavola, and M. Capizzi, Phys. Rev. B **68**, 085204 (2003).

[33] T. Prokofyeva, T. Sauncy, M. Seon, M. Holtz, Y. Qiu, S. Nikishin, and H. Tempkin, Appl. Phys. Lett. **73**, 1409 (1998).

[34] H. Ch. Alt, A. Yu. Egorov, H. Riechert, B. Wiedemann, J. D. Meyer, R. W. Michelmann, and K. Bethge, Appl. Phys. Lett. **77**, 3331 (2000).

[35] There should also be a pair of new H-stretching lines for samples that contain H and D. A decoupled H-stretching line has been seen at 3192 cm^{-1} (the isotopic sibling of the 2366 cm^{-1} line). Experimental difficulties have prevented the observation of the H-stretching counterpart of the 2224 cm^{-1} line.

[36] J. D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).

[37] V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. Bush, Ph. D'Arco, and M. Llunell, *Crystal2003 User's Manual* (University of Torino, Torino, 2003).

[38] E. Fermi, Z. Phys. **71**, 250 (1931).

[39] A. A. Kaplyanskii, Opt. Spectrosc. **16**, 329 (1964).