

# Nitrogen-hydrogen complex in GaAs<sub>x</sub>N<sub>1-x</sub> revealed by x-ray absorption spectroscopy

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(Received 10 February 2005; published 5 May 2005)

GaAsN alloys belong to a class of semiconductors with fascinating physical properties. Indeed, a small amount of nitrogen incorporation in GaAs leads to a counterintuitive and large band-gap reduction, and to an unexpected sudden increase in the effective mass of electrons. Even more surprisingly, both electronic and structural changes can be reversed fully and in a tunable manner by hydrogen incorporation. In this paper, we combine x-ray absorption spectroscopy at the nitrogen edge with *ab initio* simulations to investigate the atomic geometry of N-H complexes in hydrogenated GaAsN. In this way, we provide experimental evidence that dihydrogen-nitrogen complexes with  $C_{2v}$  symmetry are the most abundant species in hydrogenated GaAsN. This finding contradicts previous predictions of "in-line"  $N-H_2^*$  complexes as the predominant species, and accounts for recent infrared absorption experiments.

DOI: 10.1103/PhysRevB.71.201301

PACS number(s): 61.72.Bb, 61.10.Ht, 71.15.-m, 71.55.-i

Dilute nitride alloys such as GaAsN have been of tremendous recent interest because of the strong and unexpected modifications exerted by nitrogen on the physical properties of the host lattice. These changes include a giant band-gap reduction<sup>1</sup> and a decrease in the rate at which the band gap depends on external perturbations (such as hydrostatic pressure<sup>2-4</sup> and temperature<sup>4,5</sup>) and a peculiar dependence of the electron effective mass on the nitrogen concentration.<sup>6</sup> All these effects render dilute nitrides attractive for the fabrication of light emitters in the telecommunications wavelength range and of high-efficiency solar cells. Very surprisingly, the dramatic changes induced by nitrogen in dilute nitrides can be reversed fully by hydrogen irradiation.<sup>7-12</sup> Figure 1 summarizes some of the most striking effects of H irradiation as observed in GaAsN. Continuous and dashed lines are the x-ray diffraction (XRD) data of a H-irradiated and untreated GaAsN sample, respectively. As reported previously,<sup>11</sup> XRD of hydrogenated GaAsN shows a disappearance of the diffraction peaks associated with the GaAsN epilayer and a recovery of the GaAs lattice parameter. Concomitantly, H irradiation leads to a nearly full reopening of the band gap, as shown by the photoluminescence spectra shown in the inset of Fig. 1. Other important physical quantities as the electron effective mass,<sup>10</sup> and the temperature coefficient of the band gap<sup>12</sup> are strongly affected by H, too. Such effects are technologically relevant since hydrogen is present in most growth processes and mass-production steps of semiconductor devices. In addition, hydrogen could be used in dilute nitrides as an unique tool for patterning the electronic properties of the crystal on a nanometer scale.

The effects of H irradiation in GaAsN, InGaAsN, and GaPN have triggered many theoretical studies aimed at dis-

covering the microscopic hydrogen-nitrogen complex responsible for the experimental observations.<sup>13-21</sup> All present theories predict that an in-line dihydrogen-nitrogen complex, named  $N-H_2^*$ , is responsible for hydrogen-related effects in dilute nitrides. In the  $N-H_2^*$  complex [ $N-H_2^*$  (a) in Fig. 2], two strong Ga- $H_{BC}$  and N- $H_{AB}$  bonds are formed, which involve, respectively, a  $H_{BC}$  atom in bond center position (BC) between the Ga and N atoms and a  $H_{AB}$  atom in the opposite position with respect to the same nitrogen atom (antibonding position, AB). Very recently, infrared (IR) absorption measurements have shown that the local vibrational mode related to the Ga-N bond disappears in GaAsN after H irradiation.<sup>18</sup> However, no evidence for a Ga- $H_{BC}$  mode was found, contrary to the expectations of the  $N-H_2^*$  (a) model. In that study, *two* N-H stretching modes due to a *same* H-N complex have been detected, instead. It has been recently proposed, based on computation of the defect energetics, that new dihydrogen complexes,  $N-2H_{BC}^{2+}$ , may form in hydrogenated GaAsN (Ref. 19) and GaPN;<sup>20</sup> they consist of *two*  $H_{BC}$  atoms bound to a *single* N atom. One complex has a  $C_{2v}$  symmetry, indicated as  $C_{2v}$ -symm in Fig. 2. In a second  $C_{2v}$ -like complex (indicated as  $C_{2v}$ -asymm in Fig. 2), one of the  $H_{BC}$  ions is located off the N-Ga axes. The  $C_{2v}$  complexes can lead to a recovery of the band-gap energy and to a partial recovery of the lattice parameter.<sup>21</sup> On the other hand, they cannot account for the lattice parameter changes shown in Fig. 1.<sup>21</sup> The motivation of the present study is, therefore, to investigate the local structure of the N-H complex with a technique more direct and quantitative than IR spectroscopy in order to determine whether complexes with  $C_{2v}$ -like symmetry are present.

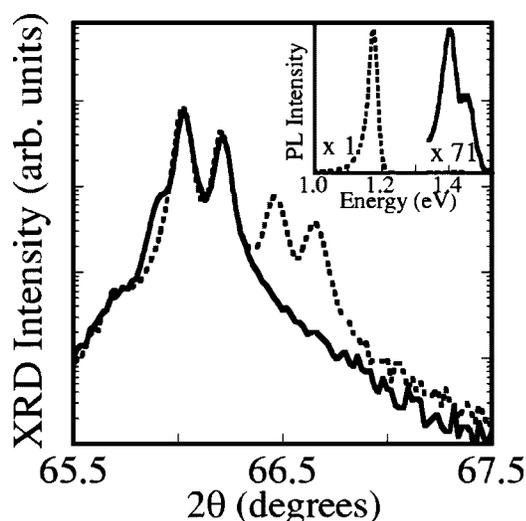


FIG. 1. XRD data near the (004) reflection for  $\text{GaAs}_{0.986}\text{N}_{0.014}$  before (dashed line) and after (continuous line) exposure to a hydrogen dose equal to  $3.0 \times 10^{18}$  ions/cm<sup>2</sup>. The inset reports the low-temperature (10 K) photoluminescence (PL) spectra for the same samples shown in the main part of the figure. In the hydrogenated sample, the low-energy peak is due to the passivated GaAsN epilayer, the high-energy shoulder is likely related to the GaAs substrate. PL multiplication factors are given.

Since the early development of x-ray absorption spectroscopy (XAS), it has been recognized that this technique could provide precious information on the local geometric arrangement of dopants and defects in semiconductors.<sup>22</sup> Up to now, the analysis of the extended part of the XAS spectrum (the extended x-ray absorption fine structure “EXAFS” region) has been used to determine the coordination of a number of dopants in semiconductors.<sup>23</sup> The use of the x-ray absorption near-edge structure (XANES) has been limited or absent in this field, most probably due to the (real and/or perceived) difficulties in simulating the spectral region in which the multiple scattering expansion of the XAS cross section does not converge. However, there is a strong interest in applying XANES since it is more sensitive to the three-dimensional structure of defects than EXAFS, which to a large extent performs a one-dimensional projection of the structure on the interatomic distance axis. For the specific problem at hand, the advantage of XAS as compared to IR spectroscopy is that XAS inherently probes all the atomic geometries present weighing the contribution of each one to the average spectrum with its relative abundance, thus avoiding the interpretative problems of IR due to the varying cross sections of vibrational modes; in fact, some IR lines (e.g., specific wagging modes) are predicted but have never actually been experimentally observed. The method we use also has a more general interest, not limited to the particular field of semiconductors, and the present study of a defect with a relatively simple structure can be considered as a test of the applicability of XANES to the determination of defective local atomic arrangements in condensed matter.

The structural properties of the N-H complexes in GaAsN have been investigated by local density functional (DFT) methods in a supercell approach by using separable

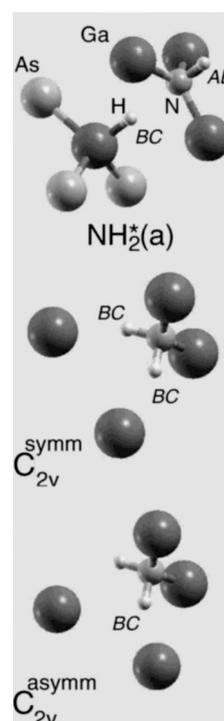


FIG. 2. (a) Sketch of the  $\text{N}-\text{H}_2^*$  (a) and  $\text{C}_{2v}$  symmetric and asymmetric complexes. The  $\text{N}-\text{H}_2^*$  (b) complex has an  $\text{N}-\text{H}_{\text{BC}}-\text{Ga}-\text{H}_{\text{AB}}$  configuration; similar in-line configurations characterize the  $\text{N}-\text{H}_{\text{BC}}$  and  $\text{N}-\text{H}_{\text{AB}}$  monohydrogen complexes.

*ab initio* pseudopotentials.<sup>24,25</sup> Geometry optimizations have been performed by fully relaxing the atomic positions in 64-atom supercells with the PWSCF code.<sup>26</sup> Further details on the theoretical methods have been reported elsewhere.<sup>19,20</sup>

GaAsN/GaAs epilayers were grown by solid source molecular-beam epitaxy on GaAs(001) substrates, with a typical thickness of 300 nm. Postgrowth atomic hydrogen irradiation was performed by a low-energy (100 eV) and low-current (a few tens of  $\mu\text{A}/\text{cm}^2$ ) Kaufman source with the samples held at 300 °C.<sup>7,8</sup> As-grown and H-treated samples were characterized by low-temperature (10 K) photoluminescence, which is excited by the 515-nm line of an  $\text{Ar}^+$  laser, dispersed by a single 1-m monochromator, and detected by Ge detector cooled at liquid nitrogen. XRD measurements were performed by using an unmonochromatized Cu rotating anode.

XANES measurements were performed on the branch line of the ALOISA beamline<sup>27</sup> of the ELETTRA synchrotron radiation facility in Trieste, Italy. The energy dependence of the N-absorption cross section was monitored by recording the intensity of N  $K\alpha$  fluorescence photons using a windowless hyperpure Ge detector. Recently, nitrogen-edge XANES and relative simulations were successfully employed by some of the present authors to study short-range ordering in InGaAsN.<sup>28</sup>

The XANES spectra were simulated in a real-space full multiple scattering approach (FMS) based on Green’s function calculations in the complex plane using the FEFF8 code.<sup>29</sup> The code employs a Barth-Hedin formulation for the exchange-correlation part of the potential and the Hedin-

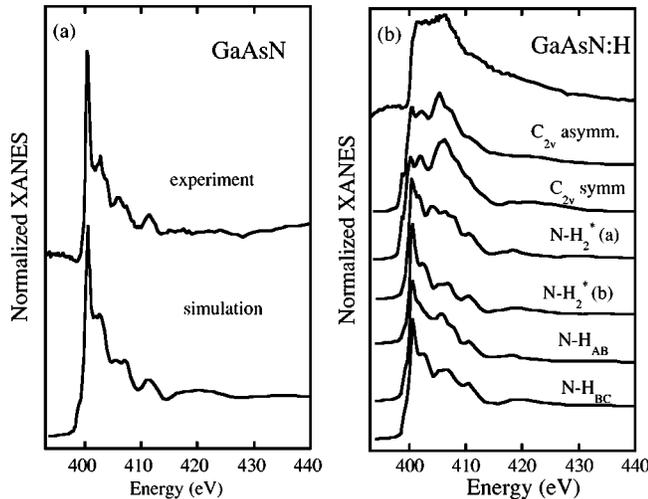


FIG. 3. (a) Experimental and simulated XANES for the as-grown sample before exposure to hydrogen; (b) experimental N  $K$ -edge XANES for the hydrogenated sample of Fig. 1 (top) and corresponding FMS simulations based on the atomic coordinates calculated via DFT in presence of the most stable monohydrogen- and dihydrogen-nitrogen complexes.

Lundqvist self-energy correction; calculation of the potential was performed by using a self-consistent field within a 4-Å radius, a distance that includes the second coordination shell of a central nitrogen in GaAsN. Atomic coordinates for each N-H complex were taken from the DFT calculations described above, repeating eight times a 64-atoms supercell and translating the positions in order to drive a N atom to the center of the cell. The clusters exploited in FMS calculations consisted of 512 atoms for GaAsN, 520 for monohydrogen complexes, and 528 atoms for dihydrogen complexes. The full multiple scattering radius was fixed to 20 Å in order to enclose all the input atoms without using any extra scattering paths. The use of such large clusters is mandatory to reproduce the region of the absorption spectrum close to the edge, where the photoelectron mean free path can reach a few tens of angstroms.

Figure 3(a) shows a comparison of the fluorescence-detected nitrogen  $K$ -edge XANES experimental spectrum with a simulation based on the atomic coordinates obtained by density functional theory (DFT) calculations for GaAs<sub>0.986</sub>N<sub>0.014</sub>. The excellent correspondence between the experimental and simulated spectra demonstrates the soundness of our method. We now consider the effect of H incorporation in GaAsN. Figure 3(b) shows the experimental nitrogen-edge XANES for hydrogenated GaAs<sub>0.986</sub>N<sub>0.014</sub> along with simulations for the most likely N-H complexes (see caption of Fig. 2 for their description). Sizable variations among the simulated XANES line shapes for the different N-H complexes can be observed. Most importantly, only the  $C_{2v}$  complexes both in the symmetric and asymmetric configurations reproduce the main features of the experimental spectrum; in particular the fact that the absorption coefficient does not decrease suddenly after the first maximum (the so-called “white line”) but rather exhibits an extra peak between 405 and 408 eV. Instead, monohydrogen (N-H<sub>BC</sub>, N-H<sub>AB</sub>) and different dihydrogen (N-H<sub>2</sub><sup>\*</sup>) com-

plexes show large discrepancies with, and cannot account for, the experimental XANES spectrum. Thus, a *firm evidence* of the predominant formation of complexes of the  $C_{2v}$ -type in hydrogenated GaAsN is obtained.

We point out that the present method allows a much more direct comparison between experiment and simulation than IR spectroscopy; a full comparison of the experimental spectrum (energy position of the spectral features, their relative intensities and width) with simulations is indeed possible. Also, the present method inherently probes all the atomic geometries present, weighing the contribution of each one to the average spectrum with its relative abundance, thus avoiding the interpretative problems of IR due to the varying cross sections of vibrational modes.

The present results (i) account for the existence of *two* N-H stretching modes related to a *same* N-H complex as found by IR measurements,<sup>18</sup> and (ii) support theoretical predictions of new dihydrogen complexes.<sup>19,20</sup> In addition, these results give support to an assignment of vibrational frequencies calculated for the  $C_{2v}$  complexes to the main IR lines.<sup>30–32</sup> We notice that a dihydrogen-nitrogen complex, similar to the present asymmetric  $C_{2v}$  complex, accounts well for the splitting experimentally observed in the IR local modes of hydrogenated-deuterated GaAsN.<sup>31,32</sup> The clear evidence reported here that the  $C_{2v}$  complexes are the most abundant ones in hydrogenated GaAsN does not exclude that other N-H complexes are present as a minor species. In fact, while both  $C_{2v}$  and N-H<sub>2</sub><sup>\*</sup>(a) complexes explain the reopening of the GaAsN band gap upon H irradiation, only N-H<sub>2</sub><sup>\*</sup>(a) complexes are predicted<sup>21</sup> so far to fully neutralize the changes in the lattice parameter reported<sup>11</sup> in hydrogenated GaAsN.

The success of our method depends on three main factors. First, the high brilliance of x-ray beams recently achieved by third generation synchrotron sources has allowed the recording of high-quality fluorescence-detected N-edge XANES spectra from dilute systems; fluorescence detection in the soft x-ray region is particularly challenging due to low fluorescence yield. Second, advances in the theoretical understanding of the x-ray absorption process have led to the availability of reliable computer codes, able to accurately simulate the XANES spectra. Third, finally, the reliability of the local density DFT methods permits one to achieve accurate results on the microstructure and energetics of defects and complexes in both crystalline and amorphous systems.

The combined experimental-theoretical method adopted here is of general interest in all research areas in which low concentrations of dopants or defects are present. Examples of possible applications include diluted magnetic semiconductors of interest for spintronics, where the site location of a metal impurity (e.g., Mn) or the formation of clusters represent a *crucial* point for understanding the physical properties of the material.

*Note added in proof.* The  $C_{2v}$  complexes considered in this paper are doubly charged. After submitting the manuscript we have performed DFT simulations on *neutral*  $C_{2v}$  complexes. These simulations indicate that neutral  $C_{2v}$  complexes (both in the symmetric and asymmetric configurations) can recover the GaAs lattice constant. However, the

$N-H_2^*$  (a) still results to be the most stable neutral dihydrogen complex, thus suggesting that it could be present as a minor species.

We are grateful to the ALOISA staff and to P. Fons for

assistance during the experiment, L. Ortega for XRD measurements, and C. Ferrero for useful advice on computational aspects. Measurements at ELETTRA were supported by the Synchrotron Radiation Committee of Istituto Nazionale per la Fisica della Materia (INFN), Italy.

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<sup>1</sup>For a review see, *Physics and Applications of Dilute Nitrides*, edited by I. A. Buyanova and W. M. Chen (Taylor & Francis, New York, 2004); *Dilute Nitrides*, edited by M. Henini (Elsevier, Oxford, UK, 2005).

<sup>2</sup>W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 1221 (1999).

<sup>3</sup>P. J. Klar, H. Grüning, W. Heimbrot, J. Koch, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, *Appl. Phys. Lett.* **76**, 3439 (2000).

<sup>4</sup>P. Perlin, S. Subramanya, D. E. Mars, J. Kruger, N. A. Shapiro, H. Siegle, and E. R. Weber, *Appl. Phys. Lett.* **73**, 3703 (1998).

<sup>5</sup>A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, *Appl. Phys. Lett.* **77**, 2870 (2000).

<sup>6</sup>F. Masia, A. Polimeni, G. Baldassarri Höger von Högersthal, M. Bissiri, M. Capizzi, P. J. Klar, and W. Stolz, *Appl. Phys. Lett.* **82**, 4474 (2003).

<sup>7</sup>A. Polimeni, G. Baldassarri Höger von Högersthal, H. M. Bissiri, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, *Phys. Rev. B* **63**, 201304(R) (2001).

<sup>8</sup>G. Baldassarri Höger von Högersthal, M. Bissiri, A. Polimeni, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, *Appl. Phys. Lett.* **78**, 3472 (2001).

<sup>9</sup>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).

<sup>10</sup>A. Polimeni, G. Baldassarri Höger von Högersthal, F. Masia, A. Frova, M. Capizzi, S. Sanna, V. Fiorentini, P. J. Klar, and W. Stolz, *Phys. Rev. B* **69**, 041201(R) (2004).

<sup>11</sup>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).

<sup>12</sup>A. Polimeni, M. Bissiri, A. Augieri, G. Baldassarri Höger von Högersthal, M. Capizzi, D. Gollub, M. Fischer, M. Reinhardt, and A. Forchel, *Phys. Rev. B* **65**, 235325 (2002).

<sup>13</sup>Yong-Sung Kim and K. J. Chang, *Phys. Rev. B* **66**, 073313 (2002).

<sup>14</sup>A. Janotti, S. B. Zhang, Su-Huai Wei, and C. G. Van de Walle, *Phys. Rev. Lett.* **89**, 086403 (2002).

<sup>15</sup>A. Amore Bonapasta, F. Filippone, P. Giannozzi, M. Capizzi, and A. Polimeni, *Phys. Rev. Lett.* **89**, 216401 (2002).

<sup>16</sup>W. Orellana and A. C. Ferraz, *Appl. Phys. Lett.* **81**, 3816 (2002).

<sup>17</sup>S. Sanna and V. Fiorentini, *Phys. Rev. B* **69**, 125208 (2004).

<sup>18</sup>Fan Jiang, Michael Stavola, M. Capizzi, A. Polimeni, A. Amore Bonapasta, and F. Filippone, *Phys. Rev. B* **69**, 041309(R) (2004).

<sup>19</sup>A. Amore Bonapasta, F. Filippone, and P. Giannozzi, *Phys. Rev. B* **68**, 115202 (2003).

<sup>20</sup>A. Amore Bonapasta, F. Filippone, and P. Giannozzi, *Phys. Rev. B* **69**, 115207 (2004).

<sup>21</sup>A. Amore Bonapasta and F. Filippone, *Phys. Rev. B* **68**, 073202 (2003).

<sup>22</sup>J. C. Knights, T. M. Hayes, and J. C. Mikkelsen, Jr., *Phys. Rev. Lett.* **39**, 712 (1977).

<sup>23</sup>See for example: K. C. Pandey, A. Erbil, G. S. Cargill III, R. F. Boehme, and D. Vanderbilt, *Phys. Rev. Lett.* **61**, 1282 (1988); D. J. Chadi, P. H. Citrin, C. H. Park, D. L. Adler, M. A. Marcus, and H. J. Gossmann, *ibid.* **79**, 4834 (1997); K. M. Yu, W. Walukiewicz, S. Muto, H. C. Jin, J. R. Abelson, C. Clerc, C. J. Glover, and M. C. Ridgway, *Appl. Phys. Lett.* **75**, 3282 (1999); V. Koteski, N. Ivanovic, H. Haas, E. Holub-Krappe, and H.-E. Mahnke, *Nucl. Instrum. Methods Phys. Res. B* **200**, 60 (2003).

<sup>24</sup>X. Gonze, R. Stumpf, and M. Scheffler, *Phys. Rev. B* **44**, 8503 (1991).

<sup>25</sup>D. Vanderbilt, *Phys. Rev. B* **41**, R7892 (1990).

<sup>26</sup>S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari, A. Kokalj, <http://www.pwscf.org/>

<sup>27</sup>L. Floreano, G. Naletto, D. Cvetko, R. Gotter, M. Malvezzi, L. Marassi, A. Morgante, A. Santaniello, A. Verdini, and F. Tommasini, *Rev. Sci. Instrum.* **70**, 3855 (1999).

<sup>28</sup>G. Ciatto, F. D'Acapito, L. Grenouillet, H. Mariette, D. De Salvador, G. Bisognin, R. Carboni, L. Floreano, R. Gotter, S. Mobilio, and F. Boscherini, *Phys. Rev. B* **68**, 161201(R) (2003).

<sup>29</sup>A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, *Phys. Rev. B* **58**, 7565 (1998).

<sup>30</sup>A. Amore Bonapasta, F. Filippone, M. Capizzi, A. Polimeni (unpublished).

<sup>31</sup>W. Beall Fowler, Kevin R. Martin, Kathryn Washer, and Michael Stavola (unpublished).

<sup>32</sup>Mao-Hua Du, Sukit Limpijumng, and S. B. Zhang (unpublished).