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Connections between local and macroscopic properties in solids: The case of N in III-V-N alloys

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Although it is well known that dilute species often significantly modify the properties of solids in which they are hosted, a basic question remains open: How critical are their local properties in determining the macroscopic ones of the host material? Here we address this issue by taking N in dilute III-V-N alloys as a paradigmatic case and propose an original approach based on synergic progress in x-ray spectroscopies, density functional theory simulations, and hydrogen exposure as a *tool* to modify local bonding. In this way we are able to clarify how local properties operate by identifying the coupling mechanism between specific atomic orbitals responsible for the changes of both deep and band edge states. The success of our approach indicates a new way to connect local and macroscopic properties.

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Dilute atomic species very often play a key role in determining the physical properties of condensed matter, dopants in semiconductors being the textbook example of the significant effects of even very dilute species. Shallow dopants are characterized by delocalized wave functions and limited local atomic distortions, their effects being mainly related to a chemical valence different from that of the host atoms. On the other hand, in deep centers strong local structural distortions are linked to highly localized wave functions which are responsible for significant modifications of macroscopic (e.g., optical) properties [1], a notable example being the DX^- center in AlGaAs [2]. This is also true in general for many defect complexes, the purposeful formation of which is a key tool to tune physical properties or the unwanted presence of which can detrimentally affect device performance. Despite this general relevance, an atomistic understanding of the origin of the modification of the host properties and, in particular, of the relationships between local interactions, structural and electronic properties of the dilute species, and macroscopic ones of the host material has remained elusive and, in particular, some basic questions are still unanswered: How critical are the local properties of dilute species in determining the macroscopic properties of the host material and how do they operate?

Here we address these issues by choosing the N impurity as a case study. When incorporated in small amounts in III-V semiconductors, N atoms produce macroscopic effects by inducing a dramatic reduction of the energy gap of the host material [3]. In dilute nitrides there is no chemical valence effect since N is an isoelectronic impurity but a strong role of local structural distortions since the atomic size of N is appreciably smaller than that of the substituted group-V atom. Up to now, little attention was paid to a possible role of N local properties because the interaction between N-induced states and the near-edge CB ones was generally believed to be the main cause of the band gap reduction.

In this paper we focus on the connection between local interactions and macroscopic properties and perform our investigations with an original approach based on synergic advances in experiment and theory. We use advanced x-ray absorption spectroscopy (XAS), valence-to-core x-ray emission spectroscopy (vc-XES) and refined density functional theory (DFT) simulations of both atomic and electronic structure (including band edge states); moreover, in an original *perturbative* approach, we use hydrogen irradiation to willfully modify the local interactions of the dilute species providing an extra degree of sensitivity. We believe the issues we address to be of general relevance in condensed matter whenever there is a significant effect of a dilute species as, for instance, in the cases of Cr doped V_2O_3, in which the Cr concentration is one of the parameters that can be tuned to produce the Mott transition [4] and N doping of graphene which shifts the characteristic Dirac cone of the electronic structure [5]. Most ingredients of our study could be extended to other contexts, for example, in cases in which there is strong vibronic coupling. Present results indeed give clear indications on the relationships between local and macroscopic properties in the case of the N impurity showing, at the same time, the great potential of combining XAS, vc-XES, and *ab initio* methods in order to increase the sensitivity to both atomic and electronic structure. Similar investigations could be performed in combined optical and x-ray time resolved measurements of excited states created by optical transitions, in which a strong coupling between electronic and nuclear degrees of freedom is known to occur; such studies are becoming possible with the advent of femtosecond free electron laser x-ray sources [6].

In addition to the striking reduction of the energy gap induced by N, the optical emission energy of dilute nitrides can

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be tailored, even at the nanoscale, by irradiating the material with low energy H ions that completely passivate N effects [7–9] due to the formation of a specific N-H defect [10–13]. These extraordinary properties explain also the strong interest and the effort spent in the description of near-edge electron states of these materials. Most of the experimental work done to date has been based on optical methods, which permit an accurate analysis of the near-edge electronic states but lack elemental sensitivity. Many different theoretical approaches have been used to predict the evolution of these states on varying the N content [14]. The band anticrossing (BAC) model [15] indicated that the origin of the giant band gap reduction is the strong interaction of a N localized state with the conduction band minimum (CBM) of the host material. More accurate descriptions followed this simple model [16]. Regarding possible links to the local structure of N some attempts have been done both by theory and experiments. The degree of localization of CBM states has been determined by analyzing the electron charge distribution [17–19], while the origin of deep N *p* valence-band states has been related to the formation of short N-Ga bonds [20]. On the other hand, the electronic structure around N has been probed by core-level spectroscopies: XAS has been used to identify the H-N defect responsible for N passivation [10–13] and XAS and XES have been used to probe both the N local VB and CB densities of states (DOS) [21]. However, previous studies addressed specific issues without reaching a comprehensive description from a local point of view.

Here we fill this gap by taking advantage of the H passivation mechanism which can significantly contribute to shedding light on the relationship between modifications acting locally on N and the host electronic structure. Present results reveal a significant contribution of local properties to the macroscopic effects induced by N and permit us to propose a unifying picture in which the local N-Ga bonding plays a key role in both the occurrence of the N-induced deep states and the effects of N on the CBM of the host material.

We investigated Ga(AsN) (1.3% N) and (InGa)(AsN) (3.4% N, 4% In) epilayers on GaAs(001). In order to induce a modification of the local structure of N, part of the epilayers were irradiated with low-energy H ions with doses leading to complete passivation of N atoms. The local structure of the as-grown and H irradiated samples was probed by off-resonance vc-XES [22] and XAS [23] at the N *K* edge. XAS and XES spectra are reported in Fig. 1 (top panel) on a common energy scale referred to the N 1*s* level [24].

XAS and XES spectra probe the changes of the N localized *p*-projected CB and VB DOS with N concentration and upon H irradiation. In Fig. 1(a) a gray shaded band marks the optical gap of as-grown samples and a red one indicates the blue shift caused by H irradiation. The higher energy peak of the XES spectra can be attributed to N 2*p*-Ga 4*p* hybridized states and the lower energy one to N 2*p*-Ga 4*s* states [25]. H irradiation drastically affects the XES line shape (and thus the local VB DOS [26]): The height of the higher energy peak decreases, the lower energy one increases, and new states on the low energy side of the VB appear; however, the local VBM is not affected by H irradiation. The XAS spectra exhibit considerable variations upon N increase and H irradiation. The intense sharp peak at the absorption edge (the so-called "white line," WL), related to strongly localized N states with *p* character within a few eV of the local CBM, shifts to lower energy with increasing N content and completely disappears upon H irradiation. The latter effect is accompanied by a strong blue shift of the XAS absorption edge, the energy of which is related to the local CBM. We find therefore a first link between local and nonlocal properties: Variations of the energy of near edge XAS spectral features follow those of the optical gap.

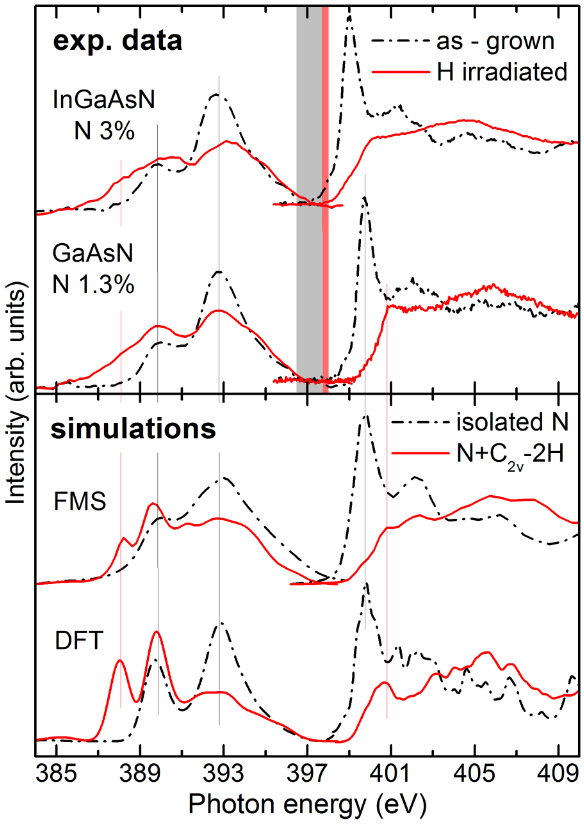

FIG. 1. (Color online) Top: experimental XES and XAS spectra at the N *K* edge of as-grown (black dash-dotted lines) and H irradiated (red continuous lines) samples. The shaded areas in the top panel mark the value of the gap for as-grown (light gray) and the blue shift induced by H irradiation (dark red). Bottom: *Ab initio* FMS and DFT simulations of XAS and XES spectra for GaAsN and the C_{2v}-2H complex.

Two complementary approaches were used to understand the local electronic structure of N and the modifications induced by H. First, starting from the atomic geometries obtained by plain density functional theory (DFT) calculations [27], we performed spectral simulations in the full multiple scattering (FMS) [28] approach in which the atomic charge density is spherically averaged. Second, we compared experimental data with results of *ab initio* DFT calculations of the spectra [29], a full potential approach. The geometries obtained from plain DFT simulations were used as input for hybrid DFT calculations with the Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation formulation [30,31]. In both FMS and full potential DFT simulations the geometry of the multiple hydrogen C_{2v}-2H complex was used [11,32,33]. The bottom panel of Fig. 1 summarizes the results obtained: FMS and

DFT spectral simulations are in excellent and good agreement with XAS and XES experimental data, respectively. The unchanged energy of the local VBM, in contrast with the modifications of the rest of the XES line shape, suggests that the involved N states are little affected by the formation of the N-H complex. FMS and DFT simulations correctly reproduce the changes of the XAS spectra upon hydrogenation, in particular the disappearance of the WL and the blue shift of the edge.

The good agreement between experiment and theory permits us to connect the modifications of the N electronic states to the evolution of the N local structure induced by the rupture of two N-Ga bonds by H. Inspection of the N local environment in the isolated N impurity and in the C_{2v}-2H complex, insets of Fig. 2, shows that an isolated N atom symmetrically attracts its four Ga neighbors from their unrelaxed positions to reduce the N-Ga distances, while in the C_{2v}-2H complex two H atoms bind to N by breaking two N-Ga bonds, thus permitting the N atom to displace towards its two remaining Ga neighbors which, in turn, relax towards their original positions in the GaAs lattice. Thus, in the C_{2v}-2H complex, the N-Ga coupling is strongly reduced due to the coexistence of the two remaining N-Ga bonds with two short and strong N-H bonds [34]. A detailed analysis performed by considering the DOS projected on N and its Ga neighbors as given by HSE calculations, see Fig 2 (top), shows indeed that the two XES peaks are mainly related to N p states at -7 and -4 eV, ranges in which s and p Ga states are also present, respectively. Upon formation of the N-H complex, the pDOSs of the same N and Ga atoms, reported in Fig 2 (bottom), show that the substitution of two Ga neighbors of N with two H atoms strongly reduces the pDOS in the region of the N p-Ga p coupling and at the same time increases the weight of the deeper N p states, in agreement with the higher electronegativity of H with respect to Ga. The lowering of the N-Ga coupling fully explains, therefore, the changes of the XES spectra observed upon hydrogenation.

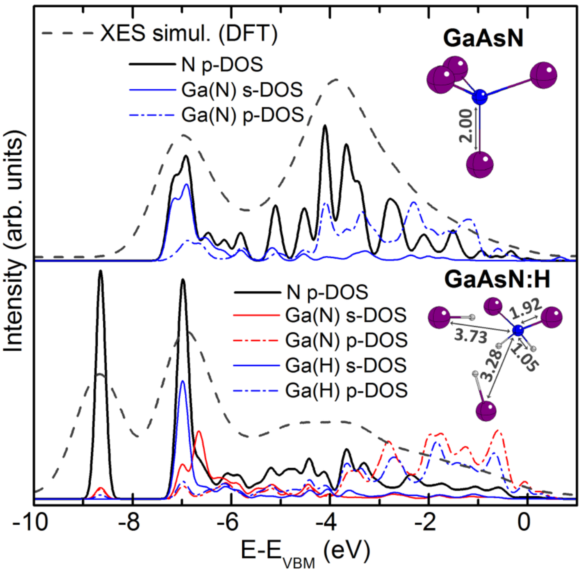

FIG. 2. (Color online) s and p state VB DOSs projected on N and its four Ga neighbors calculated by HSE-DFT. The insets illustrate the local geometries; N, Ga, and H atoms are represented by medium (blue), large (purple), and small (gray) circles, respectively and distances are given in Å. In GaAs, the Ga-As distance is 2.44 Å.

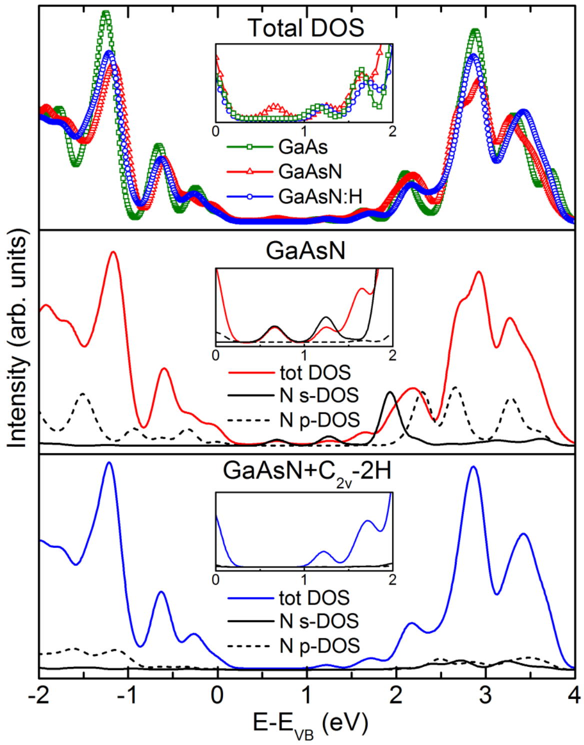

FIG. 3. (Color online) Top: Total DOSs for GaAs, GaAsN, and the C_{2v}-2H complex. The middle and bottom panels report the total and projected DOSs on N for GaAsN and for the C_{2v}-2H complex, respectively. The insets report a magnified view of the band edge regions.

The blue shift of the XAS absorption edge and the disappearance of the WL upon H irradiation parallel the corresponding shift of the band gap, suggesting that even these effects are connected to a lowering of the N-Ga coupling. We therefore directed our attention to the relationship between changes of the N local environment and the evolution of the Ga(AsN) edge states upon hydrogenation, based on the good results given by the HSE functional in describing the N effects on the GaAs band structure [35,36]. Figure 3 shows total and projected DOSs calculated for GaAs, Ga(AsN), and the C_{2v}-2H complex in Ga(AsN). In the top panel, the total DOSs for the three materials and a magnified image of the band-edge region show the reduction of the band gap induced by the introduction of N and its re-opening induced by H. In the middle panel the total DOS and the N s and p state pDOSs in Ga(AsN) are displayed: A strong contribution of N s states to the CBM is apparent. Finally, the bottom panel of Fig. 3 shows the DOSs for the C_{2v}-2H complex and illustrates how all N contributions to the band edges in Ga(AsN) are eliminated by hydrogenation. The DOS results are usefully complemented by analysis of the electron density distributions corresponding to the CBM, illustrated in Fig. 4. While the CBM is delocalized in GaAs, it is strongly localized on the N atom in Ga(AsN); similar findings were reported in previous theoretical studies

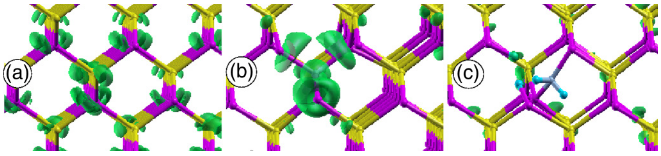

FIG. 4. (Color online) Contour plots of the square modulus of the electron wave function corresponding to the CBM calculated at the Γ point for: (a) GaAs, (b) GaAsN, and (c) the C_{2v}-2H complex. Wave function sampling was 3.5×10^{-4} electrons/(a.u.)^3 in (a) and 1×10^{-3} electrons/(a.u.)^3 for (b) and (c). Ga, As, N, and H atoms are indicated by purple, yellow, blue, and light blue spheres, respectively. The N atom (partially hidden by the isosurfaces) is at the center of (b) and is bonded to two H atoms in (c).

[20,37]. Formation of the C_{2v}-2H has the effect of destroying this localization.

All together, the above results add novel insight and go beyond the BAC-derived models, indicating a significant role of the local N-Ga interactions: The reduction of the N-Ga coupling induced by H is directly related indeed to the re-opening of the GaAs energy gap. As a confirmation, we performed a HSE calculation in which the atoms were kept fixed at the geometry of the canted C_{2v} complex (i.e., the N-H_2 complex without H saturators) but the two H atoms bonded to N were removed. Despite the energetically unstable situation, we found that also in this case the band gap re-opened, definitively confirming the key role of the rupture of N-Ga bonds. Further support to our picture is given by a recent theoretical study [38] in which the N effects on the CBM are attributed to the coupling between N-induced *s* states near the CBM. Such a coupling is hindered by the formation of the C_{2v}-2H complex.

In conclusion, our results clearly show that the N-Ga local interactions play a key role both in determining the features of the N-related deep states and in the N effects on the GaAs optical gap, thus revealing a clear connection between local and macroscopic properties. The present results substantially advance previous studies by explaining the local coupling mechanism at the base of the change in materials properties: N *p*-Ga *p* and N *p*-Ga *s* coupling in the case of N deep states and N *s*-Ga *s* coupling in the case of the CB edge. They also clarify the H passivation mechanism. At the same time, the present results show how an accurate description of the connections between local atomic bonding and electronic properties and macroscopic properties can be achieved by applying advanced x-ray spectroscopies, numerical simulation methods, and adopting an innovative *perturbative* approach consisting of hydrogen irradiation as a *tool* to modify local bonding via the rupture of chemical bonds.

From a general point of view, the direct link between local atomic environment and electronic properties found for N in dilute nitrides illustrates the significance that local properties can have for dilute species in condensed matter, stimulates similar studies in other relevant cases, and indicates a route for answering the addressed, general issues.

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[1] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, Berlin, 1999), Sec. 4.3.

[2] D. J. Chadi and K. J. Chang, Phys. Rev. B **39**, 10063 (1989).

[3] For a review see *Dilute Nitrides*, edited by M. Henini (Elsevier, Oxford, UK, 2005); *Dilute III-V Nitride Semiconductors and Material Systems*, edited by A. Erol (Springer, Berlin, 2008).

[4] A. I. Frenkel, D. M. Pease, J. I. Budnick, P. Metcalf, E. A. Stern, P. Shanthakumar, and T. Huang, Phys. Rev. Lett. **97**, 195502 (2006); S. Lupi *et al.*, Nat. Commun. **1**, 105 (2010).

[5] E. Velez-Fort, C. Mathieu, E. Pallecchi, M. Pigneur, M. G. Silly, R. Belkhou, M. Marangolo, A. Shukla, F. Sirotti, and A. Ouerghi, ACS Nano **6**, 10893 (2012).

[6] See, for example, J. Kern *et al.*, Science **340**, 491 (2013); H. T. Lemke *et al.*, J. Phys. Chem. **117**, 735 (2013).

[7] M. Felici, A. Polimeni, G. Salviati, L. Lazzarini, N. Armani, F. Masia, M. Capizzi, F. Martelli, M. Lazzarino, G. Bais, M. Piccin, S. Rubini, and A. Franciosi, Adv. Mater. **18**, 1993 (2006).

[8] R. Trotta, A. Polimeni, and M. Capizzi, Adv. Funct. Mat. **22**, 1782 (2012).

[9] R. Trotta, A. Polimeni, F. Martelli, G. Pettinari, M. Capizzi, L. Felisari, S. Rubini, M. Francardi, A. Gerardino, P. C. M. Christianen, and J. C. Maan, Adv. Mat. **23**, 2706 (2011).

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

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

[12] 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).

[13] G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni, M. Capizzi, M. Berti, G. Bisognin, D. De Salvador, L. Floreano, F. Martelli, S. Rubini, and L. Grenouillet, Phys. Rev. B **79**, 165205 (2009).

[14] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).

[15] W. Shan, W. Walukiewicz, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).

[16] E. P. O'Reilly, A. Lindsay, P. J. Klar, A. Polimeni, and M. Capizzi, Semicond. Sci. Technol. **24**, 033001 (2009).

[17] L.-W. Wang, L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **80**, 4725 (1998).

[18] T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. B **60**, R11245 (1999).

[19] P. R. C. Kent and A. Zunger, Phys. Rev. Lett. **86**, 2613 (2001).

[20] C. Persson and A. Zunger, Phys. Rev. B **68**, 035212 (2003).

[21] V. N. Strocov, P. O. Nilsson, A. Augustsson, T. Schmitt, D. Debowska-Nilsson, R. Claessen, A. Yu. Egorov, V. M. Ustinov, and Zh. I. Alferov, Phys. Status Solidi B **233**, R1 (2002); V. N. Strocov, P. O. Nilsson, T. Schmitt, A. Augustsson, L. Gridneva, D. Debowska-Nilsson, R. Claessen, A. Yu. Egorov, V. M. Ustinov, and Z. I. Alferov, Phys. Rev. B **69**, 035206 (2004).

[22] M. Zangrando, M. Finazzi, M. Zacchigna, D. Cocco, R. Rochow, and F. Parmigiani, Rev. Sci. Instrum. **75**, 31 (2004).

[23] 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).

[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.085301 for details on sample deposition and experiments.

[25] W. R. L. Lambrecht, B. Segall, S. Strite, G. Martin, A. Agarwal, H. Morkoç, and A. Rockett, Phys. Rev. B **50**, 14155 (1994).

[26] The adjective *local* referred to VB, CB, VBM, and CBM and is used to distinguish between the corresponding physical property characterizing the whole material and the same property when the N atom site is taken as a reference.

[27] P. Giannozzi *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).

[28] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58**, 7565 (1998).

[29] M. Taillefumier, D. Cabaret, A.-M. Flank, and F. Mauri, Phys. Rev. B **66**, 195107 (2002); C. Gougoussis, M. Calandra, A. P. Seitsonen, and F. Mauri, *ibid.* **80**, 075102 (2009).

[30] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[31] See Supplementary Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.085301 for details on simulation methods.

[32] L. Wen, M. Stavola, W. B. Fowler, R. Trotta, A. Polimeni, M. Capizzi, G. Bisognin, M. Berti, S. Rubini, and F. Martelli, Phys. Rev. B **86**, 085206 (2012).

[33] This complex differs from the N-H_2 complex generally referred to as a canted or asymmetric C_{2v} due to the presence of two further H atoms which saturate the dangling bonds. Full potential DFT spectral simulations show that it gives a better agreement with present experimental findings than the canted C_{2v} complex.

[34] The formation of strong N-H bonds is confirmed by estimates of bond dissociation energies and measured H stretching frequencies, see Ref. 7.

[35] V. Virkkala, V. Havu, F. Tuomisto, and M. J. Puska, Phys. Rev. B **85**, 085134 (2012).

[36] Also our results show that the HSE method significantly corrects the band gap error of the LDA and reproduces its variation induced by the introduction of N and H exposure; we find 1.25, 0.67, and 1.22 eV for the gaps of GaAs, GaAsN, and C_{2v}-2H in GaAs, respectively, which favorably compare to the experimental values.

[37] 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).

[38] V. Virkkala, V. Havu, F. Tuomisto, and M. J. Puska, Phys. Rev. B **88**, 035204 (2013).