

Importance of on-site corrections to the electronic and structural properties of InN in crystalline solid, nonpolar surface, and nanowire forms

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In this work, we employ first-principle calculations to predict the structural and electronic properties of InN nanowires comparing the results obtained at the local-density approximation (LDA) and at the LDA+ U level. Our study suggests that in the case of wurtzite InN it is important to apply an on-site Hubbard correction to both the indium d states and the nitrogen p states in order to recover the correct energy level symmetry and ordering at the Γ point of the Brillouin zone and obtain a reliable description of InN band structure. We apply the methodology to predict the electronic properties of InN nanowires and find that LDA and LDA+ U results are in qualitative agreement both in terms of confinement and surface-passivant effects.

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I. INTRODUCTION

InN is a low band-gap semiconductor that has attracted considerable attention due to its promising electronic properties such as high electron affinity, mobility, and saturation velocities. In recent years, a few experimental groups have managed to growth InN in the form of one-dimensional nanostructures [nanowires (NWs)] with diameters ranging from tens to hundreds of nanometers (see, e.g., Refs. 1–3). These nanostructures, due to their high surface/volume ratio and their strong anisotropic electronic and optical features, have been proposed as charge collectors in new generation solar cells but also as basic elements in innovative optoelectronic devices. Being able to understand and predict how surfaces and confinement effects influence the physical properties of InN is of primary importance for these applications to become real. For the above reasons, detailed investigations of InN properties have been addressed in several experimental^{4–6} and theoretical^{7–10} works, yet not much is known on the size effect on the energy gap and other electronic properties of this material.

Several measurements proved that InN in the wurtzite bulk phase has an electronic band-gap magnitude of about 0.7 eV.^{11–14} From the point of view of *ab initio* simulations, the prediction of the InN band gap is a challenging task: density-functional theory (DFT) both in the local-density approximation (LDA) and in the generalized gradient approximation (GGA) underestimates InN band gap giving rise to zero or negative values.^{15–17} In this material, similarly to other compound semiconductors containing transition or post-transition metals, DFT underestimates the position in energy below the valence-band maximum (VBM) of the cation semicore d states, and therefore overestimates their hy-

bridization with the anion- p valence states. As a result an artificially large p - d coupling pushes the valence band up in energy strongly reducing the calculated band gap. Only methods allowing corrections to LDA (GGA) such as self-interaction correction (SIC), exact exchange approaches, and quasiparticle approximation (GW) report gap values close to experiments: 0.59 eV with GW,¹⁸ 0.58 eV with SIC, and 0.82 eV with GW.⁸ However the latter methods can hardly be employed in the investigation of nanostructures like nanowires because they are computationally too demanding.

In this work, to repair the deficiency of LDA in describing the Coulomb interaction between localized states, we use the LDA+ U method^{19–21} and apply a Hubbard U correction to both the d electrons of the cation (indium) and the p electrons of the anion (nitrogen), as already done for some compound semiconductors.²² This appears to be fundamental in order to recover the correct symmetry of the electronic states close to the VBM.

The paper is organized as follows: in the next section we present the computational approach, in Sec. III we discuss the results obtained for InN bulk, nonpolar surface and nanowires, and finally in Sec. IV we summarize our results.

II. METHODS AND THEORY

In the present paper we use LDA (Ref. 23) and LDA+ U in the context of a plane-wave pseudopotential implementation [QUANTUM ESPRESSO (Ref. 24)] to describe the structural and electronic properties of InN bulk and nanowires. The In $4d$ electrons are explicitly considered as valence electrons because they are known to be important for a correct description of the structure of this material.²⁵

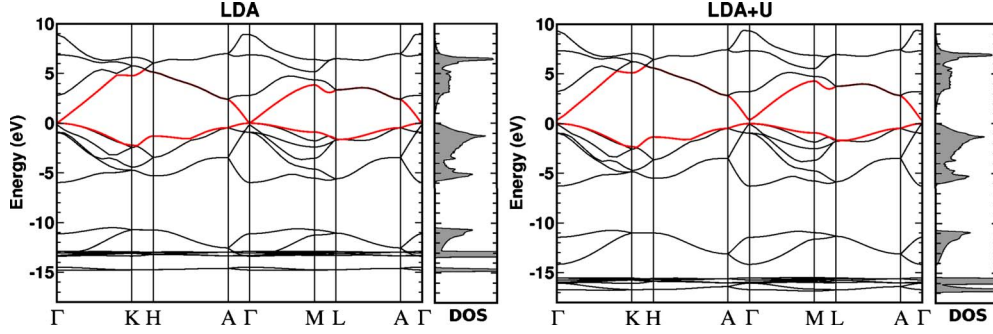


FIG. 1. (Color online) Band structure and density of states of wurtzite InN obtained with LDA (left panel) and LDA+ $U^{(d+p)}$ (right panel). The VBM is taken as energy zero.

Several theoretical studies reported that DFT and, in particular, LDA, although correctly describing InN structure, strongly underestimates InN band gap and fails in predicting the symmetry of the states close to the top of the valence band. This deficiency comes from an incorrect description of the Coulomb interaction between the localized d electrons of indium. As a consequence the semicore In $4d$ bands are too high in energy, and the Coulomb repulsion with the nitrogen p -like valence band is overestimated. This results in pushing the VBM toward higher energies and in closing the InN energy gap. Indeed our LDA calculations predict a negative sp band gap at Γ of -0.16 eV and a position of the $4d$ states of about 13 eV below VBM. On the contrary, in the case of InN, it is known from x-ray photoemission spectroscopy⁶ that the $4d$ states of indium are at about 16 eV below the VBM, the nitrogen $2s$ band lies at 12 eV from the VBM and the energy gap is about 0.7 eV.

Different approaches have been proposed to repair this deficiency and, among the others we mention the use of LDA+ U , many-body GW correction performed on the eigenstates obtained with self-interaction corrected pseudopotentials or with exact exchange functional. LDA+ U has the advantage of being computationally less demanding with respect to the other methods and, for this reason, it can be applied to systems like surfaces or nanostructures which would be hardly tractable with the other approaches.

The main idea of the LDA+ U method is to add to the LDA functional a term, E_U , corresponding to the mean-field approximation of the Coulomb interaction in multiband Hubbard model. U represents the screened Coulomb parameter. In its standard form LDA+ U aims at correcting the description of the coulomb interaction only among highly correlated states, such as d or f . Since on-site interaction U_d (from here we will indicate a Hubbard term for d electrons as U_d and for p electrons as U_p) accounts for strong interaction in narrow bands composed of spatially localized atomiclike states, adding a Hubbard term to d electrons is expected to lower their energy (in the direction of the experimental values), possibly inducing an increase in the gap.

Previous theoretical work²¹ on InN has shown that applying a U correction only to the d states of indium ($U_d = 1.9$ eV) poorly improves the band-structure description of this material: there is only a slight change in the band gap, from -0.18 eV to 0.03 eV, and both the d bands (of indium) and s bands (of nitrogen) remain well above the energy val-

ues observed experimentally. In the present paper, to recover the main InN band features, we apply a U correction also to the nitrogen $2p$ electrons. Indeed, similarly to what observed for some oxides compounds,²² in the case of InN the inclusion of the U correction on the anion appears to be fundamental for an improved description of p - d interaction and, beside inducing the band-gap opening, it corrects the symmetry of the states close to the top of the valence band, as we will show in the next paragraph. In the followings, we will denote this computational scheme as LDA+ $U^{(d+p)}$.

A major issue, when performing LDA+ U calculations, is the choice of the U parameter which defines the entity of the local potential to be applied on the selected atomic species and it is often evaluated by trying to reproduce experimental photoemission data. In our study, we systematically varied both U_p and U_d by considering their effects on the position of the $4d$ band of indium, on the position of the $2s$ states of nitrogen, on the VB width, and on the electronic band gap at Γ . These values were compared to the ones obtained experimentally and discussed in Ref. 6: the $4d$ states of indium are at about 16 eV below the VBM, the nitrogen $2s$ band lies 12 eV below the VBM, the VB width is about 6.4 eV, and the energy gap is about 0.7 eV. The values for U optimized in this process were $U_d = 6.0$ eV and $U_p = 1.5$ eV; the effects of these parameters on the bulk band structure are discussed in detail in the next paragraph.

III. RESULTS AND DISCUSSION

A. InN bulk

We optimized the wurtzite InN bulk lattice parameters consistently with the LDA+ $U^{(d+p)}$ approach described above and we obtained equilibrium values of $a = 3.505$ Å, $c/a = 1.616$, and $u = 0.378$ for a cutoff of 30 Ry and a k -point grid of $(8 \times 8 \times 8)$. These parameters are slightly smaller than the LDA values ($a = 3.524$ Å, $c/a = 1.618$, $u = 0.378$) (Ref. 26) but still close to the experimental ones [$a = 3.538$ Å, $c/a = 1.612$, $u = 0.377$ (Ref. 5)]. In Fig. 1 the band structures obtained with LDA (left panel) and LDA+ $U^{(d+p)}$ (right panel) approximations are compared. Following our choice of parameters for U and in agreement with experiments, the In $4d$ band is centered at about 16 eV below the VBM while the N $2s$ band is shifted down in energy by about 0.5 eV with respect to LDA. Correspondingly the VB width increases to

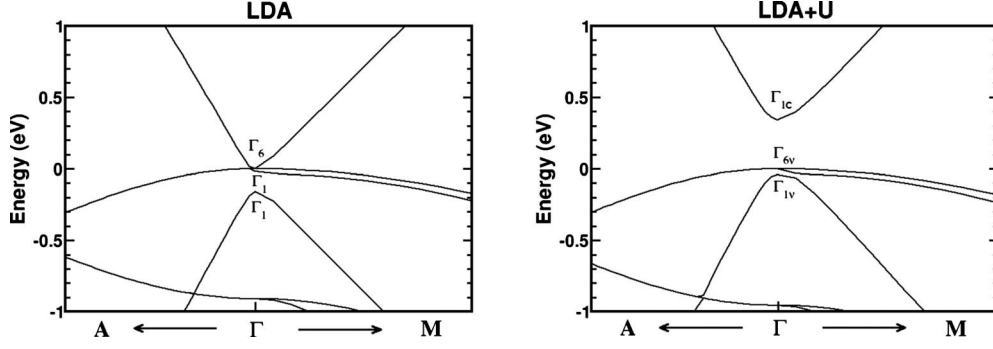


FIG. 2. Band structure of wurtzite InN bulk around the Fermi level close to the Γ point obtained with LDA (left panel) and LDA + $U^{(d+p)}$ (right panel) approaches. The VBM is taken as energy zero.

about 6.3 eV, a value that is very close to the one predicted by experiments and by many-body corrections (G_0W_0).⁶

The most important effects of including the U term on both the d and p electrons of In and N, respectively, are on the electron energy-level symmetry and ordering at the Γ point close to the energy-gap region (see Fig. 2 and Table I). Table I shows that LDA calculations predict a negative sp band gap, i.e., a negative distance of the $\Gamma_{1c}-\Gamma_{6v}/\Gamma_{1v}$ levels with a crystal-field splitting at the top of VB $\Delta_{cr}=\varepsilon(\Gamma_{6v})-\varepsilon(\Gamma_{1v})$ of 18.3 meV, in close agreement with previous LDA calculations.⁸ The LDA prediction of a negative band gap for InN is enforced by the low lying s -like Γ_{1c} “conduction band,” or, in other words, by the wrong energetical ordering of the electronic bands close to the top of the valence band; this deficiency is not healed by employing SIC pseudopotential with d electrons considered in valence⁸ (see Table I) or by applying a U correction only on the d states of indium regardless of the chosen U_d value. LDA + $U^{(d+p)}$ (right panel in Fig. 2) not only induces a gap opening at Γ (0.34 eV) but also predicts the correct energy ordering near the VBM giving two degenerate p states (perpendicular to $[0001]$ direction) at the top of the VB and an s state at the bottom of the conduction band. This is also apparent by analyzing Table I, where we compare the eigenvalues of the six highest valence and four lowest conduction states at the Γ point found in our LDA and LDA + $U^{(d+p)}$ calculations with previous results obtained with LDA-SIC pseudopotential and GW approximation.⁸ As a consequence of the correction, the calculated electron effective mass increases from $0.02m_0$ (LDA) to $0.05m_0$ (LDA + U). The latter value is in good agreement with the recently measured mass of $0.055 \pm 0.002m_0$.²⁷

From the above discussion we conclude that applying the Hubbard U correction, for both the In d electrons and the

N p electrons improves the description of the electronic features of InN bulk in agreement with the experimental and post-DFT results. In the followings, we first apply LDA + $U^{(d+p)}$ to a well documented test case, namely, the $(1\bar{1}00)$ InN surface and then we discuss the case of InN nanowires.

B. $(1\bar{1}00)$ nonpolar surface

To test the LDA + $U^{(d+p)}$ in predicting InN surface properties, we have calculated the geometry and the electronic properties of the relaxed $(1 \times 1)-(1\bar{1}00)$ InN nonpolar surface and compared them to previous theoretical results. The structure and the surface energy of this system are already well described at the LDA level and its description should not be affected by the inclusion of the Hubbard correction. Surface structures were simulated by using supercells containing 12- and 16-layer slabs and about 15 Å vacuum. Reciprocal space was sampled with an $(8 \times 8 \times 1)$ Monkhorst-Pack mesh and the geometry was relaxed until forces on atoms were less than 10^{-3} Ry/bohr. The changes in the geometry at the surface are the same for the LDA and LDA + $U^{(d+p)}$ methods: the In-N bond becomes shorter with respect to bulk by about 0.1 Å and the In-N bond axis tilts of about $7^\circ-8^\circ$ with respect to the surface plane with the In atom moving inward. The estimated surface energies are also very close: 1.50 J/m² for the LDA and 1.49 J/m² for the LDA + $U^{(d+p)}$. This shows that at the optimized lattice parameters the ground-state structural properties are not effected by the inclusion of the Hubbard correction. In Fig. 3 the surface band structures are presented. As for the case of InN bulk, it is apparent that the LDA + $U^{(d+p)}$ approach induces a gap opening and an energy shift toward lower energies of the

TABLE I. Eigenvalues of the highest valence ($v6-v1$) and the lowest conduction ($c1-c4$) bands of InN at the Γ point. LDA and LDA + $U^{(d+p)}$ eigenvalues of the present calculations are shown together with the Kohn-Sham eigenvalues obtained with LDA calculation performed with SIC pseudopotentials and the quasiparticle (QP) energies obtained from GW corrections applied at the SIC eigenstates (Ref. 8).

	$v6$	$v5$	$v4$	$v3$	$v2$	$v1$	$c1$	$c2$	$c3$	$c4$
LDA	-5.98	-0.91	-0.91	-0.02	0.00	0.00	-0.16	2.78	6.87	8.93
LDA + $U^{(d+p)}$	-6.30	-0.96	-0.96	-0.04	0.00	0.00	0.34	3.21	7.34	9.35
LDA-SIC ^a	-5.96	-0.88	-0.88	-0.08	0.00	0.00	-0.14	2.73	6.83	8.97
QP ^a	-5.96	-0.90	-0.90	-0.02	0.00	0.00	0.82	4.15	8.55	10.53

^aReference 8.

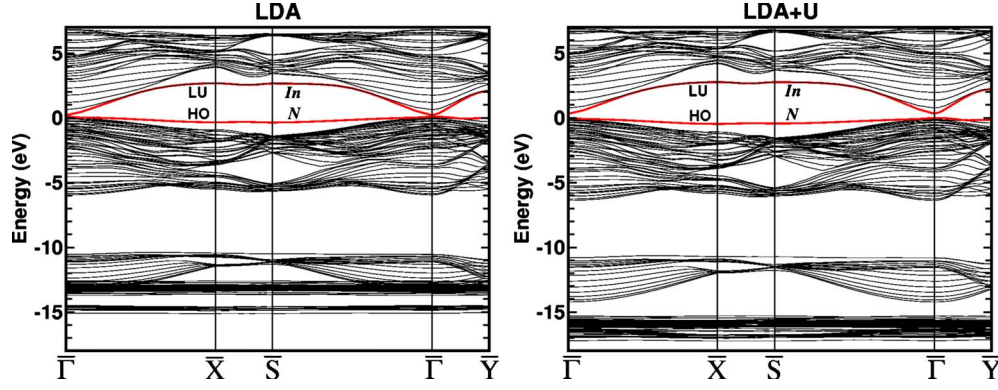


FIG. 3. (Color online) Band structure of InN (1100) surface obtained with LDA (left panel) and LDA+ $U^{(d+p)}$ (right panel) approaches. The LU state corresponds to a surface state localized on the In surface atoms and the HO state corresponds to a surface state localized on the N surface atoms. The VBM is taken as energy zero.

In d and N s bands. More interestingly, both at LDA and LDA+ $U^{(d+p)}$ level two surface states appear in the energy-gap region: the highest occupied (HO) band is a surface state with charge density localized on the N surface atom and the lowest unoccupied (LU) band is a surface state with charge density localized mainly on the In surface atom (see Ref. 28 for a detailed discussion). The HO (LU) state at the $\bar{\Gamma}$ point is degenerate with the top (bottom) of the valence (conduction) band (this is also confirmed by charge-density analysis not shown here), in agreement with previous theoretical investigations.²⁹ We also note that, at variance with the bulk system, in the case of surfaces the ordering and symmetry of the states of the surface close to the gap region at $\bar{\Gamma}$ are the same for LDA and LDA+ $U^{(d+p)}$.

The above results show that our LDA+ $U^{(d+p)}$ approach well describes the structural and electronic properties of the (1100) nonpolar surface in terms of bond distances and surface states. For this reason, this approach appears to be suitable to describe nanostructures where, due to the high surface to volume ratio, surfaces are expected to play a major role.

C. InN nanowires

We have finally applied LDA and LDA+ $U^{(d+p)}$ to study the structural and electronic properties of InN NWs grown along the [0001] axis and presenting hexagonal cross section with nonpolar (1100) lateral surfaces.¹ We considered NWs with clean and hydrogenated surfaces of three sizes (see Fig. 4): NW1 has one atom ring and a diameter $d \approx 4.1$ Å, NW2 has two rings and a diameter $d \approx 10.6$ Å while NW3 has three rings and a diameter $d \approx 17.6$ Å. All the structures were fully relaxed until the forces acting on the atoms were less than 10^{-3} Ry/bohr. The lattice parameter along the direction of the NW axis was optimized by performing several calculations at different lattice parameter c and relaxing all the atomic positions. The minimum-energy structure was obtained by fitting the total-energy values with a polynomial fit. In the case of the NWs with hydrogenated surfaces (one hydrogen for each N and In atoms at surface), we let the lattice parameter along the NW axis be the same as the wires

with clean surfaces and relaxed the position of all the atoms. In this way, we only focused on the effect of dangling-bond saturation.

In Table II we show the c lattice parameter for InN bulk and NWs relaxed at LDA and LDA+ $U^{(d+p)}$ level. Similarly to that found for ZnO wires,³⁰ with both methods the c parameter increases with decreasing the NW diameter except for the smallest nanowire (NW1) that has a c lower than InN bulk. The latter case can be understood considering that NW1 has no bulklike InN pairs since none of its atoms is fourfold coordinated. After relaxation (with both LDA and LDA+ U), the changes in InN bonds at the nanowire surface are very similar to those observed in the case of an infinite (1100) surface:²⁸ the InN bond length becomes 2.05 Å and it tilts by about 9.5°, with the In atoms relaxing inward. Upon hydrogenation the In-N bond length recovers its bulk value (~ 2.18 Å), but the In-N bond tilting is now opposite to the clean case ($\sim 5^\circ - 6^\circ$), due to the moving out of the In atom.

The band structures along the Γ -A path of the nanowires with clean surfaces calculated both at LDA and LDA+ $U^{(d+p)}$ level are presented in Fig. 5. The comparison between the two methods evidences that the effects of the U correction to the energy levels are similar to those observed for InN bulk: the band gap increases by about 0.20 eV, the VB width increases by about 0.2–0.3 eV, the 2s nitrogen band shifts downward by about 0.1 eV, and the 4d indium

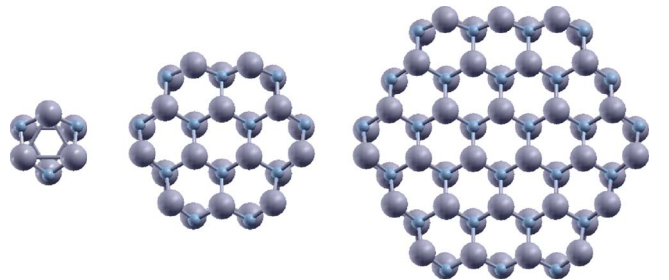


FIG. 4. (Color online) Ball and stick representation of the investigated InN nanowires: left—1 ring NW ($d \approx 4.1$ Å), middle—2 rings NW ($d \approx 10.6$ Å), and right—3 rings NW ($d \approx 17.6$ Å). Large balls represent In atoms and small balls represent N atoms.

TABLE II. Optimized c parameter for InN bulk and NWs.

c (Å)	Bulk	NW3	NW2	NW1
LDA	5.703	5.745	5.761	5.503
LDA+ U	5.664	5.720	5.745	5.565

states shift down by about 2.5 eV. The band structures of the hydrogenated NWs (not reported here) have similar features. In Fig. 6 we also report the band-gap dependence on the inverse of the NW diameter ($1/d$) for the two sets of nanowires. We note that in both cases the dependence is almost linear and that the inclusion of the U correction determines a rigid shift of the band gap (about 0.2 eV for NWs with clean surfaces and 0.35 eV for NWs with hydrogenated surfaces) that depends only slightly on the NW diameter. These results show that although underestimating the energy-gap LDA predicts a correct trend of the confinement effects. Moreover,

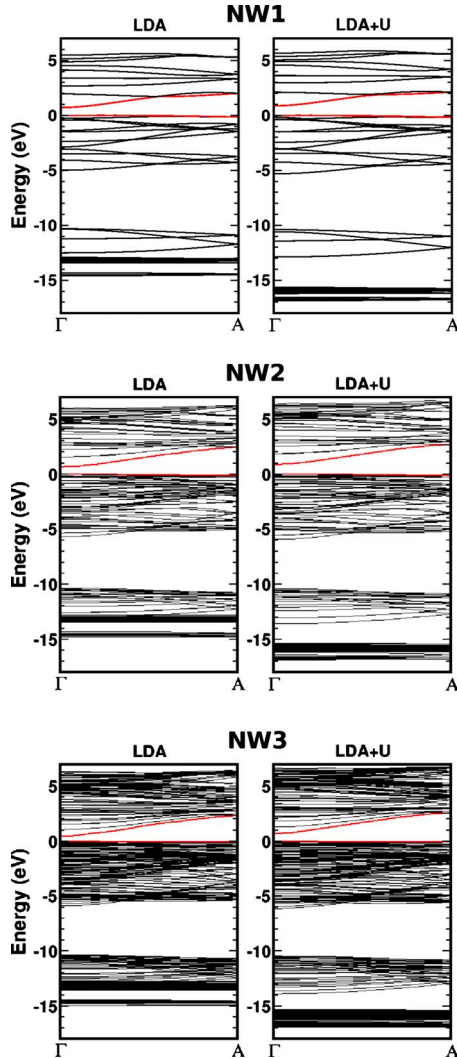


FIG. 5. (Color online) Band structures for InN nanowires with clean surfaces: top panel—1 ring NW, middle panel—2 rings NW, and bottom panel—3 rings NW. Left column—LDA and right column—LDA+ $U^{(d+p)}$. The VBM is taken as energy zero.

the larger energy gaps observed in the case of nanowires with hydrogenated surfaces imply that quantum confinement effects will be more noticeable in passivated NWs and that one might expect to see spectroscopic differences in experiments performed in different environments (e.g., solution vs ultrahigh vacuum). LDA and LDA+ $U^{(d+p)}$ predict similar confinement effects also in terms of charge-density distribution when comparing nanowires with clean and hydrogenated surfaces. In the latter case, due to surface dangling bonds saturation the electronic charge density accumulates in the center of the wire while in nanowires with clean surfaces the density is more delocalized on the surface atoms. In Fig. 7 we show, for example, the electronic charge-density isosurface of the highest occupied state for NW3 with clean and hydrogenated surfaces calculated with LDA+ $U^{(d+p)}$ (LDA yields similar results).

In spite of the similarities discussed above, some details of the electronic structures obtained with the two methods are different. In particular, an analysis of the symmetry and of the electronic charge density of the highest (lowest) occupied (unoccupied) states shows that LDA+ $U^{(d+p)}$ predicts that close to the energy-gap region, VBM and conduction band minimum (CBM), the electronic states of the nanowires have the same symmetry observed for the InN bulk (see Sec. III A): (i) the highest occupied states are two degenerate states with contribution from nitrogen p -type orbitals perpendicular to the nanowire axis (or $[0001]$ direction) and (ii) at the CBM there is nitrogen s -type orbital. The situation is different for the LDA band structures, where, in particular, for the hydrogenated wires, some mixing of the electronic states takes place that alters the correct symmetry.

IV. CONCLUSION

In this paper we proposed a generalized LDA+ U approach to study the structural and electronic properties of InN structures of different periodicity. In particular, we focused on the wurtzite InN bulk, on the $(1\bar{1}00)$ nonpolar surface, and on nanowires of increasing diameter grown along the $[0001]$ direction. We showed that in the case of InN bulk the use of U correction for both the indium d electrons and nitrogen p electrons significantly improves the agreement be-

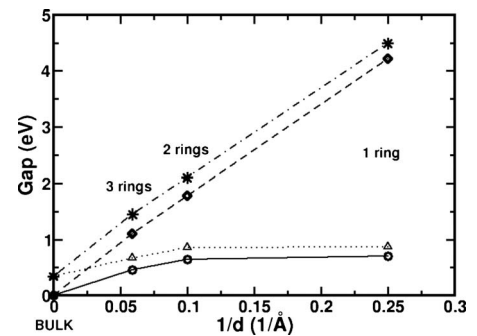


FIG. 6. Band gap vs inverse diameter ($1/d$) of InN nanowires with clean surface indicated by solid (LDA) and dotted (LDA+ $U^{(d+p)}$) lines, and for hydrogenated nanowires indicated by dashed (LDA) and dashed-dotted (LDA+ $U^{(d+p)}$) lines.

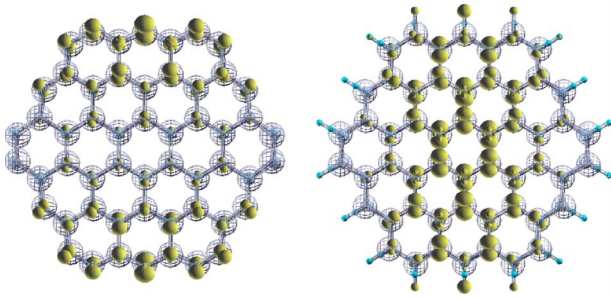


FIG. 7. (Color online) Electronic charge-density isosurface [denoted by shaded green (gray) area] for the highest occupied state in the case of LDA+ $U^{(d+p)}$: left panel—NW3 and right panel—NW3+H. Sketched globes represent atoms.

tween theory and experiment in term of band gap, valence-band width, depth of the N 2s and the In 4d bands, and symmetry of the states close to the Γ point. In the case of nonpolar surfaces, we verified that the LDA+ U approach describes the geometry of the surface with the same level of accuracy of LDA and that the inclusion of the Hubbard term, mainly affects the electronic properties of the surface inducing an energy gap opening at the Γ point. Finally we have applied LDA+ U to the case of InN nanowires and we have

shown that there exists a quasilinear dependency of the energy gap on the inverse of the wire diameter. LDA and LDA+ U give a consistent description of the nanowire geometry but, when the electronic structures are considered, LDA+ U appears to heal the symmetry of the electronic states in an energy range around the gap region. An important advantage of the LDA+ U approach, with respect to sophisticated post-DFT methods, lies in the little increase in computational effort if compared to standard DFT and in the possibility of studying and relaxing relatively large systems.

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- ¹F. Werner, F. Limbach, M. Carsten, C. Denker, J. Malindretos, and A. Rizzi, *Nano Lett.* **9**, 1567 (2009).
- ²T. Stoica, R. J. Meijers, R. Calarulo, T. Richter, E. Sutter, and H. Lüth, *Nano Lett.* **6**, 1541 (2006).
- ³S. Vaddiraju, A. Mohite, A. Chin, M. Meyyappan, G. Samanasekera, B. W. Alphenaar, and K. Sunkara, *Nano Lett.* **8**, 1625 (2005).
- ⁴V. Y. Davydov, *Phys. Status Solidi B* **229**, R1 (2002).
- ⁵W. Paszkowicz, R. Cerný, and S. Krukowski, *Powder Diffr.* **18**, 114 (2003).
- ⁶P. D. C. King *et al.*, *Phys. Rev. B* **77**, 115213 (2008).
- ⁷C. G. Van de Walle, *J. Appl. Phys.* **95**, 3851 (2004).
- ⁸J. Furthmüller, P. H. Hahn, F. Fuchs, and F. Bechstedt, *Phys. Rev. B* **72**, 205106 (2005).
- ⁹D. Segev, A. Janotti, and C. G. Van de Walle, *Phys. Rev. B* **75**, 035201 (2007).
- ¹⁰A. Janotti and C. G. Van de Walle, *Appl. Phys. Lett.* **92**, 032104 (2008).
- ¹¹J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W. J. Shaff, Y. Saito, and Y. Nanishi, *Appl. Phys. Lett.* **80**, 3967 (2002).
- ¹²R. Goldhahn, S. Shokovets, V. Cimalla, L. Spiess, G. Ecke, O. Ambacher, J. Furthmüller, F. Bechstedt, H. Lu, and W. J. Schaff, *GaN Related Alloys-2002*, MRS Symposia Proceedings No.743 (Materials Research Society, Pittsburgh, 2003), p. L5.9.
- ¹³A. Kasic, E. Valcheva, B. Monemar, H. Lu, and W. J. Schaff, *Phys. Rev. B* **70**, 115217 (2004).
- ¹⁴R. Goldhahn *et al.*, *Superlattices Microstruct.* **36**, 591 (2004).
- ¹⁵N. E. Christensen and I. Gorczyca, *Phys. Rev. B* **50**, 4397 (1994).
- ¹⁶C. Stampfl and C. G. Van de Walle, *Phys. Rev. B* **59**, 5521 (1999).
- ¹⁷F. Bechstedt, J. Furthmüller, M. Ferhat, L. K. Teles, L. M. R. Scolfaro, J. R. Leite, V. Y. Davydov, O. Ambacher, and R. Goldhahn, *Phys. Status Solidi A* **195**, 628 (2003).
- ¹⁸M. Usida, N. Haamada, K. Shiraiushu, and A. Oshiyama, *Jpn. J. Appl. Phys., Part 2* **43**, L407 (2004).
- ¹⁹V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).
- ²⁰M. Cococcioni and S. de Gironcoli, *Phys. Rev. B* **71**, 035105 (2005).
- ²¹A. Janotti, D. Segev, and C. G. Van de Walle, *Phys. Rev. B* **74**, 045202 (2006).
- ²²M. Korotin, T. Fujiwara, and V. Anisimov, *Phys. Rev. B* **62**, 5696 (2000).
- ²³J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ²⁴P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ²⁵A. F. Wright and J. S. Nelson, *Phys. Rev. B* **51**, 7866 (1995).
- ²⁶LDA+ U should be used with care in studying mechanical properties of a compound: in the present case, the decrease in lattice parameter obtained with respect to pure LDA approach leads to an increase in the elastic constants of about 10%.
- ²⁷M. Goiran, M. Millot, J.-M. Poumirol, I. Gherasoiu, W. Walukiewicz, and J. Leotin, *Appl. Phys. Lett.* **96**, 052117 (2010).
- ²⁸A. Terentjevs, G. Cicero, and A. Catellani, *J. Phys. Chem.* **113**, 11323 (2009).
- ²⁹C. G. Van de Walle and D. Segev, *J. Appl. Phys.* **101**, 081704 (2007).
- ³⁰G. Cicero, A. Ferretti, and A. Catellani, *Phys. Rev. B* **80**, 201304 (2009).