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Quantum mechanical effects in (Ga,In)(As,N) alloys

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A large supercell pseudopotential technique is used to predict optical and electronic properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys—with small x and y compositions—that are either in their disordered form or exhibiting a particular atomic ordering, namely one-dimensional nitrogen chains. In addition to the previously reported quantum couplings between electronic states with different reciprocal k points, another mechanism is found to participate in the strong decrease of the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys with respect to GaAs. This mechanism only involves the reciprocal Γ point, and is a nitrogen-induced shift of the conduction band minimum of GaAs. The existence of these two effects—quantum couplings and nitrogen-induced shift—can be easily understood within the framework of perturbation theory. Furthermore, *atomic ordering* in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys is found to strongly alter the band-gap and wave-function localization, by modifying the quantum couplings.

I. INTRODUCTION

The $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys are a key candidate material for high-efficiency multi-junction solar cells.[1] They also hold great promise for overcoming the poor temperature characteristics of conventional long-wavelength lasers.[2–5] One important feature of these quaternaries is that they can have a perfect lattice match to a GaAs substrate with the appropriate ratio of indium y to nitrogen x concentrations, thus avoiding the growth problems encountered in strained samples.

The $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and the related $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys are also of large fundamental interest because of unusual properties. For instance, the band gap of $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions, with small x and y compositions, significantly decreases when inserting more and more nitrogen atoms.[6–19] This is somewhat surprising since GaN has a much larger band gap than GaAs. The band gap of disordered $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloy lattice-matched to GaAs has even been predicted to close for large enough N compositions,[16] despite the fact that this material is entirely made of four semiconductors, i.e., GaAs, InAs, GaN, and InN.

Furthermore, *atomic ordering* has been predicted to drastically affect the optical and electronic properties of $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys.[20]

Recent experimental and theoretical studies demonstrated that $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions, with small x and y concentrations, are very peculiar because they exhibit nitrogen-induced quantum couplings between the conduction band-minimum state of GaAs and other electronic states.[17–19,21,22] These quantum couplings are currently believed to be responsible for inducing the large band-gap reduction of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ compounds when increasing the nitrogen composition. However, the mechanism responsible for the drastic effect of atomic ordering on the optical and electronic properties of anion-mixed nitride alloys is very unclear.

The aim of this paper is to provide a simple picture that explains (i) the decrease of the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys when increasing the nitrogen composition, and (ii) the strong dependency of optical and electronic properties on atomic ordering.

Our findings are as follows: (1) The insertion of nitrogen atoms into GaAs leads to a change in potential δV that already strongly pushes down the energy of the conduction-band minimum towards the valence-band-maximum energy, *without assistance of any other electronic state*. (2) Quantum couplings between the conduction band minimum of GaAs and other electronic states then reduce even more the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions. (3) The existence of these two effects can be easily understood within the framework of perturbation theory: the first mechanism is related to the first-order term in the expansion of the energy while the quantum couplings correspond to the second-order terms. (4) Atomic ordering is found to have no effect on the first mechanism, but rather strongly changes the quantum couplings. These modifications of the quantum couplings with nitrogen arrangement are responsible for the strong dependency of the optical and electronic properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys with atomic ordering.

II. METHODS

In the present study, we use 512-atom supercells of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, corresponding to $4\times4\times4$ conventional cubic cells. The number of nitrogen and indium atoms inside these cells are 4 and 12, respectively, which leads to a nitrogen composition of 1.6% and to an indium concentration of 5%. Such compositions yield a perfect lattice-match to GaAs, when assuming Vegard's law to be exact, as found in other quaternaries.[23] The indium atoms are randomly distributed on the (zinc-blende) cation sites. On the other hand, the nitrogen atomic arrangement can be of three kinds. First of all, the nitrogen atoms are randomly arranged on the anion sites in order to mimic a perfectly disordered sample, similar to the one grown in Ref. 21. Second, the nitrogen atoms all lie along a given [100] direction such as each nitrogen atom has two other nitrogen atoms as second neighbors in the anion sublattice. The nitrogen atoms have thus the following Cartesian coordinates $a(0,0,0)$, $a(1,0,0)$, $a(2,0,0)$, and $a(3,0,0)$, where a is the lattice constant. This second case corresponds to the formation of [100] chains in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. Finally, the last kind of atomic configuration is associated with nitrogen chains along a specific [110] direction, and every nitrogen atom has two other nitrogen atoms as fourth neighbors in the anion sublattice. In other words, the Cartesian coordinates of the four nitrogen atoms are $a(0,0,0)$, $a(1,1,0)$, $a(2,2,0)$, and $a(3,3,0)$. The last two atomic configurations thus correspond to a particular nitrogen ordering, namely the formation of one-dimensional nitrogen chains. This choice is done because these chains can be thought as an ''ideal'' bridge between the case of N–N *pairs* in GaAs—which are important to understand the effect of short-range-atomic order on optical and electronic properties of $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys[20]—and the case of more concentrated alloys which are of relevance to the experiment.[11,13] Furthermore, we chose these particular [100] and [110] chains because the formation of second neighbor N-N pair in GaAs is known to slightly increase the band gap with respect to the random case, while the fourth neighbor N-N pair significantly decreases that band gap.[20] The one-dimensional nitrogen chains formed along the [100] direction may thus affect the optical properties of (Ga,In)(As,N) in an opposite way than the [110] nitrogen chains. As a result, studying these two chains, as well as the random alloy, will lead to a deep understanding of the effects of nitrogen ordering on optical and electronic properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions.

For each configuration, the atoms are allowed to relax to their equilibrium positions by minimizing the strain energy, as predicted by the valence force field approach.[14,20,24–27] Having obtained relaxed configurations of large, periodic unit cells, we compute their band structures by using the generalized strain-dependent empirical pseudopotential approach of Ref. 16. This technique yields an excellent accuracy, as demonstrated by the nearly perfect reproduction of the experimental band gap of the disordered $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ quaternaries as a function of the compositions and/or as a function of pressure.[16] The ability of the empirical pseudopotential approach for treating large supercells is due mainly to the ''folded spectrum method,''[28] which provides for a computational time that scales linearly with the number n of atoms, while standard band structure methods lead to a time scaling of n^3.

To identify the coupled electronic states, we also project the alloy wave functions ψ_i on electronic states $\phi_{\nu,\mathbf{k}}$ of GaAs:

$$P_{i,\nu,\mathbf{k}}=|\langle\psi_i|\phi_{\nu,\mathbf{k}}\rangle|^2, \tag{1}$$

where ν and $\mathbf{k}$ are the band index and a vector in the first-Brillouin zone of GaAs, respectively. In the present study, the selected $\phi_{\nu,\mathbf{k}}$ are the *conduction* states that are currently believed to be responsible for the optical anomalies of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys,[17,19] namely, the Γ_{1c}, X_{1c}, and L_{1c} states of pure GaAs. In the following, these conduction states will be referred to as $\phi_{\Gamma_{1c}}$, $\phi_{X_{1c}}$, and $\phi_{L_{1c}}$, respectively.

TABLE I. Projections of the conduction-band-minimum state of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ into the Γ_{1c}, L_{1c}, and X_{1c} conduction states of GaAs [see Eq. (1)]. The first $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solution is the disordered sample, while the two others contain one-dimensional nitrogen chains formed either along the [100] or [110] direction.

System	$P_{CBM,\Gamma_{1c}}$	$P_{CBM,L_{1c}}$	$P_{CBM,X_{1c}}$
Random	0.727	0.076	0.002
[100]	0.859	0.000	0.015
[110]	0.450	0.155	0.020

III. RESULTS

A. Electronic couplings in $(\mathbf{Ga}_{1-y}\mathbf{In}_y)(\mathbf{As}_{1-x}\mathbf{N}_x)$ alloys

Table I shows the projections $P_{i,\nu,\mathbf{k}}$ for the conduction band minimum ψ_{CBM} of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions in their disordered forms or exhibiting nitrogen chains. One can see that $|\langle\psi_{CBM}|\phi_{\Gamma_{1c}}\rangle|^2$ and $|\langle\psi_{CBM}|\phi_{L_{1c}}\rangle|^2$ are quite large in the disordered solid solution. This demonstrates that $\phi_{\Gamma_{1c}}$ strongly couples with $\phi_{L_{1c}}$ to generate the conduction band minimum of the random $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. We also scanned all the excited states in this disordered alloy within an energy range of 1.5 eV above the conduction band minimum, and did not find any single localized state with significant Γ_{1c} weight. In other words, we did not find any impurity state strongly interacting with the conduction band minimum of pure GaAs. To better understand the *nature* of the interacting states, Table II shows the projections for the two excited states having the largest Γ_{1c} weights in disordered $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions. One of these two states is the conduction band minimum, and is denoted E_-. Following the notation of Refs. 18 and 21, the other state is referred to as E_+. The energies of these two states are also given in Table II, and are compared with the measurements performed in Ref. 21. Table II shows the very good agreement between predictions and experiments for both energies. By looking at the electronic charge density of the E_+ state, we further find that this interacting state is not at all an impurity level localized around nitrogen atoms, as previously thought.[21] It is of *delocalized* nature, which is consistent with the very large projection—around 80%—of E_+ into the L_{1c} state of pure GaAs. E_+ is thus derived from L_{1c}, which agrees with the results of Mattila *et al.* for nitrogen compositions larger than 0.5%.[19]

Table I also reveals that the electronic couplings between

TABLE II. Wave-function projections and energies of E_- and E_+ states in disordered $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, with $y\simeq5\%$ and $x\simeq1.6\%$. E_- and E_+ are the two excited states with the largest Γ_{1c} weights. ϵ_{theo} are the energies predicted by the present calculations, while ϵ_{exp} are the energies measured in Ref. 21.

State	$\lvert\langle\psi_i\vert\phi_{\Gamma_{1c}}\rangle\rvert^2$	$\lvert\langle\psi_i\vert\phi_{L_{1c}}\rangle\rvert^2$	$\lvert\langle\psi_i\vert\phi_{X_{1c}}\rangle\rvert^2$	ϵ_{theo} (eV)	ϵ_{exp} (eV)
E_-	0.727	0.076	0.002	1.27	1.26±0.02
E_+	0.125	0.785	0.002	1.74	1.76±0.02

TABLE III. Decrease ΔE_g of the band-gap energy with respect to GaAs, and perturbative energies of Eq. (2) for the three different $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions. The first solution is the disordered sample, while the two others contain one-dimensional nitrogen chains formed either along the [100] or [110] direction. The energy of the valence-band maximum in the three $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys is found to increase by 0.01 eV from the valence-band-maximum energy of pure GaAs.

System	ΔE_g (eV)	$\vert\langle \phi_{\Gamma_{1c}}\vert\delta V\vert\phi_{\Gamma_{1c}}\rangle\vert$ (eV)	$\frac{\vert\langle \phi_{\Gamma_{1c}}\vert\delta V\vert\phi_{L_{1c}}\rangle\vert^2}{\epsilon_{\Gamma_{1c}}-\epsilon_{L_{1c}}}$ (eV)	$\frac{\vert\langle \phi_{\Gamma_{1c}}\vert\delta V\vert\phi_{X_{1c}}\rangle\vert^2}{\epsilon_{\Gamma_{1c}}-\epsilon_{X_{1c}}}$ (eV)
Random	−0.25	−0.15	−0.03	−0.00
[100]	−0.19	−0.15	−0.00	−0.01
[110]	−0.40	−0.15	−0.10	−0.02

$\phi_{\Gamma_{1c}}$ and other conduction states of pure GaAs elements are strongly dependent on the nitrogen atomic arrangement in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. The coupling between Γ_{1c} and L_{1c} is much stronger for the [110] nitrogen chains than for the disordered sample, as evidenced by a decrease of $|\langle\psi_{CBM}|\phi_{\Gamma_{1c}}\rangle|^2$ and an increase of $|\langle\psi_{CBM}|\phi_{L_{1c}}\rangle|^2$ when going from the random case to the [110] nitrogen chains. On the other hand, this Γ-L coupling *vanishes* for the sample exhibiting chains along the [100] direction. Similarly, the coupling between Γ_{1c} and X_{1c} is very different from one sample to another one. Using the procedure developed in Ref. 29, we further find that other electronic states of pure GaAs can also couple with Γ_{1c}, depending on the atomic arrangement. For instance, the conduction-band minimum for the [110] chains has a relatively large component—around 9%—on the reciprocal k point located halfway between Γ and L. It is thus possible to *adjust, and even to turn on and off*, electronic coupling in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys by playing with the nitrogen arrangement.

B. Electronic properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys

We have investigated the effects of the couplings reported in Table I on the *electronic* properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. We found that the difference in couplings leads to a change in the conduction-band-minimum wave-function localization. The localization of the conduction-band-minimum state around nitrogen atoms significantly increases (decreases) when going from the disordered material to the [110] ([100]) nitrogen chains. Note that this trend is consistent with the Γ-L coupling: A larger coupling results in a stronger wave-function localization. This study thus demonstrates that electronic properties can be adjusted by playing with atomic arrangement in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. It is worth noting that before the idea of coupling between electronic states was proposed in 1999,[17–19,21] the concept of wave-function localization has been the mechanism suggested to explain the anomalous properties of $\mathrm{Ga}(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions.[9,14,20] The present study thus also points out that these two mechanisms are in fact related since electronic coupling induces wave-function localization.

C. Optical properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys

We now investigate the optical properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys. Table III shows that the band gap of these quaternaries is lower than the band gap of pure GaAs by more than 0.2 eV. It also drastically depends on the atomic arrangement. The band gap for the [110] chains is 0.15 and 0.21 eV lower than the band gap of disordered samples and those with [100] chains, respectively. This is quite remarkable since the nitrogen composition studied here is as small as 1.6% The valence-band-maximum energy in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ is found to be insensitive to the atomic arrangement, and is nearly equal to the valence-band-maximum energy of GaAs. Consequently, the difference in the band-gap energy between $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and GaAs, as well as, between the different $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, is almost entirely due to the conduction-band minimum.

D. Perturbation theory

To qualitatively understand the effect of the electronic couplings indicated in Table I on the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$, we analyze our results within the framework of perturbation theory at the second-order in energy:

$$\epsilon_{CBM}=\epsilon_{\Gamma_{1c}}+\langle\phi_{\Gamma_{1c}}|\delta V|\phi_{\Gamma_{1c}}\rangle+\sum_{\mathbf{k}\neq\Gamma}\frac{|\langle\phi_{\Gamma_{1c}}|\delta V|\phi_{c,\mathbf{k}}\rangle|^2}{\epsilon_{\Gamma_{1c}}-\epsilon_{c,\mathbf{k}}}, \tag{2}$$

where ϵ_{CBM} is the conduction-band-minimum energy of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, $\epsilon_{\Gamma_{1c}}$ is the conduction-band-minimum energy of pure GaAs, and δV is the difference in potential between $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ and GaAs. $\epsilon_{c,\mathbf{k}}$ and $\phi_{c,\mathbf{k}}$ are the conduction-band energy and wave function at off-center $\mathbf{k}$ vectors belonging to the first-Brillouin zone of GaAs. Note that $(\epsilon_{\Gamma_{1c}}-\epsilon_{c,\mathbf{k}})$ is negative for any off-center $\mathbf{k}$ vectors since the conduction-band minimum of GaAs occurs at Γ.

Furthermore, perturbation at the second order in energy is associated with the perturbation at the first order in wave function

$$\psi_{CBM}=\alpha\left[\phi_{\Gamma_{1c}}+\sum_{\mathbf{k}\neq\Gamma}\phi_{c,\mathbf{k}}\frac{|\langle\phi_{\Gamma_{1c}}|\delta V|\phi_{c,\mathbf{k}}\rangle|}{\epsilon_{\Gamma_{1c}}-\epsilon_{c,\mathbf{k}}}\right], \tag{3}$$

where Ψ_{CBM} is the wave function of conduction-band minimum in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, and α is a normalization coefficient. It is straightforward to derive

$$|\langle \phi_{\Gamma_{1c}}|\delta V|\phi_{c,\mathbf{k}}\rangle|^2 = \frac{|\langle \psi_{CBM}|\phi_{c,\mathbf{k}}\rangle|^2(\epsilon_{\Gamma_{1c}}-\epsilon_{c,\mathbf{k}})^2}{\alpha^2}, \quad (4)$$

with

$$\alpha^2 = |\langle \psi_{CBM}|\phi_{\Gamma_{1c}}\rangle|^2. \quad (5)$$

The second-order terms of Eq. (2) involving the couplings of Γ_{1c} with L_{1c} and X_{1c} can thus be estimated by plugging the calculated projections $|\langle \psi_{CBM}|\phi_{c,\mathbf{k}}\rangle|^2$ of Table I into Eqs. (4) and (5), and by using the well-known conduction-band structure of GaAs.[14]

Table III reports these second-order terms in energy as well as the directly calculated first-order energy $\langle \phi_{\Gamma_{1c}}|\delta V|\phi_{\Gamma_{1c}}\rangle$. One can notice two important features: (i) The first-order perturbative term in energy has an important role in the decrease of the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys with respect to GaAs. This term—which has never been addressed (to our knowledge) and which does not involve any electronic coupling—is mainly responsible for the value of the band gap in the sample exhibiting [100] chains. (ii) The difference between the band gaps of the different $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ solid solutions comes from quantum couplings between different electronic states, since $\langle \phi_{\Gamma_{1c}}|\delta V|\phi_{\Gamma_{1c}}\rangle$ is found to be insensitive to the nitrogen atomic arrangement. Note that summing the first-order perturbative energy with the second-order perturbative energies involving L_{1c} and X_{1c} does not yield the total decrease of the band gap of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys with respect to GaAs. This is probably due to the existence of other interacting states, as also indicated by the fact that the sum of the projections shown in Table I is smaller than 1. On the other hand, the trend in the band-gap energy is consistent with the trend in the electronic coupling between Γ_{1c} and L_{1c}: A large projection of the conduction-band-minimum of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys into the L_{1c} state of GaAs (see $P_{CBM,L_{1c}}$ in Table I) leads to a large value of the second-order term in energy coupling Γ_{1c} and L_{1c} [see Eq. (4)], and thus corresponds to a conduction-band minimum deeper in energy [see Eq. (2)], and, as a result, leads to a smaller band gap (see Table III).

IV. CONCLUSIONS

In summary, we theoretically investigated the effects of atomic arrangement on the electronic and optical properties of $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys, by comparing disordered samples with particularly ordered materials—namely, exhibiting one-dimensional nitrogen chains. We find that the decrease of the band gap in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys with respect to pure GaAs is due to two effects that can be described within the perturbation theory at the second-order in energy: (1) a first-order perturbative term strongly shifting the energy of the conduction-band minimum towards the energy of the valence band maximum, and (2) second-order terms which correspond to quantum couplings between the conduction-band minimum and other electronic states of pure GaAs. Finally, we have also demonstrated that nitrogen ordering leaves unchanged the first-order term, but strongly affects these second-order terms, resulting in a modification of the band-gap and wave-function localization. This study thus also demonstrates that—and explains why—playing with nitrogen arrangement can lead to an optimization of optical and electronic properties in $(\mathrm{Ga}_{1-y}\mathrm{In}_y)(\mathrm{As}_{1-x}\mathrm{N}_x)$ alloys.

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[1] S.R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J. Banas, and B. Hammons, Appl. Phys. Lett. **74**, 729 (1999).

[2] H.P. Xin and C.W. Tu, Appl. Phys. Lett. **72**, 2442 (1998).

[3] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).

[4] K. Nakahara, M. Kondow, T. Kitatani, Y. Yazawa, and K. Uomi, Electron. Lett. **32**, 1585 (1996).

[5] S. Sato, Y. Osawa, T. Saitoh, and I. Fujimura, Electron. Lett. **33**, 1386 (1997).

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

[7] M. Kondow, K. Uomi, H. Hosomi, and T. Mozume, Jpn. J. Appl. Phys., Part 2 **33**, L1056 (1994).

[8] J. Neugebauer and C.G. Van De Walle, Phys. Rev. B **51**, 10 568 (1995).

[9] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).

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

[11] A. Ougazzaden, Y. Le Bellego, E.V.K. Rao, M. Juhel, L. Leprince, and G. Patriarche, Appl. Phys. Lett. **70**, 2861 (1997).

[12] S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **72**, 1857 (1998).

[13] K. Uesugi, N. Morooka, and I. Suemune, Appl. Phys. Lett. **74**, 1254 (1999).

[14] L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. B **54**, 17 568 (1996).

[15] L. Bellaiche, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **70**, 3558 (1997).

[16] L. Bellaiche, Appl. Phys. Lett. **75**, 2578 (1999).

[17] E.D. Jones, N.A. Modine, A.A. Allerman, S.R. Kurtz, A.F. Wright, S.T. Tozer, and X. Wei, Phys. Rev. B **60**, 4430 (1999); Proc. SPIE **3621**, 52 (1999).

[18] J.D. Perkins, A. Mascarenhas, Y. Zhang, J.F. Geisz, D.J. Friedman, J.M. Olson, and S.R. Kurtz, Phys. Rev. Lett. **82**, 3312 (1999).

[19] T. Mattila, S.H.- Wei, and A. Zunger, Phys. Rev. B **60**, R11 245 (1999).
[20] L. Bellaiche and A. Zunger, Phys. Rev. B **57**, 4425 (1998).
[21] 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).
[22] L.W. Wang (unpublished).
[23] A.M. Saitta, S. de Gironcoli, and S. Baroni, Phys. Rev. Lett. **80**, 4939 (1998).
[24] L. Bellaiche, T. Mattila, L.-W. Wang, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **74**, 1842 (1999).
[25] P.N. Keating, Phys. Rev. **145**, 637 (1966).
[26] R.M. Martin, Phys. Rev. B, **1**, 4005 (1970).
[27] K. Kim, W.R.L. Lambrecht, and B. Segall, Phys. Rev. B **53**, 16 310 (1996).
[28] L.W. Wang and A. Zunger, J. Chem. Phys. **100**, 2394 (1994).
[29] L.W. Wang, L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **80**, 4725 (1998).