GaAs:N vs GaAs:B alloys: Symmetry-induced effects

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Electronic structure of GaAs with a 3% addition of B and N is studied by *ab initio* molecular dynamics. We find that the influence of B on the band gap and on its pressure dependence is weaker than that of N. Hydrostatic pressure strongly reduces the oscillator strength of the fundamental transition in GaAs:B, but not in GaAs:N. Group-theoretical analysis shows that the differences are symmetry induced, and stem from the different substitution sites of B (cation sublattice) and N (anion sublattice). For both alloys we find an additional optical transition at about 0.5 eV above the band gap involving a state derived from L_{1c}; its features agree with these of the E_+ transition in GaAs:N.

GaAs:N alloys with a small content of nitrogen are receiving a considerable interest due to potential applications in the fabrication of infrared diode lasers and efficient multijunction solar cells. Experimentally, adding a few percent (typically, 0.5 to 3) of N to GaAs leads to unexpectedly deep modifications of the electronic structure. The most important one is the reduction of the band gap;[1–7] this indicates a strongly nonlinear dependence of the band gap on the alloy composition (bowing), since the band gap of GaN is larger than that of GaAs by 2 eV. Further anomalies include non-linear pressure dependencies of the band gap[2,4] and high values of the electron effective mass.[5]

Recently, GaAs with 1–3 at. % of boron (and the lattice constant matched to GaAs) has been examined[8,9] as another candidate for infrared applications. Since B, like N, belongs to the second row of the Periodic Table, a comparable B-induced impact on the electronic structure could be expected. However, the experiment[8,9] has revealed that this is not the case: the B-induced reduction of the band gap is small, and the pressure dependence of the band gap is almost linear up to 6 GPa and close to that of pure GaAs.

To understand differences between the two alloys, we have performed *ab initio* calculations of their electronic structures. We have analyzed three issues investigated experimentally in detail, namely (i) the dependence of band gaps on the chemical composition and (ii) on hydrostatic pressure, as well as (iii) the optical properties of both alloys. We find that the different reduction of the band gap induced by B and N is mainly due to a different impact of the lattice relaxation. Next, the different pressure dependencies of the gap of GaAs:B and GaAs:N originate from symmetry-induced effects, and stem from the different substitution sites of B and N. Finally, the calculated optical absorption in both GaAs:N and in GaAs:B is similar: in both cases we find an additional strong transition at about 0.5 eV above the fundamental edge at zero pressure, forbidden in pure GaAs. Such a transition has been observed in GaAs:N.[2,3,7] As we find, the transition involves a conduction state derived from L_{1c}, which is not localized on nitrogen.

The calculations have been performed using quantum molecular dynamics.[10,11] We have employed the standard pseudopotentials.[12] The cutoff energy of 30 Ry for the plane wave basis set was sufficient to obtain convergent results. We have also used large unit cells with 64 atoms; with this

choice the substitution of one host atom by B or N corresponds to the alloy composition of 3.1 at. %. The experimental lattice constants of the end compounds were assumed, together with the alloy lattice constants chosen according to Vegard's law. Pressure dependence of the lattice constants was calculated based on Murnaghan equation of state. Compared to experiment, the values of the band gaps of GaAs at Γ, L, and X are underestimated by almost the same amount, 0.6 eV, which is a well-known consequence of the local density approximation that we use.

The obtained results are summarized in Table I. We compare first the effect of alloying by B and N on the fundamental band gap E_0. The calculations correctly reproduce the experimental findings: the change of the band gap (relative to that of pure GaAs) induced by 3% of B vanishes within the accuracy of the calculations,[13] while the presence of 3% of N reduces the gap by 0.47 eV.[14] From Table I it follows that most of the difference involves effects of structural relaxations. In fact, atomic displacements around the impurity are very similar in both systems, and consist in a symmetric decrease of the bond lengths with nearest neighbors Δl by about 12%. However, their impact on the electronic structure is the opposite: in GaAs:B the relaxation opens the gap by 0.01 eV, while in GaAs:N (Refs. 17 and 18) it closes the gap by 0.30 eV.

In order to analyze the relaxation-induced effects, we have projected wave functions from the bottom of the conduction band onto atomic orbitals.[19] The analysis of the conduction states shows that effects of electron transfer induced by the lattice relaxation act in opposite way in the two systems. In the case of GaAs:B, the lattice relaxation reduces the contribution of s orbital of B from 17% to 7%. (For comparison: in ideal GaAs the bottom of the conduction band is composed of 49% of $s(Ga)$ and 51% of $s(As)$.[19] Consequently, in a 64-atom unit cell, the contribution of $s(Ga)$ of one Ga atom to the bottom of the conduction band is 1.5%). In contrast, in the case of GaAs:N the relaxation increases the contribution of $s(N)$ from 9% to 12%. The electron transfer is one of possible sources of the calculated band-gap changes. For example, since the energy of $s(N)$ is lower than that of $s(Ga)$, the increasing contribution of $s(N)$ to the bottom of the conduction band decreases its energy, and reduces the band gap. The opposite effect occurs in GaAs:B. Furthermore, the analysis has revealed that the only

TABLE I. Effects of atomic relaxations around substitutional B and N in GaAs: ΔE_0^{rel} is the band-gap change induced by the change of the bond length Δl between the impurity and its neighbors. Q is the contribution of the s(impurity) orbital before ($n-rel$) and after (rel) the lattice relaxation. α is the contribution of the L_{1c} to $a_1(\Gamma_{1c})$.

	ΔE_0 (eV)	ΔE_0^{rel} (eV)	Δl (%)	Q^{n-rel}(%)	Q^{rel}(%)	$\alpha^{n-rel}(L_{1c})$ (%)	$\alpha^{rel}(L_{1c})$ (%)
GaAs:B	-0.11	0.01	10	17	7	1	20
GaAs:N	-0.52	-0.30	14	9	12	38	31

conduction state with an appreciable localization on the nitrogen atom is the bottom of the conduction band. In particular, there is no resonance localized at N at about 0.5 eV above the bottom of the conduction band. In the case of B we find a state at about 1.2 eV above the bottom of the conduction band, which contains 9% of B orbitals.

We have also investigated the bowing of the band gaps at wave vectors other than the Γ point. Interestingly, we find that the bowing strongly depends on the k vector. In particular, contrary to the fundamental band gap, both the E_1 and E_2 gaps that give rise to strong optical transitions in the vicinity of the L and X points, respectively, are not changed by the presence of N to within 0.05 eV. This result is in agreement with the recent optical measurements.[20,21] In the case of GaAs:B, we find a small decrease of E_1 by 0.05 eV. This nonsensitivity of the minima at L and X to the chemical perturbation stems from the very small contributions of the impurity orbitals to these states.

Before analyzing the effects of hydrostatic pressure, we provide a group-theoretical discussion of electronic states in the considered alloys. We begin by the case of pure GaAs, and observe that its point symmetry is T_d, independently whether the origin of the coordinate system is fixed on the anion or on the cation. The standard convention assumes the origin on the anion. With this assumption, the lowest conduction state at the X point in GaAs has the X_1 symmetry, and is composed of the s orbitals of anions, s_{anion}, and the p orbitals of cations, p_{cation}.[19] (To simplify the discussion, the contribution of d states is neglected.) The second state at X, situated 0.3 eV above the first one, has the X_3 symmetry, and it is a combination of s_{cation} and p_{anion}. However, the shift

FIG. 1. Calculated pressure-induced changes of conduction bands at Γ of GaAs:B. The lines are only guides for the eye.

of the origin from anion to cation interchanges the symmetry of these two states: the first one is now X_3, and the second one X_1.[22] The shift does not change the symmetry of the states from Γ and L.

Introduction of an impurity leads to three effects. First, after the substitution of a host atom by an impurity the symmetry of the system is still T_d, provided that the origin is fixed at the impurity and the lattice relaxation is symmetric (which is the case for both B and N). Consequently, the site of substitution determines the origin of the coordinate system, and therefore the symmetry of states at the X point. Second, some of degenerate states split. Finally, the impurity potential may couple states from various points of the Brillouin zone, e.g., the conduction-band minima at Γ, X, and L. The coupling is allowed or forbidden depending on the actual symmetry of the two states in question. The relevant selection rules will be discussed below.

Considering the band splitting effects, one has that there are three X minima, and the band states are threefold degenerate. The impurity potential splits the X_1-derived triplet into a $a_1(X_1)$ singlet and a $e_2(X_1)$ doublet (we use the molecular notation appropriate for diluted alloys). The X_3- derived triplet is not split, and its symmetry is $t_2(X_3)$. The L_1-derived quadruplet is split into a $a_1(L_1)$ singlet and a $t_2(L_1)$ doublet. The Γ_1 state becomes $a_1(\Gamma_1)$ singlet. The energies of the Γ-, L-, and X-derived conduction states as a function of hydrostatic pressure are shown in Fig. 1 for GaAs:B. We see that at zero pressure the $a_1(L_1)$-$t_2(L_1)$ splitting is 0.05 eV, and the $a_1(X_1)$-$e_2(X_1)$ splitting of the second conduction band at X is 0.1 eV. Similar values are obtained for GaAs:N. In this reciprocal-space picture, the impurity-induced coupling of states from various points of the Brillouin zone is monitored by projecting the states of the alloy onto the states of pure GaAs. We find that the bottom of the conduction band $a_1(\Gamma_{1c})$ contains a strong admixture of the L_{1c} states, which is 20% and 31% for B and N, respectively. The contribution of X_{1c}, about 2%, is an order of magnitude smaller, indicating a weak Γ_{1c}-X_{1c} interaction in both alloys at zero pressure.

We now turn to pressure-induced effects. For GaAs, the calculated pressure coefficients of the direct and indirect band gaps, along with the crossover pressure at which the band gap changes from direct to indirect, are in very good agreement with experiment. For both GaAs:B and GaAs:N, the pressure dependence of the band gap is weaker than in GaAs, and nonlinear.

The calculated pressure dependence of the band gap of GaAs:N is shown in Fig. 2. We find that the deformation potential of the band gap at low pressures is smaller than that of GaAs by a factor of 2, confirming the results of two recent
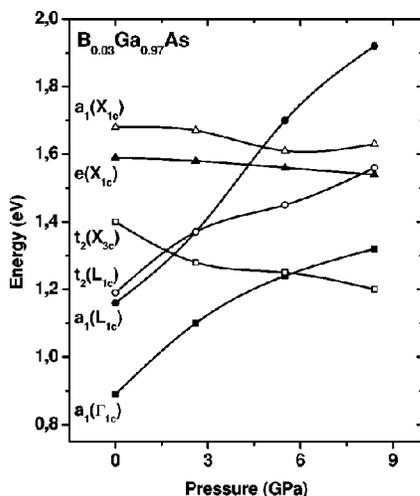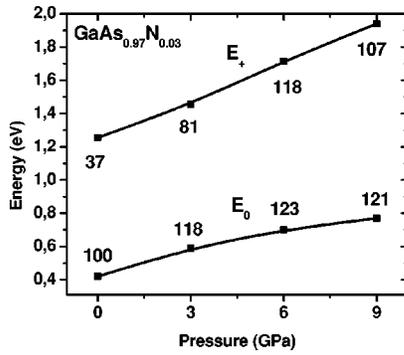
FIG. 2. Calculated pressure dependence of two dominant optical transitions in GaAs:N. Numbers give the normalized square of the interband matrix elements. The lines are only guides for the eye.
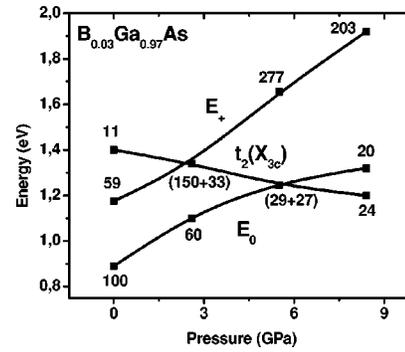

FIG. 3. Calculated pressure dependence of the dominant optical transitions in GaAs:B. Numbers give the normalized square of the interband matrix elements. The lines are only guides for the eye.

works.[4,23] These results have been correctly interpreted based on the pressure-induced changes of the GaAs band structure perturbed by the N potential.[4,23] In particular, the nonlinear pressure dependence of E_0 stems from the increasing coupling of Γ_{1c} with L_{1c} (dominant at low pressures), and with X_{1c} (dominant at pressures higher that 6 GPa). Importantly, there is no direct-to-indirect band-gap transition for pressures up to 9 GPa.

The calculated energies of the conduction bands of GaAs:B as a function of hydrostatic pressure are shown in Fig. 1. By fitting the pressure dependencies of E_0 by second order polynomials we find that at low pressures the deformation potential of GaAs:B (6.8 eV) is close to that of GaAs (8.5 eV) and larger than that of GaAs:N (4.6 eV), in agreement with experiment.[9] Moreover, in contrast to GaAs:N, the calculations predict a direct-to-indirect crossover of the band gap at about 6 GPa, see Fig. 1.

The qualitative differences between GaAs:B and GaAs:N are symmetry induced. In the case of anion-substituting N_{As}, the origin is on anion, and this is the first state at X, $a_1(X_{1c})$, which is coupled with the bottom of the conduction band. The interaction with the higher X-derived state, $t_2(X_{3c})$, is forbidden by symmetry. In contrast, in the case of the cation-substituting B_{Ga}, the interaction of $a_1(\Gamma_{1c})$ with the first X-derived state, which now is $t_2(X_{3c})$, is forbidden, and does not affect the bottom of the conduction band. For this reason these two levels may cross at 6 GPa changing the gap character from direct to indirect. The interaction with the second X-derived state, $a_1(X_{1c})$, is allowed. However, because of the greater energy separation, the coupling is weaker than in GaAs:N and does not reduce the deformation potential of GaAs:B at low pressures.

The coupling of the bottom of the conduction band Γ_{1c} with the secondary minima at L and X strongly influences optical properties of both alloys, which will now be discussed. Optical investigations of GaAs:N have shown that at energies higher than the fundamental band gap there is an additional transition denoted E_+.[2,3] To understand the origin of this feature, we have analyzed the optical absorption, which is proportional to the square of the interband momentum matrix element, $|P_{vc}|^2$. The normalized matrix elements as a function of pressure are given in Fig. 2; the value of $|P_{vc}|^2$ for the E_0 transition at zero pressure is taken as 100. The calculations reproduce two main experimental

findings.[2,3] First, we find that in addition to E_0 there is a second transition, which we interpret as E_+. Intensities of other transitions, not shown in the figure, are at least five times smaller. Second, the relative intensity of E_+ compared to E_0 increases with pressure, in agreement with the observation by Perkins *et al.*[3] Both effects stem from the N-induced modifications of the conduction states. In particular, optical transitions from the top of the valence band to $a_1(L_{1c})$ and $a_1(X_{1c})$, forbidden in pure GaAs, become allowed. At zero pressure, the E_+ feature is due to the transition to $a_1(L_{1c})$, while the transition to $a_1(X_{1c})$ is a few times weaker. With the increasing pressure, the oscillator strength of E_+ increases, since the corresponding state becomes progressively more Γ_{1c}-like. (The nonmonotonic dependence of the oscillator strength of E_+ is due to fact that we have added contributions of the transitions which energies differ by less than 0.1 eV.)

The calculated values of $|P_{vc}|^2$ for GaAs:B are shown in Fig. 3. By comparing Figs. 2 and 3 we see, in particular, that, like in GaAs:N, there is a second absorption peak E_+ from the top of the valence band to $a_1(L_{1c})$ situated about 0.3 eV above the absorption edge at zero pressure, which intensity increases with pressure. We note, however, a significant difference between the influence of pressure on the strength of the E_0 transition in the two alloys. Namely, in GaAs:N the value of $|P_{vc}|^2$ increases from 100 at zero pressure to 120 at 9 GPa, while in GaAs:B it decreases five times in this pressure range at the expense of the E_+ transition. Moreover, at pressures close to 9 GPa the fundamental transition in GaAs:N is to the $a_1(X_{1c})$ state, and it is much stronger than the fundamental transition to the $t_2(X_{3c})$ state in GaAs:B. An analogous symmetry-induced effect has been investigated by Morgan[22] for the indirect-band gap GaP. He has pointed out that zero-phonon interband optical transitions become allowed in the presence of impurities, but they are much stronger for the anion-substituting than for the cation-substituting donors because of the different symmetry of the conduction states at the X point.

Finally, we comment on a controversy regarding the state involved in the E_+ transition. The situation emerging from theoretical calculations is as follows. An isolated N impurity in GaAs induces a resonance situated 0.15–0.18 eV above the bottom of the conduction band;[24] we denote it by $a_1(N)$. According to Hjalmarson *et al.*,[25] the wave function of

$a_1(N)$ is an antibonding combination of $s(N)$ with sp^3 orbitals of the nearest neighbors, and it is localized mainly on the neighbors. Extensive calculations[23] confirm this picture, and find $a_1(N)$ at 0.18 eV above the conduction-band bottom. With the increasing concentration of N the energy of $a_1(N)$ rises. For example, for GaAs with $x = 0.8\%$ of N, $a_1(N)$ is situated 0.93 eV above the bottom of the conduction band.[23] Mattila *et al.*[23] conclude therefore that "$a_1(N)$ is too far to act as a principal source of the low-energy anticrossing observed by Shan *et al.*[2]" With the increasing content of N a second state develops from the secondary minimum at L,[4,23] which eventually evolves into the $a_1(L_{1c})$ state discussed above. This state is induced by the presence of N but *is not* localized on N, and *is not* the $a_1(N)$ resonance. Based on the facts that (i) the calculated momentum matrix elements reflect the experimental features of E_+, and (ii) the theoretical composition-dependent energy separation between $a_1(L_{1c})$ and $a_1(\Gamma_{1c})$ agrees well with the experimental difference between E_+ and E_0, see Fig. 4, we propose that $a_1(L_{1c})$ gives rise to the E_+ transition. The L-related character of E_+ is also suggested by recent experiments.[6]

On the other hand, Shan *et al.*[2] have proposed a simple model of GaAs:N band structure, which considers two interacting energy levels: one associated with extended conduction states of GaAs, and the other which is a resonance *localized* on N and identified with $a_1(N)$. Moreover, the model ignores the effects of secondary L_{1c} and X_{1c} minima, which are coupled with Γ_{1c} in the presence of nitrogen atoms. (We note that at pressures higher than about 5 GPa, the bottom of the conduction band is dominated by the X_{1c} state.) The model provides an excellent parametrization of experimental data, but its assumptions are not confirmed by theoretical calculations.
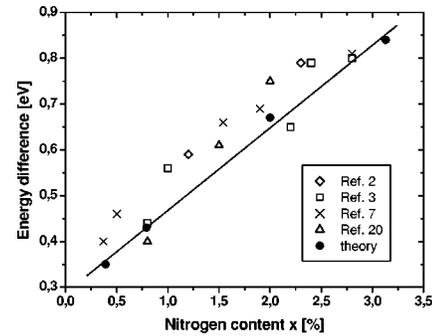

FIG. 4. Composition dependence of the experimental E_+-E_0 energy difference, and of the calculated $a_1(L_{1c})$-$a_1(\Gamma_{1c})$ energy difference for $x = 0.4$ and 0.8 (Ref. 23), 2.0 (Ref. 4), and 3.1% (this work). The line shows a linear fit to the theoretical values.

In summary, we have calculated the electronic structure of GaAs:B and GaAs:N alloys by *ab initio* methods. We find that the reduction of the GaAs band gap and its nonlinear pressure dependence induced by B is smaller than that induced by N. The obtained results are explained based on the symmetry-induced differences between the cation-substituting B and the anion-substituting N. For both alloys we find an additional optical transition involving a L_{1c}-derived state; we propose to identify it with the E_+ transition.

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[13] However, this result demonstrates a strong bowing of the $B_xGa_{1-x}As$ band gap, since the linear interpolation between GaAs and BAs predicts *an increase* of E_0 by 0.11 eV for $x = 0.03$. For GaAs:N, the reduction of E_0 relative to the linearly interpolated value is much greater, 0.52 eV.

[14] Comparison of the obtained results with experiment should be performed with caution because in the supercell method the N (or B) atoms form a superlattice, and their potential is coherent, while in a real alloy both their locations and the alloy potential are random. The long-range order reduces the band gap of alloys (Refs. 15 and 16), i.e., overestimates the bowing, and in our case the nonlinear pressure dependence of the band gap.

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