

## Quasiparticle excitations in $\text{GaAs}_{1-x}\text{N}_x$ and $\text{AlAs}_{1-x}\text{N}_x$ ordered alloys

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We have performed a quasiparticle study of the fundamental excitations in ordered alloys of III-V semiconductors,  $\text{GaAs}_{1-x}\text{N}_x$  and  $\text{AlAs}_{1-x}\text{N}_x$ . The experimentally observed anomalous redshift in  $\text{GaAs}_{1-x}\text{N}_x$  of the direct bandedge is explained here by effects arising from the 20% lattice mismatch. The fact that the bottom of the conduction band is mainly dominated by nitrogen leads to a large reduction of the fundamental gap at  $\Gamma$  as the volume increases. This reduction continues until the charge density begins to locate on the arsenic site. Based on this simple scenario, we predict that a similar redshift may be observed in the indirect gap  $\text{AlAs}_{1-x}\text{N}_x$  alloys. Also an indirect to direct band-gap transition will be observed for intermediate N concentrations. The possibility of closing the band gap is discussed in terms of the quasiparticle results.

The chemical bonds in III-V semiconductors and alloys have been the subject of intensive experimental and theoretical studies because of potential applications in optoelectronic devices and the wide range of electronic properties of these materials.<sup>1</sup> Among the III-V semiconductors, GaAs has had the major role for many technological applications in the semiconductor industry; however there is considerable interest in wider and smaller band-gap systems. Alloys made of III-V elements can exhibit very interesting and unexpected electronic properties, as is the case for  $\text{GaAs}_{1-x}\text{N}_x$  where a redshift of the photoluminescence edge has been found for small N concentration instead of the expected blueshift.<sup>2</sup> Recently we performed quasiparticle studies on the wide-band-gap semiconductors GaN and AlN (Ref. 3) and obtained good agreement with experimental results where available for both materials. This quasiparticle method has been shown to be very accurate and capable of predicting the excitations for a variety of systems: bulk semiconductor,<sup>4</sup> superlattices,<sup>5</sup> surfaces,<sup>6</sup> metals,<sup>7</sup> and molecular solids.<sup>8</sup> Based on this predictive capability and on the good matching of lattice constants we studied the band gap evolution in short-period superlattices and ordered alloys of these two semiconductors.<sup>9</sup> The results are promising in the sense of having systems with a wide range of band gaps going from 3.5 eV to 6 eV. On the other hand, mixed group III-V alloys with fixed cations such as those composed of GaN and GaAs or AlN and AlAs should, in principle, allow us to close the gap between the nitrides and arsenides, making possible the fabrication of III-V light emitting devices covering the complete spectrum. In contrast to the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys, where the components dominate the electronic structure and band gaps, in the nitride-arsenide alloys the lattice mismatch ( $\sim 20\%$ ) would have a large influence on the electronic structure. Similar effects on a small scale have been observed in the study of II-VI alloys.<sup>10</sup>

Recent photoluminescence and absorption experiments on  $\text{GaAs}_{1-x}\text{N}_x$  ( $0 < x < 0.015$ ) grown by plasma-assisted metalorganic chemical vapor deposition, show a systematic redshift of the band-edge luminescence with

increasing N content.<sup>2</sup> This is unexpected from a simple look at the electronic properties of the components. Since GaN has a 3.5-eV direct gap and GaAs has a 1.4-eV direct gap, we would expect a blueshift of the photoluminescence edge. Because of the lattice mismatch it is likely that a reconstruction of the alloy (volume effect) and, a possible rearrangement of the atoms in the unit cell (geometrical relaxation) will occur. In order to interpret these experiments we must take into account the fact that for small concentrations of N, we expect to have defect impurities where the N atom will tend to localize the charge to become  $\text{N}^-$ , then electron-hole recombination should occur. This kind of exciton on the N will show up in light emitting experiments probably as a transition close to the bottom of the conduction band in the gap region. That is, we should observe a reduced band edge in the photoluminescence. By increasing the N concentration we expect that the lattice mismatch will play the fundamental role and the previous recombination effects will be less important. For the purpose of getting blue light devices, the alloys with a mostly GaN component will be of great interest. This region was studied in the case of  $\text{Ga}_x\text{Al}_{1-x}\text{N}$  alloys<sup>9</sup> for which the band gap increased with the N concentration; however a reduction is expected for the  $\text{GaAs}_{1-x}\text{N}_x$  alloy rich in N.

The objective of the present study is to clarify the issue of the component volume difference on the quasiparticle excitations in  $\text{GaAs}_{1-x}\text{N}_x$  without geometrical relaxation. We will focus on two particular N concentrations:  $x=0.5$  and 0.25. Instead of treating the random alloy in a more appropriate description using the quasirandom structures (QS),<sup>11,12</sup> we consider only ordered alloys keeping the structural symmetry of each component [in this case the zinc-blende structure packed along the (111) direction], and we minimize the total energy as a function of the alloy volume keeping the  $c/a$  ratio of the ordered alloy equal to one. Even though this is an approximation to the actual structure and important effects coming from the internal relaxation<sup>13</sup> are neglected, we believe most of the physics relative to the experimental redshift is included in this study. The effects of geomet-

TABLE I. Calculated equilibrium lattice constant  $a_0$  (Å), for the pure elements and ordered alloys in the zinc-blende structure.

	GaN	GaAs <sub>0.5</sub> N <sub>0.5</sub>	GaAs <sub>0.75</sub> N <sub>0.25</sub>	GaAs	AlN	AlAs <sub>0.5</sub> N <sub>0.5</sub>	AlAs <sub>0.75</sub> N <sub>0.25</sub>	AlAs
Theory	4.42 <sup>a</sup>	5.12	5.30	5.61 <sup>b</sup>	4.35 <sup>a</sup>	4.91	5.28	5.61 <sup>b</sup>
Experiment	4.50 <sup>c</sup>			5.65 <sup>d</sup>				5.66 <sup>d</sup>

<sup>a</sup>As quoted in Ref. 3.

<sup>b</sup>As quoted in Ref. 21.

<sup>c</sup>Experimental data from Ref. 24.

<sup>d</sup>From Ref. 25.

rical relaxation have been addressed by Neugebauer and Van de Walle.<sup>13</sup> In a forthcoming work we will present the results of quasiparticle calculations on the geometrically relaxed structures.<sup>14</sup> We note that alloy ordering usually leads to an overestimation of the gap reduction for the alloy; this has been shown in experimental work on Ga<sub>0.5</sub>In<sub>0.5</sub>P alloys<sup>15</sup> and in the theoretical work using QS.<sup>11</sup>

The ground-state calculations are performed using the standard plane-wave pseudopotential total-energy scheme within the Kohn-Sham density functional formalism and the local density approximation (LDA) for exchange and correlation.<sup>16</sup> *Ab initio* norm-conserving pseudopotentials are used<sup>17</sup> including partial core corrections for gallium.<sup>3</sup> For all of the calculations presented here a 40-Ry cutoff energy in the plane-wave expansion is used for the LDA self-consistent charge density and wave functions. Good convergence for both total energy and electron eigenvalues is achieved with this cutoff.

The GW approximation<sup>4,18</sup> for the quasiparticle excitations is used in the calculation of the electron self-energy  $\Sigma$ . The screened Coulomb interaction is given by  $W = \epsilon^{-1}V$  where  $V$  is the bare Coulomb interaction. For the dielectric matrix we use a generalized form of the static Levine-Louie model dielectric matrix with a generalized plasmon pole model for the dynamical extension of the dielectric matrix.<sup>19–21</sup> This model requires only the dielectric constant  $\epsilon_0$  of the material as input. In principle  $\epsilon_0$  can be evaluated from *ab initio* calculations, but we have taken the experimental dielectric constant values of 5.20 and 10.9 for pure GaN and GaAs, respectively. For the mixed nitride-arsenide systems studied here, we have taken an average of the experimental values of  $\epsilon_0$ ; that is a value of  $\epsilon_0 = 8.1$  has been used throughout for the alloy quasiparticle calculations. The Levine-Louie model has been shown to give errors in band gaps of the order of few tenths of an eV,<sup>20,21</sup> the results being insensitive to small changes in the initial  $\epsilon_0$  value. On this basis we expect that the value used here for  $\epsilon_0$  will be appropriate to accurately describe the systems under study. Following previous studies<sup>3,4,21</sup> we approximate the quasiparticle wave function by its LDA counterpart. To calculate  $\Sigma$ , some cutoffs are needed: 50 bands per atom in the unit cell were used; ten  $k$  points in the irreducible zone were used for the Brillouin-zone summations; and the sum over *umklapp* processes was truncated at  $G_{\max}^2 = 16.0$  Ry.

In Table I we summarize the results of the present work on the structural properties of the zinc-blende nitride-arsenide ordered alloys. We observe that the lattice parameters of the alloys are in quite good agreement with Vergard's law. We remark again that we did

not relax the internal parameters of the alloy. Recent theoretical calculations on the GaAs<sub>0.5</sub>N<sub>0.5</sub> ordered alloy shows that the global lattice constant is very close to the one we found even though the internal positions change appreciably.<sup>13</sup> The randomness of the alloy and internal relaxation are neglected but these effects are expected to be much smaller than the global volume effect on the electronic properties.<sup>22</sup> Effects of internal relaxations have been addressed in other work.<sup>13</sup>

Let us concentrate on the experimental results for GaAs<sub>1-x</sub>N<sub>x</sub>, where an unexpected linear redshift of the photoluminescence peak was observed ( $E_{\text{peak}} = E_{\text{GaAs}}^{\text{gap}} - 12x$ ).<sup>2</sup> This fact indicates that the band gap in the alloy system has a strong nonlinear dependence on the alloy concentration  $x$ . In Table II we summarize the LDA, GW, and experimental results, where available, for these composite alloys. For the pure materials we see strong many-body correction on the fundamental band gap ( $\sim 1$  eV). This is relevant for the absolute magnitude of the band gap dependence upon concentration. On the other hand, the qualitative features of this band-gap dependence are already included in the LDA results. That is, a clear band-gap reduction is obtained up to 25% concentration of N. Remarkably, the band gap of the 50% alloy is even lower than the corresponding GaAs gap and a further reduction is obtained in going to the 25% alloy with a near closing of the LDA gap. From the present study, it is not clear at which concentration the band gap again begins to increase, and whether or not there is a range of concentrations for which the system is metallic. On the basis of the GW results the complete closing of the band gap seems unlikely to happen because of the more than 0.6-eV opening induced by the many-body

TABLE II. Calculated quasiparticle and LDA direct band gap (at  $\Gamma$ ) in eV for the ordered alloys GaAs<sub>1-x</sub>N<sub>x</sub> ( $x=0.25$  and 0.5). The value in parenthesis in the LDA column corresponds to a calculation of GaN with the same volume as the alloy (see text).

	LDA	GW	Experiment
GaN	2.1 <sup>a</sup>	3.1 <sup>a</sup>	3.2, <sup>b</sup> 3.3 <sup>c</sup>
GaAs <sub>0.5</sub> N <sub>0.5</sub>	0.4 (-0.74)	1.0	
GaAs <sub>0.75</sub> N <sub>0.25</sub>	0.06	0.7	
GaAs	0.6 <sup>d</sup> (-2.04)	1.3 <sup>b</sup>	1.52 <sup>e</sup>

<sup>a</sup>As quoted in Ref. 3.

<sup>b</sup>Optical absorption from Ref. 24.

<sup>c</sup>Photoluminescence and cathodoluminescence from Ref. 26.

<sup>d</sup>As quoted in Ref. 21.

<sup>e</sup>From Ref. 25.

corrections and also by the fact that disorder will tend to increase the band gap<sup>12,15</sup> but a more detailed study of this closing is left for a forthcoming publication.<sup>14</sup> Following these results for intermediate N concentrations, we can extrapolate to the limit of very small N concentration where experimental data is available. Then, we expect a limiting approach to the GaAs direct band-gap value from lower values. This is in clear agreement with the experimental findings.<sup>2</sup>

In order to understand better the physical mechanism behind the calculated band-gap trends, in Table II we give in parenthesis the results of a calculation for GaN with volumes equal to the 50% alloy and GaAs. As is shown, the bottom of the conduction band ( $\Gamma_{1c}$ ) has a strong volume dependence descending toward the  $\Gamma_{15v}$  top valence band, leading to the closing of the gap. This is due to the fact that the  $\Gamma_{1c}$  level has mainly antibonding character with most of the charge density located on the anion site (N). As we increase the volume the charge density becomes even more localized on the N tending to form atomlike orbitals. This leads to a lowering of this level as compared with close lying levels because of the fast decrease of its potential energy. The same kind of potential versus kinetic energy arguments have been used to explain the evolution of the band gaps in group IV semiconductors when the volume is increased.<sup>23</sup> When looking at the charge distribution at the bottom of the conduction band in the ordered alloys we find that again N clearly dominates this state. Thus, from the GaN results we expect a strong variation of this level due to the increase in volume of the alloy with respect to the pure GaN. Not until the As sites begin to accumulate some of the charge density will this band-gap lowering tendency be reversed. We note that this behavior of the  $\Gamma_{1c}$  conduction levels has also been found experimentally in Ga<sub>x</sub>In<sub>1-x</sub>P alloys under pressure,<sup>15</sup> where the  $\Gamma_{1c}$  level shows a strong pressure dependence as compared to the other close lying levels ( $X, L$ ). This different rate of change leads to a direct to indirect transition as the pressure increases.

Based on the previous results a natural extension is to study the electronic properties of similar alloys by changing the group III cation, that is Al instead of Ga in the nitride-arsenide alloys. In contrast to the Ga alloys where the constituents were direct gap materials, the Al ones are indirect gap materials. Also, AlN and AlAs show a similar lattice mismatch to GaN and GaAs (see Table I), thus a strong volume effect on the band gap evolution with concentration will also be expected. In Table III we summarize the results of our LDA and quasiparticle calculations. As before, the results in parenthesis correspond to calculations of AlN with the unit cell volume of the alloy. Clearly, the band gap at  $\Gamma$  shows a strong volume dependence as compared to the indirect band gap  $\Gamma - X$ . AlN quickly becomes a direct gap semiconductor with increasing volume. Similar to GaN, at the 50% alloy

TABLE III. Calculated quasiparticle and LDA band gaps at  $\Gamma$  and  $X$  in eV for the ordered alloys AlAs<sub>1-x</sub>N<sub>x</sub> ( $x=0.25$  and  $0.5$ ). The value in parenthesis in the LDA column corresponds to a calculation of AlN with the same volume as the alloy (see text).

	$\Gamma - X$		$\Gamma - \Gamma$	
	LDA	GW	LDA	GW
AlN	3.2 <sup>a</sup>	4.9 <sup>a</sup>	4.2 <sup>a</sup>	6.0 <sup>a</sup>
AlAs <sub>0.5</sub> N <sub>0.5</sub>	0.76 (3.01)		1.13 (1.84)	
AlAs <sub>0.75</sub> N <sub>0.25</sub>	3.47		0.45	
AlAs	1.33 <sup>b</sup> (2.62)	2.14 <sup>b</sup>	2.07 <sup>b</sup> (-0.82)	2.88 <sup>b</sup>

<sup>a</sup>As quoted in Ref. 3.

<sup>b</sup>As quoted in Ref. 21.

volume AlN in LDA shows a closing of the fundamental gap. In this case, the volume effect tends not only to reduce the band gap of the alloys but also to make it go from indirect to direct for an intermediate range of N concentrations. In that way, as a function of the N concentration, we found that small and large concentrations correspond to indirect gap semiconductors whereas at intermediate concentrations the gap is direct. Also we predict that the inclusion of low N concentrations in AlAs will lead to a similar redshift of the photoluminescence or absorption edge as occurs in GaAs.

In conclusion we have shown that the "unexpected" redshift of the band edge when a small concentration of N is added to GaAs can be explained by the increase in volume due to lattice mismatch. The lowering of the band edge is maintained until the arsenic starts playing a role in the charge density distribution of the bottom conduction band (dominated by N for intermediate concentrations). Based on the similarities between Ga-based and Al-based III-V compounds, we predict that similar redshifts may be found in AlAs<sub>1-x</sub>N<sub>x</sub> alloys. Also, we predict that for an intermediate range of concentrations the system will show a direct band-gap edge. These alloys will cover a wide range of the energy spectrum, from very small gap semiconductors to the arsenic (intermediate gap) and nitride (wide gap) semiconductors, which may be technologically important.

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