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Ab initio study of anomalous band-gap bowing in GaAs_{1-x}N_x alloys

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Abstract. A full potential self-consistent linear muffin-tin orbital method in the local density approximation (LDA) has been employed to investigate the electronic structure of the 14 ordered GaAs_{1-x}N_x alloys with $x = 0.0, 0.037, 0.074, 0.111, 0.125, 0.25, 0.375, 0.407, 0.50, 0.625, 0.75, 0.875, 0.963$ and 1.0 . The lattice parameter is seen to have a non-linear variation with the concentration of the constituent atoms. In LDA, a near closure of the fundamental energy gap appears in the concentration range 12.5–62.5% of N atoms. A strong hybridization of N s states with the Ga (s,p) and As (s,p) states is seen at the bottom of the conduction band and these states descend into the fundamental gap, filling it either partially or completely. The band gap for the random alloys also shows an anomalous bowing.

1. Introduction

Great interest has been shown in the study of the electronic properties of III–V semiconducting alloys because of their important applications in optoelectronic devices and other technological applications.

GaAs, which has a comparatively smaller band gap, plays an important role in the semiconductor industry. The alloys of III–V elements which possess wide energy gaps are important for the development of the optoelectronic devices in the high frequency region. In the case of GaAs_{1-x}N_x alloys, one expects to observe a variation of band gap from a value of 1.52 eV (GaAs) to a value of 3.3 eV (GaN). Thus a blue shift of the photoluminescence edge should have been observed experimentally with the addition of N atoms. On the contrary, a red shift of the photoluminescence edge has been observed in these alloys (Weyers *et al* 1992). In the alloys such as Al_xGa_{1-x}N, where the lattice mismatch between the end components is about 2.9%, one observes a dominant role played by the cations in determining the electronic structure and the band gaps. On the other hand, in the GaAs_{1-x}N_x alloys, the lattice mismatch is as large as 20% and the effects of various anion component concentrations are seen to be anomalous.

Compound semiconductor alloys of the type A_xB_{1-x}C are often considered to consist of a regular arrangement of A and B atoms on an fcc sublattice. However, real alloys may, in general, be random. Deviations from randomness have been observed, such as phase separation, i.e., formation of distinct AC and BC rich phases. Another case of deviation is the occurrence of order seen in both types of alloy, A_xB_{1-x}C and AB_{1-x}C_x. In the extreme case of perfect order, one may observe alternating layers of pure AC and pure BC in cation variant systems A_xB_{1-x}C or AB and AC pure layers in the anion variant systems AB_{1-x}C_x.

In an earlier paper (Agrawal *et al* 1997), we reported the results for the electronic structure of a first-principles self-consistent full potential linear muffin-tin orbital (LMTO)

calculation of the cation dominated $\text{Ga}_{1-x}\text{Al}_x\text{N}$ alloys and observed quite a little bowing in the fundamental energy gap. We extend our studies to $\text{GaAs}_{1-x}\text{N}_x$ alloys in the present article. The electronic structure of the 14 ordered systems $\text{GaAs}_{1-x}\text{N}_x$ for $x = 0, 0.037, 0.074, 0.111, 0.125, 0.25, 0.375, 0.407, 0.50, 0.625, 0.75, 0.875, 0.963$ and 1.0 have been investigated. In the local density approximation, we observe a near closure of the band gap in the concentration range $x = 0.125\text{--}0.625$ of the N atoms. This creates the possibility of the fabrication of III–V light emitting devices covering the whole optical region. Earlier, Rubio and Cohen (1995) employed a pseudo-potential theory in the local density approximation to obtain a gap of 0.06 eV for one case only, i.e., 25% concentration of N atoms. They have also performed a quasi-particle study and observed an opening of the band gap in the LDA by about 0.7 eV.

Bellaiche *et al* (1996) have discussed the electronic properties of some ordered alloys and quasirandom structures of Ga–As–N alloys by using local empirical pseudopotentials in the plane-wave pseudopotential approach. A fitting with the GW band structures, experimental band gaps and LDA deformation potentials was adopted to obtain the atomic potentials. For each composition, results were averaged over a few randomly selected configurations. They considered a bimodal distribution of bond lengths.

In contrast to Bellaiche *et al* (1996), we have investigated the electronic structure of the ordered and the random $\text{GaAs}_{1-x}\text{N}_x$ alloys by using a fully *ab initio* LMTO method without adopting any fitting procedure. Although we have adopted a unimodal distribution of bond lengths, in the majority of our calculations, the effects of bimodal distribution have been studied in a typical case and the results are not seen to be affected significantly.

In the present study, the full potential LMTO method has been used to investigate the electronic properties of the ordered $\text{GaAs}_{1-x}\text{N}_x$ alloys. For detailed information on the method used, we refer to our earlier paper (Agrawal *et al* 1997). The calculated results for the electronic structure, total density of states and band-gap bowing are shown in section 2. The main conclusions are contained in section 3.

2. Calculation and results

The lattice is a face centred cubic one. A unit cell containing eight molecular units (16 atoms) has been employed for the different crystal structures of $\text{Ga}_8\text{As}_{8-n}\text{N}_n$ alloys for $n = 0\text{--}8$. For low concentrations of N or As atoms, i.e., for $x = 0.037, 0.074, 0.111, 0.407$ and 0.963, a bigger unit cell or supercell containing 27 molecular units (54 atoms) has been employed.

The non-overlapping radii of muffin-tin spheres are chosen to be 2.17, 2.15 and 1.43 au for Ga, As and N, respectively. We use muffin-tin orbitals (MTOs) of 4s, 4p, 3d (4d) type for Ga (As) atoms and the 2s and 2p type MTOs for N. In a separate calculation, we have also considered Ga 4d states instead of Ga 3d states as valence states at several N concentrations. However, the results are not significantly changed except for a small change in the magnitude of the band gap.

For the calculation of the charge density and the potential, the LMTO envelopes are expanded in terms of the Hankel functions having the spherical harmonic components $l \leq 4$. Three values, $-0.01, -1.0$ and -2.3 Ryd for the decay factor in the Hankel functions are used in the construction of the muffin-tin orbitals for real atoms. In the interstitial region two values, -0.01 and -1.0 Ryd of the decay factor have been employed. Each supercell contains an equal number of real atomic muffin-tin spheres (MTSs) and empty MTSs. The scalar relativistic effects have been considered in all the calculations. For the exchange–correlation potential, the parametrization of Hedin and Lundqvist (1971) has been chosen.

In the present method, the wave functions of the core electrons of the atoms are relaxed, and in the self-consistent calculation in each iteration the core electron charge density is recalculated.

A deficiency of the local density theory is that the calculated value of the fundamental energy gap is about 50% of the experimental one. This originates from the fact that the excitation energies of these systems are not given by eigenvalues of the Kohn–Sham equations (Perdew and Levy 1983, Sham and Schluter 1983). The quasi-particle energies and wide band gaps have been calculated in the so-called GW approximation of the electron self-energies Σ . This self-energy is seen to be a non-local energy dependent effective potential. This is beyond the scope of the present work.

For the different structures of the ordered GaAs_{1-x}N_x alloys, the lattice parameters have been calculated by minimizing the crystal energy in our calculation. We compare these calculated lattice parameters with the available experimental values and the other calculated values in table 1. The variation is shown in figure 1. The variation is seen to be a nonlinear one. The departure from linearity is appreciable. The present calculated value for GaN is in excellent agreement with the experiment, whereas for GaAs the lattice parameter is seen to be well within 2% of the experimental value. Our calculated values are quite close to those reported for some alloys by other workers but are somewhat on the higher side. The discrepancy may arise because of the use of correlation schemes by other workers which are different from the present one.

Table 1. Variation of lattice constant with concentration of the constituent atoms in the ordered GaAs_{1-x}N_x structures. All values are measured in Å.

System (<i>x</i>)	Present	Other calc.	Expt
0.000	5.55	5.61 ^a	5.65 ^b
0.125	5.46		
0.250	5.36	5.30 ^c	
0.375	5.26		
0.500	5.14	5.12 ^c	
0.625	4.95		
0.750	4.83		
0.875	4.66		
1.000	4.50	4.42 ^d , 4.48 ^e , 4.30 ^f	4.50 ^g

^a Model dielectric function, Zhu and Louie 1991.

^b Landolt–Börnstein 1982.

^c Pseudopotential, Rubio and Cohen 1995.

^d Pseudopotential, Rubio *et al* 1993.

^e LMTO–ASA, Albanesi *et al* 1993.

^f Pseudopotential, Jenkins *et al* 1994.

^g Optical absorption, Lei *et al* 1992.

In all future calculations, the above calculated lattice parameters have been used. Further, for every ordered structure the bond lengths for the Ga–As and the Ga–N bonds are taken to be the same, i.e., we assume a unimodal distribution of bond lengths. The effect of a bimodal distribution of bond lengths is investigated in the later part of this article.

2.1. Ordered structures

The crystal lattices for all the considered ordered alloys have the zinc blende structure. In figures 2 and 3, the electronic structure is depicted for the 16- and 54-atom supercells,

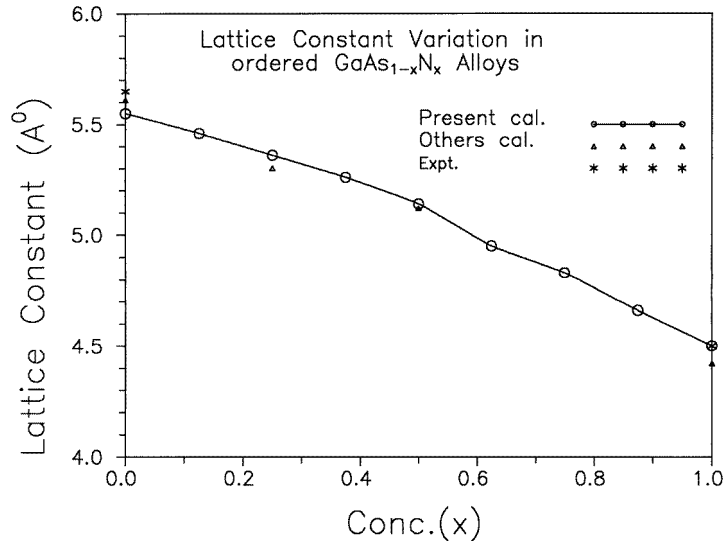


Figure 1. Lattice constant variation in the ordered $\text{GaAs}_{1-x}\text{N}_x$ alloys. Experimental data are taken from *Landolt-Börnstein* (1982) and *Lei et al* (1992). The results of other calculations are taken from *Zhu and Louie* (1991), *Rubio and Cohen* (1995) and *Rubio et al* (1993).

respectively. For brevity, we have not included the band structures for $x = 0.625$ and 0.875 in figure 2. The lengths of the primitive lattice vectors for the 16- and 54-atom supercell are, respectively, doubled and tripled as compared to those of the two-atom unit cell. This results in zone folding. Also, the number of branches increase according to the larger number of molecular units in the supercell. In figures 2 and 3, the dispersion curves are shown only in the vicinity of the fundamental energy gap. The origin of energy is chosen at the top of the valence band for each ordered alloy.

For the end component ordered structure, Ga_8As_8 , the point group symmetry is T_d and the symmetry points of the bcc Brillouin zone are W (0.5, 0.25, 0), L (0.25, 0.25, 0.25), Γ (0, 0, 0), X (0.5, 0, 0) and K (0.375, 0.375, 0). A set of 19 special k -points is selected in the irreducible part of the Brillouin zone for achieving self-consistent results. The energy gap is a direct one equal to 0.61 eV. The states just above the bottom of the conduction band correspond to the X-point of the Brillouin zone for the two-atom unit cell. This happens because of the zone folding. The valence band maximum (VBM) is composed of As p-like states whereas the conduction band minimum (CBM) is composed of the s-like orbitals mainly of Ga having some contribution from As. It may be noted that the value of energy gap for this ordered structure in the GW approximation is 1.3 eV (*Rubio and Cohen* 1995).

For the most dilute ordered structure $\text{Ga}_{27}\text{As}_{26}\text{N}$ (3.7% of N), the point group symmetry is again T_d . The N atoms lying in the adjacent 54-atom supercells are sixth neighbours among themselves. The calculated electron structure in the neighbourhood of the energy gap is shown in figure 3. The band gap is 0.44 eV. The valence band maximum is comprised of almost all the p orbitals of the three constituent atoms N, Ga and As but the main contributions are from the N and As atoms. On the other hand, the main contributors to the CBM are the antibonding mixed states of N (s), Ga (s,p) and As (s,p) orbitals. For all the other alloy systems the main contributors are the s-like orbitals of N and Ga atoms with some contribution from the As (s) orbitals.

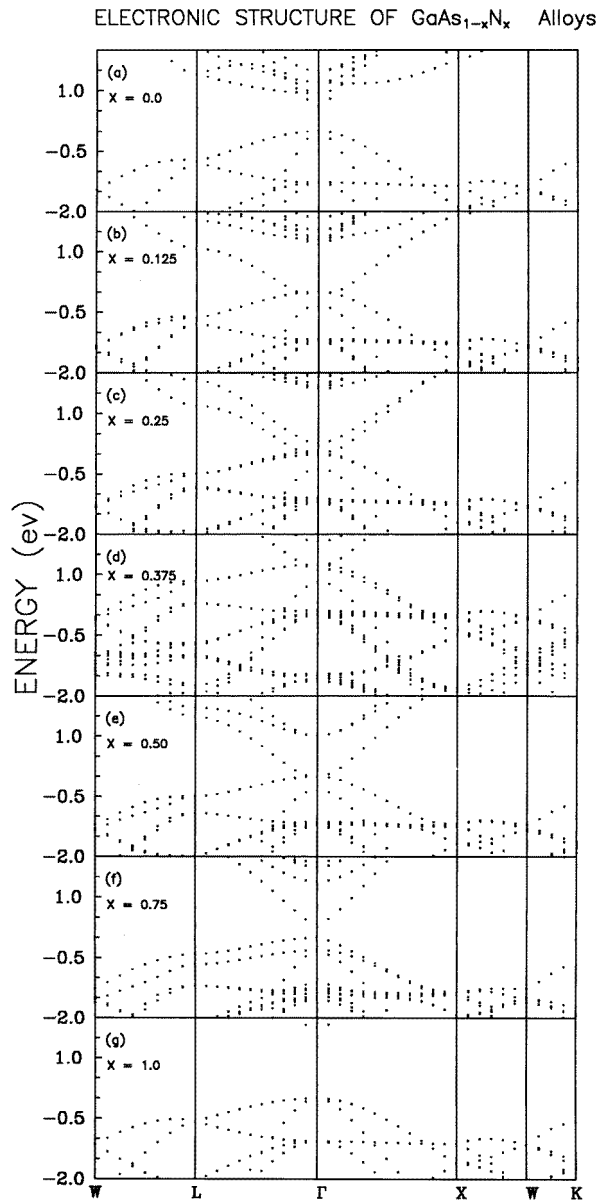


Figure 2. Electronic dispersion curves for the ordered $\text{GaAs}_{1-x}\text{N}_x$ alloys (a) $x = 0.00$, (b) $x = 0.125$, (c) $x = 0.25$, (d) $x = 0.375$, (e) $x = 0.50$, (f) $x = 0.75$ and (g) $x = 1.0$. The origin of energy has been chosen at the valence band maximum.

For the next dilute ordered structure $\text{Ga}_{27}\text{As}_{25}\text{N}_2$ (7.4% of N), two atomic configurations having different point group symmetries C_{2v} and C_{3v} were considered. In the C_{2v} symmetric configuration two N atoms are next nearest neighbours among themselves, whereas in the C_{3v} point group configuration two N atoms are fourth neighbours among themselves. For the C_{2v} and C_{3v} point group symmetries, the magnitudes of the band gap are seen to be different, i.e., 0.283 and 0.350 eV, respectively. The variation of gap is seen to be small

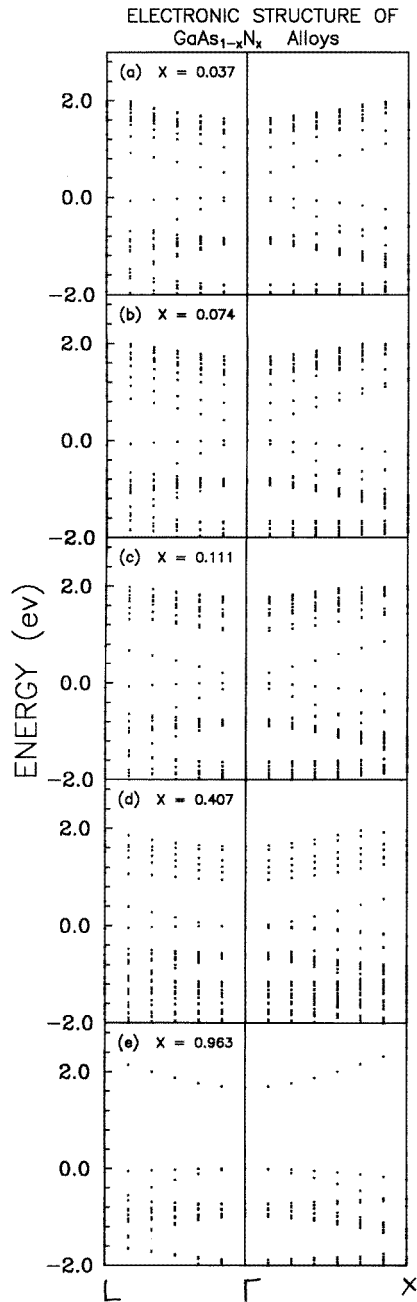


Figure 3. Electronic dispersion curves for the ordered GaAs_{1-x}N_x alloys (a) $x = 0.037$, (b) $x = 0.074$, (c) $x = 0.111$, (d) $x = 0.407$ and (e) $x = 0.963$. The origin of energy has been chosen at the valence band maximum.

for the two different locations of the two N atoms in the supercell. For brevity, we do not include the results obtained for C_{3v} symmetry in the presentation of the results.

In the Ga₂₇As₂₄N₃ ordered structure, the three N atoms are second neighbours among

themselves and the point group symmetry is C_{3v} . The magnitude of energy gap decreases to 0.11 eV. The orbital composition of the valence band maximum and that of the conduction band minimum are similar to the above discussed ordered alloys.

For the ordered GaAs_{0.875}N_{0.125} system, the symmetry is T_d . There is one N atom in the 16-atom supercell and the N atoms of the two adjacent supercells are fourth neighbours among themselves. A remarkable observation is that the band gap vanishes at this small concentration of N atoms. In the LDA, the ordered alloy becomes metallic (zero band gap) at $x = 0.125$. The hybridized s orbitals of all the atoms fill the energy gap completely. In fact, at the Γ -point where the closure of the gap is seen, the states at the VBM are comprised of mixed As (p) and N (p) orbitals. Also, the charge inside the MT sphere of N has increased. One observes a localization of charge on the N atom.

For $x = 0.25$, again two different configurations of N atoms have been chosen. In C_{2v} symmetry two N atoms are next nearest neighbours among themselves, whereas in C_{3v} symmetry the nearest two N atoms are seen to be the third neighbours among themselves. For the C_{2v} and C_{3v} point group symmetries, the band gap is seen to be 0.064 and 0.0 eV, respectively. However, we have not included the results obtained for the C_{3v} symmetry in table 2. The present value, 0.064 eV, for the energy gap obtained for C_{2v} point group symmetry is in agreement with the value of 0.06 eV reported by Rubio and Cohen (1995). The inclusion of the many body effects such as considered in the GW approximation may reveal a finite energy gap instead of the closure of the gap. Rubio and Cohen have calculated the GW value as 0.7 eV. The charge inside the MT sphere of N increases further.

For $x = 0.375$, the three N atoms are next nearest neighbours among themselves and the point group symmetry is C_{3v} . The lowest conduction states enter the valence band and the band gap is zero. The MT sphere for the N atom acquires more charge.

For the next ordered structure, the Ga₂₇As₁₆N₁₁ supercell, the point group symmetry is chosen to be C_{3v} . There are two sets of clusters of N atoms out of the total of 11 N atoms. A cluster of four atoms is far separated from another set of seven atoms. The N atoms are second neighbours among themselves in each set. The minimum separation between the N atoms in one set and the other set is equivalent to a separation between fourth neighbours. The seven atoms lying in the second set form a centred hexagon normal to the $\langle 111 \rangle$ axis. The calculated energy gap is zero and one observes a closure of the gap.

For the GaAs_{0.50}N_{0.50} ordered alloy, again the two atomic configurations having different point group symmetries T_d and C_{2v} were considered. For C_{2v} symmetry, the nearest N atoms lie in the second neighbouring lattice positions. For the T_d and C_{2v} point group symmetries, the magnitudes of the band gap are 0.00 and 0.16 eV, respectively. Rubio and Cohen (1995) have obtained a band gap of 0.4 eV without including Ga 3d states in their calculation. Their reported GW value is 1.0 eV. We do not present the results obtained for the C_{2v} symmetry in table 2. The charge in the MT sphere of N is large.

For $x = 0.625$, the point group symmetry is C_{3v} . The band gap is seen to be 0.011 eV.

For the GaAs_{0.25}N_{0.75} ordered alloy ($x = 0.75$), the point group symmetry is C_{2v} . The dispersion curves are similar to those of GaAs_{0.50}N_{0.50} alloy except that the direct band gap is 0.34 eV. The ionic gap is wide (-8 to -11 eV).

For an alloy containing 12.5% of As atoms, i.e., GaAs_{0.125}N_{0.875}, the point group symmetry is T_d in a 16-atom supercell. The band gap is seen to be 1.12 eV.

At the other end of the alloy system, for one As atom in the 54-atom supercell (Ga₂₇AsN₂₆) the point group symmetry is T_d . The electronic structure is depicted in figure 3(e). The band gap is smaller than that of the pure GaN lattice and is equal to 1.66 eV.

For the Ga₈N₈ ordered structure, the other end component of the alloys, the direct band

gap is 1.90 eV. The point group symmetry is T_d . The states lying just above the bottom of the conduction band correspond to the X-point of the Brillouin zone seen in the two-atom unit cell of GaN. The VBM originates from the N (p) states and the CBM from the antibonding mixed s-like states of N and Ga. This somewhat lower value of band gap in comparison to other results (Rubio *et al* 1993, Albanesi *et al* 1993, Jenkins *et al* 1994) may arise because of the use of different exchange–correlation potentials by other workers.

One observes an accumulation of charge or more localized charge around the N atoms in the concentration range $x = 0.111$ – 0.625 . The N atoms behave in a more atomic way. The resulting fall in the potential energy leads to the lowering of N 2s states in the fundamental energy gap, filling it partially or completely. A similar conclusion has been drawn by Rubio and Cohen (1995).

In order to see the effects of a bimodal distribution of bond lengths on the electronic structure as a typical case we perform a separate calculation for the ordered $\text{Ga}_8\text{As}_7\text{N}$ alloy. In this alloy the bond length for each GaAs and GaN bond is same and is equal to 2.38 Å in a unimodal distribution of bond lengths. In order to see the effect of the variation of bond length we have chosen a value of 2.02 Å for all the four neighbouring GaN bonds around the central N atom, keeping the bond lengths of the GaAs bonds equal to 2.38 Å. The band gap is seen to be 0.035 eV against a zero value obtained for a Ga–N bond length of 2.38 Å. Thus, the zero band gap seen in a finite concentration range of N does not seem to be affected significantly in a bimodal distribution of bond lengths.

Table 2. Band-gap variation in the ordered $\text{GaAs}_{1-x}\text{N}_x$ structures. All energies are measured in eV.

System (x)	Present	Other calc.		Expt
		LDA	GW	
0.000	0.61	0.60 ^a	1.3 ^c	1.52 ^b
0.037	0.44			
0.074	0.28			
0.111	0.11			
0.125	0.00			
0.250	0.064	0.06 ^c	0.7 ^e	
0.375	0.00			
0.407	0.00			
0.500	0.00	0.40 ^c	1.0 ^e	
0.625	0.011			
0.750	0.34			
0.875	1.12			
0.963	1.66			
1.000	1.90	2.10 ^d , 1.97 ^e , 2.32 ^f	3.1 ^d	3.20 ^g , 3.30 ^h , 3.52 ⁱ , 3.4 ^j

^a Model dielectric function, Zhu and Louie 1991.

^b Pseudopotential or quasi-particle energy, Rubio and Cohen (1995).

^c Landolt–Börnstein 1982.

^d Pseudopotential, Rubio *et al* 1993.

^e LMTO–ASA, Albanesi *et al* 1993.

^f Pseudopotential, Jenkins *et al* 1994.

^g Optical absorption, Lei *et al* 1992.

^h Photoluminescence and cathodoluminescence, Paisley *et al* 1989, Sitar *et al* 1992.

ⁱ Cathodoluminescence at 53 K on epitaxial films, Harrison 1985.

^j Optical absorption, Yoshida *et al* 1982.

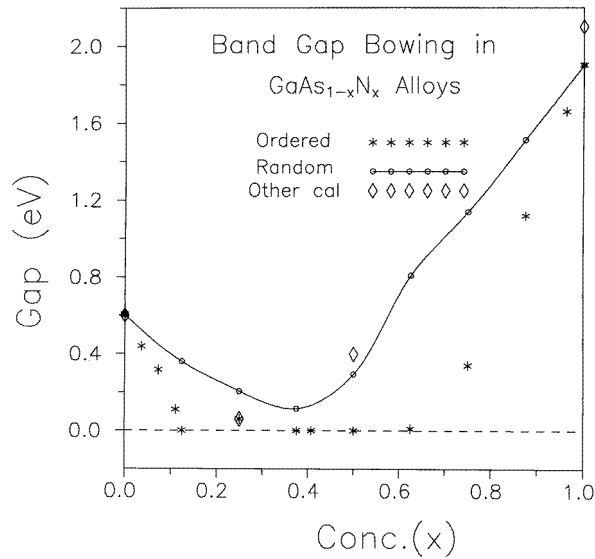


Figure 4. Variation of band gap with the concentration x for the ordered and random GaAs_{1-x}N_x alloys. The results of other calculations are taken from Zhu and Louie (1991), Rubio and Cohen (1995) and Rubio *et al* (1993).

The direct band gap energy of the GaAs_{1-x}N_x ordered alloys, for $x = 0.0, 0.037, 0.074, 0.111, 0.125, 0.25, 0.375, 0.407, 0.50, 0.625, 0.75, 0.875, 0.963$ and 1.0 is presented in table 2. A closure of gap is observed from $x = 0.125$ to 0.625 . The calculated band gaps are compared with the available experimental data for $x = 0.0$ and 1.0 and the other calculated values available for $x = 0.0, 0.25, 0.50$ and 1.0 . The variation of band gap energy with concentration x of N atoms is shown in figure 4.

Weyers *et al* have obtained an empirical linear relationship for the measured change in energy gap of GaAs_{1-x}N_x alloys up to 1.5% of N atoms. In the present calculation, the lowest concentration of N atoms is 3.7%. Assuming the Weyers *et al* relationship to be true for 3.7% of N atoms, the extrapolated decrease in bandgap for $x = 0.037$ is 0.44 eV. This denotes a change of about 30%.

In the present calculation the calculated decrease in the band gap is about 28%, which is in very good agreement with the experiment.

2.2. Random alloys

In general, one may not expect the occurrence of a particular ordered structure. A more probable situation is the occurrence of a number of various different local atomic configurations in different parts of an alloy. The alloy may be a disordered one depending upon the growth conditions. The properties of the disordered alloy may be simulated by considering the statistical mechanical distributions of the ordered structures. A cluster expansion method has been adopted (Sanchez and de Fontaine 1981, Sanchez *et al* 1984, Srivastava *et al* 1985) in the past for obtaining such a statistical mechanical description. It has been suggested that the coefficient of the cluster expansion method may be obtained by a first principles calculation of a set of ordered structures. This method which was first used for binary alloys can be extended to the ternary alloy in the case where the disorder is

assumed to occur only on one type of site, say anion or cation as is the case for the presently discussed $\text{AB}_{1-x}\text{C}_x$ alloys. One simplifies the calculation by truncating the cluster expansion at the level of nearest neighbour interactions. For a tetrahedron structure one studies the five basic structures corresponding to the nearest neighbour tetrahedron B_{4-n}C_n ($n = 0-4$). The statistical mechanical property of the alloys may be considered as the property seen for the random alloys. Any statistical property $F(x)$ at a particular concentration x may be expanded as

$$F(x) = \sum_n P_n(x) F_n \quad (1)$$

where F_n is the property for the anion tetrahedron and $P_n(x)$ is the probability of the occurrence of cluster B_{4-n}C_n .

The probability of each cluster which is in general temperature dependent should be obtained at any given temperature by minimizing the free energy with respect to the probability $P_n(x, T)$. However, we assume here a temperature independent random distribution function for the probability given by

$$P_n(x) = \binom{4}{n} x^n (1-x)^{4-n}. \quad (2)$$

A similar calculation has been done by earlier workers (Srivastava *et al* 1985, Albanesi *et al* 1993, Agrawal *et al* 1997). This is obviously a first approximation and may be expected to be valid for the case of frozen-in disorder of the gas or liquid phase from which the solid solutions are quenched.

Using (1) we have calculated the band gap for the random alloys at different concentrations of N and have included the results in figure 4. One observes a very large bowing in the energy gap curve with a minimum value of 0.114 eV at $x = 0.375$.

Our results compare very well with those obtained by Bellaiche *et al* (1996) for electronic structure. Similar to them, we observe a weak localization of the conduction band minimum wavefunctions around N atoms in the N impurity region (dilute N alloys) and a strong localization of valence band maximum wavefunctions around As atoms in the As impurity region (N dominated alloys). For some of their 'special quasirandom structures' which are different from our fixed zinc blende structures, they obtain a negative band gap in contrast to our zero band gap. These authors have obtained a minimum value of band gap equal to 0.4 eV for $x = 0.50$ random alloy in contrast to our value of 0.3 eV for the random alloy obtained here without using any fitting procedure.

3. Conclusions

The first principles full potential self-consistent linear muffin-tin orbital (LMTO) method has been employed to understand the electronic properties of 14 ordered and random $\text{GaAs}_{1-x}\text{N}_x$ alloys. The calculated lattice constant shows quite a non-linear behaviour. A large band-gap bowing is observed. A near closure of the fundamental energy gap is observed for an N atomic concentration range of $x = 0.125-0.625$. Inclusion of many body effects such as the GW approximation may open the gap by $\sim 0.7-0.9$ eV, making these alloys narrow gap materials in the N concentration range of 0.125–0.625. This closure of gap arises because of the descending of the s-like states of N hybridized with those of Ga and As atoms. The results are in agreement with those of other calculations.

Acknowledgments

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