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Electronic structure of $(GaAs)_{1-x}Ge_{2x}$: the relative importance of short-range and long-range order

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Abstract. We calculate the electronic structure of $(GaAs)_{1-x}Ge_{2x}$, for which there are contradicting theories of the short-range structure. To investigate the latter we use the cluster–Bethe-lattice method and the configuration-averaging technique of Gomez-Santos and Verges which can take into account diagonal and off-diagonal disorder as well as disorder in the short-range order parameters. Our results are in good agreement with XPS spectra, and band gap, EXAFS and x-ray diffraction measurements. They point to models in which (i) no As–As or Ga–Ga bands exist, (ii) there is perfect coordination around each atom provided the atoms are not near grain boundaries and (iii) the fraction of antisites is very low for $x < 0.2$ and then quickly goes to 0.5 at the critical value x_c at which the zincblende-to-diamond transition occurs. Furthermore we have strong evidence that short-range order is the dominant factor in the formation of not only the band gap, as reported previously, but also the valence band density of states, at least for $x < x_c$. By comparison with other calculations and experiments we show that the VCA breaks down for this class of alloys, and even the single-site CPA may be inadequate in some cases.

1. Introduction

The need for semiconductors with tailorable band gaps has led to the production of new materials with distinctly different properties from the well known group IV and III–V semiconducting alloys. One such metastable material is $(GaAs)_{1-x}Ge_{2x}$ which exhibits strong band-gap bowing (tenths of an eV) and a zincblende-to-diamond transition [1, 2]. Considerable controversy exists over its short-range structure and the origin of this deep band-gap bowing [3–8].

Two models have essentially been proposed to explain this. Newman and Dow (ND) [4] and later Newman and co-workers [5] have interpreted the band gap E_g versus composition x curve as being V shaped with a discontinuous slope at a critical $x = x_c = 0.3$. They assumed that As–As and Ga–Ga nearest-neighbour (NN) pairs exist so that at $x = x_c$ the zincblende-to-diamond transition occurs when the fraction of antisites AF = 0.5. Their analysis used (a) a simple expression for the total energy equivalent to a three-component spin model, and initially, a thermodynamic mean-field approach for its solution; and (b) the virtual crystal approximation (VCA) in the tight-binding scheme for the electronic structure. Their model gave AF = 0.085 at $x = 0$ and an almost linear variation between $x = 0$ and $x = x_c = 0.3$.

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On the other hand, a series of growth models and electronic structure calculations exist which all exclude the possibility of wrong bonds (WB), i.e. As–As and Ga–Ga bonds, and which give a critical x_c between 0.2 and 0.4 [3, 6–9].

In particular, Holloway and Davis (HD) [6] have argued that the data for the $E_g(x)$ curve are consistent with a smooth, though deeply bowed, curve and have criticized the neglect of potential fluctuations by ND when they made use of the VCA. Their Monte Carlo recursion method calculations [6] have shown that (a) the large band-gap bowing is a consequence of alloy disorder only and (b) the presence of a finite gap is inconsistent with the existence of WB since these bonds introduce enough states in the gap to annihilate it. They particularly stressed the dominance of short-range order (SRO) over long-range order (LRO) on E_g since in their calculations [8] clusters with the same SRO but different LRO gave the same E_g while the opposite (same LRO, different SRO) gave markedly different E_g.

Kim and Stern (KS) [9] have argued that, because of the metastability of the alloy, the zincblende-to-diamond transition is determined by the kinetics of growth, and not by thermodynamics, and this explains the non-uniqueness of x_c, which can vary according to the morphology of kinetic growth. In their simulations the fraction of antisites AF was almost zero for small x ($x < 0.1$) and rapidly approaches AF $= 0.5$ at $x = 0.26$ for growth in the [100] direction. KS actually calculated the order parameter S but there is one-to-one correspondence between S and AF. Similar results were obtained by Davis and Holloway [7]. AF was found to be zero in their calculations up to $x = 0.2$.

Considerable controversy remains, however, partly because of the different interpretation of the EXAFS data in the similar compound $(GaSb)_{1-x}Ge_{2x}$ [10] by Newman and co-workers [5] on the one hand and HD [7] and KS [9] on the other. Unfortunately no such data are available for $(GaAs)_{1-x}Ge_{2x}$ since its constituent atoms have almost equal scattering factors. In $(GaSb)_{1-x}Ge_{2x}$ the number of Sb NN of a Ga atom follows a $4(1-x)$ variation, but the number of Sb NN of a Ge atom is smaller than that of a $2(1-x)$ straight line. The authors of the latter papers assigned this deviation to the polycrystallinity of the sample. In grain boundaries, Ge sits preferentially on the Sb sublattice, to ease the lattice strain. Newman and co-workers on the other hand assumed the presence of WB and by an improved solution of the three-component spin model of ND showed that 5% of such bonds are consistent with the experiments for this material. To explain the calculated annihilation of the band gap—when WB are introduced—they suggested that this is a defect of the cluster calculations of HD [6] and that a more advanced configurational averaging technique like the coherent potential approximation (CPA) would not change the results of their modified VCA calculations [5]. In this version of the VCA, 'environmental effects' are introduced, but alloy disorder effects are still neglected.

However, the breakdown of the standard VCA for this class of materials was demonstrated by the CPA calculations and XPS spectra of Hass and Baird (HB) [11]. In these calculations the band gap for the ND model was drastically shorter than that calculated by the VCA and became zero at approximately $x = 0.20$–0.25, see figure 1. On the other hand, for the model with no antisites, the variation of the band gap with x showed the strong band-gap bowing seen in the experiments, if calculated by the CPA, but a much weaker bowing if calculated by the VCA. Furthermore, the XPS spectra showed a four-peak structure that is completely absent in the VCA but present in the CPA calculations, see figure 3 below. This structure is due to the fact that the differences between the atomic levels are greater than the broadening of the

individual spectral features. Obviously, a model with no antisites, especially at large x, is not realistic but it is a convenient way to eliminate WB since the CPA (but not the cluster CPA) can accept only probabilities for site occupancies but no NN correlations. It seems, therefore, that the effect of the alloy disorder and the WB is to produce, each one independently, a bowing of tenths of an eV, but the combined effect of both diminishes the gap too quickly.

In a recently published paper Gu *et al* [12] have used the same model as that of Newman and co-workers [5] but have imposed the condition that Ge is randomly distributed over both sublattices, due to the metastability of the alloy. They have deduced that the fraction of WB is 'very small', but no specific number was given. Their calculated band-gap bowing, using the modified VCA, was in reasonable agreement with experiment. However, it is not clear to us whether this bowing is partly due to the very small number of WB present—which we will show to have a dramatic effect on the band gap—or to the inclusion of environmental effects, or to both.

Experimental evidence of the value of the transition point exists in the x-ray diffraction data of Shah *et al* [13] for $(GaSb)_{1-x}Ge_{2x}$ where the (002) reflection disappears as x approaches 0.3. The order parameter was found there to vary in a way that gave AF $= 0$ for $x < 0.2$ and then a rapid increase to 0.5 at $x = 0.3$. Again no data are available for $(GaAs)_{1-x}Ge_{2x}$ because of the similarity of the scattering factors. Raman spectra [14] are less easy to interpret.

In this paper we do not aim to calculate the total energy or to simulate the growth of the material. We are simply trying to solve the one-electron problem as fully as we can; and by comparison with experiment or other calculations, we are trying to resolve the above issues related to the SRO of $(GaAs)_{1-x}Ge_{2x}$. To accomplish this we perform the configurational averaging by including diagonal and off-diagonal disorder as well as disorder in the SRO parameters, which we derive for this class of materials. This is the first calculation that includes all these elements.

Our conclusions are summarized very briefly below.

(1) We confirm the VCA breakdown found in the calculation of HB [11], but we also hint at the inefficiency of even the CPA for this class of alloys.

(2) We calculate the variation of the band gap E_g at $x = 0$ with respect to the fraction of WB for the ND model (AF $= 0.085$, see figure 2 below) and show that 5% of WB completely annihilate E_g. No such calculation exists up until now. The case of (GaAs) with antisites at or away from stoichiometry will be taken up in another paper. We only present these data here since they add weight to the theories assuming no WB and simplify our calculations in this paper.

(3) We find that not only the band gap, but also the broad characteristics of the DOS including the four-peak structure derive mainly from SRO.

(4) We find that for a homogeneous sample (non-polycrystalline) perfect SRO should be preserved. The observed deviation from the $2(1-x)$ law of Sb NN of Ge must then be attributed to the polycrystallinity of the samples.

(5) The band gap is rather insensitive to the SRO parameters provided no As–As or Ga–Ga bonds exist. This was also seen by HD [6] but no specific values for the SRO parameters were given.

(6) We give evidence that the variation of the antisite fraction between $x = 0$ and $x = x_c$ is not linear but as predicted by KS [9] and HD [7] and seen in the experiments of Shah *et al* [13].

We note that experimental results dealing with non-stoichiometric (GaAs)Ge [15]

have been published. We believe that before this material can be analysed, any pending questions related to stoichiometric (GaAs)Ge should be resolved.

2. Method

We use the recently introduced method of Gomez-Santos, Verges and co-workers [16, 17] which includes all the above-mentioned requirements, i.e. diagonal and off-diagonal disorder and, especially, disorder in the SRO parameters. The method is an improvement on the Kittler–Falicov method [18] which, in turn, was a generalization of the method of Jacobs [19]. It gives clear band gaps, with no pseudostates near the edges, and is also better than the CPA although no comparison exists with the molecular CPA for semiconducting alloys [20]. Furthermore, the method is easily generalized to real alloys with many orbitals per site. It is a direct space method requiring information only on the SRO of each atom and missing any LRO present, since it uses a Bethe lattice to simulate the effective field. However, this is not an unwelcome feature because it is exactly the influence of the SRO on the DOS of this material that we want to investigate in this paper. Since comparison with experiment is favourable in most cases we can be reasonably certain of the dominance of SRO over LRO. This issue will be discussed at length in the next section.

According to this method the local DOS of each atom is given by an expression of the form

$$\mathrm{Im}\left(z - E_i - \sum_{j=1}^{1} \phi_i^j\right)^{-1}$$

where z is an energy variable with an infinitesimal imaginary part, E_i are the diagonal tight-binding parameters of atom i and ϕ_i^j are the self-energies of atom i coming from the four tetrahedral j-directions. We are using an sp^3s^* basis set so that all the above symbols are 5×5 matrices. We allow the self-energy of each type of atom to be different on each sublattice so that we have six self-energies to calculate: three types of atoms, As, Ga and Ge, times two types of lattice position, anion and cation. This is so because we only need to calculate the self-energy of each atom in one of the four tetrahedral directions chosen arbitrarily, the other three being given by simple symmetry operations on the first one. From now on a symbol like $\phi_A^{a,(c)}$ will denote the self-energy of an A-type atom on an anion- (cation-) type of sublattice.

The equations obeyed by the ϕ depend on the NN environment of each atom. The calculation of Newman and co-workers [5] shows that 5% of As–As bonds exist from $x = 0$ up to $x = 0.5$. To test this we have calculated the DOS of pure $Ga_{0.5}As_{0.5}$ with AF = 0.085, assuming that WB may exist. The equations for this special case are those of Gomez-Santos and Verges, but modified to take into account the presence of an sp^3s^* basis on each site. As noted earlier, a complete account of these calculations will be given in another paper. Our calculated E_g with respect to the concentration of WB (see figure 2 below) shows that 5% of these bonds completely annihilate the band gap whereas 0.5%—an order of magnitude down from the value in [5]—decreases the band gap by 0.35 eV, from 1.5 to 1.15 eV. All this is in sharp contrast with experiment, so that we will assume that no WB exist for any x and the only possible bonds are As–Ga, As–Ge, Ge–Ga and Ge–Ge.

Using the method of [16] and [17] we get the following three equations for ϕ:

$$\left(z - E_{\mathrm{As}} - \sum_{i=1}^{4} S_i^{+} \phi_{\mathrm{As}}^{\mathrm{a}} S_i\right)^{-1} = p_{\mathrm{As^aGa^c}} \left(z - E_{\mathrm{As}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{As}}^{\mathrm{a}} S_i - V_{\mathrm{AsGa}} \left(z - E_{\mathrm{Ga}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ga}}^{\mathrm{c}} S_i\right)^{-1} V_{(\mathrm{GaAs})}\right)^{-1} + p_{\mathrm{As^aGe^c}} \left(z - E_{\mathrm{As}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{As}}^{\mathrm{a}} S_i - V_{\mathrm{AsGe}} \left(E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{c}} S_i\right)^{-1} V_{\mathrm{GeAs}}\right)^{-1} \tag{1}$$

$$\left(z - E_{\mathrm{Ga}} - \sum_{i=1}^{4} S_i^{+} \phi_{\mathrm{Ga}}^{\mathrm{c}} S_i\right)^{-1} = p_{\mathrm{Ga^cAs^a}} \left(z - E_{\mathrm{Ga}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ga}}^{\mathrm{c}} S_i - V_{(\mathrm{GaAs})} \left(z - E_{\mathrm{As}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{As}}^{\mathrm{a}} S_i\right)^{-1} V_{\mathrm{AsGa}}\right)^{-1} + p_{\mathrm{Ga^cGe^a}} \left(z - E_{\mathrm{Ga}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ga}}^{\mathrm{c}} S_i - V_{\mathrm{GaGe}} \left(E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{a}} S_i\right)^{-1} V_{\mathrm{GeGa}}\right)^{-1} \tag{2}$$

$$\left(z - E_{\mathrm{Ge}} - \sum_{i=1}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{c}} S_i\right)^{-1} = p_{\mathrm{Ge^cAs^a}} \left(z - E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{c}} S_i - V_{\mathrm{GeAs}} \left(z - E_{\mathrm{As}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{As}}^{\mathrm{a}} S_i\right)^{-1} V_{\mathrm{AsGe}}\right)^{-1} + p_{\mathrm{Ge^cGa^a}} \left(z - E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{c}} S_i - V_{\mathrm{GeGa}} \left(z - E_{\mathrm{Ga}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ga}}^{\mathrm{a}} S_i\right)^{-1} V_{\mathrm{GaGe}}\right)^{-1} + p_{\mathrm{Ge^cGe^a}} \left(z - E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{c}} S_i - V_{\mathrm{GeGe}} \left(E_{\mathrm{Ge}} - \sum_{i=2}^{4} S_i^{+} \phi_{\mathrm{Ge}}^{\mathrm{a}} S_i\right)^{-1} V_{\mathrm{GeGe}}\right)^{-1} \tag{3}$$

plus another three with $\phi_{\mathrm{As}}^{\mathrm{c}}$, $\phi_{\mathrm{Ga}}^{\mathrm{a}}$ and $\phi_{\mathrm{Ge}}^{\mathrm{a}}$ on the LHS, exactly symmetrical to the above, which we do not give here for economy of space. V_{AB} is the matrix containing the two-centre integrals between atoms A and B, $p_{\mathrm{A^aB^c}}$ is the conditional probability that atom A on the anion lattice has a B nearest neighbour and S_i are the symmetry operations of the tetrahedron. The tight-binding parameters are the same as those of all previous works (see [4, 6, 11]). Since our method includes off-diagonal disorder we also need the two-centre hopping elements related to As–Ge and Ga–Ge bonds. We make the approximation of taking for these matrix elements $v(\text{As–Ge}) = v(\text{Ge–Ga}) = [v((\text{GaAs}))\,v(\text{GeGe})]^{1/2}$. The fact that the bond lengths

in (GaAs) and Ge are almost the same, together with Harrison's rules [21], guarantee that such an approximation will not affect our results. In fact our inclusion of off-diagonal disorder is an improvement on all previous calculations. The equations for the ϕ are solved by an iterative method with a small imaginary part for the energy variable z.

We now come to the calculation of the conditional probabilities $p_{A^aB^c}$, i.e. of the SRO parameters. We denote by, say, $P(A^aB^c)$ the probability that we find an A-type of atom on the anion lattice and a B-type of atom on the cation lattice. To simplify the notation in the calculations we put $P(As^aGa^c) = k$, $P(Ga^cGe^a) = l$, $P(Ge^cAs^a) = m$, $P(Ge^aGe^c) = n$, $P(Ga^aGe^c) = p$, $P(As^cGe^a) = q$ and $P(As^cGa^a) = r$. Requiring that each type of atom saturates the corresponding type of bonds we get the following equations (see [18] for more details):

$$k + l = (1 - \mathrm{AF})(1 - x) \tag{4}$$

$$r + p = \mathrm{AF}(1 - x) \tag{5}$$

$$m + n + p = x \tag{6}$$

$$k + m = (1 - \mathrm{AF})(1 - x) \tag{7}$$

$$r + q = \mathrm{AF}(1 - x) \tag{8}$$

$$l + n + q = x. \tag{9}$$

We have assumed that Ge is evenly distributed between the two sublattices.

The equations are only consistent if $m = l$ and $p = q$. Therefore, only equations (4)–(6) are required, and it can be seen that given x and AF, only two parameters from the set k, l, n, r, p are required to specify the rest. The conditional probabilities may be calculated now by a simple application of Bayes theorem or by the equivalent formulae of Kittler and Falicov [18]. For example, we get

$$p_{Ga^cAs^a} = k/(1 - x)(1 - \mathrm{AF}) \qquad p_{Ge^cAs^a} = m/x.$$

If perfect SRO prevails, $k = (1 - x)^2$ and $m = x(1 - x)$, so that $p_{Ge^cAs^a} = p_{Ga^cAs^a} = 1 - x$.

The numbers of Sb NN of Ga and of Ge, measured experimentally, are equivalent to the number of As NN of Ga = $N_{(GaAs)}$ and to the number of As NN of Ge = N_{GeAs}, which are equal to $4p_{(GaAs)}$ and $4p_{GeAs}$, respectively, the latter being the conditional probabilities, irrespective of site. By similar arguments to the above, it can be easily proved that

$$\begin{aligned} N_{(GaAs)} &= 4p_{(GaAs)} = 4(k + r)/(1 - x) \\ N_{GeAs} &= 4p_{GeAs} = 4(m + q)/2x = 2(1 + p)/x. \end{aligned} \tag{10}$$

Now we assume that these quantities vary as

$$N_{(GaAs)} = 4\alpha(1 - x) \qquad \text{and} \qquad N_{GeAs} = 2\beta(1 - x). \tag{11}$$

No approximation is involved since α and β are functions of x. They are only introduced to make contact with experiment. Manipulation of equations (4) and (5) and (10) and (11) leads to

$$\beta = \alpha + (1 - \alpha)/x \tag{12}$$

which shows that given α, the value of β is determined and if $\alpha = 1$ then $\beta = 1$ also. Again we emphasize that no similar measurements are available for $(GaAs)_{1-x}Ge_{2x}$.

In our calculations we have taken α to be one of our SRO parameters. For x greater than 0.3, when the transition to diamond symmetry seems to occur, one does not need any other parameter since, then, $k = r$ and from equations (10) and (11) $k + r = 2k = \alpha(1 - x)^2$. For $x < 0.3$ we make the simplification of taking $k/r = (1 - \mathrm{AF})^2/\mathrm{AF}^2$. This is not at all necessary for the method to work but since we found that the parameter α must be very close to 1 to make positive contact with experiment, it leads to an economy of presentation. Otherwise one would have to present results in terms of both k and r, or any other pair of independent bond probabilities which would give very little additional information. Note, however, that this is an exact relationship for $x \geqslant x_c = 0.3$, a very good approximation for $x \simeq x_c$ and a bad approximation for $x \ll x_c$, as it can lead to negative probabilities if the value of AF is unrealistically high. Our results fall within the first two regions, where most of the interest lies due to the XPS results available. No such approximation has been assumed in the calculations of figures 2 or 3 (see next section).

3. Results and discussion

The effect of WB on the band gap of pure (GaAs) with AF = 0.085 (the ND model) is shown in figure 2. It was discussed in the previous section since it was a prerequisite to the formulation of equations (1)–(3). We mention it here for the sake of completeness of this section. The results of the calculation which we describe immediately below assume therefore the presence of no WB.

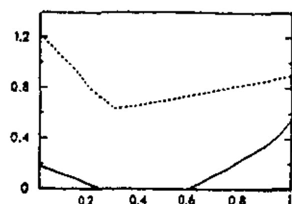

Figure 1. Comparison of VCA (broken curve) and CPA (full curve) band gaps for the ND model. After Hass and Baird [11].

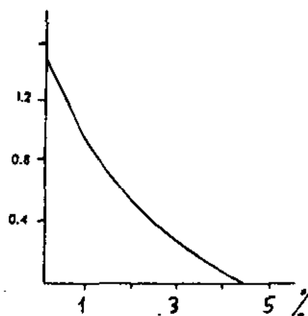

Figure 2. Variation of the band gap of $Ga_{0.5}As_{0.5}$ with respect to the concentration of anion–anion bonds for the ND model.

We have first calculated the DOS for the case of no antisites. This is shown in figure 3 while the XPS spectra are shown in figure 4. The variation of the band gap E_g with x is shown in figure 5, together with that of Hass and Baird [11] and the values measured experimentally [2]. We examine figure 5 first. It can be seen that the two curves, $E_g(x)$, are very similar. Actually, the bowing for both curves is even stronger for large x than that of the experimental points, but this is due to the rather low value for the band gap of Ge that this particular set of tight-binding parameters gives. (No fitting was employed.) All this confirms the breakdown of the VCA for

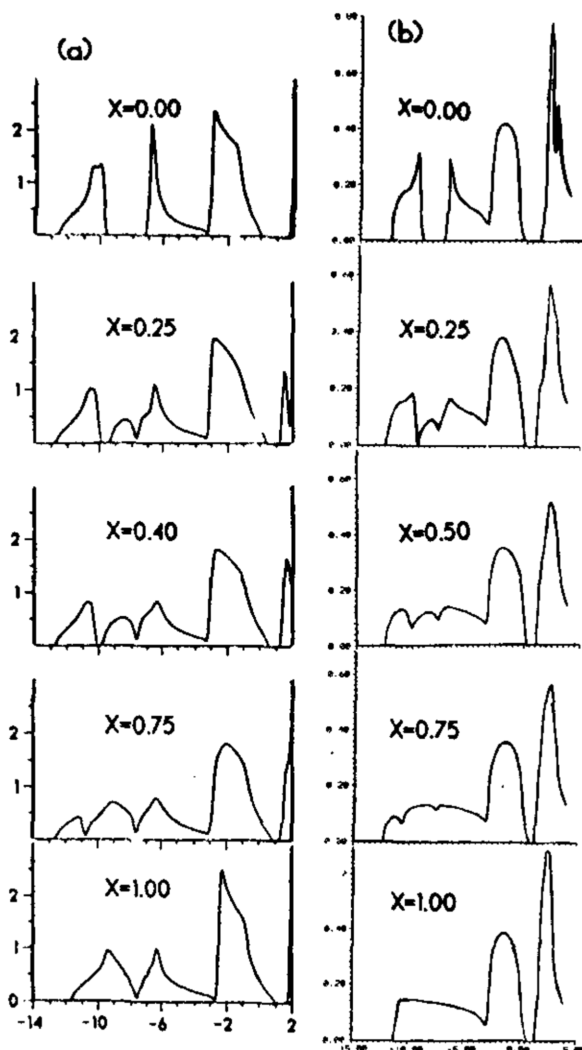

Figure 3. Density of states of $(GaAs)_{1-x}Ge_{2x}$ for AF = 0. (*a*) CPA results, after [11]; (*b*) our results.

this material and the fact that the observed strong bowing is a result of alloy disorder only.

Our DOS for the valence bands (figure 3) is again very similar to the corresponding ones of Hass and Baird [11], except for the region of $x \simeq 1$ (i.e. the end point of pure Ge), which was expected. However, they fit well with their XPS spectra. In particular, the four-peak structure is most evident near $x = 0.25$ and is fading away as x increases up to $x = 1$, which is what we get. This would not add any new information on the material had it not been for the fact that all previous calculations use a k-space approach and ours completely lack any LRO. This result generalizes to the whole DOS the original conclusions of HD [8], that the band gap is insensitive to any changes in the LRO of this material and that the SRO is the determining factor.

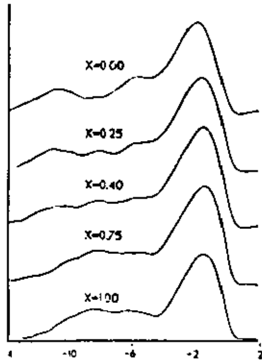

Figure 4. XPS spectra of $(GaAs)_{1-x}Ge_{2x}$.

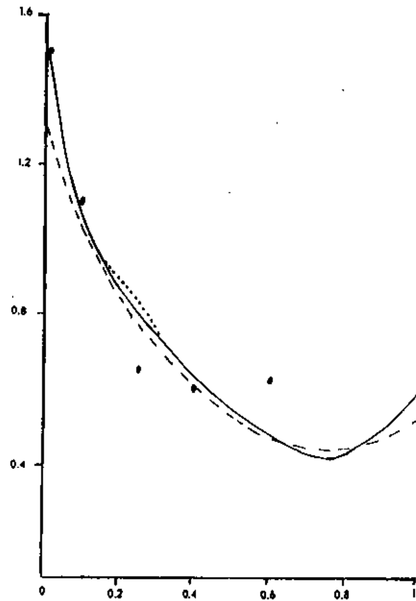

Figure 5. Variation of the band gap with x. Full curve, our results for AF = 0; broken curve, CPA results for AF = 0; dotted curve, our results for AF as in the ND model. Isolated points denote the experimental values.

As x approaches 1 our DOS tends smoothly to the DOS of amorphous Ge (or Si) while that of HB tends to the DOS of crystalline Ge. This was expected because it is known that for homopolar semiconductors the presence of rings of like-atom bonds make the contribution of LRO significant [22]. Surprisingly, the experimental curve at $x = 1$ seems to fit our results better.

Next we consider the case of non-zero AF and, in particular as given by the ND model on the one hand and the experimental value [12] and KS and HD models on the other. We present results for the DOS only for $x = 0.25$ and $x = 0.40$ (when the four-peak structure should be most evident) and for $\alpha = 1$ or $\alpha = 1.1$. Putting $\alpha = 0.9$ gives the same results as for $\alpha = 1.1$, i.e. they seem to be symmetrical about $\alpha = 1.0$. Between $x = 0.50$ and $x = 1.0$ our DOS tends smoothly to that of Ge shown in figure 3. Figures 6(a) and (b) show the DOS with AF as given by ND. It can be seen that these results contradict experiment in that the four-peak structure is missing. Also, varying the SRO parameter α makes little difference. In fact our DOS for AF = 0 is much more consistent with the XPS spectra of HB than this set. This has also been noticed by Hass and Baird when they compared their calculation with their spectra.

We now take AF = 0.05 at $x = 0.2$ which is an intentionally exaggerated average of the results in [7, 9, 12] but much lower than the ND value ($x = 0.25$ is too close to x_c, and the order parameter S is difficult to read accurately from the curves). We immediately see (figures 6(e) and (f)) that for $x = 0.20$, $\alpha = 1$ we regain the characteristic four-peak structure, but not so clearly for $\alpha = 1.1$. For $x = 0.40$ (figures 6(c) and (d)) the results are the same since the two models are identical.

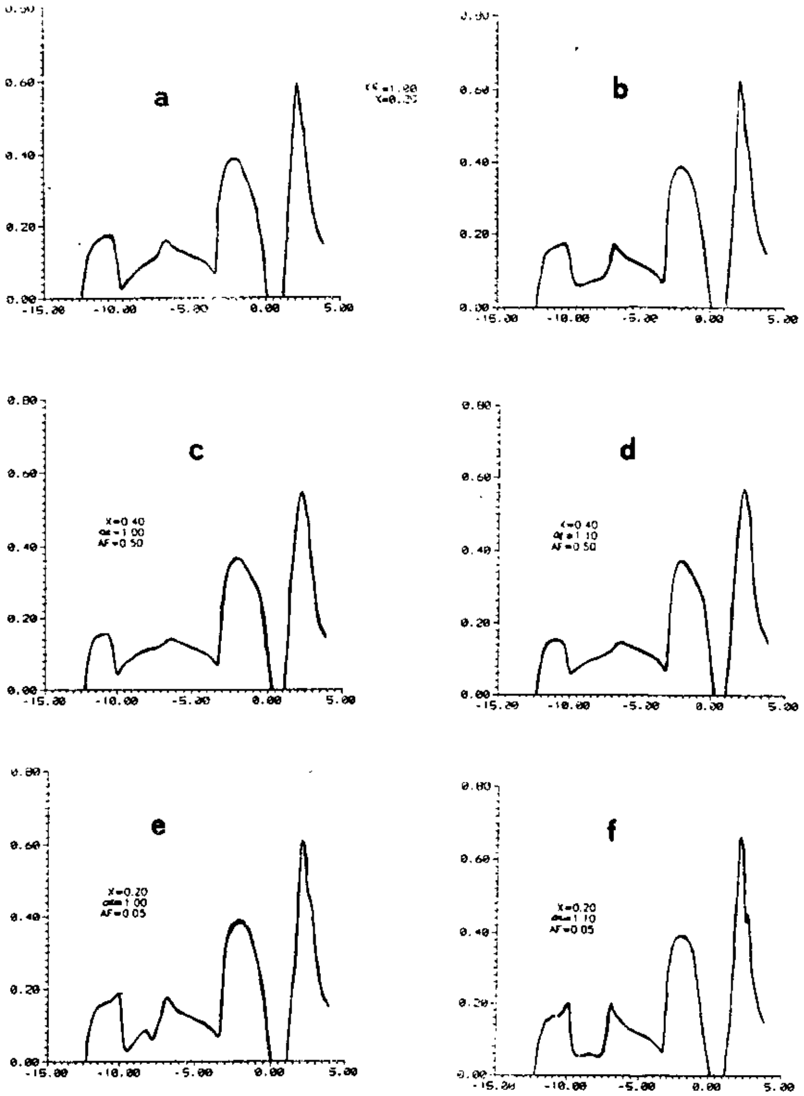

Figure 6. Density of states of $(GaAs)_{1-x}Ge_{2x}$ when AF is varied according to the ND model ((*a*) and (*b*)) or according to the KS or HD models ((*e*) and (*f*)). Parts (*c*) and (*d*) are common to both models.

Note that we are using the word model only as far as AF is concerned since we have excluded the possibility of WB. The above results suggest that the fraction of antisites must be very small for $x < 0.20$ and that the transition must be abrupt.

Also, the number of As neighbours of Ga and Ge should not deviate more than a few percent from the $4(1-x)$ and $2(1-x)$ variations, respectively, since then the characteristic feature of the DOS for x near 0.2 is lost again. This is true provided that the Ge atoms are evenly distributed on the two sublattices, as we have assumed. The observed lower value of N_{GeSb} seen in the EXAFS experiments of Stern *et al* [10] should therefore be attributed to the preferential substitution of Ge on anion sites

near dislocations and other defect sites, to ease the lattice strain, as the authors of the experimental paper claim. Note that in the calculations of Newman and co-workers [5] deviations in both $N_{(GaSb)}$ and N_{GeSb} occur.

For $x = 0.40$ the four-peak structure is missing from our results, while it is just visible in the XPS spectra. In the CPA calculations it is present for only this value of x (not higher or lower) and much reduced. This may well be a deficiency of the Bethe lattice. Note, however, that our results correctly place this feature of the DOS as being more dominant near $x = 0.20$ and fading away as x increases, as the XPS spectra show. It simply fades away faster than experiment suggests.

We now come to the final point in this section, which is the variation of the band gap with x. It can be seen from figure 5 that for the case of a linear variation in the fraction of antisites, $E_g(x)$ is not appreciably different from the case of AF = 0. Only for $x = 0.25$ is a lower bowing by 0.05 eV introduced, which is almost independent of α. Other types of variation in AF give the same result. Therefore, antisites *per se* make little difference on $E_g(x)$, provided WB are not present. This has also been observed by HD [6, 8] in their cluster calculations.

However, the CPA $E_g(x)$ of HB for the ND model (figure 1) is drastically different from our $E_g(x)$ for the same model (the same AF, which is what is only required in the CPA). The reason for this is that in the single-site CPA one cannot exclude or include quantitatively the presence of WB. A comparison of figures 1 and 5 leads us to suggest that the CPA may be inefficient for this class of alloys (but certainly not break down). When AF = 0 the two calculations give almost identical results (and both completely different from the VCA) because they refer to the same SRO, but when AF $\neq$ 0 the two methods give totally different $E_g(x)$, because the CPA cannot include, in general, any information on the SRO of the material. This does not mean that the calculated variation of the band gap by HB is wrong when AF $\neq$ 0 but one does not know what level of concentration of Ga–Ga and As–As bonds is correct. For very small concentrations, it should obviously be similar to the AF = 0 case, while for concentrations of WB greater than 5% it should give zero band gap for small x. Our results in figure 2 show that it is correct if the concentration of WB is approximately 3%.

4. Conclusions

We have calculated the electronic structure of $(GaAs)_{1-x}Ge_{2x}$, for which several growth models and theories explaining its zincblende-to-diamond transition exist. Although the method we have used is more appropriate for amorphous materials, we have derived information on the SRO of the alloy which is consistent with all experimental facts. In particular, the presence of As–As and Ga–Ga bonds should be excluded since they shorten (or annihilate) the band gap too quickly, the bowing of which is due to the effects of alloy disorder. Environmental effects may need further investigation. Furthermore, we suggest that for a monocrystalline sample, perfect coordination around the atoms must exist. Following Stern *et al* [10] we attribute the deviation of N_{GeSb} from the $2(1-x)$ law to the presence of grain boundaries. Our calculations favour the Holloway and Davis [6–8] and Kim and Stern [9] models as well as the experiments of Shah *et al* [13] in which the transition to the diamond structure occurs due to a sudden increase of the antisite fraction to 0.5, while it is almost zero for small x.

Since the above results have been obtained by a method that makes no assumption on the LRO of the material, we have strong evidence that the SRO is the dominant factor in the formation of the DOS, at least for $x < x_c$. The XPS spectra suggest that this may hold beyond x_c. The importance of SRO is in fact the reason why at least the standard VCA fails for this material and the single-site CPA is not adequate enough. This is, in turn, due to the strength of the scattering potentials. For example, As–As and Ga–Ga bonds are energetically unfavourable because the potential is too repulsive. Traditionally, the most studied semiconducting alloys are the isovalent III–V and II–VI (e.g. $GaAs_{1-x}P_x$), for which the VCA has been quite successful. We tentatively suggest that in all non-isovalent alloys—such as the one studied in this paper—only a method that can properly take into account the presence of SRO will work.

References

[1] Alferov Zh I, Zhingarev M Z, Konnikov S G, Mokan I I, Ulin V P, Vmaskii V E and Yavich B S 1982 *Fiz. Tekh. Poluprov.* **16** 831 (Engl. Transl. 1982 *Sov. Phys.–Semicond.* **16** 532)
[2] Barnett S A, Ray M A, Lastras A, Kramer B, Greene J E, Raccah P and Abels L L 1982 *Electron. Lett.* **18** 891
[3] Dyakonov M I and Raikh M E 1982 *Fiz. Tekh. Poluprov.* **16** 890 (Engl. Transl. 1982 *Sov. Phys.–Semicond.* **16** 570
[4] Newman K E and Dow J D 1983 *Phys. Rev.* B **27** 7495
[5] Gu B L, Newman K E and Fedders P A 1987 *Phys. Rev.* B **35** 9135
[6] Holloway H and Davis L C 1984 *Phys. Rev. Lett.* **53** 1511
[7] Davis L C and Holloway H 1987 *Phys. Rev.* B **35** 2767
[8] Davis L C and Holloway H 1987 *Solid State Commun.* **64** 121
[9] Kim K and Stern E A 1985 *Phys. Rev.* B **32** 1019
[10] Stern E A, Ellis F, Kim K, Romano L, Shah S I and Greene J E 1985 *Phys. Rev. Lett.* **54** 905
[11] Hass K C and Baird R J 1988 *Phys. Rev.* B **38** 3591
[12] Gu B L, Ni J and Zhu J L 1992 *Phys. Rev.* B **45** 4071
[13] Shah S I, Kramer B, Barnett S A and Greene J E 1986 *J. Appl. Phys.* **59** 1482
[14] Krabach T N, Wada N, Klein M V, Cadien K C and Greene J 1983 *Solid State Commun.* **45** 895
[15] Baird R J, Holloway H, Tamor M A, Hurley M D and Vassell W C 1991 *J. Appl. Phys.* **69** 226
[16] Gomez-Santos G and Verges J A 1987 *J. Phys. C: Solid State Phys.* **20** 5501
[17] Martin-Moreno L, Martinez E, Verges J A and Yndurain F 1987 *Phys. Rev.* B **35** 9683
[18] Kittler R C and Falicov L M 1976 *J. Phys. C: Solid State Phys.* **9** 4259
[19] Jacobs R L 1973 *J. Phys. F: Met. Phys.* **3** 933
[20] Lempert R J, Hass K C and Ehrenreich H 1987 *Phys. Rev.* B **36** 1111
[21] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Fransisco: Freeman)
[22] Joannopoulos J D and Cohen M L 1974 *Phys. Rev.* B **10** 1545