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J. Phys.: Condens. Matter 5 (1993) 8677–8688. Printed in the UK

A theoretical study of stoichiometric and As-rich amorphous GaAs

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Received 20 May 1993

Abstract. We have investigated the electronic and atomistic structure of stoichiometric and As-rich GaAs by treating this material as a ternary alloy of fourfold-coordinated As^{4+}, Ga^{3+} and threefold-coordinated As^{3+}. Using the configurational averaging technique of Verges we have calculated the density of states (DOS) of this material, not only in terms of the stoichiometric index x and proportion of As^{3+} atoms α, but also in terms of the short-range order (SRO) parameters. By correlating with experiment we obtain valuable information about the SRO. In particular, we have shown that compensation occurs at a value of α that is a function of x only. Using this value of α and assuming that less than 1% of As^{4+}–As^{4+} bonds occur (all other As–As bonds being allowed) we were able to (i) reproduce the EXAFS data and the variation of the optical gap with x and (ii) account for the observed shoulder in the lowest peak of the valence band and the subsidiary shell of As neighbours of Ga. Finally, at other values of the SRO parameters, we find features in the DOS that could explain some experiments on other amorphous III–V semiconductors.

1. Introduction

The electronic and atomistic structure of amorphous III–V compounds has been investigated intensely for more than ten years. In the last three years new work on the non-stoichiometric and alloyed forms of a-GaAs has appeared. Most of the experiments have been performed on a-GaAs but a-GaP and a-InP have also been investigated. XPS [1–5], EXAFS [6–8], combined optical and transport [9–12] and electron diffraction [13] measurements have been used to probe the structure of these materials. The main findings of these experiments are the following.

At stoichiometry these materials are best described by a continuous random network (CRN) with even-membered rings only. The band gap E_g of a-GaAs was found to be 1.15–1.2 eV, i.e. 0.2–0.3 eV lower than that of c-GaAs [4, 9]. Its density of states (DOS) is very similar to that of the crystalline compound, the only difference being an addition of states between the upper two peaks of the valence band [3]. In a previous publication [14] we have shown that this is a result of the loss of long-range order (LRO) and not of the presence of As–As bonds. Core electron spectroscopy has not revealed the presence of anion–anion or cation–cation bonds, so-called wrong bonds (WBs), in GaAs but it did so in GaP and InP.

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This is thought [12] to be due to the fact that Ga and As have almost equal atomic radii. Similarly, no drastic decrease of the conductivity upon annealing is seen in GaAs but it is seen in GaP, the optical gap of which is smaller by 50% compared to c-GaP. These drastic changes in GaP are believed to be due to WBs that act as either donors or acceptors and broaden to form bands near the original band edges.

Away from stoichiometry trivalent cation or anion sites are expected to be present depending on which atom is in excess. So far all the experiments have been performed on $Ga_{1-x}As_x$ with an As excess. The band gap of the alloy remains almost constant at 1.1–1.2 eV for the range $0.5 \leqslant x \leqslant 0.75$ [7] and is little influenced by annealing [4]. EXAFS experiments by Baker *et al* [7] showed that the coordination of As changes from four at $x = 0.5$ to 3.3 at $x = 0.85$. EXAFS experiments by Udron *et al* [6] gave 10% of the As as being threefold coordinated at $x = 0.52$. No threefold-coordinated Ga sites were detected. Also in the data of Udron *et al* , a subsidiary shell at 3.3 Å of As neighbours of Ga (and vice versa) has been detected, lying between the first shell (2.5 Å) and second shell (5.5 Å) of the tetracoordinated network. To explain this structure, the authors have not taken into account any As–As bonds but have instead invoked the presence of threefold coordinated Ga atoms.

Finally at $x = 0.60$, XPS spectra have revealed a shoulder at the lowest-lying peak of the valence band, indicative of As–As WBs [5]. This explanation was prompted by the presence—in the partial DOS of an isolated anion WB—of a corresponding splitting of this peak [15].

The theoretical work on this area [15, 16] has been entirely confined to isolated defects such as WBs and dangling bonds (DBs) and their possible complexes, despite the fact that samples as rich in As as 60–75% have been studied [5, 7]. The main results of these calculations are that isolated anion WBs produce donor states near E_c, while anion DBs produce acceptor states near E_v and vice versa for the cation defects. Furthermore, O'Reilly and Robertson [15] showed that if the material is to remain compensated as is normally the case, the ratio of the number of WBs to DBs must be $\frac{3}{2}$.

In this paper we present calculations of the electronic structure of a-GaAs, treating the semiconductor as a ternary alloy of Ga^{4+}, As^{4+} and As^{3+} sites. Our purpose is not only to fill the theoretical omissions on such matters as the variation of E_g with x and the effects of DBs and WBs on the latter, but we will also argue that specific experiments have been misinterpreted because of the lack of information on the effects of concentrated trivalent As sites on the electronic structure of this material. We will finally present a model that will coherently explain all the experimentally observed features and also give some possible explanation of the different features of other amorphous III–V alloys such as GaP. The next section, although an exposition of the method used, contains some results applicable to all a-III–V semiconductors and is essential to an understanding of our results. The purely mathematical aspects of this section are relegated to an appendix.

2. Method

We have used a Bethe lattice of variable coordination (four or three) to simulate the structure of a-GaAs, and the configurational averaging technique introduced by Verges and co-workers [17, 18] to calculate the averaged DOS, the quantity being measured by XPS. This technique has been quite successful in its application to other amorphous semiconductors [18] while

its application by one of us [19] to c-$GaAs_{1-x}Ga_{2x}$ has produced band gaps that are better than that of the coherent potential approximation (CPA). It is a definite improvement on the Kittler–Falicov method [20], giving clear gaps with no spurious bands near the band edges. The method only requires information on the short-range order (SRO) through the conditional probabilities p_{AB} that an A atom has a B nearest neighbour. As mentioned earlier, the mathematical aspects of the calculation of the DOS are relegated to an appendix. We present in this section results which are independent of any particular configurational averaging technique.

Let the probabilities of the possible bonds in a-GaAs be denoted as follows:

$$P(\text{Ga–Ga}) = k \qquad P(\text{As}^{4+}\text{–Ga}) = l \qquad P(\text{As}^{3+}\text{–Ga}) = m$$

$$P(\text{As}^{3+}\text{–As}^{4+}) = n \qquad P(\text{As}^{4+}\text{–As}^{4+}) = p \qquad P(\text{As}^{3+}\text{–As}^{3+}) = q.$$

By requiring that all possible types of atom satisfy all the possible types of bond we obtain the following equations:

$$2k + l + m = 8(1 - x)/(4 - \alpha x) \tag{1}$$

$$l + n + 2p = 8(1 - \alpha)x/(4 - \alpha x) \tag{2}$$

$$M + n + 2q = 6\alpha x/(4 - \alpha x) \tag{3}$$

where α is the proportion of As atoms which are trivalent (bond angle, 97° as in pure As), i.e. a-GaAs is modelled as a ternary alloy of the form $Ga_{1-x}As^{4+}_{(1-\alpha)x}As^{3+}_{\alpha x}$. The reader who is not familiar with deriving such equations may consult [20].

The following two regimes may be distinguished: $x = 0.5$ and $x > 0.5$. At $x = 0.5$ we have $\alpha = 0$ (according to EXAFS) so that $n = m = q = 0$ and $k = p$. Hence either the proposition of As^{4+}–As^{4+} or Ga–Ga bonds may be treated as an independent parameter. This limiting situation ($x = 0.5$) is straightforward and will only concern us at the beginning of section 3. On the other hand, for $x > 0.5$ (the As-rich regime) we take $k = 0$ and hence, given x and α, we have three equations and five unknowns so that two of the bond probabilities may be used as parameters. Of course, a calculation which would involve a minimization of the total free energy would come out with a single set of values for l, m, n, p and q but the aim of this paper is to derive these by comparison with experiment. Treating m and p as parameters we obtain:

$$l = [8(1 - x) - mc]/c \tag{4}$$

$$n = [8(2x - \alpha x - 1) - (2p - m)c]/c \tag{5}$$

$$q = [7\alpha x - 8x + 4 + (p - m)c]/c \tag{6}$$

with $c = 4 - \alpha x$. Once l, n and q are known, the conditional probabilities p_{AB} can be calculated in terms of x, α, p and m.

If l, n and q are to remain in the interval [0,1], then one finds after some lengthy but straightforward algebra that

$$4(2x - 1 - p + m)/(7 - p + m)x \leqslant \alpha \leqslant 4(4x - 2 - 2p + m)/(8 - 2p + m)x \tag{7}$$

provided that p and m are not close to unity. One can now use the above expressions to calculate the ratio of WBs to DBs, equate it to $\frac{3}{2}$ and find the value of α in terms of x, p and m at which compensation occurs. It turns out that this value of α is *independent* of p and m, and is given by

$$\alpha_c = (2x - 1)/x. \tag{8}$$

Given p, m and α, one may calculate the DOS in terms of them. Alternatively, one may treat them as parameters and see how the DOS evolves as they are changed.

3. Results and discussion

We have performed our calculation in the range $0.5 \leqslant x \leqslant 0.75$ because all of the experiments for which data are available have been performed within this range. We present our results in three stages. First, we present the case of $\alpha = 0$, which is only applicable to the stoichiometric a-GaAs, and then we examine the case $\alpha = \alpha_c$ which refers to compensated $Ga_{1-x}As_x$ and explains adequately the available experiments. Finally, we present results for some arbitrarily chosen values of α, p and m. These results describe what the properties of a-GaAs would be if it were self-doped. Although not relevant to GaAs samples on which experiments have been performed, they are, we think, representative of other III–V semiconductors in which large numbers of WBs have been detected, such as a-GaP. Before proceeding, it is worth mentioning that the data of Udron *et al* [6] will be investigated in the second state, as they refer to $x = 0.52$.

Our calculated DOS of the chemically ordered a-GaAs (i.e. with no WBs) is shown in figure 1. This result is by no means new [14]. It is only for comparison with the results to come that it is given here. The band gap E_g is 1.5 eV and the three-peak structure of the valence band (VB) is in good agreement with the XPS spectra [3] and in very good agreement with the calculated DOS of O'Reilly and Robertson [15 whose tight-binding parameters we are using. However, one should notice that the valence band width (VBW) is shorter than the experimental value at the low-energy side, extending up to −12.5 eV instead of −15 eV.

We now introduce some disorder into the material in the form of fourfold WBs (i.e. $\alpha = 0$). To sustain stoichiometry, the number of anion and cation WBs must be equal. Our DOS with 4% WBs is shown in figure 2, while the variation of E_g with WB concentration is shown in figure 3. The main difference between the DOS of figure 2 and that of figure 1 is a drastic shortening of the band gap due to the introduction of two sub-bands near the band edges E_c and E_v. If the number of cation WBs, but not that of the anion WBs, is reduced to zero (which would automatically increase x) then the sub-band at E_v disappears and vice versa, so these sub-bands correspond to the discrete energy levels of isolated WBs [15] which have broadened into bands.

The band gap at $x = 0.5$ decreases very rapidly as the ratio of WBs increases. It becomes zero at a concentration of approximately 5%. For E_g to remain at 1.1–1.2 eV a concentration of something less than 1% is required. Since in a CRN with even-membered rings one cannot have isolated WBs [21], these are introduced into the network in pairs or more. Note that since E_g is a function of substrate temperature [9] and annealing conditions, the upper bound on the presence of WBs may increase, but only very slightly (to 2%).

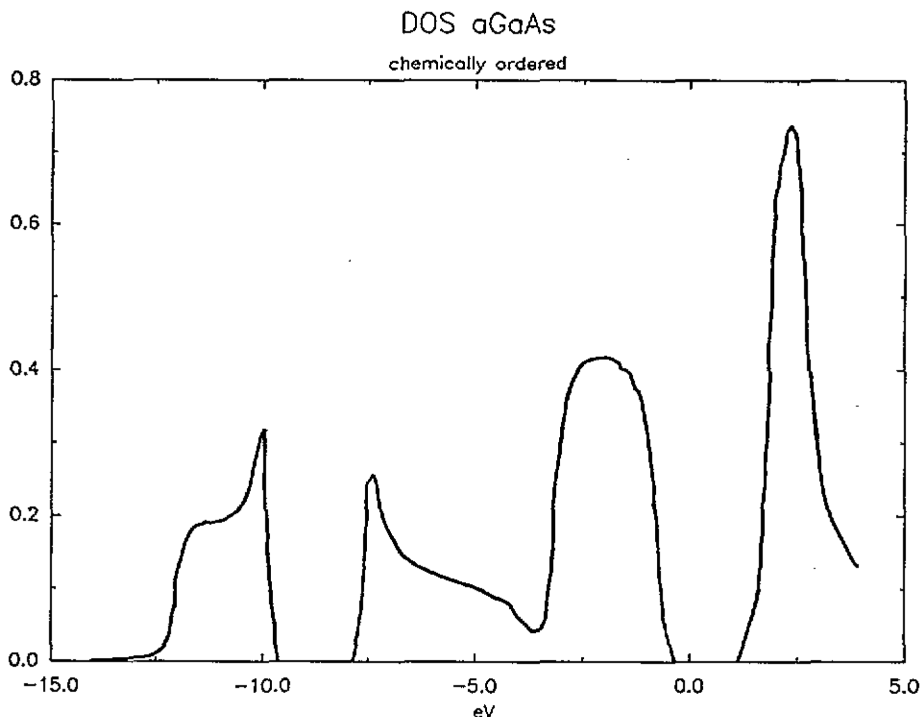

Figure 1. DOS of stoichiometric, chemically ordered, tetracoordinated a-GaAs.

A final point of this stage is the local DOS (LDOS) of an isolated WB (see the inset of figure 2). It shows a splitting of the lowest peak of the VB as calculated by other workers [15, 16]. This splitting in the *local* DOS was thought to be responsible for the observed shoulder of the same peak in the $x = 0.60$ samples. One may note for the moment that it is absent in the configurationally averaged DOS at $x = 0.5$ that contains 4% WBs. Whether this concentration is very small or the shoulder has a somewhat different origin will be seen below.

Next we examine the case of compensated non-stoichiometric GaAs ($x > 0.5$). In this case a finite proportion of As atoms will be threefold coordinated. We have shown in the previous section that this proposition is $\alpha = \alpha_c = (2x - 1)/x$ if the material is to remain compensated. It is worth commenting on this result. In principle α_c could have been a function of the two 'independent' parameters p and m, but it is not. This means that compensation does not occur at a specific configuration, but that there is an infinity of configurations at which this occurs. Note that this is not at all obvious from the start, i.e. given that the ratio WB/DB = $\frac{3}{2}$, this implies that α_c is a function of x only. This may help to understand the difficulty of self-doping.

Before proceeding, it is worth testing this value of α against the available EXAFS measurements. Figure 4 shows the total coordination of an As atom as measured by Baker *et al* [7], together with our results calculated using α_c. The agreement is more than satisfactory. In fact it would have been better if the experimental error bars were smaller. Also in the data of Udron *et al* [6], 10% of the As atoms were found to be threefold coordinated at $x = 0.52$. This compares very well with the value of 8% obtained using equation (8).

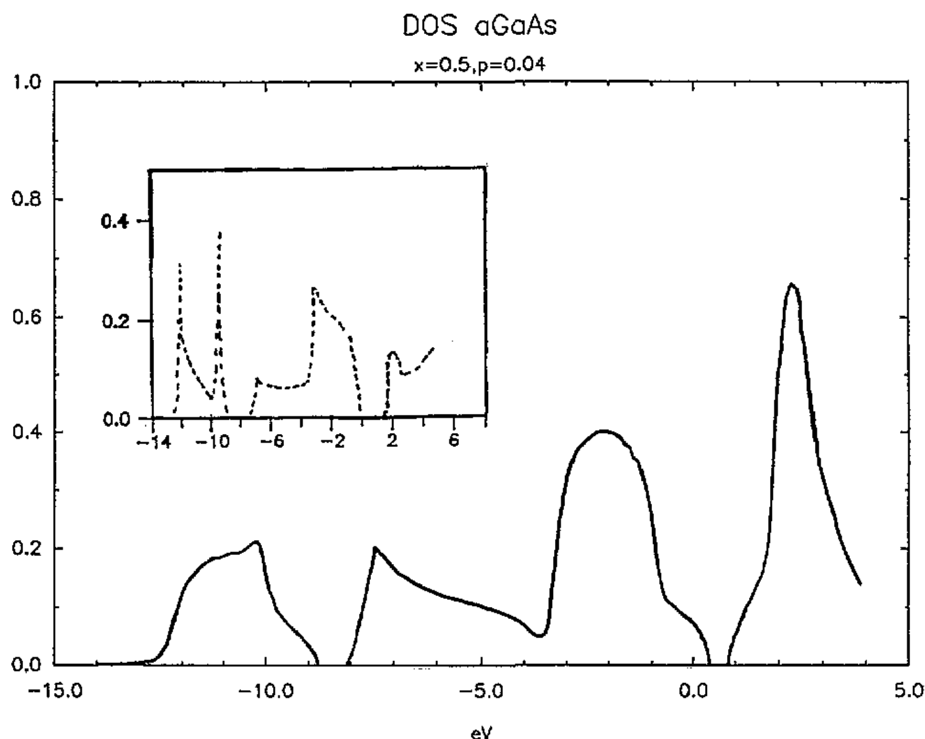

Figure 2. DOS of stoichiometric tetracoordinated a-GaAs with 4% of each type of WB.

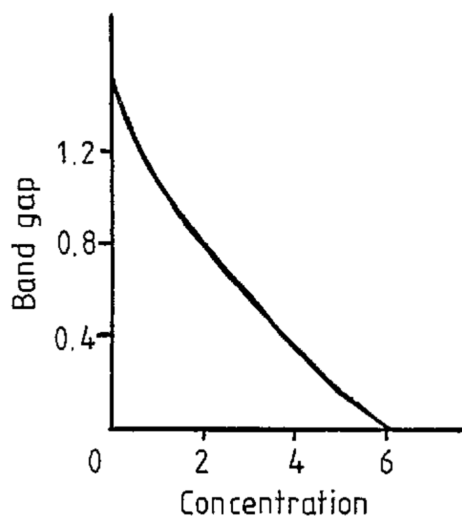

Figure 3. Variation of the band gap of tetracoordinated a-$Ga_{0.5}As_{0.5}$ with respect to the concentration of WBS.

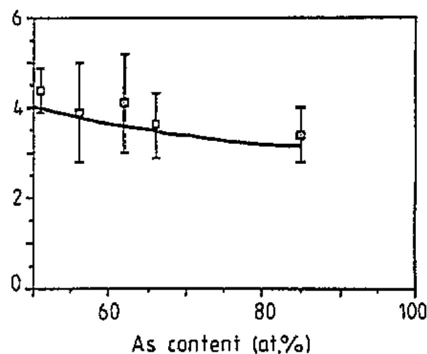

Figure 4. Nearest-neighbour coordination of As in a-$Ga_{1-x}As_x$ with respect to x. The isolated points are the EXAFS results of Baker *et al*, the continuous curve being our result, assuming compensation ($\alpha = \alpha_c$) and no As^{4+}–As^{4+} bonds.

Now that we have fixed α, it remains to fix p and m. Guided by the results of the $x = 0.50$ case, where small values of p produced a drastic decrease in E_g, we choose $p = 0$. This does not mean that WBs are absent but simply that they occur as either As^{4+}–As^{3+} or As^{3+}–As^{3+}. This choice will be tested below. For the concentration of As^{3+}–Ga bonds we choose a small value $m = x - 0.5$. Repeated tests we have performed have shown that m has almost no effect on the calculations. Putting $m = 0$ or doubling the above value made a difference of 0.05–0.1 eV which is approximately the accuracy of this type of calculation.

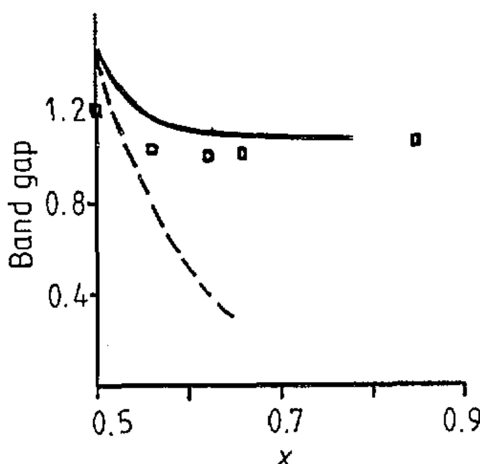

Figure 5. Variation of the band gap with x. Isolated points refer to experimental values for the optical gap. The full curve is our result for the same model as in figure 4, while the broken curve is our result for non-compensated a-GaAs with some (see text) As^{4+}–As^{4+} bonds.

We first examine the variation of E_g with x. This is shown in figure 5, together with the values of the optical gap measured by Baker *et al* [7, 10]. We observe that our choice of $p = 0$ reproduces the nearly constant value of E_g at 1.1 eV in all concentration regions except near $x = 0.5$. For this value of x we only need a concentration of 1% As^{4+}–As^{4+} to bring E_g down to 1.2 eV, as can be deduced from the results of the previous section. If p is assigned moderate values (e.g. $(2x - 1)/2$, which is halfway between $p = 0$ and the value $p = 2x - 1$ occurring when $\alpha = 0$), then E_g decreases much more quickly than experiments suggest. For example, we obtain $E_g = 0.7$ at $x = 0.58$. It seems therefore that the most likely model of a-GaAs is that at $x = 0.50$, As^{4}–As^{4+} and Ga–Ga bonds occur in concentrations of approximately 1% and as x increases, the extra As is incorporated in its trivalent form while Ga–Ga bonds disappear and some of the already present As^{4+} distort to form As^{3+} in proportions given by α_c and with less than 1% of As^{4+}–As^{4+} bonds. This is further evidenced by the typical DOS diagram shown in figure 6.

This is the DOS of $Ga_{0.4}As_{0.6}$ with no As^{4+}–As^{4+}, together with its constituent LDOSs (unweighted). The stoichiometric index was specifically chosen to be 0.6 so that it agrees with the samples from which XPS data were taken. One immediately notices the appearance, at the correct energy, of the shoulder of the lowest VB peak observed in the XPS. The height of this shoulder is very low (and hence quite distinct) only because the VBW is short, i.e. the DOS is zero in the range −15 to −13 eV. However, the origin of this shoulder is somewhat different from that adopted so far. It is evident by inspection of the LDOS that this shoulder is in fact due to the As^{3+} sites. Since some of these sites are necessarily bonded to As

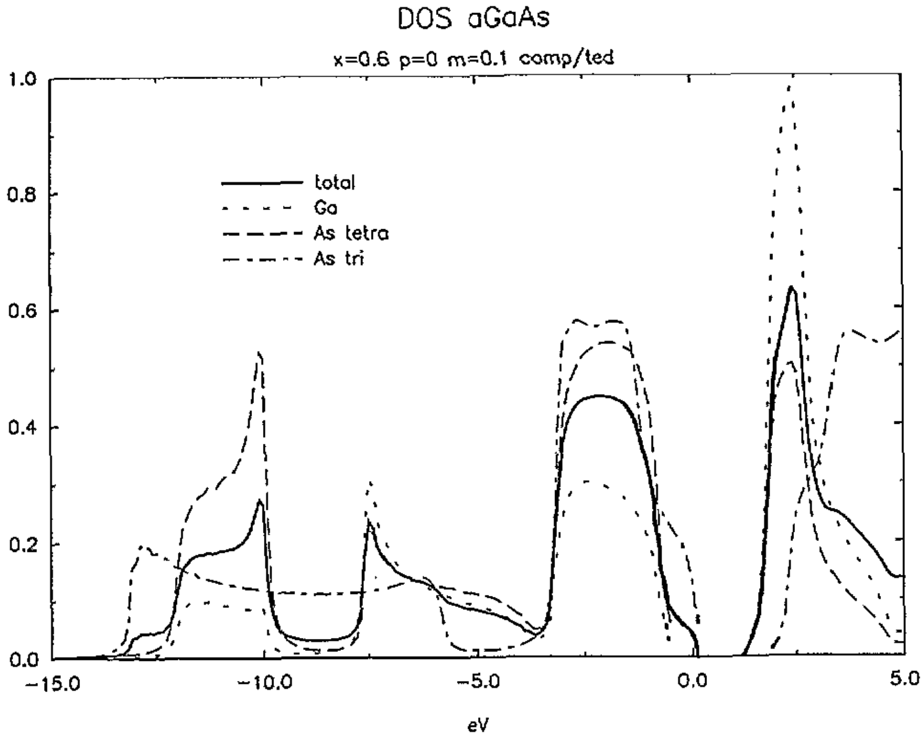

Figure 6. DOS of a-$Ga_{0.4}As_{0.6}$ with trivalent and tetravalent As. Values of parameters are as in figure 4.

atoms, one may claim that indirectly it is partly the effect of anion WBs. The new element in the interpretation is however the fact that if As^{4+}–As^{4+} bonds were present this feature would have been washed out, as will be verified below. Therefore this shoulder contains more information on structure than initially anticipated.

Note also (i) the small sub-band near E_v due to the anion DBs and (ii) the absence of any sub-band near E_c due to the fact that the As^{4+}–As^{3+} and As^{3+}–As^{3+} WB configurations give states inside the bands.

Before proceeding to the final stage of the presentation of our DOSs ($\alpha \neq \alpha_c$ and $p \neq 0$) it is worth giving an alternative explanation of the subsidiary shell of As neighbours of Ga observed in the recent data of Udron *et al* [6]. In the tetracoordinated a-$Ga_{0.5}As_{0.5}$, the first shell of As corresponds to the first-nearest-neighbour (NN) atoms and the second to the third-NN atoms. If, however, some WBs are present at $x = 0.52$, then the situation depicted in figure 7 may be realized and one may have an As neighbour of Ga which is a second-NN atom but in a distorted configuration. If to a first approximation the bond lengths of Ga–As and As–As atoms are taken to be equal to 2.45 Å, then the distance to the second shell is found to be 3.6 Å. If better bond lengths and some structural relaxation are introduced this value may easily increase or decrease by 0.1–0.2 Å.

The alternative to using no anion WBs requires (equations (1)–(3)) that the number of tricoordinated As atoms is more than 30% and also that equal amounts of Ga atoms are tricoordinated. Both are in sharp contrast with all EXAFS measurements. Thus although our model contradicts that of Udron *et al* [6] our is in much better agreement with their overall

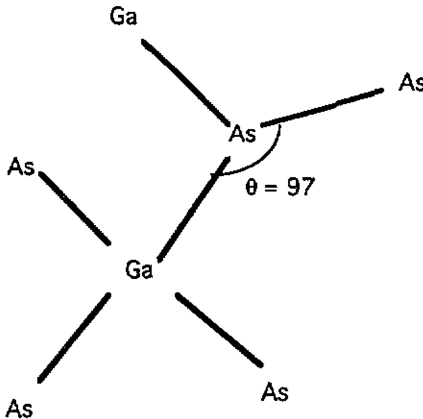

Figure 7. Possible configuration of As and Ga atoms giving a subsidiary shell of As neighbours of Ga.

data and also more direct. Note that, as previously mentioned, our prediction of $\alpha = \alpha_c = 0.08$ is very close to their observed $\alpha = 0.1$.

Finally we examine the case of non-compensated a-GaAs with a finite number of As^{4+}–As^{4+} bonds. As before we have to fix α, p and m. We choose $p = x - 0.5$ and $m = 2p$, i.e. we choose a value of p halfway between zero and the value at which $\alpha = 0$, and we double the previous value of m. Since the calculations to follow are only performed for the purpose of demonstrating the effects which will actually lift the present agreement with experiment, the particular values of the parameters used will be of no real significance. Having fixed p and m we choose α to lie in the middle of the range allowed by inequalities (7).

The DOS of $Ga_{0.4}As_{0.6}$ using these parameters is shown in figure 8. There are three features to be discussed: first, the shoulder of the lowest VB peak has disappeared because of a rounding effect due to As^{4+}–As_{4+} bonds; second, the sub-band near E_v is not clear at all because the value of α has been significantly reduced, but E_v itself has not moved significantly; third, and most important, a clear sub-band near E_c has appeared that has drastically shortened the band gap. This is due to As^{4+}–As^{4+} bonds, and is exactly the same type of sub-band as appears near E_c in figure 2. The variation of E_g with x is shown in figure 5, and we can see its rapid decrease with x. We believe that the situation described in figure 2 is probably what is happening in stoichiometric a-GaP, where a large decrease of the optical gap is seen, whereas the situation depicted here (figure 8) may possibly be observed if P-rich a-GaP can be prepared. We believe that the difference between the two compounds may be due to the difference in the atomic radii of their constituent atoms as Gheorghiu and Theye [12] originally suggested. We have nothing more to add at this point as this is beyond the scope of this paper.

4. Conclusions

We have calculated the electronic structure of a-$Ga_{1-x}As_x$ in terms of x, α and the SRO parameters. By comparison with experiment we are able to deduce the structure of this

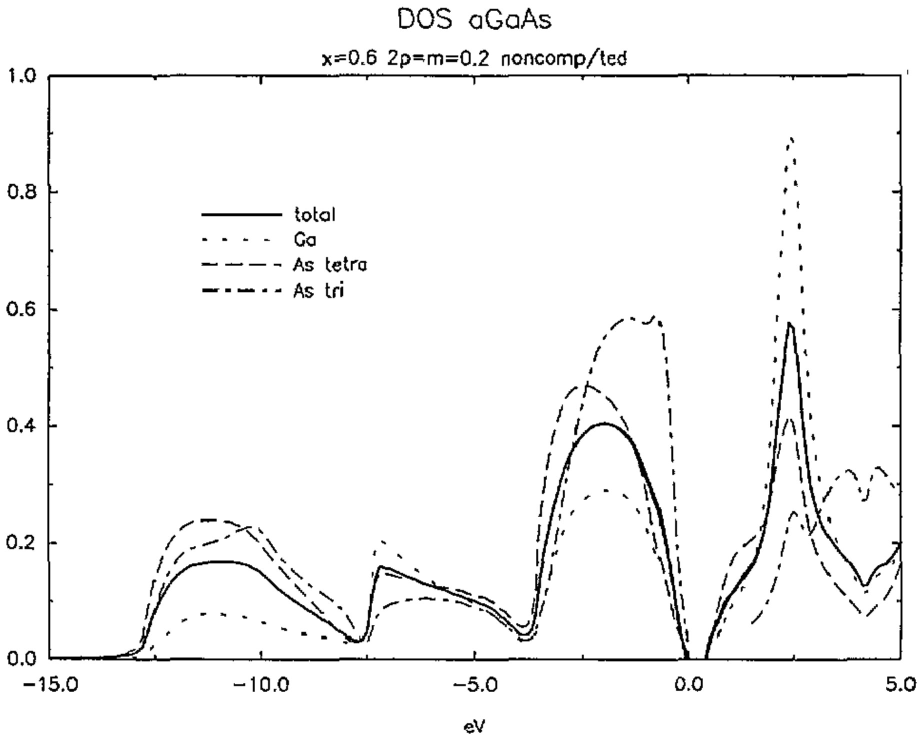

Figure 8. DOS of non-compensated a-$Ga_{0.4}As_{0.6}$ with As^{4+}–As^{4+} bonds. For the values of the parameters, see the text.

material. In particular we have shown that the value of α at which compensation occurs is a function of x only. Using this value and assuming no As^{4+}–As^{4+} bonds, we are able to account for: (i) the EXAFS data as a function of x; (ii) the optical gap as a function of x; (iii) the shoulder of the lowest peak of the VB at $x = 0.60$ and (iv) the subsidiary shell of As neighbours of Ga. It must be emphasized that not only is our model the simplest possible one—the material remains compensated with the extra As forming As–As bonds with at least one As in the $\theta = 97°$ configuration—but the same model can account for all four above-mentioned experiments with no internal inconsistencies. When non-compensation and As^{4+}–As^{4+} bonds are allowed in the DOS, one observes features which may be relevant to other amorphous III–V semiconductors.

Appendix

The configurationally averaged partial DOS due to each type i of atom is given by

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

where z is the energy variable with an infinitesimal imaginary part, E_i are the diagonal elements of the Hamiltonian, ϕ_i is the self-energy of type i of atom (Ga, As^4, As^3) in one

arbitrarily chosen bond direction and S_j are the symmetry operations which give the self-energies in the remaining $m-1$ bond direction. Evidently $S_1 = I$, the identity operation. We are using an sps* basis set on each atom so that all the above symbols are 5×5 matrices. For the tight binding parameters we use the values of O'Reilly and Robertson [15]. There is a different self-energy for the nominally anion (a) and the nominally cation (c) sub-lattice so that in all there are six unknown self-energies to calculate.

The equation for ϕ^{a}_{Ga}, $\phi^{a}_{As^{4+}}$ and $\phi^{a}_{As^{3+}}$ are given below. The equations for ϕ^{c}_{i} are symmetrical with ϕ^{a}_{i}. In the following, p_{AB} are the conditional probabilities, V_{AB} the off-diagonal matrix of the Hamiltonian S and R the symmetry operations for the tetrahedral and 97° configurations respectively and $\sum$ denotes $\sum_{i=1}^{4}$ or $\sum_{i=1}^{3}$, while $\sum'$ denotes $\sum_{i=2}^{4}$ or $\sum_{i=2}^{3}$. Using the procedure outlined in [17] and [18] we obtain

$$\begin{aligned}
&\left(z - E_{As} - \sum S_i^{+}\phi^{a}_{As^{4+}}S_i\right)^{-1} \\
&\quad = p_{As^{4+}Ga}\Bigg(z - E_{As} - \sum{}' S_i^{+}\phi^{a}_{As^{4+}}S_i \\
&\qquad - V_{AsGa}\left(z - E_{Ga} - \sum{}' S_i^{+}\phi^{c}_{Ga}S_i\right)^{-1} V_{GaAs^{4}}\Bigg)^{-1} \\
&\qquad + p_{As^{4+}As^{4+}}\Bigg(z - E_{As} - \sum{}' S_i^{+}\phi^{a}_{As^{4+}}S_i \\
&\qquad - V_{As^{4+}As^{4+}}\left(z - E_{As} - \sum{}' S_i^{+}\phi^{c}_{As^{4+}}S_i\right)^{-1} V_{As^{4+}As^{4+}}\Bigg)^{-1} \\
&\qquad + p_{As^{4+}As^{3+}}\Bigg(z - E_{As} - \sum{}' S_i^{+}\phi^{a}_{As^{4+}}S_i \\
&\qquad - V_{As^{4+}As^{3+}}\left(z - E_{As^{3+}} - \sum{}' R_i^{+}\phi^{c}_{As^{3+}}R_i\right)^{-1} V_{As^{3+}As^{4+}}\Bigg)^{-1}
\end{aligned}$$

$$\begin{aligned}
&\left(z - E_{Ga} - \sum S_i^{+}\phi^{a}_{Ga}S_i\right)^{-1} \\
&\quad = p_{GaAs^{4+}}\Bigg(z - E_{Ga} - \sum{}' S_i^{+}\phi^{a}_{Ga}S_i \\
&\qquad - V_{GaAs^{4+}}\left(z - E_{As} - \sum{}' S_i^{+}\phi^{c}_{As^{4+}}S_i\right)^{-1} V_{As^{4+}Ga}\Bigg)^{-1} \\
&\qquad + p_{GaGa}\Bigg(z - E_{Ga} - \sum{}' S_i^{+}\phi^{a}_{Ga}S_i \\
&\qquad - V_{GaGa}\left(z - E_{Ga} - \sum{}' S_i^{+}\phi^{c}_{Ga}S_i\right)^{-1} V_{GaGa}\Bigg)^{-1} \\
&\qquad + p_{GaAs^{3+}}\Bigg(z - E_{Ga} - \sum{}' S_i^{+}\phi^{a}_{Ga}S_i \\
&\qquad - V_{GaAs^{3+}}\left(z - E_{As^{3+}} - \sum{}' R_i^{+}\phi^{c}_{As^{3+}}R_i\right)^{-1} V_{As^{3+}Ga}\Bigg)^{-1}
\end{aligned}$$

$$\left(z - E_{\mathrm{As}} - \sum R_i \phi^{\mathrm{a}}_{\mathrm{As}^{3+}} R_i\right)^{-1}$$
$$= p_{\mathrm{As}^{3+}\mathrm{As}^{3+}} \Bigg(z - E_{\mathrm{As}} - {\sum}' R_i^{+} \phi^{\mathrm{a}}_{\mathrm{As}^{3+}} R_i$$
$$- V_{\mathrm{As}^{3+}\mathrm{As}^{3+}} \left(z - E_{\mathrm{As}^{3+}} - {\sum}' R_i^{+} \phi^{\mathrm{c}}_{\mathrm{As}^{3+}} R_i \right)^{-1} V_{\mathrm{As}^{3+}\mathrm{As}^{3+}} \Bigg)^{-1}$$
$$+ p_{\mathrm{As}^{3+}\mathrm{As}^{4+}} \Bigg(z - E_{\mathrm{As}} - {\sum}' R_i^{+} \phi^{\mathrm{a}}_{\mathrm{As}^{3+}} R_i$$
$$- V_{\mathrm{As}^{3+}\mathrm{As}^{4+}} \left(z - E_{\mathrm{As}} - {\sum}' S_i^{+} \phi^{\mathrm{c}}_{\mathrm{As}^{4+}} S_i \right)^{-1} V_{\mathrm{As}^{4+}\mathrm{As}^{3+}} \Bigg)^{-1}$$
$$+ p_{\mathrm{As}^{3+}\mathrm{Ga}} \Bigg(z - E_{\mathrm{As}} - {\sum}' R_i^{+} \phi^{\mathrm{a}}_{\mathrm{As}^{3+}} R_i$$
$$- V_{\mathrm{As}^{3+}\mathrm{Ga}} \left(z - E_{\mathrm{Ga}} - {\sum}' S_i^{+} \phi^{\mathrm{c}}_{\mathrm{Ga}} S_i \right)^{-1} V_{\mathrm{GaAs}^{3+}} \Bigg)^{-1} .$$

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