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## ***Ab initio* investigation of the electronic and geometric structure of zincblende $\text{Ga}_{1-x}\text{Tl}_x\text{As}$ alloys**

S Mankefors<sup>†</sup> and S P Svensson<sup>‡</sup>

<sup>†</sup> Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

<sup>‡</sup> Department of Electrical Engineering, University of Maryland, College Park, MD 20742, USA

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**Abstract.** Unique extensive *ab initio* band structure calculations have been performed to investigate the electronic and atomic structural dependency on the Tl concentration of (Tl, Ga)As. No approximations of the surrounding material are made, but the entire problem is addressed in full-scale calculations. Lattice constants, bond lengths, band structure, effective mass and bulk modulus were calculated, some for the first time ever for any material with this method. As a result of the choice of theoretical method, very detailed geometrical information on lattice distortions and bond length distributions was discovered. These symmetry-breaking lattice distortions were found to affect the band structure. The bands varied smoothly over the entire composition range, except in the region where the material changed from semiconducting to semi-metallic character; a split-off band was found to exist for a small concentration interval before the conduction band reached the valence band. The effective mass was shown to decrease for increasing Tl concentration up to 23%, supporting earlier predictions of enhanced electron transport properties in this alloy system. Calculations of bulk modulus and thermodynamic stability of the alloy indicated that the material in zincblende form may be more stable the higher the temperature is.

### **1. Introduction**

Semiconductor materials of III–V type have been extensively studied theoretically and experimentally over a number of years. Most work, however, has been devoted to materials made from the three middle row constituents, i.e. P, As, Sb, Al, Ga and In. This mainly because of the relative ease with which compounds from these elements can be synthesized.

As experimental procedures have matured, interest in materials made from the remaining elements has increased. For example, compounds containing the last group III element, thallium, have been proposed theoretically as promising candidates for long-wavelength infrared detectors [1] and heterostructure field-effect transistors [2]. However, experimental data on thallium-containing compounds are still scarce. In fact the literature contains contradictory information as to whether the materials can be synthesized [3, 4] at all. Continued work in this field should be aided by better theoretical understanding of the electronic and bond properties of the compounds. To this end we have set out to calculate the lattice constants, bond lengths, band structure, effective mass and bulk modulus of  $\text{Ga}_{(1-x)}\text{Tl}_x\text{As}$  using an *ab initio* method which yields deeper theoretical insights, compared to earlier calculations based on more approximate approaches. Even so, the precision of the arrived at band energies suffer from the inaccuracy that is still typical of all modern calculation methods, making it hard to make detailed predictions of some device properties. However, the surprising precision of the effective mass of GaAs lends some credibility to earlier predictions of high mobility in  $\text{Ga}_{(1-x)}\text{Tl}_x\text{As}$  with Tl contents up to 20 to 30%.

The energy minimization used in these extensive calculations produces distributed values for the bond lengths among the constituents that are an improvement over effective medium alloy calculations. The procedure has also been used to calculate the elastic energies of the alloy in zincblende structure, which can be used, for example, to calculate critical thicknesses in heterojunctions. Finally, we have made an approximate analysis of the stability of the alloy itself, which seems to suggest that problems with the thermodynamic stability should be expected when synthesizing alloys with high Tl contents using equilibrium methods.

## 2. Theory

### 2.1. Background

For a long time, *ab initio* calculations have played an important role in the theoretical investigations of different alloys. However, standard methods, like the coherent potential approximation [5] (CPA), making use of extensive approximations of the surrounding media. CPA has won widespread use [6–10] since the small number of required atoms makes it a very effective numerical approach. Unfortunately, using it, or other similar approximations loses important information. This is particularly true for any geometrical information; CPA, the virtual crystal approximation (VCA) and others assume equal bond lengths in all directions in a homogenous medium, something that is clearly not the case in reality. Thus, any geometrical information beyond average lattice constants cannot be extracted from these approximations. The assumption of equal bond length in all directions introduces an unnaturally high degree of symmetry, which affects the electronic structure, as will be shown in this paper.

In contrast to the CPA approach, full-scale *ab initio* calculations do provide complete geometrical information. They also allow for distortions to take place through relaxation and thus provide the correct degree of symmetry. Until recently it has been impractical to use this computational approach because of the numerical demands. However, through the on-going rapid development in computing power, it is now possible, albeit time consuming (of the order of  $\sim 10\,000$  CPU hours), to undertake large-scale *ab initio* investigations [5, 11–14] of alloys. Because of the time demand, several studies [5, 11, 12] have still been limited to a relatively small set of eight atoms. Although an improvement over approximate approaches, such a limited set does not properly allow a reduction in symmetry and proper lattice relaxation. This affects the results in a very profound way as we will show in this paper. To our knowledge, Shen *et al* [13] and Agrawal *et al* [14] are the only other investigators who have undertaken large-scale *ab initio* investigations of an alloy. However, with the continued rapid increase in computing power, and demonstrations of the value of such calculations, we expect to see the number of applications increase dramatically.

### 2.2. Modelling of the alloy

The lack of experimental data on Tl-containing compounds makes it highly interesting to apply the most refined calculation tools available to corroborate earlier predictions of promising device properties arrived at using more approximate theoretical approaches [1, 2]. Part of the attractiveness of the proposed devices is that they would use commonly available substrate materials like InP and GaAs. The active, Tl-containing, device layers would thus be of zincblende structure. In this investigation we have chosen not to address the issue of whether zincblende is the crystal configuration lowest in energy for the alloy or not. Even if a more stable structure were found its applicability to non-equilibrium synthesis techniques, for example molecular beam epitaxy (MBE), would be limited. At this early stage we have also chosen

not to include the further complication of strain, induced by growth of the alloy on a substrate with different lattice constant, even though this may be one of the practical applications of the material [2].

To describe the zincblende alloys, an ensemble of 64 atoms with different concentrations of Tl was placed inside a cubic supercell, with the side equal to twice the assumed lattice constant. Initially the atoms were placed in perfect III–V zincblende lattices, where the III-valued atoms could be chosen to be either Ga or Tl. All anion sites were occupied by As atoms. Whether the group III sites in the supercell were occupied by Tl or Ga atoms was chosen at random. The actual lattice positions for each energy calculation were generated by the modified pseudo-random number generator RAN2 [15]. The resulting supercell systems were found to have no remaining symmetry. In each case every atomic position was fully relaxed, resulting in significant lattice distortions.

Our investigation of geometries with only *some* reduced symmetry revealed deviations in both lattice constants and total energy, as compared to the non-symmetrical models. The total energy of the completely unsymmetrical random model differed both when compared to the large 64-atom symmetrical ensembles and all tested eight-atom ensembles. This effect arises because any geometrical symmetry automatically symmetrizes forces and atomic displacements, which has a non-negligible effect on the total energy. It does *not* mean that e.g. a segregation of the alloy into pure GaAs and TIAs, or any other high symmetry system cannot be lower in energy (see section 3). What it does imply, however, is that the random alloy simply cannot be properly modelled by a system containing any amount of symmetry. Consequently, results for smaller supercells (eight atoms, see Chen and Sher [5] and Jhi and Ihm [11]) must be questioned, since there is no way to completely eliminate the symmetry in these configurations. The statistics are likewise extremely poor in these investigations; the maximum number of possible configurations for a given concentration is six not counting the reduction due to the symmetry. In our 64-atom system, the average number of possible configurations is  $1.4 \times 10^8$ , and the minimum number 4960, which ensures the quality of the model.

It is important though in order to obtain valid results to ensure that the random distributions chosen are good representations of the physical reality, i.e. that the models represent the probable physical distributions. It is also important to estimate the effect of the exact choice of distribution. We have performed several tests towards this end, all indicating a high degree of insensitivity of the total energy, atomic distances etc. The variations due to the exact nature of the distribution were all considerably less than the numerical uncertainty and thus negligible, see below. Hence this approach should give reliable and useful results. Sufficient number of atoms and unsymmetrical configurations are therefore two very important features of high-precision calculations for the future.

### 2.3. Computational details

All wavefunctions and energy eigenvalues were calculated *ab initio* within density functional theory [16, 17] (DFT) using the local density approximation (LDA) as implemented by Ceperley and Alder [18] and Perdew and Zunger [19]. For the electron–ion interaction, fully separable, nonlocal pseudo-potentials (PP) were used [20, 21], based on self-consistent solutions of the relativistic Dirac equation for free atoms [22–24]. The calculations were performed using the plane-wave band structure code fhi94md.cth [25], which is a heavily modified version of fhi93cp [26] concerning the computational methods. The geometries were described by the supercell method, using the theoretical lattice constants for GaAs (5.50 Å) and TIAs (6.27 Å) in the bulk calculations and a plane wave cut-off of 12 Ryd. Bulk TIAs was

assumed to exhibit the zincblende geometry. To sample the wavefunctions of the 64-atom alloy systems we used four special Monkhorst–Pack  $k$ -points in the irreducible Brillouin zone (IBZ), corresponding to eight  $k$ -points in the full zone. In the bulk calculations six special  $k$ -points in the IBZ (27 in the full zone) were employed to describe the wavefunctions. The equilibrium geometries were considered established when all forces were smaller than  $0.005 \text{ eV \AA}^{-1}$ , corresponding to an estimated numerical uncertainty of  $\sim 0.02 \text{ \AA}$ . Smaller supercells only containing eight atoms were also calculated for comparison. The same numerical conditions as for the 64-atom alloy geometries were used.

In order to produce the random physical system, a total number of more than  $1 \times 10^9$  different distributions were produced by the use of the RAN2 pseudo-random number generator. The final distributions were subsequently chosen randomly from the 95% most common systems to avoid pathological situations. To further check the accuracy of the current approach, several different randomized geometries produced in the way above for fixed Tl concentrations were calculated using a lower cut-off of only 8 Ryd to save computing time. This kind of cut-off has earlier been found to give reliable results [27] when comparing total energies and structural constants. The fluctuations in total energy were negligible, and the averaged nearest neighbour distances (NNDs) also agreed very well for all properly randomized structures. Although good for comparisons, a 8 Ryd plane-wave cut-off is not entirely reliable when it comes to absolute values. Hence we increased the cut-off to 12 Ryd in the final calculations.

That the thicknesses of the supercells were adequate was explicitly tested by examining the partial density of states (PDOS) and atomic positions for any periodicity. All influences of any single atom disappeared within a few atomic layers, agreeing well with earlier findings on other complex structures [28–30]. Since the supercells contain eight atomic layers in all three dimensions they should accordingly be free from any artificial influence.

To produce the continuous results for the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy, we calculated the atomic and electronic structures of different  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  superstructures using the following number of Tl and Ga atoms: 3 + 29, 6 + 26, 13 + 19, 19 + 13 and 26 + 6. This corresponds roughly to 9.3%, 18.8%, 40.6%, 59.4% and 81.2% Tl in the alloy. For each composition the total energy was minimized with respect to the lattice constant using the high cutoff, and double checked by repeating the calculation at the lower cutoff with the same number of Tl atoms, but with a different atomic distribution in addition to the tests made above. In all cases the statistical differences were found to be considerably less than the numerical uncertainty.

Before going on to the results, we should discuss possible errors in the calculations due to the DFT–LDA approach. Since, to our knowledge, there are no experimental data available on TIAs, we have to look at trends in other theoretical results, summarized in table 1. The GaAs and AlAs results agree very well with traditional LDA calculations [31], but display the typical slight underestimation of bandgap and lattice constant. TIAs can be expected to be more analogous to materials with larger lattice constants, like InP and InAs. The calculated lattice constants for those materials reproduce the experimental values exactly, whereas the bandgap energies are shifted down by about the same amount as for GaAs and AlAs. Our lattice constant for TIAs of  $6.27 \text{ \AA}$  is somewhat larger than found earlier by van Schilfgaarde *et al* [1] ( $6.18 \text{ \AA}$ ) as is the bandgap,  $-1.86 \text{ eV}$ , to be compared [1] with  $-2.12 \text{ eV}$ . Considering these results it is reasonable to conclude that the calculated bandgaps for  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  are underestimated and that the lattice constants have errors that become progressively smaller for higher compositions. More exact estimations cannot be made before more experimental data exist. We therefore choose not to present any elaborate estimations of the LDA errors, but only the numerical uncertainty within the current approach. However, we expect the computations to return the correct general behaviour of the band structure as well as any other property.

**Table 1.** Calculated and experimental values for bandgaps and lattice constants (300 K).

Material	$a_{calc}$ (Å)	$a_{exp}$ (Å)	$E_{g,calc}$	$E_{g,exp}$ (eV)
GaAs	5.50	5.56	1.06	1.43
TlAs	6.27	—	-1.86	—
AlAs	5.60	5.66	1.29	2.15
InP	5.87	5.87	1.10	1.34
InAs	6.06	6.06	0.00	0.36

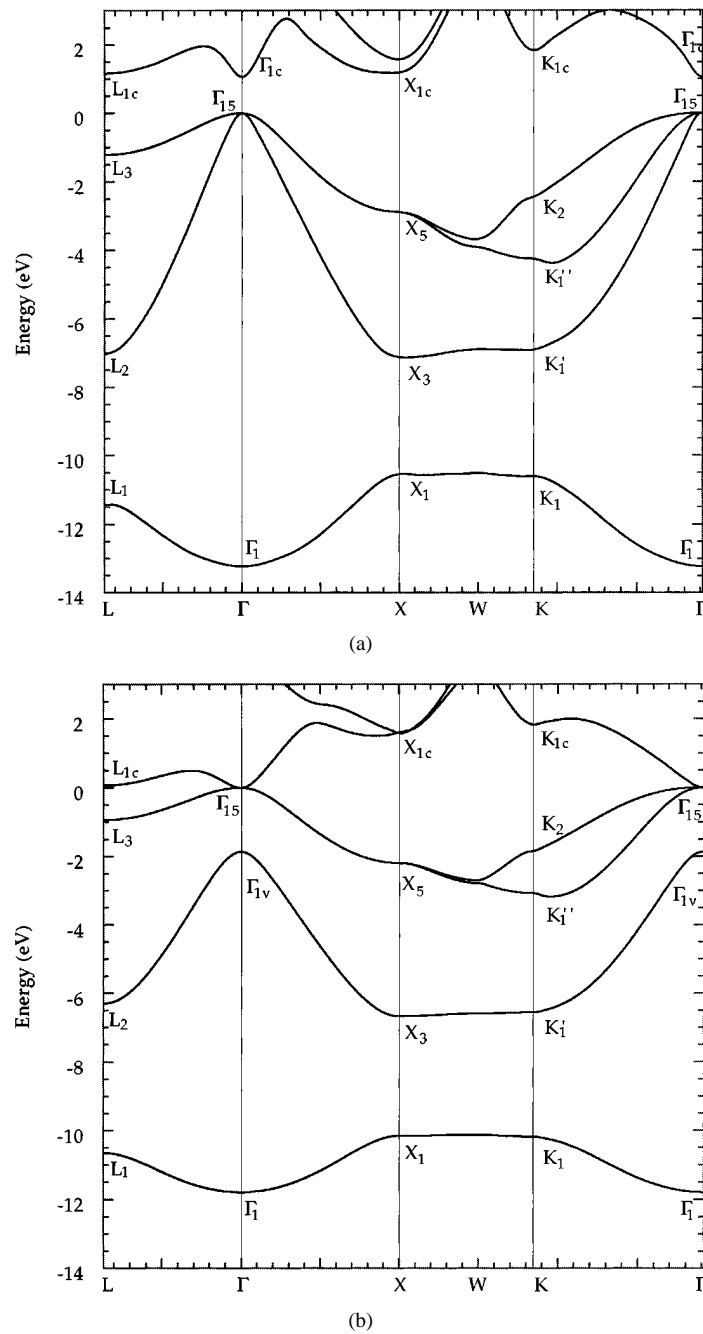
Hence only the detailed absolute values are assumed to be affected by the LDA errors. These errors are of greater significance for predictions of compositions at which the material will be suitable as a LWIR detector than they are for electron devices. Any new experimental data for a high concentration  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy will easily enable a more exact error correction though.

### 3. Results and discussion

The band structures of bulk GaAs and TlAs have been calculated and are displayed in figure 1. Because of the pronounced differences between the GaAs and TlAs in the regions of the fundamental gap, the definition of the bandgap becomes somewhat dubious, however. We have therefore chosen to *define* the ‘bandgap’ as  $E_g = |\Gamma_{1c}| - |\Gamma_{1v}|$ . This makes  $E_g$  take on the ordinary positive value in GaAs, while the ‘gap’ becomes negative in TlAs. Strictly speaking the bandgap can of course never be negative, and TlAs is a semimetal, but similar to e.g. HgTe (see [31]) it still is very descriptive to use the term ‘negative gap’. Furthermore this notation is already established in earlier work [1, 2] in this field. Using this definition of  $E_g$  we see that TlAs exhibits a very large negative ‘gap’ within the valence band, i.e. the topmost valence band point  $\Gamma_{15}$  coincides with the conduction band minimum (CBM)  $\Gamma_{1c}$ , while the  $\Gamma_{1v}$  point is separated out and pushed down. The width of the lower part of the valence band below the heteropolar gap ( $X_1 - \Gamma_1$ ) is also considerably smaller for TlAs as compared to GaAs, and the bottom of the valence band ( $\Gamma_1$ ) is situated more than 1 eV higher. This, together with the decrease in width of the upper valence bands at the K-point ( $K_2 - K_1''$ ) and the lowering of the conduction band in the L-point, are the most pronounced differences between the electronic structure of GaAs and TlAs.

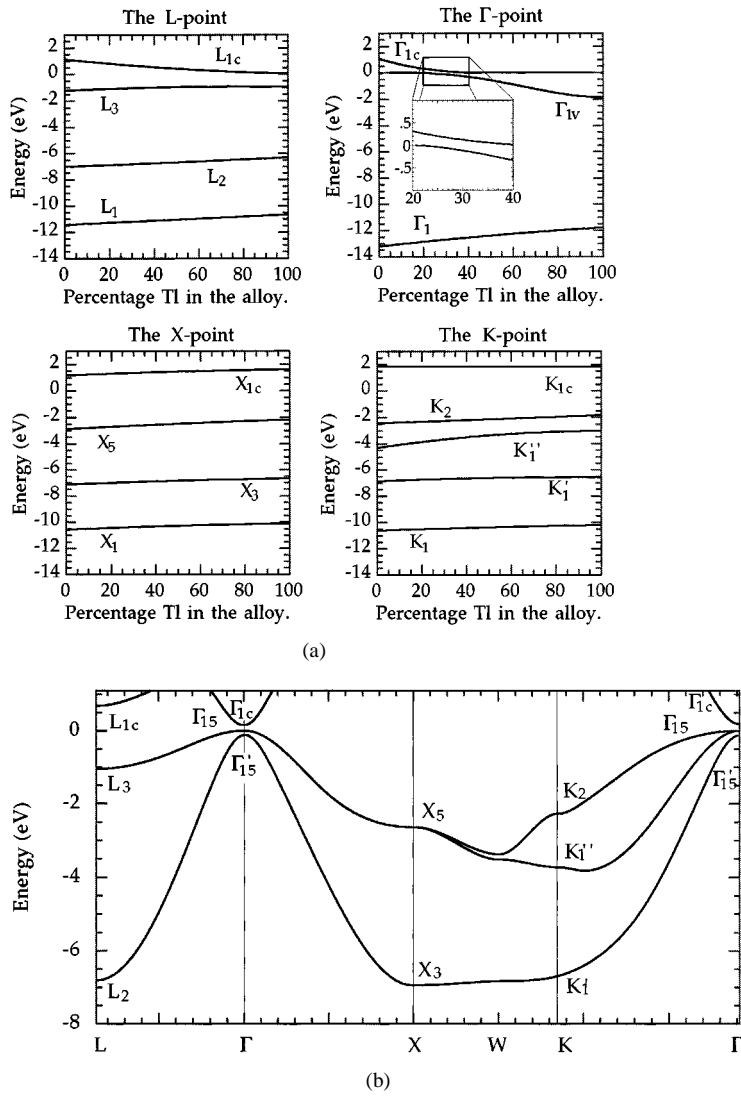
While geometrical data were straightforwardly extracted from the calculations, the electronic structure becomes extremely involved when large supercells are used. This is because the Brillouin zone (BZ) of the much larger ensemble is considerably smaller than the bulk one. Thus, the bulk bands will be folded onto this new, smaller BZ, creating a weblike structure of bands. For non-ideal cases, i.e. alloys, many bands will also be slightly shifted because of the locally different chemical environment of the individual atoms. Thus, bands that are degenerate when calculating a large supercell of pure GaAs or TlAs become non-degenerate in the alloy. This effectively broadens the bulk bands in the range of  $\sim 0.05$  eV. We have, however, chosen not to introduce any broadening of the resulting bulk alloy bands here, but consider all bands as ideal, although with an uncertainty of 0.05 eV. Resulting band values were produced by taking the centre value of the broadened electronic structures.

We interpolated all geometrical and electronic structural functions by four-degree polynomials using the least-squares-fit procedure. All differences between the individual calculations and the interpolated polynomial values were very small in absolute values and well within the numerical errors of the geometrical properties (0.02 Å) and the total energy



**Figure 1.** (a) The calculated electronic band structure of GaAs. The VBM is taken as zero energy. (b) The same as (a) but for TIAs.

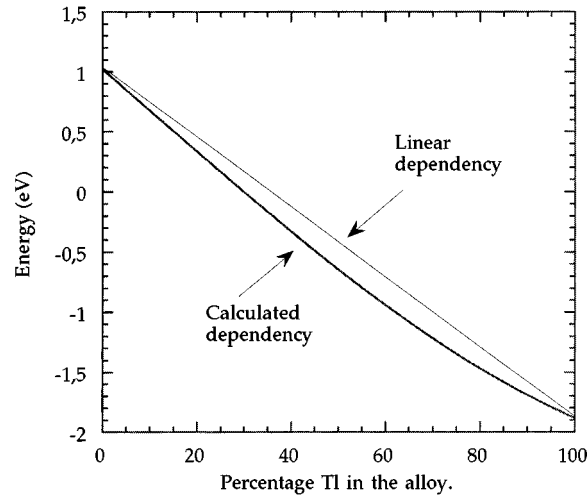
(0.05 eV) of the ensembles. This clearly indicates that the statistical error due to the limited size of the ensembles is smaller than the numerical error and can thus safely be ignored. Comparing the current geometries with different atomic distributions at a lower cutoff, as discussed in section 2.3, further confirmed these findings.



**Figure 2.** (a) The dependency of the electronic structure (critical points) on the Tl concentration in the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy. Note that  $\Gamma_{15}$  is identically zero as it defines the VBM and is therefore not displayed here. (b) The upper part of the valence band structure including the split-off band and lowest parts of the conduction band for the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy with a Tl concentration of 28.1%, see the text for details.

Our results indicate that the band structure varies smoothly between the two end cases of pure GaAs and TlAs (see figure 2(a)). The only exception is in the  $\Gamma$ -point of the conduction band,  $\Gamma_{1c}$ , and the central valence band,  $\Gamma_{1v}$ . The two upper valence bands remain degenerate at the  $\Gamma$ -point up to a Tl concentration of 23% when  $\Gamma_{1v}$  splits off from  $\Gamma_{15}$  and opens up a ‘gap’ beneath the valence band maximum (VBM). The conduction band, on the other hand, remains above the VBM, up to 35% Tl when the gap between  $\Gamma_{1c}$  and  $\Gamma_{15}$  closes up. At all higher concentrations,  $\Gamma_{1c}$  is degenerate with  $\Gamma_{15}$  and is consequently identically to zero since  $\Gamma_{15}$  defines the VBM. In reality the upper limit of 35% Tl will probably be pushed to somewhat higher concentrations since the DFT-LDA is well known to underestimate the





**Figure 3.** The bandgap as defined by  $E_g = |\Gamma_{1c}| - |\Gamma_{1v}|$  as a function of the Tl content in the alloy. A simple linear dependency is inserted for comparison.

fundamental bandgap and thus is likely to return a too small value of the  $\Gamma_{1c}/\Gamma_{15}$  distance for any concentration (see also the discussion in section 2.3). The value of 23% Tl necessary for the  $\Gamma_{1v}$  to split off from the  $\Gamma_{15}$  should be accurate though since DFT-LDA is known to return good results for the occupied states.

Still, the existence of a split-off band is unexpected in terms of group theory and since this concentration range in addition is situated in between the calculated concentrations of 18.8% and 40.6%, it might be argued that the effect is a result of the numerical framework and the interpolation done. In order to check the results more carefully we therefore calculated the bands of an ensemble with nine Tl and 23 Ga atoms (28.1% Tl concentration), using the interpolated lattice constant from the previous calculations to limit the numerical effort. In the resulting band structure we find  $\Gamma_{1c}$  to be situated 0.16 eV above and  $\Gamma_{1v}$  0.11 eV below the VBM respectively (see figure 2(b)). This is in full agreement with the prior results within numerical uncertainty. This clearly shows that  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  has a split-off band for Tl concentrations between 23% and 35%, i.e. there exist minor gaps between both  $\Gamma_{1c}/\Gamma_{15}$  and  $\Gamma_{1v}/\Gamma_{15}$  in the range of tenths of an electron volt for these concentrations. Even taking the numerical broadening of 0.05 eV into account, the effect remains. Consequently,  $E_g = |\Gamma_{1c}| - |\Gamma_{1v}|$  is not the ‘true’ bandgap in this region. Outside the 23 to 35% interval, it coincides with the common bandgap and its value varies smoothly between  $x = 0$  and 1 (see figure 3).

The reason for this apparent discrepancy with group theory is that there is no proper symmetry on the atomic level or that of the supercell itself. Only in the case of a homogenous local environment can a central atom experience full symmetry. In a real, *distorted* lattice of a mixed crystal, a central atom of any given region of the system would experience an environment which is different in different directions, both because the neighbouring atoms are statistically of different types and because the bond lengths vary due to the relaxation. It should be noted that the revelation of this effect on the band structure is due to the *ab initio* approach. CPA [5] and similar schemes replace the surrounding atoms with an effective, homogenous medium, which results in an unnaturally high degree of symmetry, forcing degeneracy upon the bands. When this is lifted, the Tl content may move the  $\Gamma_{1v}$  point down toward the  $-1.86$  eV

value of 100% TIAs. Hence, the only result of the broken symmetry is that the  $\Gamma_{1v}$  may move freely, which it does. Although the same arguments are valid for the rest of the bands, no other split-offs are seen outside the numerical uncertainty. However, it should be mentioned at this point that the spin-orbit splitting is of the same order of magnitude as the split-off band, and if included, might reduce this effect at least partly.

Although a somewhat better polynomial fit to the bandgap is obtained with more terms than two, the higher powers turn out to have relatively little weight. We can therefore neglect the third and fourth order terms used in our fit to facilitate comparison with earlier determined bowing factors  $C$ . Doing so, our calculation returned a value of  $C = 0.88$  in excellent agreement with the approximation ( $C = 0.9$ ) used by Svensson and Crowne [2].

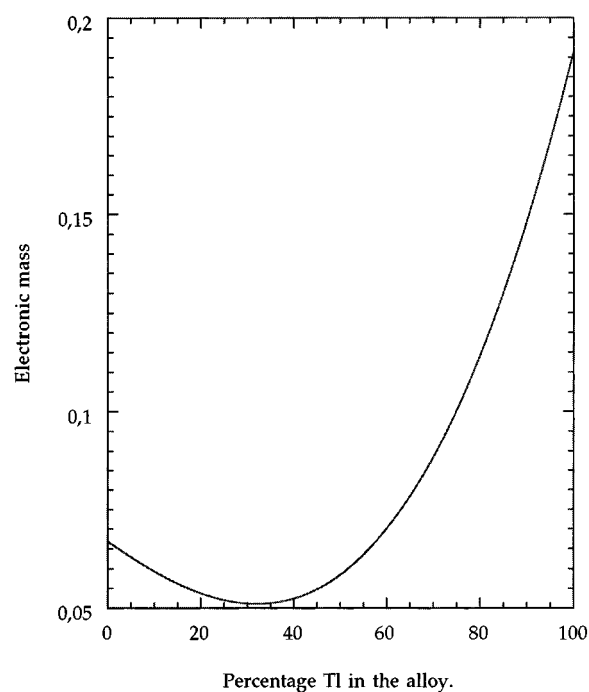
Using the curvature of the lowest conduction band around the  $\Gamma$ -point, we have calculated the effective mass,  $m^*$ , of the electrons. The two extreme cases, GaAs and TIAs show a difference of nearly a factor three in  $m^*$ , with  $0.065 m_e$  for GaAs ( $0.066 m_e$  experimentally) and  $0.191 m_e$  for TIAs. This behaviour can be easily understood in terms of the electronic structure of the two materials. GaAs has a very pronounced direct bandgap with a strong increase and relatively large local maxima in energy around the  $\Gamma$ -point, which gives the CBM a relatively high curvature. TIAs, on the other hand, has a much flatter conduction band around the  $\Gamma$ -point with a slow increase in energy toward the L- and X-point with only minor maxima in between.

For low concentrations of Tl, the alloy keeps the GaAs type of electronic structure, but exhibits progressively smaller bandgap with increasing Tl content due to the changes in electronic structure. This is simply an effect of the conduction band distorted paraboloid around the  $\Gamma$ -point becoming sharper for low concentrations. When the  $\Gamma_{1v}$ -point splits off, the decrease in  $m^*$  slows down at the same time as the electronic structure becomes more TIAs-like (see figure 4). This is not very surprising, since the conduction band can no longer move much lower in energy. At even higher Tl contents, after the bandgap closes at 35%,  $m^*$  begins to increase quickly as the rest of the conduction bands move downward to the valence band, while  $\Gamma_{1c}$  is kept fixed at the VBM. The absolute minimum of  $m^*$  is thus 32.5% Tl, just before  $\Gamma_{1c}$  reaches zero energy. This is a slightly higher concentration than that of  $E_g = 0$ , which occurs at 29% because of its different definition (i.e.  $|\Gamma_{1c}| - |\Gamma_{1v}|$ ).

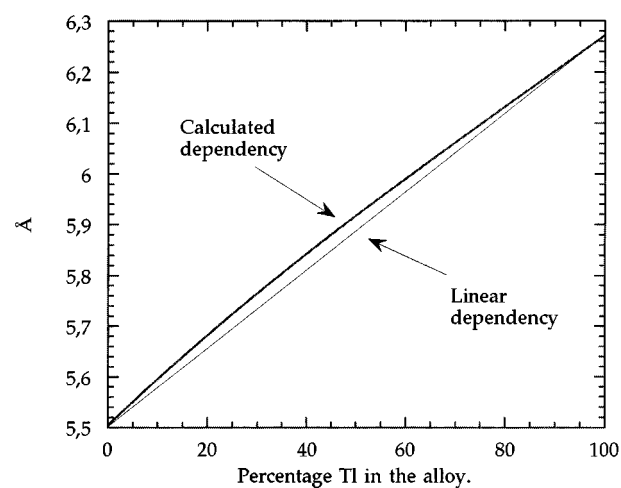
Turning to the geometrical results, which are unique to *ab initio* calculations, it might be argued again that statistical fluctuations can affect the calculations in a significant way. However, the number of bonds in our analysis is twice as many as the atoms, resulting in nearly 2000 calculated bonds, which provide more than adequate statistics. The resulting lattice constant of the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  as a function of Tl concentration is bowed slightly upward (see figure 5). This agrees very well with the downward bowing of the bandgap  $E_g$  since an increase in the lattice constant implies a decrease in the bandgap for any given atomic geometry.

Using the relationship between total energy and the lattice constant for each fixed concentration, we also calculated the bulk modulus of the (macroscopic) alloy. Transforming the dependency on the lattice constant for any given Tl concentration to a volume dependency and differentiating twice resulted in  $B = 0.821 \times 10^{11} \text{ J m}^{-3}$  for GaAs, to be compared with an experimental value of  $0.793 \times 10^{11} \text{ J m}^{-3}$ . Our value for TIAs of  $0.432 \times 10^{11} \text{ J m}^{-3}$  is slightly lower than the theoretical value of  $0.49 \times 10^{11}$  in [1], which most likely is related to our larger lattice constant. The general dependency of  $B$  on the Tl concentration is displayed in figure 6, where the  $B$ -value is bowed upward in a similar way to the lattice constant. This should be expected since the mixing of Tl and Ga forces the lattice to expand, and hence decreases the compressibility.

Investigating the geometry in more detail, i.e. the bond lengths between nearest neighbours, we notice that the major part of the increase of the lattice constant with increasing Tl

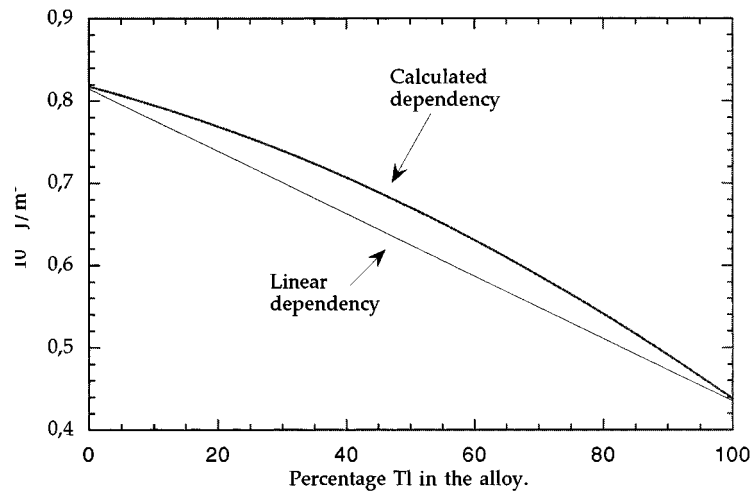


**Figure 4.** The effective electronic mass  $m^*$  of the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy for different concentrations of Tl. Numerical uncertainty is  $\pm 10\%$  of the absolute value. It should be noted though that the exclusion of spin-orbit splitting gives an additional uncertainty to this value.

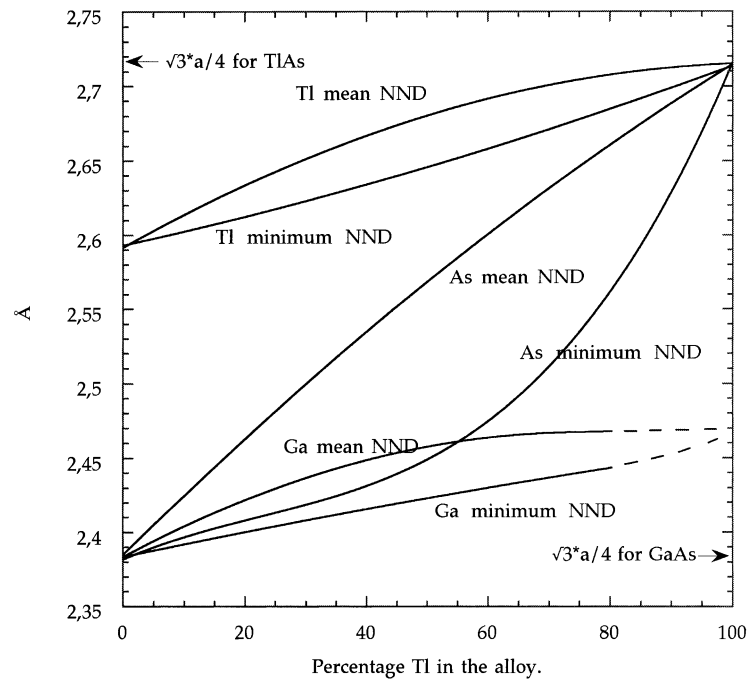


**Figure 5.** Lattice constant for the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy as a function of the Tl content.

concentration is, of course, due to the exchange of Ga to Tl atoms. However, a considerable part of the increase can also be explained in terms of greater bond lengths of both species of metal atoms to the surrounding As. It is especially interesting to note the large differences in averaged minimum and mean bond lengths for the different species (see figure 7). The maximum bond

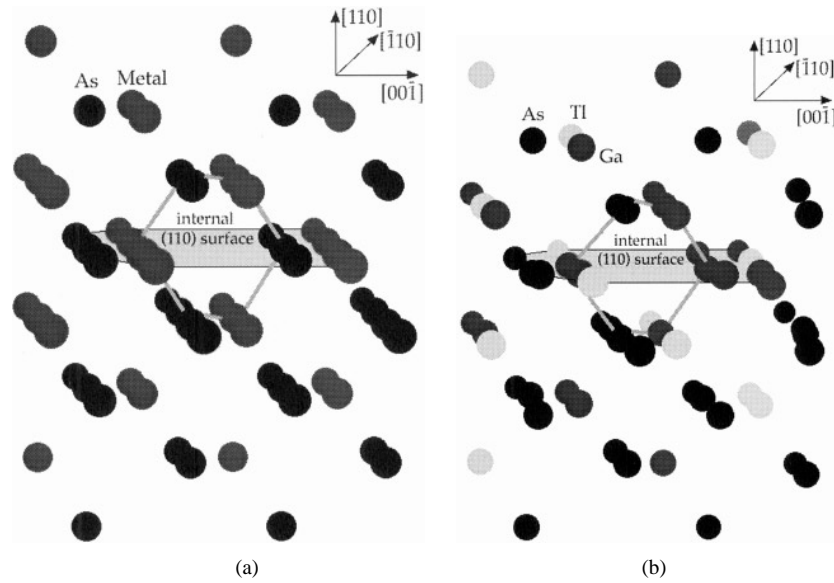


**Figure 6.** The dependency of the bulk modulus for the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy on the Tl concentration.



**Figure 7.** The averaged mean bond lengths for As, Ga and Tl atoms in the alloy. Average minimum distances for the different species to the nearest neighbours are also inserted. The maximum bond lengths show very similar dependencies on the Tl concentration, but are not included here. The bond length for Tl in pure GaAs is interpolated from the values of mixed alloys and should be interpreted as a single Tl atom in infinite GaAs. Similarly the bond length for a single Ga atom in TlAs is indicated by the dashed line.

lengths display very similar dispersions to the minimum distances. These differences clearly imply that the atoms will, in general, have considerable differences in bond lengths to different



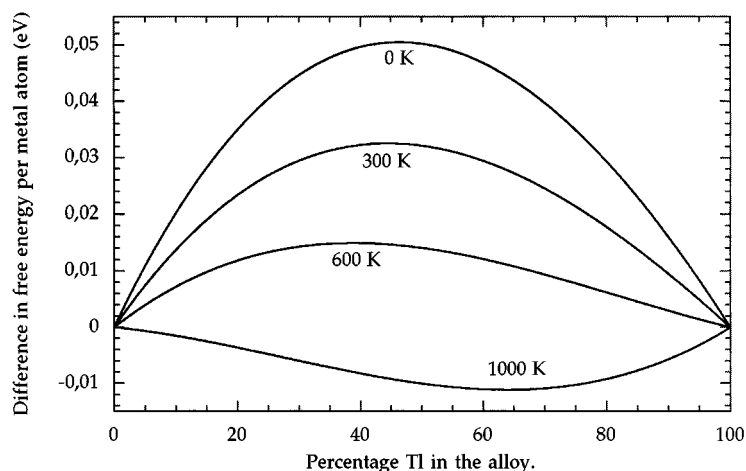
**Figure 8.** (a) The ideal zincblende geometry for a cubic supercell containing 64 atoms. (b) The same as in (a), but for a  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy with 40.6% Tl. Note the large displacements around the Tl atoms.

neighbours. The actual bond geometry for each individual atom will then depend on the exact nature of the local atomic distribution (see the discussion above) in the surrounding volume of the alloy.

Consequently, the zincblende lattice should become heavily distorted for any substantial intermixing of Ga and Tl atoms, something that is reflected in the large deviations of As bonds from the mean value in the range of 30% to 70% Tl. These distortions can be clearly seen when comparing the ideal lattices of GaAs and TlAs with one of the mixed distributions, figure 8(a) and (b). Thus, not even the lattice itself is ideal any longer for substantial mixing concentrations, which implies that not only the atomic, but also the geometrical symmetry becomes broken. This, together with the differences in local atomic distribution, is the driving force of the broadening (increase in numerical uncertainty) of the electronic bands and thus a very important feature of high-precision calculations. The same effects also enable the  $\Gamma_{1v}$ -point to split off, since the symmetry is eliminated.

Although Chen and Sher [5] used a different calculation method with eight-atom supercells in their analysis of  $\text{Ga}_{1-x}\text{In}_x\text{As}$ , our test calculations on  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  with the same small size atomic geometry returned very similar results to theirs: a linear dependency was observed in the lattice constant as a function of composition and the variations in bond lengths were much smaller than for our large systems. On the other hand the investigation on  $\text{Sn}_x\text{Ge}_{1-x}$  by Shen *et al* [13], using supercells containing 72 atoms, did find large variations in bond lengths. This clearly suggests that the linearity [5] and small variations in bond lengths most likely are numerical constructs due to the smaller ensemble, and not physical properties. These findings further stress the importance of proper randomization and sufficiently large ensembles.

Another interesting feature of figure 7 is the bond lengths at 0% Tl composition. We can call this the 'doping limit', or in other words, the limit at which a Tl atom is embedded in an infinite GaAs crystal, or vice versa. The ideal bond lengths are then  $\sqrt{3}a/4$  for the host



**Figure 9.** The difference in free energy for the alloy and the separated phase containing GaAs and TIAs particles according to the definition in equation (1). Note that the dependency of the free energy is unsymmetrical with respect to the Tl concentration for all temperatures.

crystal, or 2.382 and 2.717 Å for GaAs and TIAs, respectively. From figure 7 we see that the bond length for Tl in GaAs is 2.59 Å. Since we did not include any investigation of alloys with Tl concentrations outside the range of 9.3–81.2% Tl, it is consequently harder to make a good interpolation for the Ga NND-value for small Ga concentrations than for the Tl bond length for small Tl concentrations. Figure 7 does, however, indicate a bond length of approximately  $2.47 \pm 0.02$  Å for a single Ga atom in an extended TIAs crystal, i.e. only 0.09 Å larger than in the GaAs crystal. The reason for this effect lies in the  $sp^3$  hybridization of the TIAs (GaAs) surrounding the Ga (Tl) atom, i.e. the angular forces which work to conserve the tetrahedral angles of the bonds of the TIAs (GaAs) close to the ‘impurity’ atom. This difference in bond length is, even if not critical, important to achieve the correct electronic structure locally. Thus simple assumptions about bond lengths should also be avoided if possible in more simple approximation schemes, but taken from proper *ab initio* calculations to obtain, at least, the correct mean distance.

At this point we should also address the stability of the alloy itself. There is, as noted in the introduction, an ongoing controversy about whether Tl-containing compounds are stable [3,4]. Thus, any theoretical findings on the mixed case would be of interest. Unfortunately there is no obvious reference system. In principle, we could consider a vast number of different phases, including metallic clustering, As particles, different lattice types etc. However, as outlined in section 2.2 we limit our analysis to the case of an unstrained zincblende configuration. The question of the stability of the alloy is then reduced to whether the species separates into GaAs and TIAs particles. Neglecting interface effects between different particles, we should then find that the energy of this ‘separated phase’ is simply  $E_{sep} = (1-x)E_{GaAs} + xE_{TIAs}$ . Since the particles are homogenous, they have the minimal entropy of  $2k_B \ln(2)$  where  $k_B$  is the Boltzmann constant. Note that the entropy has been normalized to the number of (metallic) atoms. The alloy on the other hand has a non-trivial entropy  $S$ , where  $S = 2k_B \ln(2) - k_B[(1-x) \ln(1-x) + x \ln(x)]$ . Using the calculated (and normalized) total energy  $E_{alloy}$  for the alloy, the free energy  $F$  then becomes  $F_{alloy} = E_{alloy} - TS = E_{alloy} - T(2k_B \ln(2) - k_B[(1-x) \ln(1-x) + x \ln(x)])$ . For the separated phase the corresponding free energy becomes  $F_{sep} = (1-x)E_{GaAs} + xE_{TIAs} - T2k_B \ln(2)$ .

Taking the difference between  $F_{\text{alloy}}$  and  $F_{\text{sep}}$ , we arrive at

$$F_{\text{diff}} = E_{\text{alloy}} - Tk_B[(1-x)\ln(1-x) + x\ln(x)] - ((1-x)E_{\text{GaAs}} + xE_{\text{TlAs}}). \quad (1)$$

The results are plotted for several different temperatures in figure 9. As shown, the alloy phase is only stable at relatively elevated temperatures. The numerical uncertainty in the total energies results in a possible numerical error of 0.015 eV, however, which in principle could allow the alloy to be stable at considerably lower temperatures. There might also be additional systematic errors due to the DFT-LDA scheme itself that could be in the same range as  $F_{\text{diff}}$ , although nothing seems to indicate that. Hence, we do consider the results as an indication, even if somewhat vague, of the possible instability of the alloy. Using the absolute values found here, growth of any TIAs alloy should take place at relatively high temperatures to achieve a good mixing. Cooling of the sample will then lock the species in their places, resulting in a room-temperature alloy. If, on the other hand, there are other configurations more stable than the TIAs zincblende lattice assumed above, the difference in free energy will increase even further since  $E_{\text{TlAs}}$  then would decrease (see equation (1)).

#### 4. Conclusions

We performed *ab initio* calculations on the  $\text{Ga}_{1-x}\text{Tl}_x\text{As}$  alloy for a set of concentrations covering the entire range from 0% to 100%. The electronic and geometrical structural dependency on the Tl content was investigated in detail. Of particular interest was the finding of a ‘double gap’ above and below the VBM for concentrations between 23% and 35%. Apart from this effect, the electronic structure changed relatively smoothly from GaAs to TIAs. The lattice constant and bulk modulus had a positive dependency on the Tl concentration as compared to the linear combination of GaAs and TIAs. The effective mass was found to decrease monotonically up to about 23% Tl, indicating promising transport properties for electron device applications. Beyond 23%, the effective mass increases. Geometrically, we found that the lattice was subject to extensive distortions for substantial mixing concentrations. In the limit of a single Ga (Tl) atom in infinite TIAs (GaAs), the bond length differed considerably from the ideal metal-As binding lengths. Investigating the free energy of the system, we found that the alloy was unstable at zero K by a few hundreds eV/atom, probably requiring relatively elevated synthesis temperatures.

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