

# Energetics of formation of $\text{TiGa}_3\text{As}_4$ and $\text{TiGa}_3\text{P}_4$ intermediate band materials

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Using density functional theory quantum methods, total energy values and vibrational properties have been computed, and thermodynamic properties evaluated, for Ti-substituted GaAs and GaP, proposed as candidates for intermediate band photovoltaic cells. The calculations predict that the formation of these materials from the binary compounds implies an increase in total energy (that is ascribed largely to the change in coordination undergone by Ti, from six-fold to four-fold), and thus phase separation rather than mixed compound formation would be favored. However, the mentioned increase is not larger (for the arsenide case it is actually smaller) than that predicted for Mn-substituted GaAs, a material which has been experimentally made, and therefore the obtention of these Ti-substituted materials is expected to be feasible as well. Vibrational and disorder entropy contributions to the formation free energy of the ternary compounds have been also computed; they compensate partially for the total energy increase, and indicate that the thermodynamic feasibility of the materials synthesis improves for low Ti concentrations and high temperature conditions.

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## I. INTRODUCTION

Solar energy is one of the main renewable sources expected to allow, in the future, alleviation of the greenhouse effect problem and to decrease the dependence on fossil fuels. In order to reach that situation it is necessary, however, to increase significantly its efficiency, making it possible to obtain, from a given amount of incident radiant energy and at an acceptable cost, a higher amount of utilizable energy than can be gained today. To this aim, a proposal issued in recent years is the use in photovoltaic devices of intermediate band materials, i.e., compounds in which a partially filled, relatively narrow electronic band exists within the band gap of an otherwise normal semiconductor; these materials show promise of providing photovoltaic cells of unprecedented performance, as their ideal efficiency limit is 63.1%, much higher than the well-known Shockley and Queisser limit of (single junction) normal cells (40.7%).<sup>1</sup> Some of the first candidates proposed are Ti-substituted GaAs and GaP, which show such intermediate bands in accurate quantum calculations;<sup>2-4</sup> it seems then pertinent to assess, from the thermodynamic point of view, the viability of the synthesis of these compounds, especially in the more likely case of substituting Ti in the Ga position. A computational work with this aim has been carried out and is presented here.

## II. METHODS

Total energy calculations within density functional theory (DFT) were made with the plane-wave CASTEP code,<sup>5</sup>

allowing spin polarization and using the PBE functional<sup>6</sup> and ultrasoft pseudopotentials.<sup>7</sup> These latter include in the core, for the Ti atom, the  $3p$  semicore levels, but take into account an appropriate nonlinear core correction<sup>8</sup> to keep high accuracy; for the Ga atom, the  $3d$  levels were kept within the valence manifold. The plane-wave cutoff (650 eV) and the density of the Monkhorst-Pack sampling of the Brillouin cell were chosen high enough to achieve convergence in total energy better than 30 meV. Energy was minimized by relaxation of cell dimensions and atom coordinates with convergence thresholds of 0.02 meV/atom and 0.001 Å for total energy and atomic displacements, respectively.

DFT phonon calculations were made with the SIESTA code,<sup>9</sup> allowing spin polarization and using the local density approximation, norm-conserving pseudopotentials and confined atomic functions in a basis set of DZP quality with different confinement radii for  $s, s', p, p'$ , and  $d$  orbitals. The used pseudopotentials were taken to include the  $3p$  electrons and below for Ti,  $2p$  and below for P, and  $3d$  and below for Ga and As. We used here a Monkhorst-Pack sampling of  $8 \times 8 \times 8$   $k$  points for all lattices. To determine the equilibrium structure of the systems studied, all the atomic positions and the unit cell were allowed to relax by the minimization of the total energy until the largest force components were below 0.001 eV/Å and the stress was below 0.1 GPa. To determine phonon data we adopt the frozen-phonon method,<sup>10,11</sup> which requires the use of supercells where the *ab initio* force constant matrix is calculated in real space. From the thus computed forces on the ions the phonon frequencies were obtained in a grid of points of the Brillouin zone defined according to a Monkhorst-Pack sampling of  $12 \times 12 \times 6$

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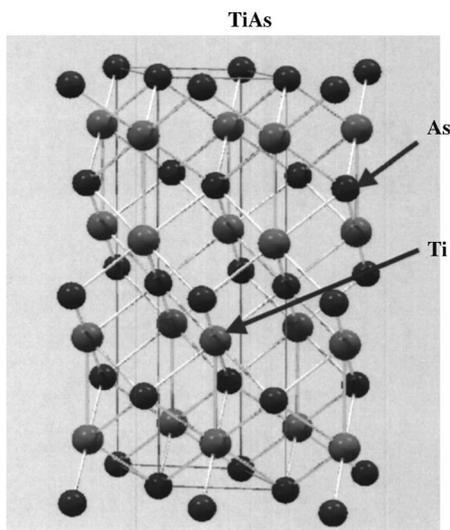


FIG. 1. Crystal structure (hexagonal) of TiAs (and TiP).

points. From this the phonon density of states was obtained, and the vibrational contributions to thermodynamic properties were computed using standard formulas.<sup>12</sup>

The starting model used for the metal-substituted compounds was, in most cases, a zinc-blende-type cubic cell with 8 atoms in which one Ga (out of four) was substituted by Ti (or by Mn where appropriate). In one case, a  $2 \times 2 \times 2$  zinc-blende supercell model (with 16 atoms in the primitive cell of the fcc superlattice) was used, where 1 of the 8 Ga atoms present was substituted by Ti. For pure TiAs and TiP, the known hexagonal structure of these compounds,<sup>13</sup> which is a hybrid stacking of hexagonal slabs of the TiN (rocksalt) and NiAs structures (Fig. 1), was used.

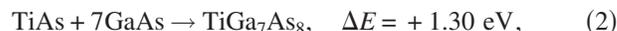
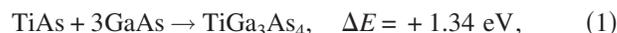
### III. RESULTS AND DISCUSSION

The electronic structure features obtained in the calculations are in agreement with the band structures and density-of-states data obtained with other DFT methods and previously published.<sup>3,4</sup> Briefly, upon introduction of Ti in the Ga site a new band appears in the gap, being located close to the conduction band (and appearing well separated from it if an accurate calculation, e.g., using the exact exchange method, is used).<sup>3</sup> This new band, formed mainly from Ti  $3d$  orbitals and with two states in it as corresponds to the  $e_g$ -type lower manifold arising from such levels in a tetrahedral environment, is half-filled with one electron, i.e., it is crossed by the Fermi level, and shows therefore the desired intermediate band characteristics. Additional ongoing calculations<sup>14</sup> show, as expected, that for lower Ti concentrations the width of this band decreases (and so does its separation from the conduction band) leading ultimately to a narrow level (i.e., with width below 0.25 eV for a 3% Ti dilution level) well separated from the conduction band, while the ferromagnetically ordered spin polarization observed for the higher Ti concentrations evolves into an independent spin behavior. These electronic structure features, which will be subject of a separate publication,<sup>14</sup> are however not the main concern of the

present work, and will not be dealt with here in detail; rather, the energetics of the compound formation is the addressed objective, and is reported in what follows.

#### A. Total energy calculations

From the total energy values computed for the Ti-substituted compounds and the pure binary ones a formation energy balance can be calculated, and yields the following values:



These data imply that all the ternary phases considered would be less stable than a mixture of the corresponding binary compounds; the energy difference is certainly much higher than the thermal energy under typical synthesis conditions (e.g.,  $kT=0.06$  eV at  $T=700$  K). Note also that the situation is less favorable for the phosphide than for the arsenide. It is worth noting here that, as exemplified by the arsenide case, this difference (per Ti atom inserted) is nearly the same for the two levels of Ti substitution examined (Ti:Ga=1:3 and 1:7); thus higher dilution is not expected to modify significantly the prediction in this respect. Also, preliminary calculations with larger cells show that locating two atoms in nearest-neighbor Ga sites (sharing one P or As bonded atom) or more separated ones (as in the above-mentioned cases) brings rather small energy differences (below 0.05 eV/Ti atom in the phosphide case) which are within the error margin expected for these methods. These results agree with the phase diagram data experimentally obtained for the Ti–Ga–As system,<sup>15</sup> which reports the formation of only binary compounds, without any clear indication of solid solution formation (at least in significant concentrations). In particular, TiAs was shown in that work to be rather stable, which would make difficult its integration into the GaAs structure.

One major reason for these positive values lies in the fact that Ti, particularly in the trivalent state of these compounds, strongly prefers octahedral (six-fold) to tetrahedral (four-fold) coordination. Indeed the hexagonal structure of TiP and TiAs (Fig. 1) is quite different from that of GaAs and GaP; in it Ti is coordinated to six P (or As) nearest neighbors, while in the proposed GaAs- or GaP-like structures a less favorable tetrahedral coordination is imposed to it. The importance of this factor can be assessed by comparing the total energy values calculated as noted earlier for the TiAs and TiP structures with those computed similarly for the same compounds in a hypothetical GaAs-type (zinc-blende) structure. According to these computations, in the geometrically fully relaxed state the formation of these phases would have the following phase change energy costs:

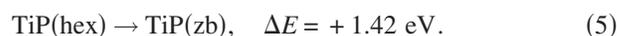


TABLE I. Distances (in Å) between M=(Ti/Ga) and X=(As/P) in MX and in TiGa<sub>3</sub>X<sub>4</sub> compounds.

$d(M-X)$ (Å)	X=P	X=As
Ti-X: hex	2.43/2.55	2.60
cub	2.405	2.485
compd	2.405	2.49
Ga-X: compd	2.355	2.50
cub	2.36	2.48

Thus most of the energy cost of Ti insertion in GaAs and GaP is due to the change of coordination. The fact that this cost is higher for the arsenide than for the phosphide may well be due to the higher size of the As atom, which besides providing a longer, weaker bond to Ti leads to a more important As-As repulsion when a larger number of atoms have to be crammed around Ti. This is reflected in an analysis of the interatomic distances in these compounds (Table I). As expected, the Ti-X distance is longer for Ti-As than for Ti-P already in the hypothetical cubic structure, but the difference increases in the real hexagonal structure; this latter increase can be ascribed to the mentioned higher As-As repulsion, which will partially counteract in the hexagonal phase the stabilization of the preferred six fold coordination of Ti. Apart from this, the data show that, when the X atom is small (the case of P) and thus does not condition so much, through mutual repulsion, the lattice dimensions, the (tetrahedral) Ti-X distance is higher than the Ga-X distance, showing that the Ti ion is larger than the Ga ion; this is probably an additional factor contributing to making unfavorable the substitution of Ga by Ti in these materials.

While these calculations would suggest that introducing Ti in these Ga-X lattices is not feasible, the fact is that, when a quite similar total energy calculation is carried out for Mn-substituted GaAs, the following balance is found:



Here MnAs is modeled in the hexagonal structure prevailing for this compound at typical synthesis temperatures (above 420 K).<sup>16</sup> Thus substitution of Ga by Mn would be predicted to be even less likely than by Ti, but the fact is that it has been experimentally verified that Mn can be introduced in GaAs substituting for Ga, even if only in small amounts (below 10%), and indeed Mn:GaAs, with ferromagnetic semimetallic character, is lately receiving huge attention due to its potential for spintronics.<sup>17</sup> Therefore one can assume, solely on these grounds, that preparing Ti-substituted GaAs (and GaP) should be at least as feasible.

## B. Vibrational properties

Phonon spectra for GaAs, GaP, TiGa<sub>3</sub>As<sub>4</sub>, and TiGa<sub>3</sub>P<sub>4</sub> using the DFT SIESTA code were computed and reported in a previous work,<sup>18</sup> where it was shown that very accurate results can be obtained with this method, at least for the semiconductors. Indeed the specific heats computed from these phonon data with the above-mentioned formulas<sup>12</sup> reproduce well the experimental data<sup>19</sup> for GaAs and GaP (Fig. 2).

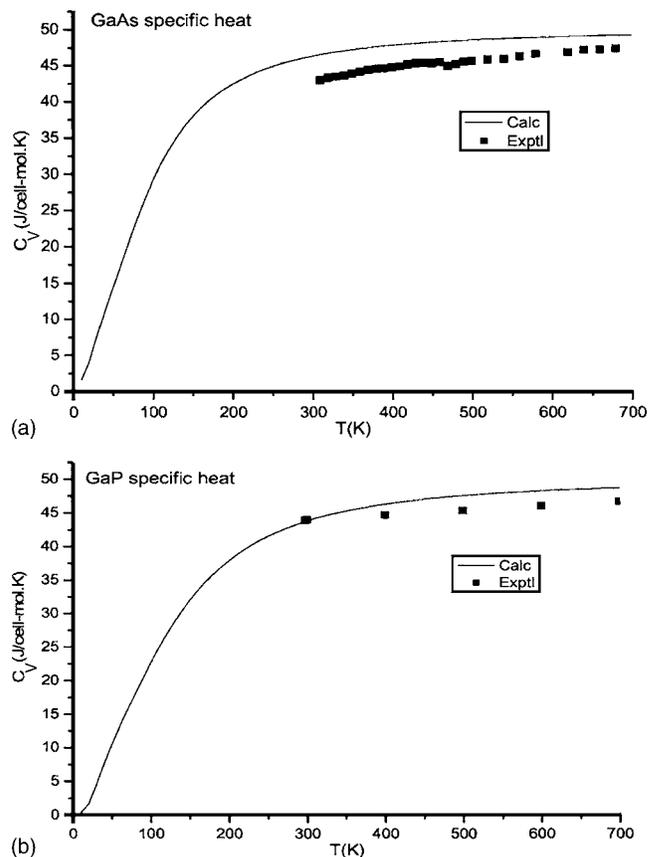


FIG. 2. Specific heats of GaP and GaAs computed from previously calculated phonon data (Ref. 18), compared to experimental results (Ref. 19).

Similar phonon calculations have been undertaken here also for the binary phases TiAs and TiP. A detailed report and analysis of the phonon dispersion curves will be given elsewhere;<sup>20</sup> here we present the phonon densities of states, which are seen to be appreciably different from those of the pure or Ti-substituted Ga-X materials (Fig. 3). This difference is again quite probably due to the different coordination and packing structure of pure TiP and TiAs (in comparison to the zinc-blende phases), and it may be presumed that there will be a noticeable influence on the vibrational contributions to free energy. These have been computed, and the variations in this magnitude predicted to occur upon formation of the TiGa<sub>3</sub>X<sub>4</sub> phases as outlined earlier are plotted as a function of temperature in Fig. 4.

These results indicate that in the ternary compound the vibrational effects contribute with a negative component to the formation free energy, making it less unfavorable particularly at the higher temperatures; but the magnitude of this effect is not large, and clearly does not suffice to compensate for the positive total energy balance presented earlier [Eqs. (1)–(3)].

## C. Dilution effects

The degree of dilution of the Ti substituent must also have an influence on the ease of mixed compound formation. For the total energy balance (as expressed per inserted Ti atom) this effect is considered to be weak, at least for Ti:Ga ratios below 1:3, judging from the nearly equal  $\Delta E$  values

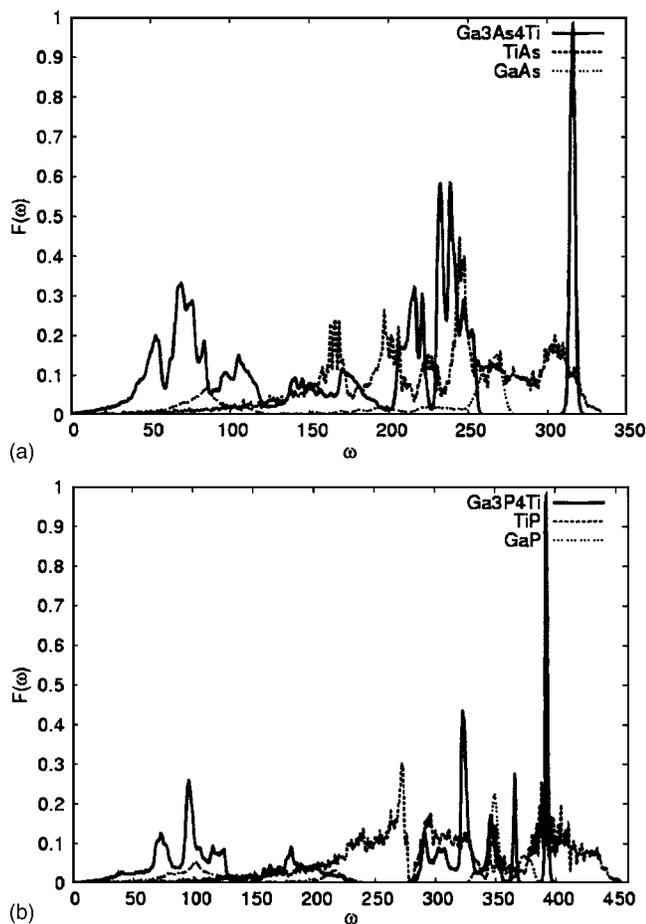


FIG. 3. Phonon density-of-states curves obtained for TiP and TiAs, compared to those obtained previously (Ref. 18) for the  $\text{GaX}$  and  $\text{TiGa}_3\text{X}_4$  phases.

computed, as shown earlier, for the  $\text{TiGa}_3\text{As}_4$  and  $\text{TiGa}_7\text{As}_8$  structures. The formation, in a disordered situation, of Ti pairs (i.e., the location of these atoms in nearest-neighbor Ga sites) might lead in principle to a change in this situation, but, as indicated by the preliminary calculations mentioned earlier, this is not particularly favored, and indeed is expected to occur only rarely in diluted systems, that are, according to the present study, the only ones likely to be achievable.

On the other hand, the possibility of disorder in the location of the partially substituting Ti atoms implies the existence of a net configurational entropy (mixing entropy). For the reasons mentioned in the preceding paragraph, modulation of this entropy term by configuration energy differences arising from interactions between substituent atoms (that could play a role for high substitution levels<sup>21</sup>) will be negligible; in these conditions, for a given Ti fraction  $x$  (in the Ga sites) this term is easily computed, leading to a contribution to the free energy of the compound that, expressed per Ti atom, amounts to

$$-T \cdot S = kT[x \ln(x) + (1-x)\ln(1-x)]/x. \quad (7)$$

A plot of this contribution as a function of temperature, computed for several values of  $x$ , is presented in Fig. 5. It can be seen that this may represent a significant quantity for low concentrations of Ti and high temperatures; but it is still

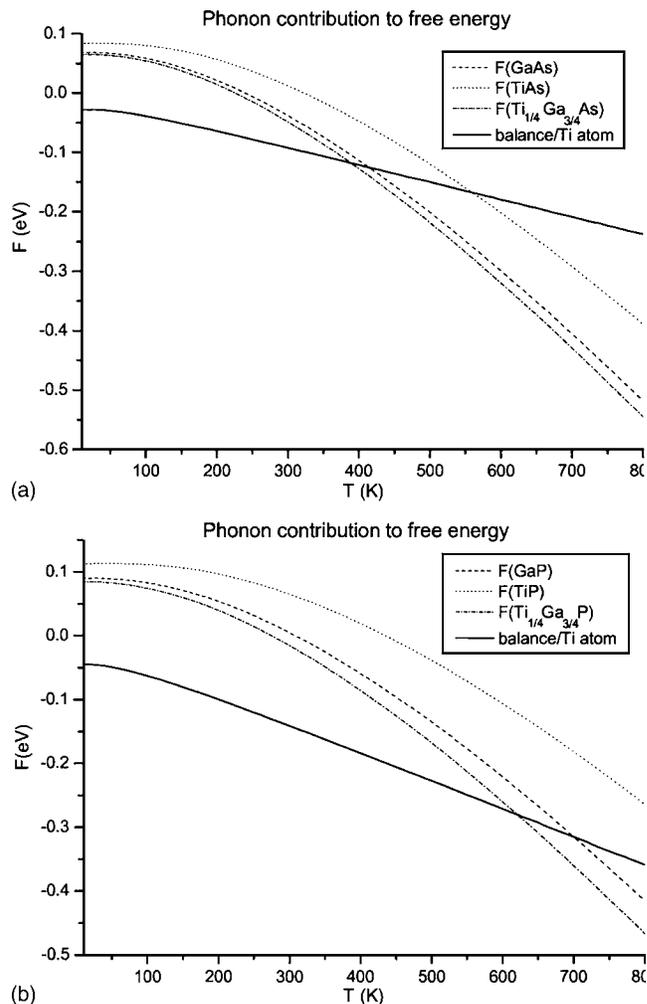


FIG. 4. Vibrational contributions to free energy for the individual phases and the balance of Ti insertion.

smaller than the total energy difference given in Eqs. (1)–(3). Even the sum of this disorder entropy-dependent component and of the vibrational component indicated earlier remains, at any practical temperature, with clearly lower magnitude than the computed total energy component.

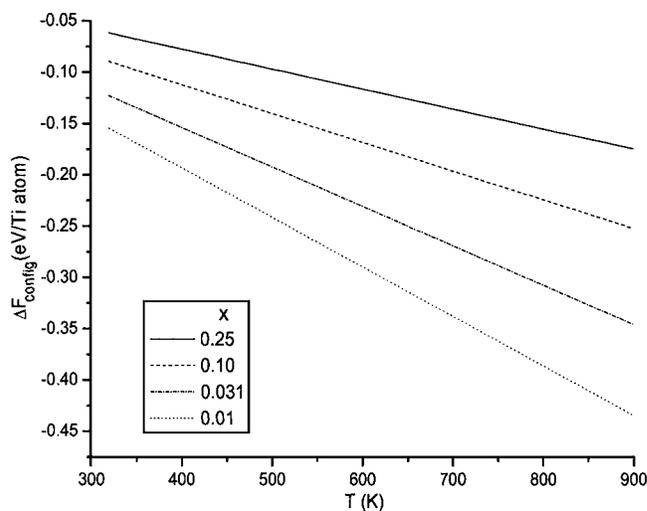


FIG. 5. Mixing entropy contribution to the free energy of insertion of Ti when forming  $\text{Ti}_x\text{Ga}_{1-x}\text{X}$ .

#### IV. CONCLUSIONS

The introduction of Ti in GaAs or GaP (substituting for Ga) is predicted to be energetically unfavored, a fact that is related to the coordination change involved and also, to some extent, to differences in atomic size; but it is not so to an extent higher than what is predicted for the introduction of Mn. Therefore, and taking into account that other works have shown the feasibility of introducing a few percent amount of Mn in GaAs before Mn clustering occurs (this clustering has been shown to be favorable in recent DFT studies<sup>22</sup>), one may expect that the preparation of Ti-substituted GaAs and GaP is possible, at least through methods similar to those used for Mn:GaAs.

Computation of phonon density of states in these systems allows one to estimate the contribution of these phonons to the free energy of formation of the compounds of interest. When added to the contribution of configurational entropy, the resulting term can compensate for a significant fraction (although not for all) of the total energy term which acts against compound formation. Thus the use of preparation methods which do not facilitate reaching thermal equilibrium, but which can lead to metastable states, can make possible the practical preparation of these materials (at least for relatively low Ti concentration), which may be useful for realizing the Intermediate Band Solar Cell concept.

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