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First-principles investigation of isolated band formation in half-metallic $Ti_xGa_{1-x}P$ ($x=0.3125-0.25$)

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Several alloy semiconductors containing a transition metal atom of the type MGa_4X_3 with $X=$As or P and $M=$Sc or Ti have been found previously to present an isolated partially filled intermediate band within the usual band gap of the host semiconductors and have been proposed as highly efficient photovoltaic materials. In this paper, we carry out an *ab initio* investigation of band structures and electronic properties for the more chemically stable $Ti_xGa_{1-x}P$ compound as a candidate for isolated intermediate band formation. We have calculated the electronic structures using self-consistent density functional theory method in both local density approximation and generalized gradient approximation (GGA) approaches and compared the GGA results with those obtained with the exact exchange method that we have implemented in the code SIESTA. Using spin-polarized localized wave functions to represent the valence electrons states and nonlocal pseudopotentials for the core electrons, we have also studied in detail the $Ti_xGa_{1-x}P$ compounds at different dilution levels of the Ti transition metal atom ($x=3.125\%,6.25\%,12.5\%,25.0\%$) and for two (cubic and tetragonal) different crystal cells. Results at the different dilutions show in all cases a fully spin-polarized structure and, except for the case of immediate Ti neighbors, indicate a rather small spin coupling between Ti atoms and confirm the presence of the isolated narrow partially filled intermediate band for this compound. They also show the higher suitability of isotropic crystal structures for obtaining in these materials the intermediate band with the desired small band width.

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I. INTRODUCTION

We have investigated recently using first-principles calculations novel candidate materials of photovoltaic interest resulting from the substitution of certain transition metal atoms in the P (or As) position of GaP (or GaAs). Band structures and electronic properties of diluted semiconductor compounds like Ga_4As_3Ti and Ga_4P_3Ti phases with zinc-blende structure have been studied in detail using an accurate *ab initio* code based on the density functional theory (DFT). The results obtained for those compounds present, in some cases, an isolated intermediate partially filled energy band located in the semiconductor band gap between a valencelike full band and a conductionlike empty band, showing both direct and indirect band gaps in their band diagrams.[1] The presence of this intermediate band allows these compounds to be proposed as highly efficient photovoltaic materials with the possibility of providing enhanced efficiencies due to both high and low energy photons absorption.[2] Using the intermediate band to enhance the use of sub-band gap energy photons, direct optical absorption probabilities of the proposed half-metallic materials have been also determined by means of quantum mechanic calculations of the transition matrix elements between the corresponding band states.[3] The calculations, using both the local density approximation (LDA) approach and the generalized gradient approximation (GGA) corrections for the exchange and correlation potential, were made with the SIESTA program.[4] However, the major LDA and GGA failure is associated with excitation energies because of the incomplete cancellation of the nonphysical self-interaction contained in the Coulomb energy and the potential. This effect is mainly manifested in an underestimation of the band-gap energies in semiconductors, and indeed, the *ab initio* calculations of band-gap properties for the GaAs and GaP semiconductors show several discrepancies with the experiments. To improve the results and correct the well-known band-gap problem, the exact exchange (EXX) method, that we have recently implemented in the SIESTA program, was applied to GaP and GaAs,[5] and more recently to the $TiGa_4P_3$ system in which the presence of a half-metallic intermediate band was confirmed in the non-spin-polarized case.[6]

On the other hand, the discovery of ferromagnetic behavior in diluted magnetic Mn III–V semiconductors makes this kind of material very promising for developing new kinds of devices with applications in spintronics.[7–12] In particular, semiconductors in which carriers are fully spin-polarized also offer the possibility of realizing spin-polarized solar cells. It would be, therefore, interesting to assess to which extent a similar situation can arise in the case of substitution with Ti.

In this paper, we present *ab initio* theoretical investigations, in both spin-polarized and non-spin-polarized approaches, of fully relaxed electronic band energy structures and parameters of the more chemically stable $TiGa_3P_4$ compound system, studied within the *ab initio* self-consistent DFT using the SIESTA program.[4] A study of the similar system $TiGa_3As_4$ has been presented elsewhere.[13] Now we address the system based on GaP since this semiconductor, having a larger band gap, may make it easier to obtain an isolated intermediate band. Furthermore the band gap of GaP is closer to the optimum for the intermediate band formation than that of GaAs.[2] At this point, it should be mentioned that a thermodynamics-based study on the feasibility of experimentally preparing Ti-doped GaAs and GaP, made by computing *ab initio* total energies with a DFT plane-wave code and estimating entropic contributions from disorder and lattice vibrations to the free energy of the system, has been carried out by us recently.[14] It was found in this work that insertion of Ti in these semiconductors is thermodynamically not very favorable, but that the situation in this respect is not worse than in the similar Mn-doped system, which has been, however, experimentally obtained; thus, these materials seem realizable.

In the present work, we use both the LDA and GGA approaches to determine the properties of these compounds and to understand the effect of spin-polarized wave functions on the calculated intermediate band properties. Because of the lack of experimental data for the $Ti_xGa_{1-x}P$ system, and in order to assess the results through a more accurate band-gap analysis, the EXX nonpolarized band energy results computed for the $x=25\%$ case are compared to those obtained using the exchange part of the nonpolarized GGA. As shown below, the results predict the formation of a partially filled intermediate band in these compounds when Ti atoms substitutes for Ga atoms once the spin polarization or some other methodological improvement as inclusion of EXX is taken into account.

Then, the effects of the Ti dilution level on the partially filled intermediate band formation and on both the width and the precise location of this intermediate band within the band gap of the host semiconductor have been investigated in the $Ti_xGa_{1-x}P$ system for a wide range of Ti atom dilution levels varying from 3.1% to 25%. The results show that an isolated intermediate band with an appreciable width is well formed in the 3–10% range dilution. Besides, the material exhibits full spin polarization of the Ti(3*d*) levels in the whole range of dilutions studied, although these $Ti_xGa_{1-x}P$ structures will probably not be magnetically ordered at practical temperatures except where the closest Ti-Ti configurations appear.

Finally, to investigate the effect of the lattice distortions in the characteristics of the intermediate band, we have carried out a comparative study of two different compounds with a tetragonal cell shape, using cell compositions $TiGa_7P_8$ and $Ti_2Ga_6P_8$ that correspond to Ti dilution levels of 12.5% and 25%, respectively.

II. MODELS AND COMPUTATIONAL DETAILS

A. Calculation methods

Band energy diagrams and total and atomic projected density of states calculations were carried out using the direct diagonalization method of the *ab initio* SIESTA code based in the formalism of the DFT. The SIESTA code makes all calculations by projecting electron wave functions and density onto a real space grid and using a numerical localized linear combination of finite-range atomic orbitals basis set.

The Kohn-Sham equations are solved self-consistently within either the LDA or (in most cases) the corrected GGA for the exchange and correlation potential, or the EXX for the exchange potential. Calculations have been carried out on either the spin-polarized or nonpolarized Kohn-Sham equations, employing for the exchange correlation potential, the local density Ceperley- Alder[15] form, as parametrized by Perdew and Zunger,[16] or the generalized gradient-corrected approximation of Perdew *et al.*[17] This method has been extensively tested for a great variety of semiconductor-type systems.[1] In spin-polarized calculations, the configuration used to start the self-consistent procedure had one unpaired electron in each Ti atom, and the electronic spin density was then allowed to evolve with eventual modification of the total spin if so dictated by the variational process. To solve the equation for the exact exchange potential in the EXX method, a modified version of the SIESTA code has been used (see Ref. 5 for details of method and implementation) in which a localized auxiliary basis set made up of a lineal combination of numerical Slater functions centered on the atomic positions and having the translational symmetry of the solid is used to represent the exchange density and the potential. The auxiliary basis set representation of the exchange density yields the correct long range $(1/r)$ behavior of the exchange potential.[6] In this calculation, a high number of auxiliary basis functions (88) have been used to represent the exchange density.

Norm-conserving pseudopotentials of Troullier and Martins[18] type, in the fully separable form of Kleinman and Bylander,[19] and with nonlinear core correction[20] have been used for representing core electrons in all atoms. In all the calculations, the reference valence configurations for the pseudopotentials used were $4s^2 4p^0 3d^2 4f^0$ for Ti, $4s^2 4p^1 3d^0$ for Ga and $3s^2 3p^3 3d^0$ for P. Pseudopotentials were generated from the neutral atoms, and optimization of all orbitals was performed and tested on a range of cutoff radii. For the comparison of the GGA and EXX exchange calculations, we have used pseudopotentials generated using the GGA and the EXX exchange, respectively, and the same correlation term has been used. A localized linear combination of finite-range pseudoatomic orbitals (basis set of the type of Sankey and Niklewski[21]) has been employed for the description of valence electrons. The basis set used to describe valence electrons was of double zeta plus polarization (DZP), quality (two *s* and six *p* orbitals for Ga and As and two *s* and ten *d* orbitals for Ti, adding five *d* orbitals more for Ga, and As and three *p* orbitals more for Ti to account for the polarization part), with different cutoff radii for the different type of orbitals of the basis set. The shift energy parameters ΔE_{PAO}, corresponding to the finite range of the pseudoatomic orbitals, were chosen to be less than 0.05 eV to ensure the energy convergence for both LDA and GGA exchange and correlation potentials and for the EXX exchange potential used. We tested also the convergence with respect to the basis set and *k*-point samplings in the calculations for all systems. For the above-mentioned real space grid, the mesh chosen corresponded in the unit cells used here to a cutoff energy of up to 200 Ry in the associated Fourier-transformed charge density. This relatively large mesh cutoff is needed to describe the localized *d* states of titanium.

B. Lattice structures

We have made calculations for an eight-atom simple cubic cell, where a single Ti atom replaces one atom of Ga in the cubic cell of GaAs; this corresponds to a dilution of 25% of the Ti atom in the Ga positions in the cell. The model is designed to have the smallest possible unit cell and be able to retain, if pertinent, the highest symmetry. Note, however, that the SIESTA code uses no symmetry, allowing thus any spontaneous distortion in geometry relaxations. Indeed in the models with cubic symmetry, we started in some cases with slightly atomic positions displaced from the ideal ones to facilitate such distortions in case these were favored.

To study the effect of dilution in the formation of the intermediate band, we have used two different supercells. The first one has cubic shape and 64 atoms in it ($2\times2\times2$ supercell of the basic GaP cubic cell); in it we have substituted different proportions of Ga atoms with Ti in order to vary the dilution level. The other one has a tetragonally shaped cell containing 16 atoms ($1\times1\times2$ supercell of the basic GaP cubic one). In these supercells, the minimum concentrations of titanium atoms, 3.12% and 12.5% of the Ga sites for the 64- and 16-atom cells, respectively, were studied. In addition, in the $2\times2\times2$ supercell, we also used a $Ti_2Ga_{30}P_{32}$ cell content (corresponding to a Ti atom dilution level of 6.25% in the Ga sites), with one Ti atom in (0,0,0) position and the second one in different positions: cell center $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, face center $(\frac{1}{2},\frac{1}{2},0)$, edge center $(\frac{1}{2},0,0)$, and also in the position closest to the first Ti atom (sharing with it through direct bond one P atom), i.e., $(\frac{1}{4},\frac{1}{4},0)$; these situations will be labeled CC, FC, EC, and CP, respectively. Similarly, in the mentioned tetragonal cell a $Ti_2Ga_6P_8$ cell content, corresponding to a Ti atom dilution level of 25%, was studied by placing Ti atoms in positions (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

For Brillouin cell sampling, we used a Monkhorst-Pack grid of $8\times8\times8$ k points in the simple eight atoms cubic unit cell, of $3\times3\times3$ k points in the 64 atom supercell and of $6\times6\times3$ for the 16 atom supercell structures.

To determine the equilibrium structure of the systems studied, all the atomic positions and the unit cell lattice dimensions were allowed to relax by minimization of the total energy until the largest force component was below 0.01 eV/Å and the stress was less than 0.1 GPa.

III. RESULTS AND DISCUSSION

A. Comparison of different approximations results for the cubic $TiGa_3P_4$ lattice

As a basic reference, we have made calculations, using both the LDA and the GGA exchange and correlation potentials, for the pure binary GaP semiconductor in the zinc-blende structure, with a DZP basis for the two atoms, and compared our results with available experimental data and with EXX results.[5] For GaP, the optimized lattice parameter constants obtained after dynamical relaxation with the LDA and GGA are 5.44 and 5.63 Å, respectively; these compare well to the experimental value[22] 5.45 Å. It is known that, in general, LDA overestimates the binding energy and GGA overestimates lattice constants. In these calculations, the LDA lattice constant agrees quite well with the experimental value, while the GGA lattice constant shows, as expected, a deviation from it, with a lattice expansion of 3.3% typical of this approximation. For the same calculations, the band-gap values obtained are 1.56 eV for LDA and 1.45 eV for GGA; both remain underestimated in comparison with the one calculated with the EXX method,[5] 2.62 eV, and, as expected, with the experimental value[20] 2.21 eV. Similar deviations between the calculated and real values of the band gap can be expected for the $Ti_xGa_{1-x}P$ systems described below, where gallium atoms in the supercell will be replaced by Ti.

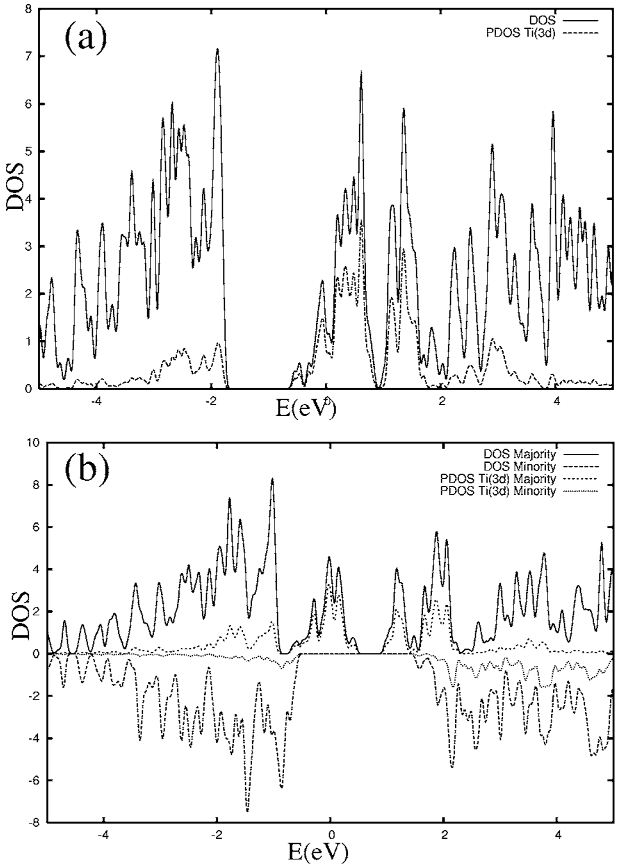

FIG. 1. $TiGa_3P_4$ total density of states (solid lines) and Ti d orbital-projected partial density of states (dotted lines), for (a) spin nonpolarized and (b) spin-polarized fully relaxed GGA calculations. Energies are measured in eV and Fermi levels have been set at the energy zero.

In Fig. 1, we present a comparison of the density of states (DOS) and the Ti projected density of states [(PDOS), computed as sum of individual projections on all Ti d orbitals] obtained for the $TiGa_3P_4$ compound, with fully relaxed geometry, in both nonpolarized and spin-polarized GGA-level calculations. In both cases, the intermediate band (IB) is mainly composed by d orbitals belonging to Ti atoms, as it is clearly shown in the Ti-projected DOS. Indeed the magnetic moment computed for the Ti atom is $1.000\mu_B$; the spin density is further delocalized on neighboring P atoms to a total extent of $-0.014\mu_B$, while the spin density in the Ga atoms amounts to $0.012\mu_B$.

For interpreting these results, one may recall that, as it is well known, in transition metals, the tetrahedral coordination implies a splitting of $3d$ valence levels so that the two-level manifold of e_g symmetry has lower energy that the three-level manifold of t_{2g} symmetry. Close inspection of the re-

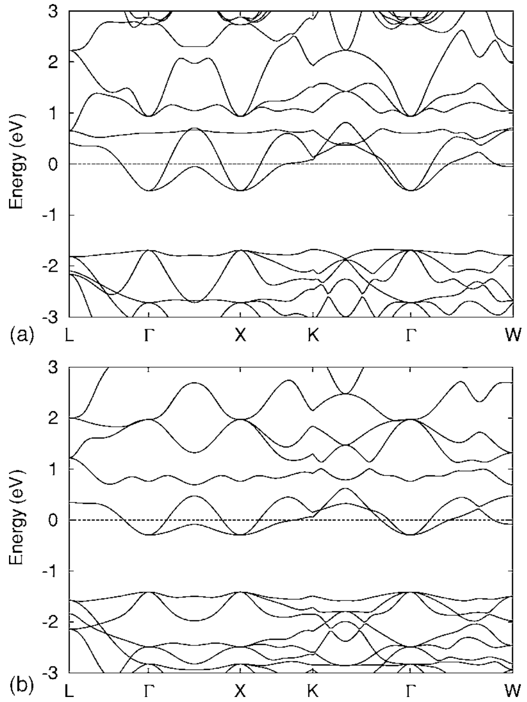

FIG. 2. Nonpolarized electronic band structure for $TiGa_3P_4$ calculated with GGA (a) and EXX (b) method displayed in the main directions of the Brillouin zone of the parent fcc structure. The horizontal line denotes the position of the Fermi level (E_F=0 eV).

sults shows that the levels forming the IB correspond to the e_g manifold, while those corresponding to the t_{2g} manifold appear overlapping the lower part of the empty conduction band; the Fermi level lies in both cases within the IB, which is partially filled and of metallic character. In the spin-unpolarized calculation, Fig. 1(a), the curve shows a broad band gap between the valence band (VB) and the IB, which overlaps the lower edge of the conduction band. However, the use of the spin-polarized Hamiltonian in the second case, Fig. 1(b), moves down the IB to a position closer to the VB, showing a clear second gap between the IB and the conduction band (CB). Moreover, this last calculation shows that the electrons in the half-filled intermediate band are all spin polarized as the majority spin. This last feature will be also apparent in all spin-polarized calculations made for this compound at different dilutions, presented in what follows. Furthermore, the total electronic energy found in the spin-polarized calculation is 0.83 eV lower than that of the spin-unpolarized one, showing that the polarization effect is a significant one.

To better assess the significance of these results, in Fig. 2 we compare, for the same $TiGa_3P_4$ system, two band energy diagrams obtained in nonpolarized calculations with no correlation included, made in one case using the exchange-only part of the GGA approach and in the other with the EXX method, using in the latter case 88 functions in the auxiliary basis representing the exact exchange term. Due to the high computational demand of the method, in this EXX calculation no geometry relaxation has been done; rather, the relaxed ionic positions and lattice parameters resulting from the GGA calculation were taken. In both cases, the Fermi level appears close to the middle of the intermediate band, occupied by a single electron. In the GGA case, Fig. 2(a), an empty Ti d band of t_{2g} character, forming the lower part of the conduction band overlaps the upper part of the intermediate band, mainly in the K-Γ direction. This is a situation similar to that found in Fig. 1(a). However, in the results obtained with the EXX method, Fig. 2(b), the intermediate band appears now well separated from both conduction and valence bands, and the band widths are smaller than those obtained the GGA case. This smaller bandwidth in the EXX case is mainly due to the absence, in this method, of the spurious residual self-interaction in the Coulomb potential, that is present in the GGA method; the elimination of this unphysical effect allows a greater degree of electron localization, leading to a reduced orbital overlap and a decrease in the bandwidth. On the other hand, it is expected, because of the approximation done in practice, that the empty t_{2g}-type manifold of Ti d levels, forming the band that appears in this calculation at 0.11 eV above the top of the intermediate band limiting the width of the second band gap, will really be located at much higher energy.

We now compare the results given by the GGA and LDA approaches in spin-polarized calculations carried out with full geometry relaxation for the $TiGa_3P_4$ compound. After total dynamical relaxation, the optimized lattice parameters of the cubic cell are 5.69 Å and 5.47 Å, respectively, showing small lattice expansions of 1.0% and 0.5%, respectively, in comparison to the values obtained for the corresponding host semiconductor with the same functionals (5.63 Å and 5.44 Å).

Then, the band diagrams of the majority and minority spin components obtained for the $TiGa_3P_4$ compound in these spin-polarized GGA and LDA calculations are compared in Fig. 3. In the second case, the (majority) spin-up channels [Fig. 3(a), left side] show that again the upper part of the e_g band, crossed by the Fermi level, is mixed in the K-Γ direction with an empty band due to the three-level manifold of Ti d states with t_{2g} symmetry forming the bottom of the conduction band. This mixing disappears when the spin-polarized GGA functional is used [Fig. 3(b)], the results presenting in this case a spin-polarized half-metallic intermediate band. This type of spin-polarized GGA calculation can be considered more realistic than the LDA-based one, and we will use it in the study of the effect of dilution presented in what follows.

B. Dilution effects

We present in Fig. 4, DOS and Ti-projected DOS data for all the 64-atom cell structures studied: the $TiGa_{31}P_{32}$ system and the four $Ti_2Ga_{30}P_{32}$ structures considered. In all cases, the calculation started with the d electrons in the Ti d shell ascribed to the majority spin, and this feature, even if it was left to evolve freely, did not change during the whole procedure of self-consistent-field (SCF) results and lattice geometry optimization. As shown in this figure, in all these more diluted cases, an intermediate band appears clearly isolated from the conduction and valence bands. In all of them except the last one, it contains two states per Ti atom (so that it can be ascribed to the e_g manifold in its d shell) and is partially

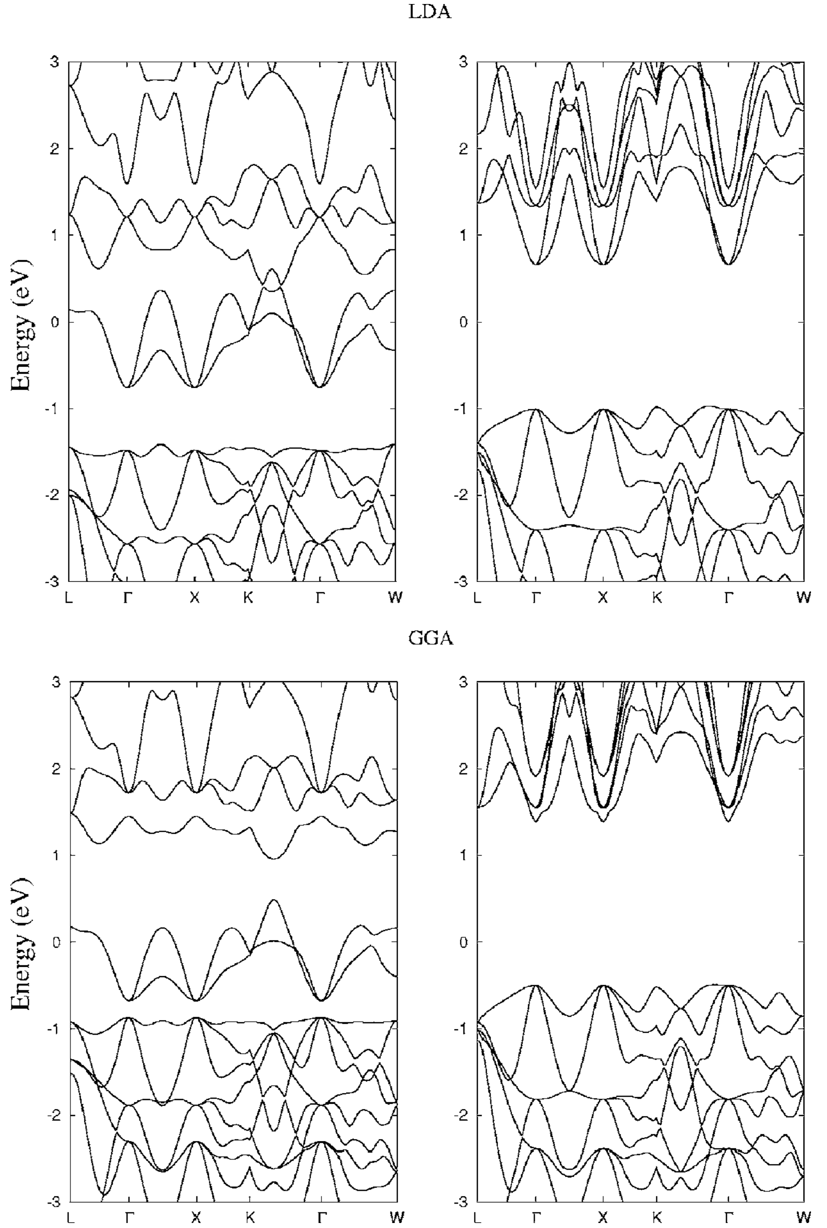

FIG. 3. Polarized band structure of 25% Ti atom dilution, as calculated with an eight-atom cubic cell using LDA (upper panel) and GGA (lower panel) represented in the corresponding fcc directions. In both cases, the majority spin is displayed on the left and the minority on the right sides. Fermi level is displayed by a horizontal line and set at the energy zero.

occupied as it is crossed by the Fermi level. In the last case, Fig. 4(e) (CP situation), the results indicate that the e_g manifold degeneracy is completely lifted (due probably to the strong distortion of the local Ti environment induced by the close Ti-Ti distance) and the IB, formed by one spin-polarized state per Ti atom, is fully occupied. For these systems, the magnetic moment on each Ti atom has been evaluated to be $1.000\mu_B$ in the CC case and the 3.12% dilution case, while in the CP case, it is $0.988\mu_B$. For the P atoms, which are nearest neighbors to Ti, the spin density amounts, in the CP case, to $-0.032\mu_B$ for the P atom shared by two Ti atoms and to around $-0.02\mu_B$ for the other six closest P atoms, while the CC case and the 3.12% dilution case the same value is obtained, $-0.018\mu_B$.

A relevant issue is whether the spins of the Ti-based electrons in these compounds have really a net tendency to be aligned in parallel form as suggested by the results in the preceding figure. To check this, additional calculations on the $Ti_2Ga_{30}P_{32}$ CC and CP structures were carried out in which the two unpaired electron spins were set to be oriented in an antiparallel way. For the CC case, the result had an energy nearly indistinguishable (the difference was <1 meV) from the parallel orientation result [that reflected in Fig. 4(b)], and its total DOS (sum of both spins) was also practically the same (results not shown), while the spin distribution found was opposite in the two Ti atoms but otherwise the same. This equivalence in energy means that in this situation, the spins of the different Ti atoms are unconnected from one another, and in the SCF procedure, it is nearly irrelevant to orient them initially parallel or antiparallel; they will thus experience no significant tendency to change it. This could be expected in view of the relatively large Ti-Ti distance, especially considering that the unpaired electron in the Ti($3d$) level, being of e_g-like symmetry, will concentrate its density mostly away from the Ti-P bond so that the phosphorus atoms will be scarcely polarized and will not be,

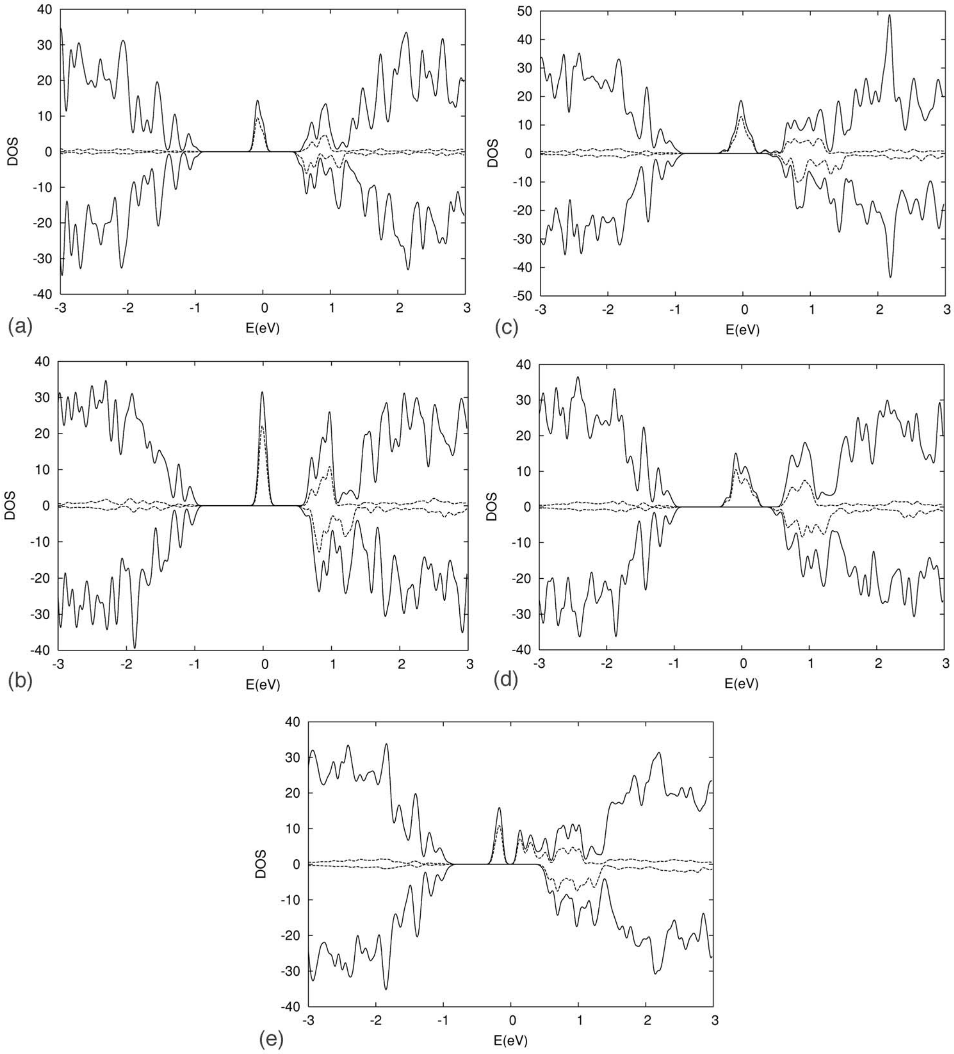

FIG. 4. Total density of states (solid lines) and Ti atoms *d* orbitals projected density (dashed lines) obtained for calculations on the 64-atom cell: (a) $TiGa_{31}P_{32}$,; (b), (c), (d), and (e) $Ti_2Ga_{30}P_{32}$ with Ti orderings of CC, FC, EC, and CP types, respectively.

therefore, an efficient intermediate for coupling the spins of the Ti atoms. This situation differs from the analogous Mn-substituted III-V compounds, where for a similar level of substitution, ferromagnetism is predicted by DFT calculations in agreement with experimental observation; the difference may be due to the stronger hybridization of Mn($3d$) electrons of the t_{2g}-type manifold, which are oriented closer to the Mn-(V element) bonds. In reality this means that this Ti-containing system will behave at finite temperatures as a paramagnet, with nearly equal populations of both spins being distributed at random in the solid.

In the CP case, on the contrary, the antiparallel spins case showed a total free energy higher than the parallel one by 135 meV. Thus the presence of a direct Ti-P-Ti link seems to produce a ferromagnetic coupling between the *d* electrons of the Ti atoms involved. In the single Ti-pair structure of this case, this would correspond to a ferromagnetic semiconductor, since zero electron density is predicted at the Fermi level, but for larger Ti clusters, a half-metallic ferromagnetic behavior might appear, with potential interest in spintronics; this phenomenon is however outside the scope of this work, which addresses the possibility of obtaining partially occupied IB structures (independent on their magnetic character) utilizable in advanced photovoltaic cells.

Clues on the possible occurrence of such clustering could be obtained comparing the energy values of the different $Ti_2Ga_{30}P_{32}$ structures obtained. The calculations made here yield free energies decreasing somewhat when the minimum Ti-Ti distance decreases, so that the (ferromagnetically ordered) CP case appears lower than the CC case by 0.20 eV. This would indicate that clustering is energetically favored. However, accurate assessment of this difference requires ensuring a high level of convergence in respect to the atomic function basis size; such study has not been made here. Rather, we take into account a similar calculation made in a related recent work[14] in which energetic evaluations using a high accuracy plane-wave DFT method have indicated, for a similar Ti-doped system, a negligible energy difference (below 5 meV) upon clustering in a 24-atom cell. Thus, the tendency to clustering would be very small. In any case, in diluted systems (the only ones likely to be thermodynamically accessible according to that same work) and under the high temperature conditions likely to be used in making this type of crystalline materials, the percentage of Ti ions involved in such pairs will be probably rather small, and thus these will be little relevant for determining the materials properties.

C. Effects of lattice anisotropy

The influence of lattice anisotropy on the IB is clearly shown in Figs. 5(a) and 5(b), presenting results obtained for the above-described tetragonal cells having contents $TiGa_7P_8$ and $Ti_2Ga_6P_8$, (corresponding, respectively, to Ti dilution levels of 12.5% and 25% substitution in Ga positions). The energy dispersion diagrams determined in these cases show in both systems a rather broad IB, having significant overlaps with other bands which avoid its isolation.

It is instructive to compare the two cases studied here having 25% Ti in Ga positions, i.e., those of Fig. 5(b), where the type of ordering established decreases the symmetry of the lattice below the cubic one, with the cubic situation reflected in Fig. 3: the situation reflected in Fig. 5(b) leads to a splitting of the Ti *d* levels of e_g-type symmetry and to a broadening of the intermediate band [see Fig. 5(b)]. These effects can probably be ascribed to the macroscopic distortions of the cell shape occurring in the tetragonal cell case, which amount to an elongation of the c/a ratio by a 2.3% and will consequently generate a lower local symmetry around the Ti atom. In the case of $TiGa_7P_8$, a lower broadening of the intermediate band [Fig. 5(a)] is produced, due probably to a lower degree of distortion of the tetragonal cell shape (a lower elongation of the c/a ratio, of $\sim 1.5\%$, is observed in this case) which will generate also a smaller decrease of the local symmetry around Ti atom. In real life, preparations of randomly Ti-substituted GaP or GaAs will never produce these same orderings; but thin film growth conditions might favor the appearance of a preferential direction in the structure which by leading to anisotropic lattice deformations could have undesirable level-broadening effects similar to those predicted here for tetragonal cell structures. These effects should, therefore, be monitored whenever the synthesis of these systems is attempted.

IV. SUMMARY

Previous spin-unpolarized DFT computations of this type of compound, using either of LDA or GGA, had shown that insertion of Ti in the P (or As) positions of GaP (or GaAs) can produce inside the band gaps of these semiconductors an additional band of the kind valid for implementing the intermediate band photovoltaic cell concept.[1] Here it is now shown that, if spin polarization and other methodological improvements are taken duly into account, one can predict the formation of an intermediate band also in the (chemically less unlikely) situation of having Ti in the Ga site. Although the computationally expensive exact exchange (EXX) approach would be needed to ensure high accuracy of the results (see Fig. 2), the examination of the differences typically appearing depending on whether such better method is used or not (in the first case narrower intermediate bands, broader gaps, and higher lying valence bands are predicted) allows us to assess the likely outcome of an accurate calculation from that of a less accurate one (without EXX).

Thus, cases in which standard LDA or GGA computations predict that the intermediate band would be located nearly contiguous to the conduction band of the host semiconductor, as is seen for example in Fig. 3, one can expect to have it located well inside the gap in an accurate evaluation.

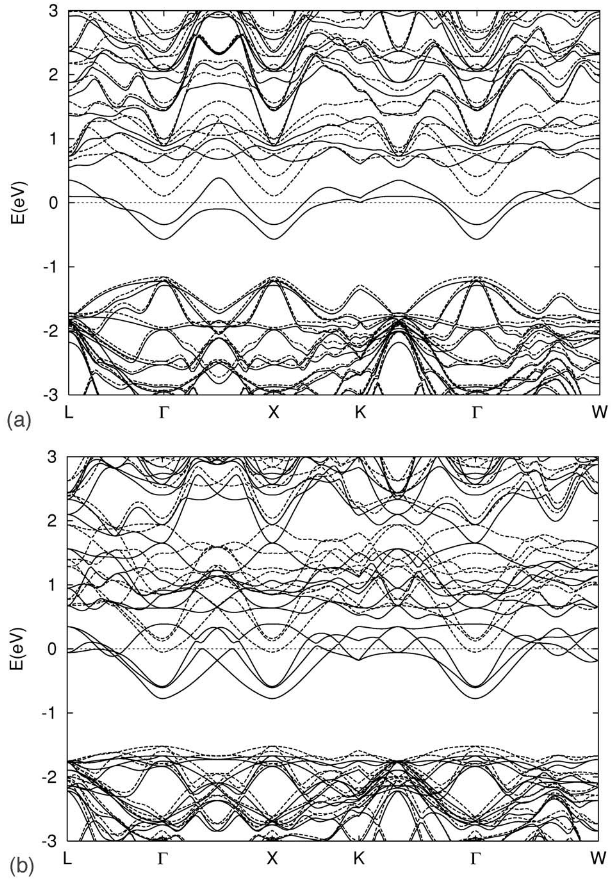

FIG. 5. GGA full relaxed spin polarized band diagrams of the majority (solid lines) and minority bands (dashed lines) obtained for (a) $TiGa_7P_8$ and (b) $Ti_2Ga_6P_8$ (16-atom tetragonal cells) displayed in directions corresponding to those of high symmetry in the Brillouin zone of the parent fcc structure. The horizontal line denotes the position of the Fermi level ($E_F = 0$ eV).

In any case, the study of dilution level effects shows that, while a 25% of Ga substitution by Ti might lead to appreciable overlap of the intermediate band with the valence (or conduction) one, lower levels in the 3–10% range can provide a well-formed intermediate band having appreciable dispersion (and thus the undesirable strong radiationless recombination typical of localized levels should not appear) but remaining well separated from the valence and conduction bands and with a width limited to an acceptable magnitude. Moreover, these last calculations show that the material exhibits spin polarization although the $Ti_xGa_{1-n}P_m$ structures do not show tendency to magnetic ordering except when two Ti atoms appear in the closest neighborhood (a situation that, being not particularly preferred according to previous calculations, is expected to be infrequent in diluted systems), so that paramagnetic behavior is mostly expected.

A significant observation is that, even within one same level of dilution (25% in this study), a Ti-substituent ordering which decreases significantly the isotropy of the material lattice can produce in it macroscopic distortions which, by facilitating a lower local symmetry around the Ti atom, lead to a splitting of levels and to a broadening of the intermediate band beyond the desirable limits. Future attempts to prepare these materials will need thus to take care so that the appearance of such anisotropy directions is not favored by the experimental procedure.

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