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First-principles electronic structure of rare-earth arsenides

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Abstract. The electronic properties of rare-earth arsenides have been calculated from first principles. In the calculations we have treated the rare-earth *f* electrons both as core-like and as valence-like electrons. We consider the changes in the energy bands and in the density of states near the Fermi level which are found to be relevant, except for the case of LuAs, and discuss this in relation with the role played from the rare-earth $5d$ derived states. Moreover we show that the rare-earth $5d$ related bands are particularly sensitive to the variation of the lattice constant; change in the lattice constant of less than 1% leads to a different behaviour with respect to the crossing of the rare-earth $5d$ derived bands and the As $4p$ derived bands along the Δ-direction. This point is discussed in connection with the possibility of having a semimetal-semiconductor transition in the rare-earth arsenides.

PACS. 71.20.-b Electron density of states and band structure of crystalline solids – 71.20.Eh Rare earth metals and alloys

1 Introduction

There is a growing interest in the study of the electronic properties of rare-earth pnictides (RE-V group compounds); this is due to the variety of their magnetic and electrical properties despite their common rocksalt structure [1]. Moreover in the case of rare-earth arsenide (REAs) materials, it has been demonstrated that they can be grown epitaxially on III-V semiconductors [2–6]. It is expected that these systems will play a role in the electronic and photonic technology as materials especially focused on electronics and photonics based on low dimensional metals and semimetals. One can envisage applications like metal base, hot-electron, or resonant tunneling transistors as well as like distributed Schottky diode array; buried ground plates and buried Schottky contacts could be improved by the successful development of these systems.

The REAs heterostructures have,also, interesting magnetic behaviour; ErAs is, for example, an antiferromagnetic semimetal, whose magnetism is induced by the nearly filled $4f$ shell [3]. Transport measurements [3] on relatively thick (200 Å) ErAs films buried in GaAs confirmed the prediction of Hasegawa and Yanase [7] of semimetallic conduction in this material. Finally it was argued that the quantum confinement could lead to a semimetal-semiconductor transition for very thin ErAs layers [4]. However, ErAs shows no semimetal-semiconductor transition when the layer thickness is reduced to 3 ML. This result was confirmed by our *ab initio* calculation of the electronic properties of ErAs/GaAs and YbAs/GaAs superlattices [8], where our main finding was that, on reducing the thickness of the REAs layer, indeed a gap opens up in the band structure of YbAs embedded in GaAs, albeit above the Fermi energy. The failure to produce a transition to semiconducting behaviour is most likely related to the complexities of the real band structure especially at the X point, and to the character of the interface between the rare-earth arsenide and the GaAs. Nevertheless, this result is very important from a technical point of view. Projected applications include transistor-like structure where electrons are injected through ultra thin semimetal films. If these films reverted to a semiconducting state, their potential impact in resonant tunneling hot-electron transistors would be lost.

From theoretical point of view, an interesting aspect of these compounds is the occurrence of localized strongly correlated $4f$ electrons for which the Local Density Approximation (LDA) in the Density Functional Theory (DFT) presents some failures. There were several attempts to improve the LDA in order to take into account strong electron-electron correlations. One of the most popular approaches is the self-interaction correction (SIC) method [9–11]. A different way to incorporate some correction effect in systems with localized *d* or *f* states was successfully done in the so-called LDA+U method [12]. In this case a simple mean-field Hubbard-like term is added to LDA functionals for the localized state.

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It should be noted, also, that the correct treatment of rare-earth 4*f* electrons in the calculations is still under discussion: should the 4*f* electrons be treated as core-like or as a part of the valence bands? Discussions on this controversy are provided in references [1,13]. These points (whether a localized or itinerant model of the *f* electrons is appropriate, and secondly whether or not the LDA provides an adequate description of these materials) affected studies on the band structure of the rare-earth-V compounds. It is interesting to note that recent studies based on the LDA+SIC method, where the *s*-*d* and *f* electrons are described on the same footing [10,11], have shown a third possibility, where part of the *f*-electron manifold is treated as itinerant and the other part as localised. In the case of YbAs the trivalent configuration has been found favorable over the divalent and the calculated equilibrium volume agrees well with the experimental one.

In the absence of available results on Er-V compounds, the first interpretations of the experimental investigations of ErAs were largely based directly on the Hasegawa and Yanase work on the Gd-V compounds [7] and on the subsequent tight-binding calculations by Xia *et al.* [14]. This was obviously not completely satisfactory. While one expects a qualitative similarity between the band structures of Gd and Er compounds, there must be quantitative differences. Recently Petukhov *et al.* have calculated the electronic structures of ErAs and $\mathrm{Er}_x\mathrm{Sc}_{1-x}\mathrm{As}$ [15] and of rare-earth pnictides [1]. In this last paper they present results of the electronic band structures and magnetic moments for several rare-earth pnictides, including GdAs and ErAs, where the 4*f* states were treated as core states. The optimum valency for Er is found to be Er^{3+} ($4f^{\,11}$). Since Er atoms have 12 *f* electrons, this can be obtained by the promotion of a 4*f* electron to a 5*d* one; thus the atomic configuration of Er atoms in the calculations is $4f^{\,11}5d^{\,1}6s^{\,2}$, which is similar to that of Gd atoms ($4f^{\,7}5d^{\,1}6s^{\,2}$). As it comes out from the ErAs calculations in the Er^{3+} configuration, the Er 5*d* bands are hybridized with the As 4*p* derived bands; as consequence one Er 5*d* band (the Δ'_2 band) dips below the As 4*p* derived band (the Δ_5 band) at X, crossing it near X, below the Fermi energy. As a result the X_3 point, that belongs to the Δ'_2 line, lies in energy below the double degenerate X_5 point ending the Δ_5 line. This is one of the main reasons for the semimetallic character of ErAs. It is worthwhile to note that in references [1,15] the calculations have been performed for the theoretical equilibrium lattice constants, determined through total energy minimisation. Earlier, Takegahara and Kaneta calculated the electronic band structure for Lu compounds [16] and YbAs and $\mathrm{Yb}_4\mathrm{As}_3$ [17], showing similar results.

In this paper, we present band structure and density of states studies of a series of monoarsenides compounds. We consider YAs, ErAs, TmAs, YbAs and LuAs. The reasons for studying this range of monoarsenides are that they show a large variety of situations with respect to the *f* electrons occupancy. Y atom has no *f* electrons but shows a similar atomic configuration to the RE atoms in monoarsenides with respect to the *d* occupancy, only when the rare-earth *f* electrons are treated as core-like; Tm and Er atoms have a nearly full 4*f* shell, 12 and 13 *f* electrons respectively, whereas Yb and Lu atoms possess a full 4*f* shell (with Lu having also a 5*d* electron). This large range will permit us to study the trends within the group of the RE elements. The case of CeAs has been not considered due to the fact that Svane *et al.* [18] have shown that in this case the ground state has 1 *f* state occupied. By taking the *f* electron in the core, the situation will be very similar to that of YAs which is present in our calculations. To our knowledge, these presented here are the first calculations in the case of YAs and TmAs.

The paper is organized as follow: Section 2 describes the computational method, Section 3 is related to the results of the band structure of ErAs, in particular with respect to their dependence on the lattice constant, in Section 4 the results for the density of states and energy band structure for all the considered monoarsenides are present and discussed, also in connection with the treatment of the *f* electrons; and finally Section 5 is devoted to the conclusions.

2 Electronic properties: the method

We have used the Density Functional Theory (DFT) [19] in the local spin density approximation (LSDA), where exchange and correlation were treated in the formulation of von Barth and Hedin [20]. The scalar relativistic linear muffin-tin orbital (LMTO) method [21] is used in the atomic sphere approximation (ASA) including the combined correction term. Empty spheres [22] were introduced in order to have closed-packed lattices. In the calculations we use, in the case of ErAs, both the experimental lattice parameter [23] and the equilibrium lattice parameter determined by total energy calculation [1,15], whereas for the other compounds we use only the experimental lattice parameter [23]. The unit cell contains 4 atoms: 1 As, 1 RE atom and two empty spheres. The radii of the atomic and empty muffin-tin spheres were all chosen to be equal. The choice of equal spheres is a natural one making the underlying sphere packing the same as in the bcc structure for which the ASA is known to be accurate; moreover this choice has been tested for a variety of cases, see for example reference [24], where LMTO calculations for 34 elemental and compound semiconductors are reported. Table 1 collects the lattice parameter and the atomic-sphere radii used in the calculations.

In the LMTO self-consistent computations we used two separate energy panels; the lowest energy panel covers the region of the RE 5*p* states, whereas the second panel contains the rest of the states. The treatment of the RE 5*p* states as valence-like band electrons is necessary because treating the RE 5*p* states as (renormalized) frozen-core states leads to non-negligible renormalization effects. These effects can be made negliglible with a different choice of atomic-sphere radii for the 4 spheres in the calculation, but these radii would be so different that errors due to spurious overlaps could not be excluded.

Table 1. Lattice parameter a and radii S of the atomic spheres used in the calculations. In all cases the lattice parameter is the experimental one, except for ErAs, where we perform calculations for both the experimentally and theoretically determined lattice parameters (see text). Also the different atomic configurations used, concerning the treatment of the f electrons as core-like or valence-like electrons, are given. For YAs, which do not possess f electrons, only one configuration has been used.

	YAs	ErAs	TmAs	YbAs	LuAs
a (Å)	5.786	5.743 (5.700)	5.711	5.698	5.680
S (a.u.)	2.692	2.672 (2.652)	2.657	2.651	2.645
(a) f core	$4p^6 4d^1 5s^2$	$4f^{11}{:}5p^6 5\mathrm{d}^1 6s^2$	$4f^{12}{:}5p^6 5d^1 6s^2$	$4f^{13}{:}5p^6 5d^1 6s^2$	$4f^{14}{:}5p^6 5d^1 6s^2$
(b) f valence	$4p^6 4\mathrm{d}^1 5s^2$	$4f^{12} 5p^6 6s^2$	$4f^{13} 5p^6 6s^2$	$4f^{14} 3p^6 6s^2$	$4f^{14} 5p^6 5d^1 6s^2$

As already pointed out in the introduction, the $4f$ electrons can be treated as part of the "pseudo" core or as part of the valence electrons. We have performed band structure and density of states calculations considering both possibilities; this help us in the determination of how the f electrons affect the band states: through the crystal potential due to its Coulomb and exchange interaction (f pseudocore), or through direct hybridization (f valence). The atomic configurations used in our calculations for both cases are, also, collected in Table 1. It is important to note that the use of the $5d$ electron in the calculations, promoting a RE f electron to a d one and treating the f electrons as partially filled core, results in a push-up of the remaining unoccupied f electron levels well above the Fermi level, thus mimicking the LDA+U approach.

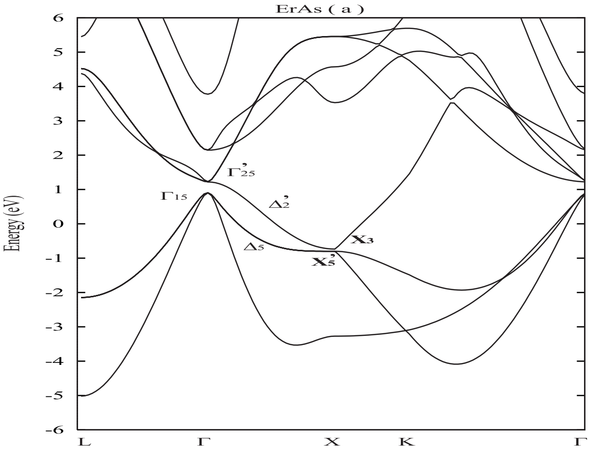

Fig. 1. Selfconsistent energy band structure of ErAs. The Er f electrons have been treated as core-like and the experimental lattice parameter $a = 5.743$ Å has been used in the calculation. The zero energy is related to the Fermi energy.

3 The energy bands of erbium arsenide: the role of the lattice parameter

In this section we will discuss our results for the energy band structure of ErAs; this is the mostly investigated compound within the REAs and its behaviour is characteristic of the entire group. In order to compare our results with previous calculations [1,15], we will limit us here to the case where the RE f electrons are treated as core-like. Thus the atomic configuration of Er is $4f^{11}{:}5p^{6}5d^{1}6s^{2}$, which means that the f electrons are treated as core electrons and that 1 f electron has been promoted to a d one in order to have a trivalent valence configuration.

Figure 1 shows our results for the energy band structure of ErAs related to the case where the experimental lattice parameter ($a = 5.743$ Å) [22] has been used in the calculation (ErAs(a)). We see that the compound is semimetallic in agreement with the previous calculations [1,15]. We note that the Fermi level is well below the Γ_{15} point (located 0.90 eV above the Fermi level), that is derived from the As $4p$ states. Even at Γ we found that the Γ'_{25} point, which originates from the Er $5d$ states, is separated, with respect to the Γ_{15} point, by an energy difference of 0.33 eV.

Particularly important is the energy bands behaviour in the Γ-X direction; here we note around the Fermi level two different lines, which play an important role in the semimetallic character of the rare-earth arsenides. The first line (the Δ_5 line that accomodates two electrons and originates from the As $4p$ electrons) starts from the Γ_{15} point and, after the cross of the Fermi level, reaches X at the double degenerate X'$_5$ point (located at -0.81 eV with respect to the Fermi level); the second line (the Δ'_2 line) is due to the Er $5d$ electrons, this line starts from the Γ'_{25} point, crosses the Fermi level near X and reaches at X the X$_3$ point (at -0.73, below the Fermi energy). Differently from the results of Pethukov *et al.* [1,15] our energy band structure do not show the crossing between the two Δ lines; a small energy difference is still present between the two lines. In order to investigate this discrepancy we have performed a second calculation for ErAs (ErAs(t)) taking as lattice parameter the theoretically estimated lattice parameter of Pethukov *et al.* [1,15]: $a = 5.700$ Å .

Figure 2 shows our results for this case.

We see now that the Δ'_2 line dips rapidly in the Γ-X direction and crosses the Δ_5 line shortly before X. Therefore the double degenerate X'$_5$ point is now located in energy above the X$_3$ point, in agreement with the Pethukov calculations [1,14]. Table 2 collects our results for these selected symmetry points at Γ and X for the two ErAs(a) and ErAs(t) different calculations. From Table 2 and Figures 1 and 2 we see that are in particular the Δ'_2 line and consequently the X$_3$ point which are affected by the change in the lattice parameter.

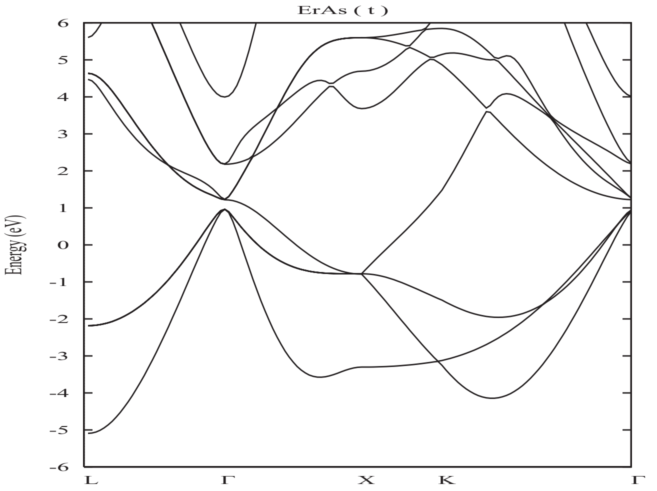

Fig. 2. Selfconsistent energy band structure of ErAs. The Er *f* electrons have been treated as core-like and the theoretical lattice parameter a= 5.700 Å has been used in the calculation. The zero energy is related to the Fermi energy.

Table 2. Selected energy states (in eV, with respect to the Fermi energy) at Γ and X points in the band structures of ErAs for calculations related to the experimentally (a) and theoretically (t) determined lattice parameter a, indicated in the table.

	ErAs(a) (a = 5.743 Å)	ErAs(t) (a= 5.700 Å)
Γ_{15}	0.90	0.96
Γ'_{25}	1.23	1.22
X_3	−0.73	−0.80
X'_5	−0.81	−0.78

It is worthwhile to note that the two calculations differ only by less than 1% in the used lattice parameter, this means that the Er 5d derived bands are particularly sensitive to changes in the pressure or to the presence of strain. We do not try to find the energy minimum in our calculations, which is beyond the realm of this work; the key point here is that the presence of pressure or strain, which produces variation in the lattice parameter and/or in the nearest neighbour distances, can originate an energy difference between the Δ'_2 and Δ_5 lines or alternatively their crossing. This result is important with respect to the possibility of producing a semimetal-semiconductor transition in REAs epitaxially grown on semiconductors. Usually the adsorbate (here the REAs) takes, at the first stage of growth, the lattice constant of the underlying substrate (the semiconductor); thus in principle it is possible to resolve the crossing of the Δ lines with appropriate conditions. Hovewer to produce a semimetal-semiconductor transition one needs not only to resolve the crossing of the Δ lines, but also to really open an energy gap (for example by rising up in energy the X points); a short discussion on this point has been presented in reference [8].

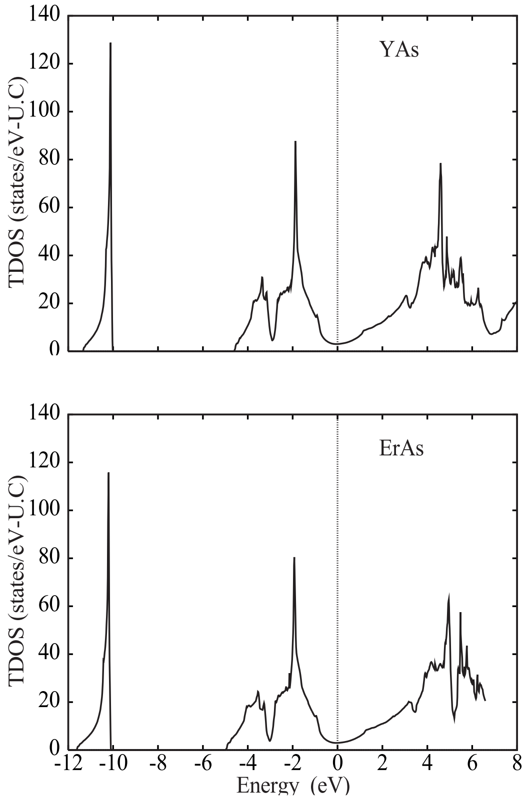

Fig. 3. Total density of states (TDOS) for YAs and ErAs. The RE *f* electrons are treated as core-like in the calculations. The zero energy is related to the Fermi energy.

4 Density of states and energy bands

4.1 *f* electrons treated as core-like electrons

Here we present our results for the density of states and the energy band structure of all the considered compounds; as pointed out before, in the calculations we have used the experimental lattice parameters collected in Table 1. Regarding the RE *f* electrons, we will show here the results obtained considering the *f* electrons as core-like. Thus a 4f electron has been promoted (as in the case of ErAs) to a 5d electrons, except for the case of LuAs; the atomic configurations used are collected in Table 1.

Figure 3 and Figure 4 show our calculated total density of states (TDOS) for YAs and ErAs and for TmAs, YbAs and LuAs respectively. All the compounds are found semimetallic in agreement with previous calculations [1,7,15–17]. The TDOS shows overall similar features. The spectra are composed mainly from three groups of states; at around 10 eV below the Fermi level we found the s-like states of As; just below the Fermi energy the As 4p derived states are predominant and show remarkable hybridization with the RE 5d derived states, originating the semimetallic character of the compounds. Finally the RE 5d derived states form the most important contribution to the empty states.

These characteristics are clearly shown in Figures 5 and 6, which display the partial density of states (PDOS)

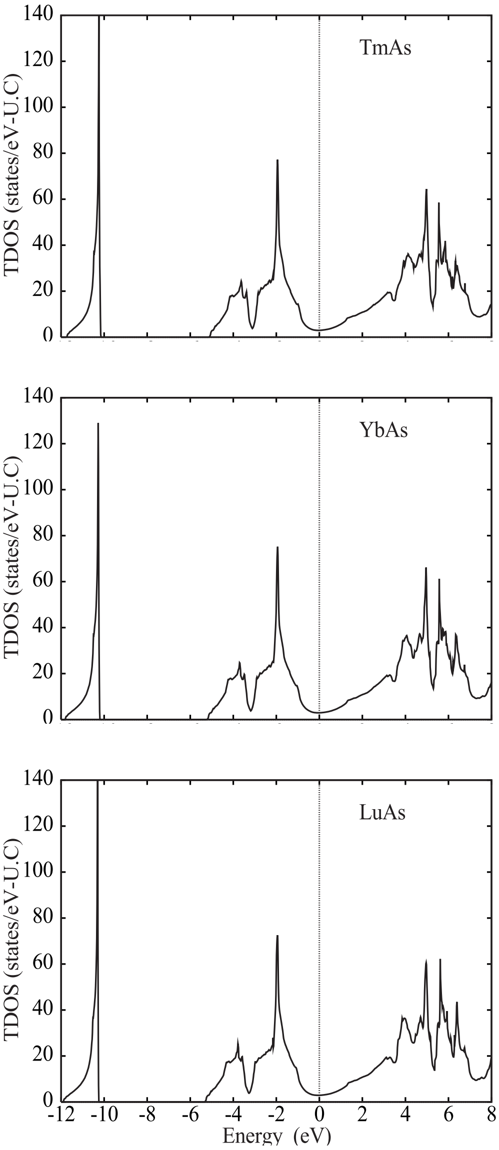

Fig. 4. Total density of states (TDOS) for TmAs, YbAs and LuAs. The RE *f* electrons are treated as core-like in the calculations. The zero energy is related to the Fermi energy.

projected on the different components of the two atoms present in the calculations, in this case *s, p, d* for both RE and As atoms (we show here the case of TmAs as an example, the results for the other compounds are very similar).

If we consider the energy band structures, these are shown in Figures 7 and 8. Also here the similarity between the different compounds is quite evident. Table 3 contains the energy values of selected *k*-points in the band structures. We note that, on going from Y to Lu, the energy separation between the Γ'_{25} and Γ_{15} points increases; the same happens for the separation between X_3 and X'_5. This trend is exactly opposed to that of the lattice parameter, that decreases on going from Y to Lu. As in the previously discussed case of ErAs, for all the compounds the

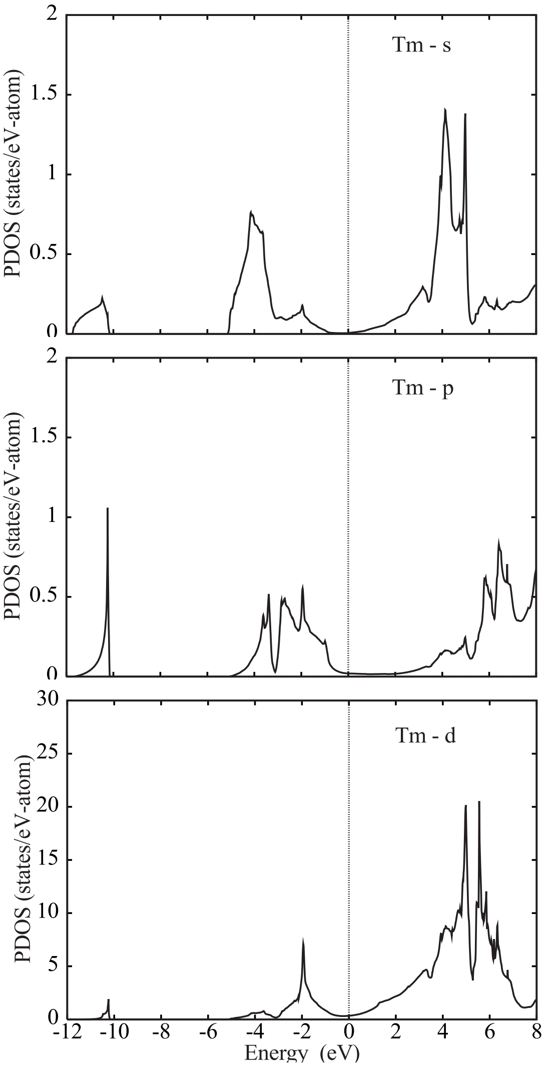

Fig. 5. Partial density of states (PDOS) projected on the different components of the Tm atom in the TmAs compound. The Tm *f* electrons are treated as core-like in the calculations. The zero energy is related to the Fermi energy.

Table 3. Selected energy states (in eV, with respect to the Fermi energy) at Γ and X points in the band structures of the monoarsenides. The upper panel is devoted to the calculations, where the *f* electrons are treated as core-like, the lower is related to the *f* valence-like calculations.

	YtAs	ErAs(a)	TmAs(a)	YbAs(a)	LuAs(a)
Γ_{15}	0.89	0.90	0.92	0.91	0.90
Γ'_{25}	1.12	1.23	1.26	1.28	1.32
X_3	−0.71	−0.73	−0.74	−0.72	−0.71
X'_5	−0.77	−0.81	−0.85	−0.90	−0.96
		ErAs(b)	TmAs(b)	YbAs(b)	LuAs(b)
Γ_{15}		1.73	1.74	1.75	0.79
Γ'_{25}		2.71	2.76	2.86	1.35
X_3		0.53	0.53	0.65	−0.65
X'_5		0.58	0.52	0.38	−0.94

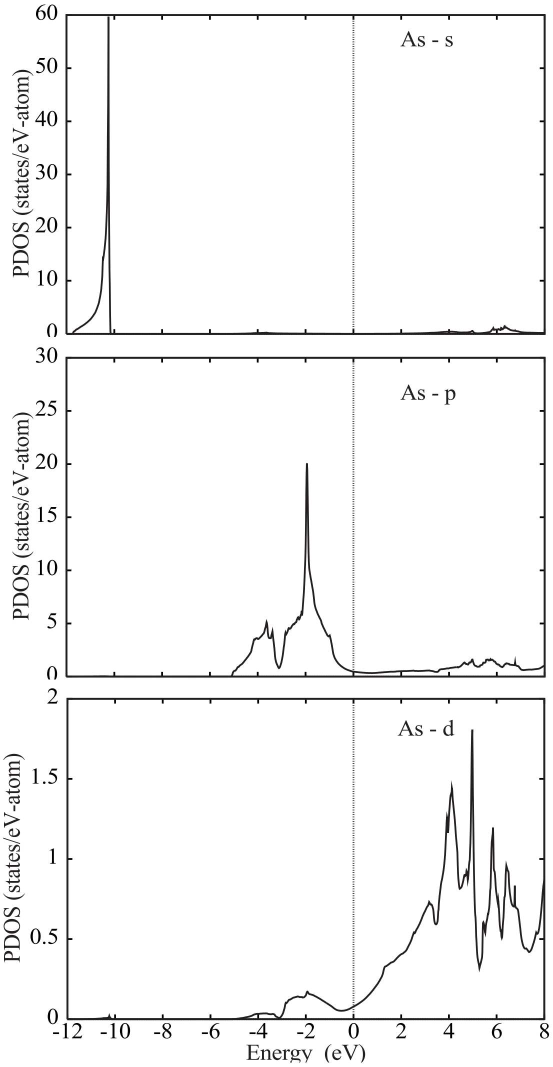

Fig. 6. Partial density of states (PDOS) projected on the different components of the As atom in the TmAs compound. The Tm *f* electrons are treated as core-like in the calculations. The zero energy is related to the Fermi energy.

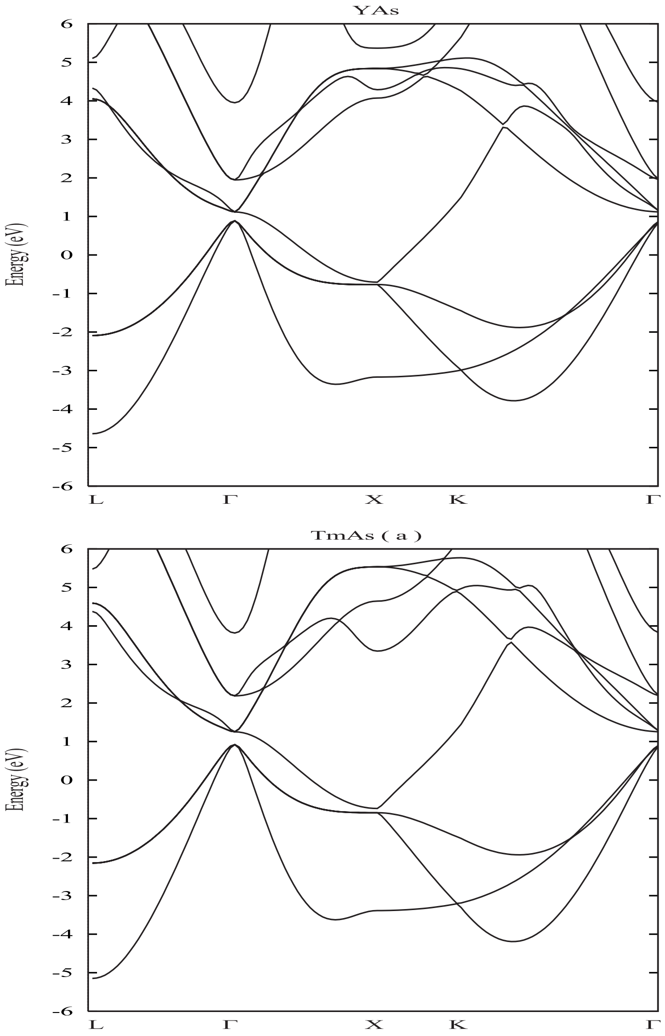

Fig. 7. Selfconsistent energy band structure of YAs and TmAs. The RE *f* electrons have been included as core-like in the calculations. The zero energy is related to the Fermi energy.

calculations at the experimental lattice parameter show no crossing of the Δ'_2 and Δ_5 lines. The result for YAs is thus in agreement with the outcome for ScAs (the two compounds are very similar differing only for the principal number of the valence *p,d,s* states) [15].

4.2 *f* electrons treated as valence-like electrons

The second possibility in the calculation of the electronic properties of REAs is the inclusion of the *f* electron in the valence. Thus we have performed total density of states, partial density of states and energy band structure calculations of ErAs, TmAs, YbAs and LuAs treating the RE *f* electrons as valence-like electrons.

We first discuss the case of LuAs; in this compound the inclusion of the *f* electrons in the valence do not imply a modification regarding the RE 5*d* presence in the atomic configuration (see Tab. 1), therefore we will expect minor changes in this case with respect to the previous one. Figure 9 shows the band structure of LuAs with the *f* electrons included as band electrons (LuAs(b)) and Table 3 collects some important band energy values. First of all we note the presence of the Lu *f* derived states at about −5 eV below the Fermi energy, moreover we see that the inclusion of the *f* electrons in the valence do not change very much the behaviour of the other bands; the energy lines and points in the band structure of Figure 9 (except for the *f* derived bands) are practically the same of the corresponding result in Figure 8 (see also Tab. 3). This result is in agreement with the LuAs density of states calculation of Takegahara [17] and with the band structure calculation of Pethukov et *al.* [1] for the similar case of GdAs, also Gd (like Lu) possesses a 5*d* electron.

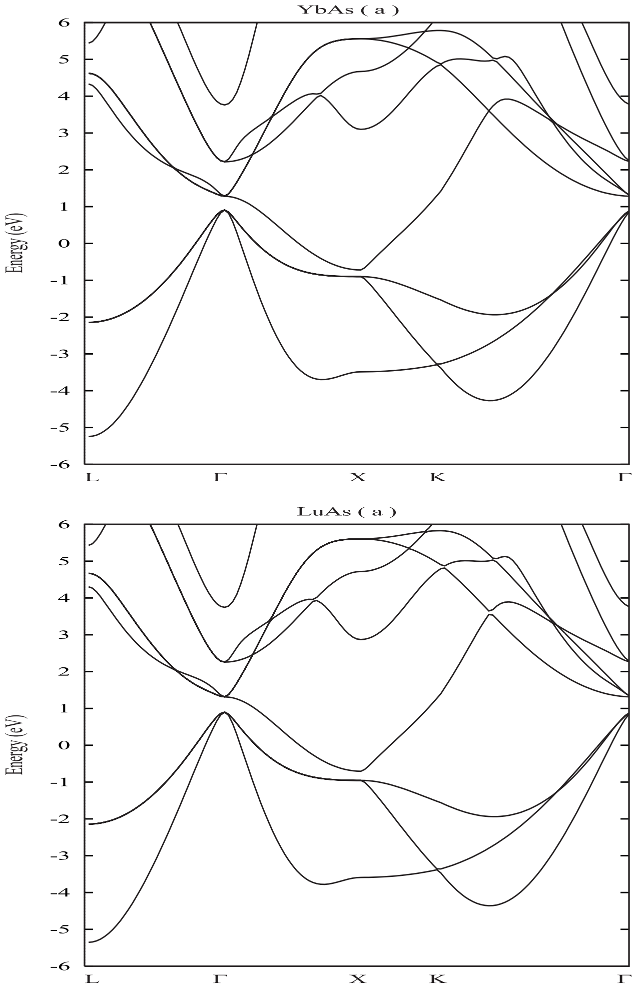

Fig. 8. Selfconsistent energy band structure of YbAs and LuAs. The RE *f* electrons have been included as core-like in the calculations. The zero energy is related to the Fermi energy.

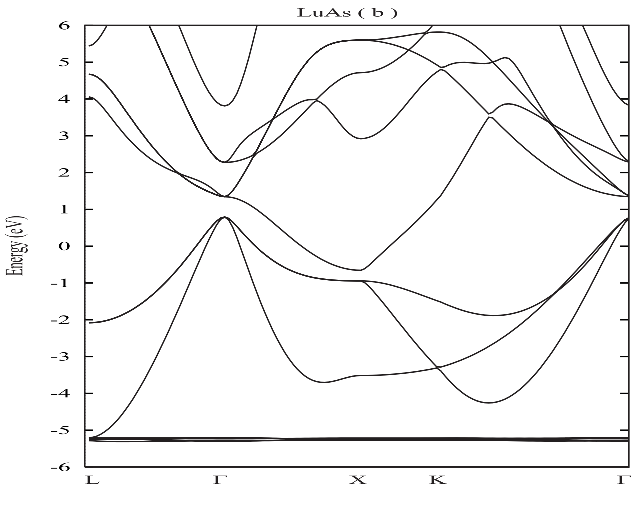

Fig. 9. Selfconsistent energy band structure of LuAs. The Lu *f* electrons have been included as valence-like in the calculation. The zero energy is related to the Fermi energy.

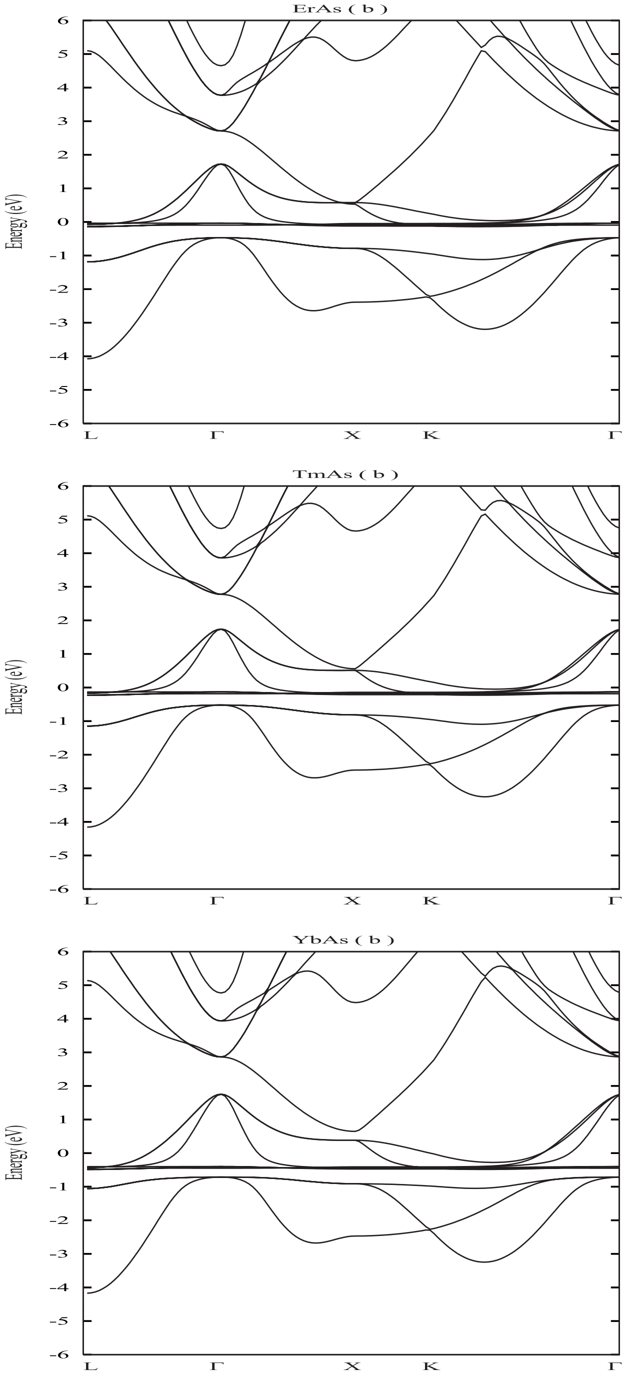

Fig. 10. Selfconsistent energy band structure of ErAs, TmAs and YbAs. The RE *f* electrons have been included as valence-like in the calculations. The zero energy is related to the Fermi energy.

The situation is completely different for the other considered REAs (ErAs, TmAs and YbAs). The band structure for these compounds, calculated including the *f* electrons as valence-like, are shown in Figure 10. The presence of the RE 4*f* derived bands changes strongly the band structure, in particular in the vicinity of the Fermi level. The *f* derived bands are, in all the three considered cases,

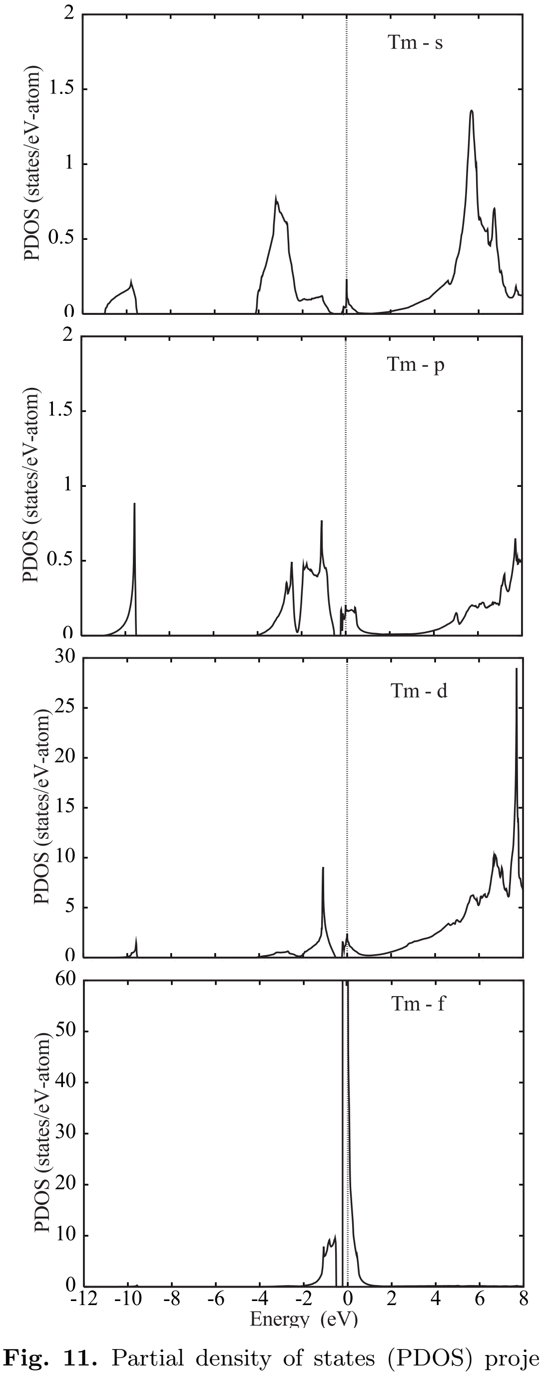

Fig. 11. Partial density of states (PDOS) projected on the different components of the Tm atom in the TmAs compound. The Tm *f* electrons have been included as valence-like in the calculation. The zero energy is related to the Fermi energy.

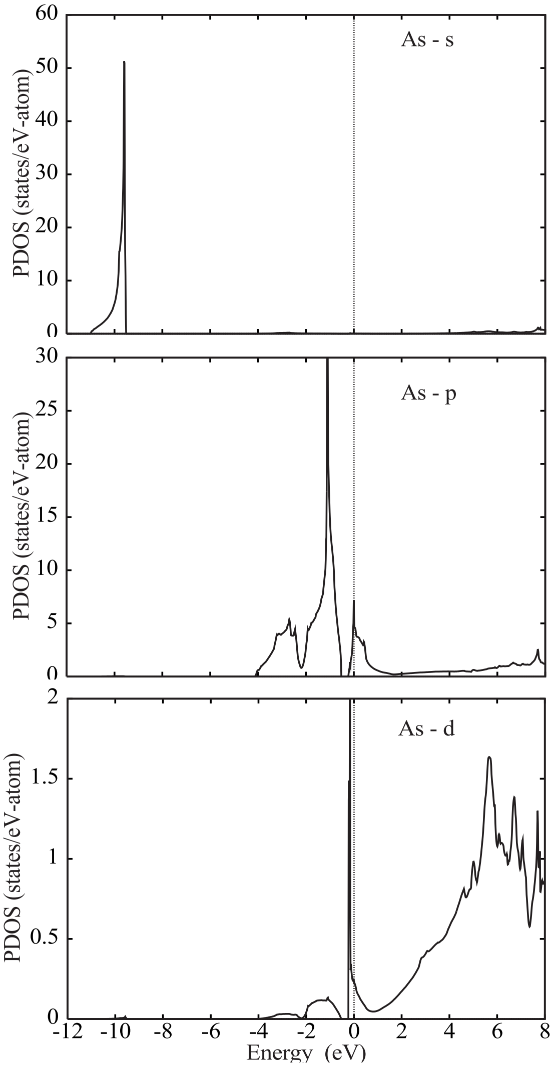

Fig. 12. Partial density of states (PDOS) projected on the different components of the As atom in the TmAs compound. The Tm *f* electrons have been included as valence-like in the calculation. The zero energy is related to the Fermi energy.

located near the Fermi level and show a strong mixing with the As 4*p* derived states. As consequence two Γ_{15} states repel each other, therefore the valence band is shifted up in energy around the Γ point. Looking at Table 3, we note that now both Γ_{15} and Γ'_{25} points are higher in energy with respect to the Fermi level by about 1 eV, this upshift is stronger for the Γ'_{25} point, consequently the energy difference between these two Γ points is enhanced with respect to the previous case (*f* electrons as core-like). Also the Δ lines are strongly affected by the presence of the *f* electrons. They now are located entirely above the Fermi level, hovewer the X$_3$-X'$_5$ energy differences is increased for YbAs, whereas is decreased for TmAs and ErAs, where now the X'$_5$ point is in energy above the X$_3$ one; this is another indication of the particular role played by the RE *d* and As *p* derived bands. The results shown in Figure 10 are in good agreement with the outcomes for similar configurations of Pethukov *et al.* for ErAs [1] and of Takegahara and Kaneta for YbAs [16]. The above discussion on the energy band behaviour is confirmed by the PDOS of TmAs shown in Figures 11 and 12, which are related to the *s, p, d* and *f* components for the Tm and *s, p, d* for the As atoms respectively (note the presence of Tm 4*f* derived bands just below and at the Fermi energy).

These results confirm that an inclusion of the f electrons as band electrons in a pure LDA calculation is not satisfactory; all the compounds, except LuAs, are no more semimetals, due to the non realistic position of the Fermi level pinned by the presence of the f electrons. A theoretical analysis which go beyond the LDA would be necessary, that allows to split in energy the occupied and unoccupied f bands, without loosing hybridization effects, this is exactly what happens using SIC, as recently shown [10,11] (see also references therein).

5 Conclusions

We have performed first-principle calculations of the density of states and the energy band structure of rare-earth arsenides. We have considered ErAs, Tm As, YbAs and LuAs covering a large range of f occupancy. Moreover we have considered the case of YAs, whose atomic configuration is quite similar to those of REAs when the RE $4f$ electrons are treated as core-like electrons. We have, also, considered the situation where the RE f electrons are treated as valence band electrons. A strong variation in the energy bands and in the density of states near the Fermi level is found; this is due to the strong mixing between RE $4f$ derived states and As $4p$ derived bands, that raises up the valence band above the Fermi level. The LuAs compound is an exception, in this case the f derived bands are located at about 5 eV below the Fermi level, this happens because, differently from the other considered REAs, Lu has a $5d$ electrons in both cases (f electrons treated as core-like or valence-like electrons). A particular role is played from the rare-earth $5d$ derived states, we have shown that they are particularly sensitive to the choice of the lattice constant in the calculations; variation of the lattice constant of less than 1% leads to a different behaviour with respect to the crossing of the rare-earth $5d$ derived bands and the As $4p$ derived bands along the Δ-direction near X. This fact can be relevant in connection with the possibility of originating a semimetal-semiconductor transition in the rare-earth arsenides.

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References

1. A.G. Pethukov, W.R.L. Lambrecht, B. Segall, Phys. Rev. B **53**, 4324 (1996).
2. R. Bogaerts, A. De Keyser, F. Herlach, F.M. Peeters, F. DeRosa, C.J. Palmstrom, D. Brehmer, S.J. Jr. Allen, Solid State Electron. **37**, 789 (1994).
3. S.J. Jr. Allen, D. Brehmer, C.J. Palmstrom, in *Rare Earth Doped Semiconductors*, edited by G.S. Pomrenke, P.B. Klein, D.W. Langer, Vol. 301 (Material and Research Society, Pittsburgh, 1993), p. 307.
4. S.J. Jr. Allen, F. DeRosa, C.J. Palmstrom, A. Zrenner, Phys. Rev. B **43**, 9599 (1991).
5. S.J. Jr. Allen, N. Tabatabaie, C.J. Palmstrom, S. Mounier, G.W. Hull, T. Sands, F. DeRosa, H.L. Gilchrist, K.C. Garrison, Surf. Sci. **228**, 13 (1990).
6. D.E. Brehmer, Kai Zhang, Ch.J. Schwarz, S.P. Chau, S.J. Allen, J.P. Ibbetson, J.P. Zhang, A.G. Petukhov, C.J. Palmstrom, B. Wilkens, Solid State Electron. **40**, 241 (1996).
7. A. Hasegawa, A. Yanase, J. Phys. Soc. Jpn **42**, 492 (1977).
8. M. Said, C.M. Bertoni, A. Fasolino, S. Ossicini, Solid State Commun. **100**, 477 (1996).
9. A. Svane, O. Gunnarsson, Phys. Rev. Lett **65**, 1148 (1990).
10. P. Strange, A. Svane, W.M. Temmermann, Z. Szotek, H. Winter, Nature **399**, 756 (1999)
11. A. Svane, W.M. Temmermann, Z. Szotek, L. Petit, P. Strange, H. Winter, Phys. Rev. B **62**, 13394 (2000)
12. V.I. Anisimov, J. Zaanen, O.K. Andersen, Phys. Rev. B **44**, 943 (1991).
13. R. Ahuja, S. Auluck, B. Johansson, M.S.S. Brooks, Phys. Rev. B **50**, 5147 (1994)
14. J.B. Xia, S.F. Ren, Y.C. Chang, Phys. Rev. B **43**, 1692 (1991).
15. A.G. Pethukov, W.R.L. Lambrecht, B. Segall, Phys. Rev. B **50**, 7800 (1994).
16. K. Takegahara, Y. Kaneta, J. Phys. Soc. Jpn **60**, 4009 (1991).
17. K. Takegahara, Physica B **186-188**, 850 (1993).
18. A. Svane, Z. Szotek, W.M. Temmermann, J. Laegsgaard, H. Winter, J. Phys. Cond. Matt. **10**, 5309 (1998).
19. P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964), W. Kohn L.J. Sham, Phys. Rev. **140**, A1133 (1965).
20. U. von Barth, L. Hedin, J. Phys. C **5**, 1629 (1972).
21. O.K. Andersen, Phys. Rev B **12**, 3060 (1975); O.K. Andersen, O. Jepsen, M. Sob, in *Electronic Band Structure and its Applications*, edited by M. Yussouff (Springer, Heidelberg, 1987), p. 1.
22. D. Glötzel, B. Segall, O.K. Andersen, Solid State Commun. **36**, 403 (1980).
23. P. Villars, L.D. Calvert *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (American Society for Metals, Metals Park, 1985).
24. N.E. Christensen, S. Satpathy, Z. Pawlowska, Phys. Rev. B **36**, 1032 (1987).