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Structural and electronic properties of non-magnetic intermetallic YAuX (X = Ge and Si) in hexagonal and cubic phases

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Abstract. The structural and electronic properties of non-magnetic intermetallic YAuX (X = Ge and Si) crystallized in hexagonal phase have been investigated using the full potential linearized augmented-plane wave (FP-LAPW) method based on the density functional theory (DFT), within the generalized gradient approximation (GGA). The calculated lattice parameters were in good agreement with experiment. Also, the structural and electronic properties of the non-magnetic half-Heusler YAuPb compound including the artificial YAuX (X = Ge and Si) calculated in cubic phase were determined. It was found that the half-Heusler YAuPb compound presented metallic character. The results showed that YAuGe in cubic phase is a semiconductor whereas the cubic YAuSi is an isolator.

Keywords. DFT; FP-LAPW; intermetallics; electronic structure; density of states.

1. Introduction

A class of compounds that has attracted a great attention in recent years is RETX, where RE is a lanthanide element, T the transition element and X the main group element. This class offers a broad variety of different structure types [1,2] with interesting electronic and magnetic properties that show heavy Fermion behaviour [3,4], half-metallic properties [5,6], mixed valent behaviour in Eu, Yb and Ce compounds [7–12], giant magnetoresistance [13] superconductivity [8,14], etc.

Approximately 50 hexagonal RETX compounds crystallize in the LiGaGe structure, which can be thought of as a RE^{n+} ion stuffing a wurtzite $(TX)^{n-}$ sublattice. In the past few years, many RETX compounds were determined as in the $CaIn_2$ structure type (random distribution of T and X atoms). Later it was found that their correct structure is LiGaGe type with T and X atoms form separate lattices [15–17]. Its crystal structure is completely described by four parameters, the hexagonal cell parameters a, c and the internal T and X atoms positional parameter z in (1/3, 2/3, z). At this point it is interesting to look at or think about hexagonal analogues of cubic $C1_b$ compounds. The prototype of this structure is known as LiGaGe (space group $P6_3mc$). A number of experimental studies have been carried out on such ternary compounds. It was found that most of the compounds are reported in the disordered $CaIn_2$ structure type. Their correct structure is the LiGaGe structure type, which belongs to a subgroup of $P6_3mc$. Cubic XYZ compounds with $C1_b$ structure crystallize in the zinc-blende structure type in space group ($F\bar{4}3m$) with a cubic cell parameter close to 6.0 Å. The least and most electronegative elements are Y at (1/2, 1/2, 1/2) and Z at (0, 0, 0) forming a rock salt lattice. X are found at (1/2, 1/2, 1/2) in the centres of tetrahedra formed by Z, as well as by Y. Connecting X and Z reveals the stuffed zinc-blende lattice of the $C1_b$ structure.

The intermetallic yttrium compounds YAuX (X = Ge and Si) are one such class of alloys belong to a large family of terminal RETX each crystallizing in a hexagonal LiGaGe-type structure, exhibits interesting structural and physical properties [18,19]. In the recent years, Lin *et al* [20] discovered several different paradigms of trivial and non-trivial topological ordering, including an intrinsically metallic nontrivial topological state in YAuPb which crystallized in the cubic $C1_b$ phase. This structure represents famous alloys called half-Heusler materials but the focus was not on the properties of these materials because it is not the subject of this paper. Most importantly, it was proposed that in the half-Heusler family the topological insulator have gained great success experimentally. Topological insulator (TI) is of a new class of materials, which has a full insulating gap in the bulk but contains topologically protected conducting states on edges or surfaces [21–24].

Here density functional calculations were carried out [25] in order to investigate the ground state of each material in its stable structure (the crystal structures have been taken from the literature, except for the cubic compounds YAuGe and YAuSi in which case the compounds are artificial). These artificial compounds either have hexagonal crystal structure. Also, a systematic investigation was performed on the band topology of YAuPb, YAuGe and YAuSi in the cubic phase.

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Table 1. Calculated lattice constants and bulk moduli for hexagonal YAuX (X = Ge and Si) and cubic YAuZ (Z = Ge, Si and Pb) using GGA.

Phase	Compounds	a (Å)	c (Å)	c/a	B (GPa)
Hexagonal (LiGaGe)	YAuGe	4.459	7.800	1.773	97.04
		4.410 [30]	7.308 [30]	1.657 [30]	—
	YAuSi	4.330	7.499	1.731	104.51
		4.288 [31]	7.544 [32]	—	—
Cubique ($C1_b$ structure)	YAuGe	6.443	—	—	95.59
	YAuSi	6.380	—	—	102.78
	YAuPb	6.737	—	—	84.18
		6.73 [33]			—

The remainder of this paper is organized as follows: in Section 2, the method and the details of the calculations are given. In Section 3, the obtained structural and electronic results for h-YAuX (X = Ge and Si) in the hexagonal structure and c-YAuPb in the cubic phase as well as the properties of c-YAuX (X = Ge and Si) in cubic $C1_b$ structure are presented and discussed. Finally, a conclusion is given in Section 4.

2. Computational method

First-principle calculations for the cubic and hexagonal phases of YAuZ (Z = Ge, Si and Pb) within density functional theory (DFT) was performed [25]. The Kohn–Sham equations were solved with the full potential linearized augmented-plane wave (FP-LAPW) technique, as implemented in the WIEN2K package [26]. In the present self-consistent calculations, a muffin-tin model for the crystal

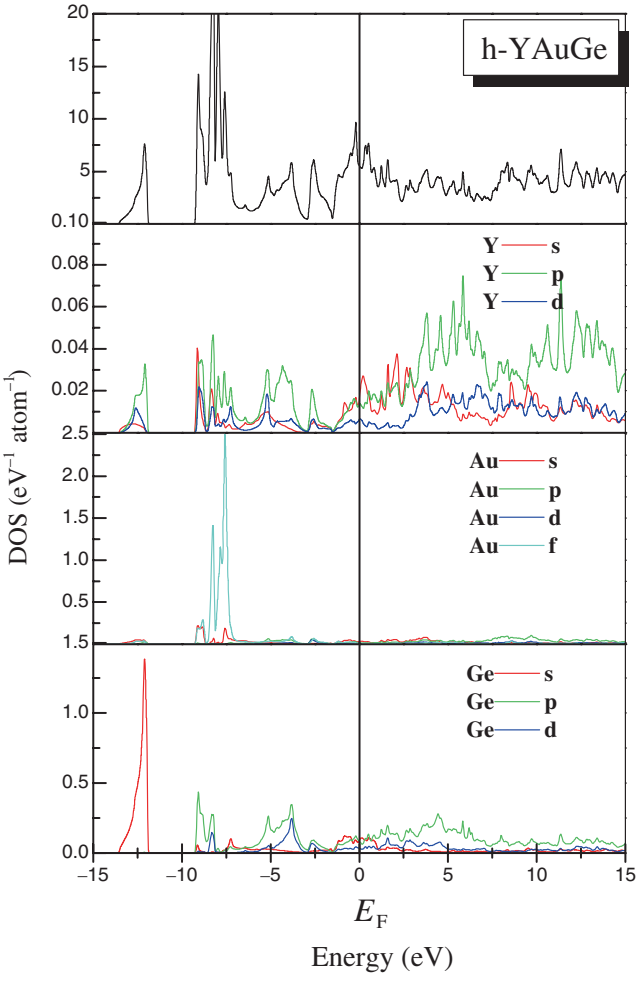

Figure 1. Total and partial density of states for YAuGe in hexagonal phase using GGA.

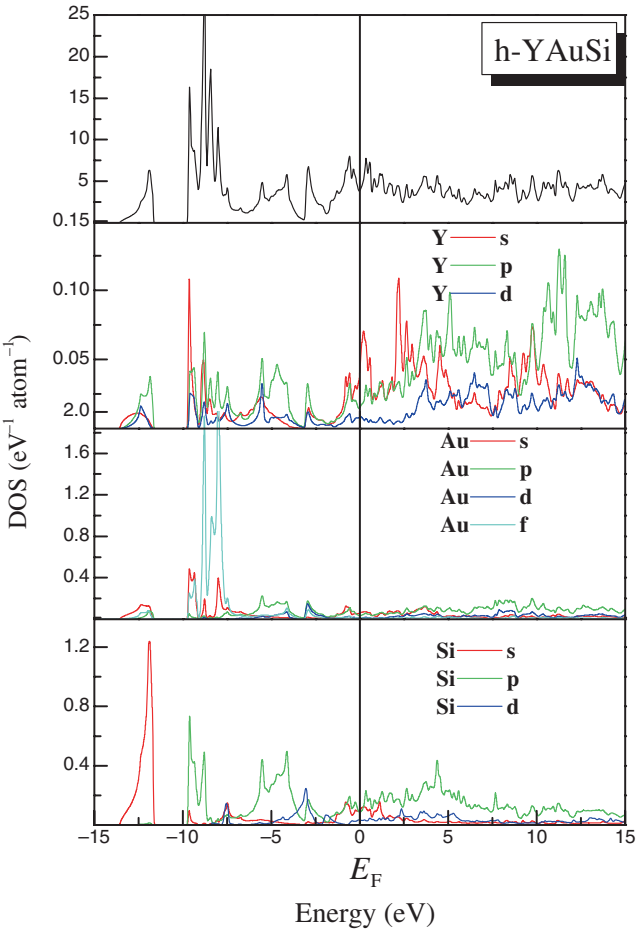

Figure 2. Total and partial density of states for YAuSi in hexagonal phase using GGA.

potential is assumed and the unit cell is divided into two regions, within and outside the muffin-tin sphere. The electrons are separated into two groups, namely the core electrons whose charge densities are confined within the muffin-tin spheres and the valence electrons. The core electron states are considered fully relativistic by solving the Dirac equation, whereas the valence electrons are just treated as scalar relativistic. In both regions of the unit cell, different basis sets are used to expand the wave function, charge density and potential. Inside the non-overlapping spheres of muffin-tin radius (RMT) around each atom, a linear combination of radial solutions of the Schrödinger equation times the spherical harmonics are used, while the plane wave basis set is used in the interstitial region. In the calculations, yttrium ($4d^1\ 5s^2$), gold ($4f^{14}\ 5d^{10}\ 6s^1$), germanium ($3d^{10}\ 4s^2\ 4p^2$), silicon ($3s^2\ 3p^2$) and lead ($4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$) states are treated as valence electrons, and the muffin-tin radii of 2.0, 2.0, 2.1, 2.1 and 2.15 a.u. were used for Y, Au, Ge, Si and Pb atoms, respectively. The exchange–correlation energy is in the form of Perdew–Burke–Ernzerhof (PBE) with generalized gradient approximations (GGA) [27]. The maximum value of angular momentum $l_{max} = 10$ was taken for the wave function expansion inside the atomic spheres. The parameter $R_{MT} * K_{max} = 8$, where R_{MT} is the smallest muffin-tin radius and K_{max} is the truncation for the modulus of reciprocal lattice vector, was used for the plane wave expansion of the wave functions in the interstitial region. The Monkhorst–Pack special k-point scheme with a 1500 special k-points in the Brillouin zone were used for YAuGe, YAuSi and YAuPb compounds. The criterion of convergence for energy was chosen as 10^{-4} (Ryd). The electron states were treated in a scalar relativistic approximation. Using the energy eigenvalues and eigenvectors at these points, the density of states (DOS) was determined by the tetrahedral integration method [28].

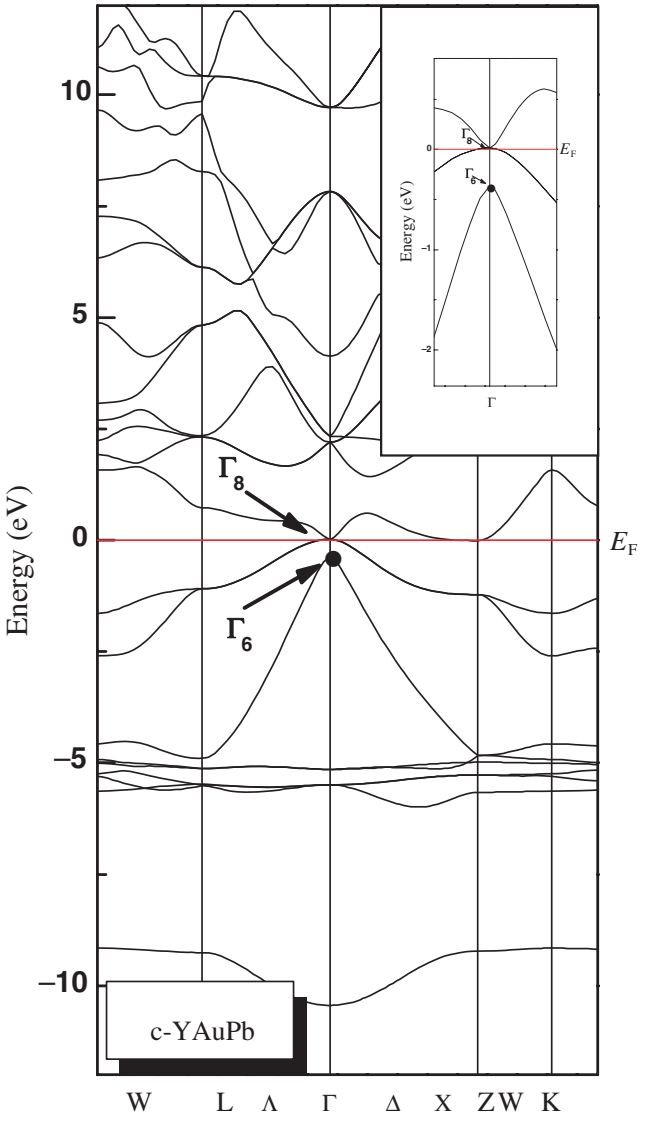

Figure 3. Calculated band structure for YAuPb.

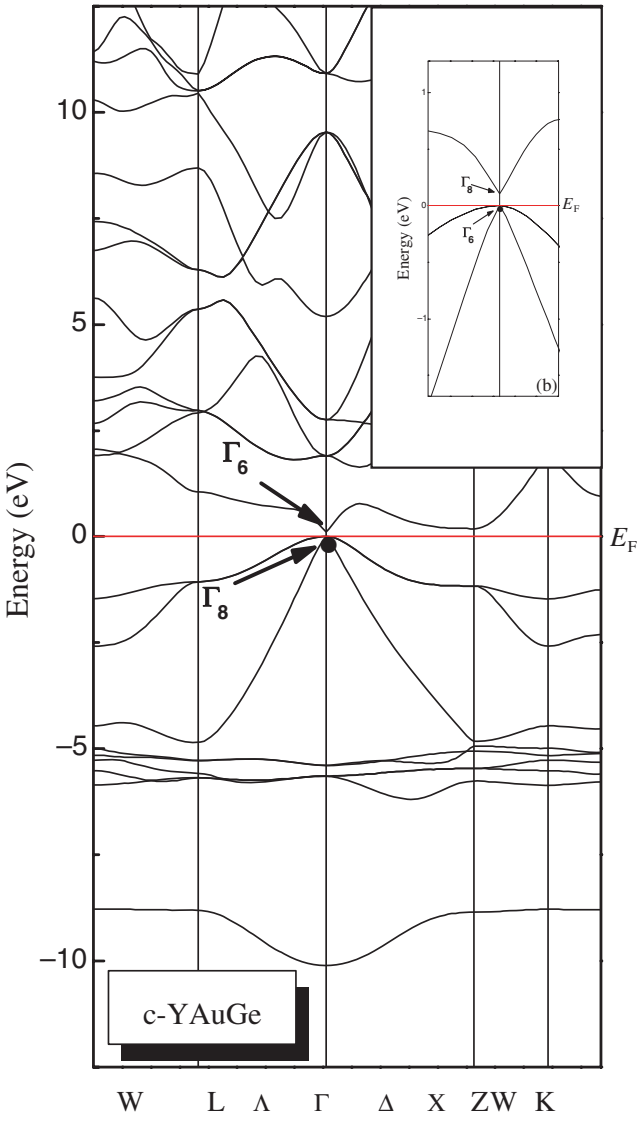

Figure 4. Calculated band structure for YAuGe in cubic phase using GGA.

3. Results and discussion

3.1 *Structural properties of h-YAuX, c-YAuX (X = Ge and Si) and c-YAuPb*

The lattice constants for YAuGe and YAuSi in both hexagonal (space group $P6_3mc$) and cubic $C1_b$ (space group $F\bar{4}3m$) structures and for YAuPb in $C1_b$ structure are optimized. The calculated total energies at many different volumes around equilibrium were fitted by Murnaghan's equation of state [29] in order to obtain the structural properties for both the hexagonal and cubic phases. It was confirmed that the non-spin-polarized configuration is lower in energy than the ferromagnetic case for all compounds in both phases. The crystal structure of RETX is completely described by four parameters, the hexagonal cell parameters a, c and the internal T and X positional parameters (1/3, 2/3, 1/2−z) where z is different for T and X. The calculated lattice constants and bulk modulus in both phases are presented in table 1 along with the experimental data [30–32]. When the c/a ratio is optimized, a maximum deviation of 7.0% from the experimental value for YAuGe alloy is found. Generally, the results are in reasonable agreement with the experimental values. However, the YAuPb alloy is considered as half-Heusler material and as it is well known, the half-Heusler alloys containing with $C1_b$ structure crystallize in the zinc-blende structure type in space group ($F\bar{4}3m$) with a cubic cell parameter close to 6.0 Å. Our calculated lattice parameter of YAuPb is very close to the available experimental data [33]. Values of 6.44 and 6.38 Å for c-YAuGe and c-YAuSi, respectively, are obtained. Comparing the calculated bulk modulus of the three materials in cubic phase, it is noted that the value obtained for c-YAuSi is much more important that reflects its hardness.

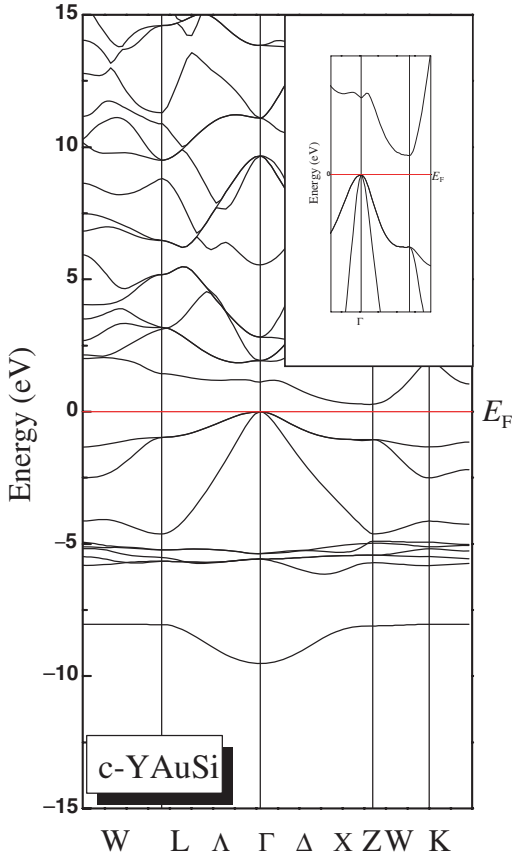

Figure 5. Calculated band structure for YAuSi in cubic phase using GGA.

3.2 *Electronic properties of h-YAuGe and h-YAuSi*

The calculated total densities of states (TDOS) and the partial density of states (PDOS) near Fermi level are presented in figure 1 for h-YAuGe and figure 2 for h-YAuSi. Here and in all following figures, energies are referred to the Fermi level (E_F). The features of the occupied densities of states for both alloys are quite similar. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level E_F for both compounds. As a result, the h-YAuX compound will exhibit metallic properties. There is a strong hybridization in the energy region from −9 eV to the Fermi level, being characteristic of Y s–p–d, Au f and Ge p states, which indicate the covalent interaction between them. The bonding bands above the Fermi level are mainly attributed to Y s–p–d states, while the Au p and Ge p orbitals contribute a little to the density of states. Therefore, it was observed from −7 to −10 eV that the Au f states split a strong sharp peak, which hybridize with other orbitals and Y p split some sharp peaks above Fermi level. It also can be seen that the

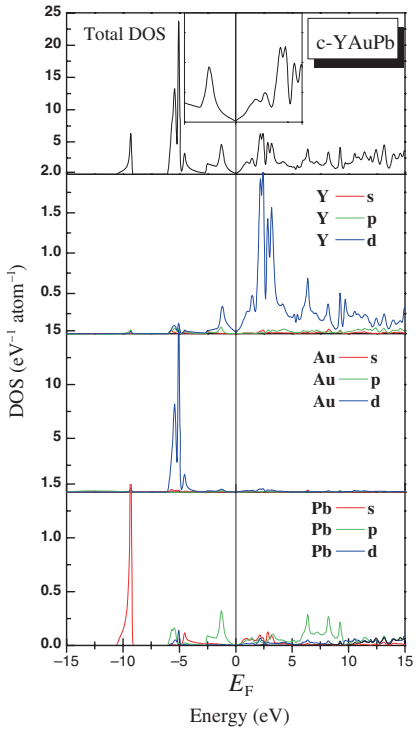

Figure 6. Total and partial density of states for YAuPb.

contributions from the d orbital of Ge and Si atoms are relatively small but not negligible in this region. Finally, Y p and Ge s states are mentioned, which are found below −10 eV but these are expected to play little role in the bonding.

3.3 *Electronic properties of c-YAuZ (Z = Ge, Si and Pb)*

Figures 3–5 present the pictures of the calculated band structures of the cubic ternary materials, c-YAuPb, c-YAuGe and c-YAuSi, respectively. A common characteristic of these materials is that the top of the valence band is located at the Γ point.

One can notice a presence of a gap above the Fermi level in all compounds except for YAuPb. The valence and conduction bands are well separated without crossing each other. The band inversion occurs in YAuPb, but low energy properties in this compound are complicated by another set of conduction bands that comes below the Fermi energy to form electron pockets near X. It is found that YAuPb presents metallic character. The results agree with the recent calculations of Lin *et al* [20] who found that YAuPb is topologically nontrivial metal (or 'topological metal'). Al-Sawai *et al* [34] studied YAuPb using the modified Becke and Johnson potentials on the local density approximation (MBJLDA) [35] based on DFT. They found that YAuPb presents a semi-metal character.

The band structure of c-YAuGe is different to that of YAuPb. It exhibits natural band ordering (s-like Γ_6 states lie above the p-like Γ_8 states) and opens a direct gap at the Γ point, indicating them to be semiconductor. The s-type bands in YAuSi are above E_F, and are unoccupied meaning that c-YAuSi is an insulator.

Figure 6 illustrates the calculated TDOS and PDOS of YAuPb in cubic phase. Comparing the DOS with the band structure it is observed that the strongest bands in the energy range around −10 eV, mainly originate from the Pb s states. The bands around Fermi level are due to a small contribution from the d states of yttrium with a strong hybridization between the s–p states of the gold and the lead. Accordingly, one can see the Pb p levels arise above the s levels, leading to an inverted band structure. The TDOS of YAuPb exhibits a zero gap in which valence and conduction bands touch at the Γ point. Figure 7 shows TDOS and PDOS of c-YAuGe, the conduction band is mainly dominated by Y d states whereas in the valance band Au d states split some sharp peaks. In this energy range the same contribution of Y and Au d states can be seen for cubic YAuSi in figure 8. Hence the density of states of c-YAuGe and c-YAuSi shows almost narrow dispersion at Fermi level which slightly separates the valence and

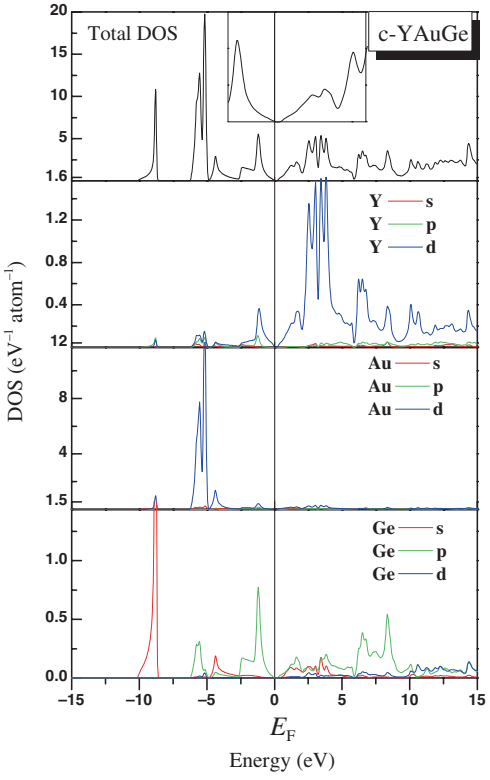

Figure 7. Total and partial density of states for YAuGe in cubic phase using GGA.

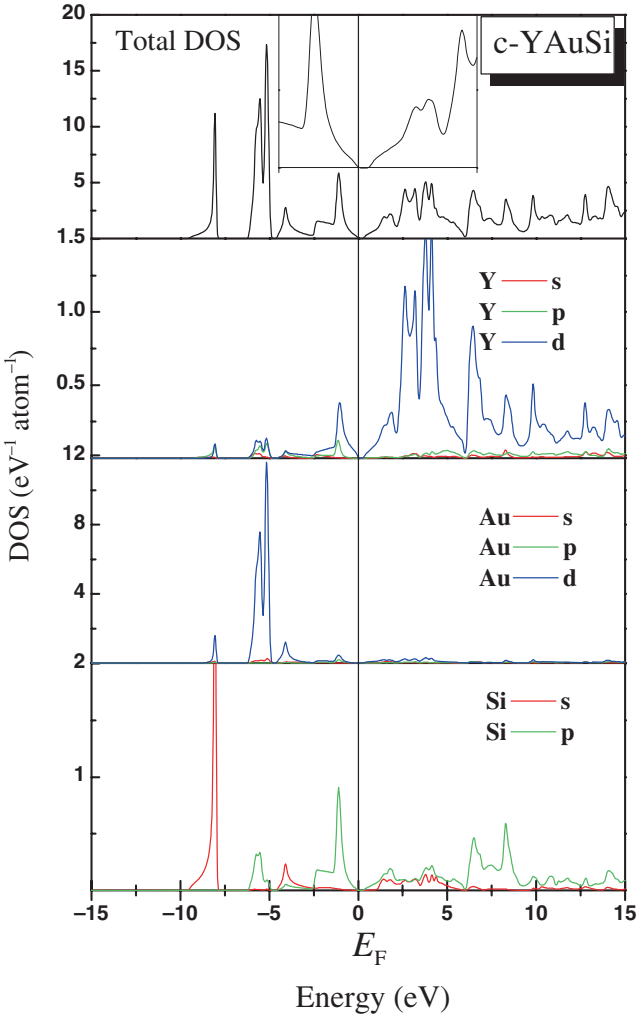

Figure 8. Total and partial density of states for YAuSi in cubic phase using GGA.

conduction bands. Thus, c-YAuGe presents a direct band gap at the Γ point and c-YAuSi shows an indirect band gap Γ–X.

4. Conclusion

In conclusion, first-principle calculations were performed based on the FP-LAPW method within the GGA to evaluate the structural and electronic properties of intermetallic hexagonal YAuGe and YAuSi compound and the half-Heusler cubic YAuPb, including the study of artificial YAuGe and YAuSi in cubic phase. The results reveal that these compounds are non-magnetic and h-YAuX (X = Ge and Si) show metallic nature. For the cubic structure we found the character of insulator material for c-YAuSi and semiconductor material for c-YAuGe whereas YAuPb presents a metallic character.

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