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2009 J. Phys.: Condens. Matter 21 025502

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IOP Publishing Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **21** (2009) 025502 (6pp) doi:10.1088/0953-8984/21/2/025502

Electronic band structures of AV_2 (A = Ta, Ti, Hf and Nb) Laves phase compounds

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Received 11 September 2008, in final form 29 October 2008
Published 9 December 2008
Online at stacks.iop.org/JPhysCM/21/025502

Abstract
First-principles density functional calculations, using the all-electron full potential linearized augmented plane wave method, have been performed in order to investigate the structural and electronic properties for Laves phase AV_2 (A = Ta, Ti, Hf and Nb) compounds. The generalized gradient approximation and the Engel–Vosko-generalized gradient approximation were used. Our calculations show that these compounds are metallic with more bands cutting the Fermi energy (E_F) as we move from Nb to Ta, Hf and Ti, consistent with the increase in the values of the density of states at the Fermi level $N(E_F)$. $N(E_F)$ is controlled by the overlapping of V-p/d, A-d and A-p states around the Fermi energy. The ground state properties of these compounds, such as equilibrium lattice constant, are calculated and compared with the available literature. There is a strong/weak hybridization between the states, V-s states are strongly hybridized with A-s states below and above E_F. Around the Fermi energy we notice that V-p shows strong hybridization with A-p states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Laves phases represent the largest group of intermetallic compounds and are found to crystallize in three structural types, which are named after the representative cubic $MgCu_2$(C15), hexagonal $MgZn_2$(C14) and hexagonal $MgNi_2$(C36). Their ideal composition is AB_2. These phases belong to the class of tetrahedrally close-packed alloys. Two of the structural features of the Laves phase which have aroused interest are, firstly, the dependence of the structure adopted on the number of valence electrons of the constituent metal atom and, secondly, the structural distortions observed in a number of the hexagonal $MgZn_2$ type phases [1]. Laves phases can be formed by main group metallic elements and transition metals as well as by lanthanides and actinides. These structures are considered as size factor compounds [2]. They are examples of topologically close-packed structures [3–6], representing the best space filling arrangement for unlike spheres A and B (in the ratio 1:2) with $r_A/r_B \cong 1.23$. Generally, among the three Laves phases (C14, C15 and C36), C15 is a low-temperature phase except for some special systems, e.g. ScF_2, for which the structure sequence is, from high to low temperature, C36, C15 and C14 [7]. Interest in the Laves phases has grown due to their promising behaviour as solid state hydrogen storage materials [8, 9]. They also have interesting magnetic and electrical properties [10–13]. The C15 Laves phase has a crystal structure that is derivative of the diamond structure, i.e. based on fcc. AV_2 (A = Ta, Ti, Hf and Nb) which crystallizes in the $MgCu_2$-type structure with space group $Fd3m$ belong to this large group of Laves compounds. They are of technological interest because of potential applications as high-temperature structural materials with excellent oxidation resistance [14]. In addition, these compounds have quite high melting temperatures and low densities [15].

Little of the theoretical research work for Laves phase compounds AV_2 (A = Ta, Ti, Hf and Nb) has been reported.

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Table 1. Structural parameters for the (C15) Laves phase.

Atom	Site	Symmetry	Coordinates
A(Mg)	8(a)	$\bar{4}3m(T_d)$	0, 0, 0, ...
B(Cu)	16(d)	$\bar{3}m(D_{3d})$	5/8, 5/8, 5/8, ...

First-principles all-electron, full potential linear muffin-tin orbital (LMTO) calculations based on total energy calculations for the C14 and C15 phases of HfV_2 have been done [15]. These calculations show that the C14 structure has a lower total energy than the C15 structure and the cohesive energy difference between C15 and C14 phases is very small (20 meV/atom). However, for HfV_2 there is no experimental observation of the C14 phase [15]. More recently, the full potential linearized augmented plane wave method has been used to study the equilibrium unit-cell volumes, bulk modulus, electronic and elastic properties for C15 AV_2 (A = Ta, Ti, Hf and Nb) [14, 16]. To the best of our knowledge there is no experimental data for the electronic properties of these compounds reported yet. As a step forward we present an *ab initio* study of the structural and electronic properties of the compounds AV_2 (A = Ta, Ti, Hf and Nb) for the C15 structure.

We start in the next section with a brief description of the method of calculation. In section 3 we discuss in detail the electronic properties for these compounds. Finally the principal conclusions are summarized in section 4.

2. Method of calculation

We performed first-principles calculations within the framework of the density functional theory for the C15 Laves phase in an AB_2 type compound. This is a very closely packed structure with 71% of the volume filled by touching spheres and the site symmetry is high for the two constituents [17]. The $MgCu_2$ type structure (C15) is face-centred cubic, belonging to the space group $Fd3m(o_h^7)$ with eight formula units per non-primitive cubic unit cell. The structural parameters are presented in table 1 [18, 19]. The A sublattice of the $MgCu_2$ structure defines a cubic diamond net, while the B sublattice can be described in terms of B_4 tetrahedra, sharing all of their vertices in such a way that each pair of fused tetrahedra adopt a staggered conformation. The energy band structures were determined self-consistently using the full potential linearized augmented plane wave (FP-LAPW) method as incorporated in the WIEN2k code [20]. In this approach one takes advantage of the analytic properties of the wavefunctions by dividing the unit cell into two distinct regions, based on the old concept of nonoverlapping muffin-tin spheres. The first contains all points inside the muffin-tin spheres around the atom, while the second is the interstitial region outside the muffin-tin spheres, the potential and the density in the interstitial region are expanded in terms of plane waves, and inside the muffin-tin spheres they are expanded in terms of spherical harmonics. Inside the muffin-tin spheres, the expansion of the non-spherical potential and charge density

Table 2. Calculated lattice parameters and electronic specific heat coefficient γ (mJ mol^{-1} K^{-2}). Cohesive energy per atom (eV), heat of formation per atom (meV) and $N(E_F)$ in comparison with the available previous calculations.

	Present work	Other work
HfV2		
Lattice parameter (Å)	7.3187	7.3156 [16]
$N(E_F)$ (states eV^{-1} unit cell)	15.8	7.51 [16] 14.55 [15]
Electronic specific heat coefficient, γ (mJ mol^{-1} K^{-2})	37.27	
Cohesive energy per atom (eV)	5.897	5.69 [15]
Heat of formation per atom (meV)	−17.99	−15.7 [15]
NbV2		
Lattice parameter (Å)	7.1542	7.1656 [16]
$N(E_F)$ (states eV^{-1} unit cell)	12.5	5.45 [16]
Electronic specific heat coefficient, γ (mJ mol^{-1} K^{-2})	29.49	
Cohesive energy per atom (eV)	6.122	
Heat of formation per atom (meV)	−46.22	
TaV2		
Lattice parameter (Å)	7.1349	7.2215 [16]
$N(E_F)$ (states eV^{-1} unit cell)	13.1	5.25 [16]
Electronic specific heat coefficient, γ (mJ mol^{-1} K^{-2})	30.90	
Cohesive energy per atom (eV)	6.5	
Heat of formation per atom (meV)	−121.8	
TiV2		
Lattice parameter (Å)	7.1186	7.1219 [16]
$N(E_F)$ (states eV^{-1} unit cell)	16.8	5.12 [16]
Electronic specific heat coefficient, γ (mJ mol^{-1} K^{-2})	39.63	
Cohesive energy per atom (eV)	5.47	
Heat of formation per atom (meV)	−85.9	

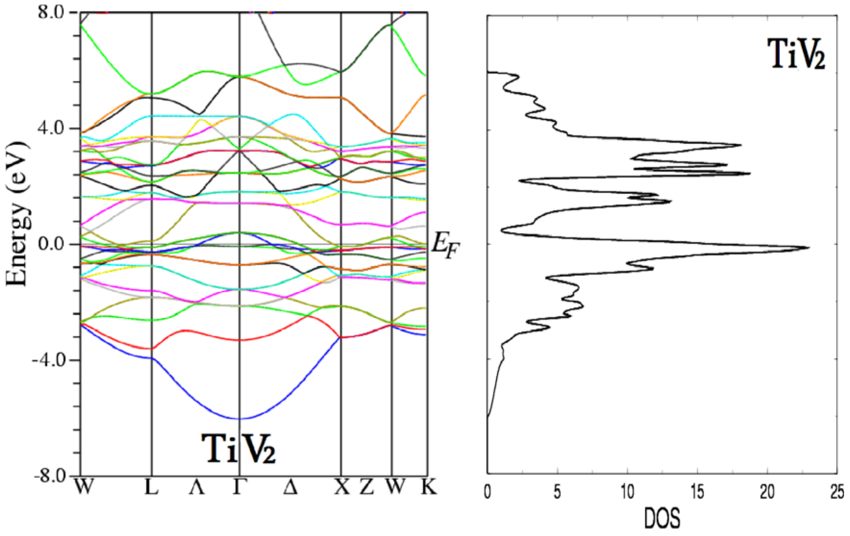

Figure 1. Calculated band structures and total densities of states (states eV^{-1} unit cell) for TiV_2 using EV-GGA.

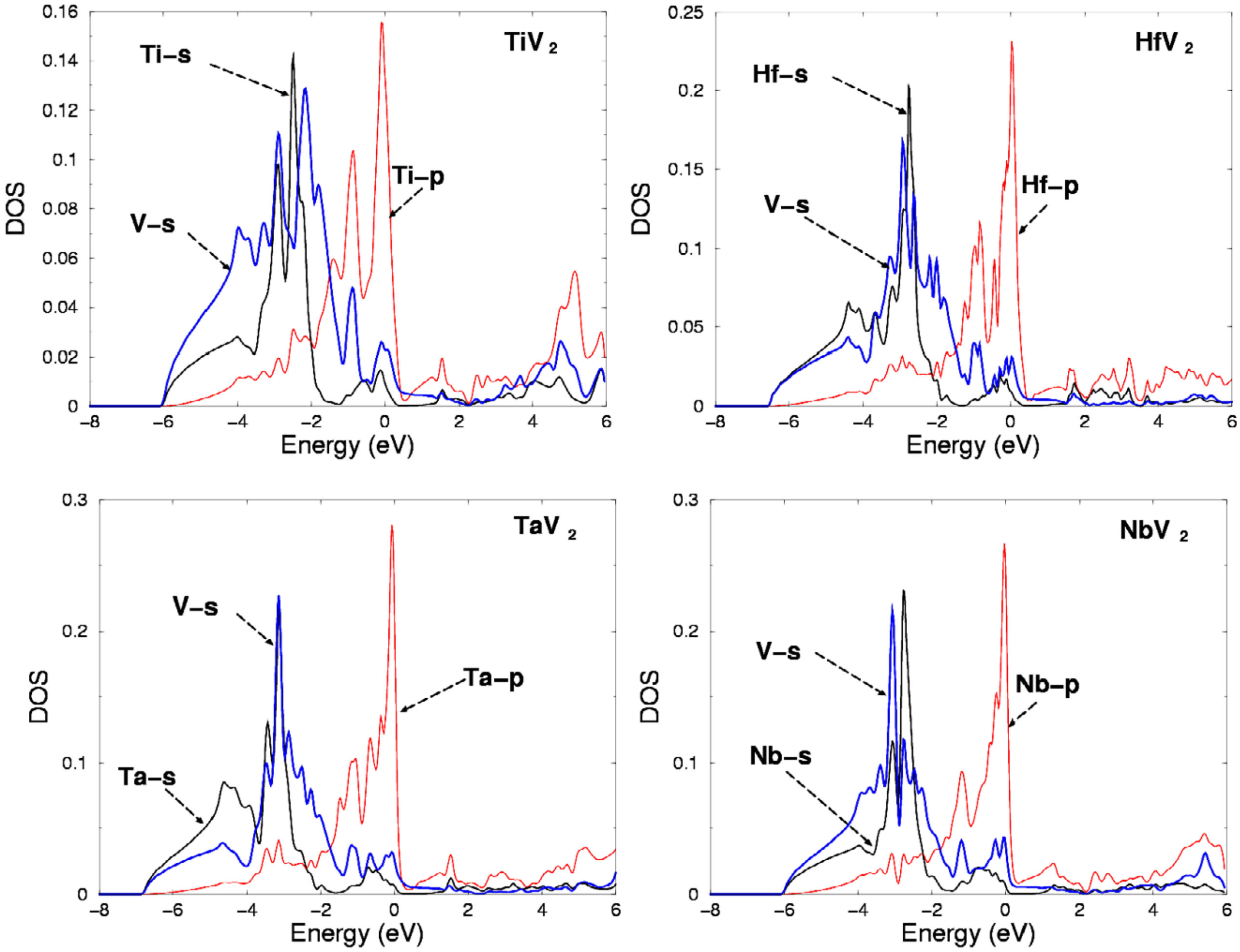

Figure 2. Calculated A-s/p and V-s partial densities of states (states eV^{-1} unit cell) for Laves phase compounds AV_2 (A = Ta, Ti, Hf and Nb) using EV-GGA.

were carried out up to $l_{max} = 10$. The exchange–correlation potential was calculated using the generalized gradient approximation (GGA) [21], which is based on exchange–correlation energy optimization to calculate the total energy. For the electronic properties we applied the Engel–Vosko (EV-GGA) scheme [22].

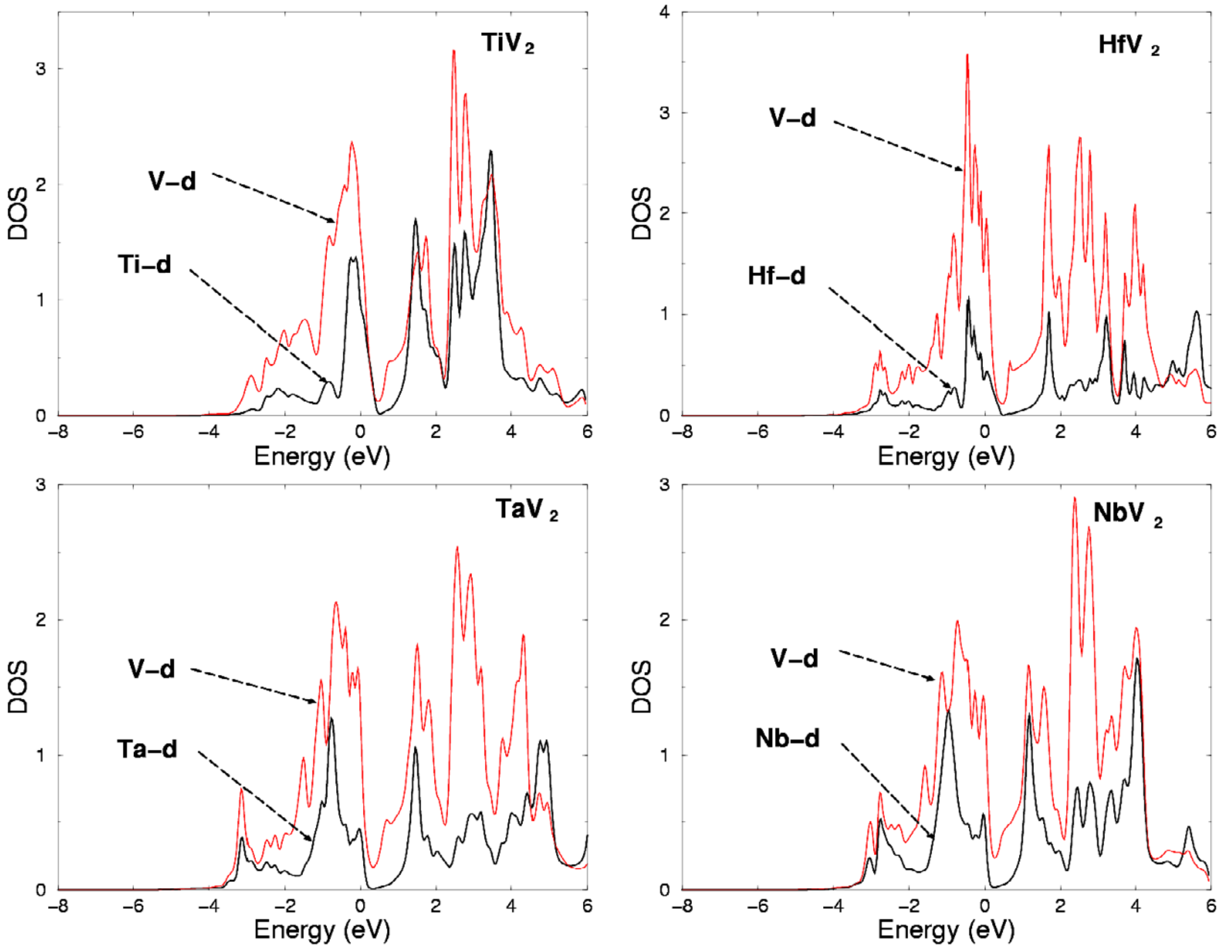

Figure 3. Calculated A-d and V-d partial densities of states (states eV^{-1} unit cell) for Laves phase compounds AV_2 (A = Ta, Ti, Hf and Nb) using EV-GGA.

We have calculated the total energy at several volumes around equilibrium. The results are fitted to Murnaghan's equation of states [23]. In this way we obtained the equilibrium lattice constant summarized in table 2.

In order to achieve energy eigenvalue convergence, the wavefunctions in the interstitial region were expanded in plane waves with a cutoff of $K_{\mathrm{max}} = 9/R_{\mathrm{MT}}$, where R_{MT} is the radius of the smallest muffin-tin sphere, which is equivalent to an energy cutoff of 16.73 Ryd for TiV_2 and 15.31 Ryd for NbV_2, TaV_2 and HfV_2. Self-consistency was obtained using 84 **k**-points in the irreducible Brillouin zone (IBZ), and the BZ integrations were carried out using the tetrahedron method [25]. The band structure and the density of states are calculated using 286 **k**-points in IBZ. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-5} Ryd.

3. Results and discussion

3.1. Band structures and densities of states

We have calculated the total energy as a function of the unit-cell volume around the equilibrium cell volume for AV_2 (A = Ta, Ti, Hf and Nb) using GGA. The calculated total energies are fitted to an empirical functional form (the third-order Murnaghan equation) [23] to obtain an analytical interpolation of our computed points from which to calculate derived structural properties. These structures can be fully defined by just the lattice parameter, **a**. The calculated structural parameters of these compounds are listed in table 2, compared with the available theoretical results. The obtained lattice parameters are in good agreement with other theoretical results [16]. Also we have calculated the cohesive energy and heat of formation ΔH for AV_2 compounds. The cohesive energies are obtained by taking the difference between the ground state energies of the isolated spin-polarized atoms and the total energy of the solid at its equilibrium volume. The cohesive energies per atom of TaV_2, NbV_2, HfV_2 and TiV_2 are predicted to be about 6.5, 6.12, 5.897 and 5.47 eV/unit cell, respectively. For Laves phases, as is generally true for most metals and other intermetallic compounds, the higher the melting temperature, the larger the cohesive energy [15]. Accordingly, we predict that TaV_2 possesses the highest melting temperature. On the other hand the heat of formation is the difference between the total energy of the compound and the sum of the total energies of the constituents in proportion to the composition. This energy is given by $\Delta H = (E_{\mathrm{AV}_2} - E_{\mathrm{A}} - 2E_{\mathrm{V}})/3$ [24]. The calculated enthalpy shows that TaV_2

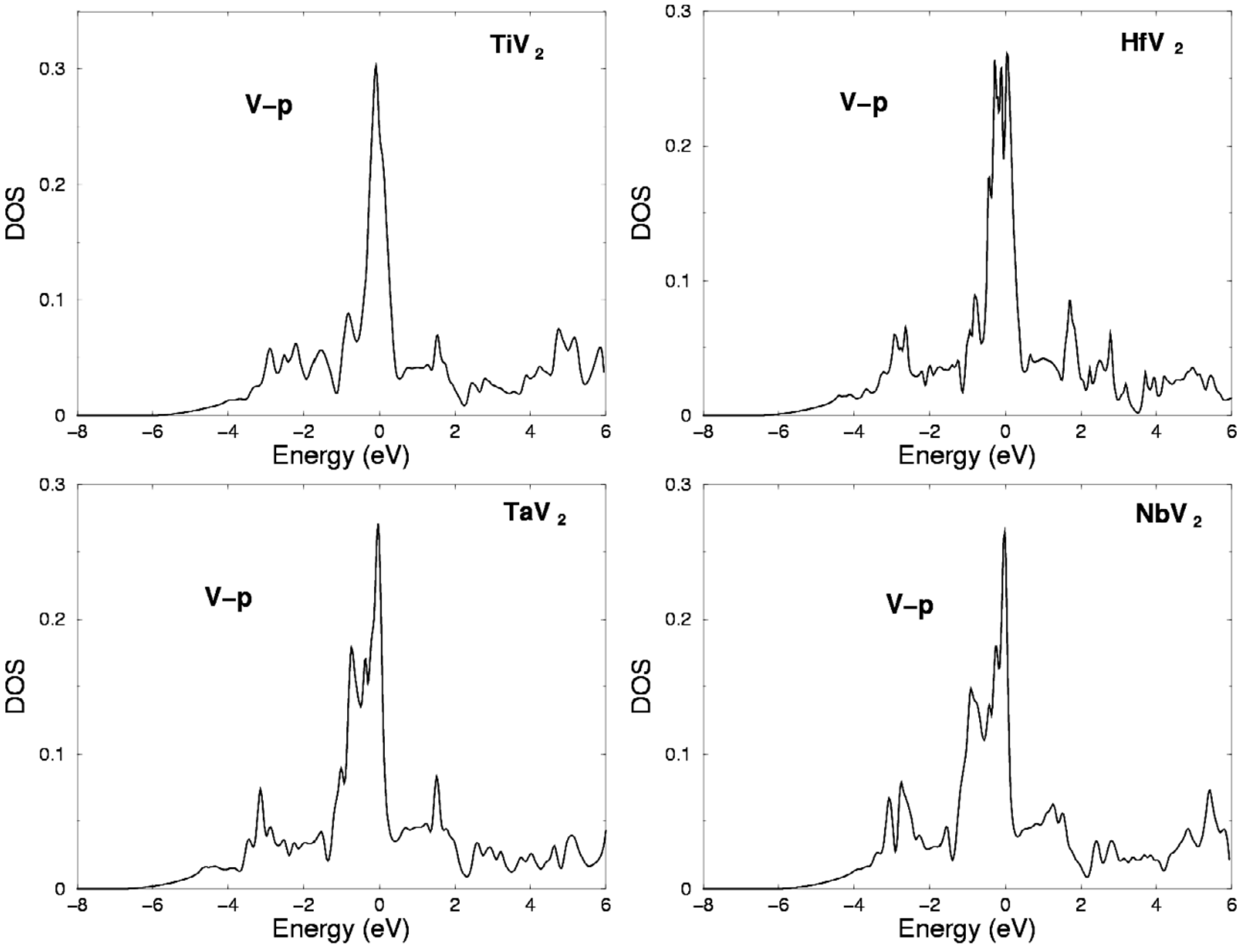

Figure 4. Calculated V-p partial densities of states (states eV^{-1} unit cell) for Laves phase compounds AV_2 (A = Ta, Ti, Hf and Nb) using EV-GGA.

is the largest compared to those of AV_2 (A = Ti, Hf and Nb) compounds. Furthermore, the large bulk modulus is found to be 193.4 GPa for TaV_2 compared with those in AV_2 compounds, which indicate that the covalent bonding existing in these AV_2 compounds strongly affects the enthalpies of formation of AV_2. In table 2 we listed our calculated cohesive energy per atom and the heat of formation per atom. In comparison with the available theoretical results [15] reasonable agreement was found.

We have calculated the band structure and total density of states (TDOS) for Laves phase compounds AV_2 (A = Ta, Ti, Hf and Nb) using EV-GGA approximations. The Fermi level is chosen to be at zero energy. As a prototype we have shown the band structure and total density of states for TiV_2 (figure 1). We find that the FP-LAPW calculation shows that these materials are metallic with increasing values of the density of states at Fermi energy ($N(E_F)$), indicating that more bands cut the Fermi energy as we move from Ti, Hf, Ta and Nb. The partial densities of states are shown in figures 2–4. From the PDOS we are able to identify the angular momentum character of the various structures. The band structure and the total density of states can be divided into two (one) groups/structures for HfV_2 and TaV_2 (TiV_2 and NbV_2). The lowest group (first group) for HfV_2 and TaV_2, which is located at −11.0 and −19.0 eV for HfV_2 and TaV_2, respectively, is mainly from Hf/Ta-f states. For all compounds the structures below and above the Fermi energy consist of A-s/p/d and V-s/p/d states. We notice that the overlapping of V-p/d, A-d and A-p states around the Fermi energy is controlling the values of $N(E_F)$, and hence the degree of metallicity of these materials. As we state in table 2, TiV_2 shows more metallic nature than HfV_2, TaV_2 and NbV_2 compounds because TiV_2 shows the highest value of $N(E_F)$ than HfV_2, TaV_2 and NbV_2, respectively. That is attributed to the fact that subtracting Nb by Ta, Hf and Ti cause it to push the occupied and unoccupied bands towards E_F, resulting in more bands cutting E_F and overlapping around it.

The electronic specific heat coefficient (γ), which is a function of the density of states, can be calculated using the expression

$$\gamma = \tfrac{1}{3}\pi^2 N(E_F) k_B^2,$$

where $N(E_F)$ is the density of states at Fermi energy and k_B is the Boltzmann constant. The calculated density of states at Fermi energy $N(E_F)$, enables us to calculate the bare electronic specific heat coefficient, in units of mJ mol^{-1} K^{-2}. The calculated values of (γ), for the investigated compounds are listed in table 2.

From the partial densities of states we notice there are significant changes in the structures of V-s/p/d states when we substitute Ti by Hf, Ta and Nb, indicating that A compounds play significant roles in changing the properties of these compounds. From the PDOS, we note that there is a strong/weak hybridization between the states. V-s states are strongly hybridized with A-s states below and above E_F. Around the Fermi energy we notice that V-p shows strong hybridization with A-p states. The trends in the band structures and densities of states (as we move from Ti to Hf, Ta and Nb) can be summarized as follows. (1) The lowest group in HfV_2 and TaV_2, which belong to the Hf-f and Ta-f states, is shifted towards lower energies by around 8.0 eV when we move from HfV_2 to TaV_2. However, in the other two compounds this group disappears because these compounds do not possess f states. (2) Moving from Ti to Hf, Ta, Nb causes a significant change in the structures of the A-s/p/d and V-s/p/d partial densities of states. (3) All the structures are shifted by around 0.5 eV towards lower energies when we move from Ti to Hf and Ta, whereas they shift toward higher energies by around 0.5 eV when we move from Ta to Nb. (4) More bands cut E_F, resulting in increasing $N(E_F)$.

Now we elucidate the feature of chemical bonding from the nature of total DOS and angular momentum projected DOS (partial DOS). We observe that the DOS (for all compounds) ranging from -5.0 eV to E_F is larger for V-d states between (2.0–3.5 states eV^{-1}), V-p states (0.28–0.31 states eV^{-1}), A-s (0.14–0.22 states eV^{-1}) and A-p (0.16–0.28 states eV^{-1}) by comparing the total DOS with the angular momentum projected DOS of V-d, V-p, A-s and A-p states as shown in figures 2–4. These results show that some electrons from the V-p, A-s and A-p states transfer into occupied states and take part in weak covalent interactions between V and A atoms, and the substantial covalent interactions between V and A atoms. The A–V bonds have basically mixed ionic and covalent characters. Accordingly, we can also say that the covalent strength of V–A bonds is stronger than those ionic bonds.

4. Conclusion

The electronic properties of the Laves phase compounds AV_2 ($A = $ Ta, Ti, Hf and Nb) were calculated using the FP-LAPW method. The density of states at the Fermi level $N(E_F)$ are controlled by the overlapping of V-p/d, A-d and A-p states around the Fermi energy. $N(E_F)$ significantly increased as we move from Nb to Ta, Hf, Ti. Substituting Ti by Hf, Ta and Nb shows that A compounds play significant roles in changing the properties of these compounds. There is a strong/weak hybridization between the states. Our calculated cohesive energy per atom and the heat of formation per atom show reasonable agreement with the available theoretical results.

Acknowledgments

This work was supported from the institutional research concept of the Institute of Physical Biology, UFB (no. MSM6007665808) and the Institute of System Biology and Ecology, ASCR (no. AVOZ60870520).

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