First-principle investigations of structural and electronic properties of TMAI (TM = Fe, Co, and Ni) transition metal aluminides

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In the present work, we have investigated the structural and electronic properties of TMAI (TM = Fe, Co, and Ni) transition metal aluminides in the B2 structure, using first-principle calculations of the density functional theory (DFT) based on the linearized augmented plane wave method (FP-LAPW) as implemented in the WIEN2k code, in which the energy of exchange and correlation are treated by the generalized gradient approximation (GGA), proposed in 1996 by Perdew, Burke and Ernzerhof (PBE). The ground state properties have been calculated and compared with other calculations, and the electronic structures of all FeAl, CoAl, and NiAl compounds exhibited a metallic behavior. It was depicted that the density of states is characterized by the large hybridization between the s-p (Al) and 3d (Fe, Co, and Ni) states, which creates the pseudogap in the region of anti-bonding states. Moreover, the band structures of FeAl, CoAl, and NiAl are similar to each other and the difference between them is in the energy level of each band relative to the Fermi level.

Keywords: *first-principle calculations; intermetallics; electronic structures*

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1. Introduction

Many technological applications require the use of new intermetallic alloys by changing their stoichiometry and their crystal structures [1], which are considered a new class of fundamental materials for industry. They are used in structural materials (automotive, aerospace), magnetic, energy storage devices (batteries, hydrogen storage, heating elements), furnace hardware, corrosion-resistant tools and dies (piping for chemical industries, cladding, coatings), and electronic devices [2].

The development of a structural material with high specific resistance is still of considerable interest in the transport industry and aviation [3]. The particular interest lies in the FeAl, CoAl, and NiAl

transition metal (TM) aluminides, which possess a number of desirable physical and mechanical properties, such as high melting point, low density, good thermal conductivity, excellent high-temperature strengths, oxidation and corrosion resistance [4, 5], and interesting optical [6] and magnetic properties [1, 7], which make them promising for the high-temperature structural applications [2, 8–10].

The FeAl, CoAl, and NiAl (TM) aluminides in the B2-type crystal structures belong to the most intensively studied intermetallic compounds [11]. Very interesting are the earlier first-principle studies [12–25] and the recent theoretical study [26] that analyzed their phase stability, elastic constants, electronic structure, phonon frequencies, and magnetic properties. In addition, the recent experimental studies that investigated the thermal conductivity for combustion synthesis of CoAl and NiAl [4],

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and the thermal spraying in the TiAl, FeAl, and NiAl [5] are also worth mentioning.

In the present study, we have investigated the structural and electronic properties of FeAl, CoAl, and NiAl with the WIEN2k code and compared them with other theoretical and experimental works, using the generalized gradient approximation (GGA-PBE) with the Perdew, Burke and Ernzerhof (PBE) parameterization for the effects of exchange and correlation.

2. Method of calculations

The calculations of the present study were performed in the framework of the density functional theory (DFT) [27, 28]. We have employed the full-potential linearized augmented plane waves (FP-LAPW) method as implemented in the WIEN2k code [29]. The generalized gradient approximation in the Perdew, Burke and Ernzerhof scheme (GGA-PBE) [30] was used for the exchange and correlation effects in order to calculate the structural parameters and electronic properties of TMAI (TM = Fe, Co, and Ni) compounds. FeAl, CoAl, and NiAl (TM) aluminides have a simple B2 (or CsCl) structure with a space group (Pm-3m), where the Fe, Co, and Ni atoms are located at position (0, 0, 0) and Al atom is at (0.5, 0.5, 0.5), as shown in Fig. 1.

Fig. 1. Crystal structure of TMAI (TM = Fe, Co, Ni).

The values of non-overlapping muffin-tin radii were chosen as 2.4 (a.u.) for (Fe, Co, and Ni) atoms, and 2.1 (a.u.) (atomic units) for Al atom. We have expanded the wave functions in the interstitial region to plane waves with a cut-off of $K_{\max} = 7.0/R_{\text{MT}}$ (where $K_{\max}$ is the magnitude of

the largest K vector in the plane wave and R_{MT} is the average radius of the muffin-tin spheres). The maximum value for partial waves inside the atomic sphere was $l_{\max} = 10$. The charge density was Fourier expanded up to $G_{\max} = 12 \text{ (a.u.)}^{-1}$. For the sampling of the Brillouin zone, the $(11 \times 11 \times 11)$ Monkhorst-Pack mesh [31, 32] was utilized in all calculations, where the self-consistent convergence of the total energy was at 0.1 mRy.

3. Results and discussions

3.1. Structural properties

The calculated total energies as a function of equilibrium volumes were fitted with the empirical Murnaghan's equation of state [33] to obtain the equilibrium lattice constant a_0 , bulk modulus B_0 and its pressure derivative B'_0 for FeAl, CoAl, and NiAl compounds. The variation of total energy-volume curves are shown in Fig. 2. Our results and various theoretical [15, 34] and experimental data [35–37] are summarized in Table 1.

Fig. 2. Variation of total energy ΔE (mRy) as a function of the volume $V \text{ (a.u.)}^3$ for FeAl, CoAl, and NiAl.

The ground state properties, such as a_0 , B_0 , and B'_0 for the studied compounds are very close to the theoretical [15, 34] and stay in good agreement with the experimental ones [35–37] as depicted in Table 1. The computed lattice constant and bulk modulus (a_0/B_0) deviate from the

Table 1. Calculated lattice constant a_0 , bulk modulus B_0 and its pressure derivative B'_0 for FeAl, CoAl, and NiAl.

compound	a_0 (Å)	B_0 (GPa)	B'_0
This work			
FeAl	2.870	179.95	4.26
CoAl	2.853	179.89	4.42
NiAl	2.894	159.32	4.34
Other calculations			
FeAl	2.869 [34] 2.903 [35]	180 [34] 136 [35]	4.00 [15]
CoAl	2.853 [34] 2.861 [36]	179 [34] 162 [36]	4.4±0.3 [15]
NiAl	2.894 [34] 2.887 [37]	159 [34] 156 [37]	4.2±0.5 [15]

theoretical calculations [34] of GGA-PBE [30] of 0.035 % / -0.027 %, 0 % / 0.49 %, and 0 % / 0.20 % for FeAl, CoAl and NiAl, respectively. Also the lattice constant deviates from experimental data [35–37] of -1.13 %, -0.27 %, and 0.24 % for FeAl, CoAl, and NiAl, respectively. We noticed that the CoAl has the smallest lattice parameter, and the bulk modulus B_0 decreases going from FeAl to CoAl to NiAl.

3.2. Electronic properties

The calculated total (T) and partial (P) densities of states (DOS) for FeAl, CoAl, and NiAl are illustrated by Fig. 3, 4, 5, and 6. The deepest regions of TDOS are dominated by the contributions of 3d (Fe, Co, and Ni) states, which are split into two parts t_{2g} and e_g symmetry states due to the crystal field of cubic structure [1, 12] as shown in Fig. 4, 5, and 6. Fig. 3 depicts that TDOS are composed by two peaks of high density, the large peak represents the bonding (t^b) states dominated by the 3d- t_{2g} (Fe, Co, and Ni) states, and the lower peak represents the anti-bonding (t^a) states dominated by the 3d- e_g (Fe, Co, and Ni) states (Fig. 4, 5, and 6). The intensities of the two peaks increase from FeAl to CoAl to NiAl as the transition metal atomic number increases going from Fe to Co to Ni.

Furthermore, we observed the large hybridization between the s-p (Al) and 3d (Fe, Co, and

Fig. 3. Total density of states for FeAl, CoAl, and NiAl. The Fermi level is set to zero (vertical dotted line).

Ni) states (Fig. 4, 5, and 6); this creates a pseudogap [20, 38] above the 3d- t_{2g} and below the e_g states which leads to a separation between the bonding and anti-bonding states [39]. The bottom of the valence band is dominated by a small contribution of s (Al) states, and their hybridization with 3d- t_{2g} (Fe, Co, and Ni) states is almost absent. In addition, it can be seen in PDOS (Fig. 4, 5, and 6) that there are significant falls in the curves of s (Al) states compared with 3d (Fe, Co, and Ni) states,

Fig. 4. Partial density of states for: (a) s of (Fe, Al), (b) p of (Fe, Al), (c) (e_g , t_{2g}), (d) of Fe, and (d) total of Fe. The Fermi level is set to zero (vertical dotted line).

Fig. 5. Partial density of states for: (a) s of (Co, Al), (b) p of (Co, Al), (c) (e_g , t_{2g}), (d) of Co, and (d) total of Co. The Fermi level is set to zero (vertical dotted line).

which explains the charge transfer from Al atom to (Fe, Co, and Ni) atoms.

Moreover, Fig. 4, 5, and 6 depict that the Fermi level (E_F) is located in the 3d bands for FeAl and CoAl, while it is moved over 3d band for NiAl [13]. In the case of FeAl, this level is situated just above the bonding states, thus, these states are almost completely filled [41]. For CoAl, the E_F is located in the pseudogap at the bottom of the anti-bonding

states, and it is situated above the occupied anti-bonding states for NiAl [19, 40]. Therefore, the bonding states are completely filled and shifted to higher binding energies for CoAl and NiAl, what explains that these latter compounds are more stable than FeAl [41].

The calculated Fermi energy (E_F) and densities of states $N(E_F)$, $3d(E_F)$, $t_{2g}(E_F)$, and $e_g(E_F)$ at Fermi level for each compound and other

Fig. 6. Partial density of states for: (a) s of (Ni, Al), (b) p of (Ni, Al), (c) (e_g , t_{2g}), (d) of Ni, and (d) total of Ni. The Fermi level is set to zero (vertical dotted line).

theoretical calculations [19, 26, 40] are summarized in Table 2. Our results depict that the difference between the values of Fermi energies of FeAl, CoAl, and NiAl barely exceeds 0.043 Ry. The $N(E_F)$ of FeAl is in good agreement with theoretical value [26] determined by GGA-PBE [30]. The computed $N(E_F)$ are consistent with other calculations for FeAl [40], CoAl [19], and NiAl [40]. However, the values of $3d(E_F)$ decrease going from

FeAl to CoAl to NiAl, in which the density of states is dominated by the major contributions of the $t_{2g}(E_F)$ states and $e_g(E_F)$ states for FeAl and (CoAl and NiAl), respectively. We can also notice that the non-null density of states, $N(E_F)$ at Fermi level, reveals the metallic conductivity of FeAl, CoAl, and NiAl [26, 42].

Fig. 7. Band structure of FeAl. The Fermi level is set to zero (horizontal dotted line).

The band structures along high symmetry direction in the first Brillouin zone of FeAl, CoAl, and NiAl are presented in Fig. 7, 8, and 9, respectively. The calculated band energies at high-symmetry points, such as Γ_1 , Γ_{12} , $\Gamma_{25'}$, R_{12} , and $R_{25'}$ with other theoretical values [19] are given in Table 3. The band energies of Γ_{12} , $\Gamma_{25'}$, and $R_{25'}$ increase with increasing in the transition metal atomic number going from Fe to Co to Ni, while R_{15} decreases from FeAl to CoAl to NiAl and R_{12} increases from CoAl to FeAl to NiAl. The width of the 3d band is calculated from the difference between two energies $R_{25'}$ and R_{12} . Our results are in good agreement with other theoretical calculations [19]. We note that this width increases from FeAl to NiAl to CoAl.

Table 2. Calculated Fermi energy E_F (Ry), and densities of states $N(E_F)$, $3d(E_F)$, $t_{2g}(E_F)$, $e_g(E_F)$ (states/ Ry cell) at Fermi level for FeAl, CoAl, and NiAl.

Compound	E_F	$N(E_F)$	$3d(E_F)$	$t_{2g}(E_F)$	$e_g(E_F)$
This work					
FeAl	0.62010	42.65	36.84	31.23	5.60
CoAl	0.65247	09.14	07.15	00.80	6.35
NiAl	0.61009	11.96	07.12	01.60	5.53
Other calculations					
FeAl		42.16 [26]			
		42.88 [40]			
CoAl		08.65 [19]			
NiAl		11.75 [40]			

Table 3. Calculated band energies at high-symmetry points (eV) with respect to Fermi level for FeAl, CoAl, and NiAl.

Compound	Γ_1	Γ_{12}	$\Gamma_{25'}$	$\Gamma_{12} - \Gamma_{25'}$	R_{12}	$R_{25'}$	$R_{25'} - R_{12}$	R_{15}
This work								
FeAl	10.32	2.20	0.18	2.02	0.93	3.29	2.36	3.13
CoAl	11.10	2.99	0.87	2.12	0.23	3.96	3.73	2.33
NiAl	11.08	3.18	1.51	1.67	0.96	4.05	3.09	1.97
Other calculations [19]								
FeAl	10.87	2.76						
CoAl	11.69	3.39	0.87	2.52	0.21	4.23	4.02	
NiAl	11.69	3.62	1.58	2.04	1.05	4.32	3.27	

4. Conclusion

The first-principle calculations of the density functional theory (DFT) within the full-potential linearized augmented plane waves (FP-LAPW) method and GGA-PBE approximation were used to investigate the structural and electronic properties of FeAl, CoAl and NiAl transition metal aluminides in the B2 structure. We disclosed that the computed ground state properties, such as the lattice constant, the bulk modulus and its first derivative, are very close to other theoretical results and stay in good agreement with the experimental ones. For the densities of states, we depicted large hybridizations between the s-p (Al) and 3d (Fe, Co and Ni), and revealed important falls in the s (Al) states at the bottom of valence band, which explain the charge transfer from Al atom to (Fe,

Co, and Ni) atoms. Moreover, we showed that the strong hybridizations between the p (Al) and 3d- t_{2g} states for FeAl, and between p (Al) and 3d- e_g states for both CoAl and NiAl, create pseudogaps that split the densities of states into two regions: the bonding and anti-bonding states. Also, the non-null densities of states around the Fermi level are principally dominated by the 3d- t_{2g} (Fe) and 3d- e_{2g} (Co and Ni) for FeAl and (CoAl and NiAl), respectively, revealing the metallic behavior of FeAl, CoAl, and NiAl. The band structures of FeAl, CoAl, and NiAl compounds are similar, and the differences between them are in the values of band energies at high-symmetry points relatively to the Fermi level. This is due to the difference in the transition metal atomic numbers of (Fe, Co, and Ni). Besides, the absence of band gaps in the band structures confirms the metallic character of FeAl, CoAl, and NiAl compounds under study.

Fig. 8. Band structure of CoAl. The Fermi level is set to zero (horizontal dotted line).

Fig. 9. Band structure of NiAl. The Fermi level is set to zero (horizontal dotted line).

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