JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 17, No. 5-6, May – June 2015, p. 827 - 833

First-principles studies on structural and electronic properties in AlX-type (X= Sc, Ti, Fe, Co, Ni,Y, Zr and Hf) intermetallic compounds

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The structural properties, phase stability and electronic structures of AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds have been systematically investigated by using first-principles calculations. The calculated equilibrium structures and enthalpies of formation in present work are in good agreement with the available experimental and other theoretical data, and the results of enthalpies of formation show that YAl is the most stable. The electronic structure was further investigated to understand the underlying mechanism of the structural stability of the AlX compounds. The results can provide helpful guidance for future measurement and design of new high-temperature structural materials.

(Received April 15, 2015; accepted May 7, 2015)

Keywords: First-principles; XAl compounds; Phase stability; Electronic structures

1. Introduction

Aluminum (Al) alloys with alloying elements Sc, Ti, Ni, Co, Y, and Zr are technologically important due to their low density and high tensile strength at high temperature, and are the most widely applied to aircraft engines, weapons, thermal nuclear reactors and power generation systems as the high-temperature structural materials [1-4]. Accordingly, phase stability, electronic and structural properties of compounds in Al alloys are critical information in designing materials with desired properties.

Recent studies show that electronic structure (chemical bonds between atoms) and energetic properties essentially determines the structural or phase stability. However, the related data of AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds is very scarce due to the complexity of sample preparation and the limitation of the experimental test [5,6]. It is very important to understand the nature of phase stability for intermetallic compounds from the view of the electronic structure.

The fundamental understanding of both the mechanical properties and phase stability of intermetallics provided by the results of quantum–mechanical electronic structure calculations has been significantly improved over the last 20 years. Ab initio or first-principles methods based upon electronic density-functional theory (DFT) [7] have been employed to derive a number of bulk and defect properties including enthalpy of formation, the relative stability of competing structures, elastic constants, lattice parameters, and the energies associated with point and planar defects [8,9].

In this paper, we attempt to calculate the structural, energetic and electronic properties of AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds by using the pseudopotential plane-wave method based on density functional theory. The stability of the compounds is revealed from the enthalpies of formation and the bonding nature in atomic or electronic scale.

2. Computational Method

All calculations were performed by using the first principles calculations based on density functional theory (DFT) [10] implemented in Quantum-ESPRESSO program package [11]. Meanwhile, the exchange and correlation energies are calculated with in the generalized gradient approximation of Perdew-Wang91 version (GGA-PW91). The Monkhorst-Pack scheme [12] was used for *k* point sampling in the first irreducible Brillouin zone (BZ). The *k* points separation in the Brillouin zone of the reciprocal space were 18×18×18, 12×12×6, 18×18×18, 18×18×18, 18×18×18, 15×12×18 and 15×12×18 for ScAl, TiAl, FeAl, CoAl, NiAl, YAl, ZrAl and HfAl, respectively. The cutoff energy for plane wave expansions was determined as 540 eV after convergence tests. The valence electronic configurations were Al ($3s^23p^1$), Sc ($3s^23p^63d^14s^2$), Ti ($3s^23p^63d^24s^2$), Fe ($3s^23p^63d^64s^2$), Co ($3s^23p^63d^74s^2$), Ni ($3s^23p^63d^84s^2$), Y ($4s^24p^64d^15s^2$), Zr ($4s^24p^64d^25s^2$) and Hf ($5s^25p^65d^26s^2$) in the calculations. The convergence criteria for geometry optimization were as follows: electronic self-consistent field (SCF) tolerance less than 5.0×10^{-7} eV/atom, Hellmann–Feynman force below 0.01eV/Å, maximum stress less than 0.05GPa and displacement within 2.0×10^{-4} Å. After the structures were optimized, the total energies were recalculated self-consistently with the tetrahedron method. The latter technique was also used to calculate the electronic density of states (DOS). The crystal structures of eight stable AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds are shown in Fig. 1.

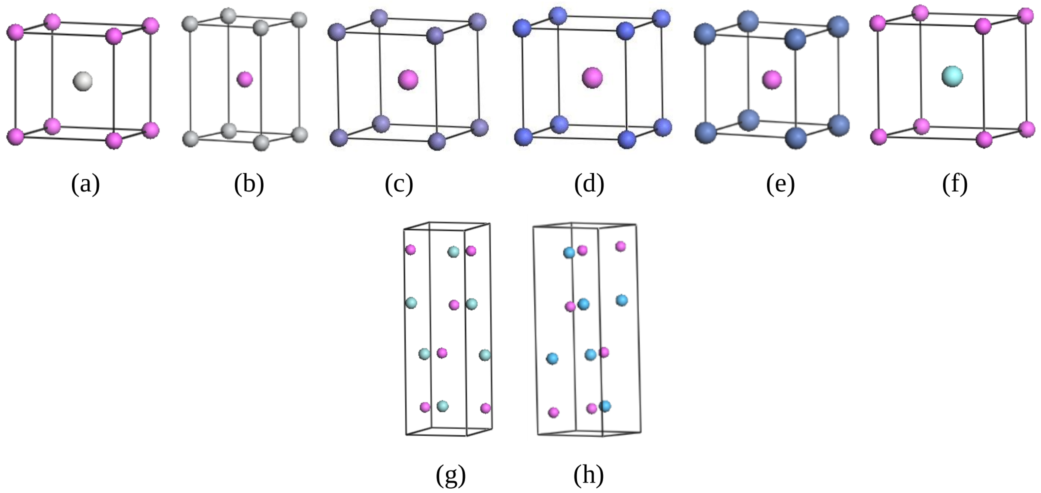


Fig. 1. The crystal structures of XAl (X= Sc,Ti, Fe, Co, Ni,Y, Zr and Hf) intermetallic compounds, (a) ScAl, (b) TiAl, (c) FeAl, (d) CoAl, (e) NiAl, (f) YAl, (g) ZrAl and (h) HfAl. The purple balls represent Al and other balls represent transition metal atoms.

3. Results and discussions

3.1 Structural properties

In this work, the original crystal structures have been built based upon the experimental crystallographic data of eight stable AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds [13-20]. Starting from the above crystal structures, the structural optimization was first performed by full relaxation of cell shape and atomic positions. The optimized lattice parameters are listed in Table 1, where the available experimental results were also presented. The calculated lattice parameters of X-Al intermetallic compounds agree very well with the available experimental data and previous calculations by Wang et al. [21] and Tao et al. [22] with an error less than 2% except for the YAl compound, which is 3.64% smaller than the experimental data. These agreements of optimized lattice parameters with the experimental values provide a confirmation that the computational methodology utilized in this work is suitable and reliable.

Table 1 Calculated and experimental lattice parameters, total energy E_{tot} and enthalpy of formation ΔH for AlX (X= Sc, Ti, Fe, Co, Ni, Y, Zr and Hf) intermetallic compounds

Alloys	Space group	Lattice parameters (Å)			E_{tot}	ΔH (kJ/mol)		
		a	b	c	(eV)	This work	Expt.	CALPHAD
ScAl	*Pm-3m*	3.376			-1333.3617	-44.26	-46[23]	
		3.380[13]						
TiAl	*P4/mmm*	2.832	2.832	4.058	-1659.9091	-40.88	-40.1[24]	-39.82[25]
		2.829[14]	2.829[14]	4.071[14]				
FeAl	*Pm-3m*	2.849			-928.4103	-27.74	-24[26]	
		2.910[15]						
CoAl	*Pm-3m*	2.850			-1101.1083	-56.88	-59.80[27]	-69.3[28]
		2.866[16]						
NiAl	*Pm-3m*	2.900			-1415.1583	-62.60	-65.7[24]	-66.13[29]
		2.877[17]						

Alloys	Space group	Lattice parameters (Å)			E_{tot}	ΔH (kJ/mol)		
		a	b	c	(eV)	This work	Expt.	CALPHAD
YAl	*Pm-3m*	3.617			-250.1284	-88.28	-89.9[30]	-86.91[25]
		3.754[18]						
ZrAl	*Cmcm*	3.418	10.887	4.257	-2678.5018	-43.72	-53[31]	-44.5[25]
		3.362[19]	10.892[19]	4.274[19]				
HfAl	*Cmcm*	3.231	10.883	4.336	-928.3614	-42.86	-39.9[32]	-45.2[33]
		3.240[20]	10.803[20]	4.278[20]				

3.2 Enthalpies of formation

In order to understand the formation stability of the binary Al-X intermetallic compounds, the enthalpies of formation for eight compounds were calculated according to the following expressions [34]:

$$\Delta H = (E_{\text{tot}} - N_{\text{Al}} E_{\text{tot}}(\text{Al})_{\text{solid}} - N_X E_{\text{tot}}(\text{X})_{\text{solid}}) / (N_{Al} + N_X) \tag{1}$$

where E_{tot} is the total energy of AlX compounds in equilibrium lattice per unit; $E_{\text{tot}}(\text{Al})_{\text{solid}}$ and $E_{\text{tot}}(\text{X})_{\text{solid}}$ are the total energy of fcc Al and transition metals in their stable state per unit cell, respectively; N_{Al} and N_{X} refer to the numbers of Al and transition metals atoms in unit cell of AlX compounds, repectively. In the present work, we calculate the single atomic energy by the following method: at first, the energy of a pure metal crystal in the solid state was calculated, then the energy was divided by the number of atoms involved in the crystal, and this result is the energy of a single atom in the pure metal. The calculated energies of Al, Sc, Ti, Fe, Co, Ni, Zr, Y and Hf pure metals for our considered systems were -52.8091 eV, -1279.6351 eV, -1606.2525 eV, -875.0262 eV, -1047.1202 eV, -1361.0515 eV, -1285.5356 eV, -195.4894 eV and –410.4832 eV, respectively.

The calculated enthalpies of formation of the eight binary compounds together with their available experimental and other theoretical calculated data [23-33] are tabulated in Table 1. The calculated enthalpies of formation reveal that YAl compound has the most negative enthalpy of formation and YAl is the most stable. Fig. 2 shows the comparison of calculated enthalpies of formation for the binary compounds in the Al-X systems with the available experimental data and calculated values from CALPHAD approach (see Table 1 for detailed values).

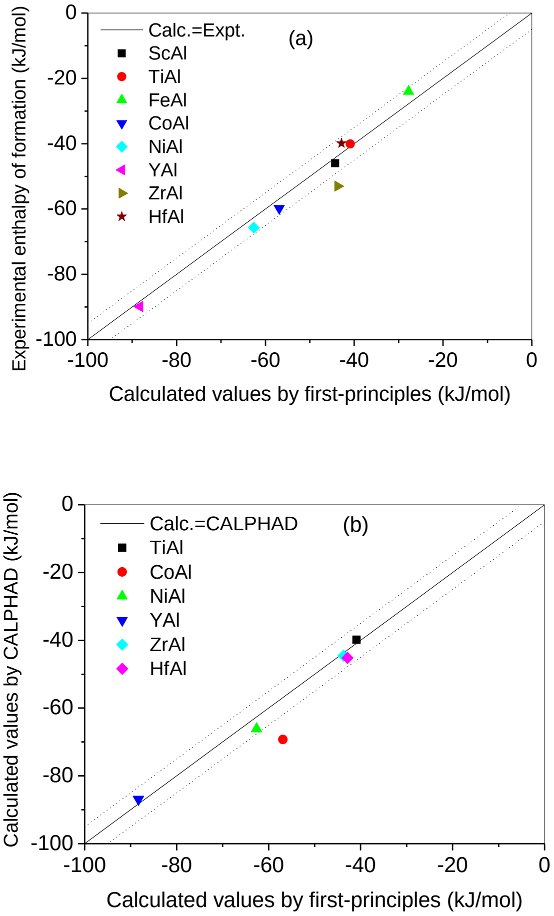


Fig. 2. Comparison of calculated enthalpies of formation in this work for the Al-X intermetallic compounds with the experimental measurements (a) and the calculated values by CALPHAD (b). The solid line shows unity (y = x), and the dashed lines present an error range of ±5 kJ/mol.

In Fig. 2, the solid line implies a perfect agreement between the present calculated and experimental values (CALPHAD calculated values), and two dashed lines are represented an error bar of ±5 kJ/mol. The calculated enthalpies of formation compare favorably with experimental data for most compounds, while the largest discrepancy between first-principles and experimental data is found for the ZrAl compound. It is worth noting that the similar observation was found in the ZrAl compounds [21] between first-principles predictions and experimental data. The disagreement between the present results and the measurements suggests further experimental validations are needed for the enthalpies of formation of ZrAl compound. The enthalpies of formation from first-principles calculations also are compared with CALPHAD approach (Fig. 2(b)) for those compounds. For most of the compounds, the differences are within ±5 kJ /mol, except for the CoAl compound. The enthalpies of formation for the CoAl compound obtained from CALPHAD approach by Dupin et al. [28] is -69.3 kJ/mol more negative than the measured value [27], while the present value agrees with the measured value [27], as shown in Table 1. This suggests that the CALPHAD-type enthalpies of formation for the CoAl compounds need to be updated.

3.3 Electronic structures

To obtain further insight into the nature of the bonding in Al-X intermetallic compounds, the density of states (DOS) and the charge density distribution for eight compounds were calculated. Fig.3 show the total densities of states (TDOS) and partial densities of states (PDOS) for Al-X intermetallic compounds, in which the Fermi level was set to zero. The values of the total DOS at Fermi level was larger than zero for all compounds, which indicated the metallic behavior.

The DOS shown in Fig. 3 reveal that, for these compounds, the part of TDOS in energy range between -4.0 eV and the Fermi level are mainly contributed by Al 3p and transition metal atoms 3d, 4d or 5d states. It indicates that the Al 3p states hybridize strongly with the transition metal atoms 3d, 4d or 5d states in the region, and atomic bonds would be formed between Al and transition metal atoms. While the part of TDOS at the lower energy region (-10.0 eV to -4 eV) are primarily contributed by the Al 3s and Al 3p states. It can be seen that the sp states of Al atoms are very strong in the lower energy region. Besides, it is worth noting that the TDOS of YAl is the presence of a valley near the Fermi level, and this valley is referred to as a pseudo-gap. The pseudo-gap may indicate the presence of covalent bonding. As a result, the maximum band-filling state is most easily reached in YAl than the other compounds, thus YAl is the most stable compound. The conclusion can be also supported by the bonding electron numbers at the Fermi level, $N(E_F)$ for these compounds. $N(E_F)$ is 1.15, 3.49, 2.32, 1.02, 0.99, 0.97, 3.21 and 2.43 for ScAl, TiAl, FeAl, CoAl, NiAl, YAl, ZrAl and HfAl, respectively. In general, $N(E_F)$ on DOS plot can be used to characterize the activity of valance electrons of the atoms in crystal. Namely, the smaller $N(E_F)$, the less is change probability of the electronic structures of the crystal when external conditions change, thus the crystal has the higher stability [34]. It is shown that the stability of YAl is highest of eight compounds.

In order to gain further understanding of the bonding characteristics of Al-X intermetallic compounds, the charge density distribution has been also investigated. Fig. 4 displays the calculated charge density distribution maps in the (111) plane for ScAl, TiAl, FeAl, CoAl, NiAl, YAl, and in the $(1\bar{1}0)$ plane for ZrAl and HfAl. In these figures, the X atoms and Al atoms are in the center position. The color indicates bonding charge value; red denotes an increase of accumulated charge after bonding, blue indicates a charge density depletion. From Fig. 4, it can be seen that the near spherical charge distribution around Al and X atoms in all compounds which indicates a metallic bonding. It is evident that there exists a overlap of charge between Al and X atoms. The overlap of bonding charge density between Al and X atoms becomes stronger and stronger from Sc to Ni (i.e. from group 3 to group 8), and indicates a covalent bonding. Although the different X transition metals affect the Al–X bonds character severely, they hardly change the Al–Al bonding. This feature implies that the d-p hybridization for Al–X bonding, which is associated with electrons characteristics of transition metals, play an important role in these intermeallics. These results are consistent with the observed hybridized states in Fig. 3.

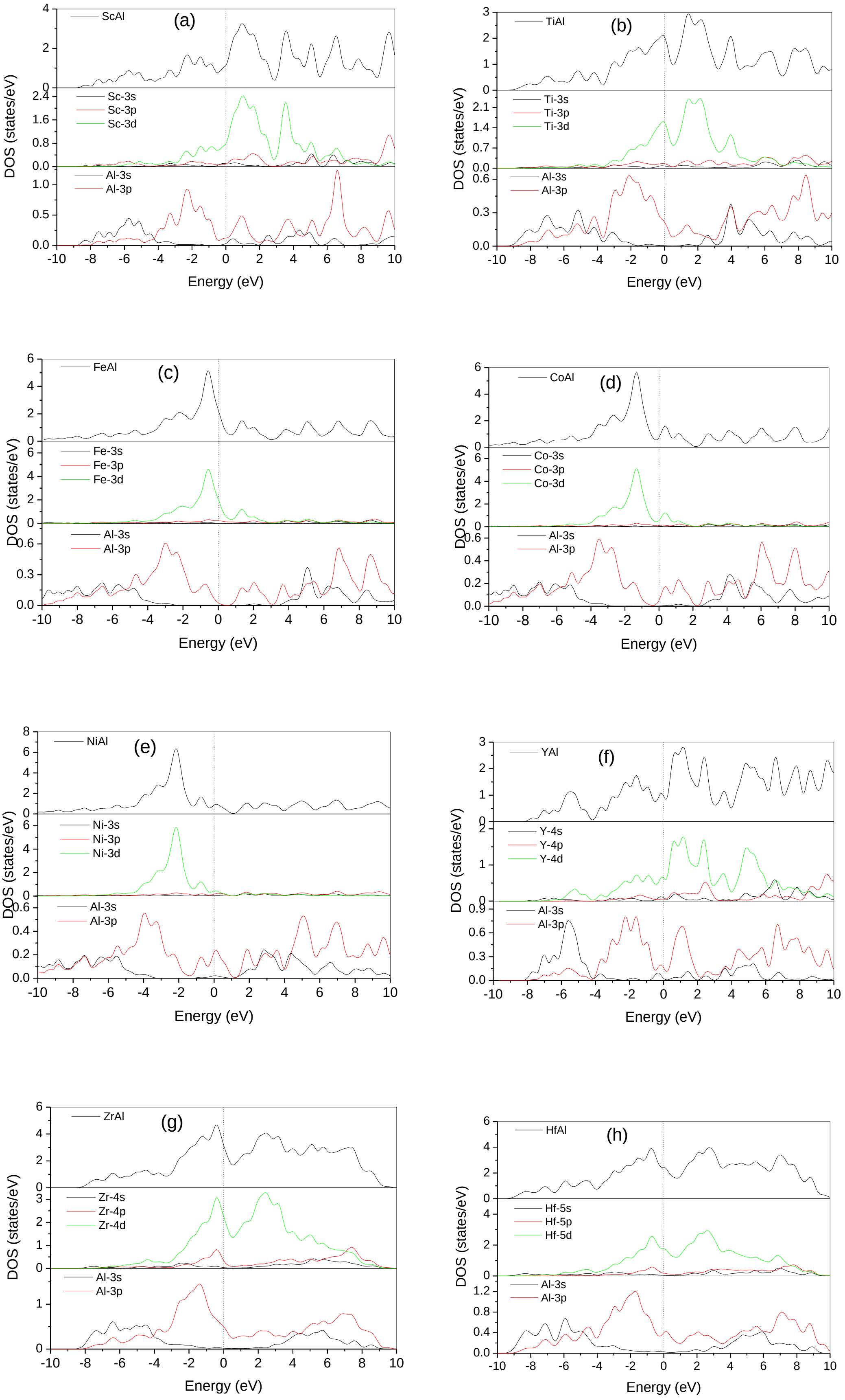
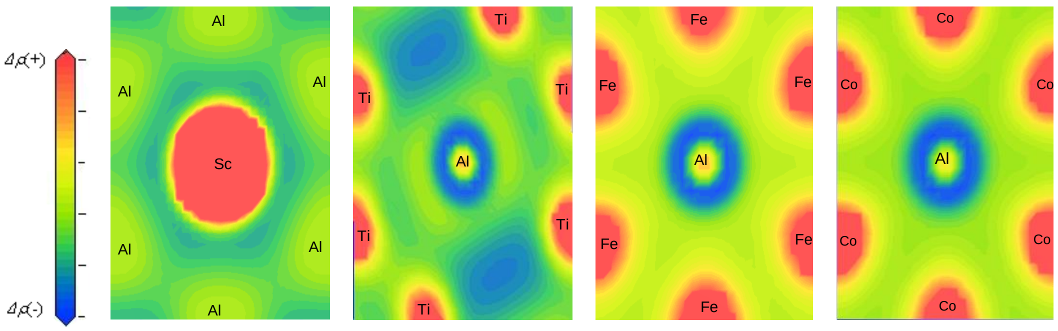
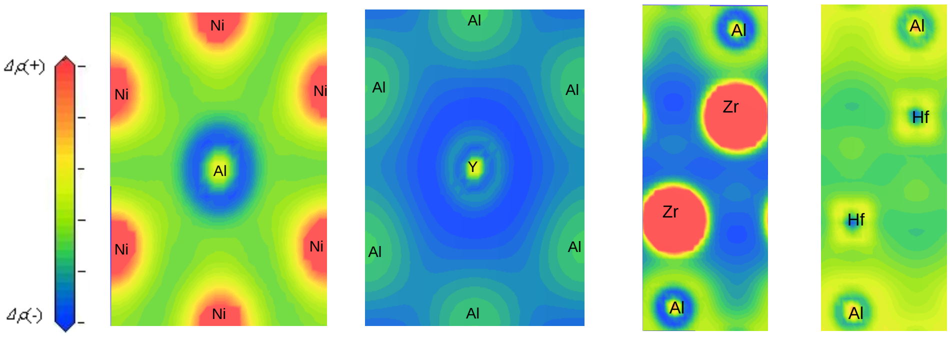


Fig. 3. Total and partial electronic densities of states near Fermi level of Al-X intermetallic compounds, (a) ScAl, (b) TiAl, (c) FeAl, (d) CoAl, (e) NiAl, (f) YAl, (g) ZrAl, (h) HfAl. The dotted lines denote the Fermi level E_F.



(a) ScAl (b) TiAl (c) FeAl (d) CoAl



(e) NiAl (f) YAl (g) ZrAl (h) HfAl

Fig. 4. The charge density distribution for Al-X intermetallic compounds in the (111) plane (ScAl, TiAl, FeAl, CoAl, NiAl and YAl) and in the $(1\bar{1}0)$ *plane (ZrAl and HfAl).*

4. Conclusions

In summary, the structural properties, phase stability, densities of states, and charge density distribution of the eight stable Al-X intermetallic compounds have been investigated using first-principles methods based density functional theory in this work. The calculated lattice parameters have a great agreement with experimental results. The calculated enthalpies of formation reveal that YAl compound has the most negative enthalpy of formation and YAl is the most stable. Electronic densities of states and the charge density have shown that Al-X intermetallic compounds exhibit metallic characteristics and the d-p hybridization for Al–X bonding becomes stronger and stronger from Sc to Ni and indicates a stronger covalent bonding. The results can provide helpful guidance for future measurement and design of new high-temperature structural materials.

Acknowledgement

The authors gratefully acknowledge the financial support by the program for Shenyang Ligong University Key Laboratory Opening Fund in advanced materials processing technology in Liaoning Province, China and by the program for Liaoning Excellent Talents in University (LNET), China.

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