



Effect of Si substitution on electronic structure and magnetic properties of Heusler compounds $\text{Co}_2\text{TiAl}_{1-x}\text{Si}_x$

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ABSTRACT

The electronic structures of Co-based Heusler compounds $\text{CoTiAl}_{1-x}\text{Si}_x$ ($x=0, 0.25, 0.5, 0.75$ and 1) are calculated by first-principles using the full potential linearized augmented plane wave (FP-LAPW) method within GGA and LSDA+U scheme. Particular emphasis was put on the role of the main group elements. In recent years, the GGA calculations of Co_2TiAl ($x=0$) and Co_2TiSi ($x=1$) indicated that they are half-metallic, but the electronic structure of this compound with $x=0.25, 0.5$ and 0.75 has not been reported yet, neither theoretically nor experimentally. The calculated results reveal that these are half-metallic and exhibit an energy gap in the minority spin state and also show 100% spin polarization. The substitution of Al by Si leads to an increase in the number of valence electrons, with increasing x . Our calculated results clearly show that with the Si doping, the lattice parameter linearly decreases; bulk modulus increases, and the total magnetic moment increases. The calculated energy gap in the minority spin state, using GGA scheme, was smaller than that obtained by using LSDA+U scheme. The outcomes of this research also show that the Co-3d DOS and therefore, the magnetic properties of compounds are dependent on electron concentration of the main group elements and it will affect the degree of p-d orbital occupation.

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1. Introduction

Half-metallic ferromagnets (HMFs) [1] have attracted scientific and technological interest due to their potential use as a highly spin-polarized current source in spintronics, magneto-electronic devices and ferromagnetic shape memory effect [2–9]. HMFs exhibit a strongly metallic behavior in one spin band (spin-up) at the Fermi energy level, E_F , and at the other spin band (spin-down), they behave like a semiconductor, which results in a 100% spin polarization at E_F [10]. They serve as a model for the understanding of band-magnetism of d-electrons due to their simple crystallographic structure and a series of interesting diverse magnetic phenomena like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy fermion behavior can be seen in these compounds [11].

The Heusler compounds as the half metallic ferromagnet are usually ternary compounds with the stoichiometric composition X_2YZ where X and Y represent transition metals and Z represents a main group element. They crystallized in the $L2_1$ structure (space group $\text{Fm}\bar{3}\text{m}$) which is depicted, as an example for Co_2TiAl compound, in Fig. 1. Besides ternary X_2YZ compounds, there exist large assortments of substitutional quaternary alloys of the type $\text{X}_2\text{Y}_{1-x}\text{Z}_x$ or $\text{X}_2\text{YZ}_{1-x}\text{Z}'_x$ [12]. The $L2_1$ crystal structure consists of four fcc

sublattices as X at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Y at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and Z at $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ [13]. However, these alloys can transform into the B_2 (disorder between Y and Z atoms) or A_2 (disorder between X, Y and Z atoms) structure or a combination of the above structures, depending on their thermodynamic equilibrium [14]. Such a mixture of atoms in Y and Z positions can destroy the half-metallic properties [15]. In the Heusler compounds, the electronic structure plays an important role in determining the magnetic properties and predicting half-metallic ferromagnetism as the temperature stability of the energy gap in the minority (spin-down) spin states is one of the important questions for materials to be used in applications. Depending on the situation of E_F , several different effects may destroy the half-metallicity at finite temperatures such as spin-rotation, the lattice parameter and defect densities changed at elevated temperatures [16].

Amongst some kinds of the Heusler alloys, the Co-based Heusler alloys Co_2YZ are especially attractive for their predicted high spin polarization and high Curie temperature [17] as well as varying magnetic moments at Co sites depending on the constituents Y and Z [18–20], making them attractive for various industrial application. As we know, Co provides the highest Curie temperature among all 3d transition metals [21]. In these compounds, the magnetic moment per Co atom ranges from 0.3 to $1.0\mu_B$ in contrast with Mn-based Heusler alloys X_2MnZ (where X is not Co) with almost constant moments of approximately $4\mu_B$ on the Mn atom [18]. It is found that the Curie temperature (T_C) of the Heusler compounds decreases linearly as the total spin moment decreases [22].

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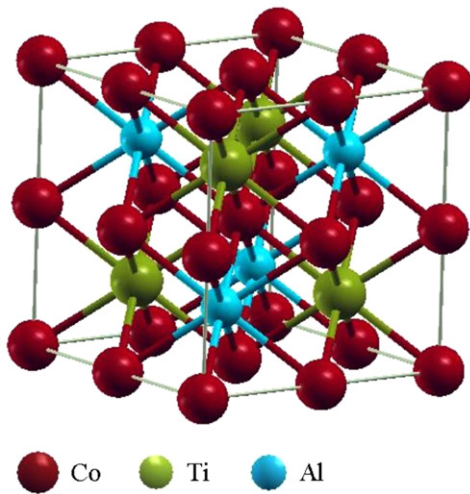


Fig. 1. L₂₁-type structure of Co₂TiAl compound.

In this paper, we have compared the obtained results of the electronic structures using two different methods i.e., GGA and LSDA+U schemes implemented in WIEN2k code [23,24]. Electronic structure calculations for the Heusler compound Co₂TiAl_{1-x}Si_x were performed using the density functional theory (DFT). The compounds with $x=0$ and $x=1$ were already discussed in Refs. [10,13,25], while no results on compounds with $x=0.25$, 0.5 and 0.75 have been reported yet, to our knowledge. For the compounds with $x=0$ and 1, Fm3m symmetry was used and the compounds with $x=0.25$ and 0.75 were calculated in Pm3m symmetry and for $x=0.5$, P4/mmm symmetry was applied.

2. Computational details

We carried out the electronic structure calculation using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2k package. The exchange-correlation potential was taken within the generalized gradient approximation (GGA) [26] and in order to study the on-site correlation at the 3d transition metals, the LSDA+U [27] method was also used. It is, in the LSDA+U scheme, recommended that the effective Coulomb-exchange parameter $U_{\text{eff}}=U-J$ be used where U is the Coulomb part (Hubbard U) and J is the exchange part [28]. The value of U_{eff} obtained by using the Novak method [29] were set to $U_{\text{Co}}=0.1421$ Ry for the complete series Co₂TiAl_{1-x}Si_x. We expand the basis function up to $R_{\text{MT}}K_{\text{max}}=8$, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the maximum modulus for the reciprocal lattice vector. The maximum value for partial waves inside the atomic sphere (l_{max}) was set to 10. The number of K points in the irreducible Brillouin zone (IBZ) for self-consistent cycles is taken as 47 and the energy and charge convergence criterions were set to 10^{-5} Ry and 10^{-4} electrons, simultaneously. In our calculations spin-orbit coupling is neglected, but it may have strong influence on the spin polarization [30] when the Z atom is a heavy element such as Sn or Sb [31].

3. Results and discussion

3.1. Equilibrium structural properties

First, in order to compute the ground state properties, we carried out a volume optimization as illustrated in Fig. 2a for GGA and Fig. 2b for LSDA+U methods. During the optimization, we initially use experimental lattice constants taken from Refs.

[10,25]. The optimized lattice constants (in Angstrom) and calculated bulk moduli obtained by total energy minimizations are presented in Table 1. The experimental measurements data are also listed for comparison. The substitution of Al by Si leads to an increase in the number of valence electrons with increasing Si content and may be considered as electron doping. Using both schemes indicate that with increasing Si content, bulk modulus increases, but the lattice parameter decreases linearly in agreement with Vegard's law (as shown in Fig. 3) due to smaller atomic radius of Si than that of Al [32,33]. Calculated lattice constants obtained from LSDA+U are slightly smaller than that of GGA approximation. Agreement between our theoretical and experimental results, especially for the case of $x=0$ (within GGA scheme) and $x=1$ (within LSDA+U scheme), is excellent in comparison to other reported theoretical results [10,13].

3.2. Electronic properties

3.2.1. Density of state (DOS)

Fig. 4a and b show the total electronic density of states (DOS) for compounds Co₂TiAl_{1-x}Si_x within the GGA and LSDA+U methods, respectively. The origin of the energy scale is located at the Fermi energy. As one can see, a half-metallic ferromagnetic ground state is found for the complete series of Co₂TiAl_{1-x}Si_x as the calculated energy gap in spin-down band is larger for the LSDA+U compared with the GGA method. Furthermore, the width of energy gap calculated within the GGA and LSDA+U methods increases slightly with the increase of Si content. For $x=0$, the low lying s-states are found at energies below -6 eV which are attributed to the Al-3s occupied states (Figs. 5 and 6). These Al-3s states are very low in energy and also well separated from other states.

As shown in Fig. 4a and b, using both methods, with increasing Si content, a new group of s-states is found at energies below -8.5 eV which is related to Si s-states. These states are separated from p and d-states by the gap that increases with increasing x . In the spin-up states, in a range between -1 and -3.5 eV, a broadly multi-peak structure is manifested due to the contribution of spin-up bonding states between Co and Ti atoms (Figs. 6 and 7). However, the majority (spin-up) states are shifted towards lower energies as the s-p element varies from Al to Si because extra electrons must occupy accessible states in spin-up states and leads to an increase in total magnetic moment as presented in Table 2. A quantitative description can be deduced from Fig. 8. The dominant contribution for these states is related to the Co-3d states.

As shown in Fig. 6, which is obtained from the GGA method, for pure Co only the spin-up band of Co-3d states is fully occupied and an exchange splitting of about 1.69 eV is manifested, consistent with Co magnetic moment in its pure state. In the majority spin states of these compounds, Co-3d DOS exhibits the itinerant characteristic cutting the Fermi level, while the Ti-3d states are mainly unoccupied and hybridize with Co-3d states as shown in Figs. 6 and 7 for the GGA and LSDA+U schemes, respectively. In the minority spin states, Ti-d states are excluded from the Ti-site. From partial Co-3d DOS, two peaks below the E_F coincided with Ti-3d for spin-up electronic states prove the strong coupling (hybridization) between these states in forming a common d band. The occupied Co-3d states contribute to both the majority and the minority density of states, whereas the occupied Ti-3d states are mostly majority. So the peaks below and above the E_F in the total density of states, are due to bonding and anti-bonding states coupled between Co and Ti atoms.

It is worth mentioning that the contribution of s-p element (p states) is relatively small in this energy range (Fig. 5). However, the hybridization between the p states of s-p element (Z atom)

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