Effect of Cr on the electronic structure of Co₃Al intermetallic compound: A first-principles study

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Abstract

The effect of doping with Cr on the electronic structure and magnetism of Co₃Al has been studied by density functional calculations. It has been found that the Cr atom has a strong site preference for the B-site in Co₃Al. With the substitution of Cr for Co, the total densities of states (DOS) change obviously: A DOS peak appears at $E_F$ in the majority spin states and an energy gap is opened in the minority spin states. The effect of Cr in Co₃Al is mainly to push the antibonding peak of the Co (A,C) atoms high on the energy scale and to form the energy gap around $E_F$, and also to contribute to the large DOS peak at $E_F$ in the majority spin direction. The calculations indicate a ferromagnetic alignment between the Co and Cr spin moments. The calculated total magnetic moment decreases and becomes closer to the Slater–Pauling curve with increasing Cr content. This is mainly due to the decrease of the Co (A,C) spin moments. At the same time, the moments of Co (B) and Cr (B) only change slightly.

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1. Introduction

In the last decade, the so-called half-metals have attracted much attention for their interesting magnetic and transport properties and possible applications in spintronics [1–3]. The half-metal is semiconductor-like in one spin band at the Fermi level, and at the other spin band it is strongly metallic, which results in a complete (100%) spin polarization of the conduction electrons at $E_F$. It is known that a lot of magnetoelectronic devices operate on an imbalance in the number of majority and minority spin carriers at the Fermi level. So half-metals can be used as spin injectors for magnetic random access memories and for other spin-dependent devices [4].

Most half-metals are ferromagnets and also called half-metallic ferromagnets (HMFs). The first predicted HMF is NiMnSb, theoretically calculated by de Groot et al. [4]. In succession, some Heusler alloys have been theoretically predicted to be HMFs and experiments have been carried out to establish their magnetic and transport properties [5–13]. Calculations have also been performed on alloys with similar structures, such as Fe₄N and Mn₄N [14]. It has been found that the Cr atom plays an interesting part in the formation of the half-metallicity. Some Heusler alloys containing Cr, like Co₂CrAl [9], Co₂CrSi [10] and Fe₂CrSi [13], have been predicted as HMFs theoretically, though the corresponding binary alloys Co₃Al and Fe₅Si are only normal ferromagnetic alloys, and the doping of Cr in other Heusler alloys may be a promising way to synthesize new HMFs. So it is important to study the effect of Cr on the electronic structures of the Heusler alloys.

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In this paper, we study the influence of Cr on the electronic structure and magnetism of the binary Co$_3$Al alloy by first-principles calculations. It is found that with the substitution of Cr for Co, an energy gap is opened in the minority spin band at $E_F$, while in the majority spin states a large densities of states (DOS) peak is formed. The calculated total magnetic moment decreases and becomes closer to the Slater–Pauling curve with increasing Cr content, due to the decrease of the Co (A,C) spin moments.

2. Computational method

We carried out the electronic-structure calculations using the pseudopotential method with a plane-wave basis set based on density-function theory [15–17]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [18]. The local-density approximation (LDA) [19,20]. The plane-wave basis set cut-off was used as 500 eV for all the cases. In all, 182 $k$ points are employed in the irreducible Brillouin zone. These parameters ensure good convergences for total energy. The convergence tolerance for the calculations was selected as a difference in total energy within the $1 \times 10^{-6}$ eV/atom. Population analysis is performed using a projection of the PW states onto a localized basis. Analysis of the resulting projected states is then performed using the Mulliken formalism [21,22]. It is known that the substitution in Heusler alloys with proper values leads to ordered structures which can be easily used for the calculations. In this paper, we use the ordered mixed compounds for the calculation, which have the chemical formula of Co$_2$(Co$_{1-x}$Cr$_x$)Al$_4$ ($x=0$, 0.25, 0.5, 0.75, 1.0). Similar calculations have been performed on Co$_8$(Mn$_{1-x}$Fe$_x$)$_4$Si$_4$ and Co$_2$Cr$_{1-x}$Fe$_x$Al alloys and compared with the fully relativistic Korringa–Kohn–Rostocker (KKR) method, with the coherent potential approximation (CPA). No significant differences in the integrated properties, such as the DOS or magnetic moments, were found between the mixed ordered compounds and random alloys [23,24].

We have used the experimental lattice constants of Co$_3$Al and Co$_2$CrAl compounds for the calculations [25]. For the intermediate part of this series of alloys, we assume that the lattice constants vary linearly with the concentration, which has been used in Ref. [26] and gives reliable results.

3. Results and discussion

The Heusler alloy crystallizes in the L2$_1$ structure and has a stoichiometric composition of X$_2$YZ, where X and Y are transition metal elements, and Z is a main group element. Generally the Heusler structure can be looked upon as four interpenetrating face-centered-cubic (fcc) lattices, in which the X atoms occupy the A (0 0 0) and C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) sites, Y atom enters the B ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) site and Z atom occupies the D ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) site in the Wyckoff coordinates. The site preference of the 3d metals in Heusler alloys has been thoroughly studied. It is found that the site preference of different 3d elements in alloys is mainly determined by the number of their valence electrons, the 3d elements with less d electrons prefer to occupy the B sites, whereas elements with more electrons prefer the (A,C) sites [27]. So here in Co$_3$Al, the Cr atoms will enter the B sites in the crystal.

In order to testify the site preference of Cr in Co$_3$Al, we assume two kinds of site preferences in Co$_3$Al, one is Cr entering the B site, the other is Cr entering the (A,C) sites. The energy difference between the two configurations is

\[ \Delta E = E_B - E_{(A,C)} \]

Table 1

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Delta E$ (eV)</th>
<th>$M_A$ ($\mu_B$)</th>
<th>$M_{S-P}$ ($\mu_B$)</th>
<th>$M_{Co (A,C)}$ ($\mu_B$)</th>
<th>$M_{Co (B)}$ ($\mu_B$)</th>
<th>$M_{Cr (B)}$ ($\mu_B$)</th>
<th>$M_{Al}$ ($\mu_B$)</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0</td>
<td>3.90</td>
<td>6</td>
<td>1.18</td>
<td>1.66</td>
<td>–</td>
<td>–0.12</td>
</tr>
<tr>
<td>0.25</td>
<td>–0.20</td>
<td>3.72</td>
<td>5.25</td>
<td>1.04</td>
<td>1.68</td>
<td>2.06</td>
<td>–0.13</td>
</tr>
<tr>
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<td>3.52</td>
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<td>0.88</td>
<td>1.72</td>
<td>2.04</td>
<td>–0.13</td>
</tr>
<tr>
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<td>3.25</td>
<td>3.75</td>
<td>0.68</td>
<td>1.76</td>
<td>2.08</td>
<td>–0.13</td>
</tr>
<tr>
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<td>–1.10</td>
<td>3.00</td>
<td>3</td>
<td>0.50</td>
<td>–</td>
<td>2.14</td>
<td>–0.16</td>
</tr>
</tbody>
</table>

$M_{S-P}$ is the value derived from the Slater–Pauling curve.
shown in Fig. 1 and also listed in Table 1. It is clear that the total energy calculations strongly suggest that Cr enters the B site, which is lower in energy and more stable. It is also found that the energy difference increases with increasing Cr content, indicating the strong site preference of Cr at the B site.

The spin-projected total DOS of the $\text{Co}_2(\text{Co}_{1-x}\text{Cr}_x)\text{Al}$ ($x = 0–1$) alloys are shown in Fig. 2. The DOS presented in the upper half part of the figure corresponds to the majority spin direction and the lower half part to the minority spin direction. The vertical line indicates the position of the Fermi level. In the total DOS, the low-energy region below $-6\,\text{eV}$ is mainly the s states of the Al atoms, which are separated from the p and d states by a dip in DOS in both spin directions and do not overlap with the 3d or 3p bands. So they are unaffected by the d–d exchange interaction and are not shown in Fig. 2. The states around $-4\,\text{eV}$ consist mainly of the p states of Al, which hybridize with the p and d states of the 3d atoms and determine the degree of occupation of p–d orbits. The DOS from $-4$ to $+2\,\text{eV}$ are mainly governed by the d states of Co and Cr, together with contributions from p electrons of Al.

It is known that the shape of the DOS strongly depends on the atomic order of the nearest neighbor shell. Thus the substitution of Cr for Co affects the d–d hybridization and leads to the reconstruction of the bands. Since Cr has fewer valence electrons than Co, to accommodate the fewer electrons, both the majority and minority spin states are shifted with respect to the Fermi level. In the majority DOS of Co$_2$Al, both the bonding and antibonding peaks are far below the Fermi level and are occupied. The DOS at $E_F$ is very low. But with increasing Cr content, the up-spin states are shifted to higher energy and a new antibonding peak appears at $E_F$, which indicates a leakage of charge from the majority states below the Fermi level to the unoccupied majority states, due to the decrease in the average number of valence electrons [28]. In the minority DOS of Co$_2$Al, the Fermi level locates at the shoulder of the antibonding peak, but with the substitution of Cr, the antibonding peak is shifted to higher energy and the states around $E_F$ decrease, and a gap is opened at $E_F$ when $x = 1$ in the end. So the substitution of Cr for Co stabilizes the energy gap in the minority spin band and makes Co$_2$CrAl a half-metal [9].

It is known that a disadvantage of the PW basis set is that, due to the delocalized nature of the basis states, it does not give enough information to understand the localization of the electrons in the system. So to make a deep study on the bonding characters, we make the Mulliken population analysis for both Co$_3$Al and Co$_2$CrAl, which are the two ending members of this series of alloys, and the results are presented in Table 2. The density functional tools of COOP, COHP or recently developed ECOV are also good choices [29–31].

The Mulliken population analysis is useful in investigating the covalent, ionic, or metallic character of bonds in a compound. The positive and negative bond overlap population values indicate bonding and antibonding states, respectively. A value close to zero indicates that there is no significant interaction between the electronic populations of the two atoms [32]. Also, a high value of the bond overlap population indicates a covalent bond, whilst a low value indicates an ionic nature [33].

We can classify mainly two kinds of bonds in Co$_3$Al or Co$_2$CrAl, which are the nearest Co (A,C)–Co (B)/Cr (B) and Co (A,C)–Al, and next-nearest Co (A)–Co (C) and Co (B)/Cr (B)-Al. It can be seen in Table 2 that all the values
of bond population are positive, which indicates their bonding nature, whether the interaction between their populations is strong or weak.

The change of the electronic structure with increasing Cr content is obviously seen in the partial DOS in Figs. 3–5. It has been reported that the covalent hybridization between the lower-energy d states of a higher-valent transition metal atom like Co and the higher-energy d states of a lower-valent transition metal like Cr is strong, and can lead to the formation of bonding and antibonding bands. The bonding hybrids are localized mainly at the higher-valent transition metal atom and the unoccupied antibonding states mainly at the lower-valent transition metal [34]. In Fig. 3, it can be seen that the change in the minority spin states is more obvious above the Fermi level. With the substitution of the lower-valent atom Cr, the unoccupied antibonding DOS peak is weakened, which results in a small magnetic splitting localized at Co (A,C) and opens the energy gap around \( E_F \). Meanwhile, the majority DOS of Co (A,C) is shifted to higher energy and the antibonding peak is moved to the Fermi level, which results in the increase of the number of the d-holes, and a new dip in DOS is opened around -0.6 eV below \( E_F \). Finally, the net effect of these changes in both majority and minority spin states leads to the decrease of the Co (A,C) spin moments with increasing Cr content.

In \( Fe_{3-x}Cr_xAl \), the moments of Co (A,C) also decrease with increasing Cr content for a similar reason [35].

Figs. 4 and 5 give the partial DOS of Cr (B) and Co (B) with different Cr content, respectively. Both Cr (B) and Co (B) have eight Co as nearest neighbors. In the cubic crystal field, the Cr and Co d states are split into a doublet.
with $e_g$ symmetry and a triplet with $t_{2g}$ symmetry, respectively, and their DOS show a two-peak structure (a bonding and an antibonding peak), which are separated by a dip in DOS. The antibonding peak of Cr (B) in the minority spin states is high above the Fermi level and the exchange splitting may be large, which results in a large local moment of Cr (B).

With the increasing Cr content, the majority DOS of Cr (B) is pushed to higher energy, and the minority spin states move slightly downward on the energy scale. The change in the partial DOS of Co (B) is also smaller than that of Co (A, C). It can be seen that they keep the two-peak structure and no new extra states appear in the whole concentration range studied. The reason is that for the B site the nearest neighbor shell is mainly determined by the Co (A, C) atoms which are unaffected by the substitution of Cr, and the DOS of the atoms at the B sites are determined mainly by the nearest neighbors.

From the partial DOS of the Co and Cr atoms, it can be seen that in the majority spin states the large DOS peak at
the Fermi level is mainly dominated by the Co (A,C) and Cr (B) spin-up states and the contribution from Co (B) is rather small. In the minority spin states, the energy gaps are opened around the Fermi level in both Cr (B) and Co (A,C) DOS, but the antibonding peak of Co (B) always locates at $E_F$, which is the main cause of the non-zero states in the minority DOS around $E_F$. So the effect of Cr in Co3Al, which may also be the same for other lower-valent atoms at the B site in the half-metallic Heusler alloys, is mainly to push the antibonding DOS peaks of the (A,C) atoms high on the energy scale and to open the energy gap around $E_F$. Sometimes the lower-valent atoms also contribute to the high DOS peak at $E_F$ directly. This has been observed in many half-metallic Heusler alloys. So though the minority gap originates mainly from the hybridization between the states of the atoms at (A,C) sites [36], the lower-valent atom at the B site also plays an important role. The change of the calculated total spin moments with increasing Cr content is listed in Table 1 and is also shown in Fig. 6. The values derived from the Slater–Pauling curve are also listed together. The Slater–Pauling curve is $M_t = Z_t - 24$, where $M_t$ is the total magnetic moment per formula unit and $Z_t$ is the total number of valence electrons. In half-metallic Heusler alloys, the Fermi level is pinned at the gap in the minority spin states and the extra valence electrons more than 24 will fill in only the majority spin states, and lead to a linear change of the spin moment with the number of valence electrons [34]. It is clear that with increasing Cr content the total spin moment decreases, the difference between which and the S–P curve becomes smaller and smaller and finally becomes the same. This is due to the formation of the energy gap at $E_F$. The decrease of the total spin moment can be attributed to the decrease of the partial moments of Co (A,C). The moments of Co (B) and Cr (B) only slightly change with increasing Cr.

In Co$_2$(Co$_{1-x}$Cr$_x$)$_2$Al, the spin moments of Cr, Co (A,C) and Co (B) are in ferromagnetic alignment in the whole concentration range studied. The Al atom at the D site only has a small negative moment ranging from $-0.12$ to $-0.16\mu_B$.

4. Conclusion

The effect of doping with Cr on the electronic structure of Co3Al has been studied by density functional calculations. It has been found that the Cr atom has a strong site preference for the B site in Co3Al. With the substitution of Cr for Co, the total DOS changes obviously: A large DOS peak appears at $E_F$ in the majority spin states and an energy gap is opened in the minority spin states. This change is mainly determined by the states of Co (A,C) and Cr (B) atoms. The DOS of Co (B) is less affected by the increasing Cr content. The effect of Cr in Co3Al is mainly to push the antibonding DOS peak of the (A,C) atoms high on energy scale, and to form the energy gap around $E_F$, and also contribute to the high DOS peak at $E_F$ in the majority spin direction. The calculation indicates a ferromagnetic alignment of the Co and Cr spin moments. The calculated total magnetic moment decreases and becomes closer to the Slater–Pauling curve with increasing Cr content. This change is mainly due to the decrease of the Co (A,C) spin moments.

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