Ab initio study of Cr substitution for Co in the Heusler alloy Co$_2$CrAl: Half-metallicity and adjustable magnetic moments

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Abstract

The effect of doping on the half-metallicity and magnetism of Co$_{2-x}$Cr$_x$CrAl ($x = 0–1$) alloys was studied by full-potential linearized-augmented plane wave (FLAPW) calculations. With increasing Cr content, a transition from the half-metallic ferromagnet (HMF) to the half-metallic completely compensated ferrimagnet (HMCCF, also called half-metallic antiferromagnet) is observed. The calculations indicate that Co$_{2-x}$Cr$_x$CrAl alloys are half-metallic within the whole range studied. Substitution of Cr for Co leads to a large antibonding peak above $E_F$ in the majority-spin band, but still keeps the energy gap in the minority-spin band. The size of the gap is mainly determined by the density of states (DOS) of atoms at the (A, C) sites. With increasing Cr content, the total spin moment decreases linearly from 3$\mu_B$/f.u. to zero, which obeys the Slater–Pauling curve quite well. The spin moment of Cr at the C site is antiferromagnetically aligned with the magnetic moments of the Cr (B) and the Co atoms. This antiferromagnetic coupling causes a monotonic decrease of the total magnetic moment.

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1. Introduction

Since the 1990s, much attention has been paid to the half-metals which have been found to exhibit interesting magnetic and transport properties and have possible application in spintronics [1–3]. Usually, a half-metal is semiconductor-like in the minority-spin band at the Fermi level $E_F$, whereas the majority-spin band is strongly metallic, which results in a complete (100%) spin polarization of the conduction electrons at $E_F$. This is interesting from both theoretical and experimental point of view. It is known that many magnetoelectronic devices operate on an imbalance in the number of majority- and minority-spin carriers at the Fermi level. Therefore, half-metals can be used as spin injectors and in other spin-dependent devices [4].

Most half-metals are ferromagnets and are also called half-metallic ferromagnets (HMFs). The first predicted HMF is NiMnSb, theoretically calculated by de Groot et al. [4]. Since then, much attention has been spent on the Heusler alloy family for new HMFs. Ishida et al. [5] have proposed that the full-Heusler alloys Co$_2$MnZ (Z = Si, Ge) are half-metallic. Later Mn$_2$VAl [6], Co$_2$MnX (X = Si, Ge, Sn) [7] and Co$_2$Msi (M = Ti, V, Cr) [8] have also attracted much attention. Recently, Co$_2$CrAl [9], Co$_2$CrGa [10,11] and Co$_2$FeSi [12] have been reported to exhibit HMF character in their electronic structure. Meanwhile, a series of half-metallic completely compensated ferrimagnets (HMCCFs, also called half-metallic antiferromagnets) have also been predicted theoretically [13–15]. HMCCFs are non-magnetic and have advantages in some technical applications.
Heusler alloys crystallize in the L2₁ structure and have the stoichiometric composition X₂YZ, 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, the Y atom enters the B (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) site and Z occupies the D (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) site in Wyckoff coordinates.

Among the work on Heusler alloys, the effect of doping on the half-metallic and magnetic properties has been thoroughly studied [16–20]. It has been found that the half-metallicity can be retained with proper substitution. Substitution of Fe for Cr in Co₃CrGa helps to stabilize the L₂₁ structure and the half-metallic properties [19]. So doping in ternary Heusler alloys offers an excellent possibility to discover new materials with half-metallicity or other interesting properties. However, to the best of our knowledge, most studies on doping of Heusler alloys are on substitution for Y atoms at the B site and there are only few reports on substitution for atoms at the (A, C) sites.

In the present study, we have performed full-potential linearized-augmented plane wave (FLAPW) calculations to investigate the effect of substitution of Cr for Co on the half-metallicity and the magnetic properties of the Heusler alloy Co₂CrAl. In the Co₂₋ₓCrₓAl system may be meaningful for practical applications.

2. Computational method

We carried out the electronic-structure calculations using the self-consistent FLAPW method based on the local spin-density approximation within the density-functional theory [21,22], where the potential and/or the charge density in the crystal are treated with no shape approximation. One hundred and eighty-two \(\mathbf{k}\) points are employed in the irreducible Brillouin zone. The self-consistent calculation stops if the charge-density deviation is less than 0.01 me/a.u. and the total energy deviation is better than 0.1 mRy per cell. The density plane-wave cut-off is \(R_{\text{K}}\)\(_{\text{max}}\) = 8.0. The electron states were treated in a scalar relativistic approximation. Using the energy eigenvalues and eigenvectors at these points, the density of states (DOS) was determined by the tetrahedral integration method [23].

As described above, in X₂YZ Heusler alloys, the X and Y atoms usually occupy the (A, C) and B sites, respectively, and the Z atom occupies the D site. The site preference of the different 3d elements in Heusler alloys is determined by their number of valence electrons [24]. For example, in Fe₃Si, the 3d elements with less d electrons than Fe prefer to occupy B sites, whereas elements with more d electrons prefer (A, C) sites, and Si occupies D site [25].

In the calculations, we assume that the extra Cr atoms that substitute for Co enter the C site in Co₂CrAl, which corresponds to Co₂₋ₓCrₓAl \((x = 0, 0.25, 0.5, 0.75, 1)\) and leads to an ordered structure and an integral occupation of the crystal sites. Similar calculations have been performed on Co₆(Mn₁₋ₓFeₓ)₃Si₄ [26] and Cr₂Cr₁₋ₓFeₓAl [18] 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 the magnetic moments, were found between the mixed ordered compounds and random alloys [26].

We have used the experimental lattice constants of the compounds Co₂CrAl and Cr₂CoAl (Refs. [27] and [28]) for the calculations. For the intermediate part of this series of alloys, we assume the lattice constants to vary linearly with concentration. A similar assumption has been used in Ref. [17] and gives reliable results.

3. Results and discussion

We will first discuss the general electronic structure of Co₂₋ₓCrₓAl \((x = 0–1)\). The calculated total DOSs are shown in Fig. 1. In all alloys, the majority-spin band is strongly metallic while the minority-spin band shows an energy gap at \(E_F\), which leads to a complete spin polarization of the conduction electrons. Thus, we can say the Co₂₋ₓCrₓAl alloys are “true” half-metals. It can be seen that the substitution of Cr for Co does not change the general shape of the DOS obviously. In the majority-spin band, the DOS at \(E_F\) slightly decreases with increasing Cr content, but it is still much higher than the minority DOS, which is important for the investigation of spin polarization. Also a high-majority DOS is preferable in high-efficiency spin projection systems [18]. Meanwhile, it can be seen that, with the substitution of Cr for Co, a DOS peak appears at about \(+2\) eV, which can be attributed to the antibonding peak of Cr (C) as presented below. The DOS of the minority-spin band is less affected by the doping with Cr than the majority DOS. The main change is a small shift of the minority DOS with respect to the Fermi level.

In Fig. 1, the states below \(-6\) eV are mainly the s states of Al, which are separated from the d states by a dip in the DOS in both spin directions and are unaffected by the d–d hybridization. The contribution of the s states is relatively small and not presented in Fig. 1. The low-energy part around \(-5\) eV consists mainly of the p states of Al, which hybridize with p and d states of the Cr and Co atoms and determine the occupation degree of the p–d orbitals. The states of the 3d atoms extend from \(-4\) to \(+2\) eV and hybridize with each other. The d states are wide on energy scale, which may result from the strong hybridization between the Co and Cr atoms. It has been reported that the covalent hybridization between the lower-energy d states of a high-valent transition metal atom like Co and the higher-energy d states of a lower-valent transition metal like Cr...
can be strong and can lead to the formation of bonding and antibonding bands [29].

More details of the change in the electronic structure can be seen in the atom-projected DOS. In order to investigate the electronic structure of these alloys further, we present in Fig. 2 the spin-projected partial DOS of Co$_2$CrAl and Cr$_2$CoAl, the two parent members of this series of alloys. In Co$_2$CrAl and Cr$_2$CoAl, the DOS of Cr (B) has a two-peak structure (a bonding and an antibonding peak) due to the bcc crystal-field effect. In the spin-up states, the two peaks are basically below the Fermi level and fully occupied. But in the spin-down states, the exchange splitting moves the antibonding peak high above the Fermi level, which results in a large magnetic moment at the Cr (B) site. The Co atoms in both Co$_2$CrAl and Cr$_2$CoAl have four Cr and four Al atoms as nearest neighbors, so that their electronic structures are similar. It is clear that in the two compounds, the gap in the DOS of Cr (B) is much wider and the shape of the energy gap in the minority spin states is mainly determined by the DOS of the atoms at A and C sites, which are two Co in Co$_2$CrAl and one Cr and one Co in Cr$_2$CoAl. This agrees quite well with the finding of Galanakis et al. [30] that the hybridization in Co$_2$MnZ compounds not only occurs between the nearest-neighbor Co and Mn 3d orbitals but also between the next-nearest-neighbor Co–Co d orbitals. This causes non-bonding states ($t_{1u}$ and $e_u$) in the minority-spin band and a gap occurs between the occupied $t_{1u}$ bands and empty $e_u$ bands.

The change of the partial DOS of Cr and Co at the C site with increasing Cr content is shown in Fig. 3. It is clear that in both spin directions the DOS of Cr (C) is relatively low at the Fermi level so that, in Co$_{2-x}$Cr$_x$CrAl, the large majority DOS peak mainly emerges from the Co and Cr (B) atoms. It has been reported that the bonding hybrids are localized mainly at the high-valent transition metal atom site and the unoccupied antibonding states mainly at the lower-valent transition metal site [29]. From Figs. 2 and 3, it can be seen that the partial DOS of Cr (C) and also Cr (B) have large antibonding peaks above the Fermi level and remain unoccupied, while the DOS of Co is mainly below the Fermi level and occupied. But it may also be noted that the partial DOS of Cr (C) lies mainly below $E_F$ in the minority-spin states and above $E_F$ in the majority-spin band. The partial DOS of Cr (B) is reversed and mainly lies above $E_F$ in the minority-spin band and basically below $E_F$ in the majority-spin band. For the Co atom, there is also an antibonding peak in the minority DOS above $E_F$. So, the contributions to the total DOS from the Cr (C) and from the Co (A) or Cr (B) are opposite, which indicates the antiparallel configuration of their spin moments.

In Heusler alloys, the ferromagnetic and antiferromagnetic moment alignments result from a competition between two physical mechanisms [31]: the intra-atomic exchange splitting of the magnetic atom d states and the inter-atomic covalent interaction of d states from different atoms at B sites. Both mechanisms affect the total energy and the coupling of the partial moments through the d bands interactions. The magnetic energy applies equally to the ferromagnetic and antiferromagnetic alignments while the covalency mechanism is only beneficial for antiferromagnetic alignment. Thus, an intrinsic part of the covalency mechanism is the mixture of states on different atoms to form the hybrid states, which implies the population of the minority-spin states and give rise to the antiferromagnetic–ferromagnetic competition [31]. In normal X$_2$YZ Heusler alloys, such as Co$_2$CrAl, the Cr atom at
B site is surrounded by eight Co atoms and the distance between the Cr atoms is not the nearest, so that the covalent interactions of the Cr–Cr atoms are not direct and only use the p states of the Z atom as an intermediary, which results in ferromagnetic coupling between the Co and Cr atoms. Upon substitution of Cr for Co, however, the Cr atoms enter the C sites and Cr (B) will have Cr (C) as nearest neighbors, so that the distance between Cr (C) and Cr (B) is small, comparable with bcc Cr (which is a typical antiferromagnet), and a strong direct covalent interaction of their d states may be expected. Hence the covalency mechanism is enhanced and an antiferromagnetic alignment between the magnetic moments of Cr (B) and Cr (C) or Co is formed.

Fig. 4 shows the concentration dependence of the total magnetic moment in Co$_2$Cr$_x$CrAl alloys. The line in Fig. 4 represents the Slater–Pauling curve obeyed by ideal half-metallic ferromagnets, that 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. It is clear that the total magnetic moment obeys the Slater–Pauling curve quite well. In full-Heusler alloys, the minority band contains 12 electrons per unit cell, from the s–p atom and the 3d atoms. So, the compounds with 24 valence electrons like Cr$_2$CoAl have 12 electrons in both spin directions and are non-magnetic. If the alloy has more valence electrons, the exchange splitting will shift the majority states to lower energies. The extra electrons only fill majority-spin states which results in a linear change of the spin moment with the number of valence electrons [29]. In Co$_{2-x}$Cr$_x$CrAl, if $x$ varies from 0 to 1, the number of valence electrons drops from 27 to 24 and the total magnetic moment decreases from 3 to 0.007$\mu_B$/f.u. This indicates a transition from a HMF to a HMCCF.

As shown in Figs. 2 and 3, the spin-up d electrons of Cr (B) hybridize with those of Co and Cr (C) and form a common d band, whereas the spin-down d electrons are excluded from the Cr (B) sites. Thus localized partial magnetic moments composed of itinerant electrons are obtained [31]. The calculated partial moments of Co$_{2-x}$Cr$_x$CrAl alloys are also shown in Fig. 4. The Cr atoms entering the C site have a large negative moment, which are antiparallel to those of Co and Cr (B). Meanwhile, the Co only has a small spin moment. A similar small Co moment was also reported in Ref. [27]. This may be attributed to the large occupied spin-down bonding states that reside preferentially at Co sites. The decrease of the total spin moment results from the antiparallel alignment of the Cr (C) moment with that of Co and Cr (B).

With increasing Cr content, the moments of Co and Cr (C) decrease and moment of Cr (B) increases. It is known that the magnetic properties of, particularly, 3d metals are very much dependent on the chemical surrounding such as the number, type and distance of the nearest neighbors of a given site. So, with substitution of Cr for Co in Co$_{2-x}$Cr$_x$CrAl alloys, the charge transfer between the higher-valent and lower-valent 3d atoms will happen, for Cr has less valence electrons than Co. This will lead to the reconstruction of the 3d bands and will affect the magnetic moments.

The present study on Co$_{2-x}$Cr$_x$CrAl indicates that, in this series of alloys, the magnetic moment can be adjusted from 3$\mu_B$ to zero without destroying the half-metallicity. This is quite meaningful for practical applications, because, with this knowledge, one can easily prepare materials for spintronics devices with strong-ferromagnetic, weak-ferromagnetic or non-magnetic properties and high spin polarization by adjusting the Cr composition.

4. Conclusions

We have studied the effect of doping on the half-metallicity and magnetism of Co$_{2-x}$Cr$_x$CrAl ($x = 0–1$) alloys using FLAPW calculations. The results indicate that Co$_{2-x}$Cr$_x$CrAl alloys are half-metallic within the whole...
range studied. Substitution of Cr for Co leads to a high antibonding peak above $E_F$ in the majority-spin band while the energy gap in the minority-spin band is retained. The width of the gap is mainly determined by the electronic states from atoms at the (A, C) sites. With increasing Cr content, the total spin moment decreases linearly from 3 $\mu_B$/f.u. to zero, which obeys the Slater–Pauling curve quite well. The moments of the Cr atoms at the C site are antiferromagnetically aligned with the magnetic moments of the Cr (B) and the Co atoms. This antiferromagnetic alignment causes a transition from a half-metallic ferromagnet to a half-metallic completely compensated ferromagnet.

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