Effect of Fe substitution on the magnetic properties of half-Heusler alloy CoCrAl

Hongzhi Luo [a,b,*], Heyan Liu [a], Xiao Yu [a], Yangxian Li [a], Wei Zhu [b], Guangheng Wu [b], Xiaoxi Zhu [c], Chengbao Jiang [c], Huibin Xu [c]

[a] School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China
[b] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China
[c] School of Material Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, PR China

ARTICLE INFO

ABSTRACT

The effect of Fe substitution for the vacant site in half-Heusler alloy CoCrAl is studied. A series of single phase $CoFe_xCrAl$ ($x = 0.0$, 0.25, 0.5, 0.75 and 1.0) alloys has been successfully synthesized. The lattice constant is found to increase almost linearly with increasing Fe content, indicating Fe atoms enter the lattice of CoCrAl instead of existing as a secondary phase. When Fe entering the vacant site, spin polarization occurs and the alloy turns from a semimetal in CoCrAl to a half-metallic ferromagnet (HMF) in CoFeCrAl. This is due to the reconstruction of the energy band with Fe substitution. The Curie temperature and saturation magnetic moments are enhanced and increase monotonically with increasing Fe content. The variation of the spin moment follows the Slater–Pauling curve and agrees with the theoretical calculation as well.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Since the last decade, 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, the so-called half-metal is semiconductor-like in minority spin states at the Fermi level E_F whereas the majority states are strongly metallic, which results in a complete (100%) spin polarization of the conduction electrons at E_F. This is interesting from both the theoretical and experimental point of view.

Till now, the half-metallic properties have been found in several kinds of materials such as full- and half-Heusler alloys [4–9], CrO_2 [10], zinc-blende compounds [11] and double perovskites [12]. Among them the Heusler alloys have ordered structure, high-Curie temperature and are easy to be prepared as thin films. All these make them promising candidates for the application in spintronic devices.

Most half-metals are ferromagnets and are also called half-metallic ferromagnets (HMFs). The first predicted HMF is NiMnSb,

a half-Heusler alloy [4]. Since then, much attention has been spent on this family for new HMFs. Among them, the doped quaternary alloys such as $Co_2(Cr_xFe_{1-x})Al$ have attracted much attention for they are suitable for technical applications [13,14]. Recently, Korth et al. reported the substitution of Fe for Ti in semiconducting half-Heusler alloy CoTiSb. Their results suggests that the doped $Co(Ti_{1-x}Fe_x)Sb$ are also promising HMFs [15].

It is known that the half-Heusler alloy XYZ crystallizes in the $C1_b$ structure. The space group is $F\bar{4}$-3m. The conventional stable structure for half-Heusler alloy is that the Y and Z atoms located at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites and form the rock salt structure, while the X atom locates in the octahedrally coordinated pocket, at one of the cube centre site $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. So there is still a vacant site $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ unoccupied. In this paper, we study the influence of doping Fe in the vacant site on the structure and magnetic properties of the semiconducting half-Heusler alloy CoCrAl. Meanwhile, the electronic structures of the two ending members of the $CoFe_xCrAl$ alloys: CoCrAl and CoFeCrAl have been studied.

2. Experimental methods

The $CoFe_xCrAl$ ingots were prepared by arc-melting, the constituent elements in a high purity argon atmosphere. The purity of

* Corresponding author at: School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China. Tel.: +86 10 8264 9247; fax: +86 10 6256 9068.
E-mail address: luohz@aphy.iphy.ac.cn (H. Luo).

the raw materials was 99.9% or higher. All the ingots were melted at least three times for homogenization. The ingots were then wrapped in molybdenum foil and sealed in a quartz tube and annealed at 973 K for 3 days under protection of argon atmosphere. Then X-ray powder diffraction (XRD) with Cu K_α radiation was used to verify the crystal structure and to determine the lattice constants. Thermomagnetic curves (TMA) were measured in a Vibrating–sample–magnetometer (VSM) with a field of 0.05 T to determine the Curie temperature (T_c). The magnetization curves were measured by SQUID magnetometer with applied field up to 5 T.

3. Results and discussion

The powder XRD patterns for CoFe$_x$CrAl are shown in Fig. 1. In all these samples, a Heusler structure is identified. As an example, we present the calculated pattern of CoFeCrAl at the bottom row for comparison. It can be seen that, besides the normal (2 2 0), (4 0 0) and (4 2 2) diffraction peaks in common cubic crystal, the superlattice reflections (2 0 0), (2 2 2) and (4 2 0) are also quite obvious, but the (1 1 1) diffraction is invisible in the experimental XRD patterns, so there may be some B2 type of disorder in the Heusler structure. With the doping of Fe, there is no other additional peak observed. The only change is that the diffraction peaks are shifted to a lower angel due to Fe entering the vacant site. The derived lattice constants of CoFe$_x$CrAl are listed in Table 1 and also shown in Fig. 4. It is clear that the lattice constant increases almost linearly with increasing Fe constant. All these suggest that Fe atoms enter the lattice of CoCrAl instead of existing as a secondary phase.

To investigate the influence of Fe in the vacant site, within the limit of the code, we studied the electronic structure of CoCrAl and CoFeCrAl, which are the two ending members of the CoFe$_x$CrAl alloys. The calculations were performed using the pseudopotential method with a plane-wave basis set [16–18]. The electronic exchange–correlation energy was treated under the local-density approximation (LDA) [19]. The calculated total and partial DOSs of CoCrAl are presented in Fig. 2(a). Generally, half-Heusler alloy with 18 valence electrons are semiconductors and non-magnetic. Their DOSs show an energy gap around the Fermi level. The total DOS of CoCrAl shows a similar character. It has a symmetrical total DOS in majority and minority spin directions

and give a paramagnetic ground state. The Fermi level locates in the energy gap in both majority and minority bands. However, it can be seen that there are still small states near the Fermi level. In order to investigate this further, we present the band structure of CoCrAl in Fig. 2(c). Since CoCrAl is paramagnetic, the majority and minority bands are same. It is clear that, close to the high symmetry points (X, W), there is a small overlap between the conduction and valence bands across the Fermi level. This makes CoCrAl a non-magnetic semimetal. There are no previous reports on the electronic structure of half-Heusler alloys containing Al. We assume this semimetal-like band may be related to the smaller lattice constant of CoCrAl compared with common half-Heusler alloys containing Sb or Sn.

It is known that in Heusler alloys the covalent hybridization between the lower-energy d states of the high-valent transition metal atom and the higher-energy d states of the low-valent transition metal can lead to the formation of bonding and antibonding bands. The bonding hybrids are localized mainly at the high-valent transition metal atom site, while the unoccupied antibonding states mainly at the low-valent transition metal site [20]. So a d–d band gap is formed near the Fermi level. In the minority spin states, there are 9 bands below the d–d gap (four from the s–p atom and five from the 3d atom). If a half-Heusler alloys has 18 valence electrons, these electrons will occupy the minority and majority bands equally. This makes the alloy non-magnetic. If there are more electrons than 18, the Fermi level will be shifted from the energy gap to the antibonding peak. Then the non-magnetic state is no longer stable and spin polarization will happen [21]. In this work, when Fe (having 8 electrons) entering the vacant site, the extra valence electrons will overlap with the d states of both Co and Cr. So the energy gap around the Fermi level will change from covalent band gap in half-Heusler alloys to a d–d band gap in full-Heusler alloys [22].

The calculated total and partial DOSs of CoFeCrAl are present in Fig. 2(b). According to the previous studies on Co$_2$(Cr$_{1-x}$Fe$_x$)Al, when Fe substituting for Cr, the extra electrons with respect to Cr and Mn compounds lead to an overlap of the Co bonding and antibonding minority d hybrids and decreases the gap width or even destroys the gap [23,24]. But for the alloys with Fe substituting for the Co site, such as CoFeMnAl, the gap is still open and the half-metallic character is retained [25]. This may also be true in CoFeCrAl alloy.

It is clear that the substitution of Fe enhances the hybridization of the 3d electrons and leads to the reconstruction of both majority and minority bands. The majority spin states are shifted to low energy and the Fermi level locates at the antibonding peak; while in the minority band, it is still pinned in the gap. The majority DOS peak comes from contributions of both (Co, Fe) and Cr up-spin states. This leads to a 100% spin polarization of the conduction electrons at E_F and a ferrimagnetic ground state. The change is also clearly seen in the partial DOS. Both the majority DOS of Co and Cr moves lower on energy scale compared with those in CoCrAl. But their minority DOS are shifted to higher energy. In the partial DOS of Cr, a two-peak structure (a bonding and an antibonding peak) is observed. In the up-spin states the

Table 1
The structure and magnetic properties of CoFe$_x$CrAl (x = 0.0, 0.25, 0.5, 0.75 and 1.0) alloys.

Composition (x)	0.00	0.25	0.50	0.75	1.00
Lattice constant (Å)	5.742	5.746	5.750	5.758	5.760
T_C (K)	18	165	292	392	460
M_s (μ_B/f.u.)	0.060	0.495	1.040	1.550	2.070
M_{S-P} (μ_B/f.u.)	0.00	0.50	1.00	1.50	2.00

M_{S-P} is the spin moment derived from the Slater–Pauling curve.
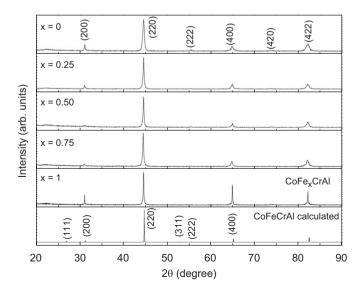

Fig. 1. X-ray powder diffraction for CoFe$_x$CrAl (x = 0.0, 0.25, 0.5, 0.75 and 1.0) alloys, the bottom row shows the calculated pattern of CoFeCrAl.