Half-metallicity and anisotropy magnetoresistance properties of Heusler alloys Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si

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**Article info**

In this paper, we investigate the half-metallicity of Heusler alloys Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si by first principles calculations and anisotropy magnetoresistance measurements. It is found that, with the increase of Cr content x, the Fermi level of Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si moves from the top of valence band to the bottom of conduction band, and a large half-metallic band gap of 0.75 eV is obtained for x=0.75. We then successfully synthesized a series of Heusler Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si polycrystalline ribbon samples. The results of X-ray diffraction indicate that the Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si series of samples are pure phase with a high degree of order and the saturation magnetic moment follows half-metallic Slater–Pauling rule. Except for the two end members, Fe$_{2}$CoSi and Fe$_{2}$CrSi, the anisotropic magnetoresistance of Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si (x=0.25, 0.5, and 0.75) shows a negative value suggesting they are stable half-metallic ferromagnets.

1. **Introduction**

Half-metallic ferromagnets were discovered by theory with a prediction of 100% spin polarization [1,2], in which the majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting. Since the first prediction of half-metallic ferromagnet in Heusler compounds in 1983 by de Groot [3], several Heusler series that possess half-metallic properties have been experimentally realized [4–6]. Full-Heusler compounds are usually presented with the general formula X$_{2}$YZ, where X and Y are the transition elements and Z represents the main group element. The cubic unit cell consists of four interpenetrating face-centered-cubic (fcc) sublattices, two of which are occupied by identical X atoms and the other two by Y and Z atoms [7]. Because of high Curie temperature, Co-based Heusler compounds are considered as the most promising candidates for half-metallic ferromagnets working at room temperature [8,9]. However, Co-based Heusler compounds have a serious inadequacy that a high L2$_{1}$ degree of order is necessary to present a high spin polarization. For example, recent experiments found that, in sputtered Co$_{2}$MnSi Heusler films, a few degree of atomic disorder between Co and Mn will cause a large reduction of the spin polarization [10]. On the other hand, the thermal excitation and spin-flip scattering can also destroy the half-metallicity in Co-based Heusler alloys. To avoid thermal excitation and spin-flip scattering of electrons to the conduction sub-band, Bakle et al. [11] proposed a method for engineering the band gap and tuning the Fermi level by doping Fe in Heusler alloys Co$_{2}$Mn$_{1-x}$Fe$_{x}$. Very recently, based on the first principles calculations, Luo et al. [12] found that Fe-based Heusler alloys Fe$_{2}$CoSi and Fe$_{2}$CrSi are two typical half-metallic ferromagnets. They also pointed out that the half-metallicity of these Fe-based Heusler alloys is insensitive to atomic disorder. However, the Fermi levels of Fe$_{2}$CoSi and Fe$_{2}$CrSi locate at the edge of valence and conduction bands, respectively. In this paper, using the first principles calculations, we investigate the band structures of a series of Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si Heusler compounds, to find the most stable half-metallic ferromagnets. The in-plane anisotropic magnetoresistance (AMR) experiments were further performed to verify the half-metallicity in this series.

2. **Experimental**

Fe$_{2}$Co$_{1-x}$Cr$_{x}$Si (x=0.0, 0.25, 0.5, 0.75, and 1) ingots were prepared by arc-melting under an Ar atmosphere. Melting was repeated several times to obtain chemically homogenous ingots. Because the flaked sample for the measurements of AMR cannot be obtained by arc-melting, the melt-spinning method was utilized to make small metal sheets from the obtained ingots. The thickness of the ribbon samples used in this work is roughly around 46 μm. Structural examination was performed by X-ray diffraction (XRD) with Cu-Kα radiation. The AMR effect in all samples was measured by the standard four-terminal method in Physical Property Measurement System (PPMS). A superconducting quantum interference device (SQUID) was used to determine the saturation magnetic moment at the low temperature of 5 K.
The calculations of density of states (DOS) and band structure have been performed on the basis of the density-functional theory (DFT) within the general gradient approximation (GGA). We also used GGA+U calculations to account for the on-site electron-electron Coulomb interaction.

3. Results and discussion

Fig. 1 shows the XRD patterns of Fe$_2$Co$_{1-x}$Cr$_x$Si with different Cr content $x$ measured at room temperature. Indexing the characteristic reflections, we find that the studied samples crystallized in face centered cubic (fcc) structure without other detectable second phases. The left part of Fig. 1 shows the XRD superlattice reflections measured by the step-scan method. The appearance of superlattices (111) and (200) indicates that our samples have a highly ordered structure[13,14], and the values of the degree of atomic ordering can be roughly estimated from the ratio of the integrated intensity of the superlattice reflections (111) and (200). It is well known that, the intensities of the B2 and L2$_1$ (or Hg$_2$CuTi) superlattice reflections are proportional to $S^2$ and $(1-2z)^2S^2$, respectively. As we have mentioned above, the chemical formula of full-Heusler alloys can be presented as X$_2$YZ (X: Fe, Y: Cr, Co, and Z: Si). The $S$ parameter represents the B2 order from the A2 structure, and $S=1$ indicates that the alloys have a perfectly B2-ordered structure. On the other hand, in the A2 structure, both the X and Y sites are randomly occupied by X and Y atoms, thus $S$ should be zero. In addition, $z$ indicates the ordering from B2 to L2$_1$. As a result, we can obtain the $S$ and $z$ values from the formulas given below[13]:

$$S = \frac{(I_{200}/I_{220})_{\text{experiment}}/(I_{200}/I_{220})_{\text{theory}}^{1/2}}{(1-2z)S = \left(\frac{(I_{111}/I_{220})_{\text{experiment}}/(I_{111}/I_{220})_{\text{theory}}}{}\right)^{1/2}}$$

The calculated values of $S$ and $z$ are shown in the inset of Fig. 1. All the studied samples exhibit almost the same $S$ value of 0.9, which indicates that nearly 5% of the X site is occupied by improper atoms (Y and Z) (A2-disorder). On the other hand, the values of $z$ are very small, showing a local maximum of 0.2 at $x=0.5$, which means that about 20% of the Y (or Z) site is occupied by Z (or Y) atoms (B2-disorder). We therefore can conclude that all the samples are approximately highly ordered L2$_1$ or Hg$_2$CuTi structure.

Based on the calculations by Luo et al. [12], the Fermi levels of Fe$_2$CrSi and Fe$_2$CoSi lie on the top of valence band and the bottom of conduction band, respectively. Therefore their half-metallicity is easily destroyed by the thermal excitation and/or spin-flip scattering. Following the idea of tuning the Fermi level position in Heusler alloys Co$_2$Fe$_{1-x}$Mn$_x$Si [11] and Co$_2$FeAl$_{1-x}$Si$_x$ [14,15], one can expect to adjust the Fermi level by doping Cr in Fe$_2$Co$_{1-x}$Cr$_x$Si. In Fig. 2(a), we show the calculated spin-resolved DOS for Fe$_2$Co$_{1-x}$Cr$_x$Si with different Cr content $x$. The upper part of each panel displays the majority spin densities and the lower one the minority spin densities. The results of DOS in Heusler alloys Fe$_2$CrSi and Fe$_2$CoSi are consistent with the previous results [12]. The majority states of Fe$_2$CrSi exhibit a rather high density in the vicinity of Fermi level that is caused by weakly dispersing, flat bands. As expected, we successfully shift the position of the

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Fig. 1. Dependence of X-ray diffraction (XRD) patterns on Cr content $x$ for Fe$_2$Co$_{1-x}$Cr$_x$Si ($x=0.0, 0.25, 0.5, 0.75$, and 1). The left inset shows the schematic Heusler structure. The right inset indicates the order parameters as a function of $x$. Here $S$ and $z$ indicate B2 and L2$_1$ degree of ordering, respectively.

Fig. 2. (a) Spin-resolved density of states (DOS) for Fe$_2$Co$_{1-x}$Cr$_x$Si ($x=0.0, 0.25, 0.5, 0.75$, and 1) from first principles calculations. The Fermi level moves from the top of $E_{\text{VB}}$ (valence band) to the bottom of $E_{\text{CB}}$ (conduction band) with increasing Cr content $x$. The Cr content $x$ dependence of $E_{\text{CB}}$ and $E_{\text{VB}}$. (b) and, the sizes of gap $\Delta E_{\text{gap}}=E_{\text{CB}}-E_{\text{VB}}$ (c). The insets in (c) show the enlarged profiles for spin-resolved DOS of Fe$_2$CoSi and Fe$_2$Co$_{0.25}$Cr$_{0.75}$Si. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Fermi level to the center of minority gap from the edge with the increase of the Cr substitution.

In order to clearly show the motion of minority spin band near the Fermi level, in Fig. 2(b), we display the energy of top valence band $E_{VB}$ (black circles) and bottom conduction band $E_{CB}$ (red circles) as a function of the Cr composition $x$. We found that, with the increase of Cr content $x$, $E_{VB}$ first decreases and reaches a local minimum at $x=0.75$ and then increases. On the contrary, $E_{CB}$ exhibits opposite tendency. We further calculated the sizes of half-metallic band gap $\Delta E_{gap}=E_{VB}-E_{CB}$, and the results are plotted as a function of $x$ in Fig. 2(c). A very small $\Delta E_{gap}$ of 0.05 eV is found for Fe$_2$CoSi; however, if Co is partially replaced by Cr, the $\Delta E_{gap}$ will rapidly increase with increasing Cr content $x$, reaching a maximum value of 0.71 eV at $x=0.75$. The enlarged profiles for spin-resolved DOS of Fe$_2$CoSi and Fe$_2$Co$_{0.25}$Cr$_{0.75}$Si are shown in the inset of Fig. 2(c). Interestingly, unlike Fe$_2$Co$_{0.25}$Cr$_{0.75}$Si having a large half-metallic band gap, for Fe$_2$CoSi, there exists only a touching point at the Fermi level in the down-spin channel.

Fig. 3 shows the saturation magnetization values ($M_s$) as a function of Cr composition $x$. The inset shows the typical magnetization of all the samples measured at 5 K by a SQUID magnetometer. The $M_s$ values are 4.88, 4.14, 3.58, 2.78 and 2.1 (in $\mu_B$/formula unit) for $x=0$, 0.25, 0.5, 0.75 and 1, respectively. These experimental values straightforwardly follow the half-metallic Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3. Based on the first principles calculations, Galanikis et al. [16,17] proposed that the $M_s$ of half-metallic Huesler alloys follows the Slater–Pauling rule as shown in Fig. 3.

Very recently, Kokado et al. [18] have systematically investigated the sign of the anisotropy magnetoresistance (AMR) of ferromagnetic materials. As a result, they found that, for half-metallic ferromagnets, the dominant scattering is $s \uparrow \rightarrow d \uparrow$ or $s \downarrow \rightarrow d \downarrow$, which causes the sign of the AMR to be negative [19,20]. Subsequently, Yang et al. [21] measured the AMR ratio in Heusler Co$_2$(Fe,Mn)Si epitaxial films, and pointed out that the AMR effect can be an indicator of half-metallicity or non-half-metallicity, which can easily be achieved without having to make any microfabricated device structures. In our work, we also examined the half-metallic properties of Fe$_2$Co$_{1-x}$Cr$_x$Si by AMR effect measurement. The results of normalized in-plane magnetoresistance as a function of magnetic field are displayed in Fig. 4. Here a constant current of 5 mA and a magnetic field up to 5 T were applied to the sample plane in the following two configurations: (a) parallel ($\rho_{||}$) and (b) perpendicular ($\rho_{\perp}$) to the current direction. Besides the MR values, the sign of MR is independent of the configuration between the current and magnetic field. The MR of all the samples exhibits no tendency to saturation even at a field of 5 T. It is found that the MR sign of Fe$_2$CoSi is positive and it reaches a value of about 1%. However, the MR sign of other samples is negative. Moreover, the positive MR is almost ten times larger than those with the negative MR sign. Based on the MR measurements, we have calculated the AMR ratio, and the results are shown in Fig. 5. Here the AMR ratio was defined as AMR=$[\rho_{\perp}-\rho_{\parallel}]/\rho_{\parallel}$. We found that, the AMR ratio of Fe$_2$Co$_{1-x}$Cr$_x$Si ($x=0.25$, 0.5, and 0.75) shows a negative value, which suggests that the dominant scattering is $s \uparrow \rightarrow d \uparrow$ (see the DOS of Fe$_2$Co$_{1-x}$Cr$_x$Si in Fig. 2). Referring to the AMR description proposed by Kokado et al. [18], the negative AMR sign indicates
the half-metallic nature of this series. However, for the two end members, Fe$_2$CoSi and Fe$_2$CrSi, the positive AMR ratio is obtained which suggests that the half-metallic properties may be destroyed easily because of their Fermi level located at the edge of the gap.

4. Conclusion

In summary, using the first principles calculations, we have studied the electronic band structure and the magnetic transport properties of Heusler alloys Fe$_2$Co$_{1-x}$Cr$_x$Si. We found that the Fermi level of Fe$_2$Co$_{1-x}$Cr$_x$Si moves from the top of valence band to the bottom of conduction band with increasing Cr content. A large half-metallic band gap of 0.75 eV is obtained for Fe$_2$Co$_{0.25}$Cr$_{0.75}$Si; the Fermi energy is located in the middle point of the minority states with a large band gap of 0.75 eV. The fabricated Heusler Fe$_2$Co$_{1-x}$Cr$_x$Si ribbon samples are all pure fcc phase with a high degree of order. The saturation magnetic moment of all samples increases linearly with increasing Cr content, and straightly follows the half-metallic Slater–Pauling rule. To characterize the half-metallic property, we have further investigated the in-plane anisotropic magnetoresistance (AMR) of the ribbon samples. The negative AMR values are found among the three Fe$_2$Co$_{1-x}$Cr$_x$Si alloys ($x=0.25$, 0.5, and 0.75), meaning they are stable half-metallic ferromagnets.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant nos. 51071172 and 51171207) and the National Basic Research Program of China (973 Programs: 2012CB619405).

References