Mn₂CoSb compound: Structural, electronic, transport and magnetic properties

Xuefang Dai*a,b,*, Guodong Liu*a, Lijie Chen*a, Jinglan Chen*a, Guangheng Wu*a

a State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China
b School of Material Sciences and Engineering, Hebei University of Technology, Tianjin 300130, People’s Republic of China

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Abstract

High-ordered Mn₂CoSb compound has been synthesized successfully by a melt-spinning technique. The band structure calculation shows that Mn₂CoSb is a true half-metallic ferromagnet characterized by an indirect Γ–X band gap of about 0.4007 eV around the Fermi level for minority-spin electrons. The calculated magnetic moment is 4.00 µB per formula unit, which is close to the experimental value of 3.92 µB. The electronic resistivity shows a power-law $T^{-1.33}$ temperature dependence at low temperature. The $T^{-1.5}$ dependence of the magnetization was observed at low temperature, which is expected from Bloch’s law.

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1. Introduction

Half-metals are defined as magnetic materials showing a band gap at the Fermi energy for one spin direction. The first half-metallic ferromagnet (HMF) was predicted by de Groot et al. in the Heusler alloys in 1983 [1]. Since then, the exotica exhibiting a complete (100%) spin polarization at the Fermi level have attracted much attention due to their potential application in spin-electronic devices [2]. Both experimental and theoretical investigations to seek for new members of this family of HMFs were carried out zealously and many new and exciting results were reported during the last two decades [3–10]. Half-metallic characteristics arise from a strong magnetic band splitting. The conduction electrons are 100% spin polarized at the Fermi level [11]. However, in reality this complete spin polarization is not always observed. Since the experimental search for half-metals is tedious and the verification of the expected spin polarization is involved, electronic structure calculations have played an important role in this area. In this work, we synthesized a compound Mn₂CoSb by a melt-spinning technique. The study mainly focused on its structure, electronic structure, magnetic and transport properties. A half-metallic characteristic was predicted in the Mn₂CoSb alloy.

2. Experimental and computational details

We prepared the precursor ingot with composition of Mn₂CoSb by melting pure metals in the argon atmosphere. Subsequently, the ribbon was melt-spun at a linear velocity of about 12 m/s. Usually, the as-spun ribbons have a width of 2–3 mm and a thickness of 50 µm. The structure of the samples was determined using powder X-ray diffraction (XRD). The resistivity was measured using the four-point DC technique. The saturation magnetization measurements were carried out using a superconducting quantum interference device magnetometer (SQUID) in fields up to 5 T. The ac magnetic susceptibility measurements were carried out to determine the Curie temperature of the materials.

The electronic structure of Mn₂CoSb was calculated by the self-consistent full-potential linearized-augmented plane-wave (LAPW) method based on the local spin-density approximation
(LSDA) within the density functional theory [12,13]. Fifty \( k \) points in the irreducible Brillouin zone are used to achieve self-consistency in the calculation. The self-consistency is better than 0.01 me/a.u. for charge density and spin density, and the stability is better than 0.1 mRy for the total energy per cell. The experimental lattice constant is used in the electronic structure calculations. The muffin-tin sphere radii \( R \) used are 2.6 a.u. for Sb and 2.2 a.u. for Mn and Co atoms. The density plane-wave cutoff is \( R_{\text{max}} \) = 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 was determined by the tetrahedral integration method [14,15].

3. Results and discussions

3.1. Structure

Fig. 1 shows the X-ray diffraction patterns of the Mn\(_2\)CoSb sample. Many peaks can be observed except the principal cubic structure diffraction peaks in the XRD pattern of precursor ingots as shown in Fig. 1(a), indicating the other phases were formed in the precursor ingots. On the other hand, the pure cubic structure in ribbons was confirmed evidently as shown in Fig. 1(b). All diffraction lines can be indexed with the cubic structure. The (111) and (200) peaks correspond to the order-dependent superlattice reflections. Therefore, the presence of the (111) and (200) peaks indicates the high-ordered alignment of atoms in the Mn\(_2\)CoSb alloy [16]. The crystal structure of the Heusler alloys is based on a cubic structure with four interpenetrating f.c.c. sublattices A, B, C, D (Fig. 2(a)). Similar to the Mn\(_2\)NiSn alloy [17], a high-ordered structural model was established for Mn\(_2\)CoSb alloy as shown in Fig. 2(b). In this structural model the A and C sublattices are occupied by Mn and Co atoms respectively, which is different from the conventional L2\(_1\) structure where both A and C sublattices are occupied by Mn atoms as shown in Fig. 2(c). Here, the MnMnCoSb and MnCoMnSb representing the basis along the diagonal direction in two unit cells are used to distinguish these two structures shown in Fig. 2(b) and (c). Rietveld refinement has been employed to estimate the phase compositions of Mn\(_2\)CoSb synthesized by a melt-spun method. Using the MnMnCoSb-type structural model, the Rietveld refinement results were shown in Fig. 1(b). It was clear that the melt-spun Mn\(_2\)CoSb alloy was in single phase with the MnMnCoSb structure. The MnMnCoSb structure was used to carry out the calculation on electronic structure and magnetism. The calculated results are quite consistent with the experimental data. The lattice parameter was found to be \( a = b = c = 5.9042 \) Å. The value was used in the following calculation on the electronic structure.

3.2. Electronic structure

The spin-dependent bands along high-symmetry directions in the Brillouin zone for Mn\(_2\)CoSb were shown in Fig. 3. It can be seen that the majority spin band structure is strongly metallic, while the minority spin band structure shows an insulating behavior. It is clear that there is an indirect \( \Gamma-X \) band gap of about 0.4007 eV around the Fermi level for minority carriers. The Fermi level lies 0.1335 eV above the minority spin valence band maximum (VBM) which is the minimum energy required to flip a minority spin electron from the VBM to the majority spin Fermi level, which is very important and often referred to as the “spin-flip gap (HM gap)” [18]. The non-zero HM gap indicates our Mn\(_2\)COsB alloy is a typical HM alloy. With the help of DOS (as shown in Fig. 4), the lowest valence band (from \(-13 \) eV to \(-11 \) eV in both the majority and minority spin states) is due to a band consisting almost entirely of Sb 5s electrons and is separated with respect to the other hybridized bands, being basically unaffected by the Mn–Mn and Mn–Co d electron exchange interaction. The bands are omitted from plotting the band graph. The upper dispersed bands are due to the strong hybridization of Mn–Mn and Mn–Co d electrons, including a contribution from Sb p states in the occupied valence.

As seen from Fig. 4 the valence band extends more than 5 eV below the Fermi level. In the majority-spin component, Mn atoms occupying B sites (Mn(B)) 3d states are occupied and hybridized with Co 3d electrons. On the other hand, in the minority-spin part, local and mostly non-hybridized Mn(B) 3d states are found at about 1.3 eV above \( E_F \). The Sb atom provides s–p states to be hybridized with d electrons and determines the degree of occupation of p–d orbitals. The peaks between \(-6 \) and \(-5 \) eV consist of Sb 5p states strongly mixed with Mn occupying A sites (Mn(A)) and Co 4s states. There is a large exchange splitting between the spin-up and spin-down bands of the Mn(B) d states, which leads to large localized spin magnetic moments at the Mn(B) site and to the polarization of the Mn 3d bands away from the Fermi level. For Mn(A) atoms, the high-density region is situated near the Fermi level. The intra-atomic exchange interaction was weakened seriously, which leads to the disenablement of localized spin magnetic moments at the Mn(A) site. The calculated magnetic moments of the atoms Mn(A), Mn(B), Co and Sb are 0.10 \( \mu_B \), 3.06 \( \mu_B \),...
Fig. 2. The generalized Heusler structure with four interpenetrating f.c.c. sublattices A, B, C and D (a). The structural models of Mn$_2$CoSb: the MnMnCoSb-type high-ordered structure (b) and the conventional L2$_1$ structure (MnCoMnSb-type) (c).

Fig. 3. Majority spin (left column) and minority spin (right column) band structures for Mn$_2$CoSb alloy at the experimental lattice constant of 5.8620 Å.

Fig. 4. Calculated spin-projected DOS plots for Mn$_2$CoSb: (a) total and projected on (b) Mn(A), (c) Mn(B), (d) Co, and (e) Sb atoms. The upper halves of each panel display the spin-up states and the lower halves the spin-down states.

0.82 $\mu_B$ and $-0.02 \mu_B$, respectively. Thus the total spin magnetic moment is 4.00 $\mu_B$ per formula unit, which is equal to the integral number of Bohr magnetons expected for a half-metallic ferromagnet. In addition, the total energy calculated with experimental lattice constants for MnCoMnSb-type is 0.42 eV/cell higher than that of MnMnCoSb-type structure, which confirms that the Mn$_2$CoSb alloy favors MnMnCoSb structure instead of MnCoMnSb.

3.3. Transport properties

Fig. 5 shows the temperature dependence of resistivity. In the overall temperature range, the resistivity decreases upon the temperature decreasing and characterizes a typical metallic behavior. By assuming the functional form $\rho = \rho_0 + cT^n$ ($\rho_0$ is residual resistivity and $\rho_L(T) = cT^n$ is the temperature dependent part of resistivity) for our data, a plot of $\ln(\rho - \rho_0)$ as a function of $\ln T$ will yield a curve whose slope corresponds to the exponent $n$. Obviously, the curve can be divided into two parts by an inflection at about 70 K. At low temperature ($T < 70$ K), the results exhibits a $T^n$ behavior with $n = 1.33$. No $T^2$ term was found in this temperature range, which is in accord with the behavior of NiMnSb, PtMnSb and Mn$_2$VAl alloys [19,20]. In the conventional metallic ferromagnets, the resistance usually has a term proportional to $T^2$, which is ascribed to one-magnon scattering of conduction electrons (spin-flip scattering) [21]. However, in the case of half-metallic ferromagnets, there is no $T^2$ contribution to the resistance in the same temperature range because of the absence of spin-down states at $E_F$ which prevents the spin-flip scattering for spin-up charge carriers due to single-magnon excitations. At higher temperature, the
resistivity follows $T$ behavior, which can be reasonably interpreted by the conventional electron–phonon scatterings.

For our sample, the residual resistivity is large and up to 98 $\mu\Omega$ cm, while the residual resistivity ratio (RRR), $\rho_{300K}/\rho_{5K}$, is 2.2, much lower than that of the other predicted HMF, for example, Co$_2$MnSi single crystal where the RRR is up to 6.5 [22]. It is well known that the impurities and defects are the primary factors to affect the residual resistivity and RRR. For our Mn$_2$CoSb sample, the excellent half-metallic behavior results from a high-ordered alignment for all kinds of atoms in the compound. Raphael and Orgassa reported a small antisite disorder could result in the gap disappearance and the dramatic decrease of RRR [22,23]. In our melt-spun Mn$_2$CoSb sample, it is a reasonable estimation that there exist a relatively large amount of antisite defects due to the fast cooling condition in the melt-spinning process. So, the disorder defects in Mn$_2$CoSb can possibly have a remarkable effect on the half-metallicity and the electronic transport properties.

3.4. Magnetism

The magnetization curve at 5 K is shown in Fig. 6(a). The magnetization is saturated in the magnetic field of about 1800 Oe. The saturation magnetization measured at 5 K in a field of 5 T on a melt-spun sample is found to be 75.34 emu/g, corresponding to 3.92 $\mu_B$ per formula unit Mn$_2$CoSb. This value is very close to the integral number of Bohr magnetons expected for a half-metallic ferromagnet. This confirmed that the Mn$_2$CoSb is a HMF. The small difference between the prediction of the band calculation and the experimental result is probably attributed to the antisite disorder and the microstructure formed in the melt-spinning process [24,25].

Fig. 6(b) shows the temperature-dependent magnetization of a melt-spun Mn$_2$CoSb ribbon in the temperature from 5 K to 300 K. We separately fit the data to the functional form $M_S(T) = M_S(0)(1 - AT^n)$ with $n = 2.47$ for experimental data. The data for $T < 50$ K as a function of $T^{1.5}$ are shown in the inset graph. The solid line is a linear fit to the data, indicating the $T^{1.5}$ dependence of the magnetization at low temperature range.
in the alloy Mn$_2$CoSb by the ac magnetic susceptibility measurements.

4. Summary

A new high-ordered compound Mn$_2$CoSb was synthesized successfully by a melt-spinning technique. Its electronic band structure, transport and magnetic properties have been studied in this work. It was demonstrated, using band structure calculations, the Mn$_2$CoSb compound is a true HMF due to a spin-flip gap of 0.1335 eV in the bands for the minority-spin electrons. The experimental magnetic moment of 3.92 $\mu_B$ is very close to the calculated value of 4.00 $\mu_B$ per formula unit, which is equal to the integral number of Bohr magnetons expected for a half-metallic ferromagnet. It is different from conventional metallic ferromagnets in that the electronic resistivity of Mn$_2$CoSb follows a $T^{1.33}$ behavior at low temperature. Temperature dependence of resistivity for Mn$_2$CoSb reveals a small RRR, which reflects the relatively large amount of Co–Mn antisite defects. At low temperature the temperature dependence of magnetization exhibits a $T^n$ behavior with $n = 1.5$, which is consistent with Bloch’s law.

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References


