Magnetization and spin polarization of Co$_{2-x}$Fe$_x$MnSi Heusler alloys

Iduru Shigeta, Shinpei Urakawa, Masakazu Ito and Masahiko Hiroi
Department of Physics and Astronomy, Kagoshima University, Kagoshima 890-0065, Japan
E-mail: shigeta@sci.kagoshima-u.ac.jp

Abstract. We report magnetization and spin polarization of Co$_{2-x}$Fe$_x$MnSi Heusler alloys. Co$_{2-x}$Fe$_x$MnSi Heusler alloys are theoretically predicted to be half-metals (HM's) and generally possess high Curie temperature. The fact that the saturation magnetization of Co$_{2-x}$Fe$_x$MnSi for 0 $\leq$ $x$ $\leq$ 1.5 obeys the Slater-Pauling rule reveals that those compounds are experimentally expected to be HM's. Therefore, the spin polarization of Co$_{2-x}$Fe$_x$MnSi Heusler alloys was determined by the Andreev reflection technique using Co$_{2-x}$Fe$_x$MnSi/Pb planar-type junctions. The obtained differential conductance was able to be fitted very well by the modified Blonder-Tinkham-Klapwijk theory. From analysis of spin polarization measurements, we have found the spin polarization of $P = 0.50$ for $x = 0.5$ and $P = 0.52$ for $x = 1.25$, respectively. Consequently, the spin polarization was less dependent of different concentrations of $x$.

1. Introduction
Ternary $X_2YZ$ type alloys that crystallize in cubic $L2_1$ structure are referred to as Heusler alloys, where $X$ is a high valent transition metal atom, $Y$ is a low valent transition metal atom, and $Z$ is an $sp$ atom [1]. They have been attracting interests by reason of their potential use as half-metals (HM's) [2], ferromagnetic shape memory alloys [3], and thermoelectric materials [4]. Especially, Heusler alloys are regarded as the most promising half-metallic materials for spintronics applications because of their high Curie temperature ($T_C$) and low coercivity [5]. From first-principle band structure calculations, the Heusler alloys Co$_2$MnSi and Fe$_2$MnSi were predicted to be HM's if the ferromagnetic states are assumed [6]. Recently, Sakuraba et al. reported a large tunneling magnetoresistance (TMR) value of 570% at 2 K from a Co$_2$MnSi/Al-O/Co$_2$MnSi magnetic tunnel junction (MTJ) [7], which was attributed to the half-metallicity of the Co$_2$MnSi Heusler alloy. However, the TMR value showed a strong temperature dependence of only 67% at room temperature. The low room temperature TMR of the MTJ using Co$_2$MnSi was caused by the presence of an extra density of states near the Fermi level. Another possible reason for the degradation of half-metallicity is the presence of disorder in the $L2_1$ structure of Heusler alloys. At present, in spite of prediction of HM's by the theoretical works, HM's have not been realized yet for any materials at room temperature.

In this paper, we focus on magnetization $M$ and spin polarization $P$ of Co$_{2-x}$Fe$_x$MnSi. A differential conductance was measured by the Andreev reflection technique using ferromagnetic Co$_{2-x}$Fe$_x$MnSi Heusler alloy/superconducting Pb planar-type junctions. The $P$ value was determined by analysis of an experimentally obtained conductance with a theoretical calculation by the modified Blonder-Tinkham-Klapwijk (BTK) theory [8].
2. Experimental procedure
Polycrystalline Co$_{2-x}$Fe$_x$MnSi samples were fabricated by arc-melting high purity constituent elements under high purity argon atmosphere [9]. The phase characterization was carried out by $\theta-2\theta$ X-ray diffraction (XRD) using CuK$\alpha$ radiation. The parameters for these crystal structures have been refined by the Rietveld profile fitting program RIETAN-FP [10]. Magnetization $M$ of Co$_{2-x}$Fe$_x$MnSi was measured as a function of temperature $T$ and magnetic field $\mu_0 H$ by a commercial superconducting quantum interference device magnetometer (MPMS, Quantum Design). We have fabricated planar-type junctions by depositing Pb through a metal mask patterned with counterelectrodes on the polished surface of polycrystalline Co$_{2-x}$Fe$_x$MnSi samples. All Pb thin films were kept to 150 nm thick, which was longer than the coherence length $\xi_0 = 87$ nm of Pb [11]. We have measured differential conductance $G(V)$ of the prepared planar-type junctions by the conventional modulation method [12].

3. Results and discussion
The crystal structure of the $L_2_1$ ordered full-Heusler $X_2YZ$ alloy consists of four face-centered-cubic sublattices with $X$ atoms at $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$ and $(\frac{3}{4} \frac{3}{4} \frac{3}{4})$, $Y$ atoms at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$, and $Z$ atoms at $(000)$ in Wyckoff coordinates. The crystal structure of Co$_{2-x}$Fe$_x$MnSi Heusler alloys has been refined by the Rietveld analysis of obtained XRD patterns. Figure 1 illustrates the profile fit and difference patterns for Co$_{1.5}$Fe$_{0.5}$MnSi at room temperature. The solid line is calculated intensities, solid circles overlying them are the observed intensities, and $\Delta y_i$ is the difference between the observed and calculated intensities. The short vertical lines mark the positions of possible Bragg reflections of the $L_2_1$ structure. We have observed the (111) and (200) reflections, which are related to an atomic order in the $L_2_1$ structure. The observed intensities agree with the results calculated as the Heusler $L_2_1$ structure. Therefore, the polycrystalline samples obtained in this study are single phase of the ordered Heusler $L_2_1$ structure. The unit cell dimension was refined to be $a = 0.56642(3)$ nm for Co$_{1.5}$Fe$_{0.5}$MnSi. The global $R$ factors were $R_{wp} = 16.9\%$ ($S = R_{wp}/R_e = 1.15$) and $R_p = 12.1\%$. Phase-dependent $R$ factors were $R_B = 4.8\%$ and $R_F = 6.4\%$ for Co$_{1.5}$Fe$_{0.5}$MnSi. Figure 2 represents the resulting lattice constants of Co$_{2-x}$Fe$_x$MnSi as a function of concentration $x$, where the solid line is a guide to the eye. The lattice constant $a$ increases with increasing $x$ monotonically, but it is very small change.

We have measured magnetization of Co$_{2-x}$Fe$_x$MnSi. Figure 3 shows $M(H)$ as a function of magnetic field $\mu_0 H$ for $x = 0.5$ and $x = 1.0$ at $T = 5.0$ K. The $M(H)$ curves were almost saturated at $\mu_0 H = 1$ T for samples which were considered to be simple ferromagnetic.

![Figure 1. Rietveld refinement patterns of the Co$_{1.5}$Fe$_{0.5}$MnSi Heusler alloy.](image-url)
Therefore, measurements of $M(T)$ as a function of temperature $T$ were also performed under $\mu_0 H = 1$ T. Figure 4 represents $M(T)$ under $\mu_0 H = 1$ T for $0 \leq x \leq 1.8$. The $M(T)$ curves in figure 4 are regarded as the $T$ dependence of saturation magnetization. The saturation magnetization $M_0$ extrapolated to $T = 0$ K is obtained as $M_0 = 4.9 \mu_B$ per formula unit for Co$_2$MnSi. With decreasing $x$ the $M(T)$ curve shifts upward, and this means that $M_0$ increases with decreasing $x$, and accordingly $T_C$ is also presumed to increase monotonically to $T = 985$ K [5], which is the $T_C$ of Co$_2$MnSi. First-principle band structure calculations predict that Co$_2$MnSi and Fe$_2$MnSi Heusler alloys are to be HM's if the ferromagnetic state is assumed [6]. Based on the theoretical prediction, we have investigated the saturation magnetization of Co$_{2-x}$Fe$_x$MnSi and have found that for $0 \leq x \leq 1.5$ they indeed obey the Slater-Pauling rule $M_t = (Z_t - 24)\mu_B$/f.u. [9], where $M_t$ is the total spin magnetic moment per formula unit and $Z_t$ is the total number of the valence electrons per formula unit [13]. This indicates the possibility that Co$_{2-x}$Fe$_x$MnSi for $0 \leq x \leq 1.5$ is expected to be HM's. Therefore, these results motivate us to investigate spin polarization of Co$_{2-x}$Fe$_x$MnSi for $0 \leq x \leq 1.5$.

From the previous studies, HM's are expected for the Co$_{2-x}$Fe$_x$MnSi Heusler alloys, then


we have measured spin polarization \( P \) of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi} \) by using the Andreev reflection technique \([12]\). The experimentally obtained conductance was analyzed by the modified BTK theory \([8]\). Figures 5 and 6 show the resulting conductance \( G(V)/G_n \) of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi}/\text{Pb} \) planar-type junctions for \( x = 1.25 \) and \( x = 0.5 \) at \( T = 1.2 \) K, where differential conductance \( G(V) \) is in the superconducting state and \( G_n \) is in the normal state. The open circles are the experimental data and the solid lines are the theoretical calculations, respectively. The good fitting results were obtained, as shown in figures 5 and 6. From analysis by the modified BTK theory, we were able to determine spin polarization \( P = 0.52 \) for \( x = 0.75 \) and \( P = 0.50 \) for \( x = 1.5 \), respectively. The results indicate that the spin polarization is less dependent of different concentrations of \( x \). The resulting values of fitting parameters are also presented in figures 5 and 6, where \( \Delta \) is the energy gap of the superconducting Pb thin film, \( Z \) is the potential barrier height at the junction interface, and \( \chi^2 \) is the normalized sum of squared deviations between the experimental data and theoretical calculation \([12]\). With regard to the energy gap of Pb, \( \Delta = 0.80-0.95 \) meV is smaller than \( \Delta = 1.36 \) meV in the previous report \([14]\). The reduction in \( \Delta \) can be comprehended by the proximity effect at the junction interface between the ferromagnet and superconductor. Finally, we note the origin that the experimental \( P \) values of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi} \) compounds were lower than \( P = 1 \) in the theoretical predictions \([6]\) and \( P \sim 1 \) in the particular TMR devices only at low temperatures \([7]\). The main reasons that are thought for the reduction in \( P \) values are probably the interfacial effects and the compositional effects near the junction interface.

4. Conclusions

The fact that the saturation magnetization of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi} \) Heusler alloys became to follow the Slater-Pauling rule for \( 0 \leq x \leq 1.5 \) reveals that those compounds are to be HM’s. Therefore, we have determined spin polarization \( P \) of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi} \) by the Andreev reflection technique. The spin polarization of \( \text{Co}_{2-x}\text{Fe}_x\text{MnSi} \) was \( P = 0.52 \) for \( x = 1.25 \) and \( P = 0.50 \) for \( x = 0.5 \), respectively. The \( P \) values were less dependent of different concentrations of \( x \). So far, contrary to the theoretical predictions, HM’s have not been realized yet in Co-based Heusler alloys except for the particular TMR devices only at low temperatures. The suppression in \( P \) values probably attributes to the interfacial effects and the compositional effects near the junction interface.

**Figure 5.** Normalized conductance \( G(V)/G_n \) of the \( \text{Co}_{0.75}\text{Fe}_{1.25}\text{MnSi}/\text{Pb} \) junction at \( T = 1.2 \) K. The open circles are the experimental data. The solid line is the fitting result of the modified BTK theory.

**Figure 6.** Normalized conductance \( G(V)/G_n \) of the \( \text{Co}_{1.5}\text{Fe}_{0.5}\text{MnSi}/\text{Pb} \) junction at \( T = 1.2 \) K. The open circles are the experimental data. The solid line is the fitting result of the modified BTK theory.
Acknowledgments
We would like to thank S. Fujii for his helpful advice and discussion. This research was partially supported by the JGC-S Scholarship Foundation (No. 2133) and the Grant-in-Aid for Young Scientists (B) (No. 21740259) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References
[1] Heusler F 1903 *Verh. Dtsch. Phys. Ges.* 5 219
[2] Katsnelson M I, Irkhin V Y, Chioncel L, Lichtenstein A I and de Groot R A 2008 *Rev. Mod. Phys.* 80 315
[3] Ishikawa H, Sutou Y, Omori T, Oikawa K, Ishida K, Yoshikawa A, Umetsu R Y and Kainuma R 2007 *Appl. Phys. Lett.* 90 261906
[4] Nishino Y, Deguchi S and Mizutani U 2006 *Phys. Rev. B* 74 115115
[5] Webster P 1971 *J. Phys. Chem. Solids* 32 1221
[6] Ishida S, Fujii S, Kashiwagi S and Asano S 1995 *J. Phys. Soc. Jpn.* 64 2152
[7] Sakuraba Y, Hattori M, Oogane M, Ando Y, Kato H, Sakuma A, Miyazaki T and Kubota H 2006 *Appl. Phys. Lett.* 88 192508
[8] Ji Y, Strijkers G J, Yang F Y and Chien C L 2001 *Phys. Rev. B* 64 224425
[9] Kondo Y, Yano I, Shigeta I, Ito M, Hiroi M, Manaka H and Terada N 2009 *J. Phys.: Conf. Ser.* 150 042099
[10] Izumi F and Momma K 2007 *Solid State Phenom.* 130 15
[11] Poole C K, Farach H A and Creswick R J 2000 *Handbook of Superconductivity* (San Diego: A Harcourt Science and Technology Company)
[12] Shigeta I, Murayama O, Hisamatsu T, Brinkman A, Golubov A A, Tanaka Y, Ito M, Hilgenkamp H and Hiroi M 2011 *J. Phys. Chem. Solids* 72 604
[13] Galanakis I, Dederichs P H and Papanikolaou N 2002 *Phys. Rev. B* 66 174429
[14] Kittel C 2004 *Introduction to Solid State Physics* 8th ed (United States of America: John Wiley and Sons)