Effects of Substituted Elements on Spin Reorientation in Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$

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The spin reorientation and Curie temperature of Mn$_2$FeSb$_{1-y}$Sn$_y$ (0 ≤ x, y ≤ 0.15) compound were investigated by magnetization measurements. Spin reorientation temperature increased from 255 K at x = 0 to 383 K at x = 0.15, whereas it almost unchanged by Sn substitution. Curie temperature decreased down to 318 K with both Fe and Sn substitution. Substitution of Fe stabilized the ferrimagnetic state with magnetic moment lying in c-plane. Substitution of Sn induced the antiferromagnetic phase at low temperature. It was found that the magnetic hysteresis derived from quasi first-order magnetic phase transition exhibited at x ≥ 0.10 or T ≥ 300 K.

[doi:10.2320/matertrans.MT-MN2019016]

(Received December 20, 2019; Accepted April 6, 2020; Published May 22, 2020)

Keywords: Mn$_2$Sb, spin reorientation, first-order magnetic transition

1. Introduction

Ferrimagnetic (FRI) Mn$_2$Sb-based compounds with a tetragonal Cu$_2$Sb-type structure have been paid attention due to the first-order magnetic transition (FOMT) with small volume change. The configuration of magnetic moment in Mn$_2$Sb and related compounds with Cu$_2$Sb-type structure is shown in Fig. 1. There are magnetic moments $m$ of two Mn atoms, which were called $m_\text{Mn(I)}$ at 2a-site and $m_\text{Mn(II)}$ at 2c-site. $m_{\text{Mn(I)}}$ and $m_{\text{Mn(II)}}$ are reported to be 2.1 $\mu_B$ and 3.9 $\mu_B$, respectively, and aligned antiparallel each other. The triple layer of magnetic moments, $m_\text{Mn(II)}$-$m_\text{Mn(I)}$-$m_\text{Mn(II)}$, aligned parallel along the c-axis (FRI(I) state). The triple layer of magnetic moments aligned perpendicular to c-axis (FRI(II) state). This change of configuration of magnetic moments was spin reorientation (SR), which occurred in the vicinity of $T_{\text{SR}} = 250$ K. The SR in Mn$_2$Sb-based compound is related to sign of magnetic crystalline anisotropy constants $K_1$ and $K_2$.

Substituting 3d-elements (Cr, Co and V) for Mn or Sn/Ge for Sb result in the first-order magnetic transition (FOMT) from the FRI to antiferromagnetic (AFM) state with discontinuous volume change. Meanwhile, FOMT does not appear for Ti- and Fe-substitution. As seen in Fig. 1, the $m_{\text{Mn(II)}}$-$m_{\text{Mn(I)}}$-$m_{\text{Mn(II)}}$ triple layers align antiparallel each other in the AFM state. FOMT, which is accompanied with the small change of unit cell, is benefit for the reversibility on the magnetic cooling materials based on magnetocaloric effect. That is because the loss due to small thermal hysteresis.

Recently, Nwodo et al. reported that another magnetic hysteresis in the vicinity of 320 K in Mn$_{1.9}$Fe$_{0.1}$Sb$_{1-y}$Sn$_{y}$ (0 ≤ x, y ≤ 0.15). At the transition temperature, latent heat and discontinuous change of lattice parameters were not observed. Therefore, it was called quasi first-order phase transition (QFOMT). Since there is a report that the spin reorientation from easy axis to an easy-plane was first-order transition, Nwodo et al. proposed that the QFOMT of Mn$_{1.9}$Fe$_{0.1}$Sb$_{0.9}$Sn$_{0.1}$ was derived from SR. However, although the Mn$_{1.9}$Fe$_{0.1}$Sb$_{0.9}$Sn$_{0.1}$ exhibited QFOMT, the important factor for exhibiting QFOMT is unclear. In this paper, for investigating the factor for exhibiting QFOMT in Fe- and Sn-modified Mn$_2$Sb, magnetic phase diagram of Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ was produced. In particularly, substitution effects on the $T_C$ and $T_{\text{SR}}$ were focused on.

2. Experimental Procedure

Polycrystalline Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ (0 ≤ x, y ≤ 0.15) was prepared as follows. A mixture of nominal amounts of pure elements (3N–Mn, 4N–Fe, 4N–Sb, and 5N–Sn) was arc-melted in an argon atmosphere. The obtained samples were sealed in a quartz tube in an Ar atmosphere, and were annealed at 923 K for 1 day. After that, the sample was quenched into ice water by breaking the quartz tube. X-ray powder diffraction (XRD) experiments were performed using Cu K$_\alpha$ radiation at room temperature. Magnetization

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measurements were carried out by a superconducting quantum interference device (SQUID) magnetometer for $10 \leq T \leq 360$ K and vibrating sample magnetometer (VSM) for $300 \leq T \leq 770$ K. In this study, thermomagnetization curves using SQUID magnetometer were performed by the warming process after zero-field cooling (ZFCW) and field cooling (FC) protocol. AFM-FRI transition temperature $T_t$ was determined by the cross section of the largest slope of the tangent line and the baseline for ZFCW process. $T_{SR}$ and $T_C$ were determined by the peak of the $dM/dT$ curve.

3. Results and Discussions

Figure 2 shows the typical XRD patterns for Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ at $x = 0.05$ (a) and 0.15 (b). The main diffraction peaks were indexed by the tetragonal Cu$_2$Sb-type structure. The weak peaks derived from MnSb phase with hexagonal NiAs-type structure was detected. The stronger peaks of MnSb were observed at $y$-rich region, such as Mn$_{1.85}$Fe$_{0.15}$Sn$_{0.90}$Sn$_{0.10}$ and Mn$_{1.95}$Fe$_{0.05}$Sb$_{0.85}$Sn$_{0.15}$.

Figure 3 shows the temperature dependence of magnetization of Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ at 0.1 T. Solid and dashed line indicate the ZFCW and FC processes, respectively. The inset shows enlarged view in the vicinity of $T_{SR}$.

Effects of Substituted Elements on Spin Reorientation in Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ at $x = 0.05$ (a) and 0.15 (b). The main diffraction peaks were indexed by the tetragonal Cu$_2$Sb-type structure. The weak peaks derived from MnSb phase with hexagonal NiAs-type structure was detected. The stronger peaks of MnSb were observed at $y$-rich region, such as Mn$_{1.85}$Fe$_{0.15}$Sn$_{0.90}$Sn$_{0.10}$ and Mn$_{1.95}$Fe$_{0.05}$Sb$_{0.85}$Sn$_{0.15}$.

Figure 3 shows the temperature dependence of the magnetization ($M-T$ curve) of Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ ($0 \leq x \leq 0.15$, $0 \leq y \leq 0.15$). In Fig. 3(a), the reduction of $M$ due to the FOMT between the AFM and FRI state was observed for $10 \leq T \leq 150$ K. With increasing $y$, the $T_t$ shifted to higher temperature. The FOMT suppressed with increasing $x$. However, small drops in $M-T$ curves were observed for $T < 50$ K for $y = 0.15$ even in high $x$ (see Fig. 3(c) and (d)).
SR of Mn$_2$Sb was determined to be 255 K, which is consistent with previous reports.\textsuperscript{1)} The magnetic hysteresis of QFOMT was observed at $T_{SR}$ for higher $x$ than 0.1.\textsuperscript{11)} It is found that QFOMT appeared when $T_{SR}$ existed in high temperature region over 300 K. Meanwhile, $y$-$T_{SR}$ relation was not observed clearly.

Figure 4 shows the $M$-$T$ curve for $300 \leq T \leq 770$ K in a magnetic field of 0.1 T. $T_C$ of Mn$_2$Sb was evaluated to be 549 K, which was good agreement with Ref. 6). $T_C$ of impurity MnSb-based phase was about 587 K\textsuperscript{14)} and it was not observed. $T_C$ decreased monotonically with increasing both $x$ and $y$. At $x \neq 0$ and small $y$ region, a cusp was observed just below the drop of $M$ around $T_C$. The origin of this cusp was not clarified. However, the cusp disappeared by increasing $y$.

Figure 5 shows the magnetic phase diagram of Mn$_{1-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ in the function of $x$ (a) and $y$ (b). Open symbols indicate the composition which exhibited QFOMT.

Figure 4 $M$-$T$ curves of Mn$_{1-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ at 0.1 T ($300 \leq T \leq 770$ K). The inset shows the enlarged view in the vicinity of $T_C$, which indicated by the arrows.

Fig. 5 Magnetic phase diagrams for Mn$_{1-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ in function of $x$ (a) and $y$ (b). Open symbols indicate the composition which exhibited QFOMT.
As seen in Fig. 5, the AFM state appeared only at low $x$ and high $y$ regions. Comparing the slope of $x$-$T_C$ and $y$-$T_C$ lines, Sn-substitution was more effective for the reduction of $T_C$, although both Fe and Sn-substitution reduced $T_C$. The reduction rates of $T_C$ at constant $y$ and $x$ were 70 K/$x$ and 194 K/$y$, respectively. The increase of $x$ led to enhancement of $T_{SR}$ at the rate of 465 K/$x$, whereas $T_{SR}$ did not clearly change by substituting Sn. As shown in Fig. 5(a) and (b), it was found that $T_{SR}$ strongly depended on $x$ and continuously increased with increasing $x$. QFOMT appeared when $x$ was over 0.1 and when $T_{SR}$ was higher than 300 K. Therefore, it is suggested that the QFOMT was related to SR.

It was considered that Fe-substitution changed the magnetic crystalline anisotropy constants. According to Mössbauer spectroscopy, the value of quadrupole splitting in Mn$_{1.98}$Fe$_{0.02}$Sb at 300 K and 80 K are reported to be $-0.12$ mm/s and $0.10$ mm/s, respectively. On the other hand, hyperfine fields in Mn$_{1.98}$Fe$_{0.02}$Sb at 300 K and 80 K are reported to be 80 kOe and 50 kOe, respectively. Since SR depend on the magnetic crystalline anisotropy constant $K_1$ and $K_2$, Mössbauer spectroscopy experiment for Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ is necessary for investigating the relationship between SR and QFOMT in microscopic viewpoint.

It is clearly observed that Fe and Sn stabilized the FRI and AFM phases, respectively. Meanwhile, both Fe- and Sn-substitution reduced $T_C$. According to the first-principle calculation study for As-modified Mn$_2$Sb, interatomic distances between the Mn atoms and their the nearest neighbors were more effective for stability of AFM and FRI states than composition change. It is suggested that exchange interaction decreased due to the modification of Fe and Sn substitution, leading to the reduction of $T_C$. Meanwhile, stabilization of AFM or FRI state was due to the change of the lattice parameters.

4. Conclusion

The effects of Fe- and Sn-substitution on the magnetic properties of Mn$_{2-x}$Fe$_x$Sb$_{1-y}$Sn$_y$ was investigated. The magnetic phase diagrams at $x$- and $y$-section were presented. Substitution of Sn atom did not change $T_{SR}$, although $T_C$ monotonously decreased with increasing Sn content at the rate of 194 K/$y$. $T_{SR}$ increased with increasing $x$ and QFOMT appeared for $x \geq 0.1$, suggesting the relation between QFOMT and SR.

Acknowledgments

The magnetization measurements were performed at the Institute for Solid State physics, the University of Tokyo and Institute for Materials Research, Tohoku University.

REFERENCES