Magnetic properties of $Mn_{2}Sb_{1-x}Z_{x}$ (Z = Ge, Sn)

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Magnetic properties of $Mn_2Sb_{1-x}Z_x$ (Z = Ge, Sn)

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Abstract:
Magnetization and electrical resistivity measurements were carried out for polycrystalline $Mn_2Sb_{1-x}Ge_x$ ($0.05 \leq x \leq 0.2$) and $Mn_2Sb_{1-x}Sn_x$ ($0.08 \leq x \leq 0.15$) in magnetic fields up to 16 T in the 4.2–600 K temperature range in order to investigate the magnetic and the electrical properties under magnetic fields. $Mn_2Sb_{0.95}Ge_{0.05}$ and $Mn_2Sb_{0.9}Sn_{0.1}$ showed a first-order magnetic transition from a ferrimagnetic (FRI) to an antiferromagnetic (AFM) phase in the vicinity of T_t = 172 K and 190 K, respectively, with decreasing temperature in a zero magnetic field. With increasing x, T_C decreased slightly and T_t increased. The electrical resistivity changes abruptly by 87% for $Mn_2Sb_{0.95}Ge_{0.05}$ and 43% for $Mn_2Sb_{0.9}Sn_{0.1}$ at T_t. The magnetic phase diagrams of $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ are presented.

Keywords: Mn_2Sb, magnetic properties, kinetic arrest effect, first order phase transition

I. Introduction

Mn_2Sb compound with a Cu_2Sb-type tetragonal structure (space group: P4/nmm) is ferrimagnetic (FRI) at temperatures below $T_C \sim 550$ K.[1–3] The crystal and spin structures are shown in Fig. 1.[3] There are two crystallographically non-equivalent sites for Mn atoms, Mn1 (2a-site) and Mn2 (2c-site), which are tetrahedrally and octahedrally surrounded by Sb atoms. The Sb atom occupies the 2c-site. Neutron-diffraction study shows the presence of triple layers (Mn2-Mn1-Mn2) along the *c*-axis and antiparallel magnetic moments on Mn1 and Mn2. The magnetic moments of Mn atoms are $2.1\mu_B$/Mn1 and $3.9\mu_B$/Mn2, leading to the FRI state in Mn_2Sb.[2]

The substitution of various elements (V, Cr, Co, Cu and Zn) for Mn, as well as (As, Ge and Sn) for Sb, results in a first-order magnetic transition from the FRI to an antiferromagnetic (AFM) state at the transition temperatures T_t (~100–300 K) for cooling process.[1–15] The moments of all triple layers are parallel in the FRI state whereas the arrangement is antiparallel in the AFM state.[2,3] The lattice parameters, the magnetization M, the electrical resistivity ρ, *etc*. of these substitution compounds change abruptly and are accompanied by a FRI-AFM transition.[4–7] In addition, the magnetoresistance and the magnetostrictive effects of these compounds were observed at temperatures below T_t and are accompanied by a field-induced AFM-FRI transition.[5–7] Therefore, these compounds have attracted attention as magnetic field-controlled materials.

Recently, the dynamics of the FRI-AFM transition in $Mn_{1.85}Co_{0.15}Sb$ was reported to be arrested by applying a magnetic field μ_0H, the so-called kinetic arrest effect (KA effect).[6] In our previous study, we also confirmed that the structural property of $Mn_{1.8}Co_{0.2}Sb$ were affected by the KA effect under magnetic fields.[7,14] On the other hand, detailed reports on the KA effect for the magnetic and the electrical properties of $Mn_2Sb_{1-x}Z_x$ (Z = Ge or Sn) are few compared to those on $Mn_{1-x}Co_xSb$. In order to estimate the potential of $Mn_2Sb_{1-x}Z_x$ for applications, its magnetic and electrical properties for these compounds in high magnetic fields must be clarified. In this report, we present the experimental results of the

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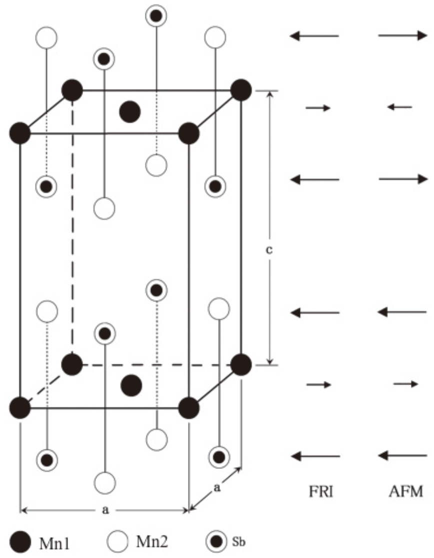

Fig. 1. Crystal structure and arrangement of Mn1 and Mn2 moments in the ferrimagnetic (FRI) and the antiferromagnetic (AFM) state in Mn_2Sb based compound. The length of the arrow represents the magnitude of the magnetic moment of the atom.[3)]

magnetic and the electrical properties of $Mn_2Sb_{1-x}Z_x$ (Z = Ge, Sn; $0.05 \le x \le 0.2$) under high magnetic fields up to 16 T.

2. Experimental

Polycrystalline $Mn_2Sb_{1-x}Ge_x$ ($0.05 \le x \le 0.2$) and $Mn_2Sb_{1-x}Sn_x$ ($0.08 \le x \le 0.15$) was prepared by arc-melting a mixture of nominal amounts of pure elements (Mn, 3N; Co, 3N; Sb, 4N) in an argon atmosphere. The obtained button-shaped ingot was turned over and re-melted several times. After that, the ingot was annealed at 923 K for 24 h in a quartz tube with a vacuum and then slowly cooled to room temperature (RT). The obtained sample was confirmed to be a single phase of a Cu_2Sb-type structure by X-ray powder diffraction (XRD) measurements at RT. The lattice parameters *a* and *c* were determined to be 0.4077 nm and 0.6455 nm at RT, respectively, which are comparable to the reported data.[5)]

The magnetization *M* measurements were carried out using *a* superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in the temperature *T* range from 10 to 330 K and magnetic fields $\mu_0 H$ up to 5 T. Using a vibrating sample magnetometer (VSM), we performed *M* measurements for RT $\le T \le$ 620 K under $\mu_0 H \le 1$ T by using a 10-T cryocooled superconducting magnet. The electrical resistivity ρ was measured by using a standard four-probe technique for $4.2 \le T \le 280$ K and $0 \le \mu_0 H \le 16$ T with an 18-T superconducting magnet.

3. Results and discussion

Figure 2 shows the concentration, *x*, dependence of the lattice parameters *a* and *c* for $Mn_2Sb_{1-x}Ge_x$ (a) and $Mn_2Sb_{1-x}Sn_x$ (b) at RT. The parameters were estimated by the 2θ positions of the 220 and the 004 reflection peaks. Both *a* and *c* decrease with increasing *x* for $Mn_2Sb_{1-x}Ge_x$. We confirmed that the compound of $x = 0.2$ was AFM at RT whereas other compounds were FRI. For $Mn_2Sb_{1-x}Sn_x$, *c* decreases slightly with increasing *x*, but *a* is almost constant for *x*.

The temperature dependence of the magnetization of $Mn_2Sb_{0.95}Ge_{0.05}$ (a) and $Mn_2Sb_{0.9}Sn_{0.1}$ (b) for $\mu_0 H = 0.1$ T and 5 T is shown in Fig. 3 as typical *M-T* data. Here, the measurements were made in field cooling (FC; solid curve), field cooled warming (FCW; solid curve) and field warming after zero-field cooling (ZFCW; broken curve). As shown in Fig.3 (a), the data of $Mn_2Sb_{0.95}Ge_{0.05}$ for $\mu_0 H = 0.1$ T indicate that a first-order phase transition from a FRI to an AFM phase occurs in the vicinity of 172 K (= T_t) with a thermal hysteresis of approximately 15 K. When a field of $\mu_0 H = 5$ T was applied, T_t of $Mn_2Sb_{0.95}Ge_{0.05}$ decreases to 150 K and the width of the hysteresis is approximately 10 K. As shown

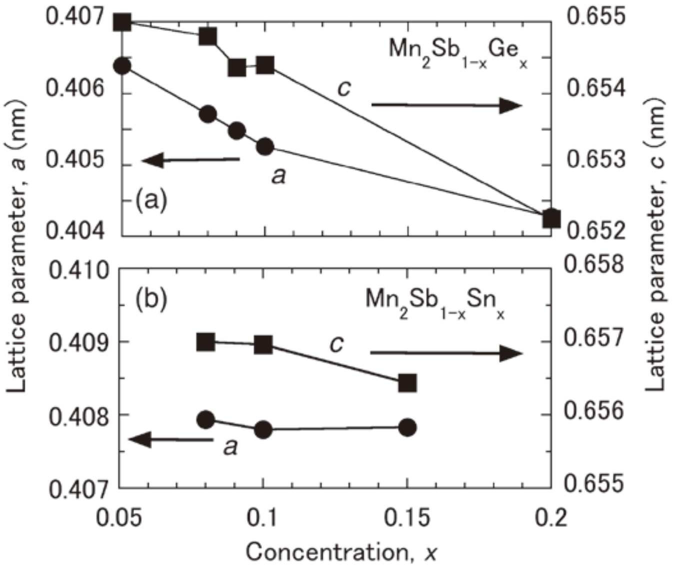

Fig. 2. Concentration x dependences of the lattice parameters a and c of $Mn_2Sb_{1-x}Ge_x$ (a) and $Mn_2Sb_{1-x}Sn_x$ (b) at room temperature.

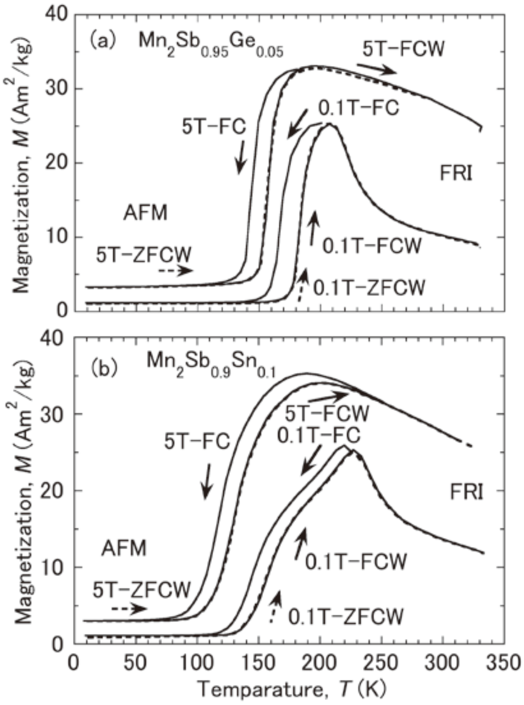

Fig. 3. Temperature dependence of the magnetization of $Mn_2Sb_{0.95}Ge_{0.05}$ (a) and $Mn_2Sb_{0.9}Sn_{0.1}$ (b) for magnetic fields of $\mu_0H = 0.1$ and 5 T. The measurements were made in field cooling (FC; solid curve), field cooled warming (FCW; solid curve) and field warming after zero-field cooling (ZFCW; broken curve).

in Fig.3 (b), a first-order phase transition of $Mn_2Sb_{0.9}Sn_{0.1}$ occurs in the vicinity of 190 K (= T_t) with a thermal hysteresis of approximately 15 K for $\mu_0H = 0.1$ T. When a field of $\mu_0H = 5$ T was applied, T_t of $Mn_2Sb_{0.9}Sn_{0.1}$ decreases to 128 K and the width of the hysteresis is approximately 15 K.

Figure 4 shows the temperature dependence of the electrical resistivity ρ (ρ-T curve) of $Mn_2Sb_{0.95}Ge_{0.05}$ (a) and $Mn_2Sb_{0.9}Sn_{0.1}$ (b) for a zero magnetic field and $\mu_0H = 16$ T, which is shown as typical ρ-T data. Here, ZFC and ZFW mean zero-field cooling and zero-field-warming measurements, respectively. A first-order phase transition from a FRI

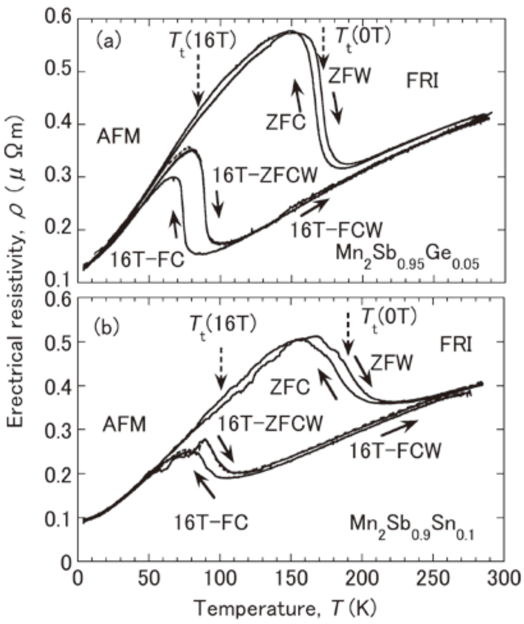

Fig. 4. Temperature dependence of the electrical resistivity of $Mn_2Sb_{0.95}Ge_{0.05}$ (a) and $Mn_2Sb_{0.9}Sn_{0.1}$ (b) for a zero magnetic field and μ_0H = 16 T. The measurements were made in zero-field cooling (ZFC), zero-field warming (ZFW), field cooling (FC), field cooled warming (FCW) and field warming after zero-field cooling (ZFCW). The broken allows indicate the determined transition temperature T_t between the antiferromagnetic (AFM) and ferrimagnetic (FRI) phases.

(low resistivity) to an AFM (high resistivity) state occurs with decreasing temperature. The broken allows in Fig. 4 indicate determined transition temperatures, T_t, for a zero field and μ_0H = 16 T. For $Mn_2Sb_{0.95}Ge_{0.05}$, ρ changes abruptly by 87% (=[(ρ(185 K) - ρ(150 K))/ ρ(185 K)] =$\Delta\rho/\rho$) in the vicinity of T_t = 172 K. $\Delta\rho/\rho$ of $Mn_2Sb_{0.9}Sn_{0.1}$ was estimated to be 43% in the vicinity of T_t = 190 K. This value of $\Delta\rho/\rho$ for $Mn_2Sb_{0.9}Sn_{0.1}$ is consistent with that of a previous report for $Mn_2Sb_{1-x}Sn_x$.[11)]

Figure 5 shows the magnetic phase diagrams of $Mn_2Sb_{1-x}Ge_x$ (a) and $Mn_2Sb_{1-x}Sn_x$ (b). The Curie temperatures, T_C, were determined by an inflection point of M-T curves for T > 290 K using VSM. The transition temperatures, T_t, under μ_0H = 16 T were determined by the middle point of the thermal hysteresis for the ρ-T curves, as shown by the broken allows in Fig. 4. For $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$, T_C decreases slightly with increasing x whereas T_t increases except for $Mn_2Sb_{0.85}Sn_{0.15}$. When a magnetic field of μ_0H = 16 T was applied, T_t of both substituted systems shifts to lower temperature side.

The FRI-AFM transition temperatures, T_t, of $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ decrease by applying a magnetic field. When a magnetic field is applied to these systems, a decrease of Gibbs free energy of the FRI phase is larger than that of the AFM phase because of a gain in the Zeeman energy. This leads that the FRI-AFM transition temperature decreases with increasing magnetic fields. The decrease of T_t by applying magnetic fields is similar to that of $Mn_{2-x}Co_xSb$.[6,7,13,14)] However, we cannot observe any characteristic property of the KA effect for $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ even in a high magnetic field of 16 T. In $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$, the values of M for FCW at 5 T (5T-FCW; solid curve) are same values for ZFCW at 5 T (5T-ZFCW; broken curve), as shown in Fig. 3. This behavior is quite different from that of $Mn_{2-x}Co_xSb$. In $Mn_{2-x}Co_xSb$, the value of M for FCW at 5 T is much larger than that for ZFCW at 5 T.[7,13)] In addition, the ρ-T curves of $Mn_2Sb_{0.95}Ge_{0.05}$ and $Mn_2Sb_{0.9}Sn_{0.1}$ for μ_0H = 16 T are traced on those for μ_0H = 0 T at low temperature; that is, the value of ρ at low temperature is independent on the cooling process under a magnetic field, as seen in Fig. 4.

In contrast to the obtained results on $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$, the values of M and ρ of $Mn_{2-x}Co_xSb$ at the temperatures below T_t depend strongly on the cooling process under a magnetic field.[6,7)] This reason is that a residual

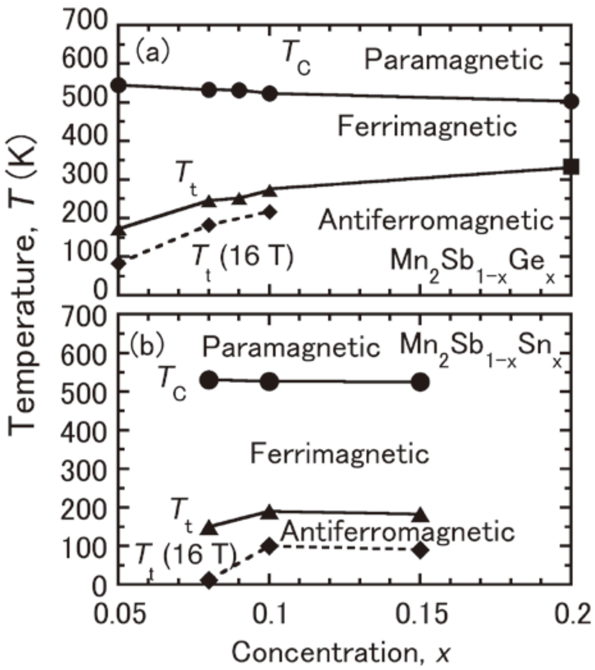

Fig. 5. Magnetic phase diagrams of $Mn_2Sb_{1-x}Ge_x$ (a)[15] and $Mn_2Sb_{1-x}Sn_x$ (b). The Curie temperature T_C was determined by the magnetization measurements for $\mu_0H = 1$ T. The transition temperature T_t for a zero magnetic field and $\mu_0H = 16$ T were determined by the electrical resistivity measurements.

FRI phase (metastable phase) exists in the AFM phase (stable phase) under a magnetic field even at low temperature, and the content of the residual FRI phase depends strongly on the intensity of the magnetic field.[6,7,13,14] This behavior of $Mn_{2-x}Co_xSb$ is thought to be due to the critically slow dynamics induced by the magnetic field, which is called the KA effect induced by a magnetic field.[6] However, the origin of the field-induced KA effect is still unclear.

The first-order AFM-FRI/ferromagnetic transition and the field-induced KA effect were reported for $Mn_{1.85}Co_{0.15}Sb$[6], $Mn_{1.8}Co_{0.2}Sb$[7], $Ce(Fe_{0.96}Al_{0.04})_2$[16], $Ce(Fe_{0.96}Ru_{0.04})_2$[17], $Pr_{0.5}Ca_{0.5}MnO_3$[18], $Ni_{45}Co_5Mn_{36.7}In_{13.3}$[19] and $Ni_{37}Co_{11}Mn_{42.5}Sn_{9.5}$[20]. In these compounds, substituting various elements for the magnetic atoms modified the magnetic sublattice. On the other hand, $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ exhibit a first-order FRI-AFM transition without the KA effect. $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ are formed by substituting a small amount of nonmagnetic Ge and Sn for nonmagnetic Sb, respectively. In addition, the lattice change in $Mn_{1.8}Co_{0.2}Sb$ and $Mn_2Sb_{0.8}As_2$ at T_t is ~0.6% or less.[7,9] Considering these results, therefore, we suppose that the KA effect under a magnetic field is mainly due to the instability of the magnetic states rather than the structural or elastic properties.

In this study, we confirmed that $Mn_2Sb_{1-x}Ge_x$ ($0.05 \le x \le 0.2$) and $Mn_2Sb_{1-x}Sn_x$ ($0.08 \le x \le 0.15$) exhibit the first-order phase transition without KA effect. For $Mn_2Sb_{0.95}Ge_{0.05}$, ρ changes abruptly by 87% in the vicinity of T_t. Therefore, $Mn_2Sb_{1-x}Ge_x$ compounds will be one of the candidates for high performance materials controlled by magnetic fields.

4. Summary

Magnetization and electrical resistivity measurements were carried out for polycrystalline $Mn_2Sb_{1-x}Ge_x$ ($0.05 \le x \le 0.2$) and $Mn_2Sb_{1-x}Sn_x$ ($0.08 \le x \le 0.15$) for $4.2 \le T \le 620$ K and $0 \le \mu_0H \le 16$ T. The lattice parameters a and c of $Mn_2Sb_{1-x}Ge_x$ decreased with increasing x. For $Mn_2Sb_{1-x}Sn_x$, c decreases slightly with increasing x, but a was almost constant. The Curie temperature T_C for $Mn_2Sb_{1-x}Ge_x$ decreased from 545 K ($x = 0.05$) to 504 K ($x = 0.2$). For $Mn_2Sb_{1-x}Sn_x$, T_C decreased slightly from 531 K ($x = 0.08$) to 526 K ($x = 0.15$). For $Mn_2Sb_{1-x}Ge_x$, the first-order magnetic transition temperature T_t between a ferrimagnetic and an antiferromagnetic phase increased from 172 K ($x = 0.05$) to 334 K ($x =$

0.2). For $Mn_2Sb_{1-x}Sn_x$, T_t increased from 150 K (x = 0.08) to 190 K (x = 0.1), and then T_t was almost constant for x. When a magnetic field was applied, T_t decreased. The magnetic phase diagrams of $Mn_2Sb_{1-x}Ge_x$ and $Mn_2Sb_{1-x}Sn_x$ were presented.

Acknowledgments

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