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Magnetic and electrical properties of $Mn_2Sb_{1-x}Z_x$ (Z = Ge, Sn) under high pressures and high magnetic fields

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Abstract:
High pressures and high magnetic field effects on magnetic and electrical properties of polycrystalline $Mn_2Sb_{0.92}Ge_{0.08}$, $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ were investigated. These compounds showed a first-order magnetic transition between the ferrimagnetic (FRI) and antiferromagnetic (AFM) phases for 150–250 K temperature range in a zero magnetic field. The pressure dependence of the AFM/FRI transition temperature was estimated to be -5.1×10^{-2} GPa^{-1} for $Mn_2Sb_{0.92}Ge_{0.08}$. The electrical resistivity changed abruptly by 50% for $Mn_2Sb_{0.92}Sn_{0.08}$ and by 71% for $Mn_2Sb_{0.85}Sn_{0.15}$ at the transition temperature. We confirmed the negative magnetoresistance over 60% for the Sn-substituted compounds.

Keywords: Mn_2Sb, first-order magnetic transition, pressure effect, negative magnetoresistance

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.[1–17] 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 the FRI-AFM transition.[4–7,15,16] In addition, the magnetoresistance and the magnetostrictive effects of these compounds were observed at temperatures below T_t and were accompanied by a field-induced AFM/FRI transition.[5–7,15,16] Therefore, these compounds have attracted attention as magnetic field-controlled materials.

Recently, the thermal FRI/AFM transition in $Mn_{1.85}Co_{0.15}Sb$[6] and $Mn_{1.8}Co_{0.2}Sb$[7,14] was reported to be arrested by applying a magnetic field B, called "kinetic arrest effect (KA effect)"[6] or "thermal transformation arrest (TTA) effect". On the other hand, Shimada *et al.*[15] and Koyama *et al.*[16] reported that $Mn_2Sb_{1-x}Z_x$ (Z = Ge or Sn) does not exhibit the TTA effect. The substitution of Co for Mn as well as Ge and Sn for Sb results in a lattice contraction and a first-order magnetic transition from the FRI to an antiferromagnetic (AFM).[15,16] Therefore, in order to clarify the origin of the TTA effect and to estimate the potential of $Mn_2Sb_{1-x}Z_x$ for applications, it is necessary to clarify the magnetic and

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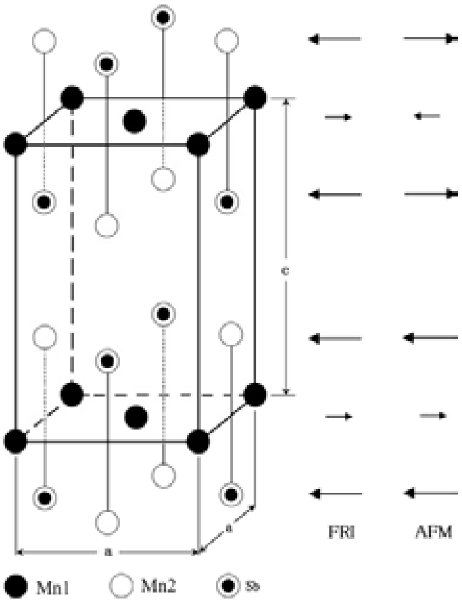

Fig. 1. Crystal structure and arrangement of Mn1 and Mn2 moments in the ferrimagnetic (FRI) and the antiferromagnetic (AFM) states in Mn_2Sb based compound. The length of the arrow represents the magnitude of the magnetic moment of the atom.[3)]

electrical properties for these compounds in high magnetic fields and high pressures. In this report, we present the experimental results of the magnetic properties of $Mn_2Sb_{0.92}Ge_{0.08}$ under high pressures up to 1 GPa and the electrical properties of $Mn_2Sb_{1-x}Sn_x$ ($x = 0.08$ and 0.15) under high magnetic fields up to 16 T.

2. Experimental

Polycrystalline $Mn_2Sb_{0.92}Ge_{0.08}$, $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ were 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 ingots were 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. The obtained sample was confirmed to be a single phase of a Cu_2Sb-type structure by X-ray powder diffraction (XRD) measurements at room temperature.

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 B up to 5 T. The electrical resistivity ρ was measured by using a standard four-probe technique for $4.2 \le T \le 280$ K and $0 \le B \le 16$ T with an 18-T superconducting magnet. The initial permeability μ was measured by an AC transformer method using a piston-cylinder type pressure cell under hydrostatic pressures P up to 1 GPa for $77 \le T \le 400$ K.

3. Results and discussion

Figure 2 shows the temperature dependence of the magnetization of $Mn_2Sb_{0.92}Ge_{0.08}$ for $B = 0.1$ T and 5 T. 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). The data of $Mn_2Sb_{0.92}Ge_{0.08}$ for $B = 0.1$ T show that a first-order phase transition from a FRI to an AFM phases occurs in the vicinity of 230 K ($= T_t$) with a thermal hysteresis of approximately 15 K. This transition temperature T_t of $Mn_2Sb_{0.92}Ge_{0.08}$ is larger than that ($T_t = 172$ K) of $Mn_2Sb_{0.95}Ge_{0.05}$. When a magnetic field of 5 T was applied, T_t of $Mn_2Sb_{0.92}Ge_{0.08}$ decreases to 210 K, and the width of the hysteresis did not change and was approximately 15 K. This phenomenon is different from that of $Mn_2Sb_{0.95}Ge_{0.05}$. The width of the hysteresis of $Mn_2Sb_{0.95}Ge_{0.05}$ at T_t expands by applying magnetic fields.[16)] As seen in Fig.2, $Mn_2Sb_{0.92}Ge_{0.08}$ does not exhibit the TTA effect observed in $Mn_{2-x}Co_xSb$[7,13,14)].

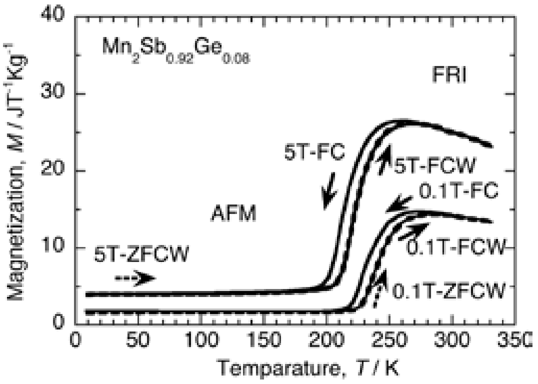

Fig. 2. Temperature dependence of the magnetization of $Mn_2Sb_{0.92}Ge_{0.08}$ for $B = 0.1$ T and 5 T. The measurements were made in field cooling (FC; solid curve), field cooled warming (FCW; solid curve) and field warming after zero-field cooling (ZFCW; broken curve).

Figure 3 shows the temperature dependence of the initial AC permeability μ (μ-T curve) of $Mn_2Sb_{0.92}Ge_{0.08}$ under various pressures up to 1 GPa. Here, the measurements were carried out for heating process. The first-order AFM/FRI transition temperature for heating process, T_t*, was estimated by the inflection point on the μ-T curve for heating process. In this figure, the vertical arrows indicate the determined T_t* in various pressures.

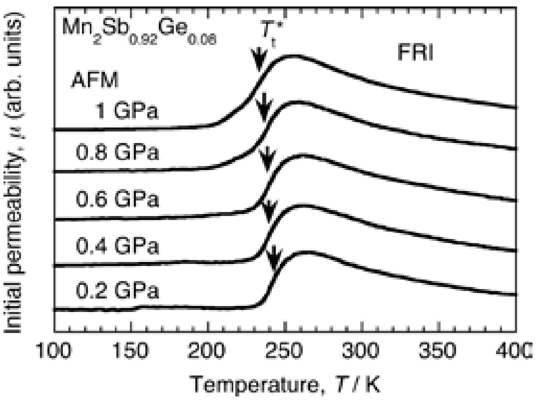

Fig. 3. Temperature dependence of the initial AC permeability μ (μ-T curve) of $Mn_2Sb_{0.92}Ge_{0.08}$ under various pressures up to 1 GPa. The measurements were carried out for heating process. The vertical arrows indicate the determined AFM/FRI transition temperature for heating process T_t*.

Figure 4 shows the pressure dependence of the AFM/FRI transition temperature for heating process. As seen in this figure, T_t* decreases linearly with increasing a pressure P, and the line in this figure is calculated by the least-square method using a linear function. The AFM/FRI transition temperature for heating process under 0.1 MPa and a zero field was estimated to be 246 K by the linear extrapolation of T_t* *vs*. P. The pressure dependence of T_t* was estimated to be $\mathrm{d}\ln T_t^*/\mathrm{d}P = -5.1\times10^{-2}$ GPa⁻¹. This result on the pressure effect with the lattice contraction indicates that the AFM interaction is suppressed by applying a pressure, but the FRI interaction is enhanced. This result is inconsistent with the previous report[16)] on the substitution effect with the lattice contraction for $Mn_2Sb_{1-x}Ge_x$. According to a report by Koyama *et al.*, the lattice parameters a and c of the Ge-substituted $Mn_2Sb_{1-x}Ge_x$ compound contract with increasing x, and the AFM/FRI transition temperature T_t increases while the Curie temperature T_C decreases.[16)] Their result indicates that the AFM interaction is enhanced but the FRI interaction is suppressed with the lattice contraction by the substitution of Ge for Sb in $Mn_2Sb_{1-x}Ge_x$.

For Co-substituted compounds, $\mathrm{d}\ln T_t^*/\mathrm{d}P$ was estimated to be −0.16 GPa⁻¹ for $Mn_{1.9}Co_{0.1}Sb$[18)] and +0.3 GPa⁻¹ for $Mn_{1.8}Co_{0.2}Sb$[19)]. The absolute value of $\mathrm{d}\ln T_t^*/\mathrm{d}P$ for $Mn_2Sb_{0.92}Ge_{0.08}$ is much smaller than that for $Mn_{1.9}Co_{0.1}Sb$ or

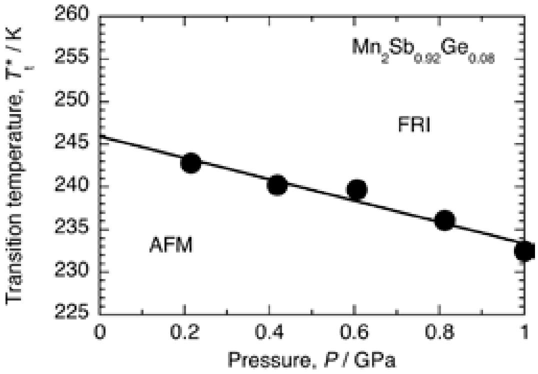

Fig. 4. Pressure dependence of the AFM/FRI transition temperature for heating process.

$Mn_{1.8}Co_{0.2}Sb$. Considering the substitution and pressure effects as mentioned above, the AFM/FRI transition is probably due to modification of hybridization among Mn-3d, Sb-p and Ge-p electrons as well as simple change of the distance among magnetic Mn ions.

Figure 5 shows the temperature dependence of the electrical resistivity ρ (ρ-T curve) of $Mn_2Sb_{0.92}Sn_{0.08}$ (a) and $Mn_2Sb_{0.85}Sn_{0.15}$ (b) for a zero magnetic field and $B = 16$ T. Here, ZFC and ZFW mean zero-field cooling and zero-field-warming measurements, respectively. A first-order magnetic transition from a FRI (low resistivity) to an AFM (high resistivity) states occurs with decreasing temperature for $Mn_2Sb_{0.92}Sn_{0.08}$ under a zero field and for $Mn_2Sb_{0.85}Sn_{0.15}$ under 0 and 16 T. The broken arrows in this figure indicate the determined AFM/FRI transition temperature T_t. For $Mn_2Sb_{0.92}Sn_{0.08}$ under a zero magnetic field, ρ changes abruptly by 50% ($=[(\rho(173\ \mathrm{K}) - \rho(122\ \mathrm{K}))/\rho(173\ \mathrm{K})] = \Delta\rho/\rho$) in the vicinity of $T_t = 150$ K. On the other hand, $\Delta\rho/\rho$ of $Mn_2Sb_{0.85}Sn_{0.15}$ under a zero magnetic field was estimated to be 71% in the vicinity of $T_t = 183$ K. These values of $\Delta\rho/\rho$ for $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ are consistent with that of a previous report for $Mn_2Sb_{1-x}Sn_x$.[11,16] When a high magnetic field of 16 T was applied to $Mn_2Sb_{0.92}Sn_{0.08}$, the AFM/FRI magnetic transition disappeared even at 4.2 K, indicating that the FRI state is stable for $4.2 \leq T \leq 280$ K.

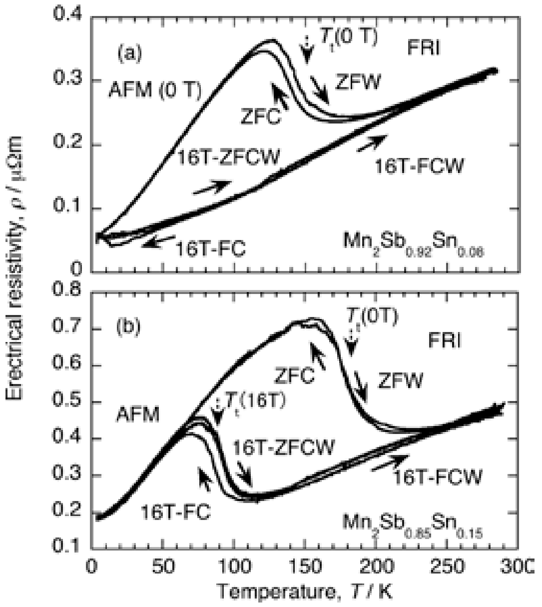

Fig. 5. Temperature dependence of the electrical resistivity ρ of $Mn_2Sb_{0.92}Sn_{0.08}$ (a) and $Mn_2Sb_{0.85}Sn_{0.15}$ (b) for a zero magnetic field and $B = 16$ T. The measurements were made in zero-field cooling (ZFC), zero-field warming (ZFW), field cooling (FC), field cooled warming (FCW) and field warming after zero-field cooling (ZFCW). The broken allows indicate the determined transition temperature T_t between the AFM and FRI phases.

Figure 6 shows the magnetic field dependence of the transverse magnetoresistance ratio $\Delta\rho/\rho(0)$ $[= (\rho(0) - \rho(B))/\rho(0)]$ for $Mn_2Sb_{0.92}Sn_{0.08}$ at 100 K (a) and $Mn_2Sb_{0.85}Sn_{0.15}$ at 144 K (b) in magnetic fields up to 16 T. The measurements were made in field increasing process. A large negative magnetoresistance was observed, when a magnetic field of $B = 16$ T was applied. The change in $\Delta\rho/\rho$ was over −60% under our conditions. The obtained values of $\Delta\rho/\rho$ were larger than that of $Mn_2Sb_{1-x}Ge_x$[15] and of $Mn_2Sb_{1-x}Sn_x$[11]. Considering previous results, the negative magnetoresistance relates closely to the metamagnetic transition.[11,15]

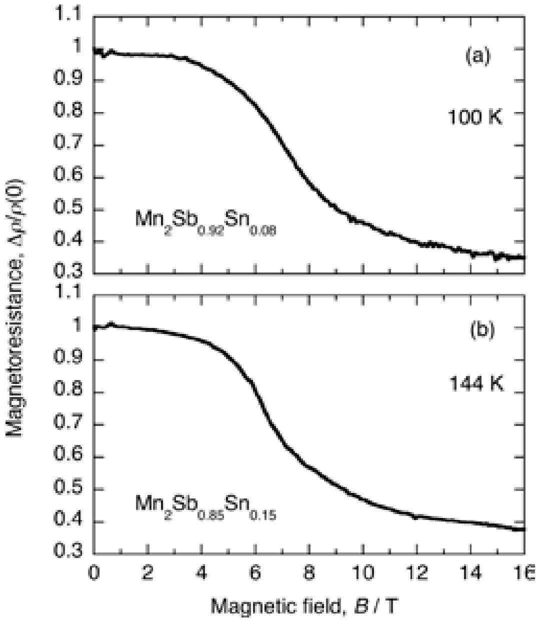

Fig. 6. Magnetic field dependence of the transverse magnetoresistance $\Delta\rho/\rho(0)$ for $Mn_2Sb_{0.92}Sn_{0.08}$ at 100 K (a) and $Mn_2Sb_{0.85}Sn_{0.15}$ at 144 K (b) in magnetic fields up to 16 T. The measurements were made in field increasing process.

The AFM/FRI 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, the decrease of the 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 AFM/FRI 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 could not observe any characteristic property of the TTA effect for $Mn_2Sb_{1-x}Ge_x$ for $B \leq 5$ T and $Mn_2Sb_{1-x}Sn_x$ for $B \leq 16$ T. In $Mn_2Sb_{1-x}Ge_x$. The value of magnetization M for FCW at 5 T (5T-FCW; solid curve) was same value for ZFCW at 5 T (5T-ZFCW; broken curve), as shown in Fig. 2. 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.[6,7,13] In addition, the ρ-T curves of $Mn_2Sb_{0.85}Sn_{0.15}$ for $B = 16$ T are traced on those for $B = 0$ T at low temperature in the AFM phase; that is, the value of ρ at low temperature in the AFM phase is independent on the cooling process under a magnetic field, as seen in Fig. 5.

In contrast to the obtained results on $Mn_2Sb_{1-x}Sn_x$, the values of ρ of $Mn_{2-x}Co_xSb$ at the temperatures (AFM phase) below T_t depend strongly on the cooling process under a magnetic field.[6,7] This reason is that a residual 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 TTA effect induced by a magnetic field.[6] Koyama *et al.* suggested that the TTA effect under a magnetic field was mainly due to the instability of the magnetic states rather than the structural or elastic properties.[13–17] The results of first-principals total-energy calculations for $Mn_{2-x}Co_xSb$[20,21], $Mn_{2-x}Cu_xSb$[22] and $Mn_2Sb_{1-x}As_x$[23] suggested that the environment around the Mn atoms and the lattice distortion play an important role in the stabilization of the magnetic state. Thought the origin of the field-induced TTA effect is still unclear, we confirmed that the magnetic and electrical properties of $Mn_2Sb_{0.92}Ge_{0.08}$, $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ could be controlled by magnetic fields and pressures without the TTA effect.

4. Summary

The magnetization measurements in $B \leq 5$ T and the initial permeability measurements under high pressures up to 1 GPa were carried out for $Mn_2Sb_{0.92}Ge_{0.08}$, and the electrical resistivity was measured for $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ for $B \leq 16$ T and $4.2 \leq T \leq 270$ K. $Mn_2Sb_{0.92}Ge_{0.08}$ showed a first-order AFM/FRI transition at 230 K with a thermal hysteresis of 15 K. The AFM/FRI transition temperature decreased by applying magnetic field. The AFM/FRI transition temperature also decreased linearly with increasing pressures. The pressure dependence of the AFM/FRI transition temperature of $Mn_2Sb_{0.92}Ge_{0.08}$ was estimated to be -5.1×10^{-2} GPa^{-1}. At the transition temperature, the electrical resistivity changed abruptly by 50% for $Mn_2Sb_{0.92}Sn_{0.08}$ and by 71% for $Mn_2Sb_{0.85}Sn_{0.15}$. The values of the negative magnetoresistance of $Mn_2Sb_{0.92}Sn_{0.08}$ and $Mn_2Sb_{0.85}Sn_{0.15}$ were over 60%.

Acknowledgments

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