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磁気特性についての研究 

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Magnetic properties of Mn$_2$Sb$_{1-x}$Z$_x$ ($Z = \text{Ge, Sn}$)

Keiichi KOYAMA*1*, Daisuke SHIMADA1, Hiroki ORIHASHI1, Daisuke MITSUNAGA1, Masahiko HIROI1, Kazuyuki MATSUBAYASHI2, Yoshiya UWATOKO2, Reisho ONODERA3, Shojiro KIMURA3 and Kohki TAKAHASHI3

Abstract:
Magnetization and electrical resistivity measurements were carried out for polycrystalline Mn$_2$Sb$_{1-x}$Ge$_x$ (0.05 $\leq x \leq 0.2$) and Mn$_2$Sb$_{1-x}$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$_2$Sb$_{0.95}$Ge$_{0.05}$ and Mn$_2$Sb$_{0.9}$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$_2$Sb$_{0.95}$Ge$_{0.05}$ and 43% for Mn$_2$Sb$_{0.9}$Sn$_{0.1}$ at $T_t$. The magnetic phase diagrams of Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$Sn$_x$ are presented.

Keywords: Mn$_2$Sb, magnetic properties, kinetic arrest effect, first order phase transition

I. Introduction
Mn$_2$Sb compound with a Cu$_2$Sb-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 2.1µB/Mn1 and 3.9µB/Mn2, leading to the FRI state in Mn$_2$Sb.2,3

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 $\rho$, 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$_{1-x}$Co$_x$Sb was reported to be arrested by applying a magnetic field $\mu_0 H$, the so-called kinetic arrest effect (KA effect).6 In our previous study, we also confirmed that the structural property of Mn$_{1-x}$Co$_x$Sb was 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$_2$Sb$_{1-x}$Z$_x$ ($Z = \text{Ge or Sn}$) are few compared to those on Mn$_{1-x}$Co$_x$Sb. In order to estimate the potential of Mn$_2$Sb$_{1-x}$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
magnetic and the electrical properties of Mn$_2$Sb$_{1-x}$Z$_x$ (Z = Ge, Sn; 0.05 ≤ x ≤ 0.2) under high magnetic fields up to 16 T.

2. Experimental

Polycrystalline Mn$_2$Sb$_{1-x}$Ge$_x$ (0.05 ≤ x ≤ 0.2) and Mn$_2$Sb$_{1-x}$Sn$_x$ (0.08 ≤ x ≤ 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$_2$Sb-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 ≤ $T$ ≤ 620 K under $\mu_0 H$ ≤ 1 T by using a 10-T cryocooled superconducting magnet. The electrical resistivity $\rho$ was measured by using a standard four-probe technique for 4.2 ≤ $T$ ≤ 280 K and 0 ≤ $\mu_0 H$ ≤ 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$_2$Sb$_{1-x}$Ge$_x$ (a) and Mn$_2$Sb$_{1-x}$Sn$_x$ (b) at RT. The parameters were estimated by the 2$\theta$ positions of the 220 and the 004 reflection peaks. Both $a$ and $c$ decrease with increasing $x$ for Mn$_2$Sb$_{1-x}$Ge$_x$. We confirmed that the compound of $x = 0.2$ was AFM at RT whereas other compounds were FRI. For Mn$_2$Sb$_{1-x}$Sn$_x$, $c$ decreases slightly with increasing $x$, but $a$ is almost constant for $x$.

The temperature dependence of the magnetization of Mn$_2$Sb$_{0.95}$Ge$_{0.05}$ (a) and Mn$_2$Sb$_{0.9}$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$_2$Sb$_{0.95}$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$_2$Sb$_{0.95}$Ge$_{0.05}$ decreases to 150 K and the width of the hysteresis is approximately 10 K. As shown
in Fig. 3 (b), a first-order phase transition of \( \text{Mn}_2\text{Sb}_{0.9}\text{Sn}_{0.1} \) occurs in the vicinity of 190 K \((T_t)\) with a thermal hysteresis of approximately 15 K for \( \mu H = 0.1 \) T. When a field of \( \mu H = 5 \) T was applied, \( T_t \) of \( \text{Mn}_2\text{Sb}_{0.9}\text{Sn}_{0.1} \) decreases to 128 K and the width of the hysteresis is approximately 15 K.

Figure 4 shows the temperature dependence of the electrical resistivity \( \rho \) (\( \rho - T \) curve) of \( \text{Mn}_2\text{Sb}_{0.95}\text{Ge}_{0.05} \) (a) and \( \text{Mn}_2\text{Sb}_{0.9}\text{Sn}_{0.1} \) (b) for a zero magnetic field and \( \mu H = 16 \) T, which is shown as typical \( \rho - T \) data. Here, ZFC and ZFW mean zero-field cooling and zero-field-warming measurements, respectively. A first-order phase transition from a FRI
(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 $\mu_0H = 16$ T. For Mn$_2$Sb$_{0.95}$Ge$_{0.05}$, $\rho$ changes abruptly by 87% ($\Delta \rho/\rho = [(\rho(185\text{ K}) - \rho(150\text{ K}))/\rho(185\text{ K})]$) in the vicinity of $T_t = 172$ K. $\Delta \rho/\rho$ of Mn$_2$Sb$_{0.9}$Sn$_{0.1}$ was estimated to be 43% in the vicinity of $T_t = 190$ K. This value of $\Delta \rho/\rho$ for Mn$_2$Sb$_{0.9}$Sn$_{0.1}$ is consistent with that of a previous report for Mn$_2$Sb$_{1-x}$Sn$_x$.11)

Figure 5 shows the magnetic phase diagrams of Mn$_2$Sb$_{1-x}$Ge$_x$(a) and Mn$_2$Sb$_{1-x}$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 $\mu_0H = 16$ T were determined by the middle point of the thermal hysteresis for the $\rho$-$T$ curves, as shown by the broken allows in Fig. 4. For Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$Sn$_x$, $T_C$ decreases slightly with increasing $x$ whereas $T_t$ increases except for Mn$_2$Sb$_{0.85}$Sn$_{0.15}$. When a magnetic field of $\mu_0H = 16$ T was applied, $T_t$ of both substituted systems shifts to lower temperature side.

The FRI-AFM transition temperatures, $T_t$, of Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$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 $T_C$ by applying magnetic fields is similar to that of Mn$_2$Co$_x$Sb.6,7,13,14) However, we cannot observe any characteristic property of the KA effect for Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$Sn$_x$ even in a high magnetic field of 16 T. In Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$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$_2$Co$_x$Sb. In Mn$_2$Co$_x$Sb, 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 $\rho$-$T$ curves of Mn$_2$Sb$_{0.95}$Ge$_{0.05}$ and Mn$_2$Sb$_{0.9}$Sn$_{0.1}$ for $\mu_0H = 16$ T are traced on those for $\mu_0H = 0$ T at low temperature; that is, the value of $\rho$ 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$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$Sn$_x$, the values of $M$ and $\rho$ of Mn$_2$Co$_x$Sb at the temperatures below $T_t$ depend strongly on the cooling process under a magnetic field.6,5) This reason is that a residual
Magnetic properties of Mn$_{2-x}$Z$_x$ ($Z = \text{Ge, Sn}$)

FRI (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. This behavior of Mn$_{2-x}$Co$_x$Sb 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. 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, Mn$_{1.8}$Co$_{0.2}$Sb, Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$, Ce(Fe$_{0.96}$Ru$_{0.04}$)$_2$, Ni$_{45}$Co$_5$Mn$_{36.7}$In$_{13.3}$, and Ni$_{17}$Co$_{11}$Mn$_{42.5}$Sn$_{9.5}$. In these compounds, substituting various elements for the magnetic atoms modified the magnetic sublattice. On the other hand, Mn$_{2-x}$Ge$_x$ and Mn$_{2-x}$Sn$_x$ exhibit a first-order FRI-AFM transition without the KA effect. Mn$_{2-x}$Ge$_x$ and Mn$_{2-x}$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$_{2-x}$As$_x$ at $T_t$ is ~0.6% or less. 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$_{2-x}$Ge$_x$ (0.05 $\leq x \leq 0.2$) and Mn$_{2-x}$Sn$_x$ (0.08 $\leq x \leq 0.15$) exhibit the first-order phase transition without KA effect. For Mn$_{2-x}$Ge$_x$, the Curie temperature $T_C$ decreased from 545 K ($x = 0.05$) to 504 K ($x = 0.2$). For Mn$_{2-x}$Sn$_x$, $T_C$ decreased slightly from 531 K ($x = 0.08$) to 526 K ($x = 0.15$). For Mn$_{2-x}$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$_2$Sb$_{1-x}$Sn$_x$, $T_c$ increased from 150 K ($x = 0.08$) to 190 K ($x = 0.1$), and then $T_c$ was almost constant for $x$.

When a magnetic field was applied, $T_c$ decreased. The magnetic phase diagrams of Mn$_2$Sb$_{1-x}$Ge$_x$ and Mn$_2$Sb$_{1-x}$Sn$_x$ were presented.

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