Magnetic and Structural Properties of Metamagnetic $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ Compound

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The magnetic and structural properties of ferromagnetic $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ were investigated by magnetization and X-ray powder diffraction measurements in magnetic fields up to 5 T. The compound showed first-order transition between the paramagnetic and ferromagnetic state with a thermal hysteresis of approximately 24 K, which was accompanied by the martensitic transformation from the hexagonal Ni_2In -type structure to the orthorhombic TiNiSi -type structure in the vicinity of 275 K. The cell volume expanded by 4.1% during the martensitic transformation. The magnetic moment of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ was estimated to be $111 \text{ Am}^2 \text{ kg}^{-1}$ ($3.7 \mu_{\text{B}}/\text{f.u.}$) at 10 K. The compound showed both metamagnetic transition and magnetic field-induced martensitic transformation. [doi:10.2320/matertrans.M2015382]

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1. Introduction

Stoichiometric MnCoGe is a ferromagnet with a Curie temperature T_{C} of 355 K.¹⁾ The compound has the martensitic phase (M-phase) with an orthorhombic TiNiSi -type crystal structure at room temperature, and has a diffusionless transformation to the parent phase (P-phase) with a hexagonal Ni_2In -type structure at $T_{\text{M}} = 470 \text{ K}$.¹⁾ This structural transformation is a thermoelastic and martensitic one with a large (approximately 3.9%) volume change.^{1,2)} It has been reported that the crystal structure parameters, magnetic moment, T_{C} , and T_{M} of this compound strongly depend on its Mn and Co composition.^{1,2)} The magnetic moment of the orthorhombic structure is larger than that of the hexagonal structure.^{1,3,4)}

The T_{C} and T_{M} of MnCoGe -based compounds have been controlled by substitution of Al⁵⁾ or V⁶⁾ for Co, off-stoichiometric composition,^{2,7,8)} interstitial modification,⁹⁾ and external pressure.²⁾ The off-stoichiometric $\text{Mn}_{1.07}\text{Co}_{0.92}\text{Ge}$ compound with $T_{\text{C}} = 275 \text{ K}$ exhibits a martensitic transformation from the P-phase to the M-phase at $T_{\text{M}} = 210 \text{ K}$.⁷⁾ The cell volume expands by 5.3% and the magnetic moment increases by 24% at T_{M} , accompanied by the martensitic transformation.⁸⁾ Koyama *et al.* observed the magnetic field-induced martensitic transformation of $\text{Mn}_{1.07}\text{Co}_{0.92}\text{Ge}$ just above T_{M} .⁷⁾ The magnetic and structural properties of $\text{Mn}_{1.07}\text{Co}_{0.92}\text{Ge}$ are similar to those of Ni_2MnGa ,¹⁰⁾ Ni-Mn-Sn ,^{11,12)} and NiCoMnIn ,¹³⁾ which are known as magnetic-field-controlled functional materials.

Recently, it was reported that substituting a small amount of Co with iron in MnCoGe decreased T_{M} and T_{C} .^{14–16)} However, while Ni_2In -type structure (P-phase) MnFeGe was found to be ferromagnetic with $T_{\text{C}} = 160 \text{ K}$, martensitic transformation was not observed.¹⁵⁾ The reported results suggested that $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ with $x \sim 0.08$ ¹⁵⁾ and $x = 0.22$ ¹⁶⁾ showed a first-order magnetic transition accompanied by martensitic transformation from the paramagnetic P-phase

to the ferromagnetic M-phase. $\text{MnCo}_{0.94}\text{Fe}_{0.06}\text{Ge}$ exhibits the first-order magnetic transition and a large change in ΔS ($\sim -27.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta B = 5 \text{ T}$) at $\sim 315 \text{ K}$.¹⁵⁾ In our previous studies, the phase diagram of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ suggested that compounds with $0.07 < x < 0.1$ will show magnetic phase transition from the paramagnetic P-phase to the ferromagnetic M-phase, accompanied by martensitic transformation in the vicinity of T_{C} .¹⁷⁾ However, the magnetic and structural properties of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ with $0.07 < x < 0.1$ have not yet been clarified in detail.

X-ray diffraction measurements carried out under high magnetic fields in a wide temperature region provide very useful information on the structural properties of magnetic-field-controlled functional materials.^{7,12)} In this study, we performed magnetization and X-ray powder diffraction measurements of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ in high magnetic fields up to 5 T to clarify the dependence of its fundamental properties on magnetism and crystal structure.

2. Experimental

A polycrystalline sample of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ was prepared by arc-melting the pure constituent elements (Mn, 3N; Co, 3N; Fe, 4N; Ge, 5N) in an argon atmosphere. The obtained button-shaped sample was sealed in an evacuated quartz tube, and was then heat treated at 1123 K for 120 h for homogenization. After the heat treatment, the sample was slowly cooled to room temperature for 10 h. The quality of the sample was examined by X-ray powder diffraction (XRPD) measurements at room temperature. The sample was confirmed to be $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ and contained co-existing P- and M-phases at room temperature. In contrast, $\text{MnCo}_{0.93}\text{Fe}_{0.07}\text{Ge}$ and $\text{MnCo}_{0.9}\text{Fe}_{0.1}\text{Ge}$ were found to have a single M-phase and P-phase at RT, respectively.¹⁷⁾

Differential scanning calorimetry (DSC; NETZSCH) was carried out under an N_2 atmosphere in a temperature range of 200–575 K. Magnetization measurements were performed using a superconducting quantum interference device magnetometer (Quantum Design) at 10–390 K and a magnetic field B up to 5 T.

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XPRD measurements with $\text{CuK}\alpha$ radiation were carried out under a magnetic field up to 5 T at 10–325 K¹⁸⁾ using a high-field X-ray diffractometer. The powder sample was fixed on a copper sample holder with Apiezon grease. The diffraction data were taken at $36^\circ \leq 2\theta \leq 46^\circ$ with a step size of 0.02° . We confirmed that the powder sample was not removed by the magnetic force during the measurements.

3. Results and Discussion

Figure 1(a) shows the DSC curves obtained for $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$. Exothermic and endothermic peaks with a thermal hysteresis were observed during cooling and heating within the temperature range of 240–330 K, which corresponded to the martensitic and reverse transformations, respectively. For comparison, the DSC curves for $\text{MnCo}_{0.93}\text{Fe}_{0.07}\text{Ge}$ are shown in Fig. 1(b). The DSC curves for $\text{MnCo}_{0.93}\text{Fe}_{0.07}\text{Ge}$ exhibited small exothermic and endothermic peaks that corresponded to the magnetic transition at T_C ($= 320$ K), in addition to the martensitic and reverse transformation. The peaks at T_C did not show thermal hysteresis, indicating that the transition was second order. In contrast, DSC curves for $\text{MnCo}_{0.9}\text{Fe}_{0.1}\text{Ge}$ only showed magnetic transition at $T_C = 280$ K.¹⁷⁾ Based on the DSC peaks for $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ in Fig. 1(a), the martensitic transformation starting and finishing temperatures, M_s and M_f , and the reverse transformation starting and finishing temperatures, A_s and A_f , were determined to be 283 K, 241 K, 279 K, and 313 K, respectively. The values of M_s , M_f , A_s and A_f were defined by the intersection of the baseline and the tangent line with the largest slope of the peaks.

Figure 2 shows the temperature dependence of the magnetization of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ at 0.05 T, 1 T, and 5 T. The first-order magnetic transition with a thermal hysteresis of approximately 24 K was observed at $250 \leq T \leq 300$ K. When the magnetic field was applied, the transition temperature shifted towards a higher-temperature. The magnetization was about $111 \text{ Am}^2\text{kg}^{-1}$ at 1 T and 10 K, which corresponds to $3.7 \mu_B$ per formula unit. This result is consistent with the results of neutron diffraction experiments ($2.8 \mu_B/\text{Mn}$ and $1.0 \mu_B/\text{Co}$)³⁾ and electronic structure calculations ($2.98 \mu_B/\text{Mn}$ and $0.78 \mu_B/\text{Co}$)⁴⁾ for the orthorhombic structure.

Figure 3 shows the magnetization curves of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ in fields up to 5 T at various temperatures. Here, the measurements were carried out after zero-field cooling from 350 K (paramagnetic P-phase). $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ shows the ferromagnetic behavior for $T \leq 260$ K and the paramagnetic behavior for $T \geq 280$ K. Metamagnetic transitions with a hysteresis were observed in the vicinity of 270 K.

Figure 4 shows the typical XPRD profiles of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ at several temperatures for the cooling (a) and heating (b) processes in a zero field. Here, hkl_h and hkl_o denote the Miller indices for the hexagonal Ni_2In -type (P-phase) and the orthorhombic TiNiSi -type (M-phase) structures, respectively. Strong Bragg peaks of the P-phase were observed in the high temperature range of 300–325 K. Small orthorhombic M-phase peaks were also detected because this temperature range was within $A_s < T < A_f$. The peaks of the M-phase started to appear and develop with decreasing temperature from 290 K. In contrast, the hkl_h intensity of the

Fig. 1 DSC curves for $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ (a) and $\text{MnCo}_{0.93}\text{Fe}_{0.07}\text{Ge}$ (b). Heating and cooling rates were 10 K/min. The vertical arrows indicate the defined temperatures for martensitic and reverse transformations (M_s , M_f , A_s and A_f).

Fig. 2 Temperature dependence of the magnetization of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ at 0.05 T, 1 T and 5 T. The vertical arrows indicate the measuring process.

Fig. 3 Magnetization curves of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ at various temperatures between 260 K and 290 K. The arrows indicate the heating and cooling process.

Fig. 4 X-ray powder diffraction profiles of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ at various temperatures for cooling (a) and heating (b) processes from 325 K to 10 K under a zero magnetic field. hkl_h and hkl_o denote the Miller indices for the hexagonal Ni_2In -type structure and the orthorhombic TiNiSi -type structure, respectively.

P-phase became smaller with decreasing temperature from M_s . The intensity of the orthorhombic M-phase peaks did not change below 200 K ($< M_f$). This result indicated that the fraction of the M-phase increased between M_s and M_f . However, a small amount of the P-phase remained at 10 K. This may have been caused by partial distortion at low temperature resulting from the pulverization of the original specimen into the powder sample. With increasing temperature, the intensity of the M-phase peaks decreased above 275 K ($\sim A_s$) and was negligibly small over 310 K ($\sim A_f$). In contrast, the intensity of hexagonal P-phase peaks rose above 275 K. These characteristic temperatures obtained from the XRPD measurements are consistent with the martensitic and reverse transformation temperatures M_s , M_f , A_s , and A_f estimated from the DSC measurements.

Figure 5 shows the temperature dependence of the unit cell dimensions of the sample in a zero field. Here, the axes and volumes of two structures are related by $a_{\text{ortho}} = c_{\text{hex}}$, $b_{\text{ortho}} = a_{\text{hex}}$, $c_{\text{ortho}} = \sqrt{3}a_{\text{hex}}$ and $V_{\text{ortho}} = 2V_{\text{hex}}$.¹⁾ The broken arrows in this figure indicate thermal hysteresis, based on the variation of the peak intensity of the XRPD patterns between the hexagonal (P-phase) and orthorhombic (M-phase) structures. No peculiar thermal contraction behavior of either phase was observed, even at $M_f \leq T \leq A_f$. However, the lattice parameters of the M-phase were almost constant for

Fig. 5 Temperature dependence of the unit cell dimensions for $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ in a zero magnetic field. The circles and squares indicate the data for the hexagonal and orthorhombic structures, respectively. The open and closed symbols indicate the data for the heating process and the cooling process, respectively. The arrows indicate the guide to the eye for the change of lattice parameters in martensitic transformation.

$T < 150$ K. This behavior is similar to that previously reported for $\text{Mn}_{1.07}\text{Co}_{0.92}\text{Ge}$.⁷⁾ The value of a_{ortho} increased by 11.9% along the c_{hex} axis at 276 K with decreasing temperature, while the other lattice parameters shrank by 0.5% ($c_{\text{ortho}}/\sqrt{3}$) and 6.5% (b_{ortho}) along the a_{hex} axes, leading to a cell volume change of 4.1%. This volume change was in good agreement with that (3.9–4.4%) reported previously for stoichiometric MnCoGe compounds^{1,2)} but is smaller than that (5.5%) of $\text{Mn}_{1.07}\text{Co}_{0.92}\text{Ge}$.⁷⁾

Figure 6 shows the typical XRPD profiles of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ under a magnetic field up to 5 T at 276 K. At this temperature, the profiles exhibited the two-phase coexistence of the hexagonal P-phase (hkl_h) and the orthorhombic M-phase (hkl_o). No remarkable 2θ -shift of the diffraction peaks was observed, indicating that the lattice parameters of both phases were independent of magnetic field strength. The magnetic field dependence of the ratio of the integrated intensities of the 211_o (M-phase) and the 102_h (P-phase) diffraction peaks is shown in Fig. 7. In this figure, the closed and open symbols indicate the data for the increasing and decreasing field processes, respectively. As seen in Figs. 6 and 7, the intensity of the M-phase was slightly enhanced with a magnetic field strength up to 5 T, while the intensity of the P-phase was suppressed. During the decrease to a zero field, the intensity of the M-phase peak remained unchanged,

Fig. 6 X-ray powder diffraction profiles of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ in magnetic fields up to 5 T at 276 K. hkl_h and hkl_o denote the Miller indices for the hexagonal Ni_2In -type structure and the orthorhombic TiNiSi -type structure, respectively.

Fig. 7 The magnetic field dependence of the ratio of the integrated intensity of the 211_o (I_{211o}) and 102_h (I_{102h}) diffractions. The closed and open symbols indicate the data for the increasing and decreasing field process, respectively.

while that of the P-phase peak did not recover completely. This irreversible process is consistent with the magnetization process with a large hysteresis observed at 270 K, as shown in Fig. 3. Namely, the obtained results suggested that $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ exhibited field-induced martensitic transformation from the paramagnetic P-phase to the ferromagnetic M-phase. Moreover, a high magnetic field of over 5 T is required to lead the complete field-induced martensitic and reverse transformations just above A_f .

As shown in Figs. 1–7, the magnetic properties of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ are closely related to the structural transformation between the hexagonal (P-phase) and orthorhombic (M-phase) structures. That is, our results clearly show that $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ exhibits first-order magnetic transition

from the paramagnetic P-phase to the ferromagnetic M-phase and field-induced martensitic transformation at room temperature. Our magnetic data are in good agreement with previous reports on magnetization measurements,^{1,2,4,7)} neutron diffraction experiments,³⁾ and band structure calculations.⁴⁾

The magnetization measurements of MnCoGe showed that the magnetic moment ($\sim 3.8 \mu_B/\text{f.u.}$) for the orthorhombic structure is larger than that ($\sim 2.6 \mu_B/\text{f.u.}$) for the hexagonal structure.^{1,4)} The electronic structure calculations also showed that the magnetic moments of Mn and Co are $2.98 \mu_B/\text{Mn}$ and $0.78 \mu_B/\text{Co}$ for the orthorhombic MnCoGe and $2.88 \mu_B/\text{Mn}$ and $0.04 \mu_B/\text{Co}$ for the hexagonal one.⁴⁾ In addition, Johnson reported that the T_C (265 K) of hexagonal $\text{Mn}_{0.95}\text{CoGe}$ is smaller than that ($T_C = 355$ K) of orthorhombic MnCoGe .¹⁾ In our previous works, the T_C (280 K) of hexagonal $\text{MnCo}_{0.9}\text{Fe}_{0.1}\text{Ge}$ was found to be smaller than that (321 K) of orthorhombic $\text{MnCo}_{0.93}\text{Fe}_{0.07}\text{Ge}$.¹⁷⁾ Considering these previous results, our findings suggest that $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ shows martensitic transformation from the P-phase with a low magnetic moment ($\sim 2.6 \mu_B/\text{f.u.}$) and low T_C (~ 280 K) to the M-phase with a high magnetic moment ($\sim 3.8 \mu_B/\text{f.u.}$) and high T_C (~ 320 K), accompanied by a large volume change of 4.1% in the vicinity of 280 K. That is, when a magnetic field is applied to this compound, the decrease in free energy in the high magnetic moment ferromagnetic M-phase is larger than that in the low magnetic moment paramagnetic P-phase because of the addition of the Zeeman energy. This caused the shift of the first-order magnetic transition temperature to a higher temperature (see Fig. 2), the metamagnetic transition with a large hysteresis (see Fig. 3), and the field-induced martensitic transformation (see Figs. 6 and 7) observed under an applied magnetic field.

However, the difference between the magnetic moment ($\sim 3.8 \mu_B/\text{f.u.}$) of the M-phase and the magnetic moment ($\sim 2.6 \mu_B/\text{f.u.}$) of the P-phase is small, only $1.2 \mu_B/\text{f.u.}$ Additionally, because the T_C of these phases are close, the difference between their magnetic moments is probably smaller than $1.2 \mu_B/\text{f.u.}$ at room temperature. As seen in Fig. 2, indeed, the magnetization of the paramagnetic P-phase was rapidly induced by the application of the magnetic field, whereas the induced magnetization of the ferromagnetic M-phase was small. As a result, the difference between the magnetizations of the phases became smaller at the first-order magnetic transition temperature. This may be a disadvantage for gaining the Zeeman energy. Therefore, a high magnetic field is required to complete the field-induced martensitic transformation and to exploit the potential of this compound sufficiently.

4. Conclusions

We performed magnetization and XRPD measurements on $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ under fields up to 5 T. A first-order transition between the paramagnetic and ferromagnetic states with a thermal hysteresis of approximately 24 K was observed in the vicinity of 275 K, which increased with the magnetic field. The magnetic moment of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ was estimated to be $111 \text{ Am}^2\text{kg}^{-1}$ for 1 T at 10 K, which corresponds to $3.7 \mu_B/\text{f.u.}$ The metamagnetic transition was observed at 270 K, which was in the vicinity of the magnetic

transition temperature. $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ exhibited martensitic transformation from the hexagonal Ni_2In -type to the orthorhombic TiNiSi -type structure and its reverse transformation at $240 < T < 320$ K. During the transformation from the hexagonal to orthorhombic structure, the cell volume expanded by 4.1%. The results of the X-ray diffraction and magnetization measurements indicated that the magnetic field induced the martensitic transformation at 276 K.

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