

Magnetic Properties of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$)

著者	ONOUÉ Masahira, OHZONO Kosuke, MITSUI Yoshifuru, HIROI Masahiko, UMETSU Y Rie, UWATOKO Yoshiya, KOYAMA Keiichi
journal or publication title	Reports of the Faculty of Science, Kagoshima University
volume	49
page range	11-15
year	2016-12-30
URL	http://hdl.handle.net/10232/00032112

Magnetic Properties of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$)

Masahira ONOUE¹⁾, Kosuke OZONO¹⁾, Yoshifuru MITSUI¹⁾, Masahiko HIROI¹⁾,
Rie Y UMETSU²⁾, Yoshiya UWATOKO³⁾, Keiichi KOYAMA^{1)*}

Abstract:

Magnetization and Mössbauer spectroscopy measurements were performed for $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$) to clarify its fundamental properties of the magnetism. The magnetic moments m for $x = 0.08$ was estimated to be $3.70 \mu_B/\text{f.u.}$ at 10 K. The compound showed a first-order magnetic transition (FOMT) from the martensitic phase with high magnetic moment to the parent phase with low magnetic moment in the vicinity of $T_t = 275$ K with increasing temperature under magnetic field of $\mu_0 H = 1$ T. From Mössbauer measurement for $x = 0.12$, the valence of Fe atom was found to be Fe^{2+} . The obtained results were discussed on the basis of the mean-field calculation for the parent and martensitic phases.

Keywords: Magnetism in Solids, mean-field calculation, first order transition, Mössbauer effect

1. Introduction

Ferromagnetic MnCoGe-based compounds are magnetic functional materials which show the magnetic-field-induced martensitic transition. When the first order magnetic transition (FOMT) was accompanied by the martensitic transition, the magnetovolume and magnetocaloric effects were observed.^{1–3)} MnCoGe-based compound exhibits a martensitic transformation from a hexagonal Ni_2In -type (P-phase) to orthorhombic TiNiSi -type structure (M-phase). The martensitic transition temperature T_M is extremely sensitive to the stoichiometry of MnCoGe⁴⁾. It has been reported that the Curie temperature T_C and T_M of the MnCoGe-based compounds were controlled by substitution of Al⁵⁾ or V⁶⁾ for Co, off-stoichiometric composition^{1,7,8)}, interstitially modified⁹⁾ and external pressure⁷⁾.

Recently, it was reported that T_M and T_C decreased by a small amount of iron substitution for Co in $\text{MnCoGe}^{10–12)}$. $\text{MnCo}_{0.94}\text{Fe}_{0.06}\text{Ge}$ showed a FOMT at $T \sim 275$ K¹⁰⁾. The FOMT is accompanied by large entropy change ΔS of -27.5 J $\text{kg}^{-1} \text{K}^{-1}$ ¹⁰⁾. By the Mössbauer measurement, it was revealed that substituted iron atoms prefer to occupy Co site to Mn site¹¹⁾. Ozono *et al.* reported that the FOMT of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ occurs simultaneously with the martensitic transformation for $0.08 \leq x \leq 0.09$ in the vicinity of room temperature¹²⁾.

In this study, we performed magnetization and Mössbauer spectroscopy for $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$) measurements in order to understand the magnetic properties.

2. Experimental

Polycrystalline $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$) compounds were prepared by arc-melting the pure consistent 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 (RT) for 10 h. The quality of the sample was examined by X-ray powder diffraction (XRD) measurements at RT. Magnetization measurements were performed using a superconducting quantum interference device magnetometer (Quantum Design) at 10–390 K and magnetic field $\mu_0 H$ up to 5 T.

⁵⁷Fe Mössbauer spectroscopy measurements were performed using a triangular wave drive motion of ⁵⁷Co resonance

1) Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan

2) Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

3) Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan

* Corresponding author:

鹿児島大学大学院理工学研究科 物理・宇宙専攻 小山佳一

〒890-0065 鹿児島県鹿児島市郡元2丁目21-35

e-mail: koyama@sci.kagoshima-u.ac.jp

source at 290 K. The velocity scale was calibrated by α -Fe, which is hyperfine magnetic field ($H_{\text{hf}} = 33.1$ T), and the offset value of the isomer shift (IS) = 0.07 mm/sec. The Mössbauer spectra were analyzed by least-squares method using the hyperfine parameters.

3. Results and discussion

Fig. 1 shows the temperature T dependence of the magnetic moment m (m - T curve) of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ under magnetic fields of $\mu_0 H = 1$ T and 5 T. The FOMT was observed between 250 K and 300 K. The transition temperature was determined to be $T_i = 275$ K for $\mu_0 H = 1$ T, which increases with increasing H . The magnetic moment m was determined to be $3.70 \mu_{\text{B}}/\text{f.u.}$ at 10 K for $\mu_0 H = 5$ T, which is consistent with the results of neutron diffraction experiments ($2.8 \mu_{\text{B}}/\text{Mn}$ and $1.0 \mu_{\text{B}}/\text{Co}$)¹³⁾ and electronic structure calculations ($2.98 \mu_{\text{B}}/\text{Mn}$ and $0.78 \mu_{\text{B}}/\text{Co}$)¹⁴⁾ for the martensitic phase (M -phase) of MnCoGe .

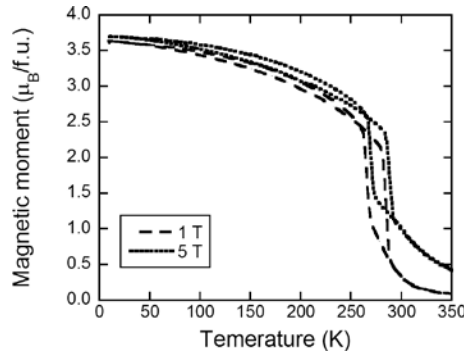


Fig. 1. Temperature dependence of the magnetic moment of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ under magnetic fields of $\mu_0 H = 1$ T (broken line) and 5 T (dotted line).

In order to understand the observed FOMT, we calculated the temperature dependence of the magnetic moment m in various magnetic fields on the basis of a simple mean-field model for the P-phase with low magnetic moment and M-phase with a high magnetic moment. Here, we assumed that the orbital angular momentum was quenched, and m originated from the thermal average of the total spin angular momentum S of the magnetic atoms. In this model, $m(T, H)$ at temperature T and applied magnetic field H was expressed as follow:

$$m(T, H) = 2S\mu_B B_J(\alpha), \quad (1)$$

where

$$\alpha = \frac{2S\mu_B(\lambda Nm + \mu_0 H)}{k_B T}, \quad (2)$$

and N is the number of magnetic atoms per unit volume, $B_J(\alpha)$ the Brillouin function, λ the molecular field constant, and k_B the Boltzmann constant¹⁵⁾. For P- and M-phases, m of MnCoGe was reported to be $2.92 \mu_{\text{B}}/\text{f.u.}$ and $3.76 \mu_{\text{B}}/\text{f.u.}$, respectively¹⁴⁾. In this study, therefore, the calculation was performed by using the parameter of $S = 3/2$ for the P-phase and $S = 2$ for the M-phase.

Fig. 2 shows the temperature dependence of the reduced magnetic moment $m(T)/m(0)$ for the calculated magnetic moments of the M-phase, $m_{\text{M}}(T)$, and P-phase, $m_{\text{P}}(T)$, for $\mu_0 H = 1$ T (a) and for 5 T (b). Here, the calculated $m(T)/m(0)$ of the M-phase and P-phase is normalized by the value of $m_{\text{M}}(T)$ at 10 K, $m_{\text{M}}(10\text{K})$. The experimental data deduced from Fig. 1 are also presented. In this calculation, using the parameters $\lambda = 177$ K for M-phase and $\lambda = 220$ K for P-phase, the calculations represented the experimental m - T data well, as seen in Fig. 2. The obtained results suggest

that the FOMT of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ is the transformation between the M-phase with high m and high T_C , and the P-phase with low m and low T_C .

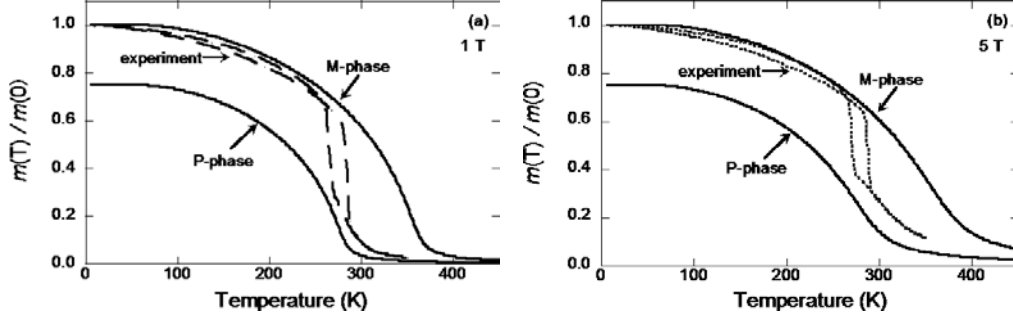


Fig. 2. Temperature dependence of the reduced magnetic moment $m(T)/m(0)$ for the calculated magnetic moments of the M-phase, $m_M(T)$, P-phase, $m_P(T)$, and the experimental data (Fig. 1) for $\mu_0 H = 1$ T (a) and for 5 T (b). The calculated $m(T)/m(0)$ of the M-phase and P-phase is normalized by the value of $m_M(T)$ at 10 K. Solid curves and broken (or dotted) curves indicate the calculated and experimental curves, respectively.

The magnetic entropy change ΔS_m during FOMT was estimated from the temperature dependence of the magnetization M (M - T curves) of $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ through the Maxwell relation,

$$\Delta S_m = \int_0^H \left(\frac{\delta M}{\delta T} \right)_H dH \quad (3)$$

Fig. 3 shows the magnetic entropy change ΔS_m vs. temperature curves. Here, ΔS_m was evaluated using the M - T data under a magnetic field $\mu_0 H$ from 0.5 T to 5 T for the 0.5 T/step. The inset of Fig. 3 shows the M - T curves for various magnetic field of $1 \leq \mu_0 H \leq 5$ T in the vicinity of T_C . The estimated ΔS_m was $-14 \text{ Jkg}^{-1}\text{K}^{-1}$ at 5 T, which was lower than the other Fe-substituted MnCoGe system for $\Delta S_m = -27.5 \text{ Jkg}^{-1}\text{K}^{-1}$ at 5 T¹⁰⁾.

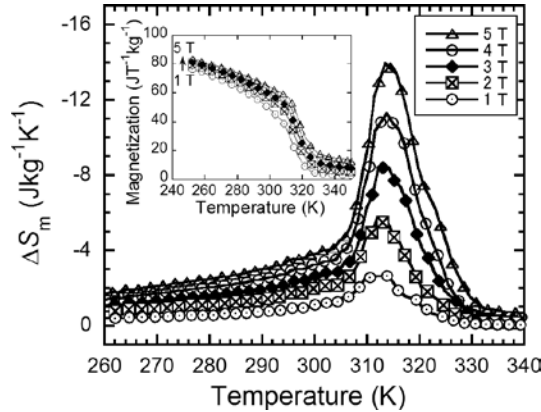


Fig. 3. Magnetic entropy change ΔS_m vs. temperature curves. Here, ΔS_m was evaluated using the M - T data as shown in the inset.

In order to estimate the contribution of ΔS_m at T_C , we calculated the magnetic free energy on the basis of the simple mean field model. The magnetic free energy per molecule F of the system is expressed by

$$F = k_B T \ln Z - m(\lambda N m + \mu_0 H), \quad (4)$$

where, Z is the partition function defined as

$$Z = T_r \exp \left[\frac{-2\mu_B S (\lambda N m + \mu_0 H)}{k_B T} \right] \quad (5)$$

The free energy F and the magnetic entropy $S_m (= -\Delta F/\Delta T)$ were calculated by eqs. (4) and (5). Fig.5 shows the temperature dependence of the calculated S_m of M -phase and P -phase. The maximum ΔS_m was estimated to be $-8.6 \text{ Jkg}^{-1}\text{K}^{-1}$ at 264 K for 5 T, which is approximately 61% of the experimental value ($-14 \text{ Jkg}^{-1}\text{K}^{-1}$) $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ exhibits the large volume change of 4.1% at T_i^{12} . These results indicate that the contribution of the magnetic entropy change to the total entropy change is smaller than the entropy change due to the structural transition.

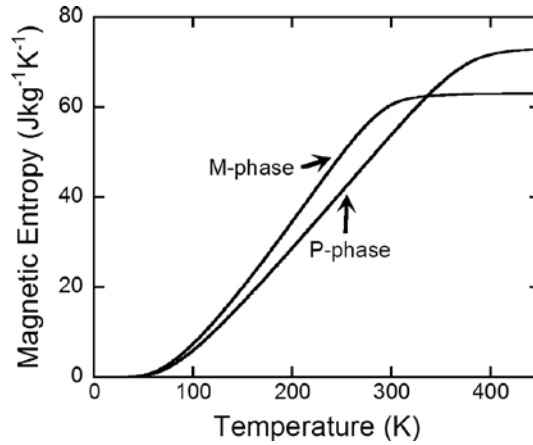


Fig. 4. Temperature dependence of the calculated S_m of M -phase and P -phase. The maximum ΔS_m from the M - to P -phase was estimated to be $-8.6 \text{ Jkg}^{-1}\text{K}^{-1}$ at 264 K.

Fig. 5 shows Mössbauer spectrum of $\text{MnCo}_{0.88}\text{Fe}_{0.12}\text{Ge}$ at 290 K. The crystal structure of $\text{MnCo}_{0.88}\text{Fe}_{0.12}\text{Ge}$ was hexagonal (P -phase), and the Curie temperature was 275 K¹². Assuming that Fe atoms occupy 69% in Co-site and 31% in Mn-site in the hexagonal structure (P -phase), the experimental spectrum was represented well by the calculation. The previous report of Mössbauer spectroscopy for $\text{MnCo}_{0.96}\text{Fe}_{0.04}\text{Ge}$ showed that Fe atoms occupy 80% in Co-site and 20% in Mn-site in the orthorhombic structure (M -phase)¹¹. Our result for the hexagonal structure is consistent with the previous report for the orthorhombic structure. The isomer shift (IS) and the quadrupole splitting (QS) for hexagonal $\text{MnCo}_{0.88}\text{Fe}_{0.12}\text{Ge}$ were evaluated to be IS = 0.12 mm/s and QS = 0.82 mm/s of Co-Site, and IS = 0.25 mm/s and QS = 0.91 mm/s of Mn-Site, respectively. The obtained results suggested that Fe^{2+} ions with $S = 0$ state (low spin state) exist in $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ compound with the hexagonal P -phase.

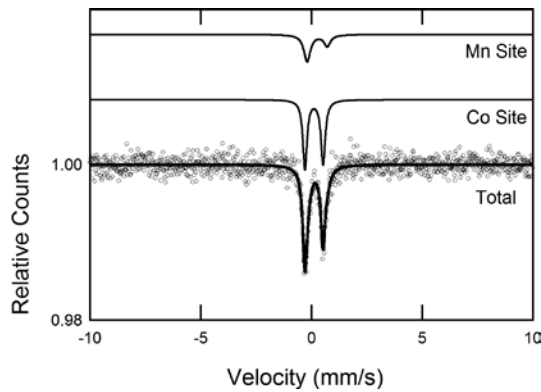


Fig. 5. The Mössbauer spectrum and sub-spectral fits for $\text{MnCo}_{0.88}\text{Fe}_{0.12}\text{Ge}$ at 290 K.

4. Conclusion

Magnetic properties of $\text{MnCo}_{1-x}\text{Fe}_x\text{Ge}$ ($x = 0.08, 0.12$) were investigated. $\text{MnCo}_{0.92}\text{Fe}_{0.08}\text{Ge}$ exhibited a first order magnetic transition (FOMT) in the vicinity of 275 K. In order to understand the FOMT, the magnetizations for the P- and M-phases were calculated by a simple mean-field theory. The calculated magnetizations indicated that the FOMT is due to the transformation between the P-phase with small m and low T_C , and the M-phases with large m and high T_C . The magnetic entropy change of the FOMT was estimated to be $-14 \text{ Jkg}^{-1}\text{K}^{-1}$. From Mössbauer spectroscopy for $\text{MnCo}_{0.88}\text{Fe}_{0.12}\text{Ge}$ (P-phase) suggested that Fe atoms occupy 69% in Co-site and 31% in Mn-site in the hexagonal structure, and Fe^{2+} atoms with $S = 0$ state existed in the compound.

Acknowledgments

The magnetization measurements were carried out at the Institute for Solid State Physics, the University of Tokyo. The Mössbauer spectroscopy experiments were performed at Division of Isotope Science, Natural Science Centre for Research and Education, Kagoshima University. This work was supported in part by the KAKENHI 16H04547 and 16K14374.

REFERENCES

- 1) K. Koyama, M. Sakai, T. Kanomata, K. Watanabe: *J. Appl. Phys.* **43** (2004) 8036-8039.
- 2) J.T. Wang, D.S. Wang, C.F. Chen, O. Nashima, T. Kanomata, H. Mizuseki, Y. Kawazoe: *Appl. Phys. Lett.* **89** (2006) 262504.
- 3) E.K. Liu, W. Zhu, L. Feng, J.L. Chen, W.H. Wang, G.H. Wu, H.Y. Liu, F.B. Meng, H.Z. Luo, Y.X. Li: *EPL*. **91** (2010) 17003.
- 4) Johnson V: *Inorg. Chem.* **14** (1975) 1117–1120.
- 5) W. Zhang, O. Tegus, Y. Wu, Yirgeltu, H. Yan, S. Lin: *J. Mater. Sci. Technol.* **25** (2009) 781–784.
- 6) G.H. Meng, O. Tegus, W.G. Zhang, L. Song, J.L. Huang: *J. Alloy. Compd.* **497** (2010) 14–16.
- 7) T. Kanomata, H. Ishigaki, T. Suzuki, H. Yoshida, S. Abe, T. Kaneko: *J. Magn. Magn. Mater.* **140-144** (1995) 131–132.
- 8) P.E. Markin, N.V. Mushnikov, E.G. Gerasimov, A.V. Proshkin, A.S. Volegov: *Phys. Metals. Metallogr.* **114** (2013) 893–903.
- 9) N.T. Trung, L. Zhang, L. Caron, K.H.J. Buschow, E. Brück: *Appl. Phys. Lett.* **96** (2010) 172504.
- 10) G.J. Li, E.K. Liu, H.G. Zhang, Y.J. Zhang, J.L. Chen, W.H. Wang, H.W. Zhang, G.H. Wu, S.Y. Yu: *J. Magn. Magn. Mater.* **332** (2013) 146–150.
- 11) Q.Y. Ren, W.D. Hutchison, J.L. Wang, R. Cobas, J.M. Cadogan, S.J. Campbell: *Hyperfine Interact.* **231** (2015) 75–84.
- 12) K. Ozono, Y. Mitsui, M. Hiroi, R.Y. Umetsu, K. Takahashi, K. Matsubayashi, Y. Uwatoko, K. Koyama: *Mater. Trans.* **57** (2016) 316–320.
- 13) S. Niziol, A. Bombik, W. Bazela, A. Szytula, D. Fruchart: *J. Magn. Magn. Mater.* **27** (1982) 281–292.
- 14) S. Kaprzyk, S. Niziol: *J. Magn. Magn. Mater.* **87** (1990) 267–275.
- 15) Chikazumi S: “Physics of Ferromagnetism” Oxford University Press (1997) 118–124.