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# Magnetocaloric and structural properties of $SmMn_2Ge_2$

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**Abstract**

We have performed detailed magnetization, specific heat and powder X-ray diffraction measurements under magnetic fields, for obtaining information on the magnetic and the structural properties of re-entrant ferromagnet $SmMn_2Ge_2$ with the $ThCr_2Si_2$-type tetragonal structure. The lattice parameter $a$ decreases by about 0.1%, while the parameter $c$ increases slightly by about 0.02% in the antiferromagnetic (AFM) state, compared with the ferromagnetic (FM) and re-entrant ferromagnetic (RFM) states. In the AFM state, the structural distortion recovers by applying a magnetic field, accompanied with the metamagnetic transition from the AFM to the forced FM states. The results of a magnetocaloric effect indicate that the magnetic entropy change at these phase transitions is mainly due to the change of the Sm magnetic state.


*Keywords:* Magnetic entropy; Magnetic phase transition; Powder X-ray diffraction

## 1. Introduction

Compounds $RMn_2Ge_2$ (R = rare earth element) crystallize in the $ThCr_2Si_2$-type body-centered tetragonal structure, which is characterized by R–Ge–Mn–Ge–R-stacked layers along the $c$-axis. It was reported that the magnetic properties of $RMn_2Ge_2$ are very sensitive to the intralayer Mn–Mn distance $R^a_{Mn-Mn}$ [1]. The magnetic interaction between interlayer Mn–Mn ions is ferromagnetic (FM) for $R^a_{Mn-Mn} > 0.285$ nm, whereas it is antiferromagnetic (AFM) for $R^a_{Mn-Mn} < 0.285$ nm at room temperature [1]. In $SmMn_2Ge_2$, $R^a_{Mn-Mn}$ is slightly larger than this critical value of 0.285 nm at room temperature, so that the compound shows re-entrant ferromagnetism: FM phase in $T_2$ (∼150 K) < $T$ < $T_C$ (∼350 K), AFM phase in $T_1$ (∼100 K) < $T$ < $T_2$ and re-entrant ferromagnetic (RFM) phase below 100 K [1–4].

Fujii et al. explained this re-entrant ferromagnetism in terms of the strong temperature dependence of the Mn–Mn and Sm–Mn exchange interactions. With decreasing temperature from $T_C$, the FM phase transforms into the AFM one at $T_2$ because $R^a_{Mn-Mn}$ decreases due to the thermal contraction and is shorter than the critical value of 0.285 nm. In the AFM phase, the Sm moments are regarded as the disordered state because of feeling no exchange field from the Mn sublattice with the AFM Mn–Mn coupling. The FM Sm–Sm coupling is enhanced below $T_1$, which becomes sufficiently strong to break the AFM Mn–Mn coupling via the FM Sm–Mn coupling, so that the RFM phase appears. A few of the spin structure models have been reported so far [1,2]. However, these models do not explain the magnetic properties of $SmMn_2Ge_2$ completely.

As we know, the magnetic entropy change is one of useful information to study the magnetic phase transition. In this paper, we present our recent results on the magnetocaloric properties deduced by the detailed magnetization and specific heat measurements and on the structural properties

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determined by high-field X-ray diffraction measurements for $SmMn_2Ge_2$.

## 2. Experimental

The polycrystalline sample of $SmMn_2Ge_2$ was prepared by arc-melting the mixture of stoichiometric amounts of the pure elements (Sm, 3N; Mn, 4N; Ge, 5N) in an argon atmosphere. In order to ensure homogeneity, the ingot was turned over and re-melted several times. The ingot was wrapped by a Ta foil and then was annealed at 900 K for 6 days in an evacuated quartz tube. Magnetization measurement was performed by a SQUID magnetometer (Quantum Design) at $5 \leq T \leq 300$ K in fields $B$ up to 1 T. Specific heat measurements were carried out by a relaxation method. High-field powder X-ray diffraction experiments with Cu Kα radiation were carried out at $8.6 \leq T \leq 290$ K and at 4 T [6]. The sample was confirmed to be a single phase of the $ThCr_2Si_2$-type structure except for a very weak Sm oxide phase at room temperature.

## 3. Results and discussions

Fig. 1 shows the temperature dependence of the magnetization at 0.1 T. The re-entrant ferromagnetism with thermal hysteresis is observed at $B = 0.1$ T, which is similar to results reported in literatures [2–5], although our stability range of the AFM phase is narrower than that reported by Fujii et al. using a single crystal [1]. The phase transition temperatures are determined to be $T_1 = 100$ K (from RFM to AFM) and $T_2 = 150$ K (from AFM to FM). The Curie temperature $T_C$ of this sample cannot be determined in our temperature range. By applying a magnetic field of 1 T, the AFM phase disappears and the forced ferromagnetic (FFM) phase is observed, as shown in the inset of Fig. 1.

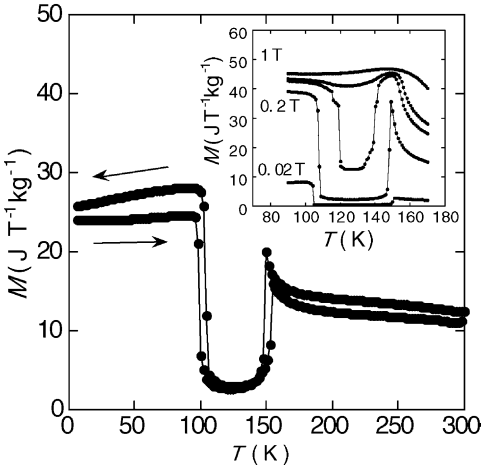


Fig. 1. Temperature dependence of the magnetization at 0.1 T. The data are taken in cooling and heating processes. The inset shows the typical magnetization vs. temperature curves with heating process under various magnetic fields of 0.02, 0.2, 0.4, 0.5 and 1 T.

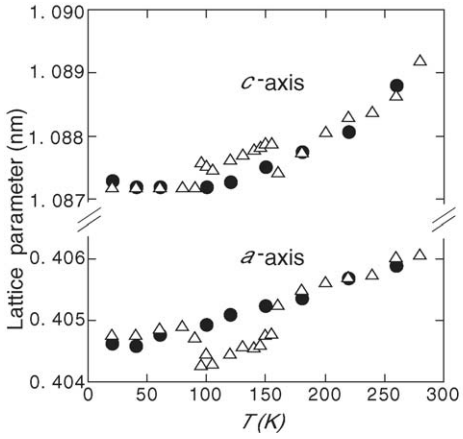


Fig. 2. Temperature dependence of the lattice parameters $a$ and $c$ in zero field (open triangles) and 4 T (solid circles).

Temperature dependence of the lattice parameters $a$ and $c$ in zero field and 4 T is shown in Fig. 2. We confirmed that the crystal structure is the $ThCr_2Si_2$-type in each magnetic phases from the profile data taken at temperatures from 20 to 290 K under zero field and 4 T [7]. With decreasing temperature from 290 K, both $a$ and $c$ decrease like the normal thermal contraction in the FM phase of $T > T_2$. On further cooling through $T_2$, $a$ contracts abruptly by 0.1% in the AFM phase, and then, it expands again by the same amount, accompanied with appearance of the RFM phase at $T_1$. In contrast to this, $c$ expands slightly by 0.04% at $T_2$ with cooling, and then, it also contracts at $T_1$. Below $T_1$, $c$ is almost constant for decreasing temperature. The observed behavior in zero field is consistent with the previous reports [2,4,5]. In the AFM phase, the unit cell volume $V$ is smaller than that in the FM phase by $\Delta V/V \sim 0.3\%$. By applying a magnetic field of 4 T, the AFM phase transforms to the FFM phase, and the lattice parameters decrease continuously with decreasing temperature like the normal thermal contraction. In addition, it seems that the lattice parameters in the FM and RFM phases are almost independent of magnetic fields up to 4 T. The obtained results indicate that the magnetic property relates closely to $R^c_{Mn-Mn}$ (interlayer Mn–Mn distance) as well as $R^a_{Mn-Mn}$, although the effect on $R^c_{Mn-Mn}$ is very small. It should be noted that the thermal hysteresis and two-phase coexistence on the structural properties cannot be confirmed in our detailed measurements at the vicinity of $T_1$ and $T_2$ [7]. Therefore, we believe that the compound dose not exhibit the structural phase transition but small striction accompanied with the magnetic phase transition.

Fig. 3(a and b) shows the magnetic entropy change $\Delta S_M$ versus temperature curves at the vicinity of $T_1$ and $T_2$ in a field change of 1 T, respectively. Here, $\Delta S_M$ is estimated by the magnetization measurements through the Maxwell relation $(dS_M/dB)_T = (dM/dT)_B$. We

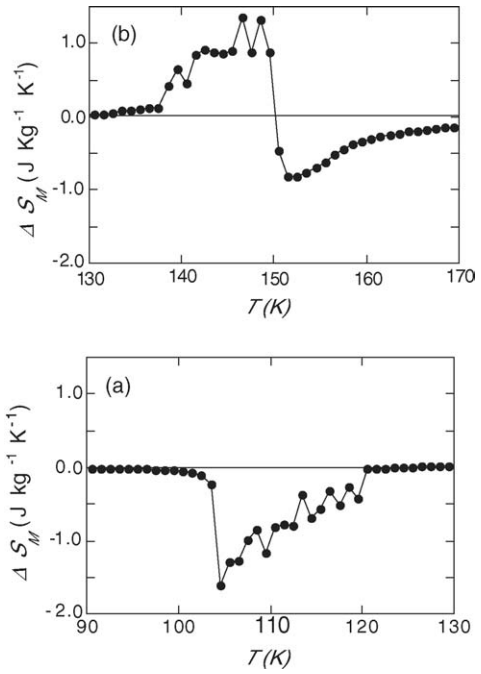


Fig. 3. Magnetic entropy change $\Delta S_M$ in field change of 1 T vs. temperature curves at the vicinity of: (a) 100 K (=$T_1$) and (b) 150 K (=$T_2$).

estimated $\Delta S_M(T_1) = -1.4\,J\,K^{-1}\,kg^{-1}$ for the RFM–AFM phase transition at $T_1$ and $\Delta S_M(T_2) = +1.3\,J\,K^{-1}\,kg^{-1}$ for the AFM–FM one at $T_2$. We also estimated to be $\Delta S_M(T_1) = -0.8\,J\,K^{-1}\,kg^{-1}$ and $\Delta S_M(T_2) = +1.1\,J\,K^{-1}kg^{-1}$ using Clausius–Clapayron's equation. Recent specific heat measurements for this sample are consistent with these results, which will be reported in future. The absolute values of $\Delta S_M(T_1)$ and $\Delta S_M(T_2)$ are much smaller than 14 $J\,K^{-1}\,kg^{-1}$ of $R\ln 2$ for a simple spin state ($S = 1/2$) or 37 $J\,K^{-1}\,kg^{-1}$ of $R\ln 6$ for a Sm moment ($J = 5/2$). These small $\Delta S_M(T_1)$ and $\Delta S_M(T_2)$ can be explained qualitatively by the following scenario on the basis of the molecular field model in R–Mn two-sublattice [8,9].

Considering the results of Refs. [8,9], it is expected that the condition of $|J_{Mn–Mn}|$ (Mn–Mn exchange constant) $\gg |J_{Sm–Mn}|$ (Sm–Mn exchange constant) $\gg |J_{Sm–Sm}|$ (Sm–Sm exchange constant) in $SmMn_2Ge_2$. The Sm moment comes easily to fluctuate with heating from low temperature, so that the almost full magnetic entropy ($R\ln 6$) of the Sm moment is released for $T < T_1$. This fluctuation also leads that the FM Sm–Mn coupling becomes unstable and is overcome by the AFM Mn–Mn coupling at $T_1$. However, the magnetic entropy change due to the Mn moment is hardly released because of the strong $J_{Mn–Mn}$ for $T < T_1$ [9]. As seen in Fig. 3(a), the sign of $\Delta S_M(T_1)$ is negative, suggesting that an applied magnetic field reduces the magnetic entropy in the AFM phase. That is, this negative $\Delta S_M(T_1)$ is due to a magnetic phase transition from an ordered state to a disordered state with heating process. Therefore, we believe that the small negative $\Delta S_M(T_1)$ is caused mainly by a magnetic phase transition from an ordered state (with thermal fluctuation) to a disordered state on the Sm moments with heating process.

On the other hand, the sign of $\Delta S_M(T_2)$ is positive, suggesting a magnetic phase transition from the disordered state to an ordered one. However, it should be noted that we cannot neglect the contribution of the Mn sublattice to $\Delta S_M$ in this temperature [9]. Kaneko et al. reported that $\Delta S_M$ (in zero field) due to the Mn sublattice is $+3.3\,J\,K^{-1}\,kg^{-1}$ for $La_{0.3}Y_{0.7}Mn_2Ge_2$ which has almost the same $R^a_{Mn–Mn}$ of $SmMn_2Ge_2$ and exhibits an AFM–FM transition at about 170 K [10]. The entropy change estimated by our specific heat measurement is $+1.4\,J\,K^{-1}\,kg^{-1}$ around $T_2$ in zero magnetic field. Therefore, the contribution of the Sm-sublattice to $\Delta S_M$ is evaluated to be $-1.9\,J\,K^{-1}\,kg^{-1}$ in zero magnetic field. The absolute value of this small $\Delta S_M$ is consistent with $\Delta S_M(T_2)$ determined by the magnetization measurement at the vicinity of $T_2$ in present work. This indicates that the Sm moments are regarded as the ordered state with thermal fluctuation in the FM phase because of feeling the exchange field from the Mn sublattice. That is, the small positive $\Delta S_M(T_2)$ is mainly originated by the magnetic phase transition from the disordered state to an ordered state on the Sm moments with heating process. On the other hand, the sign of $\Delta S_M$ is negative just above $T_2$ as seen in Fig. 3(b), which may be mainly due to the contribution of the magnetic entropy change in the Mn sublattice.

Consequently, our results show that the FM, AFM, RFM and FFM properties relate closely to the lattice parameters $c$ as well as $a$ in $SmMn_2Ge_2$. The magnetocaloric effects observed are understood in the temperature and atomic distance dependence of the Sm–Sm, Sm–Mn and Mn–Mn exchange interactions with the thermal fluctuation. Considering the fluctuation of both Sm and Mn magnetic moments as mentioned above, the results on magnetocaloric properties can be also explained on the basis of the magnetic structures proposed in Refs. [1,2].

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