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Magnetic Properties and Magnetocaloric Effect of $R_{1-x}R'_xMn_2Ge_2$ Compounds

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The magnetic and magnetocaloric properties of $Sm_{1-x}Gd_xMn_2Ge_2$ compounds with $0 \leq x \leq 0.10$ have been studied. $SmMn_2Ge_2$ is antiferromagnetic below the Néel temperature T_N ($\approx$ 400 K). Further cooling leeds to canted ferromagnetic phase below $T_C = 341$ K. With decreasing temperature, two metamagnetic phase transitions are observed: F2–AF1 at $T_2 = 153$ K and AF1–F1 at $T_1 = 106$ K. The maximum values of magnetic entropy change $|\Delta S_m|$ are found to be 1.5 J K^{-1} kg^{-1} at T_1 and 2.0 J K^{-1} kg^{-1} at T_2 in $SmMn_2Ge_2$. The MCE is found to increase with Gd concentration, $|\Delta S_m(T_1)| = 3.3$ J K^{-1} kg^{-1}, while $|\Delta S_m(T_2)|$ is slightly enhanced for $x = 0.1$. The magnetocaloric effect is found to be positive at T_1 and negative at T_2.

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1. Introduction

The term "magnetocaloric effect" (MCE) is generally associated with adiabatic temperature changes or an isothermal entropy change of magnetic material due to the application of a magnetic field. In recent years the MCE have been extensively studied in search for suitable materials applicable for new magnetic refrigeration. For obvious reasons, the magnetic materials that show a large MCE around room temperature and in low magnetic fields are especially desirable. The most important feature of these materials is that they undergo a simultaneous first-order structural and magnetic phase transition, which leads to a giant magnetic entropy change in its ordering temperature.

Up to date, the most useful room temperature magnetic working substances are materials on the basis of rare earth and 3*d* metals such as: Laves phases RM_2 (R — rare earth, M = Al, Co, Ni), $Gd_5(Si_{1-x}Ge_x)_4$, $Mn(As_{1-x}Sb_x)$, $MnFe(P_{1-x}As_x)$, $La(Fe_{13-x}Si_x)$ [1, 2].

The simplest experimental technique to determine ΔS_m and ΔT_{ad} is by magnetization measurements, using the Maxwell relations

$$\Delta S_m(T, \Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H\,, \tag{1}$$

$$\Delta T_{ad}(T, \Delta H) = -\int_{H_1}^{H_2} \left(\frac{T}{C(T,H)}\right)_H \left(\frac{\partial M(T,H)}{\partial T}\right) \mathrm{d}H\,. \tag{2}$$

If the temperature derivative of the magnetization is negative, as is the case of regular ferromagnetic materials, the thermodynamic formulation of the ΔS_m and ΔT_{ad} predicts $\Delta S_m < 0$, $\Delta T_{ad} > 0$ (the direct MCE), i.e. the sample heats up when the external magnetic field is applied adiabatically. On the other hand, if the temperature derivative of the magnetization is positive, an opposite effect occurs, i.e. $\Delta S_m > 0$, $\Delta T_{ad} < 0$ (the inverse MCE), the sample cools down when the external magnetic field is applied adiabatically [3].

The direct giant MCE appears in $Gd_5Si_2Ge_2$ — this compound undergoes a first-order magneto-structural transition at 276 K, which can be induced not only by changing the temperature, but also by changing the magnetic field or pressure. The inverse MCE exists in different kinds of magnetic arrangements, in antiferromagnetic compounds it is associated with antiparallel disorder of magnetic sublattices [4, 5].

In the case of ternary rare earth intermetallic compounds the observed magnetostructural transition is explained by strong dependence of the exchange constant on interatomic spacing. This magnetostructural coupling complicates the thermodynamics of the system, because it introduces additional mutual dependences between the specific volume and the magnetization. Giant magnetocaloric effect has been observed in $ErRu_2Si_2$ which is associated with field induced metamagnetic transition from antiferromagnetic to ferromagnetic state. The maximum value of entropy change $-\Delta S_m^{max}$ for the field change of $\Delta H = 7$ T are evaluated to be 19.3 J/(kg K) [4].

In this work we have studied the magnetocaloric properties deduced from magnetization measurements of $Sm_{1-x}Gd_xMn_2Ge_2$ for $x = 0$ and $x = 0.1$. $R_{1-x}R'_xMn_2Ge_2$ compounds crystallize in the body centered tetragonal $ThCr_2Si_2$-type structure with the space group $I4/mmm$, which can be described as a stacking of monoatomic layers in the direction of the *c*-axis according the sequence R–Ge–Mn–Ge–R. These compounds are of particular interest, because both R and Mn atoms carry a magnetic moment. The total value of the Mn moment is about (2.4–3.3) μ_B for the RMn_2Ge_2 compounds [6–8].

The high sensitivity of exchange parameters to the intralayer Mn–Mn spacing R^a_{Mn-Mn} (or parameters of

unit cell) leads to complex and very interesting magnetic phase diagrams of these compounds. The sequence of magnetic phases, which occurs in $SmMn_2Ge_2$, and $Sm_{1-x}R'_xMn_2Ge_2$ (R′ — Gd, Y) compounds is shown in a schematic way in Fig. 1. Types of the magnetic structures are shown in Fig. 2. These structures are described using the notation introduced by Venturini et al. [7]. AFmc (AF1) describes the antiferromagnetic mixed commensurate structure, which is characterised by antiferromagnetic interplane coupling of the in-plane ferromagnetic components and by the commensurate ordering of the antiferromagnetic in-plane components. Fmc (F2) presents the ferromagnetic mixed commensurate structure. AFl describes the antiferromagnetic layer magnetic structure.

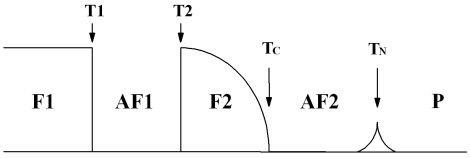

Fig. 1. The magnetic phase sequence for $SmMn_2Ge_2$ and $R_{1-x}R'_xMn_2Ge_2$ (R, R′ — rare earths) compounds. P — paramagnetic phase, AF2 — antiferromagnetic collinear structure, F2 — canted ferromagnetic structure, AF1 — canted antiferromagnetic structure, F1 — reentrant ferromagnetic phase of Mn and Sm sublattice [6–9].

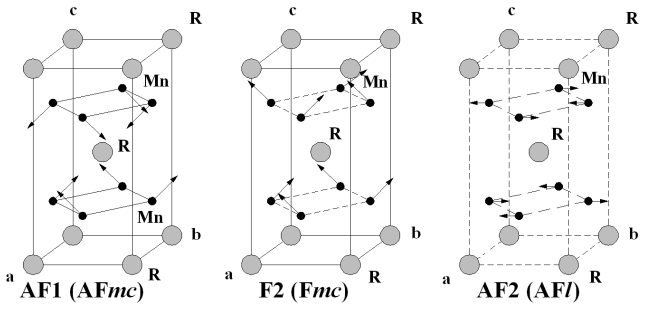

Fig. 2. The magnetic structures of the Mn sublattice in the $R_{1-x}R'_xMn_2Ge_2$ compounds from neutron diffraction study [7].

The critical lattice spacing criteria, determining the type of magnetic exchange are as follows [6–9]: $R^a_{\mathrm{Mn-Mn}} > 0.286$ nm, the intralayer in-plane coupling is antiferromagnetic and the interlayer coupling is ferromagnetic, 0.282 nm $< R^a_{\mathrm{Mn-Mn}} < 0.285$ nm, intralayer in-plane coupling remains antiferromagnetic but the the interlayer coupling is also antiferromagnetic. The critical value $R^a_{\mathrm{Mn-Mn}}$ for metamagnetic transition AF–F is between 0.285 and 0.286 nm.

In $SmMn_2Ge_2$, $R^a_{\mathrm{Mn-Mn}} = 0.287$ nm is slightly larger than critical value at room temperature, so that the compound shows re-entrant ferromagnetism: AF2 phase (between $T_{\mathrm{N}} = 385$ K and $T_{\mathrm{C}} = 341$ K), F2 phase (between $T_{\mathrm{C}} = 341$ K and $T_2 = 153$ K), reentrant antiferromagnetic AF1 phase (between $T_2 = 153$ K and $T_1 = 106.5$ K) and reentrant ferromagnetic F1 phase (below $T_1 = 106.5$ K). The values of the lattice parameters, temperatures of the magnetic phase transitions of $Sm_{1-x}Gd_xMn_2Ge_2$ samples are given in Table I [9].

TABLE I

Structural parameters and temperatures of the magnetic phase transitions of Sm_{1-x} $Gd_xMn_2Ge_2$ [9].

	$x = 0$	$x = 0.10$
a [nm]	0.4062(5)	0.4058(5)
c [nm]	1.0895(3)	1.0883(3)
c/a	2.681	2.682
V [nm^3]	0.1797(4)	0.1792(4)
$R^a_{\mathrm{Mn-Mn}}$ [nm]	0.2872(3)	0.2869(3)
T_1 [K]	106.5	96
T_2 [K]	153	161
T_{C} [K]	341	340

2. Experimental and results

Magnetic measurements are performed on the polycrystalline samples whose characterizations are reported in Ref. [9]. Magnetization is measured by means of a modified Faraday metod in the temperature range 78–400 K in the magnetic field up to 1.08 T. The temperature dependence of the magnetization of the $SmMn_2Ge_2$ and $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ compounds is displayed in Fig. 3.

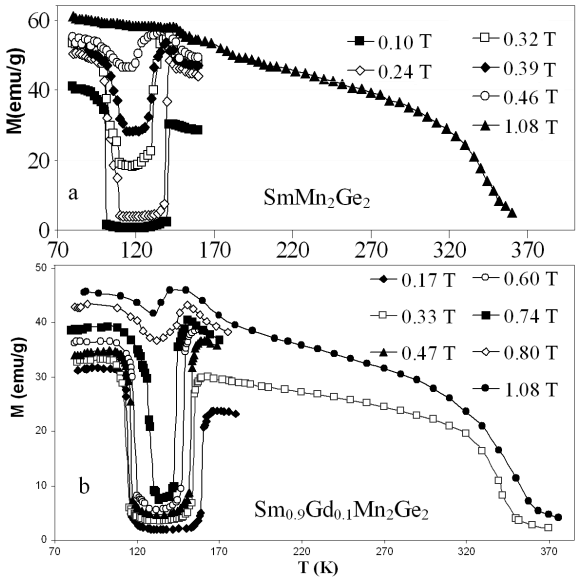

Fig. 3. Temperature dependence of the magnetization of (a) $SmMn_2Ge_2$ and (b) $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ compounds for field change of 0.10–1.08 T [9].

The crystalline structure is identical for $SmMn_2Ge_2$ and $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ compounds, except the changes

in the lattice parameters. The decrease in the lattice parameter is attributed to the smaller ionic radius of Gd (0.1787 nm) compared to that of Sm (0.1852 nm). When the value of intralayer Mn–Mn spacing $R^a_{\mathrm{Mn-Mn}}$ approaches the critical value at room temperature, the temperatures of metamagnetic transition AF1–F2 increase.

In this paper, we express the MCE as an isothermal magnetic entropy change ΔS_{m}, obtained from the magnetization data. The magnetic entropy change $\Delta S_{\mathrm{m}}(T_1)$, $\Delta S_{\mathrm{m}}(T_2)$ was estimated for polycrystalline $SmMn_2Ge_2$, $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ for first-order magnetic phase transition at T_1 and T_2.

Based on the Maxwell relation, the isothermal magnetic entropy change is given by relation (1). For discrete fields and temperature intervals, Eq. (1) can be approximated by the following expression:

$$\Delta S_{\mathrm{m}}(T, \Delta H) = \sum \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \,, \qquad (3)$$

where M_{i+1} and M_i are the magnetization values measured at T_{i+1} and T_i respectively, when the magnetic field changed is ΔH_i.

Figure 4 (a and b) shows the magnetic entropy change ΔS_{m} for $SmMn_2Ge_2$ compound at the vicinity of T_1 and T_2, respectively. It can be seen that the entropy change is negative (positive MCE) for the metamagnetic phase transition F1–AF1 at $T_1 = 106.5$. The maximum value of entropy change is equal to $|\Delta S_{\mathrm{m}}(T_1)| = 1.5$ J K^{-1} kg^{-1}.

A particularly interesting feature (common to all the $SmMn_2Ge_2$-like compounds) is the positive entropy change (negative MCE) at temperature $T_2 = 153$ K. The magnetic phase transition AF1–F2 at temperature T_2 is connected with the ordering at Mn sublattice. The interlayer Mn–Mn exchange interaction changes the sign from negative to positive as the interatomic distance $R^a_{\mathrm{Mn-Mn}}$ exceeds critical value at T_2. We estimated $|\Delta S_{\mathrm{m}}(T_2)| = 2.0$ J K^{-1} kg^{-1} for AF1–F2 phase transition at T_2.

When substituting Gd partially for Sm (for $0 \leq x \leq 0.10$) it is found that the temperature dependence of magnetization behavior is nearly the same as in $SmMn_2Ge_2$ (Fig. 3). The lattice parameters decrease with increasing x and for $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ the interatomic distance is equal to $R^a_{\mathrm{Mn-Mn}} = 0.2869$ nm at room temperature. With an increase in Gd content the range of antiferromagnetic order AF1 (AFmc) increases. For $x = 0.10$ the metamagnetic phase transition AF1–F2 occurs at temperature $T_2 = 161$ K and for the same intralayer Mn–Mn spacing $R^a_{\mathrm{Mn-Mn}} \approx 0.286$ nm being critical distance. The same effect was observed when applying hydrostatic pressure for $SmMn_2Ge_2$ [9–11].

Figure 5 shows the magnetic entropy change ΔS_{m} at the first-order magnetic phase transitions for $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$. For the magnetic phase transition F1–AF1 at $T_1 = 96$ K we estimated $|\Delta S_{\mathrm{m}}(T_1)| = 3.3$ J K^{-1} kg^{-1} and the entropy change is negative (positive MCE). With increasing Gd content the value of entropy change increases at T_1.

At $T_2 = 161$ K, the magnetic state transforms from AF1 to the F2 state, and the positive entropy change (negative MCE) was observed. The maximum value of entropy change $|\Delta S_{\mathrm{m}}(T_2)|$ is 2.3 J K^{-1} kg^{-1} and varies slightly with x. This indicates that the contribution to the magnetic entropy change at high temperatures is mainly connected with Mn sublattice.

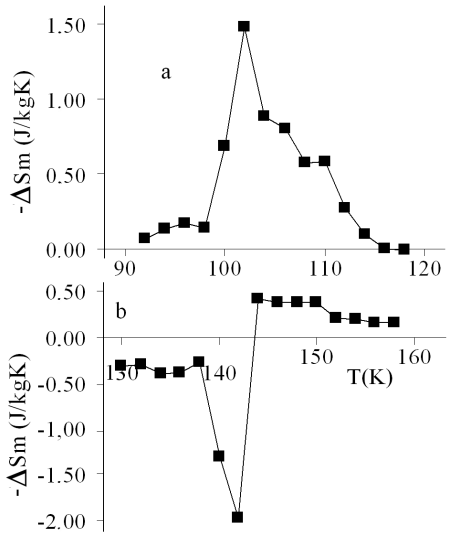

Fig. 4. Magnetic entropy change ΔS_{m} in magnetic field change of 0.10–1.08 T for $SmMn_2Ge_2$ compound at the vicinity of the (a) F1–AF1 and (b) AF1–F2 magnetic phase transitions.

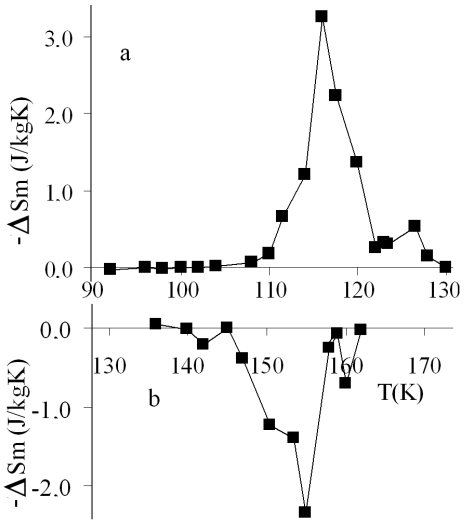

Fig. 5. Magnetic entropy change ΔS_{m} in magnetic field change of 0.17–1.08 T for $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ compound at the vicinity of the (a) F1–AF1 and (b) AF1–F2 magnetic phase transitions.

3. Discussion

The results of $|\Delta S_{\mathrm{m}}(T_1)|$ and $|S_{\mathrm{m}}(T_2)|$ obtained in this work can be compared to the value determined from

Clausius–Clapeyron equation [9]:

$$\frac{\mathrm{d}T_{\text{F-AF}}}{\mathrm{d}p} = \frac{\Delta V}{\Delta S}\,. \tag{4}$$

The values of $\mathrm{d}T_1/\mathrm{d}P$ and $\mathrm{d}T_2/\mathrm{d}P$ were determined from pressure dependence of T_1 and T_2 temperatures [9–11]. The changes of the unit cell volume at the temperature phase transitions T_1 and T_2 are $\Delta V/V \approx 0.25\%$ and $\approx 0.30\%$, respectively. Data are given in Table II [9–11].

TABLE II

Thermodynamic parameters of the first-order phase transition of Sm_{1-x} $Gd_xMn_2Ge_2$ [9–11].

	$x = 0$	$x = 0.10$
T_1 [K]	106.5	96
T_2 [K]	153	161
$\mathrm{d}T_1/\mathrm{d}P$ [K/GPa]	$-(170 \pm 20)$	$-(100 \pm 20)$
$\mathrm{d}T_2/\mathrm{d}P$ [K/GPa]	$+(171 \pm 20)$	$+(188 \pm 20)$
P_{cr} [GPa]	1.00 ± 0.05	0.92 ± 0.05
T_{cr} [K]	332 ± 2	330 ± 2

The values of ΔS_{m} calculated on the basis of Clausius–Clapeyron equation and using the Maxwell relations are listed in Table III.

TABLE III

ΔS_{m} at the first-order phase transitions of Sm_{1-x} $Gd_xMn_2Ge_2$.

	ΔS_{m} [J K^{-1} kg^{-1}] from Maxwell relations		ΔS_{m} [J K^{-1} kg^{-1}] from Clausius–Clapeyron equation	
	T_1	T_2	T_1	T_2
$SmMn_2Ge_2$	−1.5	2.0	−2.4	2.6
$Sm_{0.9}Gd_{0.1}Mn_2Ge_2$	−3.3	2.3	−3.3	3.0

These values are comparable, and much smaller than $R\ln 2$ for a simple spin state ($S = 1/2$) or $R\ln 6$ for a Sm moment ($J = 5/2$).

We estimated $|\Delta S_{\text{m}}(T_1)| = 1.5$ J K^{-1} kg^{-1} for the F1–AF1 phase transition at T_1. This value is similar to the data $|\Delta S_{\text{m}}(T_1)| = 1.4$ J K^{-1} kg^{-1} [12] and $|\Delta S_{\text{m}}(T_1)| = 1.6$ J K^{-1} kg^{-1} [13]. The sign of $|\Delta S_{\text{m}}(T_1)|$ is negative, suggesting that an applied magnetic field reduced the magnetic entropy in the AF1 phase. This fact is due to magnetic phase transition from an order state to a disorder state on the Sm sublattice and change of magnetic order in Mn sublattice. At the magnetic phase transition temperature T_2, the value of $|\Delta S_{\text{m}}(T_2)| = 2.0$ J K^{-1} kg^{-1} is positive and greater than 1.3 J K^{-1} kg^{-1} in Ref. [12].

The entropy change estimated for $Sm_{0.9}Gd_{0.1}Mn_2Ge_2$ at T_1 is $|\Delta S_{\text{m}}(T_1)| = 3.3$ J K^{-1} kg^{-1}. A similar increase in the MCE has been observed in $Gd_{1-x}Sm_xMn_2Ge_2$ with an increase in Gd content [14, 15].

In order to obtain the information about magnetic states of $SmMn_2Ge_2$ the pressure effect on MCE was discussed in [13]. $|\Delta S_{\text{m}}(T_1)|$ increases from 1.2 J K^{-1} kg^{-1} at the atmospheric pressure to 4.92 J K^{-1} kg^{-1} for $P = 0.5$ GPa. Basing on the experimentally obtained (P, T) magnetic phase diagrams [9–11, 16], values of critical temperature T_{cr} and the critical pressure P_{cr} (i.e. the Fmc phase disappears) were obtained (Table II). From these results the relative change of the unit cell volume as function of external pressure was estimated to be $\Delta V = \kappa P$, where $\kappa = -3.8 \times 10^{-3}$ nm^3/GPa. An increase in Gd content $x = 0.10$ is equivalent to the hydrostatic pressure $P \approx 0.14$ GPa. The magnetocalorical effect is found to increase with Gd concentration (or with hydrostatic pressure) at T_1. The MCE associated with the Mn sublattice at T_2 is slightly enhanced.

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