Negative magnetocaloric effect at the antiferromagnetic to ferromagnetic transition of Mn3GaC

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Negative magnetocaloric effect at the antiferromagnetic to ferromagnetic transition of Mn_3GaC

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The magnetocaloric effect of Mn_3GaC, which shows an antiferromagnetic to ferromagnetic transition at 165 K has been investigated. In this compound, magnetocaloric effect obtained at the transition is opposite to that of ordinary ferromagnetic systems, namely, negative magnetocaloric effect. It was found that a large magnetic entropy change, ΔS_{mag}, of 15 J/kg K is obtained under an applied field of 2 T. The adiabatic temperature change, ΔT_{ad}, reaches 5.4 K in a field change of 2 T. At higher magnetic fields, both ΔS_{mag} and ΔT_{ad} retain a large value over wide temperature range, exhibiting characteristic temperature dependence of a trapezoidal shape. These features are attributed to a sharp first-order transition retained in high magnetic fields as well as small magnetocrystalline anisotropy. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1587265]

I. INTRODUCTION

In recent years, on the background of growing social interest in environmental and energy issues, much attention has been paid on the studies concerning the magnetic refrigeration technology. Magnetic refrigeration has a number of ecological advantages over the conventional gas refrigeration such as high efficiency or no use of environmentally harmful gases, so it is expected to be a probable alternative refrigeration method. Magnetic refrigeration utilizes the magnetocaloric effect, the nature of magnetic solids that when exposed to a magnetic field, entropy of the substance varies owing to the change of magnetic moment alignment. For the achievement of a high efficiency magnetic refrigerator, it is strongly desired to develop the magnetic working materials with a large magnetocaloric effect at a relatively low magnetic field (hopefully up to 2 T, which can be attained by a permanent magnet). Up to now, most of magnetocaloric effect studies have been performed on ferromagnetic materials near their Curie temperatures. In particular, the report of giant magnetocaloric effect of $Gd_5Si_2Ge_2$ near room temperature region, which undergoes a first-order ferromagnetic to paramagnetic transition[1] had a great impact on this field. Focusing on a first-order ferromagnetic (or ferrimagnetic) to paramagnetic transition, we have recently reported giant magnetocaloric effect of MnAs[2] near room temperature and large magnetocaloric effect of $ErCo_2$[3] below 30 K. Subsequently, a magnetic entropy change of materials exhibiting a first-order ferromagnetic to paramagnetic transition has been reported extensively.[4,5] However, there are only few materials known to undergo a first-order magnetic transition between ferromagnetic and paramagnetic states. This indicates that the subject of our investigation should be inevitably restricted. Now, we focus on a first-order magnetic transition between antiferromagnetic and ferromagnetic states. Previously, magnetocaloric effects on FeRh alloy were investigated by Annarazov *et al.* They found a large magnetocaloric effect accompanied by the first order magnetic transition near room temperature.[6] This motivated us to study a magnetocaloric effect of the first-order antiferromagnetic to ferromagnetic magnetic transition. In the present study, we have chosen Mn_3GaC. This compound undergoes an antiferromagnetic to ferromagnetic transition around the temperature of $T_t = 160$ K.[7] In previous studies, the entropy jump at the antiferromagnetic to ferromagnetic transition in zero field was reported to be 17 J/kg K.[8,9] On the other hand, the field dependence of T_t has been found to be large, being $dT_t/dH = 4$ K/T.[10] The former suggests that a large magnetic entropy change will be obtained when a magnetic field is applied on this compound. The latter may lead to a large adiabatic temperature change. Therefore, these results suggest a large magnetocaloric effect of Mn_3GaC.

II. EXPERIMENT

The starting materials used for the preparation of Mn_3GaC are 3 N pure manganese, 6 N pure gallium, and 4 N pure carbon. Powders of these elements were carefully mixed in the desired proportion and sealed in an evacuated silica tube, the wall of which were coated with the carbon to avoid a reaction of the compound with the silica tube. Then the mixture was heated at 750 °C for 7 days. The reacted product was ground, mixed and heated again in vacuum at 750 °C for another 7 days. The compound thus prepared was checked by x-ray diffraction and electron-probe microanalysis (EPMA). This compound has the cubic structure of a perovskite-type, in which the Mn atoms are located at the face-centered positions. All of the observed diffraction lines were indexed with the cubic perovskite structure. The lattice parameter was determined to be $a = 3.894 \pm 0.001$ Å. From the result of EPMA, we verified that the prepared sample is in the single phase and the other phases are negligible.

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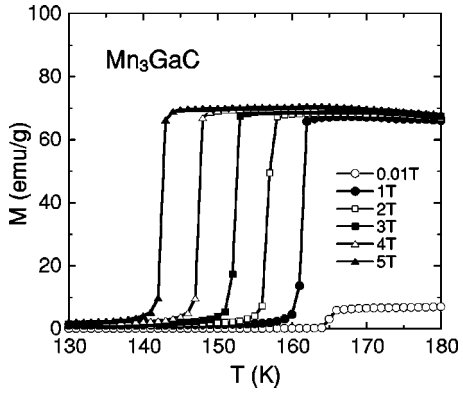

FIG. 1. Temperature dependence of magnetization of Mn_3GaC at various fields. The data were taken on increasing temperature.

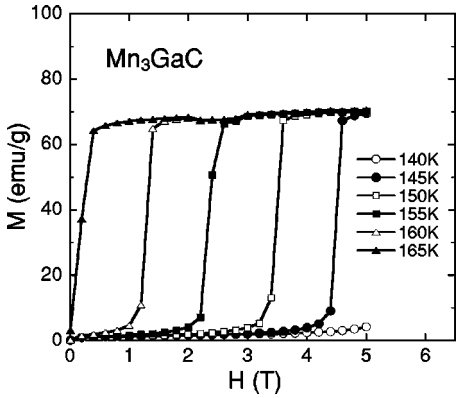

FIG. 2. Magnetization curves of Mn_3GaC near transition temperature T_t. The data were converted from $M-T$ curves in various magnetic fields.

From a general thermodynamical equation, the isothermal entropy change, ΔS_{mag}, can be described by the Maxwell relation, as

$$\Delta S_{\mathrm{mag}} = \int_0^H \left(\frac{dM}{dT}\right)_H dH. \tag{1}$$

One can calculate the magnetic entropy change by the numerical integration using magnetization values measured as functions of field and temperature. The temperature dependence of magnetization was measured in the field of 0.01 T and from 0.2 to 5 T with an interval of 0.2 T using a commercial superconducting quantum interference device magnetometer.

The adiabatic temperature change, ΔT_{ad}, was evaluated in the following way; the zero-field total entropy $S_{H=0}$ can be obtained from the specific heat data in zero field. Adding up $S_{H=0}$ and ΔS_{mag}, the total entropy at a certain field is obtained as a function of temperature. The ΔT_{ad} is given as the isentropic distance of two entropy curves with and without magnetic field.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the magnetization at various magnetic fields. With increasing temperature Mn_3GaC undergoes a first-order antiferromagnetic to ferromagnetic transition and magnetization shows an abrupt increase at T_t. The T_t is 165 K at a field of 0.01 T. The transition temperature is lowered with increasing fields almost linearly at the rate of about 5 K/T. It is noteworthy that a sharp first-order transition is retained up to the highest fields studied. Small thermal hysterisis of about 2 K was observed between the heating and cooling process. The magnetization curves at various temperatures are depicted in Fig. 2. The compound exhibits a metamagnetic transition below T_t. The critical field is increased almost linearly with decreasing temperature. The temperature dependence of the magnetic entropy change calculated from magnetization data is presented in Fig. 3. One must note that the sign of the magnetic entropy change is positive. This is because the ferromagnetic state is a high-temperature phase in this compound, so that applying magnetic field increases the entropy. In this sense, the magnetocaloric effect of the present compound is opposite to that of ordinary ferromagnetic systems. Mn_3GaC exhibits negative magnetocaloric effect, i.e., heats up when demagnetized and cools down when magnetized. In the $\Delta S_{\mathrm{mag}}-T$ curves, spikes were observed around 155 and 160 K. These spikes are probably artifacts due to the procedure to evaluate ΔS_{mag}, in which summation with a finite field interval was employed instead of integration. Neglecting spikes, the peak value of ΔS_{mag} reaches 15 J/kg K under an applied field of 1 T, which is in agreement with the entropy jump in zero field estimated from a heat capacity measurement.[9] The magnitude of ΔS_{mag} is comparable to that of a candidate for magnetic refrigerant materials in this temperature range, e.g., $(Tb_{1-x}Gd_x)Al_2$.[11] This large magnetic entropy change originates from a large value of dM/dT at T_t, as shown in Eq. (1). The maximum value of ΔS_{mag} is not dependent on a magnetic field, whereas the peak width increases almost linearly with increasing field. Consequently, the temperature dependence of ΔS_{mag} under high applied fields shows a trapezoidal shape. This is due to a sharp transition retained at even higher fields.

To estimate the adiabatic temperature change, we calculated the total entropy curve as a function of the temperature under several finite fields, as shown in Fig. 4. The entropy curve in zero field is calculated using numerical data of heat capacity measurement from the literature.[9] Figure 5 shows the temperature dependence of the adiabatic temperature change. Owing to strong dependence of T_t on a magnetic

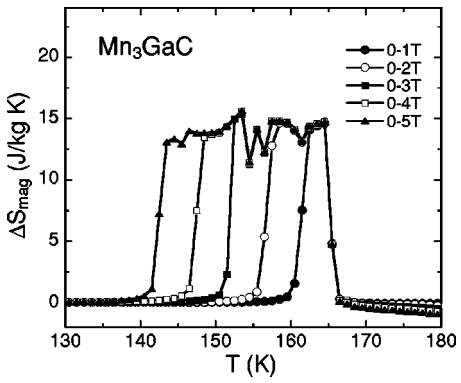

FIG. 3. Magnetic entropy change caused by a magnetic field, ΔS_{mag}, of Mn_3GaC as a function of temperature.

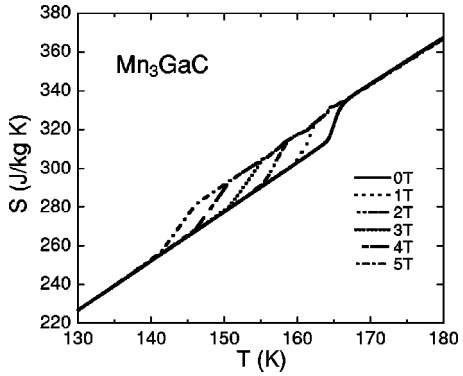

FIG. 4. Total entropy curves in several magnetic fields.

field, ΔT_{ad} in low fields below 2 T shows quite a large value of 2.7 K/T at its peak. Whereas, in high fields above 3 T, the peak value of ΔT_{ad} is saturated and only a peak width increases, resulting in a plateau. This trend is similar to the $\Delta S_{mag}-T$ curves.

Now, we discuss the origin of large ΔS_{mag} and ΔT_{ad} mentioned earlier. To yield large ΔS_{mag}, it is necessary that the entropy jump at a transition in zero field is large, in other words, there should be a considerable difference in the entropy between two magnetic states. According to the results of neutron diffraction, the magnetic moment of Mn atom in this compound is $1.8\mu_B$ in the antiferromagnetic state and $1.2\mu_B$ in ferromagnetic state.[12] This indicates that the magnetic moment of Mn atom strongly depends on magnetic state, suggesting an itinerant electron character. The significant difference in the Mn moment between the antiferromagnetic and ferromagnetic states mainly counts for the entropy difference between two magnetic states.

Another important feature of the results is the temperature dependences of ΔS_{mag} and ΔT_{ad}, that is, the peak value reach their maximum at a relatively low magnetic field and the curves become plateau in high fields. It is essential that a sharp first-order transition retained in high magnetic fields is responsible for this characteristic. In addition, small magnetocrystalline anisotropy may play an important role. Magnetic anisotropy should affect magnetocaloric properties of polycrystalline materials significantly. If magnetic anisotropy

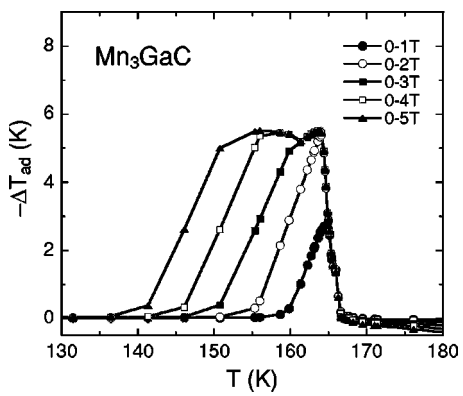

FIG. 5. Temperature dependence of adiabatic temperature change, ΔT_{ad} of Mn_3GaC.

is large enough to fix magnetic moments along the magnetization easy axis in a high field, the component of effective field on each grain is widely distributed. This makes the transition of polycrystalline samples broadened in a magnetic field, resulting in a loss of magnetocaloric effect. As for Mn_3GaC, the magnetocrystalline anisotropy is considered to be small. Therefore, a sharp first-order transition is realized even in high fields and large ΔS_{mag} and ΔT_{ad} are kept over a wide temperature range. Consequently, the temperature dependence of magnetocaloric effects becomes a plateau. In terms of small magnetocrystalline anisotropy, $3d$ transition metal based compounds are favorable. Among $4f$ compounds, materials containing Gd, whose magnetic anisotropy is always negligible, and some others meet the requirement.

IV. CONCLUSION

In conclusion, we found a negative and large magnetocaloric effect in Mn_3GaC in relatively low fields. The magnetocaloric effects of the compound in high magnetic fields exhibit a characteristic temperature dependence of a flat shape. In the active magnetic regenerator system, which is a most feasible prototype of magnetic refrigerator today, it is likely to combine several materials to cover a large temperature span. The flat temperature dependence of magnetocaloric effect is preferable for designing of a practical refrigerant unit in a wide temperature range. In addition to the large magnetocaloric effect, the T_t of Mn_3GaC can be changed by substituting $3d$ elements for Mn or Al for small portion of Ga.[13,14] These characteristics suggest that Mn_3GaC can be an appropriate candidate for the magnetic refrigerant for corresponding temperature range.

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