Magnetocaloric Effect: Direct Measurement

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Abstract. We present the study of magnetocaloric effect of $Gd_{60}Mn_{40}$ alloy. This alloy was prepared from Gd and Mn of 3N purity. The stoichiometric mixture of these elements was melted in mono-arc furnace in ultra-high purity argon atmosphere and remelted several times to ensure homogeneity of the sample. The crystal structure of the sample was investigated by powder x-ray diffraction. We used the direct method to measure the adiabatic temperature change, ΔT, and the magnetisation isotherms to calculate the isothermal entropy change, ΔS. Direct measurement was performed in magnetic field of 4.7 T in temperature range from 261 to 307 K. We obtained the maximum temperature change $\Delta T_{max} = 3.5$ K at 284 K. We measured temperature dependence of magnetisation in small magnetic field 0.03 T and evaluated the transition temperature $T_C = 289$ K. We measured magnetic field dependence of magnetization in temperature range from 265 to 305 K in magnetic field up to 5 T and we evaluated the entropy change according to the Maxwell relation.

Introduction

Magnetic cooling technique is now considered as a serious alternative for conventional refrigeration. This technique is based on the magnetocaloric effect (MCE) which is one of the basic physical properties of magnetic solids [1,2]. Great number of materials with the significant MCE was found in recent years [3,4], but the Gd still remains one of the most suitable material for real application in refrigeration or heat transport technologies. The MCE can be characterised as the adiabatic temperature change or the isothermal entropy change of materials when varying the external magnetic field. Both the sign and the extent of the temperature or entropy change between the initial and final state of the material depend on numerous intrinsic and extrinsic factors. For the application is important not only size of the MCE but also the temperature position of its maxima, which is usually connected with the magnetic transition of studied material. Hence the transition temperature defines the temperature range of possible application.

In the present work we have studied the MCE of the Gd-Mn alloys with the Mn concentration of 40 at.%. We used two different methods to determine MCE—the direct measurement of the temperature changes and the magnetization measurement. We compare and discuss the results obtained from these measurements.

Pure gadolinium crystallizes in hexagonal structure with the crystallographic space group $P6_3/mmc$. It undergoes the second order magnetic phase transition from the paramagnetic state to the ferromagnetic state with magnetic moments along the hexagonal c-axis (easy direction) at the Curie temperature T_C =293 K. The change of the easy direction from the c-axis to the easy cone takes place at 240 K [5]. The Gd and Mn form several binary intermetalic compounds. The $GdMn_2$ was also previously studied from point of view of MCE but the magnetic transition temperatures ($T_C \approx 35$ K and $T_N \approx 105$ K) [6,7] exclude it from the room-temperature application. The Gd-Mn alloys were studied in concentration range of Mn up to 20 at. % [8]. The Gd-Mn alloys form two-phase sample with α-Gd and $GdMn_2$ phases [8]. The decrease of the transition temperature from 292 K to 272 K accompanied with only a small change of the isothermal entropy change was observed.

Experimental

The $Gd_{60}Mn_{40}$ sample was prepared by arc-melting of stoichiometric mixture of pure element (3N for Gd and Mn) in ultra high-purity Ar atmosphere. The sample was remelted several times. The structure of the sample was checked by the x-ray powder diffraction.

The temperature dependence of the sample magnetisation was measured on MPMS measurement system from Quantum Design. The transition temperature of the sample was determined from this dependence as the temperature where the maximum of the first derivative occurred. The entropy change of the sample was determined from the magnetisation isotherms measured in a wide temperature range from 265 to 305 K according to equation derived from the Maxwell relation.

$$\Delta S_m = \int_{H_i}^{H_f} \frac{\partial M}{\partial T} dH \ . \tag{1}$$

The accuracy of this determination of MCE was widely discussed in literature [9–13].

The direct measurement of the sample temperature change was performed on simple cryostat consists of a container with liquid nitrogen and a sample holder. Temperature of the holder is controlled by a heater in the temperature range from 450 K down to 80 K. The magnetic field is produced by superconducting magnet with maximal field of 5 T. The elevator is used to fix the cryostat inside or outside the magnet. The rate of change of magnetic field reaches 10 T/s. The temperature difference of the sample and the sample-holder is recorded. The temperature change of the sample is then obtained by fitting the data by the theoretical cure.

$$\Delta T(t) = \Delta T_0 + \Delta T_{\max} * \left[1 - \exp\left(\frac{-t}{\tau}\right)\right]. \tag{2}$$

The sample is fixed on a silon wire and the cryostat is continually pumped during the measurement to approach adiabatic condition.

Results and Discussion

The temperature dependence of the sample magnetisation measured in a small magnetic field (of 0.03 T) is shown in Fig. 1. Two magnetic transitions are visible. First magnetic transition occurs at $T_C = 289$ K. This transition can be attributed to the magnetic ordering of Gd phase in the sample.

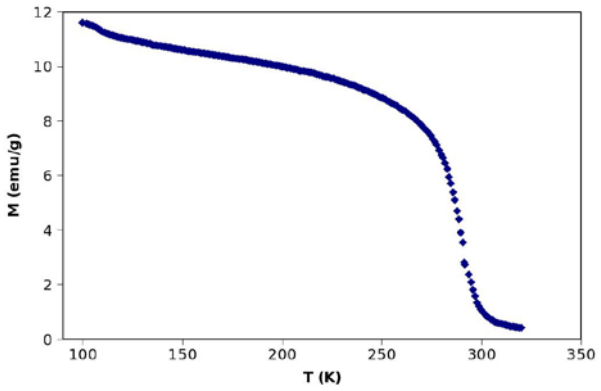

Figure 1. The temperature dependence of $Gd_{60}Mn_{40}$ sample magnetisation measured in magnetic field of 0.03 T.

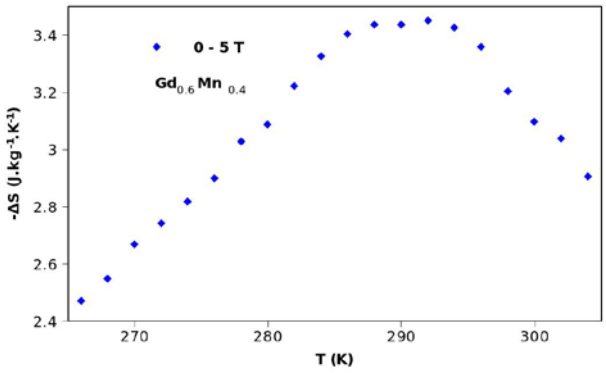

Figure 2. The isothermal entropy change plotted for a field change of 5 T.

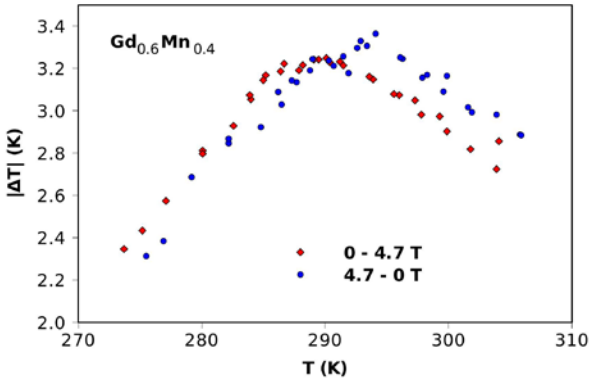

Figure 3. The adiabatic entropy change of $Gd_{60}Mn_{40}$ sample.

The transition temperature is slightly different from that in pure Gd but not as much different as in [8]. This difference is due to the different concentration of Mn impurity in this phase. The second transition occurs around $T_1 = 105$ K. This transition can be identified as the magnetic ordering of the $GdMn_2$ phase. The transition temperature T_1 correspond quite well with the Néel temperature of $GdMn_2$ published in literature [8].

The magnetisation isotherms were measured in temperature range from 265 to 305 K with temperature step of 2 K. The evaluated isothermal entropy change is shown in Fig. 2.

The maximum of the entropy change occurs around the transition temperature $T_C = 289$ K. The temperature dependence of the entropy change corresponds with the paramagnetic to ferromagnetic transition. The shape of this dependence shows a good agreement with that published in the literature for smaller content of Mn. The size of the entropy change is significantly decreased.

The result of the direct measurement of the temperature change is shown in Fig. 3.

The maximum of the temperature change occurs around the transition temperature T_C. The position of maxima differs in case of removing and applying the magnetic field. This difference can be ascribed to the different value of heat capacity in zero field and in field. The temperature change as well as the entropy change is significant in large temperature region which results in high value of the relative cooling power (RCP). The RCP can be calculated as the area below the $\Delta S(T)$ curve in temperature region where the $\Delta S(T)$ is greater than half of the maximum entropy change. We can roughly estimate that the RCP is 230 $J \cdot kg^{-1}$ from our measurement.

Conclusion

The magnetocaloric properties of $Gd_{60}Mn_{40}$ were measured. The maximum of the MCE corresponds with transition temperature T_C. The direct measurement of the adiabatic temperature change was performed. The obtained result shows decrease of the MCE from values obtained on pure Gd [14]. Despite this the $Gd_{60}Mn_{40}$ alloy is still a good candidate for application in room-temperature refrigeration.

Acknowledgments: The work was supported by the Grant Agency of the Czech Republic under the Grant No. 202/09/H041.

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