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Comparative analysis of magnetic and caloric determinations of the magnetocaloric effect in $Mn_{0.99}Co_{0.01}As$

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Abstract. The results from direct and indirect determinations of the magnetocaloric parameters of $Mn_{0.99}Co_{0.01}As$ have been analyzed. The isothermal entropy change (ΔS_T) due to external magnetic field changes has been determined through direct measurements of the heat absorbed by the sample when the field is removed under isothermal conditions. It has also been calculated from isothermal magnetization and isofield heat capacity measurements. In addition to that, the adiabatic temperature change (ΔT_S) has been obtained from direct measurements and from isofield heat capacity measurements. The different results of both ΔS_T and ΔT_S are compared. Due to the presence of a first-order phase transition, the studied sample exhibits giant magnetocaloric effect at room temperature. The observed maximum values, $-\Delta S_{T,\max} = 32.1$ J/kg·K and $\Delta T_{S,\max} = 17.7$ K for a field change from 0 to 6 T, suggest that the Co-doped MnAs compounds are promising candidates for the preparation of useful materials for magnetic refrigeration near room temperature.

1 Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) has been proposed as a competitive cooling technology to replace the conventional vapor-compression refrigeration due to low environmental impacts and high energy efficiency. In the past years, much attention has been paid to magnetic refrigeration near room temperature. To achieve that, one of the most important subjects is to find out materials with large MCE. Normally, anomalous MCE is expected to be observed at the Curie temperature in a ferromagnet, since the first derivative of magnetization M with respect temperature T, at a constant magnetic field B, $|(\partial M/\partial T)_B|$, reaches a maximum, leading to a large value of the isothermal entropy change (ΔS_T), according to the thermodynamic Maxwell's relation: $(\partial S/\partial B)_T = (\partial M/\partial T)_B$. In particular, materials undergoing first-order phase transitions (FOPT) exhibit giant MCE, because in this case the derivative $(\partial M/\partial T)_B$ becomes infinite. Therefore, a great deal of attention has been focused on materials with FOPT [1–4].

In most papers, ΔS_T is obtained from magnetization measurements based on the Maxwell relation. However, it has been proved that the quite common careless use of the Maxwell relation leads to very high and spurious peaks of ΔS_T in the transition region for materials with hysteresis [5–7]. Hence, the use of alternative methods, such as direct and specific-heat techniques, becomes very valuable in the MCE determinations. Moreover, the MCE is quantified with two fundamental parameters [8], ΔS_T and the adiabatic temperature change (ΔT_S), where ΔT_S is the temperature change of the material induced by a field change ΔB. An evaluation of ΔS_T alone, without considering ΔT_S, does not provide the information needed for cooling applications. Thus, both parameters are required to be precisely characterized in order to identify a material being good enough as a refrigerant or not. Measurements of the heat capacity ($C_{p,B}$) at different constant magnetic fields are advisable since, from them, both parameters can be deduced.

The binary compound MnAs undergoes a FOPT from ferromagnetic (FM) phase to paramagnetic (PM) phase combined with a structural transition from the hexagonal NiAs-type structure to the orthorhombic MnP-type structure at 317 K upon increasing temperature. The inverse transition takes place at 306 K on a cooling process at zero field [9]. The MCE of MnAs and its derivatives, with slight substitutions of Fe, Cu, and Cr for Mn, or Si and Sb for As [3, 10–16], have been extensively studied using magnetization data. As a result of an incorrect application of the Maxwell relation, some fallacious conclusions saying that the MnAs-based compounds exhibit "huge" or "colossal" MCE ($|\Delta S_{T,\max}| \sim 300$ J/kg·K) were made [11, 12, 15]. In this paper, we report on a giant MCE at room temperature (~295 K) in $Mn_{0.99}Co_{0.01}As$, using three different methods, i.e., isothermal magnetization, heat capacity, and direct measurements. The resulting values of

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ΔS_T and ΔT_S from the three methods are compared and analyzed.

2 Experimental

The compound was arc melted under argon atmosphere, then heat treated in a resistive furnace at 1,340 K, followed by annealing at 1,070 K and water quenched to ambient temperature, as described in detail elsewhere [11]. The X-ray diffraction pattern at room temperature indicates that the sample crystalizes in a single hexagonal phase. The heat capacity was measured under magnetic field in an adiabatic calorimeter through step points at equilibrium temperatures and also with a quasi-static scanning technique, called thermograms [17]. The second technique has some advantages for studying materials undergoing FOPT, e.g., allowing to obtain $C_{p,B}$ not only on heating processes but also on cooling ones, and also providing more precise $C_{p,B}$ values at the transition. The direct measurements of ΔS_T and ΔT_S were carried out using the same calorimeter. Magnetization as a function of temperature and magnetic field was measured with a Quantum Design SQUID (PPMS) magnetometer.

In the present study, three different measuring protocols have been used in the magnetization and direct measurements, described as follows:

(1) Protocol 1: A measurement is performed with a field change from 0 to B and then back to 0 at a low starting temperature T_l, at which the sample is in fully FM phase at zero field. Then the sample is heated to T_i at zero field and then a measurement is performed following the same field sequence as used at T_l. The procedure is repeated until the temperature reaches T_h, at which the sample is in fully PM phase at zero field.

(2) Protocol 2: The sample is heated from T_l to T_i at a constant field B. A measurement is performed when the magnetic field is brought back to 0 at T_i. After that, the sample is cooled down to T_l again, and then heated up to the next temperature T_{i+1} ($T_i < T_{i+1}$) at constant B. A measurement is performed at T_{i+1} following the same field sequence as used at T_i. The procedure is repeated until the temperature reaches T_h.

(3) Protocol 3: The sample is cooled at zero field from T_h to T_i. Then, a measurement is performed adiabatically with a field change from 0 to B starting at T_i. After that, the sample is heated up to T_h again, and then cooled down to the next temperature T_{i+1} ($T_i < T_{i+1}$) at zero field. A measurement is carried out at T_{i+1} following the same field sequence as used at T_i. The procedure is repeated until the temperature reaches T_h.

3 Results and discussion

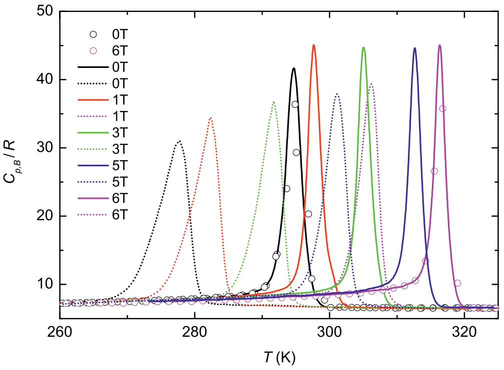

Figure 1. (Color online) Temperature dependence of $C_{p,B}$ for $Mn_{0.99}Co_{0.01}As$ at constant fields. Open circles: data determined using the step technique. Solid and dotted lines: heating and cooling thermograms, respectively. R is the gas constant.

Fig. 1 shows the temperature dependence of $C_{p,B}$ obtained near the FOPT at constant magnetic fields of 0, 1, 3, 5, and 6 T on heating and cooling processes for $Mn_{0.99}Co_{0.01}As$. An excellent agreement is observed between the data determined with the step method and the thermograms at 0 T and 6 T, but the thermograms data are more informative, in particular, at the transition. For all the studied fields, the $C_{p,B}$ curves exhibit sharp peaks and large hysteresis, implying the occurrence of FOPT.

For each $C_{p,B}$ curve, the transition temperature T_t is taken at the corresponding peak. The resulting values of T_t are listed in Table 1. We found that with 1% at. substitution of Co for Mn, the transition temperature on heating (T_t^h) decreases from 317.0 K for MnAs to 294.7 K, which is desirable for magnetic refrigeration at room temperature. However, the hysteresis is enlarged by the Co doping, which is disadvantageous for high efficiency refrigeration. T_t shifts to high temperature with applying magnetic field at a rate of $dT_t^c/dB = 4.7$ K/T for cooling processes, and $dT_t^h/dB = 3.7$ K/T for heating processes. These values are similar in MnAs [18]. The faster increase of T_t on cooling than on heating leads to a reduction of the hysteresis, specifically, from 17.1 K at 0 T to 10.1 K at 6 T. The enthalpy change at the transition (or latent heat) was calculated using $\Delta H_t = \int_{T_s}^{T_t}(C_{p,B} - C_{p,B}^{FM})dT + \int_{T_t}^{T_f}(C_{p,B} - C_{p,B}^{PM})dT$, where T_s and T_f are the starting and finishing temperatures of the transition, respectively; $C_{p,B}^{FM}$ and $C_{p,B}^{PM}$ are the heat capacities in the FM and PM phases near the transition, respectively. Then, the entropy change at the transition for these sharp peaks is written as $\Delta S_t = \Delta H_t/T_t$. The resulting values of ΔH_t and ΔS_t for different fields are listed in Table 1. It is found that the values of ΔH_t and ΔS_t on cooling are higher than on heating at a given magnetic field, whereas both, simultaneously, decrease with increasing field for heating and cooling processes. The magnitudes of ΔH_t and ΔS_t are close to those for MnAs [10]. The observation of large values of ΔH_t and ΔS_t foretells a giant MCE in $Mn_{0.99}Co_{0.01}As$.

The isothermal entropy change of $Mn_{0.99}Co_{0.01}As$ has been determined independently with the following three methods: (1) using the Maxwell relation in the form

Table 1. Transition temperatures, transition enthalpies, and transition entropies on heating and cooling processes. Maximum isothermal entropy changes and maximum adiabatic temperature changes derived from the entropy curves for $Mn_{0.99}Co_{0.01}As$.

B (T)	T_t^c (K)	$-\Delta H_t^c$ (J/g)	$-\Delta S_t^c$ (J/kg·K)	$-\Delta S_{T,\max}^{in}$ (J/kg·K)	$\Delta T_{S,\max}^{in}$ (K)	T_t^h (K)	ΔH_t^h (J/g)	ΔS_t^h (J/kg·K)	$\Delta S_{T,\max}^{de}$ (J/kg·K)	$-\Delta T_{S,\max}^{de}$ (K)
0	277.6	9.0	32.4			294.7	7.0	23.8		
1	282.4	9.0	31.9	21.4	3.6	297.7	6.9	23.2	18.2	2.6
3	291.7	8.7	29.8	30.0	10.8	305.0	6.7	22.0	24.3	8.6
5	301.1	8.1	26.9	32.0	16.8	312.6	6.1	19.5	26.2	13.2
6	306.2	7.5	24.5	32.1	17.7	316.3	5.7	18.0	26.9	14.3

^{h} and ^{c} denote heating and cooling processes, respectively.

^{in} and ^{de} denote increasing and decreasing fields, respectively.

$\Delta S_T = \sum_i \frac{M_i(T_{j+1})-M_i(T_j)}{T_{i+1}-T_i}\Delta B_i$, where the isothermal magnetization data was measured following protocol 1; (2) using the expression $\Delta S_T = Q/T$, valid for equilibrium thermodynamics, where Q represents the heat absorbed by the sample when removing the field isothermally, what we call direct determination of ΔS_T, and was carried out following protocol 2; (3) using the equation $\Delta S_T = \int_0^T \frac{C_{p,B}(T)-C_{p,0}(T)}{T}dT$, where $C_{p,0}$ and $C_{p,B}$ are the heat capacity data measured at magnetic fields 0 and B.

To be precise, for irreversible processes as happen in first-order transitions, there is an entropy dissipation to be added to ΔS_T, such as $\Delta S_{diss} = E_{diss}/T$, where E_{diss} is the dissipated energy, that can be estimated from the magnetization loops or the entropy loops obtained from the corresponding heating and cooling cycles of $M(B)$ and $C_{p,B}(T)$. In the present case, the correction values E_{diss}/T calculated for the direct determinations and the calorimetric derivations of ΔS_T were found to be smaller than 0.5 J/kg·K. Figs. 2(a) and (b) display the plots of ΔS_T for field changes of 1, 3, 5, and 6 T derived from $C_{p,B}$ on cooling and heating processes, respectively. The cooling curves exhibit higher maxima than the heating curves, as seen in Table 1. For a field change of 6 T, the maxima of $|\Delta S_T|$ are found to be 26.9 J/kg·K and 32.1 J/kg·K for heating and cooling processes, respectively. These values are quite reasonable when compared with the latent heats of the transition at zero field. For the sake of comparison, the ΔS_T data determined from direct measurements, for a field change from 6 T to 0, are also plotted in Fig. 2(b). One can see that there is an excellent coincidence for the data obtained using these two techniques.

Figures 2(c) and 2(d) show the plots of ΔS_T calculated from the magnetization data with increasing and decreasing fields, respectively, following protocol 1. In order to compare with ΔS_T derived from $C_{p,B}$, here we only present the data for field changes of 1, 3, 5 and 6 T (the measurements were carried out with maximum fields up to 9 T). The expected spurious peaks of ΔS_T are observed in Fig. 2(c), due to inadequate application of the Maxwell relation to the magnetization data, using the expression previously shown. The observed maximum value, $-\Delta S_{T,\max}$ = 138 J/kg·K for a field change of 6 T, is comparable to the literature values for $Mn_{1-x}Fe_xAs$ [11] and $Mn_{1-x}Cu_xAs$ [12]. On decreasing field, no spurious ΔS_T peaks are obtained, since each demagnetization curve starts from a fully FM state in the phase transition region and only the data below 6 T are considered. Thus, these ΔS_T values on decreasing field are well consistent with the results obtained from $C_{p,B}$ and the direct measurements, shown in Fig. 2(b). These slightly higher values than the results derived from the calorimetric measurements can be argued as coming from a higher contribution of the correction term in the magnetic derivation of ΔS_T.

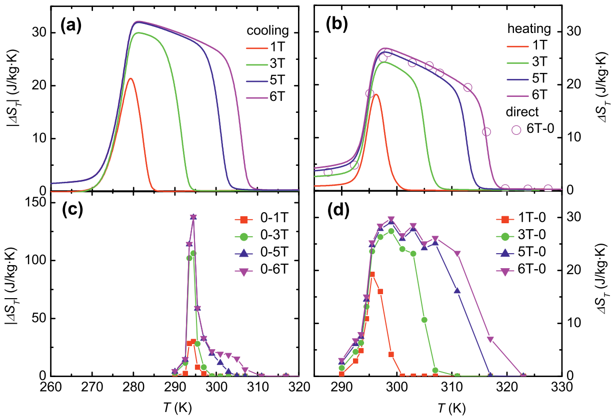

Figure 2. (Color online) Temperature dependence of the isothermal entropy change for $Mn_{0.99}Co_{0.01}As$ for several field changes. (a) ΔS_T obtained from isofield $C_{p,B}$ measurements on cooling. (b) lines: ΔS_T obtained from isofield $C_{p,B}$ measurements on heating; open symbols: the ΔS_T data obtained from the direct measurements. (c) and (d) the ΔS_T data obtained from magnetization measurements on increasing and decreasing fields, respectively.

Figure 3 shows the temperature dependence of the adiabatic temperature change for $Mn_{0.99}Co_{0.01}As$ obtained by directly measuring the temperature increment in the sample upon an adiabatic application of field. It also shows the calculated ΔT_S from the entropy curves derived from the $C_{p,B}$ data. Since the direct measurements were carried out on increasing field using protocol 3, the resulting ΔT_S values coincide with those from the cooling $C_{p,B}$ curves. The values obtained for ΔT_S are higher than those reported for MnAs [3, 10], and also higher than those for Gd [19], that has been regarded as one of the best materials for magnetic

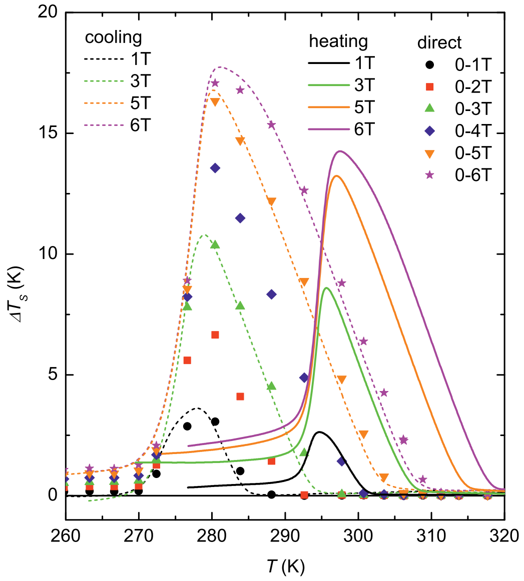

Figure 3. (Color online) Temperature dependence of the adiabatic temperature change for $Mn_{0.99}Co_{0.01}As$ with different field changes. The solid and dotted lines denote the data determined from the isofield $C_{p,B}$ on heating and cooling, respectively. The symbols denote the data obtained from direct measurements.

refrigeration at room temperature. For some typical field changes, the values of $\Delta T_{S,\mathrm{max}}$ are listed in Table 1.

Such a giant MCE of $Mn_{0.99}Co_{0.01}As$ originates from the occurrence of a field-induced magneto-structural FOPT. The giant room-temperature MCE suggests that the Co-doped MnAs compounds are potential candidates for the derivation of useful refrigerants near room temperature. A decrease of the large hysteresis would be necessary through some processing or additional doping.

4 Conclusions

The presence of hysteresis in the $C_{p,B}$ and magnetization curves indicates that the nature of the transition is first-order. The large latent heat of the FOPT together with its T_t field dependence imply a giant MCE in $Mn_{0.99}Co_{0.01}As$. Three different methods, including magnetization, $C_{p,B}$, and direct measurements, have been employed to determine the MCE of the studied compound. Application of the Maxwell relation on the magnetization data measured using protocol 1 produces spurious peaks in the resulting ΔS_T curves. The direct measurements of ΔS_T and ΔT_S gave results coinciding with those derived from $C_{p,B}$ measurements. The compound exhibits giant MCE with maximum values, $-\Delta S_{T,\mathrm{max}} = 32.1$ J/kg·K and $\Delta T_{S,\mathrm{max}} = 17.7$ K for a field change from 0 to 6 T, which indicates these Co-doped compounds are potential candidates for obtaining good materials for room-temperature magnetic refrigeration.

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