Tuning the giant inverse magnetocaloric effect in Mn$_{2-x}$Cr$_x$Sb compounds

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Structural, magnetic, and magnetocaloric properties of Mn$_{2-x}$Cr$_x$Sb compounds have been studied. In these compounds, a first order magnetic phase transition from the ferrimagnetic to the antiferromagnetic state occurs with decreasing temperature, giving rise to giant inverse magnetocaloric effects that can be tuned over a wide temperature interval through changes in substitution concentration. Entropy changes as high as 7.5 J/kg K have been observed, and a composition independent entropy change is obtained for several different concentrations/workng temperatures, making these compounds suitable candidates for a composite working material.

In the past few decades, with the discovery and development of materials presenting first order magneto-structural transitions around room-temperature, refrigeration based on the magnetocaloric effect (MCE) has become an environmentally friendly and efficient alternative to gas-compression-based refrigeration.

The MCE presents itself as the magnetic entropy and adiabatic temperature changes observed when a magnetic material is submitted to an external magnetic field change. While it is intrinsic to all magnetic materials, it is maximal around magnetic phase transitions, particularly coupled magneto-structural first-order phase transitions, in which case it is called giant MCE. Most materials presenting a giant magnetocaloric effect rely on order-disorder type phase transitions coupled to discontinuous structural changes.

Materials such as MnAs,$^1$ Gd$_4$(Si$_2$Ge$_2$),$^2$ and MnCoGe-based compounds$^{3-5}$ present crystal symmetry changes with large volume variations. On the other hand, the most promising materials for applications show only a discontinuity in lattice parameters with smaller or no volume changes at all, as is the case for La(Fe,Si)$_{13}$ (Ref. 6) and (Mn,Fe)$_2$P$_2$(Si)$_7$, respectively.

However, large entropy changes can be originated not only from order-disorder transitions but also from a number of order-order first-order phase transitions, such as spin flip, spin reorientation, and antiferro to ferro or ferrimagnetic phase transitions.

Mn$_2$Sb (Ref. 8) is a ferrimagnet with $T_C$ around 550 K and tetragonal Cu$_2$Sb-type structure (space group D$_{4h}^7$P4/nmm). In this system, the magnetism is solely due to the Mn atoms, which occupy two non-equivalent crystallographic sites 2$a$ and 2$c$, hereon referred as Mn$_I$ and Mn$_{II}$, respectively. The magnetic structure, as described by Cloud et al.,$^9$ consists of Mn$_I$ and Mn$_{II}$ sublattices stacked in triple layers in a Mn$_I$-Mn$_{II}$-Mn$_{II}$ structure which repeats along the c-direction. Both sublattices show ferromagnetic intralayer interactions, with the Mn$_{II}$ moment being roughly twice that of Mn$_I$, both parallel to the tetragonal axis. However, adjacent Mn$_I$-Mn$_{II}$ layers couple antiparallel while adjacent Mn$_{II}$-Mn$_{II}$ layers couple parallel to each other, resulting in a ferrimagnetic Mn$_I$-Mn$_{II}$-Mn$_{II}$ configuration.

It is well known that for Mn compounds the exchange interaction is strongly dependent on the interatomic spacing. Therefore, below a critical distance between adjacent Mn$_I$ layers, due to the Pauli exclusion principle, the interlayer exchange interactions must change sign and become antiferromagnetic with a $[1][1]$ configuration, in a phenomenon known as exchange inversion.$^{10}$ The transition from the ferri to the antiferromagnetic state is accompanied by the rotation of the moments from the direction parallel to that perpendicular to the tetragonal axis. As this translates into a decrease of the magnetization during lattice contraction or cooling, a so-called inverse transition is observed.

For pure Mn$_3$Sb, normal thermal contraction is not sufficient to trigger exchange inversion, but if a substitution is introduced which decreases the lattice parameters, the critical distance at which exchange inversion takes place may become accessible. Exchange inversion can be achieved by a number of different substitutions both in the Mn as in the Sb sites. They can be smaller atoms which contract the lattice: Cr, Co, V, and Cu on the Mn site, and As, Ge, and Sn on the Sb site, or a larger atom which drastically changes the thermal expansion of the lattice, as is the case of Bi substitution on the Sb site. As the interlayer exchange interaction changes sign, the variation of the c lattice parameter becomes critical. At the transition, a large discontinuous change of the c parameter is observed, which is compensated by an opposite variation of the a parameter, resulting in small volume changes.

How much the c parameter is decreased can be controlled through the amount of substitution, making it possible to tune the temperature at which the exchange inversion...
occurs and therefore the working temperature of a given compound.

In this paper, we report on the properties of the Mn$_{2-x}$Cr$_x$Sb series of compounds which present the so-called inverse magnetocaloric effect, associated with a first-order phase transition between antiferro and ferrimagnetic states.

Polycrystalline Mn$_{2-x}$Cr$_x$Sb was prepared from high purity elements: Mn and Sb in pieces (Alfa Aesar 99.9% and 99.999%, respectively) and Cr in flakes (Johnson Matthey 0.03% oxide impurity). The 3 g buttons were molten from 5 to 6 times and turned upside down in between melts to ensure homogeneity. Weight losses as low as 0.5% were observed. The buttons obtained by arc-melting were then sealed in quartz ampoules under Ar atmosphere and annealed for 120 h at 1073 K. Heating and cooling to and from the annealing temperature was performed at a rate of 5 K/min.

The samples were structurally characterized at room temperature through X-ray diffraction (XRD) measurements using Cu-K$_\alpha$ radiation which were analyzed using FullProf’s implementation of the Rietveld refinement method. The magnetic and magnetocaloric properties around the antiferro-ferrimagnetic transition were measured on a Quantum Design MPMS 5 SQUID magnetometer. The Curie temperatures were measured in a Lake Shore VSM. Other isofield magnetization measurements were performed in a Quantum Design PPMS. The magnetic entropy change was calculated from isothermal magnetization data using the Maxwell relations. All magnetization measurements were performed on powder samples with masses ranging from 10 to 20 mg.

Calorimetry measurements were performed using the setup built and reported by Klaasse and Brück as well as a commercial TA instruments Q2000 DSC. In the setup built by Klaasse and Brück, the sample must be shaped as a slab 4 x 4 x 1 mm (≈60 mg). For the commercial DSC, the samples were measured as powder with masses from 30 to 50 mg.

Four compositions of Mn$_{2-x}$Cr$_x$Sb were studied $x = 0.06; 0.08; 0.10; \text{ and } 0.12$, with transition temperatures within the range from 220 K to 340 K. These concentrations were chosen as to avoid a second antiferromagnetic phase appearing at low temperature for $x < 0.05$ while keeping a large magnetization jump. For higher Cr concentrations (approximately $x > 0.12$), the magnetization jump at the transition decreases considerably, yielding much lower entropy changes.

XRD at room temperature shows that all four samples crystallize in the tetragonal Cu$_2$Sb-type of structure (see Figure 1). The lattice parameters obtained from Rietveld refinement are presented in Table I. Increasing Cr content increases the $a$ and decreases the $c$ lattice parameter. For $x > 0.10$, $c$ is below the critical distance $c_{\text{crit}} \approx 6.53$ Å for which the antiferromagnetic phase is accessible in Mn$_{2-x}$Cr$_x$Sb compounds, and therefore, the transition temperature $T_t$ is above room temperature (see Figure 2). The weak reflection marked in Figure 1 is attributed to a small amount of second phase, identified as MnSb precipitate which crystallizes in the hexagonal Ni$_2$In-type of structure (space group D$_{6h}^{19}$-P 63/mmc). This ferromagnetic impurity has a $T_C$ around 585 K and is responsible for the rather high magnetic response in the antiferromagnetic state (see Figure 2).

Isofield magnetization measurements (see Figure 2) and Arrott plots (see Figure 3) reveal very sharp first-order phase transitions with very low thermal hysteresis (less than 2 K for all compositions reported). In contrast to some of the main giant MCE materials, the magnetic transition in these compounds is not accompanied by a change in crystallographic symmetry, but only a jump in lattice parameters. This results in a lower energy barrier at the phase transition which is one of the main factors contributing to thermal hysteresis, which in turn is also lower.

![FIG. 1. X-ray diffraction patterns at room temperature for the Mn$_{2-x}$Cr$_x$Sb compounds. The red arrow identifies the reflection attributed to the MnSb secondary phase.](image)

![FIG. 2. Temperature dependence of the magnetization.](image)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Vol (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>4.07952(3)</td>
<td>6.53651(3)</td>
<td>108.784(1)</td>
</tr>
<tr>
<td>0.08</td>
<td>4.08075(3)</td>
<td>6.53330(2)</td>
<td>108.796(1)</td>
</tr>
<tr>
<td>0.10</td>
<td>4.08708(3)</td>
<td>6.52545(3)</td>
<td>109.003(1)</td>
</tr>
<tr>
<td>0.12</td>
<td>4.08859(3)</td>
<td>6.51117(2)</td>
<td>108.844(1)</td>
</tr>
</tbody>
</table>
The transition temperature from the antiferro to the ferrimagnetic state $T_t$ is very sensitive to composition and increases with increasing Cr content at a rate of 8.2 K/at.%Cr. Unlike $T_t$ which quickly increases with increasing Cr substitution, the transition temperature between the ferri and paramagnetic states $T_C$ slowly decreases with increasing Cr content at a rate $-2.3$ K/at.%Cr. Therefore, increasing Cr substitution effectively brings the antiferro to ferri and the ferri to paramagnetic transitions together. However, for all compositions studied, $T_C$ remains far above $T_t$ and does not hinder the use of the inverse transition in applications.

The thermodynamical quantities are summarized in Table II. The saturation magnetization (right above the transition temperature at 5 T) decreases linearly with increasing Cr content, as the amount of Mn is decreased. This decrease reflects directly on the magnitude of the entropy change (see Figure 4 and Table II), which also decreases with increasing Cr content.

Notice that, unlike most magnetocaloric materials, the entropy change due to the isothermal application of an external magnetic field is positive for Mn$_{2-x}$Cr$_x$Sb compounds. This reflects the fact that field favors the high-temperature high-magnetization ferrimagnetic phase, shifting $T_t$ to lower temperatures with increasing field. Since the structural entropy increases with increasing field, manifest in the latent heat, the total entropy in field is higher than in zero field. Consequently, an adiabatic field increase will lower the temperature of the system. Therefore, this magnetocaloric effect is called inverse in contrast with the most frequently observed conventional MCE where an adiabatic field increase will increase the temperature of the system.

Entropy changes are found to be composition independent over the composition interval studied, ranging from 7.5 J/kg K to 5.5 J/kg K for a magnetic field change from 0 to 5 T. These values are comparable to those found in elemental Gd (Ref. 2) and in some La(Fe,Si)$_{13}$ (Ref. 6) compositions. This means that using different compositions of Mn$_{2-x}$Cr$_x$Sb it is possible to produce a composite material presenting a table-like effect (i.e., a plateau in the $\Delta S$ curve) over a temperature interval of approximately 100 K. Applications for such composite material could be found where cooling is required over large temperature spans in spite of a lower cooling power.

The specific heat was measured for the sample with $x = 0.06$ and is presented in Figure 5. The latent heat content of the peak (minus an “eye-ball”-shaped background) is 275 J/mol, and the entropy change due to the transition in the absence of an external magnetic field can be estimated to be approximately 5.1 J/kg K. The difference with the value in Table II can be attributed to the reported systematic errors made by the step wise methods in determining the latent heat of first order transitions, resulting in too low values. Magnetic field shifts the first order phase transition to lower temperatures widening the entropy change peak (and thus

![FIG. 3. Arrott plots around the phase transition temperature for all compositions.](image)

![FIG. 4. Temperature dependence of the entropy change for a 2 T (open symbols) and 5 T (closed symbols) magnetic field changes.](image)

![FIG. 5. Heat capacity as a function of temperature for the sample $x = 0.06$.](image)

**TABLE II. Thermodynamic quantities.**

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_t$ (K)</th>
<th>$T_C$ (K)</th>
<th>$\Delta S_m$ (J/kg K)</th>
<th>$dT_t/dH$ (K/T)</th>
<th>$M_S$ (Am$^2$/kg)</th>
<th>$\Delta T_{max ad}^+$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>232 520</td>
<td>7.5 3.9</td>
<td>36</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td>272 510</td>
<td>7.3 4.3</td>
<td>33</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>305 505</td>
<td>6.2 3.7</td>
<td>29</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.12</td>
<td>333 490</td>
<td>5.5 4.1</td>
<td>27</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
increasing the cooling power) but does not significantly increase its maximum.

Another important feature for applications is the rate at which the transition temperature shifts due to the external magnetic field, $\delta T_t / \delta B$ (see Table II). As a magnetocaloric material is cycled in and out of a magnetic field, the reversibility of the cycle will depend on the thermal hysteresis as well as $\delta T_t / \delta B$. The Mn$_{2-x}$Cr$_x$Sb compounds show low thermal hysteresis and large $\delta T_t / \delta B$ being ideal for applications. Moreover, the first order ferrimagnetic to antiferromagnetic phase transition is accompanied by discontinuous jumps in both $a$ and $c$ lattice parameters in opposite senses, resulting in volume changes from 0.1% to 0.02% in the studied range. In first order phase transitions where discontinuities in the thermal evolution of the crystal lattice are intrinsic, small volume changes are critical in keeping physical stability during cycling.

This shift is not only important in determining the operating conditions for applications but it also provides an upper bound to the value of the adiabatic temperature change $\Delta T_{ad}^{max}$. The upper bound to $\Delta T_{ad}$ can be calculated using $\delta T_t / \delta B$, $M_S$, and the specific heat value just before (or after) the latent heat peak of the first order phase transition (see Figure 5). For the studied compounds, the upper bound is found at $\approx 6$ K in a field change of 1 T (see Table II), higher values than found for materials such as La(Fe$_x$Si)$_{13}$ (Ref. 6) and (Mn$_x$Fe)$_2$(P$_y$Si)$_1$.7

In summary, we have studied the Mn$_{2-x}$Cr$_x$Sb compounds showing a first order magnetic phase transition between antiferro and ferrimagnetic states which can be tuned by substitutions. The order-order transition gives rise to a moderate giant inverse magnetocaloric effect which is found to be composition-independent within a large range of compositions and temperatures. These compounds are produced from cheap and abundant elements using a simple and straightforward process making them economically attractive for applications. Furthermore, together with small volume changes and large $\delta T_t / \delta B$ and $\Delta T_{ad}^{max}$, the composition-independent entropy changes make these compounds ideal for applications where heat pumping over large temperature ranges is necessary, such as small scale laboratory devices for N$_2$ liquefaction.

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