Low-field-induced high entropy change in Ni$_2$(Mn,Cu)Ga$_{0.84}$Al$_{0.16}$ magnetocaloric materials

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Abstract

Ferromagnetic Ni$_2$MnGa-based materials have been subject of intense study due to the strong coupling of structural and magnetic transitions, named a magnetostructural transformation, present in some off-stoichiometry compounds. This property is promising for numerous applications, such as solid state cooling and energy harvesting. In this work the magnetic and thermal properties of the polycrystalline Heusler compounds Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga$_{0.84}$Al$_{0.16}$ with martensitic transition and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.84}$Al$_{0.16}$ with magnetostructural transformation were investigated by magnetization and heat flow measurements, both as a function of temperature and magnetic field. It is found that these materials present high values of entropy change around room temperature under 0 – 1 T magnetic field change.
Introduction

A magnetostructural transformation, the coupling of structural and magnetic ordering transition change, often increases the magnetocaloric and ferromagnetic shape memory potential of some compounds due to the considerable magnetic field dependence of the magnetostructural transition.[1] With this coupling, a high total entropy change ($\Delta S$) can be achieved in a structural transformation between a magnetically ordered phase (ferromagnetic) and a magnetically misaligned phase (paramagnetic or antiferromagnetic). Among the main materials which present magnetostructural transitions, Heusler alloys based on Ni-Mn-X ($X =$ Ga, In, Sn and Sb) have received particular attention.[2] Some ferromagnetic Ni$_2$MnGa-based Heusler alloys are well known due to interesting properties, such as martensitic transformations [3] and large magnetic-field-induced deformations due to direct or reverse martensitic transitions [4,5,6] as well as reorientation of the martensite variants by twin boundary motion.[7,8,9] These materials also present an enhanced magnetocaloric effect (MCE) in some off-stoichiometry compounds.[10,11,12]

Ni$_2$MnGa crystallizes in a cubic L2$_1$-type structure (space group Fm-3m) with a room temperature lattice parameter $a = 5.825$ Å and a low temperature martensitic structure.[3] It shows a continuous transition between a ferromagnetic martensite phase and a paramagnetic austenite phase at 376 K, as well as a martensitic transition around 200 K.[5] Small additions of Ni in the Mn site leads to the appearance of a magnetostructural transition when both structural and magnetic transitions are very close in temperature, in this case around 333 K.[10]
possibility to have these transitions near the same temperature was also reported in 
Ni$_2$Mn$_{1-x}$Cu$_x$Ga alloys, where values of entropy change as large as -60 J/Kg$^{-1}$K$^{-1}$ were 
measured for 0 – 5 T of magnetic field change.[11,13,14,15]

In order to reduce the cost for production of the alloy while retaining its major 
properties, it is desirable to replace Ga by a different element. In our case, we chose 
Al.[16] Aluminum addition in Ni$_2$MnGa$_{1-x}$Al$_x$ alloys yield a coexistence of L2$_1$ 
(ferromagnetic) and B2 (antiferromagnetic) structures, leading to a predominant 
antiferromagnetism when $x > 0.30$.[17,18] The fabrication method and annealing 
processes are important factors contributing to the alloy’s magnetic and structural 
properties, as well as ensuring predominance of the ferromagnetic L2$_1$-type 
structure.[17] The alloy Ni$_2$Mn$_{1-x}$Cu$_x$Ga$_{0.9}$Al$_{0.1}$, with Al concentration of 10% on the 
Ga site, was previously studied.[19] In these compounds, the crystallographic 
and magnetic transitions coexist at around 295 K for $x = 0.20$, resulting in $\Delta S = -9.5$ JKg$^{-1}$K$^{-1}$ 
under a 0 – 5 T magnetic field change. Although the use of Al in this alloy 
dramatically reduces the maximum of $\Delta S$ when compared to the Al free materials, the 
refrigerant capacity (RC) is larger, about 110 J/Kg. Taking into account the amount 
of material with the same RC, a reduction in cost of 26% is achieved when compared 
with the compound without Al, Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga.

Polycrystalline Ni$_2$Mn$_{0.7}$Cu$_{0.3}$Ga$_{0.84}$Al$_{0.16}$ was recently studied.[20] This 
particular composition presents relevant properties for ferromagnetic shape memory 
applications with values of magnetic-field-induced deformation as large as 2.6% at 
room temperature, a remarkable value for a polycrystalline material. This compound 
presents an austenite phase with L2$_1$-type cubic unit cell of the Fm-3m space group
and a martensite phase with a L1₀ non-modulated tetragonal structure, which is considered the lowest energy structure (ground state) for the martensitic phases of these Heusler alloys. Due to an abrupt magnetostructural transition under a low magnetic field of 0.25 T, the transformation is partially induced and the material presents a giant strain of 1.6% at 297.4 K.

In the present investigation, we studied the magnetocaloric properties of Ni₂Mn₀.₇Cu₀.₃Ga₀.₈₄Al₀.₁₆ cited above, as well as the composition Ni₂Mn₀.₇₅Cu₀.₂₅Ga₀.₈₄Al₀.₁₆. The latter is similar to the well known Ni₂Mn₀.₇₅Cu₀.₂₅Ga, with partial Ga replacing by Al. The effect of using a higher Al content when compared to the study by Mejia et al [18] in Ni₂Mn₁₋ₓCuₓGa-based alloy is discussed. The work is based on magnetization and heat flow measurements.

**Experimental Methods**

Two samples pellets of 1.5 g with composition Ni₂Mn₀.₇₅Cu₀.₂₅Ga₀.₈₄Al₀.₁₆ and Ni₂Mn₀.₇₀Cu₀.₃₀Ga₀.₈₄Al₀.₁₆ were made using conventional arc melting process in 99.999% pure argon atmosphere and metallic elements with purity better than 4N. The samples were re-melted 3 times, with care not to keep the arc for more than five seconds, thereby avoiding large losses due to Mn vaporization. Initially, Mn losses of approximately 3% at the end of the melting process were observed, and to account for this, we added an excess of Mn before melting to ensure the correct stoichiometry. To achieve a better sample homogenization, two thermal treatments were applied. The samples were wrapped with tantalum foil and encapsulated in quartz tubes under a low argon pressure of 0.2 atm. The first thermal treatment was
done for 72 h at 1273 K and the second for 24 h at 673 K, both at a rate of 3 K/min and quenching in room temperature water at the end of each process. Isothermal and isofield magnetization measurements were made using a Vibrating Sample Magnetometer in a Physical Properties Measurement System (PPMS) from Quantum Design Inc. A Peltier differential scanning calorimeter device was built to measure heat flow under magnetic field in the PPMS platform. A similar apparatus is described in Ref. 21. Additional heat flow measurements were made using a commercial Differential Scanning Calorimeter (DSC), model Q2000 from TA Instruments Inc, in order to compare the results with the home made Peltier based DSC. The enthalpy change in the transition, obtained by the integrating the data of heat flow as a function of time, coincides within 2.2% when comparing the results of the Peltier Cell and the commercial DSC.

**Results and Discussion**

The temperature dependence of the magnetization measured in ZFC (zero field cooled) and FCC (field cooled cooling) modes under a magnetic field of 20 mT is shown in Fig. 1. The compound with \( x = 0.25 \) presents a magnetic transition in the austenite phase with \( T_C = 296 \) K on cooling. As the temperature decreases, a ferromagnetic martensite phase takes place from the ferromagnetic austenite one at 262 K, with thermal hysteresis of 6 K. Partial Ga replacement by Al at 16% separates the magnetostructural transformation of the Ni\(_2\)Mn\(_{0.75}\)Cu\(_{0.25}\)Ga compound [11] into a first order martensitic and a second order magnetic transformation, with 33 K of temperature difference.
For $x = 0.30$, the martensite phase is ferromagnetic while the austenite phase is paramagnetic, due to a magnetostructural transition that starts at 297 K on cooling, with thermal hysteresis of 9 K. The different magnetic ordering between the structural phases is a relevant property for magnetocaloric and ferromagnetic shape memory materials because it tends to increase the magnetization difference between the phases in the transformation.

In addition, ZFC and FCC magnetization measured at higher magnetic fields, from 20 mT up to 5 T, are shown in Fig. 2. Here, we notice in panel (a) that the $x = 0.25$ sample presents martensitic transformation among two ferromagnetic phases. Due to larger magnetocrystalline anisotropy, the martensite phase for $x = 0.25$ presents lower magnetization at small magnetic fields while the opposite is observed at high fields. This higher magnetocrystalline anisotropy is associated to the variants of martensite that impose constrains to the structure.\[5,10\] Since the magnetization process of these type of materials is strongly related to the structure, this higher magnetocrystalline anisotropy imposes a barrier to the magnetization at low magnetic field and a higher magnetic field needs to be applied to overcome this barrier. As seen in the Fig. 2 (a), a magnetic field of 0.3 T is enough to the martensite magnetization surpass the austenite magnetization.

On the other hand, this behavior associated to the magnetocrystalline anisotropy is not observed for $x = 0.30$ because this material transforms from a paramagnetic austenite to a ferromagnetic martensite. In this case, the benefit of a para-ferro transition is the increase of the magnetization difference between the phases, which is much higher for $x = 0.30$ when compared to the $x = 0.25$ sample, as observed in
Fig. 2. The higher the magnetization difference between the phases implies that a lower magnetic field is necessary to induce the transformation. This yields an increase of the energy that the material can release under an external stimulus due to the magnetic contribution, which favors the composition $x = 0.30$ in terms of magnetocaloric properties.

For both samples, isothermal magnetization measurements up to 9 T are shown in Fig. 3. Prior to each measurement the material was heated to the high temperature austenite phase and then cooled to the target temperatures displayed in Fig. 3. For $x = 0.25$, shown in panel (a), at 262 K and 270 K the material shows the ferromagnetic property of both martensite and austenite phases. All isotherms measured between these two temperatures display a magnetic-field-induced martensitic transformation. The temperature dependence of the critical field presents a linear behavior, with slope of 1.5 T/K. In inset of Fig. 3 (a), the energy loss as a function of temperature is shown. It was calculated by using the area between the curves of increasing and decreasing fields (the latter is not shown) for temperatures in which $H_C < 5$ T. Technically, this energy loss reduces the energy exchanged by the material in cyclical applications. Therefore, this curve is useful to identify more efficient temperatures for application purposes.

In the results for the sample $x = 0.30$, seen in Fig. 3 (b), the data at 293 K shows a ferromagnetic-like curve, while at 306 K it exhibits a predominant paramagnetic behavior. The measurements from 298 K to 304 K reveal that the magnetostructural transition is induced by the magnetic field. For this compound, the critical field also varies linearly with temperature, and the slope of the critical field is
1.0 T/K. Again, as noticed in Fig. 2, the magnetization difference between the phases is larger for $x = 0.30$ than for $x = 0.25$. In addition, the energy loss is presented in the inset of the Fig. 3 (b). It shows that 298 K is the temperature with lower energy loss, around 19 J/kg.

In order to quantify the total entropy change $\Delta S$ of the samples under a magnetic field change, heat flow measurements were performed using a Peltier Cell as a thermal probe. This experimental set up allow us to measure the thermoelectric voltage associated with the energy released or absorbed by the material in an isothermal process, while the transformation is induced by the magnetic field.

Examples of the measured voltage data are show in Fig. 4, for both $x = 0.25$ and $x = 0.30$ samples. These curves were obtained with different protocols of magnetic field change, while the probe measures the heat exchange. In the first one, show in Fig. 4 (a) for $x = 0.25$, the magnetic field varies in two steps, for 0 to 2 T and from 2 to 5 T. In the next case, displayed in Fig. 4 (b) corresponding to the $x = 0.30$ sample, the magnetic field changes continuously from 0 to 5 T. Finally, in Fig. 4 (c), again for $x = 0.30$, the magnetic field is changed in several discrete steps. The satellite peaks of heat released by the samples as the magnetic field varies in all parts of Fig. 4 signals that the transformation for both samples takes place in multiple steps.

From each isothermal measurement, we extract the heat exchanged and calculate $\Delta S$,[21] as shown in Figs. 5 (a) and (b) as a function of temperature and magnetic field. The values of maximum $\Delta S$ and the RC were obtained for 0 - 2 T and 0 - 5 T, and are summarized in Table 1. The RC values were calculated by integrating
the ΔS(T) peak at half of the maximum height. Also in Figs. 5 (a) and (b), we plotted the magnetic entropy change ΔS\text{mag} for 0 – 2 T calculated from the magnetization data.\[22\] In the case with a magnetostructural transformation, for x = 0.30, ΔS\text{mag} has a maximum value very close to the maximum of ΔS obtained from calorimetric data. On the other hand, for x = 0.25 the maximum value of ΔS\text{mag} is considerably lower than the maximum of ΔS from calorimetric data. We believe that this behavior is related to the nature of the transformation. In the sample x = 0.25, with martensitic transition, both phases are ferromagnetic, therefore a considerable part of the transition enthalpy comes from the lattice rearrangement, which has a non magnetic origin. On the other hand, for x = 0.30, with magnetostructural transformation, the magnetic contribution to the total entropy change is large, since the parent phase is paramagnetic and the product phase is ferromagnetic. Therefore, the total entropy change is mostly magnetic and magnetization measurements yield reliable values of ΔS.

In light of these results, it is relevant to comment on the differences between our values of ΔS and RC compared with those found for Ni\textsubscript{2}(Mn,Cu)(Ga,Al) materials in the literature. In Ni\textsubscript{2}Mn\textsubscript{0.75}Cu\textsubscript{0.25}Ga \[11\] and Ni\textsubscript{50}Mn\textsubscript{18.5}Cu\textsubscript{6.5}Ga\textsubscript{25}\[12\], they reported extremely large values of entropy change, twice as high as the ones obtained here for 0-5 T change. Indeed, Ga replacement by Al decreases the maximum ΔS.\[19\] On the other hand, RC = 84 J/kg for Ni\textsubscript{2}Mn\textsubscript{0.75}Cu\textsubscript{0.25}Ga \[11\] and 94.6 J/kg for Ni\textsubscript{50}Mn\textsubscript{18.5}Cu\textsubscript{6.5}Ga\textsubscript{25}\[13\] while our material with x = 0.30 presents RC = 120 J/Kg. Therefore, doping with Al decreases the maximum of ΔS but increases the full width at half maximum (FWHM) of the ΔS(T) peak, leading to a higher RC.\[19\] When
compared to the material Ni$_{2}$Mn$_{0.8}$Cu$_{0.2}$Ga$_{0.9}$Al$_{0.1}$ of Ref. 18, we observe that our material, with more Al, presents considerably larger $\Delta S$ and RC. Our values of $\Delta S$ and FWHM are intermediate among those reported for Ni$_{2}$Mn$_{1-x}$Cu$_{x}$Ga and Ni$_{2}$Mn$_{1-x}$Cu$_{x}$Ga$_{0.9}$Al$_{0.1}$ alloys, but the combination of both parameters, in our case, yield a maximized RC.

The magnetic field dependence of $\Delta S$ for $x = 0.25$ at 264 K and $x = 0.30$ at 298 K are shown in the insets of Figs. 5 (a) and (b), respectively. At these temperatures, around 90% of the $\Delta S$ for $0 – 5$ T is achieved with only $0 – 1.5$ T field change. This low field saturation of the entropy change at those temperatures is achieved due to the abrupt nature of the transformation. For example, for $x = 0.30$ and at $\mu_0 H = 1$ T, the material presents $\Delta S = -15$ Jkg$^{-1}$K$^{-1}$. The materials under study in this work present $\Delta S$ values larger than the compound with 0.1 Al content [19] due to their sharper transformation. These high values of $\Delta S$ under magnetic field change of $0 – 1$ T, which is considered a low magnetic field in the area of magnetocaloric research, are compatible with the extremely large strain under low magnetic fields previously observed.[20] For comparison, the values of $\Delta S$ for our material as well as for other compounds in the literature with large $\Delta S$ under $0 – 1$ T are compiled in Table 2.

Conclusions

The magnetocaloric properties of Ni$_{2}$Mn$_{0.75}$Cu$_{0.25}$Ga$_{0.84}$Al$_{0.16}$ and Ni$_{2}$Mn$_{0.7}$Cu$_{0.3}$Ga$_{0.84}$Al$_{0.16}$ compounds were studied. The materials present a ferromagnetic martensite phase that evolves from ferromagnetic austenite for $x = 0.25$ and from paramagnetic austenite for $x = 0.30$. In addition to the large strain
reported in the literature, these polycrystalline samples also have large entropy change, $\Delta S = -14 \text{ Jkg}^{-1}\text{K}^{-1}$ in the martensitic transformation for $x = 0.25$ and $\Delta S = -21 \text{ Jkg}^{-1}\text{K}^{-1}$ in the magnetostructural transition for $x = 0.30$, both under 0 - 2 T field change. Large values of $\Delta S$ under moderate magnetic fields are attributed to the sharp nature of the magnetostructural transformations. In addition, compared to the previous studied $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$ and $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}_{0.9}\text{Al}_{0.1}$ alloys, our material presents a higher refrigerant capacity, achieving 120 J/Kg for 0 – 5 T field change. The composition $\text{Ni}_2\text{Mn}_{0.7}\text{Cu}_{0.3}\text{Ga}_{0.84}\text{Al}_{0.16}$ reaches $\Delta S = -15 \text{ Jkg}^{-1}\text{K}^{-1}$ at 298 K for 0 – 1 T. A comparison with well know magnetocaloric materials presenting large values of entropy change around room temperature, for the same magnetic field change, shows that our compound with $x = 0.30$ presents a high low-field-induced entropy variation. However, other relevant parameters such as the adiabatic temperature change, $\Delta T_{AD}$, and hysteresis must be taken in to account for application purposes.

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Figure 1: Temperature dependence of ZFC (full symbols) and FCC (open symbols) magnetization under 20 mT field. The material with $x = 0.25$ presents magnetic and martensitic transitions while the compound with $x = 0.30$ presents magnetostructural transformation at room temperature.
Figure 2: Magnetization as a function of temperature for several magnetic fields. For $x = 0.25$ (a), the ferromagnetic martensite phase has a lower magnetization than the ferromagnetic austenite phase at 20 mT, and higher magnetization for fields above 0.3 T. On the other hand, the material $x = 0.30$ (b) presents a transformation from ferromagnetic martensite to paramagnetic austenite. The data for 20 mT was multiplied by two to improve visualization.
Figure 3: Magnetization as a function of magnetic field for (a) $x = 0.25$ and (b) $x = 0.30$. Both martensitic ($x = 0.25$) and magnetostructural ($x = 0.30$) transitions are induced by magnetic field changes. Inset: temperature dependence of the energy loss calculated by increasing and decreasing (not shown) magnetization for each isotherm.
Figure 4: Output voltage measured in a Peltier cell associated with the heat released by the samples (a) \( x = 0.25 \) and (b, c) \( x = 0.30 \) under magnetic field change at 264.5 K and 299 K, respectively. In (a), the magnetic field increases in two steps, from 0 to 2 T and 2 to 5 T, while in (b) the magnetic field increases continuously from 0 to 5 T. Another example of measurement, used to calculate \( \Delta S \) as a function of magnetic field, is seen in panel (c), where various magnetic field steps were applied. This data allows us to obtain the total isothermal entropy change under a magnetic field variation.
Figure 5: Temperature dependence of the total entropy change $\Delta S$ (measured with the Peltier calorimeter) and magnetic entropy change $\Delta S_{\text{mag}}$ (obtained from magnetization data), for (a) $x = 0.25$ and (b) $x = 0.30$, measured with 0 - 2 T and 0 - 5 T field change. The insets show the magnetic field dependence of the total entropy change $\Delta S$. 
Table 1: Total entropy change (ΔS) and refrigerant capacity (RC) under 0 to 2 T and 0 to 5 T for x = 0.25 and x = 0.30 samples.

| Cu (x) | ΔS (JKg⁻¹K⁻¹)          | RC (JKg⁻¹)          |
|--------|-------------------------|---------------------|
| 0.25   | -14 (0 – 2 T) / -21 (0 – 5 T) | 10 (0 – 2 T) / 51 (0 – 5 T) |
| 0.30   | -21 (0 - 2 T) / -30 (0 - 5 T) | 22 (0 - 2 T) / 120 (0 - 5 T) |

Table 2: Entropy change under 0 to 1 T, comparing our sample with selected compounds in the literature. Listed values for ΔS refer to either total or magnetic entropy change; details are given in each reference. Positive ΔS values are related to an inverse magnetocaloric effect.

| Composition                   | ΔS (Jkg⁻¹K⁻¹) | T (K) |
|-------------------------------|--------------|------|
| Mn₁Fe₀.₉₅P₀.₆₁Si₀.₃₃B₀.₀₆ [Ref. 23] | -19          | 267  |
| Ni₂Mn₀.₇Cu₀.₃Ga₀.₈₄Al₀.₁₆ [this work] | -15          | 298  |
| Ni₃₇.₅Co₁₂.₅Mn₃₅Ti₁₅ [Ref. 24] | 15           | 290  |
| LaFe₀₁₁.₄₇Mn₀₂₅Si₁₂₈H₁₁.₆₅ [Ref. 25] | -14          | 304  |
| Mn₁Fe₀.₉₅P₀.₆₀₅Si₀.₃₃B₀.₀₆₅ [Ref. 22] | 12.5         | 274  |
| Mn₁Fe₀.₉₅P₀.₆₃₃Si₀.₃₃B₀.₀₇ [Ref. 22] | 11.5         | 279  |
| Gd₅Si₂Ge₂ [Ref. 26]            | -11          | 272  |
| Mn₁₂₅Fe₀.₇₀P₀.₅₁Si₀.₄₉ [Ref. 27] | 10.5         | 278  |
| Mn₀₈₅Fe₁₈₁P₀.₆₂Si₀.₃₂B₀.₀₆ [Ref. 22] | 10.1         | 310  |
| Mn₁₂₀Fe₀.₈₈P₀.₇₅Ge₀.₂₅ [Ref. 26] | 10           | 282  |
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