Magnetocaloric behavior of Mn rich Ni\textsubscript{46}Cu\textsubscript{2}Mn\textsubscript{43}In\textsubscript{11} alloy

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Abstract: In this work, we studied the magnetic entropy change ($\Delta S_M$) across the martensite transformation (MT) in Mn-rich Ni\textsubscript{46}Cu\textsubscript{2}Mn\textsubscript{43}In\textsubscript{11} alloy. This compound undergoes a MT and a magnetic phase transition around the temperatures ($T_M$=) 272 K and ($T_{CA}$=) 325 K, respectively. A large field induced shift (=0.28 K/kOe) of the MT temperatures is observed. An application of magnetic field ($H$ =) of 50 kOe causes a large $\Delta S_M$ of 20 J/kg-K and -4.4 J/kg-K around $T_M$ and $T_{CA}$, respectively. We also found that the change in magnetic field induced isothermal $\Delta S_M(H)$ is mainly depends on the induced austenite phase fraction by the applied magnetic field at that temperature. Possible reasons for the observed behaviours are comprehensively discussed.

Keywords: Magnetization, Huesler, magnetic entropy, phase transition.

1. Introduction

In recent times, non-stoichiometric Ni-Mn-Z (Z=Sn,In) intermetallic compounds has attracted much attention due to their potential applications in the field of magnetic refrigeration, spintronics and magnetic read head etc [1-5]. It is believed that such novelties are primarily due to the presence of a strong coupling between the structural, the magnetic and the electronic degrees of freedom [2]. It is also well-known that these types of systems are characterized by first-order martensitic transition (MT) at $T_M$ as well as a second-order paramagnetic (PM) to ferromagnetic (FM) transition at the Curie point ($T_{CA}$). The $T_{CA}$ in these systems must be higher than their $T_M$ ($T_{CA}>T_M$) to realize the magneto-functionality around the $T_M$, i.e., the material should be in a magnetically well ordered state when MT takes place during cooling [6-7]. The MT in these materials also alters the magnetic state in which material may lose its ferromagnetism or attain a state having antiferromagnetic (AFM)-like correlation below the MT. Since the MT occurs between the magnetically order (austenite) to a magnetically disorder (martensite) state consequently a large change in the magnetization ($\Delta M$) and hence a large magnetic entropy change ($\Delta S_M$) is expected to achieve across the MT [8]. It is noteworthy that the high $\Delta M$ is one of the necessary conditions for any material to be a good magnetocaloric material (MCM). The presence of large $\Delta S_M$ produces the magnetocaloric effect (MCE) in these materials has great potential applications in the cooling technology without any harmful impact on the environment unlike the vapour compression based refrigerator. It is also well known that the MCE is a thermal response of a magnetic material against the variation of an external magnetic field and usually expressed in terms of $\Delta S_M$ in an isothermal process, or adiabatic temperature change ($\Delta T_{ad}$). As we already mentioned earlier that a large $\Delta S_M$ can be achieved across the MT therefore the researchers paid significant efforts in designing Ni-Mn based MCM with a strong magneto-structural coupling at MT. The studies also focused on the improvement of another vital MCE parameter, called the refrigeration capacity (RC) or the relative cooling power (RCP), which quantifies the amount of
heat transferred from cold to hot sink through the ideal refrigeration cycle [9]. In order to achieve a large RCP, it is important to widen the MT temperature range as this determines the working temperature range of a MCM. Upto now, the expensive rare-earth metal Gd, which experiences a second-order magnetic transition near room temperature, is regarded as a benchmark refrigerant material in magnetic refrigerator prototype [10, 11]. Since these rare earth systems are costly, researchers are considering Ni-Mn based intermetallic compounds as an alternative to its rare earth counterpart. But the problems in Ni-Mn based materials are, the $T_M$ in these systems is much lower than the room temperature (RT) for most of the Ni-Mn based martensite compounds and also the narrow MT width makes them low cooling efficient materials. In search for a better MCM with improved magneto-functionalities for more useful applications within the family of Ni-Mn we have synthesized the Ni$_{44}$Cu$_2$Mn$_{43}$In$_{11}$ compound and studied its magnetic and magnetocaloric properties.

2. Experimental details

The ascast sample was prepared by using tri-arc melting furnace from pure metals (99.995%, Alfa Aesar) in argon atmosphere. The sample was then annealed at 1173 K for 24 hrs in vacuum followed by quenching in normal water for homogenization. The crystal structure was determined using room temperature powder X-Ray diffraction (XRD) (Bruker D8 advance diffractometer). The nominal compositions of the annealed alloy was confirmed by energy dispersive X-Ray analysis (EDX) attached with a field emission scanning electron microscope (FESEM) within the error of ±0.1 at.%. Calorimetric measurements were done using Differential Sacnning Calorimetry (DSC). The magnetic measurements were carried out using Physical Property Measurement System (PPMS, Quantum Design) in the temperature range $T=5$-380 K and the field range $H=0$-90 kOe.

3. Result and discussions

The temperature dependent dc susceptibility $\chi(T)$ measurements were conducted using the zero field cooled warming (ZFCW) and the field cooled cooling (FCC) protocols and the results are shown in Fig.1. In the measurement of ZFCW $\chi(T)$, we first cooled the sample under zero magnetic field down to $T= 5$ K and then applying a magnetic field ($H = 100$ Oe) we recorded the $\chi(T)$ during warming the sample upto 395 K whereas the FCC $\chi(T)$ was measured in subsequent cooling of the sample. The $\chi(T)$ data show multiple features depending on the change in magnetic phases due to the thermal variations. At $T= 330$ K, the sample shows a sharp upturn with the decreasing temperature, which corresponds to the paramagnetic (PM) to ferromagnetic (FM) transition within the austenite phase, called Curie temperature of austenite phase ($T_{CA}$). On further cooling, $\chi(T)$ starts to decrease and a sharp fall is observed around $T_{ms}$. The fall in $\chi(T)$ is possibly due to the loss of ferromagnetism and the sample presumably becomes PM or AFM below the MT [12, 13]. On the other hand $\chi(T)$ starts to increase around $T_{as}$ during warming the material and a thermal hysteresis between the $\chi_{ZFCW}(T)$ and $\chi_{FCC}(T)$ curve appears in the temperature range of 245-310 K. Such hysteresis signifies the first order nature of MT. All the characteristic transition temperatures, i.e., the austenite start and finish temperatures ($T_{as}$ and $T_{af}$) and the martensite start and finish temperatures ($T_{ms}$ and $T_{mf}$) are labelled in Fig.1. Now below the MT, the compound continues to be in a low magnetic phase and eventually shows a spin glass type magnetic ground state below $T=65$ K. To validate the transformations characteristics we have carried out differential scanning calorimetry (DSC) in the absence of any magnetic field. The thermodynamic heat profiles pertaining to endothermic and exothermic peak are obtained during the heating and cooling cycles,
respectively (inset of Fig.1). The exothermic and endothermic transformation peaks represent forward (austenite phase to martensite phase transition) and reverse (martensite phase to austenite phase transition) MT, respectively. The values of the characteristic MT temperatures obtained from the magnetic measurement are in good agreement with our calorimetric measurements. Small discrepancy between the results of magnetic and calorimetric measurement can be ascribed to the influence of some factors such as the different thermal contacts of the samples with the thermocouples in the DSC and PPMS instruments and the two tangent procedures used for the determination of the characteristic temperatures etc. After the baseline correction of our calorimetric data we have quantified the transition entropy change using the following equation:

\[ S(T) = \int_{T_1}^{T_2} \frac{1}{T} \left( \frac{dQ}{dT} \right) dT \quad \ldots \ldots \quad (1) \]

where \( T_1 \) and \( T_2 \) denote the temperatures well below and above the phase transition, respectively and \( \left( \frac{dQ}{dT} \right) \) is the heat capacity. Using this equation we have numerically calculated the transition entropy change (\( \Delta S_{tr} \)) with the value of 17.7 J/kg-K. It is also important to mention that in the measurement of \( \chi(T) \), \( \chi(T) \) starts to drop below the \( T_{CA} \) and the thermal hysteresis even exists in temperature range \( T_{ms}/T_{af} \) to \( T_{CA} \) but we did not observed any trace of this hysteric region in our calorimetric and resistivity measurements.

Figure 1. The XRD Temperature variation of dc susceptibility at H=100 Oe and the inset shows the Differential Scanning Calorimetry (DSC) in heating and cooling run.

We have further measured the thermo-magnetization M(T) curves using field cooled cooling (FCC) and field cooled warming (FCW) protocols in the temperature range \( T=150-395 \) K under different applied fields (see the Fig.2). It can be seen from the Fig.2 that the magnetization difference (\( \Delta M=M|_{T_{mf}}-M|_{T_{ms}} \)) between the austenite and martensite phases keeps on increasing with the increase of the magnetic field. Also the M(T) below \( T_{mf} \) remains nearly temperature independent for all the applied fields which signifies the low magnetic behaviour of this phase. It is also evident from the Fig.2 that the characteristic martensite transformation temperatures shift towards the lower temperatures side with the application of magnetic field. The change in \( T_{ms} \) with magnetic field \( H \), i.e., \( \frac{dT_{ms}}{dH} \) is found to be 0.28 K/kOe. This observed value of \( \frac{dT_{ms}}{dH} \) has good agreement with the one we obtained using the Clausius-Clapeyaron (C.C) equation 2. If we consider the FCC M(T) curve for \( H=70 \) kOe then the \( \Delta M \) comes out to be 55 emu/g and from our DSC measurement we found the \( \Delta S_{tr} \) is 17.7 J/kg-K.

\[ \frac{dT_{ms}}{dH} = -\frac{\Delta M}{\Delta S_{tr}} \quad \ldots \ldots \quad (2) \]
Therefore, if we use these values in C.C equation, \( \frac{dT_{ms}}{dT} \) comes out to be 0.31 K/kOe which is very close to that obtained from direct determination of T_{ms} shift. The shift in T_{ms} is easy to understand by considering the change in the free energy during the MT. We know that the reverse martensitic transformation (RMT) is motivated by the chemical free energy difference between the martensite and austenite phases and the elastic energy stored in the martensite phase. Therefore, one can express the Gibbs free energy difference between the martensite and austenite phases during the RMT (martensite to austenite transformation) as

\[
\Delta G^{M\rightarrow A} = \Delta G^{ch}_{M\rightarrow A} + \Delta G^{el}_{M\rightarrow A} + \Delta E_{irr}^{M\rightarrow A} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (3)
\]

where \( \Delta G^{M\rightarrow A} \) represent the total Gibbs free energy difference between the two phases and it should be \(< 0\) to trigger the RMT [14, 15]. While \( \Delta G^{ch}_{M\rightarrow A} \) represent the chemical free energy difference, \( \Delta G^{el}_{M\rightarrow A} \) is the elastic energy stored in the martensite phase and \( \Delta E_{irr}^{M\rightarrow A} \) is the dissipation energy generated by defects in the system. Now when we apply a magnetic field, an additional and magnetic contribution to the free energy comes into play a crucial role in the total Gibbs free energy equation. Then the modified Gibbs free energy difference can be rewritten as follows [16]

\[
\Delta G^{M\rightarrow A} = \Delta G^{ch}_{M\rightarrow A} + \Delta G^{el}_{M\rightarrow A} + \Delta E_{irr}^{M\rightarrow A} + \Delta G_{mag}^{M\rightarrow A} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (4)
\]

where \( \Delta G_{mag}^{M\rightarrow A} \) is the Zeeman energy difference between the martensite and austenite phases and can written as

\[
\Delta G_{mag}^{M\rightarrow A} = -HM_{S}^{A} - (-HM_{S}^{M}) = H(M_{S}^{M} - M_{S}^{A}) \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (5)
\]

**Figure 2.** Temperature variation of magnetization under different applied fields and inset shows the variation of ΔT with applied field.

Here \( M_{S}^{A} \) and \( M_{S}^{M} \) are the saturation magnetizations of the austenite and martensite phases, respectively. In our studied compound the martensite phase is weak-magnetic, and the austenite is a strong FM (\( M_{S}^{A} \) > \( M_{S}^{M} \)), which results in \( \Delta G_{mag}^{M\rightarrow A} < 0 \). Therefore, the magnetic field favours the RMT, leading to a decrease in transformation temperatures. Using the same ideas one can also explain the increase of the thermal hysteresis width (ΔT) across the MT with measuring H (see the inset of Fig.2). For a given M(T) curve (say H=70 kOe), the ΔM is little higher for FMT (austenite to martensite) than that for RMT. Therefore, the shifts of T_{ms} and T_{mf} to the lower temperature side are larger than the shifts of T_{as} and T_{af} which eventually leads to the increase in ΔT with magnetic fields. Similar hysteresis loops were obtained at 50 K and 100 K.

To find out the effect of magnetic fields on the ΔSM we have conducted the isothermal M-H measurements in the temperature range of T=220-275 K. up to a magnetic field of H= 90 kOe.
From the M-H curves we have calculated the magnetic field induced $\Delta S_M$ using the following equation:

$$\Delta S_M(T_{av})_{\Delta H} = \frac{\Delta H}{2\Delta T} (\Delta M_1 + 2 \sum_{k=1}^{n-1} \Delta M_k + \Delta M_n) \cdots \cdots \cdots \cdots \cdots \cdots \cdots (6)$$

where $T_{av}$ and $\Delta T$ represents the average temperature and temperature difference between two ZFC M-H curves, respectively. $\Delta H$ is the changing step in the applied field and $\Delta M_k$ is the difference in magnetization at the field $k\times H$ between two isothermal curves, where $k$ is the step number of applied field, $k=1$ and $k = n$ are the step correspond to $H=0$ and the last step of maximum field, respectively. $\Delta S_M$ versus $H$ at several temperatures is shown in Fig.3. From the Fig.3 we can see that when the system is far below of its MT region i.e. below 240 K, only a small part of martensite phase is transformed into the austenite by the available magnetic field and thus the induced $\Delta S_M$ remains low and unsaturated. In this region even a magnetic field as large as 90 kOe is not enough to produce a complete field induced martensite to austenite transformation. Now as we move towards the MT region, more fractions of the martensite phase is now start to convert into the austenite phase by the available field and $\Delta S_M(H)$ starts to increase up to $T=250$ K. Whereas for the temperatures just below of martensite temperature $T_M = \frac{1}{2}(T_{ms} + T_{af})$, a field of a lower values than $H=90$ kOe is sufficient to produce saturated $\Delta S_M$. With the increase of temperatures, the austenite phase fraction increases and $\Delta S_M$ starts to the decrease again due to the decrease of the induced austenite phase fraction. So, one can conclude from Fig.3 that the induced $\Delta S_M$ is proportional to the induced austenite phase fraction.

**Figure 3.** Magnetic field variation of Isothermal $\Delta S_M$.

Apart from the magnetic entropy change $\Delta S_M$, the relative cooling power (RCP) of a magnetic material is another important parameter as it measure the efficiency of the material to be used as a refrigerant in magnetic refrigerator. The RCP is defined as: $\text{RCP} = \Delta S_M(\text{max}) \times \delta T_{\text{FWHM}}$, where $\delta T_{\text{FWHM}}$ is the full-width-at-half-maximum of the $\Delta S_M(T)$ curve. There are several approaches to determine RCP, though all of them target the range of working temperature [17]. Therefore there is further need to correlate MT with $\Delta S_M$ as well as with the working temperature range. Amorphous materials with second order transition favour large RCP and low magnetic entropy change opposite to the crystalline materials with first order transition [18]. The key concern is to develop magnetic refrigerant with high magnetic entropy change without compromising the working temperature range. Since this system shows two different types of transition i.e., MT (at
and magnetic transition (at \( T_{CA} \)), it can show both the inverse and conventional MCE. Both, the conventional magnetocaloric effect (negative \( \Delta S_M \)) and the inverse magnetocaloric effect (positive \( \Delta S_M \)) can be used in the refrigeration cycling.

Figure 4. Temperature variation of \( \Delta S_M \) at different applied field and inset shows the field variation of \( \Delta S_M \) and the RCP.

To quantify the \( \Delta S_M(T)H \) and the RCP of our material we obtained a series of magnetization isotherms \( M-H \) in the temperature range of 220-360 K with an interval of 3K and calculated the \( \Delta S_M \) using the Maxwell relation. The temperature dependence of \( \Delta S_M \) for this compound up to \( H=5T \) are presented in Fig.4. With a magnetic field change of 50 kOe, a positive \( \Delta S_M \) with a maximum value of 20 J/kg K and a negative \( \Delta S_M \) with a maximum value of -4.4 J/kg-K are observed around the \( T_M \) and \( T_{CA} \), respectively. The positive and negative values of \( \Delta S_M(T)H \) indicate the existence of inverse and direct MCE in this system. Plots of the magnetic field dependence of \( \Delta S_M(T)H \) across the \( T_M \) and \( T_{CA} \) and also the RCP across the MT are shown in the inset of Fig.4. A strong field dependence of both the \( \Delta S_M \) and RCP across the MT is observed. We have obtained a RCP value of 215 J/kg across the MT for the field change of 50 kOe which is comparatively very high considering Ni-Mn based systems. Moreover, in contrary to what was expected in this kind of material, the temperature of the negative peak shifts towards higher temperatures than \( T_{CA} \). The \( \Delta S_M \) has the characteristic shape of a first and second-order phase transitions both expanded over a large temperature range.

Conclusions:
In summary, the magneto-structural martensite transitions and magnetic entropy change of Mn-rich Ni_{44}Cu_{2}Mn_{43}In_{11} were studied. A strong field dependence of \( \Delta S_M \) and RCP across the MT is observed. From the field induced behaviour of \( \Delta S_M \) it is evident that the magnetic field induced austenites phase contributing more in the total \( \Delta S_M \). The observed large RCP in this system can be useful for practical applications as magnetic refrigerant material.

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