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Large Magneto-Caloric Effect in Ni-Co-Mn-In systems at room temperature

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Abstract

Magneto-Caloric properties were studied both in Ni-Co-Mn-In alloys and single crystals. A large inverse Magneto-Caloric Effect at room temperature was observed in a $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal. A large magnetic entropy change is found in such Ni-Co-Mn-In single crystal ($\Delta S_m = 30 \text{ J/KgK}$) at 355 K and under a magnetic field of 7 T during the first order magneto-structural transition. The net refrigerant capacity obtained higher than $270 \pm 25 \text{ J/Kg}$ for 7T is very encouraging for magnetic refrigeration applications.

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Keywords : Magnetocaloric effect, Martensitic transformation, Heusler single crystal

1. Introduction

Magnetic refrigeration has been seriously investigated since several years, particularly due to numerous advantages compared to gas refrigeration systems [1]. The magnetic refrigeration is based on the MagnetoCaloric Effect (MCE) that results from the application or removal of a magnetic field to a magnetic material. Such MCE is characterized by the coupled variations of two quantities: the isothermal entropy change ΔS and the adiabatic temperature change ΔT_{ad} . MagnetoCaloric efficiency has been demonstrated in various material systems [2-8].

Heusler alloy systems such as Ni-Mn-Ga and Ni-Mn-X (X=In, Sn and Sb) [9,10] are of great interest due to large magnetic field-induced strains correlated with other interesting effects, like the existence of a large inverse MCE [7,11-13]. Among Heusler Ni-Mn-X (X=In, Sn and Sb) alloy systems, Ni-Co-Mn-In is extensively studied because of the first-order magnetic transition from ferromagnetism to AntiFerromagnetism (AF) or non magnetism, during the Martensite-Austenite (M-A) transformation. This suggests the potential of Ni-Co-Mn-In alloys as

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MagnetoCaloric (MC) materials [14]. The entropy change (ΔS) of this Heusler system is comparable to those of the $Gd_5Si_2Ge_2$ [2], $MnAsSb$ [3] and $La(Fe,Si)_{13}$ [5] alloys, known as potential MC materials and currently investigated for magnetic refrigeration applications. In this study, we compare the results in entropy change (ΔS) and Refrigerant Capacity (RC) obtained in alloys and single crystals. The $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal shows a high entropy change ΔS above 300K over a large temperature range.

2. Experimental

$Ni_{45}Co_5Mn_{37.5}In_{12.5}$ alloy was prepared by induction melting. Samples were cut from the quenched alloy for characterization and single crystals were grown from the rest of the alloy with success using the Bridgman technique. For the alloy and the single crystal, a composition of $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ was determined by Energy Dispersive X-ray spectroscopy.

Hard X-ray diffraction studies at a temperature $T = 423$ K (austenite state) have shown that the as-grown crystal is of good quality with a mosaic distribution close to 15 arc minutes. In addition, no strong variation in the mosaic distribution of the sample has been observed when applying several thermal cyclings between 300 K and 423 K.

Magnetization versus temperature (300K-550K) and magnetization loop (0-7T) measurements were performed using an extraction type magnetometer.

Electrical resistivity properties were measured with the four probes method. The sample was cut to $3 \times 2 \times 0.5$ mm³ dimension. The current injected for the measurement was 50 mA and the distance between voltage taps was 1 mm. Samples were inserted in a cryostat working at regulated temperatures between 77K and 500K.

3. Results and discussion

Figure 1 shows the electrical resistivity versus temperature curve between 290 K and 400K for $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal. The Martensitic-Austenitic (M-A) and A-M temperature transformation occur at a temperature $T_{M-A} = (As + Af)/2 = 362$ K for heating variation and $T_{A-M} = (Ms + Mf)/2 = 351$ K for cooling variation. Ms, Mf, As and Af correspond respectively to Martensitic start, Martensitic finish, Austenitic start and Austenitic finish. The transition width is of about 15 K. In inset is represented the resistivity versus temperature for the alloy with the same composition. It can be noticed that the resistivity of the austenitic and the martensitic phases of the alloy are higher than those of the single crystal. The alloy grain boundaries contribute for a large part to the resistivity increase.

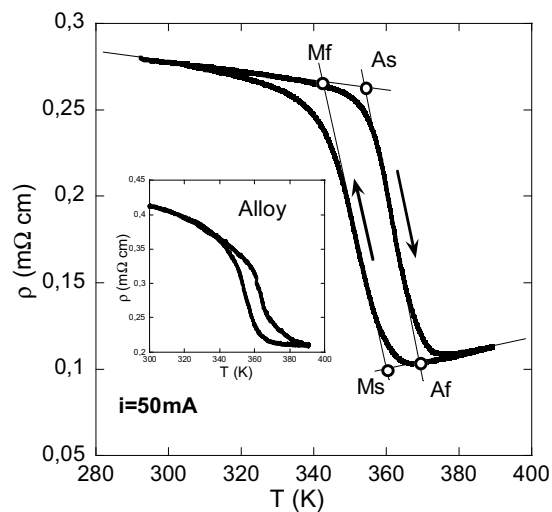


Fig. 1: Resistivity versus temperature curve for the $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal for heating and cooling variations. In inset, is shown the variations for $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ alloy.

Thermomagnetization curves for $H=200\text{mT}$ and 7T are shown on figure 2a. The Curie temperature was determined as $T_c=411\text{ K}$ by the derivative method. From the measurement at 0.2T , the transformation temperatures M_s , M_f , A_s and A_f , determined by the tangent method, are respectively 378K , 358 K , 368 K and 383 K . Such values confirm the M-A temperature transformation determined by electrical measurements. In figure 2a, only the heating variations are shown for single crystal and alloy. Although the transformation temperature is the same for single crystal and alloy, the magnetization difference of the austenitic and martensitic phases changes from the alloy to the single crystal. At 7T , the magnetization of $85\text{ Am}^2/\text{kg}$ for the parent phase of the single crystal decreases strongly down to $5\text{ Am}^2/\text{kg}$ when transforming into the martensite phase. This magnetization jump (ΔM) behavior is interesting for MC properties. The high ΔM between both phases is due to the good composition homogeneity and the low structural defect concentration in the single crystal. Indeed the slow cooling rate applied during the crystal growth ensures a homogeneous occupancy of Mn sites with respect to the crystallographic cell structure, i.e. with respect to the Mn sub-lattice responsible for the AF exchanges [15]. In Mn based Heusler alloys, magnetic moments is concentrated at the Mn atoms and the magnetic interaction strongly depends of the Mn atomic distance. Consequently, the strength of the magnetic interaction is disturbed by the change in the Mn-Mn distance particularly when structural disorder exists at the lattice scale. Thus, magnetic properties in austenite and martensite phases lead to a maximum in ΔM . In opposition, because of rapid cooling rate during alloy preparation, the amount of structural defects is higher in alloys. As a result, high values of ΔM cannot be reached easily even after annealing at high temperature for polycrystalline samples.

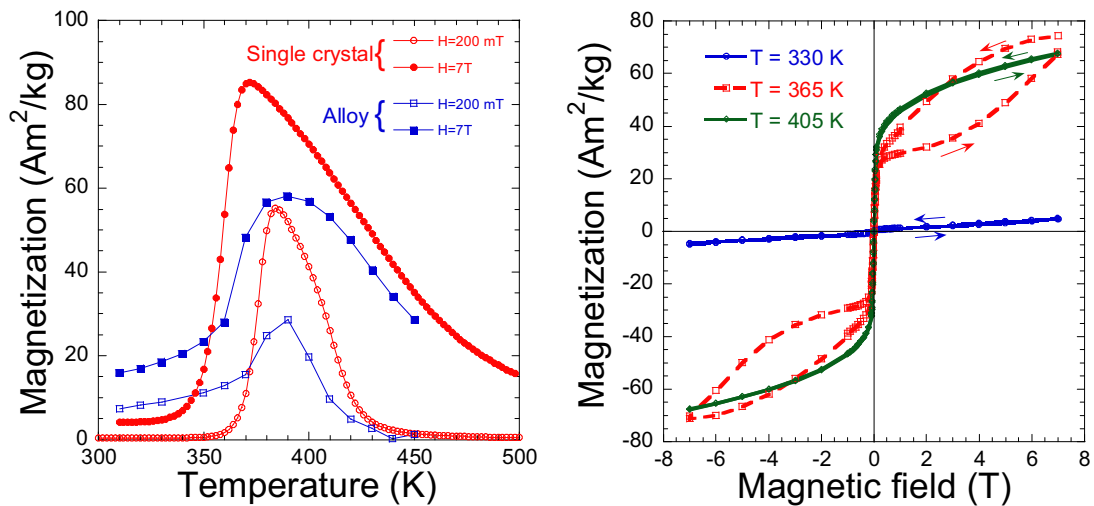


Fig. 2: a) Temperature dependence of magnetization at $H=0.2\text{T}$ and $H=7\text{T}$ for $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal (in red) and alloy (in blue). b) Isothermal magnetization loops for $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal for selected temperature values.

Figure 2b shows the $M(H)$ curves for the single crystal for different temperatures when heating the sample from 330K up to 405K with maximum magnetic field of 7T . Isothermal $M(H)$ measurements were performed by varying H from 0 to 7T , then from 7T to -7T and finally from -7T to 7T . The large hysteresis is due to the first order M-A transition and is typically observed in other magnetic systems [17,18].

It can be seen that the curves for 330 K (in the martensite phase), and 405 K (in the austenite phase) exhibit respectively weak magnetic and ferromagnetic behaviors. However the hysteresis observed for 365 K is due to the transfer from the martensite phase to the austenite phase by applying the magnetic field. Such a behavior corresponds to a metamagnetic shape memory effect in the case of Ni-Co-Mn-In Heusler alloys [10,19] and is comparable to the metamagnetic transition in MnAs and FeSiLa [20] for which very interesting magnetocaloric properties have been reported.

The entropy variation has been determined from the magnetization curves using the Maxwell relationship, as

$$\Delta S(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

The entropy versus temperature for single crystal and alloy for $H_{\max} = 2T, 5T$ and $7T$ are shown on figure 3a. It should be noted the high value of 30 J/KgK obtained for 355 K at $7T$ in the single crystal compared to 10 J/KgK for the alloy at the same temperature and magnetic field (see figure 3b). The values determined for the single crystal are comparable to those reported by different groups working on Ni-Mn-X ($X=\text{In, Sn, Sb}$) and Ni-Co-Mn-In systems [7,11-13,20-23], but it should be noticed that such magnetocaloric performance occurs at a temperature above 300 K which is very interesting for several cooling applications.

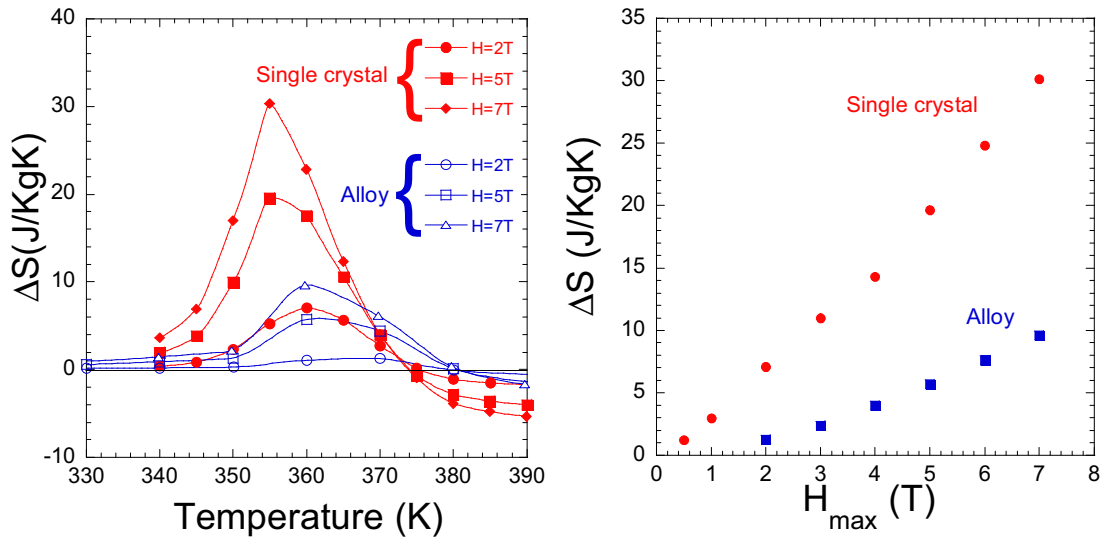


Fig. 3: a) Temperature dependence of the entropy variation ΔS for selected values of applied magnetic field for $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal (in red) and alloy (in blue). ΔS has been determined using the Maxwell relation.

b) Entropy variation ΔS versus maximum magnetic field applied to the $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal (in red) and alloy (in blue).

The Refrigerant Capacity (RC) provides an estimation of the heat transfer in an ideal refrigeration cycle [26,27]. It depends of the ΔS versus T curve and is defined as

$$RC = \int_{T_1}^{T_2} (\Delta S(T))_{\Delta H} dT \quad (2)$$

where T_1 and T_2 correspond respectively to the cold and hot temperatures during the cycle. From the data presented in figure 4, the calculation leads to a RC of 324 J/Kg at an applied magnetic field of 7 T . According to the different accuracy estimations, the RC is calculated with an accuracy of $\pm 9 \%$. The net RC obtained by subtracting the average hysteretic losses (54 J/Kg from the $M(H)$ cycles) leads to $270 \pm 25 \text{ J/Kg}$ at $7T$. Such values presented here for the single crystal are the highest values ever observed in Heusler compounds [11,28] and they are slightly lower than those obtained for the best MC systems [8,29-31].

4. Conclusions

Large entropy change ΔS has been obtained in $\text{Ni}_{45}\text{Co}_5\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal for Heusler systems in a large temperature window above 300K. Compared to alloys for which magnetization difference of the martensitic and austenitic phases is lower, the Mn atomic distance homogeneity of the single crystal enhances the AF exchange in the martensitic phase and induces a large magnetization difference between austenitic and martensitic phases. For the single crystal, the high net refrigerant capacity estimated taking into account hysteretic losses is about 270 ± 25 J/Kg for 7T. Such value shows the high potentiality of Heusler system as MC materials for temperature window above 300K.

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