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Abstract
Depending on the starting equilibrium temperature, the application of a magnetic field on a sample of Ni–Mn–Sn produces sample heating or cooling during adiabatic experiments. The competition between endothermal and exothermal effects is observed close to the martensite-to-austenite magnetostructural phase transition. A model assuming the coexistence of two phases and a field dependence of their volume allows to compute the evolution of entropy and heat capacity during the phase transition. The correct fitting of the results suggests that the field-induced reduction of the martensite-to-austenite transition temperature is responsible for the observed sign switching of the magnetocaloric effect.

Keywords
entropy, magnetocaloric effects, manganese alloys, martensitic transformations, nickel alloys, solid-state phase transformations, tin alloys

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Field-driven structural phase transition and sign-switching magnetocaloric effect in Ni–Mn–Sn

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Depending on the starting equilibrium temperature, the application of a magnetic field on a sample of Ni–Mn–Sn produces sample heating or cooling during adiabatic experiments. The competition between endothermal and exothermal effects is observed close to the martensite-to-austenite magnetostructural phase transition. A model assuming the coexistence of two phases and a field dependence of their volume allows to compute the evolution of entropy and heat capacity during the phase transition. The correct fitting of the results suggests that the field-induced reduction of the martensite-to-austenite transition temperature is responsible for the observed sign switching of the magnetocaloric effect. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2790829]

The recent discovery of materials presenting a giant magnetocaloric effect (MCE) at room temperature has increased the chances for applications of high efficiency solid-state cooling based on adiabatic demagnetization. While the MCE is generally associated with exothermal effects upon the application of field, materials presenting an endothermal response (inverse MCE) have been recently discovered.[1–3] The comprehension of this effect requires a deeper understanding of the thermodynamics associated with the MCE. Large MCE values are found in materials undergoing a first order structural transition in conjunction with a second order magnetic transition.[4–6] MCE is particularly high in materials containing rare earth elements but it was also observed in the Ni–Mn–As, Ni–Mn–Ga Heusler alloys, as well, and in the Ni–Mn–Sn system, where inverse MCE features were reported.[2]

In this letter we observe and analyze the unusual behavior of Ni–Mn–Sn which presents both positive and negative MCE features during adiabatic experiments. A simple modeling scheme shows that the peculiar MCE behavior is due to changes in the volume ratio of the structural phases induced by magnetic field. This influence corresponds to modifications of the phase transition temperature and the specific heat of the sample.

A 10 mm diameter by 20 mm tall arc-melt and chill-cast sample of nominal composition $Ni_{50}Mn_{37}Sn_{13}$ was obtained and divided in two parts. One half was used to study the microstructure and the other half was heat treated at 900 °C for 72 h and quenched in water for magnetic measurements and thermal analysis. The average composition, calculated from Energy Dispersive Spectroscopy spectra, was found to be $Ni_{48.3}Mn_{37.5}Sn_{14.2}$. Differential scanning calorimetry (DSC) performed at heating/cooling rates of 10 K/min in the absence of magnetic field show a clear structural phase transition from martensite to austenite (Fig. 1). Specific heat values $c_{p0} \approx 430$ J kg^{-1} K^{-1} in the martensite phase and $c_{p1} \approx 420$ J kg^{-1} K^{-1} in the austenite phase were determined. The temperature dependence of the magnetization was measured with a vibration sample magnetometer and an alternating gradient force magnetometer in the range from 150 to 520 K. (Fig. 1). A custom built cryomagnet insert was used to measure the adiabatic temperature change under an applied field ramp from 0 to 7 T. The sample temperature was stabilized at different values T_{start} before each measurement sequence, consisting in a linear increasing field ramp from 0 to 7 T followed by a decreasing linear ramp from 7 to 0 T at a rate of 1 T/min (Fig. 2).[6] DSC analysis on the $Ni_{48.3}Mn_{37.5}Sn_{14.2}$ system reveals (see Fig. 1) that in zero field martensite-to-austenite (M-A) transition start temperature is found at A_s=307 K, the peak at A_p=314 K while the transition finish is at A_f=317 K. A base line shift associated with a second order transition is observed in the cooling curve at the Curie point T_{CA}=314.7 K. In the heating curve the second order transition is superimposed to the endother-

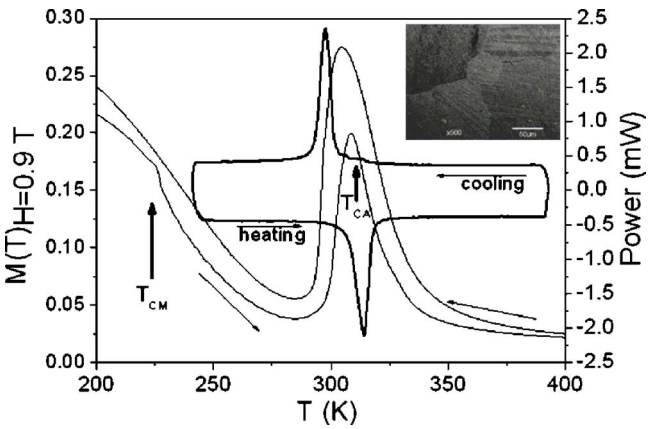

FIG. 1. Temperature dependence of the magnetization with applied field H=0.9 T after a zero field cooling (left y scale); T_{CM} is the Curie point in the martensite, and T_{CA} is the Curie point in the austenite. DSC curves at 10 K/min endothermic down (right y scale). Inset: Electron micrograph showing the polycrystalline nature of the Ni–Mn–Sn sample, grain size, and martensite twinning (lighter/darker bands).

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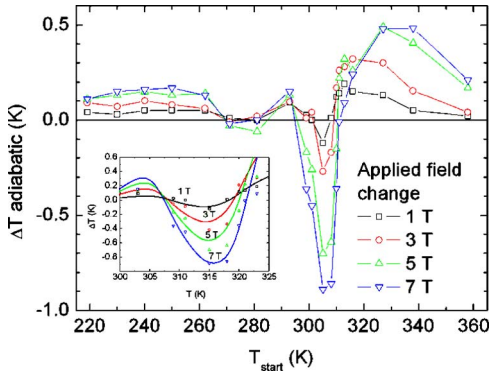

FIG. 2. (Color online) Adiabatic temperature changes measured upon the application of magnetic field up to 7 T starting from the equilibrium temperature T_{start}. Inset: A subset of the experimental data points is compared to analytical curves see Eqs. (2) and (3).

mic peak associated with the first order transition and showing the magnetostructural nature of the M-A phase transition at 314 K.

The observed temperature dependence of the magnetization $M(T)_H$ is consistent with the measured DSC curves and with the data reported in recent literature.[2,7] An evident $M(T)$ peak is found in close proximity with the M-A transition at T_{CA} (Fig. 1). The transformation from a martensite phase with a lower magnetization to an austenite phase with a higher magnetization is associated with the inverse MCE. During adiabatic tests, the occurrence of the inverse MCE was clearly identified as a temperature decrease during the application of an increasing magnetic field. The adiabatic temperature variation $\Delta T(T_{start})=T-T_{start}$ due to a magnetic field change $\Delta H \leqslant 7$ T presents a peak with an amplitude $\Delta T=-0.9$ K at $T_{start} \approx 305$ K, in correspondence with the M-A magnetostructural transition (Fig. 2). This behavior is compatible with recent results[2] obtained on a sample of the same composition and showing a sign reversal in the entropy change at the M-A transition temperature. Nonetheless a more detailed analysis of the $\Delta T(T_{start})$ curves in the temperature range between $T=308$ K and $T=312.9$ K reveals an unexpected change in the slope of the $\Delta T(H)_{T_{start}}=T(H)-T_{start}$ curves when plotted as a function of the increasing applied field H (Fig. 3 data points).

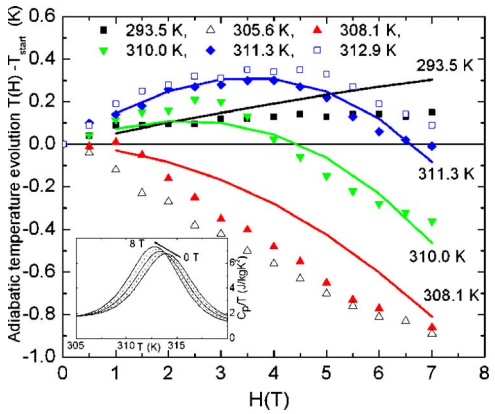

FIG. 3. (Color online) Field evolution of the adiabatic sample temperature $T(H)-T_{start}$ during a field ramp from 0 to 7 T at different starting temperatures T_{start} [points: experiment; lines: model of Eqs. (2) and (3)]. Inset: Field evolution of the c_p/T curves see Eqs. (2) and (3): $T_0=313.2$ K, $a=0.3$ K^{-1} $S_L=35$ J kg^{-1} K^{-1}, $c_{p0}=430$ J kg K^{-1}, $c_{p1}=420$ J kg K^{-1}, and $H=0,2,4,6,8$ T.

The temperature variations associated with the inverse MCE and the coexistence of endothermal and exothermal processes can be described using a model with two field dependent quantities and a fitting constant. The model assumes that magnetic field can influence the temperature evolution of the structural phase transition. During the martensite-to-austenite phase transition the volume ratio of the two phases at a certain temperature T can be modified by a magnetic field. We define $x(T)$ as the volume ratio of the sample occupied by the austenite phase, at temperature T, then $[(1)-x(T)]$ represents the volume fraction occupied by the martensite phase. At temperatures well below the M-A phase transition temperature $x=0$ whereas at temperatures in the fully transformed state $x=1$. It follows that the specific heat and the specific entropy at the phase transition can be defined as

$$\frac{c_p}{T}=\frac{c_{p0}}{T}+\frac{(c_{p1}-c_{p0})}{T}x(T)+s_L\frac{dx(T)}{dT},$$

$$s(T)=s_0+c_{p0}\ln(T)+(c_{p1}-c_{p0})\int\frac{1}{T}x(T)dT+s_Lx(T), \tag{1}$$

where $s_L=35$ J kg^{-1} K^{-1} and $s_Lx(T)$ is the increase of entropy connected to the first order phase transformation. c_p/T is defined as a mixture of the heat capacity of the two phases. In order to obtain a satisfactory fitting of the c_p/T curves obtained from DSC data at zero field (derived from Fig. 1) we assume that the volume fraction of the austenite phase increases for increasing values of T as

$$x(T)=\left(\frac{1}{2}\tanh[a(T-T_0)]+\frac{1}{2}\right), \tag{2}$$

where T_0 is the phase transition temperature and a is a fitting constant connected to the thermal span of the phase transition. The effect of magnetic field on the equilibrium between the structural phases is introduced as a shift in the temperature of the phase transition $T_0=313.2$ K. In the current martensite-to-austenite phase transition a positive shift of T_0 will correspond to a stabilization of the martensite phase whereas a negative shift of T_0 will correspond to an earlier growth of the austenite phase. A satisfactory fit of the experimental $\Delta T(H)_{T\text{start}}$ data points (see Fig. 3 lines with temperature values) is obtained introducing in Eq. (2) a field dependence for T_0:

$$T_0(\mu_0H)=T_0-[0.14(\mu_0H)]\text{ K}, \tag{3}$$

with a negative T_0 shift at a rate of −0.14 K/T. Magnetic field promotes the growth of the austenite phase with higher magnetization and entropy. In order to correctly reproduce the slope changes in ΔT associated with the coexistence of endothermic and exothermic effects, a quadratic field dependence of the parameter s_L is introduced in Eq. (1):

$$s_L(\mu_0H)=s_L+[0.04(\mu_0H)^2]\text{ J kg}^{-1}\text{ K}^{-1}, \tag{4}$$

see lines in Fig. 3. The inset of Fig. 3 shows c_p/T curves computed from Eq. (1): the field dependence of T_0 and s_L implies a linear shift toward lower temperatures and a quadratic increase of c_p/T.[8]

In this letter we have shown that, depending on the initial balance of the two available structural phases and asso-

ciated with temperature and thermal cycling history, positive, negative, or sign-switching MCE features can be observed in a polycrystalline sample of $Ni_{50}Mn_{37}Sn_{13}$. A simple modeling scheme shows that the observed field and temperature evolution of the adiabatic temperature change can be described by a field-induced shift of the structural phase transition temperature. The model results also indicate that the simple superposition of exothermal effects associated with the second order phase transition and endothermic effects associated with the first order one may be sufficient to produce the observed MCE behavior. Future work will be devoted to the direct measurement of heat capacity in the presence of field and to modeling of magnetostructural phase transitions in different systems. This will allow to establish and assess reliable experimental techniques for the characterization of MCE materials and to clarify the connection between isothermal entropy and adiabatic temperature changes estimated and measured using different experimental techniques.

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