Stress- and magnetic field-induced entropy changes in Fe-dope Ni–Mn–Ga shape-memory alloys

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Abstract

Isothermal stress- and magnetic field-induced entropy changes in a Fe-doped Ni–Mn–Ga alloy have been measured in the limits of low applied stress and magnetic field. We have obtained that in this limit while elastocaloric is conventional, giving rise to an increase of entropy when a stress is applied, magnetocaloric effect is inverse, which means that entropy decreases by application of an applied magnetic field. This inverse effect is a consequence of the magnetostructural coupling driven by the martensitic transition.

Ni–Mn–Ga close to the 2-1-1 stoichiometric composition is the archetypical Heusler alloy which shows a martensitic transformation with associated shape-memory properties.[1] The interest in this material arises from the fact that a large response to external stimuli is found in the vicinity of the transition. Actually, the coupling of magnetic and structural degrees of freedom enables a cross-variable response which means that both stress and magnetic field are effective in inducing the transition, giving rise to large deformations and changes of magnetization.[2] These changes provide additional fascinating properties to this class of materials such as elastocaloric[3] and magnetocaloric[4] properties, which are of interest for near-room-temperature refrigeration

applications.5 Therefore, understanding magnetostructural coupling is not only important at a fundamental level, but, indeed, has important technological implications.

In the present letter we compare isothermal stress- and magnetic field-induced changes of entropy in Fe-doped Ni–Mn–Ga which have been obtained from thermomechanical and calorimetric (under applied magnetic field) measurements. Ni–Mn–Ga alloys are brittle materials, but Feaddition enables improvement of its toughness withoutsacrificing its magnetic and thermoelastic properties.[6,7] Entropy changes provide relevant information on the magnetostructural coupling mechanism and enable us to quantify elastocaloric and magnetocaloric effects in the studied material.

A polycrystalline $Ni_{52.6}Mn_{21.9}Ga_{24.2}Fe_{1.3}$ ingot was obtained by arc melting pure metals under argon atmosphere. Slices cut from the ingot were encapsulated under vacuum in quartz glass and annealed at 1073 K for 72 h and quenched in ice water. The slices were then spark-machined into samples for thermomechanic and calorimetric measurements. The studied alloy undergoes a martensitic transition at M_s=327 K (in the absence of applied stress and magnetic Field). We checked the crystallographic structure by means of x-ray diffraction which revealed that the martensitic phase has a modulated (monoclinic) 14M structure.

Stress-induced entropy changes have been estimated from measurements of the elongation L of the sample during the temperature induced martensitic transition (L versus T) by keeping an applied uniaxial force F constant. For these experiments we used a standard flat specimen for tensile test experiments. The length of the sample gauge was l=5.90 mm and its cross-section ϕ =3.51 mm^2. Special grips were designed to adapt to the specimen. The upper grip was attached to a load cell and the lower grip

held a dead load (which enabled control of the applied force). Elongation was measured by a strain gauge attached to the sample. The setup was placed inside a cryofurnace in order to control temperature. In Fig. 1 we show examples of the measured *L* versus *T* curves during the forward martensitic transition on cooling at selected values of the force F corresponding to a stress σ=F/ ϕ (the cross-section ϕ is assumed constant). From these curves the isothermal stress-induced entropy change is obtained using the expression

$$\Delta S(T,\sigma) = \int_0^{\sigma} \left(\frac{\partial S}{\partial \sigma}\right)_T d\sigma = \int_0^{F=\sigma\phi} \left(\frac{\partial L}{\partial T}\right)_F dF, \qquad (1)$$

where the Maxwell relation

$$(\partial S/\partial \sigma)_T = V(\partial \varepsilon/\partial T)_\sigma = \phi(\partial L/\partial T)_F$$

(ε=L/l and V=ϕl is the guage volume) is taken into account. From data in Fig. 1, numerical computation of the above integral yields the stress-induced entropy changes[8] depicted in Fig. 2.We obtain that application of a stress induces an entropy reduction (conventional elastocaloric behavior). This is indeed the expected behavior consistent with the fact that the martensitic transition is shifted to a higher temperature by application of a stress (see inset of Fig. 1). The magnitude of the entropy reduction increases with the applied stress and, for a given stress, shows a maximum close to the temperature T_m of the inflection point of the *L* versus *T* curves.

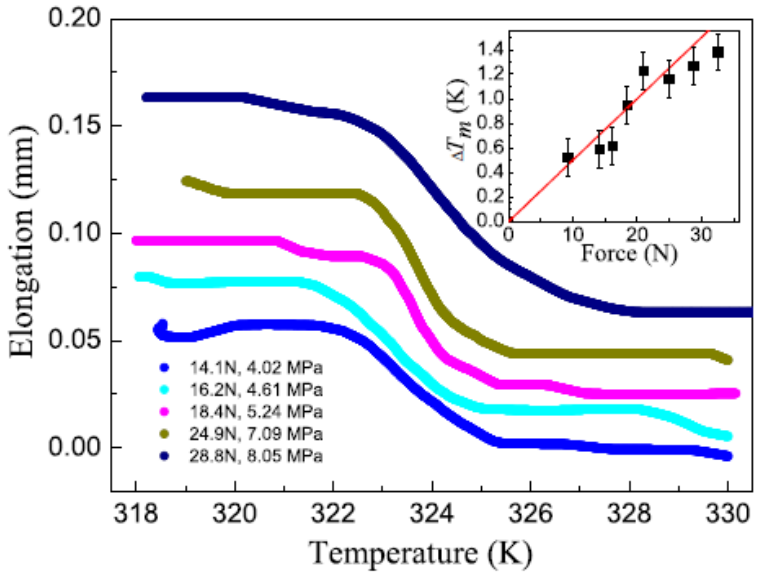

FIG. 1. (Color online) Elongation $L(T,\sigma)$ as a function of temperature in the region of the martensitic transition for selected values of the applied force. The inset shows the temperature change ΔT_m of the inflection point of the elongation curves as a function of the applied force.

Isothermal magnetic field-induced entropy changes were obtained from calorimetric measurements. We have used a specially designed differential scanning calorimeter that enables application of magnetic fields up to 1 T, while temperature is swept at rates of □0.5 K/min.[9] A small sample of mass m_c=0.125 g was used for these experiments. From the calorimetric curves the excess of entropy of the high-temperature phase was obtained as S(T,H)=$\int_{Ti}^{T}$(1/T)(dq/dT)dT, where dq/dT is the heat released per unit temperature and T is a temperature in the range between the start (M_s) and finish (M_f) of the martensitic transition and T_i is a temperature close to Mf. Entropy curves for selected values of the applied field are shown in Fig. 3. The isothermal magnetic field-induced entropy change is then computed as

$$\Delta S(T,H) = S(T,H) - S(T,H=0). \qquad (2)$$

The obtained entropy changes as a function of temperature for selected values of the magnetic field are given in Fig. 4. In this case application of a magnetic field induces an entropy increase corresponding to an inverse magnetocaloric effect.[4] Indeed this increase of entropy is consistent with the decrease of Tm (defined as the temperature of the calorimetric peak) with H (see inset of Fig. 3).

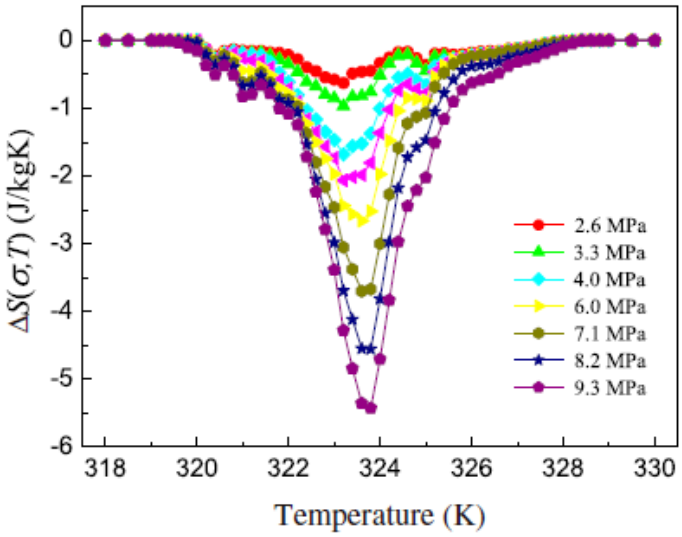

FIG. 2. (Color online) Stress-induced changes of entropy as a function of temperature for selected values of the applied force.

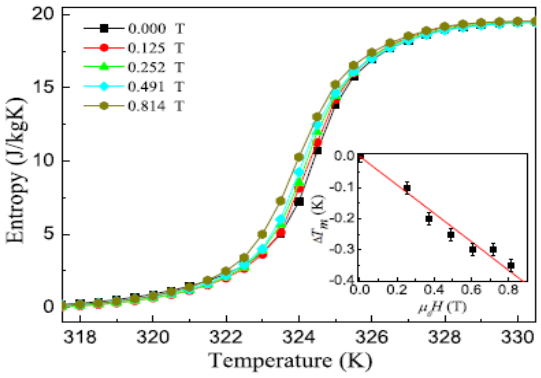

FIG. 3. (Color online) Entropy $S(T,\sigma)$ (referred to the entropy of the cubic phase) as a function of temperature in the region of the martensitic transition for selected values of the applied magnetic field. The inset shows the temperature change ΔT_m of the inflection point (calorimetric peak) as a function of the applied field.

The obtained elastocaloric and magnetocaloric effects in the studied Fe-doped Ni–Mn–Ga alloys have their origin in the large changes of L and magnetization M which simultaneously occur at the martensitic transition. They are, respectively, quantified by the derivatives $(\partial L/\partial T)_{F,H}$ and $(\partial M/\partial T)_{H,F.}$ Fig. 5 we show the peak values ΔS_{max} of the stress- and magnetic field-induced entropy change curves as a function of stress and magnetic field, respectively. In the studied range of applied generalized forces, both fields have the opposite effect on the corresponding induced entropy changes. A linear variation with rates $\Delta S_{Max}/\sigma \approx 4.4$ K/T L kg is found. The maximum available induced entropy change associated with the martensitic transition should correspond to ΔS_t(=19.5 J /K kg). Linear extrapolations of data in Fig. 5 indicate that in the case of the elastocaloric effect this maximum entropy content should be reached for stresses $\sigma \geq 39$ MPa, while in the case of the magnetocaloric effect a magnetic field $\mu_0 H \geq 4.4$ T should be required. In this last case, however, linear extrapolation is not expected to provide a good estimation since it is well known that for high enough fields dT_m/dH becomes positive for alloys of composition close to the composition of the present studied system.

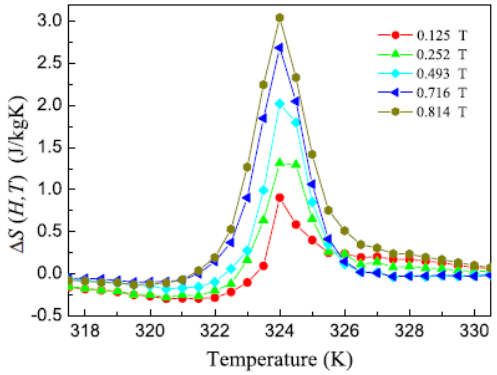

FIG. 4. (Color online) Magnetic field-induced changes of entropy as a function of temperature for selected values of the applied magnetic field.

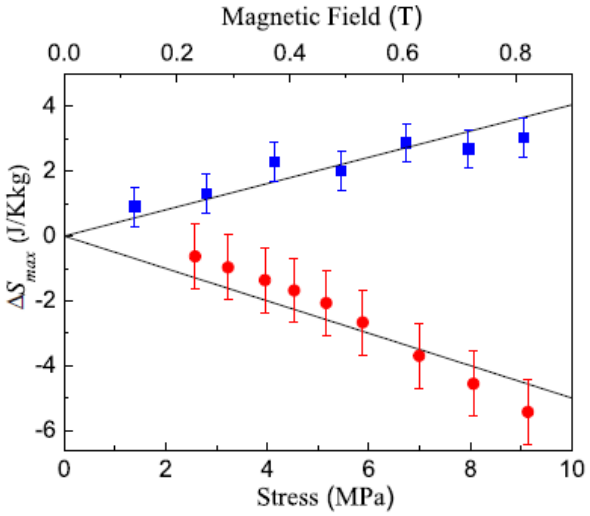

FIG. 5. (Color online) Peak values of the stress- and magnetic field-induced changes of entropy as a function of the applied stress and the applied magnetic field.

For an alloy $Ni_{46.2}Mn_{20.2}Ga_{25.0}Fe_{1.0}$, it has been reported[6] that for fields $\mu_0 H \geq 1.5$ T the transition temperature increases with the field at a rate $dT_m/d\mu_0 H$ 0.78 K/T. Therefore, the magnetic fieldinduced entropy change in this range of applied fields is expected to rise with increasing field. As in nearly stoichiometric Ni–Mn–Ga (Ref. 10) and Ni–Fe–Ga,[11] the inverse magnetocaloric effect observed in Fe-doped Ni–Mn–Ga for low applied fields is a consequence of an anomalous magnetization behavior due to the magnetostructural coupling. While in most systems undergoing magnetostructural transitions, the coupling between structure and magnetism arises from modifications of exchange interactions resulting from changes in lattice parameters,[12] in nearly stoichiometric Ni–Mn–Ga the coupling is, to a large extent, controlled by the symmetry induced change of magnetic anisotropy at the transition. This coupling is responsible for the magneticshape-memory effect displayed by these materials.[2] Systems showing 10M and 14M martensitic structure (as present Fedoped Ni–Mn–Ga), are almost

magnetically isotropic in the high temperature cubic phase and show large uniaxial anisotropy in the martensitic phase (with the easy axis along the short c-axis). This change of magnetic anisotropy gives rise to a reduction of the magnetization when the transition occurs at low applied fields. This reduction is responsible for the small decrease of transition temperature with magnetic field and thus for the inverse magnetocaloric effect, as obtained in the studied Fe-doped Ni–Mn–Ga alloy. A comparable small decrease of transition temperature at low applied magnetic fields was also reported in Ref. 13 for Ni–Mn–Ga transforming to a 14M structure.

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8. Entropy changes per unit mass are given using the mass of the sample gauge □V. A mass density □ =7.6 g/cm3 has been estimated.

9. The calorimeter used in the present study is a simplified version, adequate for near-room-temperature measurements, of the calorimeter described in J. Marcos, F. Casanova, X. Batlle, A. Labarta, A. Planes, and L. Mañosa, Rev. Sci. Instrum. 74, 4768 □2003□.

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