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Inconvenient magnetocaloric effect in ferromagnetic shape memory alloys

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ABSTRACT

Critical analysis available in the literature experimental results on magnetocaloric effect in ferromagnetic shape memory alloys Ni–Mn–X (X = Ga, In, Sn, Sb) is given. Based on a model developed by Pecharsky et al. [22], it is shown that the isothermal magnetic field-induced entropy change in the Ni–Mn–X alloys should not greatly exceed 30 J/kg K. Considering thermodynamics of temperature- and magnetic field-induced martensitic transformations, it is demonstrated that a contribution of the structural subsystem to the magnetocaloric effect in the Ni–Mn–X alloys studied so far is irreversible in magnetic fields below 5 T. This makes ferromagnetic shape memory alloys an inconvenient system for the practical application in modern magnetic refrigeration technology.

1. Introduction

Recently, a considerable interest has been paid to the magnetocaloric effect in ferromagnetic shape memory alloys (FSMAs) [1,2]. Particularly, a large isothermal magnetic field-induced entropy change ΔS_m comparable to or larger than in the giant magnetocaloric materials $Gd_5(Si_{1-x}Ge_x)$, $La(Fe_{1-x}Si_x)_{13}$, etc., has been reported for Heusler-based ferromagnetic shape memory alloys Ni–Mn–X (X = Ga, In, Sn, Sb) which undergo a first-order magnetostructural phase transition. It is worth noting that most of the papers deal with ΔS_m estimated from the Maxwell relation. Judging by the discrepancy of ΔS_m reported for the same composition [3,4], by the results of "direct" measurements [5,6] and theoretical studies [7–9], and by atypically large magnitude of ΔS_m in some compositions [4,10–13] the use of Maxwell relations alone can be in some cases inappropriate for a reliable estimation of the magnetic field-induced entropy change in the mixed-phase state of FSMAs.

Despite of the large magnetic field-induced entropy change, experimentally measured adiabatic temperature change ΔT_{ad} in the vicinity of the magnetostructural phase transition appeared to be rather small in FSMAs ($\Delta T_{ad} \sim 1-3$ K) [14–19]. This is practically the same as that near conventional second order magnetic phase transition [17,20,21] and is considerably smaller than that in Gd. Moreover, ΔT_{ad} appeared to be dependent on magnetic and thermal history of sample [18,21].

A model for description of the main features of the magnetocaloric effect in the vicinity of first order magnetic phase transitions was developed in Ref. [22]. Considering behavior of the total entropy S of a system in zero and non-zero magnetic field as a function of temperature and assuming that S does not depend on the magnetic field beyond the phase transition region, it was demonstrated that maximal value of the isothermal magnetic field-induced entropy change ΔS_m^{max} is determined by a total entropy change S upon the phase transition, $|\Delta S_m^{max}| \sim \Delta S$. In the framework of the model, the adiabatic temperature change ΔT_{ad} is related to the sensitivity of the phase transformation temperature to the external magnetic field, $\Delta T_{ad} \sim T_0' - T_0$, where T_0' and T_0 is the phase transition temperature in non-zero and zero magnetic field, respectively (see Fig. 1).

Using available in the literature experimental data, a critical discussion on isothermal magnetic field-induced entropy change and the adiabatic temperature change in ferromagnetic shape memory alloys is given. Using the model developed in Ref. [22], it shall be shown that the maximal value of $|\Delta S_m^{max}|$ in ferromagnetic shape memory alloys should not greatly exceed 30 J/kg K. Considering thermodynamic features of temperature- and magnetic field-induced martensitic transformation, it shall be demonstrated that in a modest magnetic field both the isothermal magnetic field-induced entropy change and the adiabatic temperature change should suffer from irreversibility which makes ferromagnetic shape memory alloys an inconvenient system for practical application in the magnetic refrigeration technology.

2. Isothermal magnetic entropy change

In ferromagnetic shape memory alloys, specifically in the Ni–Mn–Ga system, martensitic phase transformations occurring in ferromagnetic matrix are usually accompanied by a moderate

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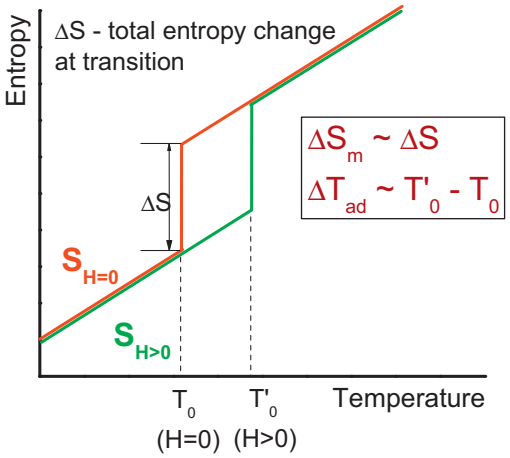

Fig. 1. Features of magnetocaloric effect at first order magnetic phase transitions [22].

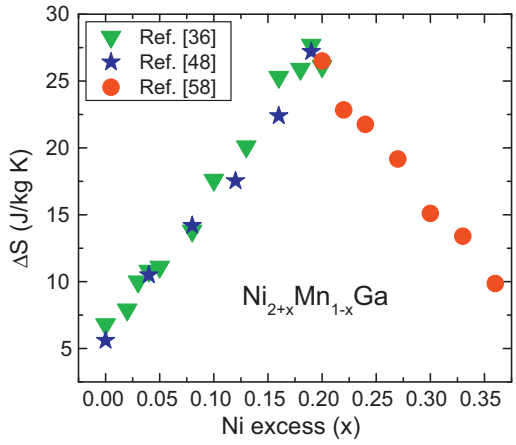

Fig. 3. Total entropy change ΔS in the $Ni_{2+x}Mn_{1-x}Ga$ alloys as a function of Ni excess x.

magnetic field-induced entropy change $|\Delta S_m| \sim 6-11$ J/kg K (for a magnetic field change $\mu_0(\Delta H) = 4-5$ T) [23–25]. A larger ΔS_m has been observed in the compositions for which the martensitic transformation is accompanied by a magnetic transition from ferromagnetic to paramagnetic state [26–30]. Moreover, as has been mentioned in Section 1, some compositions were reported to exhibit very large values of the isothermal magnetic field-induced entropy change which exceed those observed in so called giant magnetocaloric materials (Fig. 2) [31]. To shed a light on the reliability of these data, one has to recall that maximal value of the isothermal magnetic field-induced entropy change ΔS_m^{max} is directly related to the total entropy change ΔS upon martensitic phase transformation. Since martensitic transformations in ferromagnetic shape memory alloys are thermoelastic, ΔS can readily be determined from, e.g., results of differential scanning calorimetry (DSC) as $\Delta S = E/T_0$ where E is enthalpy of the transformation, T_0 is the thermodynamic equilibrium temperature determined as $T_0 = (M_s + A_f)/2$, where M_s and A_f is martensite start and austenite finish temperatures, respectively.

Shown in Fig. 3 is the total entropy change in $Ni_{2+x}Mn_{1-x}Ga$ as a function of Ni excess x, determined from DSC measurements [36,58]. In the stoichiometric Ni_2MnGa $\Delta S \approx 6.5$ J/kg K is rather small. Upon substitution of Mn for Ni, the total entropy change increases up to ≈27.6 J/kg K in a $Ni_{2.19}Mn_{0.81}Ga$ composition and then gradually decreases with further deviation from the stoichiometry. Since in $Ni_{2+x}Mn_{1-x}Ga$ ($x < 0.19$) the martensitic transformation temperature approaches the Curie temperature T_C^A, it has been suggested [36] that the enhancement of ΔS is due mainly to the contribution from magnetic subsystem. The reduction of ΔS observed in the compositions with $x > 0.20$ is presumably accounted for by the dilution of the magnetic subsystem and the rise of the thermodynamic equilibrium temperature T_0.

It is seen from Fig. 3 that the total entropy change in the $Ni_{2+x}Mn_{1-x}Ga$ ($0.18 \le x \le 0.27$) alloys undergoing first order magnetostructural phase transition does not exceed 28 J/kg K. This agrees with the results for related compositions, $Ni_{55.4}Mn_{20.0}Ga_{24.6}$ ($\Delta S \approx 23$ J/kg K) [10] and $Ni_{54.8}Mn_{20.3}Ga_{24.9}$ ($\Delta S \approx 22.3$ J/kg K) [37]. In Ga-deficit alloys, the total entropy change at the magnetostructural phase transition was reported to be ≈19.4 J/kg K in $Ni_{53.1}Mn_{26.6}Ga_{20.3}$ [38] and ≈16.6 J/kg K in $Ni_{50}Mn_{30}Ga_{20}$ [39]. Analysis of the available experimental data on ΔS in other ferromagnetic shape memory alloys [40–43] indicates that ΔS usually does not exceed 30 J/kg K.

Considering that $|\Delta S_m^{max}| \sim \Delta S$ [22,42], one should not expect to observe isothermal magnetic field-induced entropy change which is significantly larger than this value, i.e., for the Ni–Mn–X ferromagnetic shape memory alloys $|\Delta S_m^{max}|$ is limited by 30 J/kg K (Fig. 2). It should be realized that this estimation is valid for rather strong magnetic fields (typically above 5 T) which are sufficient to overcome temperature hysteresis of the martensitic transformation and completely convert structural state of the system.

In addition to the total entropy change, there are several processes which contribute to the isothermal entropy change of magnetically ordered substances. They are contributions from processes of domain wall displacements, magnetocrystalline anisotropy and paraprocesses [44]. However, it must be noted that in 3*d* transition alloys and compounds all these contributions are very small as compared even to the conventional magnetocaloric effect and can therefore be neglected. Besides these, one can count for a contribution from the dependence of the magnetic order parameter on the magnetic field which is the origin of conventional magnetocaloric effect in the vicinity of Curie temperature T_C. However, it is worth considering when the first order magnetostructural phase transition is located near (virtual) Curie temperature of either low- or high-temperature phase. Since in FSMAs the magnetostructural transition temperature T_{MS} usually coincides neither with Curie temperature of martensite T_C^M nor with Curie temperature of austenite T_C^A, the contribution from the conventional

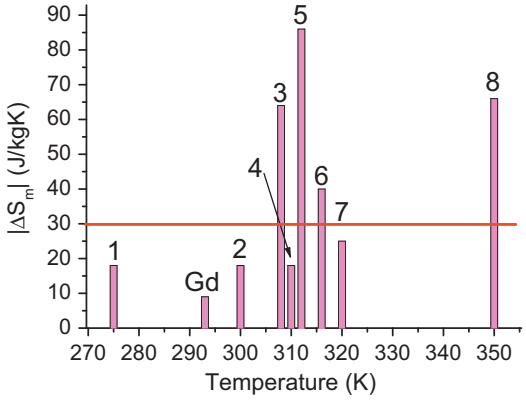

Fig. 2. Reported values of isothermal magnetic field-induced entropy change ΔS_m (for a magnetic field change $\mu_0(\Delta H) = 5$ T) in materials undergoing first order magnetic phase transitions: 1 – $Gd_5(Si_2Ge_2)$ [32], 2 – $Ni_{50}Mn_{37}Sn_{13}$ (at.%) [27], 3 – $Ni_2Mn_{0.75}Cu_{0.25}Ga$ [11], 4 – $MnFeP_{0.45}As_{0.55}$ [33], 5 – $Ni_{55.4}Mn_{20}Ga_{24.6}$ (at.%) [10], 6 – MnAs [34], 7 – $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ [35], 8 – $Ni_{2.19}Mn_{0.18}Ga$ [4]. ΔS_m in prototypical magnetocaloric material gadolinium (Gd) which undergoes a second order magnetic phase transition, is shown for the sake of comparison [31]. Horizontal line marks maximal value of the total entropy change at first order magnetic phase transitions in ferromagnetic shape memory alloys Ni–Mn–X (X = Ga, In, Sn, Sb).