Magnetocaloric effect in ferromagnetic Heusler shape-memory alloys

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Abstract. In this paper the magnetocaloric behaviour of Ni-Mn-based Heusler alloys is discussed in relation to their shape-memory and superelastic properties. We show that the magnetocaloric effect in these materials originates from two different contributions. The first, associated with the mechanism which makes feasible the magnetically induced rearrangement of martensite variants, controls the magnetocaloric effect at low applied fields, while the latter is dominant at higher fields and is essentially related to the possibility of magnetically inducing the martensitic transition. The occurrence of the inverse magnetocaloric effect associated with these two contributions is also considered.

1. Introduction
Ferromagnetic Heusler alloys undergoing a martensitic transition show giant magnetostriction, which is related to either a field-induced reorientation of martensitic twin-related variants (the magnetic shape-memory effect) or to magnetic superelasticity, which originates from the possibility of inducing the transition by means of a magnetic field. Prototypical examples of systems showing magnetic the shape-memory effect and magnetic superelasticity are Ni$_2$MnGa [1] and Mn-rich Ni$_2$Mn$_{1.4}$In$_{0.6}$ [2] respectively. Associated with the martensitic transition, these materials also display interesting magnetocaloric effects which are related to the thermal response to magnetization changes. These changes are commonly induced by the application or removal of an externally applied magnetic field and the magnetocaloric effect is measured as a temperature change when the field is applied adiabatically or as an entropy change when it is applied isothermally [3].

In the present paper we will discuss the magnetocaloric properties exhibited by Heusler alloys of the Ni-Mn-based family. These materials display either conventional or inverse magnetocaloric effect depending on specific composition and, in some cases, on the strength of the applied field. We will show that this behaviour is a direct consequence of the coupling between magnetic and structural degrees of freedom.
2. General features and results

In what follows the magnetocaloric effect will be quantified by means of the isothermal entropy change which results from the application of a magnetic field $H$. It can be expressed as,

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

(1)

where the Maxwell relation $(\partial S/\partial H)_T = (\partial M/\partial T)_H$ has been used. Therefore, $\Delta S(T, H)$ can be obtained from magnetization measurements performed in a conveniently selected range of temperatures. Fig. 1 shows $M(H)$ isothermal curves for an almost stoichiometric Ni$_2$MnGa single crystal in a temperature range about the martensitic transition ($T_M \approx 180K$).

![Figure 1. $M(H)$ curves at temperatures in the range of the martensitic transition (from 160 K to 190 K). $H$ is applied along the [001] direction.](image1)

![Figure 2. Field-induced entropy change as a function of temperature at selected values of the maximum applied field along the [001] direction.](image2)

From the magnetization data in Fig. 1 the field-induced entropy change is obtained as a function of temperature and selected values of $H$ by using eq. (1). The derivative and integral involved in the calculations were performed numerically. Results are shown in Fig. 2. Interestingly, the $\Delta S(H, T)$ curves show peaks that arise from discontinuities in the transformation path. These discontinuities are characteristic of martensitic transitions in shape-memory alloys [4, 5]. In order to compare the magnetocaloric effect in different Heusler systems, it is convenient to calculate an average field-induced entropy change over the transition range $\Delta T$, for each $H$. This expression is obtained as,

$$\langle \Delta S(H) \rangle = \frac{1}{\Delta T} \int_{\Delta T} \Delta S(T, H) dT.$$

(2)

In Fig. 3 we show this average field-induced entropy change for five alloys of compositions close to the Ni$_2$+xMn$_{1-x}$Ga line. Along this line, with increasing $x$, $T_M$ increases and approaches the Curie temperature $T_c$ (for $x \approx 0.2$, $T_M \approx T_c$). Except for alloy with $T_M \approx T_c$ (alloy 5), the entropy change first increases with $H$, reaches a positive maximum, and decreases linearly for high fields. In particular, the initial increase of $\langle \Delta S \rangle$ is rather large for alloys 1 and 2 with composition closer to the 2-1-1 stoichiometry. It has been shown that this increase is related to the decrease of $\Delta M(H)$ observed at low applied fields, which is a consequence of the magnetostructural interplay driven by the strong uniaxial magnetocrystalline anisotropy of the martensitic phase [6, 7]. At higher fields, $\langle \Delta S(H) \rangle$ decreases linearly with increasing field. In alloy 5 an almost linear decrease of $\langle \Delta S(H) \rangle$ is observed in the full range of the field. Actually,
the linear decrease is due to the fact that for this alloy family the magnetic moment of the martensite is larger than the magnetic moment of the high temperature cubic phase.

Besides Ni-Mn-Ga, martensitic transformations have been reported in other ferromagnetic Heusler alloys. Within the Ni-Mn-Z family, Ni-Mn-Sn and Ni-Mn-In display very interesting properties. These alloys undergo a martensitic transition in the composition region Ni\textsubscript{2+\epsilon}Mn\textsubscript{2-\epsilon}Z\textsubscript{\epsilon}, with \epsilon < 0.25 (Mn-rich region) far from stoichiometry. The interesting composition range is a narrow interval close to \epsilon/a \simeq 8 where, on cooling, these systems first become ferromagnetic and on further cooling undergo a martensitic transition [8]. For Ni\textsubscript{2}Mn\textsubscript{1.4}Sn\textsubscript{0.6} and Ni\textsubscript{2}Mn\textsubscript{1.44}In\textsubscript{0.56} an average field induced entropy change has been obtained following the same procedure as in the Ni-Mn-Ga family. Results are shown in Fig. 4. In these systems \langle \Delta S(H) \rangle linearly increases within the full range of the applied field. This inverse magnetoelastic effect is a consequence of the decrease of the magnetic moment which takes place at the magnetostructural transition. Interestingly, this mechanism enables the reverse martensitic transition to be induced by means of an applied field (the change of transition temperature with the applied magnetic field is particularly strong in the case of the Ni-Mn-In alloy). The drop in the magnetic moment has been shown to originate from the tendency of the excess Mn atoms (with respect to the 2-1-1 stoichiometry) to introduce antiferromagnetic exchange coupling caused by the change in the Mn-Mn distance as the martensitic phase gains stability. It is worth noting that a large drop of magnetic moment in Ni-Mn-In is basic feature that makes possible the magnetic superelastic behaviour displayed by this alloy [2]. In contrast, as the magnetic anisotropy is low in Ni-Mn-In and Ni-Mn-Sn, field-induced reorientation of martensitic variants is not operative in these systems [9].

Figure 3. (a) Averaged field-induced entropy change as a function of the applied field \textit{H} for alloys of compositions close to the Ni\textsubscript{2+\epsilon}Mn\textsubscript{1−\epsilon}Ga line. \epsilon increases from alloy 1 (\epsilon \simeq 0) to alloy 5. For alloy 5, \textit{T}_{M} \simeq \textit{T}_{c}. (b) Expanded view of the low-field region.

Figure 4. Average field-induced entropy change as a function of the field \textit{H} for Ni\textsubscript{2}Mn\textsubscript{1.4}Sn\textsubscript{0.6} (squares) and Ni\textsubscript{2}Mn\textsubscript{1.36}In\textsubscript{0.64} (circles).
3. Discussion and summary

Results presented in this paper show that the magnetocaloric effect associated with the martensitic transition in Ni-Mn based Heusler alloys is determined by two contributions. The former is an extrinsic contribution which is a consequence of the magnetostructural interplay at the length scale of martensitic variants driven by the magnetic anisotropy of the martensitic phase. The latter is intrinsic and is controlled by the change of magnetization taking place at the transition. In nearly stoichiometric Ni$_2$MnGa the first contribution is dominant, while it plays a minor role in Ni-Mn-Ga alloys undergoing the martensitic transition close to or above the Curie point. The extrinsic contribution is also irrelevant in Ni-Mn based alloys such as Ni-Mn-Sn and Ni-Mn-In. In these alloys, however, due to transition-induced antiferromagnetism, the magnetocaloric effect is inverse. Therefore, in these materials cooling occurs by adiabatic magnetization.

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