Tailoring magnetic and magnetocaloric properties of martensitic transitions in ferromagnetic Heusler alloys

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Ni$_{50}$Mn$_{34}$In$_{16}$ undergoes a martensitic transformation around 250 K and exhibits a field induced reverse martensitic transformation and substantial magnetocaloric effects. We substitute small amounts Ga for In, which are isoelectronic, to carry these technically important properties to close to room temperature by shifting the martensitic transformation temperature.

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There is growing interest in searching for materials other than Ni-Mn-Ga which may have interesting properties concerning applications relevant to magnetic-field-induced strains. Such search on Ni-Mn based Heusler systems has led to the observation of giant magnetocaloric effects (MCE) [1, 2, 3, 4, 5, 6], large strains related to field-induced transformations, and substantial contribution to the understanding of martensitic transformations in ferromagnetic Heusler materials. The valence electron concentration $(e/a)$ dependence of $M_s$ in NiMnX is linear, but with different slope for each X-species [7]. Therefore, it should be possible to manipulate $M_s$ not only by varying $e/a$, but also by holding $e/a$ constant and replacing one X species with another. In this manner one may have the possibility of shifting and adjusting favorable features occurring around the martensitic transformation of a particular alloy to higher or lower temperatures. Ni$_{50}$Mn$_{34}$In$_{16}$ ($(e/a) \approx 7.87$) shows a field induced reverse martensitic transformation at $M_s \approx 250$ K and associated with it, a large field induced strain and a magnetocaloric effect [8]. In view of technical interest, it would be desirable to shift the transition temperature to around room temperature without altering the favorable features. On the other hand, in view of understanding the electronic properties of such systems close to the martensitic transformation, it would be interesting to understand to what extent the valence electron concentration can be employed as a meaningful parameter. To test this possibility, we substitute 2% Ga for In in Ni$_{50}$Mn$_{34}$In$_{16}$. From interpolation at constant $(e/a)$, this amount of Ga is expected to shift $M_s$ to around room temperature. We compare in this study the magnetic and magnetocaloric properties of the isoelectronic compounds Ni$_{50}$Mn$_{34}$In$_{16}$ [8] and Ni$_{50}$Mn$_{34}$In$_{16}$Ga$_2$ an discuss to what extent the features around $M_s$ are preserved. The magnetocaloric properties are studied from the entropy-change as well as from direct temperature-change measurements.

The samples were prepared by arc melting pure metals under argon atmosphere. They were annealed at 1073 K for 2 hours and quenched in ice-water. The compositions of the alloys were determined by energy dispersive x-ray analysis.

Temperature dependent magnetization measurements $M(T)$ were carried out in 5 mT in the temperature range $4 < T < 400$ K, and magnetization isotherms $M(\mu_0 H)$ around the martensitic transformation were obtained in magnetic-fields up to 5 T using a superconducting quantum interference device magnetometer. The entropy change $\Delta S$ was obtained from the magnetization isotherms, and the direct temperature-change was measured with an adiabatic magneto-calorimeter.

Figures [a] and [b] show $M(T)$ in 5 mT taken on a zero-field-cooled (ZFC), field-cooled (FC), nd field-heated (FH) sequence for Ga0 and Ga2 respectively. The curves corresponding to the ZFC and FC states for both samples deviate below $T_C^{M}$, whereas no appreciable deviation is found below $T_C^{A}$. The deviation below $T_C^{M}$ is related to the anisotropy that develops in the non-cubic martensitic phase of the alloys, so that cooling in zero-field and cooling in finite field lead to different spin configurations with different $M(T)$. For Ga0, $T_C^{A} \approx 308$ K.
and this decreases to about 293 K for Ga2. On the other hand \( M_s \) increases from about 243 K for Ga0 to about 275 K for Ga2, but the fundamental features of the curve remain similar.

\[ M(T) \] has been also measured in several fields \( \mu_0 H \geq 1 \) T to compare the field rate of shift of \( M_s, dM_s/dH, \) of both samples. The results are shown in Fig. 2a. The heavy lines are drawn through the points joining the onset of decrease in \( M(T) \) with decreasing temperature. These mark \( M_s \) for each measuring field. The slope of these lines at these magnetic-field ranges give \( dM_s/dH \approx -6 \text{ KT}^{-1} \) and \( dM_s/dH \approx -2 \text{ KT}^{-1} \) for Ga0 and Ga2 respectively. \( M(T) \) curves in 5 T for the FC and FH states are shown in Fig. 2b. The thermal hysteresis for Ga2 narrows with respect to that of Ga0. Furthermore, it is also seen that the magnetization in the martensitic state decreases when Ga is added.

The magnetization isotherms in the vicinity of \( M_s \) in Figs. 3a and 3b show that the overall magnetization is lower in Ga2 than in Ga0. The data shown with open circles in both figures correspond to \( M(\mu_0 H) \) for \( T < M_s \) (values printed in italic), and the filled circles correspond to \( T > M_s \). The metamagnetic-like character of the feature in \( M(\mu_0 H) \) at temperatures \( T < M_s \) is associated with a field-induced reverse martensitic transformation. \( M(\mu_0 H) \) initially increases with increasing field with decreasing curvature, until it reaches an inflection point at a field corresponding to the onset of the field-induced transformation. Above this point, \( M(\mu_0 H) \) begins to increase faster with increasing magnetic-field. For Ga2, the field-induced transformation begins to take place at lower fields than those needed for Ga0, so that the steep rise in \( M(\mu_0 H) \) begins already below 1 T. The narrower hysteresis in \( M(T) \) for Ga2 compared to broader hysteresis for Ga0 is the cause for the lower threshold of the transformation in Ga0.

Using the data in Fig. 3 the field induced entropy change \( \Delta S \) is determined by integrating numerically \( \Delta S(T, H) = \mu_0 \int_0^H (\partial M/\partial T)_H dH. \) \( \Delta S(T, H) \) for Ga0 and Ga2 is shown in Figs. 1a and 1b. For both samples \( \Delta S(T, H) \) is positive below \( M_s \) (inverse MCE) and negative around \( T^3 \) (conventional MCE) with the crossover taking place at the temperature corresponding to \( M_s \) determined from Figs. 1a and 1b. The magnitude of the entropy change below \( M_s \) remain nearly unchanged for both samples, with a maximum value of 8 Jkg\(^{-1}\)K\(^{-1}\). Above \( M_s \), \( \Delta S \) of Ga0 reaches a slightly higher value than that of Ga2, both being about \(-5 \) Jkg\(^{-1}\)K\(^{-1}\) under 5 T. As expected, both samples cool on applying a magnetic-field below \( M_s \) and heat on applying a field around \( T_C \), as seen from the results of the direct magnetocaloric measurements in Figs. 3a and 3b for both samples. The maxima in \( \Delta T \) below \( M_s \) are nearly the same for both samples reaching a value of \(-2 \) K in 5 T. Around \( T^3 \), the maximum value is about 3.5 K for Ga0 and is slightly larger than 2 K for Ga2. This difference is consistent with the difference in \( \Delta S \) above \( M_s \).

Investigations on quaternary Heusler-based systems have been undertaken previously both to improve ma-
serve at a high temperature a favorable MCE property. We find indeed that at constant temperature change around 300-350 K in NiMn-based Heusler alloys. Nevertheless, the desired temperature is limited to a particular alloy can be brought to a desired temperature change around 300-350 K. Presently, this desired temperature is limited to about 100 K.

FIG. 5: Temperature dependence of the measured temperature change around $M_s$ and $T_C$ for a) Ga0 and b) Ga2.

Material properties and to examine the interplay between magnetic and structural properties around the martensitic transformation $T_C$. We provide in this study a method based on the varying $e/a$ dependence of $M_s$ for different group III-V elements, by which $M_s$ can be shifted so that favorable properties of a particular alloy can be brought to a desired temperature. Presently, this desired temperature is limited to below room temperature, since $T_C$ is limited to about 300-350 K in NiMn-based Heusler alloys. Nevertheless, we find indeed that at constant $e/a$, it is possible to preserve at a high temperature a favorable MCE property of Ni$_{50}$Mn$_{34}$In$_{16}$ occurring at a low temperature by substituting an element isoelectronic to In, namely Ga. The next step would be to devise a method to manipulate $T_C$, such as that involving the addition of small amounts of Co. Some work already gives evidence that replacing Ni with small amounts of Co tends to increase $T_C$.

We find in the present studies that the maximum absolute values of $\Delta S$ and $\Delta T$ on both sides of $M_s$ for Ga0 and Ga2 are nearly the same. $dM_s/dH$ is smaller for Ga2 than for Ga0 meaning that the MCE on Ga2 should be smaller. It appears that the narrower temperature hysteresis for Ga2 with respect to that of Ga0 facilitates the field induced reverse transformation. As discussed in previous studies, the narrow hysteresis is favorable for a large MCE, and much effort is invested in reducing hysteresis-losses. The reduced hysteresis in Ga2 compensates for its lower $dM_s/dH$ as compared to that of Ga0. As can be seen from the fast rise of the magnetization with increasing magnetic-field already in low-fields in Fig. 3 a lower threshold field for Ga2 is required than that for Ga0 to induce a transformation with an external field.

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