Large magnetic entropy change in a Heusler alloy Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ single crystal

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A large magnetic entropy change $|\Delta S|$ has been observed in Heusler alloy Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ single crystal near the martensitic structural transition temperature of 300 K with applied field along [001] direction. The obtained $|\Delta S|$ under an applied field of 5 T reaches 18.0 J/Kg K (corresponding 146 mJ/cm$^2$ K). A more important result is that $|\Delta S|$ can achieve constant increase of 4.0 J/Kg K for the field increase of every tesla. The very large magnetic entropy change is attributed to the abrupt change of magnetization when the first-order martensitic-austenitic structural transition takes place. The phenomena of the large magnetic entropy change and the easy adjustment of the martensitic-austenitic transition-temperature indicate that the non-rare-earth based Ni-Mn-Ga single-crystal materials may have potential applications as magnetic refrigerants.

Magnetic refrigeration has attracted much attention due to its superiority over the gas refrigeration on energy savings and environmental concerns. A study of magnetocaloric effect in various magnetic solids is gaining worldwide attention.1–16 Historically, many ferromagnets concerning second-order transition were investigated in an attempt to achieve large magnetocaloric effect (MCE), of which the rare-earth elemental Gd was considered to be the only useful material as room-temperature magnetic refrigerants for a long time owing to its large MCE near room temperature.15 Recently, the MCE involving a first-order phase transformation has attracted much investigation.6,8,17,18 Several systems undergoing a first-order magnetic transition have been found to show very large MCE.8 Usually, a first-order magnetic-phase transition concentrates magnetic entropy change to a narrower temperature range in comparison with that of a second-order magnetic-phase transformation. Gd$_x$(Si$_{1-x}$Ge$_x$)$_4$ ($x \approx 0.5$) alloys reported in literature [9,10] show giant magnetocaloric effects at a wide temperature range between ~50 and ~280 K and it has been confirmed that the nature of the phase transition, which is responsible for the large magnetocaloric effect, is a first-order transition from a monoclinic to an orthorhombic structure.15 In this paper, we report the investigation of magnetic entropy change in Heusler alloy Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ single crystal, which also involves a first-order transition.

Heusler alloys Ni-Mn-Ga have attracted considerable interests due to the observation of shape-memory effect and superelasticity in these materials.20–22 Recently, large field-induced-strains in single-crystal Ni-Mn-Ga alloys have also been observed near structural transition points.21,23 As well-known, ferromagnetic Heusler non-rare-earth based Ni-Mn-Ga alloys undergo a first-order structural transition from tetragonal martensite to cubic austenite on heating (or the reverse process on cooling), which brings about a fundamental difference in the magnetic behavior of the low-temperature martensitic and high-temperature austenitic state, causing an abrupt change of the magnetization. The simultaneous change of structure and magnetic properties at transition temperature should strongly influence the magnetic entropy change. We have observed a considerable magnetic entropy change $\Delta S$ in a sample of Ni$_{51.5}$Mn$_{22.7}$Ga$_{25.8}$ polycrystalline.14 The achieved $\Delta S$ is positive, which reaches 4.1 J/kg K under a low field of 0.9 T. Single crystal, compared with polycrystalline, can reduce the intergrain boundaries and defects to the lowest limit and show sharper change of magnetization at structural-transition point. From this viewpoint and considering the strong interest for room-temperature magnetic refrigerants, we chose Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ single crystal with a transition point at 300 K on heating, and found a very large magnetic entropy change $|\Delta S|$.

The composition of the material was modified from the stoichiometric Heusler alloy, Ni$_3$MnGa, in order to obtain a material with martensitic transformation temperature near room temperature. The starting material was prepared by arc melting appropriate amounts of Ni, Mn, and Ga with the purity better than 99.9% in a high-purity (99.999%) Ar atmosphere. The single crystals were grown at a rate of 18 mm/h by a Czochralski instrument24 with a Cu crucible system, which is cold by water.25 The Ar pressure during preparing the single crystals was about 1 atm with a base vacuum of about $5 \times 10^{-5}$ Pa. The single crystals were oriented by back-reflection Laue diffraction and cut into small cylinders for magnetic measurements by ac susceptibility and superconducting quantum interference device with field along [001] direction (c axis) of martensitic state. The composition of the present sample was checked as Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with error limit of ±0.1. The lattice parameter was determined as $a=b=5.923$ Å, $c=5.556$ Å (250 K), and $a=b=c=5.828$ Å (350 K) for martensitic and austenitic state, respectively, based on x-ray diffraction measurements. Shown in Fig. 1 is the temperature dependence of the ac susceptibility $\chi$, which exhibits very sharp changes at austenitic-martensitic and magnetic transition points. The transition from martensitic to austenitic phase on heating or the reverse process on cooling is indicated by the abrupt changes of $\chi$. At the Curie temperature $\chi$ sharply decrease. The marked $T_M$, $T_A$, $T_C$, and temperature hysteresis $\Delta T$ in Fig. 1 are 292 K, 297 K, 345 K, 6 K, respectively.
Shown in Fig. 2 is a series of isothermal $M$-$H$ curves measured at different temperatures with field along [001] direction of martensitic state. The method of setting temperature is of approaching the setting values by slow heating. The sweep rate of the field is slow enough to ensure the thermal equilibrium during the measurements. The isothermal $M$-$H$ curves from $T = 297$ K to 310 K manifest the whole transformation process. It is clear that at low temperature below the transition point, for example $T = 297$ K, the magnetization is hard to saturate, which is a character of the martensitic phase, while at high temperature above transition point, for example $T = 310$ K, the magnetization is easy to saturate, indicating the austenitic phase. The temperature range at which both martensitic and austenitic states coexist is from 299 to 305 K. The magnetic-hysteresis-loop measurements near the structural transition point indicate that the coercive field is less than 200 Oe and the ratio of the remnant to saturation magnetization is less than 7% for martensitic state, while for austenitic state the coercive field less than 20 Oe and the ratio of the remnant to saturation magnetization less than 1% were confirmed, which agrees well with the previous reports.\cite{26,27} Hence the $M$-$H$ curves can be considered roughly reversible at any temperature near the transition point.

The crossing point for the $M$-$H$ curves of martensite at 297 K and austenite at 310 K is about at 0.23 T, as shown in the inset of Fig. 2. The transition from martensitic to austenitic state brings about an increase of magnetization below 0.23 T and a decrease of magnetization above 0.23 T. It has been demonstrated that the magnetic entropy change can be obtained using Maxwell relation as follows even for a system with first-order transition\cite{9,17,18}

$$
\Delta S(T,H) = S(T,H) - S(T,0) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH. \tag{1}
$$

It is clear that the integral value of $\Delta S$ is positive below 0.23 T. When the applied field reaches 0.45 T the positive $\Delta S$ is offset, and further increasing field above 0.45 T results in the net negative $\Delta S$. The interesting behavior of the magnetic entropy change should be ascribed to the fundamental magnetic properties of the sample. In polycrystalline Ni$_{51.5}$Mn$_{22.7}$Ga$_{25.8}$,\cite{14} the crossing point for the $M$-$H$ curves of martensite and austenite is at the higher field of about 0.9 T. It is understandable that the magnetic entropy change under a field below 0.9 T is positive. It is found that the magnetic properties of Heusler alloys Ni-Mn-Ga are sensitive to the composition of Ni, Mn, and Ga, exhibiting a variation of the crossing point in the $M$-$H$ curves of martensite and austenite. The intrinsic origin of the phenomenon needs further investigation.

Plotted in Fig. 3 is the dependence of the peak values of $|\Delta S|$ on the applied field. It is found that the $|\Delta S|$ increases linearly with field at a rate of $\sim 4.0$ J/kg K T when the field...
The density of Gd near room temperature.

The large magnetic entropy change $|\Delta S|$ in Ni-Mn-Ga single crystal is associated with the first-order phase transition, the nature of which is the simultaneous occurrence of a magnetic and a structural transition. This is similar to that in Gd$_2$Ge$_2$Si$_2$.\footnote{Gd$_2$Ge$_2$Si$_2$}
For the present Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ sample the thermal hysteresis of the transition on heating and cooling is about 6 K, which is smaller than that of Fe-Rh (12 K), and wider than that of Gd$_5$Si$_2$Ge$_2$ (2 K) Ref. 9 that is roughly reversible and thus can be used as a magnetic refrigerant material. Usually, the $M$-$H$ curves of single crystal Ni-Mn-Ga samples on altering field are roughly reversible for both martensitic and austenitic state.\cite{26,27} Thermal hysteresis of single crystal Ni-Mn-Ga can be improved by controlling the composition and the crystal-growth technique. A small thermal hysteresis of 3 K has been observed in a recent report.\cite{27} A more exciting characteristic of the ferromagnetic Heusler Ni-Mn-Ga is that the martensitic-austenitic transition temperature can be easily controlled by adjusting the contents of Ni, Mn, Ga elements, which may help us in obtaining significant $|\Delta S|$ in a wide temperature range. In short, the discovery of so large magnetic entropy change in a non-rare-earth based alloy Ni-Mn-Ga single crystal near room temperature is of importance for practical magnetic-refrigerant applications.

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