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^3 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-austensitic structural transition takes place. The phenomena of the large magnetic entropy change and the easy adjustment of the martensitic-austensitic transition-temperature indicate that the non-rare-earth based Ni-Mn-Ga single-crystal materials may have potential applications as magnetic refrigerants.

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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.[8,9,17,18] Several systems undergoing a first-order magnetic transition have been found to show very large MCE.[8,9] 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. $Gd_5(Si_xGe_{1-x})_4$, $x \leqslant 0.5$ 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.[19] 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 ΔS in a sample of $Ni_{51.5}Mn_{22.7}Ga_{25.8}$ polycrystalline[14] The achieved ΔS 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_2MnGa, 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 instrument[24] 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 vaccum of about 5×10^{-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 χ, 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 χ. At the Curie temperature χ sharply decrease. The marked T_M, T_A, T_C, and temperature hysteresis ΔT in Fig. 1 are 292 K, 297 K, 345 K, 6 K, respectively.

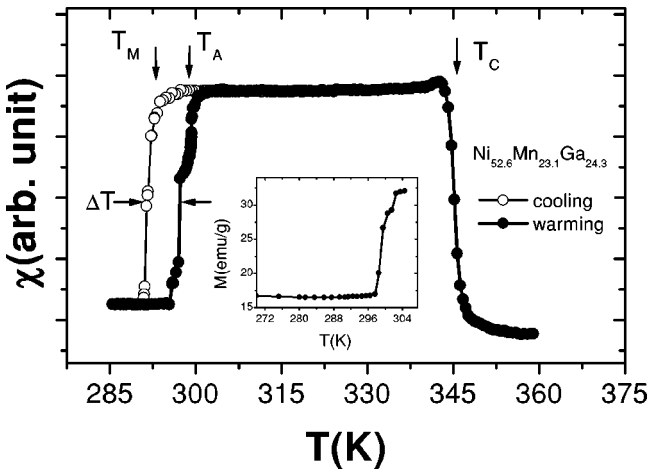

FIG. 1. Ac magnetic susceptibility χ as a function of temperature on cooling and heating. The inset is the temperature dependence of magnetization with a field of 500 Oe along [001] direction measured on heating.

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

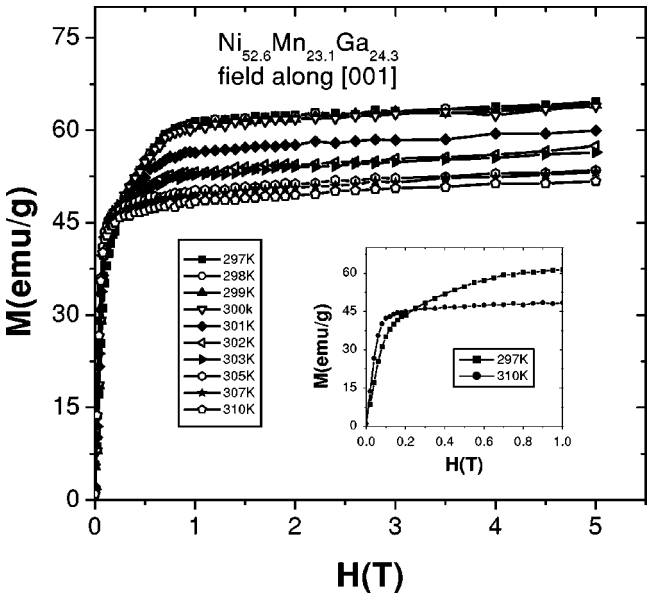

FIG. 2. The isothermal M-H curves with field along [001] direction at different temperatures. The inset is the detailed M-H curves at 297 K and 310 K.

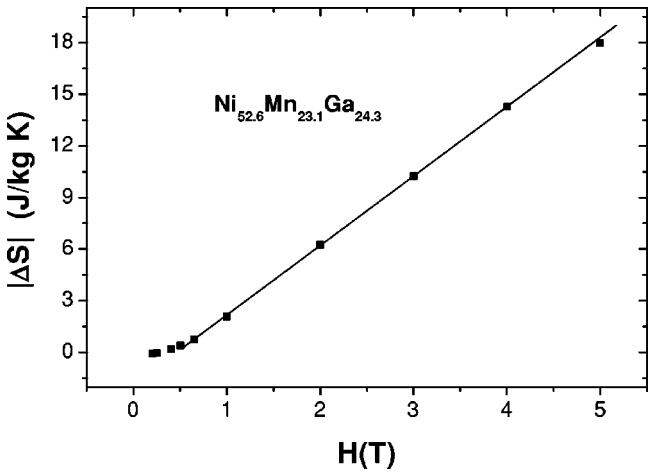

FIG. 3. The dependence of the peak values of $|\Delta S|$ for the applied field along the c axis of the martensitic phase.

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.[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[9,17,18]

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

It is clear that the integral value of ΔS is positive below 0.23 T. When the applied field reaches 0.45 T the positive ΔS is offset, and further increasing field above 0.45 T results in the net negative ΔS. The interesting behavior of the magnetic entropy change should be ascribed to the fundamental magnetic properties of the sample. In polycrystalline $Ni_{51.5}Mn_{22.7}Ga_{25.8}$,[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

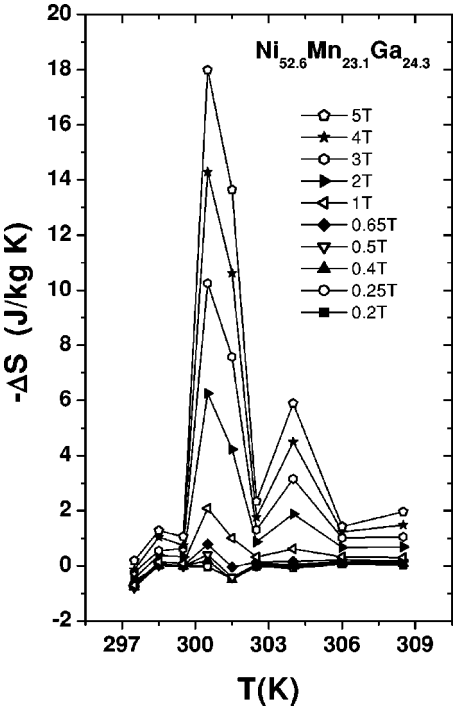

FIG. 4. Magnetic entropy change $-\Delta S$ as a function of temperature under different applied fields along the *c*-axis of the martensitic phase.

exceeds 1 T, which is attributed to the fact that both martensite and austenite have been magnetically saturated at a field of 1 T (Fig. 2). Shown in Fig. 4 is a series of $\Delta S(T)$ under different applied fields from 0.2 T to 5 T. All $\Delta S(T,H)$ curves show two peaks and the higher one is at $T_A(300\ \mathrm{K})$. The curve at 5 T gives a peak value of $|\Delta S| \sim 18.0$ J/kg K. It is known that the $|\Delta S|$ of $Gd_5Si_2Ge_2$ and Gd are ~ 18.5 and ~ 9.7 J/kg K at 276 K and 293 K, respectively, under a same field.[9] Since the cooling-power per unit volume is a critical parameter for a magnetic refrigerator, we give the $|\Delta S|$ by volumetric units, which are ~ 146, ~ 136, and ~ 77 mJ/cm^3 K for $Ni_{52.6}Mn_{23.1}Ga_{24.3}$, $Gd_5Si_2Ge_2$, and Gd, respectively, under a same field of 5 T. The density of $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ and $Gd_5Si_2Ge_2$ used in the unit transformation is estimated according to their structural symmetry and lattice parameter.[28,29] Obviously, the $|\Delta S|$ of present $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ with field along [001] direction is roughly comparable with that of $Gd_5Si_2Ge_2$ and notably exceeds that of Gd near room temperature.

It is worthy to note that the existence of two steps in the change of ac susceptibility χ on heating in Fig. 1 results in two peaks of $\Delta S(T,H)$ shown in Fig. 4. The inset of Fig. 1 is the temperature dependence of magnetization on heating under a field of 500 Oe, which shows two jumps as expected and in agreement with the χ-T curve on heating. The two magnetization jumps in one sample can be a consequence of the coexistence of two crystallographic phases. It is known that the structural transition temperature of Ni-Mn-Ga is very sensitive to the composition and the single crystal grown by present method usually has a small distribution of composition. Although the sample cut from the single-crystal boule for magnetization measurements is very small, ~ 13.53 mg in weight, two phases with small difference of composition may coexist, resulting in two-adjacent transitions. From the isothermal M-H curves shown in Fig. 2 it is also found that with increasing temperature two abrupt decreases of saturated magnetization occur. The scope of the first decrease from 300 to 302 K is 7.5 emu/g, and that of the second from 303 to 305 K is 2.35 emu/g, resulting in the difference of the two ΔS peak heights. Due to the influence of the applied field the peak positions of ΔS slightly shift to higher-temperature compared with the jump positions of ac susceptibility χ on heating. It is easy to understand that the proportion of the two phases directly influences the decrease scope of saturated magnetization and, further, the height of the two ΔS peaks. This fact also tells us that the large values of $|\Delta S|$ and the wide temperature range with large $|\Delta S|$ may be achieved by controlling the composition distribution and improving the technological process of single-crystal growth.

Usually, the saturated magnetization of low-temperature martensite is higher than that of high-temperature austenite by $10 \sim 20\%$.[21,22] For the present sample, due to the possibility of two-phase coexistence, two-abrupt decreases of magnetization take place with increasing temperature. The combined result makes the saturated magnetization of martensitic state at low temperature 297 K is 45% higher than that of austenitic state at high temperature 310 K. Further study on the detailed structural analysis of the present sample is on the way and the result will be published elsewhere.

The origin of so large $|\Delta S|$ should be attributed to the considerable jump of magnetization caused by the first-order structural transition from martensitic to austenitic phase on heating. It is known that both low-temperature martensite and high-temperature austenite are ferromagnet. When the structural transition from tetragonal martensite to cubic austenite occurs the dependence of magnetization on applied field changes strongly. In this transformation process the tetragonal unit-cell expands along c axis and contracts along the other two (In martensitic state, $c/a \sim 0.94$ and c axis is the easy axis[27]). The lower symmetry in martensitic phase enhances the magnetocrystalline anisotropy, and due to the magnetoelastic interaction the elastic energy stored by martensite gives rise to the magnetic anisotropy, which dominate the magnetization process,[30] as a result, causing a harder magnetization saturation and the saturated magnetization of the former is higher than that of the latter, as shown in the M-H curves in Fig. 2. The previous measurements on Ni-Mn-Ga[27] indicated that the application of fields in the martensitic-state produces any of the following processes: magnetic domain-wall motion, variant nucleation, twin-boundary motion, and magnetization rotation. From the approximately reversible M-H curves of the present sample at the martensitic state it can be inferred that the reversible processes dominate in the magnetization process.

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 $Gd_5Ge_2Si_2$.[19]

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),[5] and wider than that of $Gd_5Si_2Ge_2$(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.[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.[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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