

Large Barocaloric Effect with High Pressure-Driving Efficiency in a Hexagonal MnNi_{0.77}Fe_{0.23}Ge Alloy

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The hydrostatic pressure is expected to be an effective knob to tune the magnetostructural phase transitions of hexagonal MM'X alloys (M and M' denote transition metals and X represents main group elements). We perform magnetization measurements under hydrostatic pressure on an MM'X martensitic MnNi_{0.77}Fe_{0.23}Ge alloy. The magnetostructural transition temperature can be efficiently tuned to lower temperatures by applying moderate pressures, with a giant shift rate of -151 K/GPa. A temperature span of 30 K is obtained under the pressure, within which a large magnetic entropy change of -23 J·kg⁻¹K⁻¹ in a field change of 5 T is induced by the mechanical energy gain due to the large volume change. Meanwhile, a decoupling of structural and magnetic transitions is observed at low temperatures when the martensitic transition temperature is lower than the Curie temperature. These results show a multi-parameter tunable caloric effect that benefits the solid-state cooling.

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In recent years, there has been great interest in hexagonal MM'X (M and M' denote transition metals and X represents main group elements) alloys due to the realization of magnetostructural transition,^[1] magnetocaloric effects (MCE),^[2,3] negative thermal expansion^[4] and magneto-strain^[5] near room temperature in these systems. The hexagonal MM'X alloy MnNi_{0.77}Fe_{0.23}Ge was reported as a system with martensitic and magnetic transitions coupled together, which occurs at about 266 K on cooling from a paramagnetic (PM) parent phase with the Ni₂In-type structure to ferromagnetic (FM) martensite phase with the TiNiSi-type structure.^[1] With the coupling of magnetic and structural degrees of freedom, a large MCE was reported on the transition. As we know, the MCE is intensively studied due to its applications in magnetic refrigeration, thermomagnetic motors, controlling of drug delivery, and so on.^[6–8] It is desirable to find external parameters to tune or enhance the MCE. For a hexagonal MM'X family, there is a remarkable character, i.e., giant volume expansion with values of 2–5% during the structural transition upon cooling.^[1,3,9] A hydrostatic pressure can drive this transition to lower temperatures as the mechanical energy gain ($\Delta P \cdot \Delta V$) in the total Gibbs free energy tends to shift the equilibrium point of the phase transition. Thus, besides the chemical substitution,^[10,11] vacancy,^[12,13] magnetic field^[14] and strain,^[15] the hydrostatic pressure is widely used^[10,11,16–21] to tune a phase transition. In fact, as a clean means the pressure can be used to induce many physical behaviors.^[22–26] The studies on MCE include not only a wide temperature range but also a shift in transition temperature

by external parameters, such as hydrostatic pressure, which can tune the transition to the required working temperature.^[21]

In this study, we investigate the effect of hydrostatic pressure on magnetism, martensitic transition and MCE based on a hexagonal MM'X alloy MnNi_{0.77}Fe_{0.23}Ge. The magnetostructural transition temperature can be efficiently tuned to lower temperatures, with a driving efficiency of -151 K/GPa. A temperature span of 30 K is obtained under the pressure, within which a magnetic entropy change of about -23 J·kg⁻¹K⁻¹ for a magnetic field change of 5 T is observed. A decoupling of structural and magnetic transitions occurs when the martensitic transition temperature is lower than the Curie temperature of parent phase at higher pressures. These results indicate that the caloric effect of this system can be tuned by multiple external parameters.

Polycrystalline ingots were prepared by arc melting high-purity metals under argon atmosphere. The ingots were then annealed at 1123 K for five days and slowly cooled at a rate of 1 K/min to room temperature to avoid stress in samples. The structure of measured sample was examined by x-ray diffraction (XRD) using Cu K_{α} radiation. Magnetization measurements were performed using a Quantum Design superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM) equipped with pressure cell in fields up to 5 T in the temperature range of 5–300 K and for pressures up to 1.280 GPa. Daphne 7373 was used as the pressure transmitting medium. In order to determine the pressure in the pressure cell more accurately, a piece of Pb was loaded together with the proper size bulk sample as the super-

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conducting transition temperature under certain pressure for Pb is known.^[27]

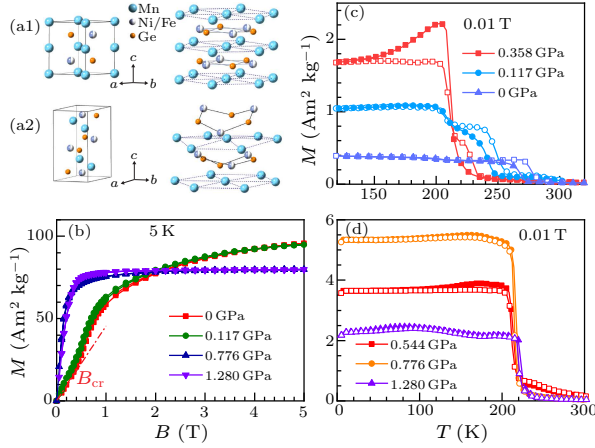


Fig. 1. (a1) and (a2) Primitive cell and a structure sketch of hexagonal parent and orthorhombic martensite phases. (b) Magnetic field dependence of the magnetization (M - H) curves at 5 K under different pressures. (c) and (d) Temperature dependence of the magnetization (M - T) in a magnetic field of 0.01 T under different pressures. The solid and open symbols represent the cooling and heating process, respectively.

At ambient pressure, $\text{MnNi}_{0.77}\text{Fe}_{0.23}\text{Ge}$ undergoes a martensitic transition at about 266 K according to the previous report.^[1] The structures of high-temperature parent and low-temperature martensite phase are shown in Figs. 1(a1) and 1(a2). The parent phase crystallizes in a Ni_2In -type hexagonal structure with a space group of $P6_3/mmc$ (194) while the martensitic phase crystallizes in a TiNiSi -type orthorhombic phase with $Pnma$ (62).^[28–30] The volume change during the transition is about 2.7%.^[1] In the right panel of Figs. 1(a1) and 1(a2) we sketch the atom position relation of two phases. The structural transition occurs via distortions of Ni/Fe-Ge hexagonal rings and Mn-Mn zigzag chains.^[3] Magnetic field dependence of the magnetization (M - H) curves at 5 K under several pressures are shown in Fig. 1(b). Metamagnetic behavior occurs at about 0.4 T under low pressures (0 and 0.117 GPa), which is also consistent with the previous report.^[1] The martensite phase in the Mn-Ni-Fe-Ge system will form a spiral antiferromagnetic (AFM) structure under zero field at low temperature.^[1,2] In addition, the M - H in this system shows metamagnetic transition from spiral AFM to FM at 5 K. In a different fashion, the M - H curves under 0.776 and 1.280 GPa show FM behavior of the parent phase, indicating the suppression of martensitic transition by high pressure. Martensite phase exhibits higher saturation field and magnetization than those of the parent phase. The former characteristic may be due to the higher anisotropy in the martensite phase. The different saturation magnetization is related to the different distances between neighboring Mn atoms in the two phases.^[18,31,32] However, the pressure-induced changes in magnetization in both the phases (parent and martensite) are small, suggesting a minor variations of the exchange interaction, which may be attributed to a slight modification of the electronic density of states at the Fermi level under the

present pressures.^[11]

The variations of magnetization and martensitic transition behaviors under different pressures are depicted by temperature dependence of the magnetization (M - T) in a magnetic field of 0.01 T, as shown in Figs. 1(c) and 1(d). The M - T curves under 0 and 0.117 GPa show clear temperature hysteresis, which is associated with the forward and reverse martensitic transition temperatures, indicating a first-order nature of the transition. The martensitic transition temperature is determined by the extreme point of the first order differential of the M - T curve. The forward martensitic transition temperature (T_M) at ambient pressure is 267 K, which is consistent with the previous report.^[1] At T_M , it is a magnetostructural transition, the parent phase in PM state transforms to the martensite phase in FM order. There is a magnetization change without hysteresis around 209 K under 0.117 GPa, which should be the Curie temperature of residual parent phase. The change in the magnetization between parent and martensite phases becomes larger with increasing pressure. Such an increase is a consequence of the lower martensitic transition temperature, at which the magnetization of FM martensite increases.

The M - T curve under 0.358 GPa is slightly complicated due to the near decoupling of structural and magnetic phase transitions. When the temperature decreases, one can see the Curie temperature of parent phase (T_C^A) and entangled martensitic transition temperature at about 212 K. However, due to the larger span of structural phase transition than a magnetic one, we can still see a “tail” of the martensitic transition. Thus there is a decrease of magnetization soon after T_C^A and T_M due to the lower magnetization of martensite compared to the parent phase in a low magnetic field of 0.01 T. On the heating process, the first drop of magnetization is associated with the Curie temperature of residual parent phase, while the second drop at about 228 K is due to the reverse martensitic transition from martensite to PM parent phase. The M - T curves show only a transition without hysteresis above 0.544 GPa (Fig. 1(d)), indicating the occurrence of the suppression of martensitic transition by higher pressures, which is consistent with the above analysis about the M - H curves. The martensitic transition is shifted to lower temperatures by pressure and finally vanishes at about 210 K. As this temperature is relatively high, there should be other factors that suppress the structural transition besides the high pressure.

The variation of magnetic order of the parent phase should be one reason. It seems that the martensitic transition will vanish when the FM transition of parent phase happens first during temperature decreasing. This suppression behavior has been observed in other $\text{MM}'\text{X}$ compounds.^[1,9,12] The interpretation could be that the parent phase is more stable at the FM state than the PM one. Thus the energy barrier between the FM parent and martensite phases becomes difficult to overcome. In the present case, this suppression behavior occurs under the condition of the hydrostatic pressure loading. Note that the sudden drops of magnetization at very low temperatures in Fig. 1(d) are associated with the superconducting

transitions of Pb as a pressure probe.

Figure 2(a) shows the pressure dependence of martensitic transition temperature and Curie temperature of the parent phase. T_M and T_C^A are determined by the extreme points of the first order differential of the $M-T$ curve. The large error bars under 0.321 and 0.330 GPa are due to the entanglement of the structural and magnetic transitions. As one can see, T_M decreases while T_C^A increases with increasing pressure. An increasing pressure leads to a shrinking of the cell volume and enhanced exchange interactions between moments on Mn atoms, which result in the rising of T_C^A . The pressure dependence of Curie temperature shows the similar behavior to the MnCoGe system.^[35] The application of hydrostatic pressure stabilizes the hexagonal parent phase because there is a big expansion of the volume during the martensitic structural transition upon cooling, which is common in hexagonal MM'X alloys.^[3] Pressures above 0.544 GPa eventually suppress the martensitic transition.

The shift with pressure of T_M is approximately calculated to be -151 K/GPa in the MnNi_{0.77}Fe_{0.23}Ge system, where $dT_t/dP = [T_M(0.358 \text{ GPa}) - T_M(0 \text{ GPa})]/0.358 \text{ GPa}$. Figure 2(b) compares the shift of T_M or T_C (both are denoted as T_t) and the transition related magnetic entropy change ($|\Delta S_m|_{\max}$) for a field change of 2 T in some systems. Here we do not distinguish the structural and magnetic transitions as we now study the capacity of pressure to tune the transitions, which is associated with the tuning of related magnetocaloric effects. Among all referenced systems here, MnNi_{0.77}Fe_{0.23}Ge exhibits a prominent response of transition temperature with pressure. Therefore, for this alloy, it is easier to drive the martensitic transition by applying moderate hydrostatic pressures. Moreover, the large value of dT_t/dP indicates that the magnetostructural tran-

sition could be induced reversibly between the T_M at ambient pressure and the reverse martensitic transition temperature (T_A) at a proper pressure, for example, 0.117 GPa. Due to the above characteristic, MnNi_{0.77}Fe_{0.23}Ge as well as its related systems are proper platforms for research of barocaloric effect and applications.^[36–38]

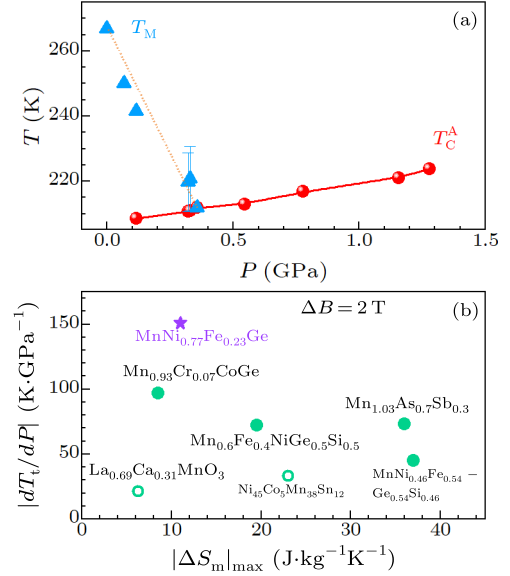


Fig. 2. (a) Pressure dependence of the martensitic transition temperature and Curie temperature of the parent phase. The orange dotted line is a guide for the eyes. (b) The value of $|dT_t/dP|$ and $|\Delta S_m|_{\max}$ (for a magnetic field change of 2 T) in several systems, where the temperatures of structural and magnetic transitions are denoted as T_t . The magnetic entropy changes are taken as the maximum values under different pressures for different systems. The solid symbols correspond to the negative dT_t/dP and ΔS_m while the open symbols to the positive values. Data is taken from Refs. [11,17,19,21,33,34].

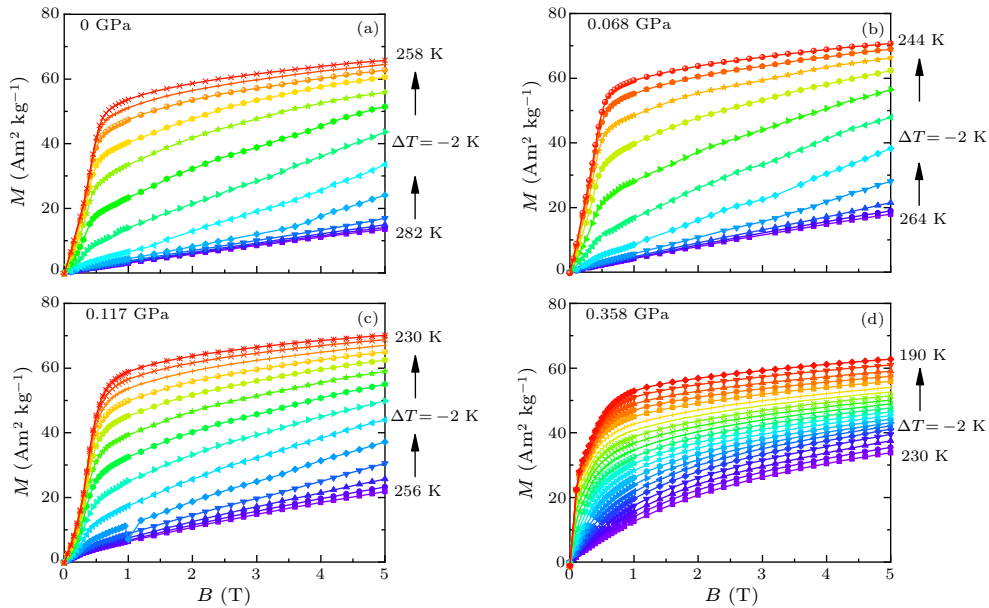


Fig. 3. Magnetic isothermals in a temperature interval of -2 K measured under 0, 0.068, 0.117 and 0.358 GPa.

We performed magnetic isothermal measurements during cooling in a loop process^[39] to avoid the influence of the magnetization history. The magnetic isothermals with a temperature interval of -2 K are shown in Fig. 3.

The study of magnetocaloric effect (MCE) in the $\text{MnNi}_{0.77}\text{Fe}_{0.23}\text{Ge}$ system at ambient and under hydrostatic pressures was based on the Maxwell relation.^[39] The magnetic entropy change associated with the magnetic field variation can be expressed as

$$\Delta S_m(T, B) = \int_0^B \left(\frac{\partial S}{\partial B} \right)_T dB = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB. \quad (1)$$

The magnetic field induced martensitic transformation in $\text{MnNi}_{0.77}\text{Fe}_{0.23}\text{Ge}$ is not reversible, i.e., the martensite phase induced by magnetic field loading will not transform to parent phase totally during demagnetization process. Thus we concentrate on the process in which the parent phase transforms to the martensite phase driven by increasing magnetic field. We calculated the magnetic entropy change of the magnetization process through Eq. (1) using magnetic isothermals data shown in Fig. 3.

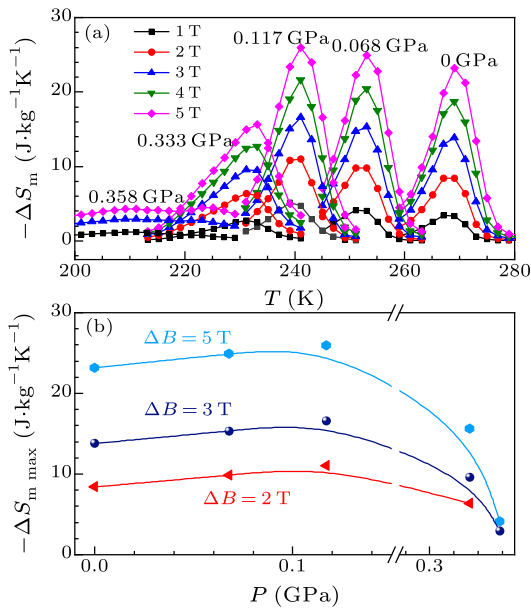


Fig. 4. (a) Temperature dependence of the magnetic entropy changes ($-\Delta S_m$) with magnetic field variation from 1 to 5 T under different pressures. (b) The maximum of the magnetic entropy changes ($-\Delta S_{m\max}$) under different pressures for a field change of 2 T, 3 T and 5 T.

Figure 4(a) shows the entropy changes in several magnetic field variations under different pressures. The entropy change is reduced under 0.333 GPa and approaches nearly zero under 0.358 GPa due to the suppression of the martensitic transition by high pressures. However, the ΔS_m reveals a nearly unchanged value in the range of about -23.2 to $-26.0\text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for a field change of 5 T (Fig. 4(b)) over the pressure range from 0 to 0.117 GPa. The conserved and tunable

MCE under hydrostatic pressure can offer indications to the practical applications of caloric materials.

In summary, the study of magnetostructural transition and MCE under hydrostatic pressure in $\text{MnNi}_{0.77}\text{Fe}_{0.23}\text{Ge}$ reveals that hydrostatic pressure can efficiently shift the magnetostructural transition temperature and thus the related MCE in this system. The decoupling of structural and magnetic phase transitions occurs at about 0.358 GPa, below which the MCE can be conserved and tuned by moderate pressures in a temperature range from 240 to 270 K. This characteristic can be useful in practical applications as one can tune the MCE to the required temperature range by applying moderate pressures. More importantly, the remarkable ability to shift the magnetostructural transition temperature by hydrostatic pressure indicates a promising barocaloric effect driven by pressure loading around the magnetostructural phase transition in this alloy with a large volume change.

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