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Magnetic properties and magnetocaloric effects in $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds

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Abstract

We have studied the magnetic properties and magnetocaloric effects in the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds with $x = 0.2, 0.22, 0.3, 0.4$ and 0.5 . X-ray diffraction patterns show that the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds crystallize in the hexagonal Fe_2P -type crystal structure. The magnetic moments of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds measured at 5 K and 5 T increase with increasing Ge content. The Curie temperature increases strongly and the magnetic entropy change has a maximum around 233 K for the compound with $x = 0.22$, which is about 19 and 31 $\text{J kg}^{-1} \text{K}^{-1}$ for a field change of 2 and 5 T, respectively.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently developed new magnetic refrigerant materials [1–5] are promising for room-temperature magnetic refrigeration, which takes advantage of the entropy difference between the magnetized and demagnetized state of magnetic refrigerant materials. They represent an energy-efficient and environmentally friendly alternative to the vapour-cycle refrigeration technique in use today. The research on magnetic refrigerant materials has been focused on new materials with a first-order phase transition, because the magnetocaloric effect (MCE) is proportional to $\partial M/\partial T$, which is large in a first-order phase transition region. Therefore, a large MCE is expected in a first-order phase transition region. The hexagonal Fe_2P -type $\text{MnFeP}_{1-x}\text{As}_x$ compounds exhibit a large magnetic entropy change which is due to a first-order phase transformation, and are one of the most promising materials for room-temperature

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magnetic refrigeration applications. It is well known that a first-order phase transition involves a more or less strong thermal hysteresis, which has an unfavourable effect on the magnetic refrigeration cycle. In order to develop new potential magnetic refrigerants, it is essential to enhance the MCE and to simultaneously reduce the thermal hysteresis. The $\text{MnFeP}_{1-x}\text{As}_x$ compound system shows advantages compared to other available materials, comparing the magnetocaloric properties and considering the cost of the materials. However, the toxic element As in the $\text{MnFeP}_{1-x}\text{As}_x$ compounds raises the question whether the material can be an environmentally friendly commercial material or not. This led us to study the replacement of As by nontoxic elements in this compound system. Tegus *et al* reported the reduction of the As content in $\text{MnFeP}_{0.7}\text{As}_{0.3-x}\text{Ge}_x$ [6] and $\text{MnFeP}_{0.5}\text{As}_{0.5-x}\text{Si}_x$ [7]. They found that the As can be replaced by Ge and Si. On the basis of these studies, Dagula *et al* studied the MCE of the $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ compounds [8]. They found that the $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ compounds exhibit large MCE and tunable Curie temperature around room temperature. These studies bring the material a step forward, closer to commercial applications. But the introduction of Ge and Si in the Fe_2P -type $\text{MnFeP}_{1-x}\text{T}_x$ ($\text{T} = \text{Ge}, \text{Si}$) lattice leads to some unfavourable effects, such as the virgin effect (when cooling the material for the first time, one observes a much lower Curie temperature than in the heating run and in any further cooling and heating runs). Additionally it leads to a large thermal hysteresis (the thermal hysteresis between the heating and cooling curves of the temperature dependence of the magnetization), and to rather high critical field for the field-induced first-order transition. In this work, we report on the effects of the P and Ge ratio on the magnetic and magnetocaloric properties of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds.

2. Experimental details

Polycrystalline samples of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds with $x = 0.2, 0.22, 0.3, 0.4$ and 0.5 were prepared by ball milling and solid-state reaction as described in previous work [9]. The starting materials used here are Mn powder (purity 99.7%), iron powder (purity 99.7%), red P powder (purity 99.999%) and Ge (purity 99.999%). A mixture of the starting materials was ball milled in a high-energy vibratory mill in a vacuum better than 2×10^{-6} mbar for 100 h. The samples were sintered at 1000°C for 5 h and homogenized at 650°C for 50 h. X-ray diffraction (XRD) data were collected on a Philips diffractometer with $\text{Cu K}\alpha$ radiation. The magnetic measurements were performed by using a Quantum Design SQUID magnetometer in the temperature interval from 5 to 400 K. The magnetic entropy change is derived from the magnetization measurements made at discrete temperatures by using the equation

$$\Delta S_m(T, B) = \sum_i \frac{M_{i+1}(T_{i+1}, B) - M_i(T_i, B)}{T_{i+1} - T_i} \Delta B, \quad (1)$$

where $M_{i+1}(T_{i+1}, B)$ and $M_i(T_i, B)$ represent the values of the magnetization in a magnetic field B at the temperatures T_{i+1} and T_i , respectively. B is the applied field.

3. Results and discussion

Figure 1 shows the powder XRD patterns of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds with $x = 0.2, 0.3, 0.4$ and 0.5 taken at room temperature. The result shows that the reflections can be identified with the Fe_2P -type phase, indicating that the compounds crystallize in the Fe_2P -type phase. However, in the case of the compounds with $x = 0.2$ and 0.3 , there is a minor impurity phase with visible reflections as indicated by arrows. A refinement analysis of the x-ray data shows that the impurity phase belongs to the pseudo-binary system $(\text{Mn}_{1-x}\text{Fe}_x)_{3+\delta}\text{Ge}$ with a hexagonal DO_{19} type structure [10]. The peak intensity of the impurity phase becomes weak

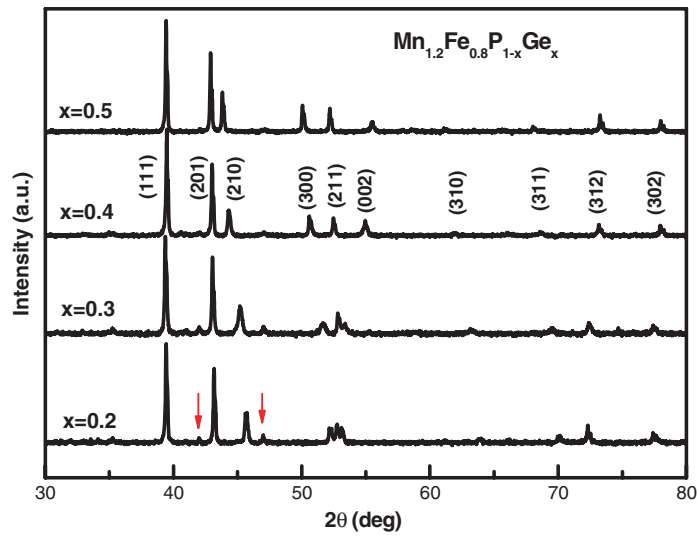


Figure 1. X-ray diffraction patterns of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds with $x = 0.2, 0.3, 0.4$ and 0.5 taken at room temperature.

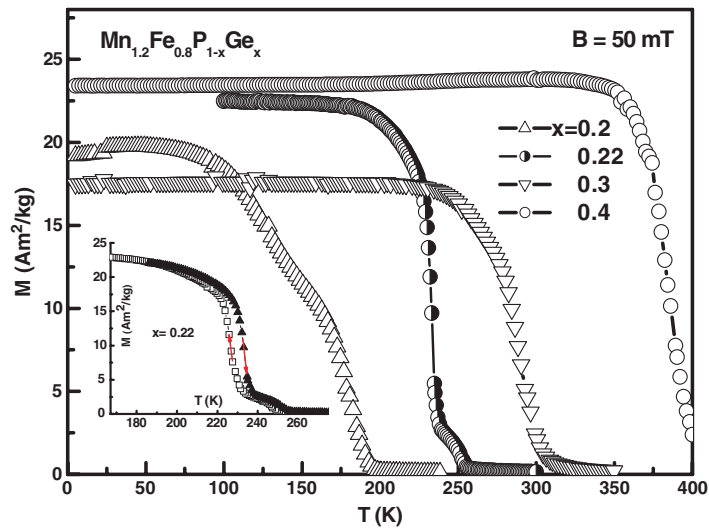


Figure 2. Temperature dependence of the magnetization of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ measured in a field of 50 mT. The inset shows the thermal hysteresis of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ compound.

with increasing Ge concentration, indicating that the main phase becomes more pure. From the shifts of the (300) and (002) reflections, we can easily derive that the lattice parameter a increases and the parameter c decreases with increasing Ge content.

The temperature dependence of the magnetization of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds with $x = 0.2, 0.22, 0.3$ and 0.4 measured with increasing temperature in a field of 50 mT is shown in figure 2. The inset shows the magnetization of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ measured in a field of 50 mT with increasing temperature and decreasing temperature. It is clear that there exists a large thermal hysteresis, about 6 K, between the two curves, indicating that the transition is of first order. The Curie temperature is determined as the temperature where

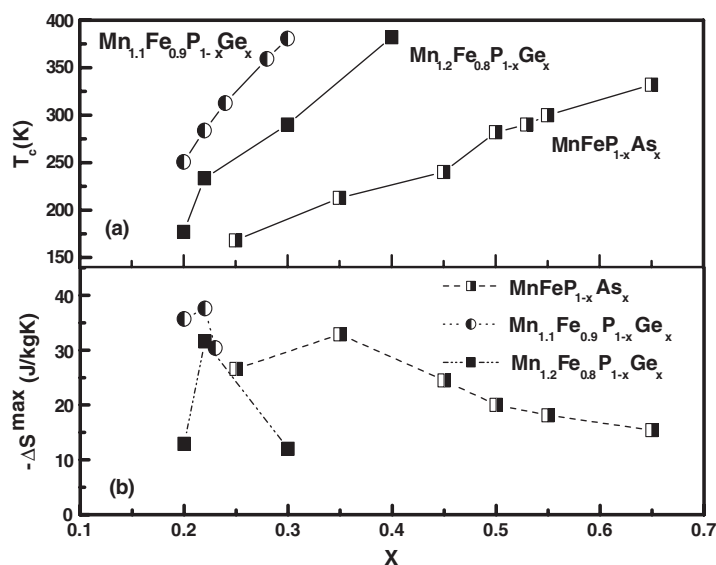


Figure 3. Composition dependence of the Curie temperature (a) and the maximum values of the magnetic entropy change (b) of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$, $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ [8] and $\text{MnFeP}_{1-x}\text{As}_x$ [9].

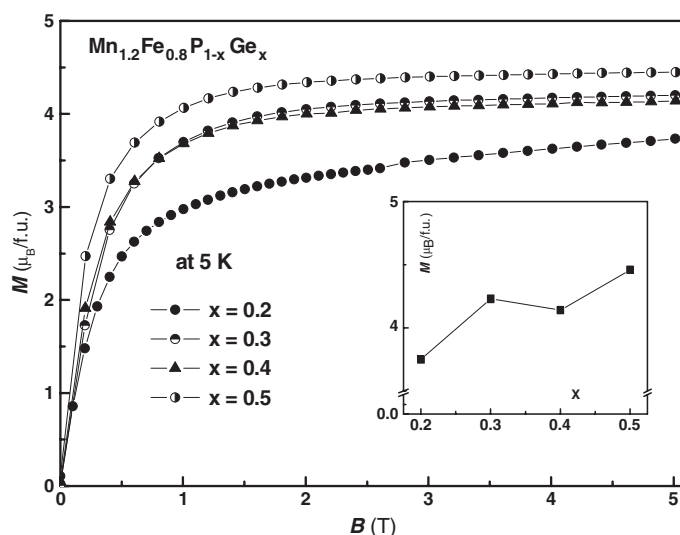


Figure 4. Field dependence of the magnetization of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ measured at 5 K.

the first derivative of the magnetization with respect to temperature has an extreme value. In this way, we determine the Curie temperature of the compounds as 177, 233, 290 and 382 K for $x = 0.2, 0.22, 0.3, 0.4$, respectively. The Curie temperature of the compound with $x = 0.5$ is higher than the maximum measurement temperature of our SQUID magnetometer. The bumps appearing in the magnetization curves are probably due to the impurity phase. For example, as shown in the inset of figure 2, there is a small bump with a transition temperature around 251 K in the magnetization curve for the compound with $x = 0.22$. A

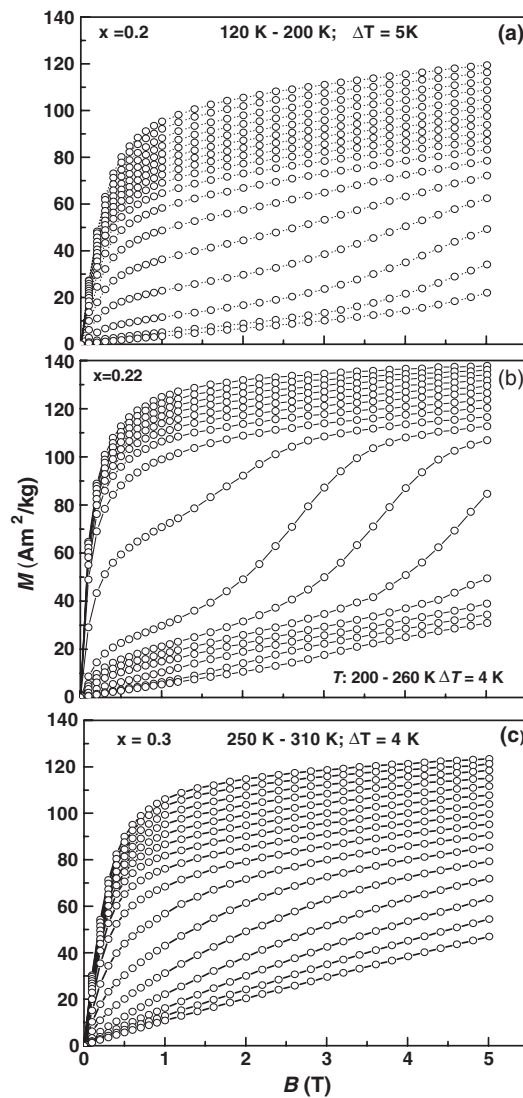


Figure 5. Isothermal magnetization curves of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.8}\text{Ge}_{0.2}$ (a), $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ (b) and $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$ (c) on increasing field in the vicinity of their Curie temperatures.

closer analysis of the $M(T)$ curve shows that no hysteresis is involved in the bump part of the curve, indicating that the transition is of second order. Considering the small value of the magnetization and the transition temperature, the impurity phase is most likely one of the hexagonal $(\text{Mn}_{1-x}\text{Fe}_x)_{3+\delta}\text{Ge}$ compounds reported in [10].

Figure 3(a) shows the composition dependence of the Curie temperature of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds, in comparison with those of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ [8] and $\text{MnFeP}_{1-x}\text{As}_x$ [9], given in the same figure. It can be seen that the Curie temperature is very sensitive to the variation of the P/Ge ratio, and the slope of the composition dependence is the same as in the case of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$, but much steeper than that of the compounds with As. The concentration dependence of the maximum values of the magnetic entropy change in a field change of 5 T is shown in figure 3(b).

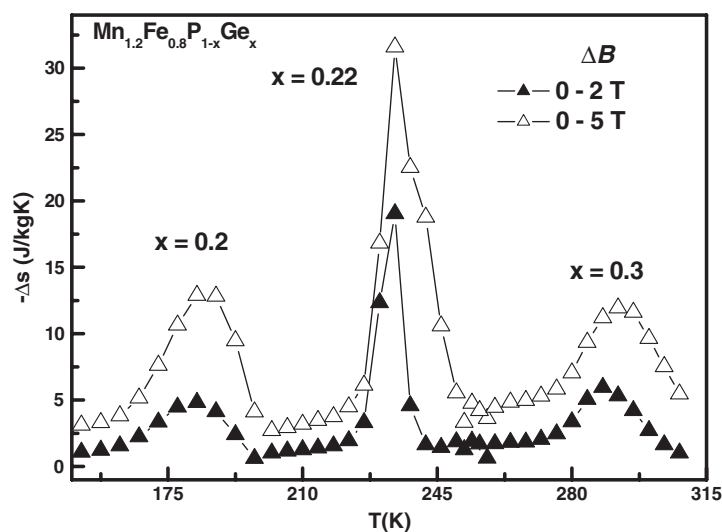


Figure 6. Magnetic entropy changes of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ ($x = 0.2, 0.22$ and 0.3) for magnetic field changes of 0–2 and 0–5 T.

The composition dependence of the magnetization at 5 K is shown in figure 4. The inset shows the magnetization at 5 K and 5 T. It can be seen that the magnetization slightly increases with increasing of the Ge content. The slightly lower value of the magnetization for the compound with $x = 0.2$ is probably due to the influence of the second phase. This increase of the magnetization can be related to the electronic structure change of the 3d atoms due to the change of lattice parameters.

Figure 5 shows the isothermal magnetization curves collected around the Curie temperature in external magnetic fields up to 5 T for $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.8}\text{Ge}_{0.2}$, $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ and $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$. In the cases of the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.8}\text{Ge}_{0.2}$ and $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ compounds, the magnetization curves measured below the Curie temperature are typical for a ferromagnetic material, but the curves behave differently above the Curie temperature. The features show that there is a metamagnetic transition triggered by the external magnetic field. This feature is quite obvious in $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.78}\text{Ge}_{0.22}$ and disappears in $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$.

From the magnetization data, we derived the magnetic entropy change of the compounds with $x = 0.2, 0.22$ and 0.3 arising from the change of the external magnetic field under isothermal conditions. The results are shown in figure 6. For the sample with $x = 0.22$, we obtain large values of the magnetic entropy change, up to 19 and 31 $\text{J kg}^{-1} \text{K}^{-1}$ for field changes of 2 and 5 T at 233 K. These values are slightly higher than those of the $\text{MnFeP}_{0.55}\text{As}_{0.45}$ compound [9]. For the compositions with $x = 0.2$ and 0.3 , we observe temperature dependences of the magnetic entropy change with broadened profiles and relatively smaller, maximum values equal to about 13.0 and 12.2 $\text{J kg}^{-1} \text{K}^{-1}$ for a field change of 5 T, respectively. This indicates that the sharper the field-induced transition the larger is the magnetic entropy change. Therefore, we can conclude that the metamagnetic transition is the origin of the large magnetocaloric effect.

In order to investigate the thermal hysteresis in this compound system, we have also measured the temperature dependence of the magnetization of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$ in fields of 1, 2, 3 and 4 T, which is shown in figure 7. The inset shows the field dependence of the Curie temperature. It can be seen that there exists a thermal hysteresis, which is about 4 K, between

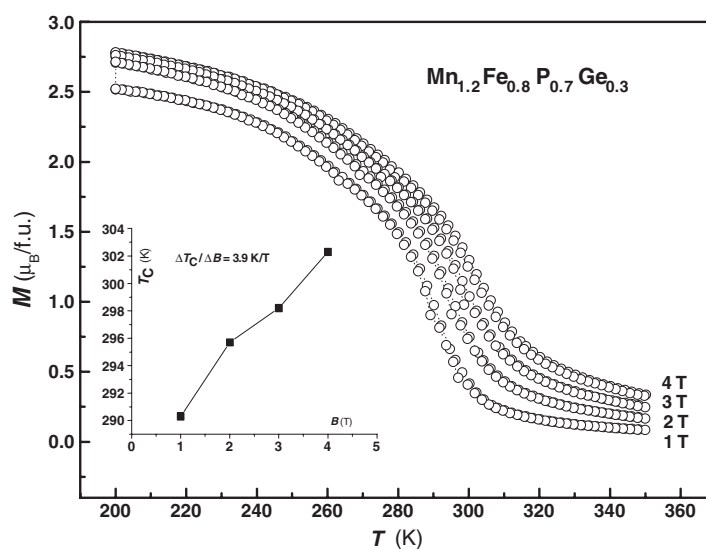


Figure 7. Temperature dependence of the magnetization of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$ measured with increasing temperature and then decreasing temperature.

the curves of magnetization measured with increasing temperature and decreasing temperature. The shift of the transition temperature with increasing field is another important parameter for investigating potential high-performance magnetic refrigerants. The field dependence of the increase rate of the Curie temperature, $\Delta T_C / \Delta B$, is about 3.9 K T^{-1} for $x = 0.3$. This is lower than the value, 5 K T^{-1} , of the compound $\text{MnFeP}_{0.45}\text{As}_{0.55}$ [11], indicating that the relative cooling power, $\text{RCP}(S) / \Delta B$ [12], in $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$ could be also lower than that of $\text{MnFeP}_{0.45}\text{As}_{0.55}$.

In conclusion, the $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Ge}_x$ compounds exhibit large MCE in the temperature range from 177 to 290 K. The maximum isothermal magnetic entropy changes are 19 and $31 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x = 0.22$ for field changes of 2 and 5 T, respectively. The thermal hysteresis is about 4 K, and the shift of the transition temperature is 3.9 K T^{-1} for $x = 0.3$. The metamagnetic first-order phase transition is the main origin of the large MCE. Taking into account the fact that T_C in the compounds can be strongly changed by the variation of composition, we thus have the possibility of designing composites with tunable working temperature which can operate in a wide temperature region.

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