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Structural, magnetic, and magnetocaloric properties of the MnFe(P,Ge) compounds were systematically studied on both bulk alloys and melt-spun ribbons. The experimental results show that the critical behavior of the phase transition can be controlled by changing either the compositions or the annealing conditions. The thermal hysteresis is found to be tunable. It can reach very small values, while maintaining a large magnetocaloric effect in a large range of working temperatures and under field changes that may be produced by conventional permanent magnets. Consequently, an effective way in producing ideal magnetic refrigerants for room-temperature applications is suggested. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3095597]

Magnetic refrigeration based on the magnetocaloric effect (MCE) is considered as one of the most promising technologies to replace vapor-compression refrigeration due to its low environmental impact and expected high-energy efficiency.[1,2] Nowadays, magnetocaloric materials undergoing a first-order field-induced magnetostructural transition are intensively investigated because of their potential applications at room temperature (T_{room}).[3–6] However, as a common feature of compounds with a first-order magnetic transition (FOMT), the observed large MCE is often accompanied by a considerable thermal hysteresis (ΔT_{hys}), which might make the compounds unsuitable for applications because a real refrigerator is expected to operate at rather high cycle frequencies.

Recently, several efforts have been made for tuning ΔT_{hys} in the pseudobinary system $Gd_5(Si_xGe_{1-x})_4$ which reveals a ΔT_{hys} of 8–10 K.[7,8] It was found that ΔT_{hys} can significantly be reduced by hydrogen insertion[9] or the addition of $3d$ elements.[10] Nevertheless, the FOMT behavior and the consequent MCE diminish drastically when increasing the hydrogen and/or the transition element concentrations. More recently, Sun *et al.*[11] concluded that the large ΔT_{hys} of 10–30 K exhibited by MnAs can be reduced or even eliminated by substituting Cr for Mn atoms. However, it is still unclear whether the MCE magnitude and the ΔT_{hys} value of Cr substituted MnAs are tunable by varying the Cr content. After the discovery of the giant MCE in $MnFeP_{1-x}As_x$,[4] many efforts have been spent to replace As by nontoxic components. Although the introduction of Si and Ge atoms into the lattice of $MnFeP_{1-x}As_x$ retains a giant MCE around T_{room}, an enhanced ΔT_{hys} was observed.[12–15] In this letter, we show that it is possible to reduce ΔT_{hys} of MnFe(P,Ge) without losing the favorable magnetocaloric properties.

Polycrystalline MnFe(P,Ge) samples were prepared by melt spinning and high-energy ball milling, as described in earlier reports.[12–16] Bulk samples of $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ ($x=0.19, 0.22, 0.25$) were sintered at 1100 °C for 10 h and then homogenized at 650 °C for 60 h before they were quenched into water at T_{room}. The sample with $x=0.25$ was also prepared with quenching from 1000 °C. Bulk $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ ($y=0.84, 0.82, 0.80, 0.74$) samples were quenched from 1100 °C after 60 h annealing. $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ ($y=0.80, 0.78, 0.76, 0.70$) melt-spun ribbons were produced at 40 m/s surface speed of the Cu wheel. The as-spun ribbons were subsequently quenched into water after annealing at 1100 °C for 15 min. Powder x-ray diffraction (XRD) of the samples was made at T_{room} in a Philips PW-1738 diffractometer with Cu $K\alpha$ radiation. Electron probe microanalysis (EPMA) was performed on some bulk samples in order to obtain further information about their homogeneity and the stoichiometry. The magnetic measurements were done on a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS 5XL).

The EPMA analysis confirms that the main phase of the bulk MnFe(P,Ge) samples, which is crystallized in the hexagonal Fe_2P-type structure (space group $P\bar{6}2m$), is homogeneous. Also, a small amount (~ 4 vol %) of secondary phase Mn_2O_3 is detected.[17] The temperature dependence of the magnetization (M-T) for $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ ($x=0.19, 0.22, 0.25$) is shown in Fig. 1(a). In agreement with the results reported by Brück *et al.*,[12] it is found that the value of T_c increases about linearly with increasing the Ge concentration, from $T_c=260$ K for $x=0.19$ to $T_c=296$ and 330 K for $x=0.22$ and 0.25, respectively. The corresponding values of ΔT_{hys} between the magnetic transitions observed on heating and cooling for $x=0.19$, 0.22, and 0.25 are 6, 4, and 2 K, respectively. For $\Delta B=0-2$ T, the isothermal magnetic entropy changes (ΔS_m) are -13.8, -20, and -13 J kg^{-1} K^{-1} for $x=0.19$, 0.22, and 0.25, respectively [Fig. 1(b)]. Note the difference for the two samples with the same composition $x=0.25$ annealed at 650 and 1000 °C for 60 h before quenching into water. The magnetic transition of the sample quenched from 1000 °C (◔) is more pronounced,
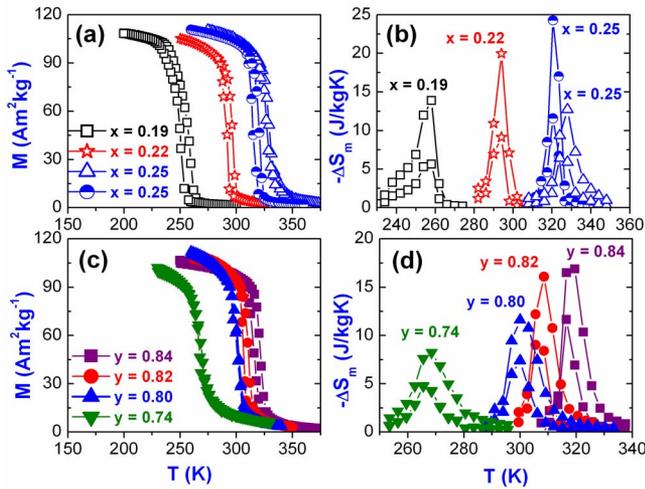
FIG. 1. (Color online) *M-T* curves measured in magnetic field *B*=0.5 T for bulk compounds of $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ (a) and $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ (c). Magnetic entropy changes as a function of temperature under the field changes of 0–1 T (lower curves) and 0–2 T (upper curves) calculated for $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ (b) and $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ (d). The sample with *x* =0.25 was quenched from 650 °C (△) and 1000 °C (◑) for a comparison.

and the values of ΔT_{hys} and T_c are 5 and 320 K, respectively. For this sample, a large ΔS_m of −24.3 J kg^{-1} K^{-1} is observed [Fig. 1(b)]. It appears that the increase in the quenching temperature (T_q) simultaneously leads to an enhanced ΔT_{hys} and a lower T_c. In other words, the higher T_q employed for MnFe(P,Ge) results in a more pronounced FOMT behavior.

Although hysteretic behavior is a characteristic for a FOMT in MnFe(P,Ge), it can be reduced by means of changing the Mn/Fe ratio. Shown in Fig. 1(c) are the *M-T* curves for the bulk samples of $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ (*y*=0.84, 0.82, 0.80, 0.74) with various Mn/Fe ratios. Both T_c and ΔT_{hys} decrease with increasing the Mn content. While T_c varies from 322 to 310 and 302 K for the samples with *y*=0.84, 0.82, and 0.80, the value of ΔT_{hys} also varies from 5 to 3 and ~0 K, respectively. The temperature dependences of ΔS_m are presented in Fig. 1(d). The maximal ΔS_m, for a field change ΔB=0–2 T, are −17 J kg^{-1} K^{-1} (*y*=0.84), −16 J kg^{-1} K^{-1} (*y*=0.82), and −12 J kg^{-1} K^{-1} (*y*=0.80). The reversible *M-T* curve of the sample with *y*=0.8 evidences that the ΔT_{hys} of MnFe(P,Ge) can even be eliminated, while maintaining a large MCE near T_{room}. It is worth noting

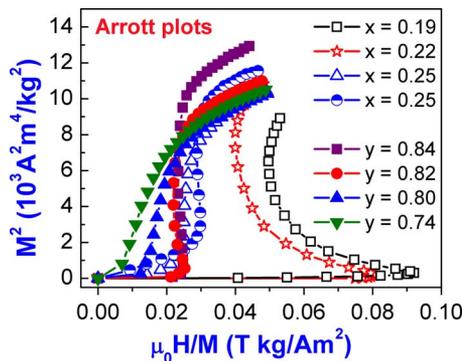FIG. 2. (Color online) Arrott plots of $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ (open symbols) (see Fig. 1) and $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ (filled symbols) (see Fig. 1) bulk samples obtained from increasing field isothermal magnetizations measured in the vicinity of their critical temperatures. In addition, the Arrott plot of the sample *x*=0.25 quenched from 1000 °C (◑) is presented for a comparison.

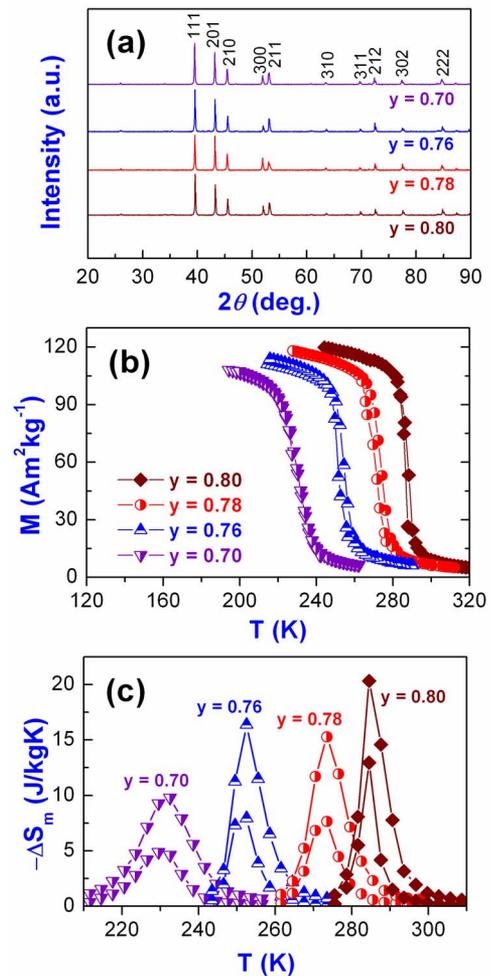FIG. 3. (Color online) $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ melt-spun ribbons: room-temperature XRD patterns (a), *M-T* curves measured in magnetic field *B* =0.5 T (b), magnetic entropy changes under the field changes of 0–1 T (lower curves) and 0–2 T (upper curves) (c).

that, when increasing the Mn content up to (2−*y*)=1.26, the value of ΔT_{hys} almost does not change (~0 K) and the MCE magnitude is retained at about −8.2 J kg^{-1} K^{-1} in the vicinity of T_c=269 K. This implies that the FOMT is weakened and the second-order magnetic transition (SOMT) becomes dominant at a sufficiently high Mn/Fe ratio.

The Arrott plot method is effective for obtaining information on the phase transition type. In Fig. 2, plots obtained in the vicinity of T_c for the bulk compounds with *x*=0.19 and 0.22, which were quenched from T_q=650 °C, clearly show a negative slope with different inflection points. Such S-shaped curves confirm the occurrence of a FOMT in these samples.[16] It is seen that the S shape is less pronounced in the curve for the sample with *x*=0.25. Alternatively, the critical behavior at a FOMT can also be described in terms of the Bean–Rodbell model.[18] Mössbauer spectral analyses made on compounds such as $MnFeP_{1-x}As_x$ (Ref. 19) and $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ (Ref. 17) have confirmed the first-order character, as displayed by the values of the so-called order-parameter η, decreases with increasing the Ge concentration. Therefore, the magnetic transition in the sample with *x* =0.25 accompanied by a small ΔT_{hys} can be understood as a weakened FOMT. However, when comparing the Arrott plot for sample *x*=0.25 quenched from 650 °C with that quenched from 1000 °C, one sees that the FOMT in Mn-

TABLE I. Variations in the lattice parameter ratio c/a, critical temperature (T_c), thermal hysteresis (ΔT_{hys}), maximal isothermal magnetic entropy change ($-\Delta S_m$), and RCP under the field change $\Delta B = 0-2$ T of $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ melt-spun ribbons compared with that of Gd (after Ref. 4).

y	c/a	ΔT_{hys} (K)	T_c (K)	$-\Delta S_{m,max}$ (J kg^{-1} K^{-1})	RCP (J kg^{-1})
0.80	0.5626	1	288	20.3	151
0.78	0.5638	2	274	15.3	162
0.76	0.5646	2	254	16.4	151
0.70	0.5651	0	230	9.8	155
Gadolinium[a]		0	293	4.2	166

[a]Reference 4.

Fe(P,Ge) can be enhanced by increasing the T_q. In connection with the above discussion, a similar argument can be used for the bulk $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ samples, which were quenched from $T_q = 1100$ °C. Here, the Arrott plots reveal a weakened FOMT for the samples with $y = 0.84$ and 0.82. However, neither a negative slope nor an inflection point is observed for the sample with $y = 0.80$ and $y = 0.74$, revealing a SOMT behavior.

Finally, we turn our attention to the structural and magnetocaloric properties of the $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ melt-spun ribbons with nominal compositions of $y = 0.80$, 0.78, 0.76, and 0.70, which were quenched from 1100 °C. Refinement of the XRD patterns displayed in Fig. 3(a) for all ribbons shows that all reflections can be indexed on the basic of a single phase Fe_2P-type structure with no minor impurity phase being present. A more detailed analysis of the lattice parameters confirms that the c/a ratio increases with increasing the Mn/Fe ratio, which usually results in a change in T_c. The M-T curves for these samples are plotted in Fig. 3(b). In a large range of working temperatures from $T_c = 230$ K to $T_c = 288$ K, when varying the Mn/Fe ratio, the ΔT_{hys} value is retained to be very small ($\Delta T_{hys} = 1-2$ K), or even it is eliminated altogether for the sample with $y = 0.7$. A maximal ΔS_m of -20.3 J kg^{-1} K^{-1} is recorded for the sample with $y = 0.8$ for $\Delta B = 0-2$ T. In the sample with $y = 0.70$, the predominance of the SOMT gives rise to a lower ΔS_m equal to -9.8 J kg^{-1} K^{-1} [Fig. 3(c)]. The variations in c/a ratio, T_c, ΔT_{hys}, $-\Delta S_m$, and relative cooling power (RCP), computed by the Wood and Potter method,[20] for several ribbons with different Mn/Fe ratio are summarized in Table I. The values of adiabatic temperature change (ΔT_{ad}) obtained from pulsed-field and specific-heat measurements are in the same order of magnitude with those of Gd, $Gd_5(Ge,Si)_4$, La(Fe,Si)H, and MnFe(P,As).[21,1,2]

In conclusion, by varying the compositions and annealing conditions, a small ΔT_{hys} and a large MCE were simultaneously obtained in the MnFe(P,Ge) compounds when the magnetic transition is controlled to be close to the border separating the first- and second-order transition regimes. Modification in preparation techniques can therefore play a

very important role when searching for the ideal materials that can be used for magnetic refrigerators operating at T_{room}. In this connection it is worth to mention that we have done experiments with a pulsed-field magnet, verifying that the MnFe(P,Ge) alloys can be used as refrigerants working at high thermal cycling frequencies.[21] The combination of these materials into a multimaterial active magnetic regenerator can enlarge temperature span and produce a higher cooling power.[22] The present finding that ΔT_{hys} of the MnFe(P,Ge) compounds can be suppressed without losing the large MCE in these low-cost materials brings practical magnetic cooling at T_{room} a step closer.[23]

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[23]See EPAPS Document No. E-APPLAB-94-065910 for comparison of magnetization curves obtained either in an adiabatic or isothermal process, the ΔTad of the first-order magnetic transition MnFe(P,Ge) compounds were calculated. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.