Tunable thermal hysteresis in MnFe(P,Ge) compounds

Trung, N.T.; Ou, Z.Q.; Gortenmulder, T.J.; Tegus, O.; Buschow, K.H.J.; Brück, E.

DOI
10.1063/1.3095597

Publication date
2009

Document Version
Final published version

Published in
Applied Physics Letters

Citation for published version (APA):
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. Nowadays, magnetocaloric materials undergoing a first-order field-induced magnetostructural transition are intensively investigated because of their potential applications at room temperature \(T_{\text{room}}\). 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 \(\Delta T_{\text{hys}}\), 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 \(\Delta T_{\text{hys}}\) in the pseudobinary system \(\text{Gd}_6(\text{Si}_{1-x}\text{Ge}_x)_{14}\), which reveals a \(\Delta T_{\text{hys}}\) of 8–10 K. It was found that \(\Delta T_{\text{hys}}\) can significantly be reduced by hydrogen insertion or the addition of 3d elements. 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. concluded that the large \(\Delta T_{\text{hys}}\) 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 \(\Delta T_{\text{hys}}\) value of Cr substituted MnAs are tunable by varying the Cr content. After the discovery of the giant MCE in \(\text{MnFeP}_{1-x}\text{As}_x\), many efforts have been spent to replace As by nontoxic components. Although the introduction of Si and Ge atoms into the lattice of \(\text{MnFeP}_{1-x}\text{As}_x\) retains a giant MCE around \(T_{\text{room}}\), an enhanced \(\Delta T_{\text{hys}}\) was observed. In this letter, we show that it is possible to reduce \(\Delta T_{\text{hys}}\) of \(\text{MnFeP(Ge)}\) without losing the favorable magnetocaloric properties.

Polycrystalline \(\text{MnFeP(Ge)}\) samples were prepared by melt spinning and high-energy ball milling, as described in earlier reports. Bulk samples of \(\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x\) \((x=0.19,0.22,0.25)\) were sintered at \(1100^\circ\text{C}\) for 10 h and then homogenized at \(650^\circ\text{C}\) for 60 h before they were quenched into water at \(T_{\text{room}}\). The sample with \(x=0.25\) was also prepared with quenching from \(1000^\circ\text{C}\). Bulk Mn_{2−y}Fe_{1+y}P_{0.75}Ge_{0.25} \((y=0.84,0.82,0.80,0.74)\) samples were quenched from \(1100^\circ\text{C}\) after 60 h annealing. Mn_{2−y}Fe_{1+y}P_{0.75}Ge_{0.25} \((y=0.80,0.78,0.76,0.70)\) melt-spun ribbons were produced at \(40 \text{m/s}\) surface speed of the Cu wheel. The as-spun ribbons were subsequently quenched into water after annealing at \(1100^\circ\text{C}\) for 15 min. Powder x-ray diffraction (XRD) of the samples was made at \(T_{\text{room}}\) 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 MnFeP(Ge) samples, which is crystallized in the hexagonal Fe$_2$P-type structure (space group $P\overline{6}2m$), is homogeneous. Also, a small amount \((\sim 4 \text{ vol}\%\) of secondary phase Mn$_3$O$_5$ is detected. 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., it is found that the value of \(T_c\) increases about linearly with increasing the Ge concentration, from \(T_c=260 \text{ K}\) for \(x=0.19\) to \(T_c=296\) and \(330 \text{ K}\) for \(x=0.22\) and \(0.25\), respectively. The corresponding values of \(\Delta T_{\text{hys}}\) between the magnetic transitions observed on heating and cooling for \(x=0.19,0.22\), and \(0.25\) are 6, 4, and \(2 \text{ K}\), respectively. For \(\Delta T=0–2 \text{ T}\), the isothermal magnetic entropy changes \((\Delta S_m)\) are \(-13.8, -20\), and \(-13 \text{ J Kg}^{-1}\text{K}^{-1}\) 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 \(1000^\circ\text{C}\) for \(60 \text{ h}\) before quenching into water. The magnetic transition of the sample quenched from \(1000^\circ\text{C}\) (●) is more pronounced,
and the values of $\Delta T_{\text{hys}}$ and $T_c$ are 5 and 320 K, respectively. For this sample, a large $\Delta S_m$ 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 $\Delta T_{\text{hys}}$ 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$_{2-x}$Fe$_x$P$_{0.75}$Ge$_{0.25}$ ($y=0.84, 0.82, 0.80, 0.74$) with various Mn/Fe ratios. Both $T_c$ and $\Delta T_{\text{hys}}$ 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 $\Delta T_{\text{hys}}$ also varies from 5 to 3 and $\sim$0 K, respectively. The temperature dependences of $\Delta S_m$ are presented in Fig. 1(d). The maximal $\Delta S_m$, for a field change $\Delta B=0$ to $2$ 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 $\Delta T_{\text{hys}}$ of MnFe(P,Ge) can even be eliminated, while maintaining a large MCE near $T_{\text{room}}$. It is worth noting that, when increasing the Mn content up to $(2-y)=1.26$, the value of $\Delta T_{\text{hys}}$ almost does not change ($\sim 0$ 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. 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. 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 $\eta$, decreases with increasing the Ge concentration. Therefore, the magnetic transition in the sample with $x=0.25$ accompanied by a small $\Delta T_{\text{hys}}$ 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-

FIG. 1. (Color online) $M$-$T$ curves measured in magnetic field $B=0.5$ T for bulk compounds of Mn$_{2-x}$Fe$_x$P$_{0.75}$Ge$_{0.25}$ (a) and Mn$_{1.1}$Fe$_{0.9}$P$_{1-x}$Ge$_x$ (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$_{2-x}$Fe$_x$P$_{0.75}$Ge$_{0.25}$ (b) and Mn$_{1.1}$Fe$_{0.9}$P$_{1-x}$Ge$_x$ (d). The sample with $x=0.25$ was quenched from 650 °C (△) and 1000 °C (○) for a comparison.
TABLE I. Variations in the lattice parameter ratio $c/a$, critical temperature ($T_c$), thermal hysteresis ($\Delta T_{hys}$), maximal isothermal magnetic entropy change ($-\Delta S_m$), and RCP under the field change $\Delta \theta=0$–$2$ T of Mn$_2$Fe$_{0.75}$Ge$_{0.25}$ melt-spun ribbons compared with that of Gd (after Ref. 4).

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

$^a$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$_2$Fe$_{0.75}$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$_2$Fe$_{0.75}$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$_2$P-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 $T_q=230$ K to $T_q=288$ K, when varying the Mn/Fe ratio, the $\Delta T_{hys}$ 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 $\Delta S_m$ of $-20.3$ J kg$^{-1}$ K$^{-1}$ is recorded for the sample with $y=0.8$ for $\Delta \theta=0$–$2$ T. In the sample with $y=0.70$, the predominance of the SOMT gives rise to a lower $S_m$ equal to $-9.8$ J kg$^{-1}$ K$^{-1}$ [Fig. 3(c)]. The variations in $c/a$, $T_c$, $\Delta T_{hys}$, $-\Delta S_m$, and relative cooling power (RCP), computed by the Wood and Potter method, for several ribbons with different Mn/Fe ratio are summarized in Table I. The values of adiabatic temperature change ($\Delta T_{ad}$) 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)$_{2}$H, and MnFe(P, As).!

In conclusion, by varying the compositions and annealing conditions, a small $\Delta T_{hys}$ 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. The combination of these materials into a multimaterial active magnetic regenerator can enlarge temperature span and produce a higher cooling power. The present finding that $\Delta T_{hys}$ 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.

This work was financially supported by the Dutch Technology Foundation (STW).

23See EPAPS Document No. E-APPLAB-94-065910 for comparison of magnetization curves obtained either in an adiabatic or isothermal process, the $\Delta T$ 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.