From first-order magneto-elastic to magneto-structural transition in (Mn,Fe)\textsubscript{1.95}P\textsubscript{0.50}Si\textsubscript{0.50} compounds

N. H. Dung,\textsuperscript{a} L. Zhang, Z. Q. Ou, and E. Brück

Fundamental Aspects of Materials and Energy (FAME), Faculty of Applied Sciences, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

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We report on structural, magnetic, and magnetocaloric properties of Mn\textsubscript{x}Fe\textsubscript{1.95-x}P\textsubscript{0.50}Si\textsubscript{0.50} (x \geq 1.10) compounds. With increasing the Mn:Fe ratio, a first-order magneto-elastic transition gradually changes into a first-order magneto-structural transition via a second-order magnetic transition. The study also shows that thermal hysteresis can be tuned by varying the Mn:Fe ratio. Small thermal hysteresis (less than 1 K) can be obtained while maintaining a giant magnetocaloric effect. This achievement paves the way for real refrigeration applications using magnetic refrigerants.


Nowadays, advanced magnetocaloric materials often undergo a first-order magnetic transition (FOMT),\textsuperscript{1-4} because the FOMT is associated with an abrupt change in crystal lattice which enhances magnetocaloric effects (MCEs) via a spin-lattice coupling. The FOMT can be divided into first-order magneto-structural transition (FOMST), which exhibits a structure change coupled with a magnetic transition as observed for Gd\textsubscript{5}(Ge\textsubscript{x}Si\textsubscript{1-x})\textsubscript{13} compounds.\textsuperscript{5,6} Ni\textsubscript{0.50}Mn\textsubscript{0.50}Sn\textsubscript{x} (Ref. 7), and MnCoGeB\textsubscript{x},\textsuperscript{8} or first-order magneto-elastic transition (FOMET) for which the crystal structure remains unchanged but the lattice constants suddenly change at the magnetic transition, as observed for MnFeP\textsubscript{1-x}As\textsubscript{x} (Ref. 9) and La(Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{13} compounds.\textsuperscript{10,11}

Fe\textsubscript{2}P-based compounds are known as giant magnetocaloric materials with a FOMET. Most studies have recently focused on (Mn,Fe)\textsubscript{2}(As,Ge) compounds.\textsuperscript{1-3,9,12,13} However, the limited availability of Ge and toxicity of As hold these materials back from real refrigeration applications. Substitution of Si for As and Ge becomes one of the most prominent studies towards making a high performance room-temperature magnetic refrigerant. Some efforts have been made to reduce thermal hysteresis (\(\Delta T_{\text{hys}}\)) which was found to be very large (\(\Delta T_{\text{hys}} \approx 35\) K) in the MnFeP\textsubscript{0.50}Si\textsubscript{0.50} alloy.\textsuperscript{14} Here, we report on (Mn,Fe)\textsubscript{1.95}P\textsubscript{0.50}Si\textsubscript{0.50} compounds when changing the Mn:Fe ratio with emphasis on the behavior of magnetic and structural transitions. We observe a previously unknown FOMST and a modified FOMET favorable for real refrigeration applications.

The (Mn,Fe)\textsubscript{1.95}P\textsubscript{0.50}Si\textsubscript{0.50} alloys were prepared by ball-milling. Proper amounts of Mn (99.9%), Si (99.999%) chips, binary Fe\textsubscript{2}P (99.5%), and red-P (99.7%) powder were mixed and ball-milled for 10 h. The fine powder was then pressed into small tablets and sealed in quartz ampoules in an Ar atmosphere of 200 mbar. The samples were sintered at 1373 K for 2 h and then annealed at 1123 K for 20 h before being oven cooled to room temperature. Magnetic measurements were carried out using the reciprocating sample option (RSO) mode in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 5XL). X-ray diffraction patterns were obtained by a PANalytical X-pert Pro diffractometer with Cu K\textalpha\ radiation, secondary flat crystal monochromator, and X’celerator real time multiple strip (RTMS) detector system.

The room-temperature x-ray diffraction measurements pointed out that all the samples crystallize in the hexagonal Fe\textsubscript{2}P-type structure (space group P-6\textsubscript{2}m). A very small amount of cubic (Mn,Fe)\textsubscript{2}Si (space group Fm\textsubscript{3m}) was also detected and hardly affects the results of magnetic measurements.\textsuperscript{15} The temperature dependence of the magnetization for the Mn\textsubscript{x}Fe\textsubscript{1.95-x}P\textsubscript{0.50}Si\textsubscript{0.50} compounds measured in a field of 1 T is shown in Fig. 1(a). For x < 1.40, the \(M-T\) curves show very sharp ferro–paramagnetic transitions. A clear \(\Delta T_{\text{hys}}\) confirms the first-order nature of these transitions. The \(\Delta T_{\text{hys}}\) can be tuned from 5 K, 2 K to 1 K by varying the Mn:Fe ratio from x = 1.20, 1.25 to 1.30, respectively. Figure 1(b) shows the isothermal magnetic entropy change (\(\Delta S_{m}\)) as a function of temperature under a field change \(\Delta B\) of 0-1 T and 0-2 T for the x = 1.20, 1.25, 1.30, 1.40 samples. Here, the \(\Delta S_{m}\) is calculated using magnetization isotherms through the Maxwell relations.\textsuperscript{4} Apparently, the absolute value of \(\Delta S_{m}\) is lower in the sample with more Mn. However, it should be noted that the x = 1.30 sample which has a very small \(\Delta T_{\text{hys}}\) still displays a large \(\Delta S_{m}\) of 15 J kg\textsuperscript{-1} K\textsuperscript{-1} under a 2 T field change. This value is 4 times higher than that of the benchmark material Gd.\textsuperscript{16}

Figure 1(c) illustrates Arrt plots derived from the magnetization isotherms in the vicinity of the transition temperature for the x = 1.20, 1.25, 1.30, 1.40, and 1.50 samples. The S-shaped magnetization curves revealing relevant high-order terms in the Landau free energy expansion\textsuperscript{13} prove a FOMT for x < 1.40. However, neither a negative slope nor an inflection point is observed for the x = 1.40 and 1.50 samples, confirming a second-order magnetic transition (SOMT). Thus, replacing some Fe with Mn can lower the energy barrier in the FOMT, and the FOMT gradually changes into a SOMT when the energy barrier becomes lower and finally vanishes.
x = 1.20, 1.30, 1.40, and 1.50. For the x = 1.20 and 1.30 samples, a discontinuity of the diffraction peaks at the transition temperature indicates a jump of lattice constants. The sample with larger MCE exhibits a stronger peak shift at the critical temperature. Additionally, the (300) and (002) peaks are shifted in the opposite direction which implies that the lattice constants a and c change in opposite sense. The steep change of lattice constants coupled with the magnetic transition confirms a FOMET. On the other hand, a continuity of the peaks with respect to temperature is observed for the x = 1.40 and 1.50 samples, demonstrating a SOMT. This observation is in good agreement with the results from the Arrot plots.

The ferromagnetic order of the Mn$_x$Fe$_{1.95}$P$_{0.50}$Si$_{0.50}$ compounds remains until Fe is completely replaced by Mn (see Fig. 1(a)). Note that the existence of the $\Delta T_{hys}$ for x $\geq$ 1.90 indicates the reoccurrence of a FOMT. However, structural measurements show that these samples have a different type of FOMT. On cooling below room temperature, we find that the paramagnetic hexagonal phase is transformed into a paramagnetic body-centered orthorhombic (bco) phase (space group Ima2). Further cooling makes this orthorhombic structure transform back into the hexagonal structure in a FOMST. The orthorhombic structure is similar to that found in Fe$_2$(P,Si) compounds. The re-entrant hexagonal structure in the FOMST points to a preference of the ferromagnetism for the hexagonal rather than the orthorhombic structure. Figure 2(b) illustrates the structural transformation on heating for the x = 1.95 sample without Fe. The orthorhombic phase exists over a temperature range from 125 K to 290 K between two ferromagnetic and paramagnetic hexagonal phases. A quite large structural transition zone at which both the hexagonal and orthorhombic phases exist explains why we could not see a sharp magnetic transition in the FOMST (see Fig. 1(a)). The MCE at the FOMST is, therefore, not so large with $|\Delta S_m| \sim 6$ J kg$^{-1}$ K$^{-1}$ under $\Delta B = 0$ T for the Mn$_{1.95}$P$_{0.50}$Si$_{0.50}$ compound.

Since hexagonal Mn$_x$Fe$_{2-x}$P (x > 1.35) is antiferromagnetic, the present study indicates that the Si addition supports a ferromagnetic order. The enhancement of the ferromagnetism by replacing P with Si was also observed in Fe$_2$(P,Si).

Because of a strong coupling between the crystal and magnetic structure, the magnetic-ordering temperature ($T_C$) can be defined as the temperature at which we see a very clear change in tendency of the thermal evolution of the lattice constants or the structure. In some cases of the FOMT, $T_C$ can also be determined from extremes of the first derivative of the isofield magnetization with respect to temperature. Shown in Fig. 3 is the phase diagram of the Mn$_x$Fe$_{1.95}$P$_{0.50}$Si$_{0.50}$ compounds. It is found that the temperature range over which the orthorhombic phase exists becomes narrower and disappears as x is lower than a critical
value which is extrapolated to be about $x = 1.88$. $T_C$ decreases almost linearly with increasing $x$ for the FOMET, gradually for the SOMT, and drops faster in a very narrow composition range of the FOMST. The Mn(3g)–Fe(3f) inter-layer exchange coupling is believed to be responsible for a ferromagnetic order in MnFe(P,Si) compounds.\cite{Bruack2005}

For the Mn-rich compounds, since the Mn atom favors the 3g site, excess Mn enters the 3f site. The reduction of $T_C$ demonstrates that the replacement of Mn for Fe weakens the Mn (3g)–Fe/Mn (3f) inter-layer exchange coupling in the hexagonal Mn-rich compounds. Therefore, the ferromagnetism will be enhanced and $T_C$ of hexagonal Fe$_2$P$_{0.8}$Si$_{0.2}$ with even less Si content (about 510 K) was found to exceed that of the Mn-rich compounds.\cite{Bruack2005, Bruack2008}

In summary, by varying the Mn:Fe ratio, the (Mn,Fe)$_{1.95}$P$_{0.50}$Si$_{0.50}$ compounds change from a FOMET into a FOMST through a SOMT. The study also shows the preference of the hexagonal Fe$_2$P-type structure for the ferromagnetic order and a strong coupling between the crystal and magnetic structure. Although the MCE from the FOMST is not so large, the existence of the FOMST with the re-entrant hexagonal structure is very interesting for further study on exchange coupling in Fe$_2$P-based materials. Moreover, small $\Delta T_{hys}$ with a giant MCE can be achieved in a FOMET favorable for real magnetic refrigeration applications in the near future.

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\begin{thebibliography}{99}
\bibitem{Supplement} See supplemental material at http://dx.doi.org/10.1063/1.3634016 for x-ray diffraction pattern of the Mn$_{1.95}$Fe$_{0.5}$P$_{0.50}$Si$_{0.50}$ compound and magnetic entropy change of the Mn$_{1.95}$P$_{0.50}$Si$_{0.50}$ compound.
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