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Structure, magnetism, and magnetocaloric properties of $MnFeP_{1-x}Si_x$ compounds

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$MnFeP_{1-x}Si_x$ compounds with $x=0.10, 0.20, 0.24, 0.28, \ldots, 0.80, 1$ were prepared by high-energy ball milling and solid-state reaction. The structural, magnetic, and magnetocaloric properties are investigated as a function of temperature and magnetic field. X-ray diffraction studies show that the samples in the range from $x=0.28$ to 0.64 adopt the hexagonal Fe_2P-type structure with a small amount of second phase which increases with increasing Si content. The samples with lower Si content show the orthorhombic Co_2P-type structure. Magnetic measurements show that the paramagnetic-ferromagnetic transition temperatures range from 214 to 377 K. Of much importance is the fact that these compounds do not contain any toxic components and exhibit excellent magnetocaloric properties. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2836958]

I. INTRODUCTION

Magnetic refrigeration has attracted much attention in recent years as a promising and environmentally friendly alternative to conventional gas-compression cooling. Regarding this aspect, promising materials for magnetic cooling are $MnFeP_{1-x}As_x$ compounds,[1] presenting small hysteresis, a large magnetocaloric effect, and easy tunability of the Curie temperature by changing the P/As ratio. However, these compounds contain arsenic which is a known toxic element. Because these compounds are found to be insoluble in concentrated hydrochloric acid, the As is not a problem as long as it is in the compound. However, it may be difficult to avoid releasing of the As component to the environment. Recently, a great deal of efforts has been spent on substituting other elements for As in order to make the compound safer. Partially replacing As by Ge leads to an enhancement of the ordered magnetic moment. However, the extremely strong dependence of the Curie temperature on the Ge concentration may present a problem as a small variation in the composition of the magnetic refrigerant may strongly alter its performance.[2] When partially replacing As by Si,[3] an enhancement of the magnetocaloric effect (MCE) is obtained while keeping a good tunability of the Curie temperature with the Si content. However, the thermal hysteresis is markedly increased, which is unfavorable for magnetic-cooling applications. In MnFe(P,As) compounds, As can be completely replaced by a combination of Si and Ge.[4] The resulting materials show a large MCE near room temperature in low fields. The nonlinear dependence of the Curie temperature on the Si content and the peculiar hysteresis behavior need further study. In this work, we have investigated compounds in which As is totally replaced by the readily abundant, cheap, and nontoxic Si. The structural, magnetic, and magnetocaloric properties of the $MnFeP_{1-x}Si_x$ compounds are presented.

II. EXPERIMENTAL METHOD

Polycrystalline samples of $MnFeP_{1-x}Si_x$ with nominal compositions x ranging from 0.10 to 1 were prepared by high-energy ball milling under Ar atmosphere for one week. The compounds with $x<0.5$ were prepared from Fe_2P and elemental Mn, Si, and P. For all compounds with higher Si contents, Fe powder was used instead of the compound. After milling, the powder was pressed into pellets which were sealed in quartz ampoules under 100–200 mbar Ar atmosphere. Subsequently, the pellets were sintered at 1100 °C for 5 h, followed by annealing at 650 °C for 50 h. Finally, they were slowly cooled down to room temperature or quenched from different temperatures. Powder x-ray diffraction (XRD) of the samples was performed at room temperature in a Philips PW1700 diffractometer with Cu $K\alpha$ radiation. Rietveld refinement was performed using the PHILIPS X'PERT PLUS software. Electron probe microanalysis (EPMA) measurements were performed on some samples in order to obtain further information about their compositions. Magnetic measurements were carried out in a superconducting quantum interference device magnetometer in the temperature range of 5–400 K and in magnetic fields up to 5 T.

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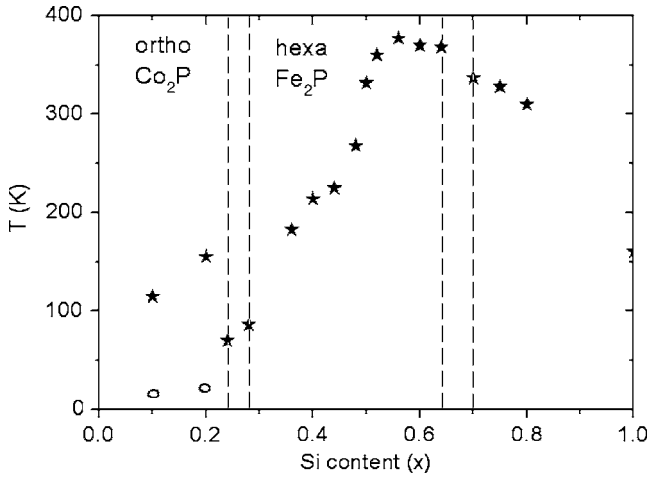

FIG. 1. Composition dependence of the ordering temperature, determined with increasing temperature, of $MnFeP_{1-x}Si_x$ compounds. The filled circles indicate the AFM-FM phase-transition temperatures.

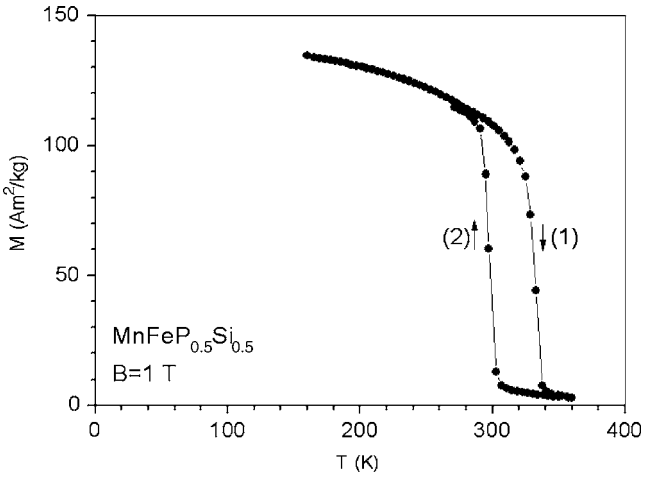

FIG. 2. Temperature dependence of the magnetization of $MnFeP_{0.50}Si_{0.50}$, measured in a field of 1 T. (1) on heating the sample and (2) on cooling the once-cooled sample.

III. RESULTS AND DISCUSSION

Figure 1, which is based on magnetic measurements carried out in a field of 1 T and on XRD patterns taken at room temperature, shows the composition dependence of the ordering temperature and a tentative phase diagram of the $MnFeP_{1-x}Si_x$ system. When the Si concentration is lower than 24%, the compounds crystallize in the orthorhombic Co_2P-type structure. There are two critical temperatures in this region. Initially, the sample is in an antiferromagnetic (AFM) state at low temperature. As the temperature is increased up to the first critical point, the ferromagnetic (FM) state is obtained. The AFM-FM phase transition temperatures are 19 and 25 K for $x=0.1$ and $x=0.2$, respectively. With further increase of temperature, a FM-PM (paramagnetic) phase transition takes place.

We have focused our attention on the composition range of $0.28 \leqslant x \leqslant 0.64$ for which a hexagonal Fe_2P-type structure (space group $P\bar{6}2m$) is obtained. XRD patterns taken on the samples with x between 0.28 and 0.48 reveal that the compounds contain a small amount of second phase which has been identified to be cubic Fe_2MnSi (space group $Fm3m$). The fraction of this phase increases with increasing Si content. EPMA results taken from $x=0.50$ and $x=0.52$ samples indicate that these samples are inhomogeneous. There is about 18% of the second phase $Mn_{1.0}Fe_{2.1}Si_{0.8}$ which is in a good agreement with the XRD results. In the Fe_2P-type structure region, a FM-PM phase transition is observed, and the ordering temperature (T_C) gradually increases with increasing Si concentration from 214 K for $x=0.4$ to 377 K for $x=0.56$. With further increase of the Si concentration, T_C decreases. The dependence of T_C on the Si concentration is unusual, but in good agreement with previous results.[3,4]

Ther XRD patterns of the samples with $x \geqslant 0.64$ show that the structure is no longer hexagonal Fe_2P type. The crystal structure in this region has not yet fully been and is subject of future investigation.

The temperature dependence of the magnetization of the compound $MnFeP_{0.50}Si_{0.50}$ is displayed in Fig. 2. The measurements were carried out in the following way: first the sample is cooled down from room temperature to 150 K in zero field, then the magnetization was measured in a field of 1 T with increasing temperature up to 360 K and, after this, with decreasing temperature down to 270 K. The magnetic transition shows a clear thermal hysteresis as evidence of a first-order transition which is related to a large magnetocaloric effect. The ordering temperature was determined as the temperature where the first temperature derivative of the magnetization has its extreme value. The result, as found on increasing temperature is displayed in Table I. The thermal hysteresis (ΔT_{hys}) between the transitions observed on heating and the second-cooling process for some of the investi-

TABLE I. Variation of the lattice parameters (a and c), c/a ratio, ordering temperature found on increasing temperature, saturation magnetization at 5 K, thermal hysteresis, and isothermal magnetic-entropy change (for a field change of 2 T) in $MnFeP_{1-x}Si_x$ compounds.

x	a (nm)	c (nm)	c/a	T_C (K)	M_S (μ_B/f.u.)	ΔT_{hys} (K)	$-\Delta S_M$ (J kg^{-1} K^{-1})
0.44	0.6022	0.3482	0.5782	225	3.5	37	7
0.48	0.6040	0.3468	0.5742	268	3.6	21	10
0.50	0.6082	0.3431	0.5641	332	3.8	35	30
0.52	0.6111	0.3401	0.5565	360	3.8	23	29
0.56	0.6181	0.3422	0.5536	377	3.7	12	8
0.60	0.6101	0.3502	0.5740	370	3.6	18	20

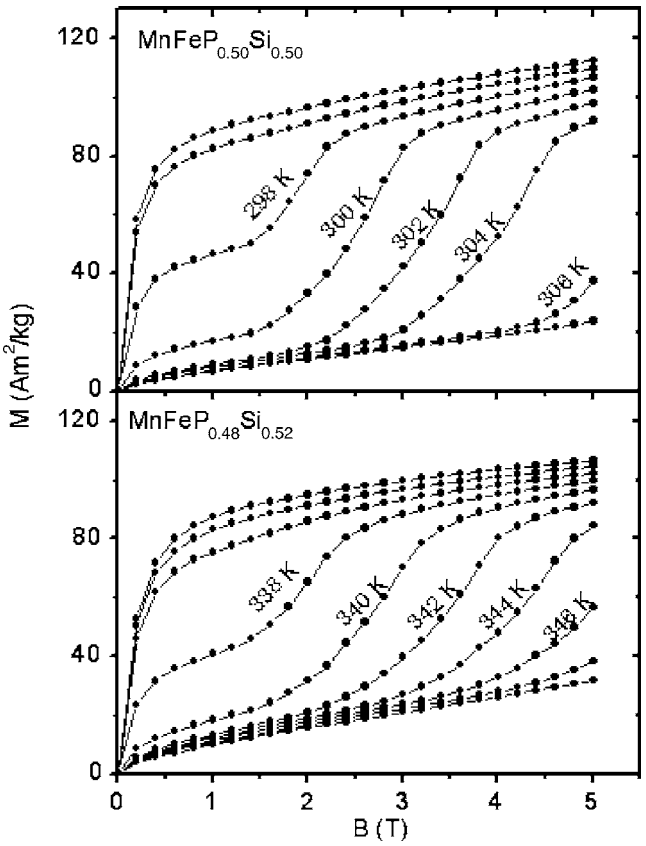

FIG. 3. Isothermal magnetizations of $MnFeP_{0.50}Si_{0.50}$ and $MnFeP_{0.48}Si_{0.52}$, measured with increasing field in the vicinity of the Curie temperature.

gated $MnFeP_{1-x}Si_x$ compounds is displayed in Table I, the values being larger than those for the $MnFeP_{0.5}As_{0.5-x}Si_x$ (Ref. 3) and MnFe(P,Si,Ge) compounds.[4]

The field dependence of the magnetization of the compounds $MnFeP_{0.50}Si_{0.50}$ and $MnFeP_{0.48}Si_{0.52}$ measured with increasing field, are shown in Fig. 3. S-shaped magnetization curves, corresponding to a magnetic field-induced transition, are observed in both the $x=0.50$ and the $x=0.52$ samples. This behavior is similar to that reported for $MnFeP_{1-x}As_x$ compounds (Ref. 5) and $Gd_5(Ge_{1-x}Si_x)_4$ compounds (Ref. 6). From these two measurements, the magnetic-entropy change can be derived by using the Maxwell relation,[6–8]

$$\left(\frac{\partial S_M}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B.$$

Figure 4 displays the temperature dependence of the magnetic-entropy change $(-\Delta S_M)$ for the compounds $MnFeP_{0.50}Si_{0.50}$ and $MnFeP_{0.48}Si_{0.52}$. The calculated maximum values of $-\Delta S_M$ for $x=0.50$ sample are 14, 30, and 42 J kg^{-1} K^{-1} for field changes from 0 to 1 T, 0 to 2 T, and 0 to 3 T, respectively. The values for $x=0.52$ are 14, 29, and 37 J kg^{-1} K^{-1}. Compared with $MnFeP_{0.5}As_{0.5-x}Si_x$ and related compounds, it is interesting that we have achieved larger $-\Delta S_M$ values, especially when considering that these

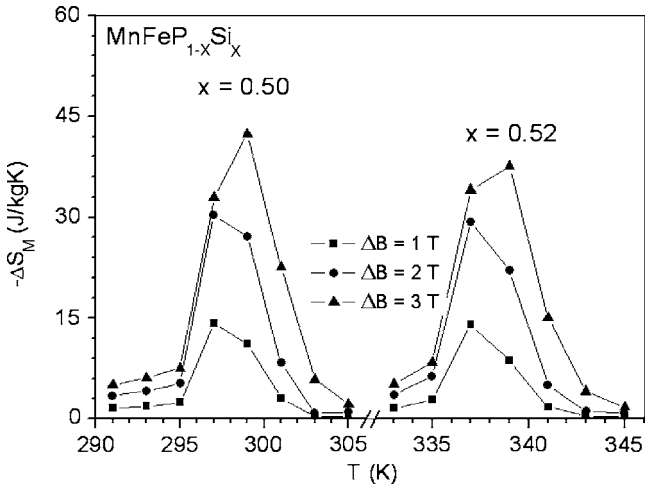

FIG. 4. Magnetic-entropy change of $MnFeP_{0.50}Si_{0.50}$ and $MnFeP_{0.48}Si_{0.52}$.

values are found in compounds containing safe and cheap components, although with a much larger thermal hysteresis.

IV. CONCLUSIONS

We have studied the structural, magnetic, and magnetocaloric properties of $MnFeP_{1-x}Si_x$ compounds. The structures were found to be of the hexagonal Fe_2P type in the range from $x=0.28$ to 0.64, and the orthorhombic Co_2P type for $x \leqslant 0.24$. We have achieved large magnetocaloric effects for $x=0.50$ and $x=0.52$. However, more efforts should be done to make samples with better homogeneity. The MnFe(P,Si) samples in the investigated range have large thermal hysteresis values which imply difficulties for cooling cycles. Although the samples have large MCEs, for some of them they are accompanied by comparatively high working temperatures which may be useful for heat-pumping applications.

ACKNOWLEDGMENTS

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