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Mössbauer spectroscopy study on the magnetic transition in $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$

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The magnetic transition has been studied in $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ by magnetic measurements and ^{57}Fe Mössbauer spectroscopy. The alloy crystallizes in the hexagonal Fe_2P-type structure with lattice constants of $a=6.0476(4)$ Å and $c=3.4766(7)$ Å. Both bulk magnetization measurements and Mössbauer spectroscopy show that the as-prepared sample has a significantly lower transition temperature on first cooling ($T_C^1 \approx 200$ K) than after it has undergone thermal cycling to 20 K ($T_C^{20\text{ K}}=240$ K). The behavior of the material stabilizes after the first cooling/heating cycle and no further changes are observed in T_C. Working with a stabilized sample, we find that the temperature dependence of the hyperfine field, $B_{hf}(T)$, is more rapid than that predicted by a simple mean field Brillouin function, and in addition, $B_{hf}(T)$ shows a thermal hysteresis of 10 K upon cooling versus heating. These results show that the magnetic transition at T_C is definitely first order and suggest that there is an additional irreversible magnetostructural change during the first cooling process of the as-prepared sample. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3067496]

I. INTRODUCTION

Room temperature magnetic refrigeration, based on the magnetocaloric effect (MCE), has attracted much attention because of its energy saving potential and being environmentally friendly.[1–4] Some $MnFeP_{1-x}As_x$ with the hexagonal Fe_2P-type structure show a large MCE, related to a first order magnetic transition around their Curie temperature T_C.[5] In addition, T_C of $MnFeP_{1-x}As_x$ can be tuned between 168 and 332 K by changing P/As ratio between 1.5 and 0.5 without losing the large MCE. $MnFeP_{1-x}(Si,Ge)_x$ with an Fe_2P-type structure show MCE as large as that of $MnFeP_{1-x}As_x$,[6–9] and are environmentally friendly materials because of the replacement of the toxic arsenic by germanium and/or silicon. The large MCE originates from a field induced first order magnetostructural transition in the MnFe(P,Si,Ge) compounds. Better knowledge of the magnetostructural transition will be helpful in understanding and improving the magnetocaloric properties of these materials. The first order magnetic transition has been studied by neutron diffraction and ^{57}Fe Mössbauer spectroscopy in $MnFeP_{1-x}As_x$.[10–12]

Up to now, no further research results have been reported on $MnFeP_{1-x}Ge_x$ except for some magnetic measurement results.[7–9,13] As part of our work on magnetocaloric materials, we investigate the magnetocaloric compound $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ using Mössbauer spectroscopy.

II. EXPERIMENTAL METHODS

Polycrystalline sample with a nominal composition of $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ was prepared by the spark plasma sintering (SPS) technique. Mn powder (99.99 wt %), Fe powder (99.99 wt %), red P powder (99.3 wt %), and Ge powder (99.9999 wt %) were mixed and alloyed via a high energy ball milling process. The milled powders were collected into a graphite mold and consolidated into bulk sample. The SPS sample preparation details have been reported elsewhere.[14] The crystal structure was checked by powder x-ray diffraction with a Cu $K\alpha$ radiation. The unit cell dimensions and other structural parameters were refined by Rietveld fitting method using the GSAS code.[15] Magnetic measurements were carried out in a Quantum Design physical properties measurement system.

The Mössbauer spectra for the $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ sample were obtained in a standard transmission geometry with a 1 GBq ^{57}CoRh source on a constant acceleration spectrometer, which was calibrated against an α-iron foil at room temperature. A vibration-isolated closed cycle refrigerator was used to obtain temperatures between 20 and 300 K. Spectra were fitted using a standard nonlinear least-squares minimization method.

III. RESULTS AND DISCUSSION

As expected, x-ray diffraction analysis confirmed that the alloy $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ crystallizes in the hexagonal Fe_2P type structure with space group $P\bar{6}2m$ except for a small amount of impurity MnO (less than 1%), which probably originated from the starting materials or from the oxidation of Mn during the preparation process. The lattice constants are $a=6.0476(4)$ Å and $c=3.4766(7)$ Å for the main phase. Rietveld fitting indicates that the Mn atoms fill the $3g$ sites and part of the $3f$ sites while the Fe atoms occupy the

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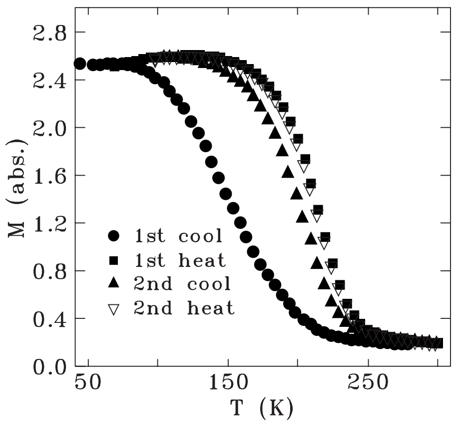

FIG. 1. Temperature dependence of magnetization, $M(T)$, for $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ under a magnetic field of 10 mT.

rest of the $3f$ sites. P and the Ge atoms randomly occupy the $2c$ and $1b$ sites.

Figure 1 displays the temperature dependence of magnetization, $M(T)$, for $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$. With decreasing temperature, a paramagnetic-ferromagnetic (PM-FM) transition starts at about 200 K for the as-prepared sample and ends at about 100 K. These results imply that this magnetic transition may co-occur with a structural change and may need a very large overcooling as driving force. After it has undergone thermal cycling to 20 K, the ferromagnetic to paramagnetic (FM-PM) transition will be completed at about 240 K during the subsequent warming process. For the second thermal cycle, the PM-FM transition starts at about 230 K during cooling process while FM-PM transition ends at 240 K during heating process. Further thermal cycles have no effect on T_C. In other words, the as-prepared sample shows a significantly lower transition temperature on first cooling ($T_C^1 = 200$ K) than after it has undergone thermal cycling to 20 K ($T_C^{20\text{ K}} = 240$ K). A similar effect of T_C is also observed in $MnFeP_{1-x}Si_x$ and $MnFe(P,Ge)_{0.89}Ge_{0.11}$.[6,7]

In order to gain more insight on the magnetic transition in $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$, the temperature dependent Mössbauer spectra were measured. Figure 2 displays the Mössbauer spectra for the as-prepared $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ sample during cooling process. At 200 K, the magnetic subspectrum appears. From 200 to 180 K, there is a coexistence of magnetic and PM subspectra, a sign of a first-order magnetic transition. The spectra are very broadened during the above temperature range. All the magnetic Mössbauer spectra (lower than 180 K) could be fitted with two Lorentz line shaped magnetic sextets with hyperfine fields of about 20 T and one Gaussian-broadened magnetic sextet with a hyperfine field of about 10 T. The main difference between the two Lorentz line shaped magnetic sextets are their different quadrupole shifts.

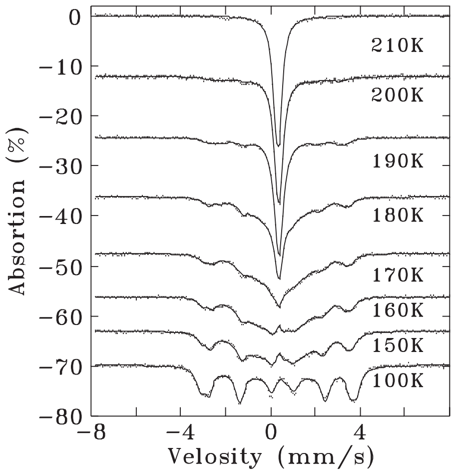

FIG. 2. Temperature dependence of Mössbauer spectra for the as-prepared $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ during cooling process.

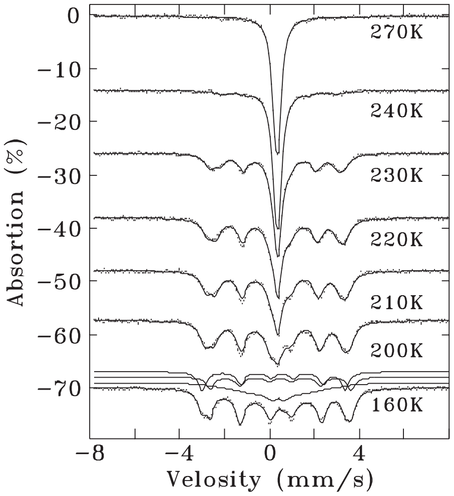

FIG. 3. Temperature dependence of Mössbauer spectra for $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ during warming process after cooling to 20 K.

Figure 3 shows the Mössbauer spectra for $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ during the subsequent warming process. The magnetic sextets disappear around 240 K. The magnetic sextets coexist with PM doublet between 200 and 230 K. In this temperature range, the spectra are simply the sum of magnetic sextets and PM doublet, not as the broadening behavior in the first cooling process (Fig. 2). For further thermal cycles, the Mössbauer spectra show the same feature as that in Fig. 2. As an example, the decomposed subspectra at 160 K are also displayed in Fig. 3. It includes two Lorentz line shaped magnetic sextets and one Gaussian-broadened magnetic sextet.

Figure 4 displays the temperature dependence of the hyperfine field B_{hf} and the absorption area of the PM doublet for the $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ compounds. As mentioned above, the fitted magnetic spectra have two Lorentz magnetic sextets and one Gaussian-broadened magnetic sextet. For clarity, $B_{\text{hf}}(T)$ for the Lorentz magnetic sextet with the smaller quadrupole shift is not shown. As shown in Fig. 4, the hyperfine field of the Lorentz magnetic sextets $[B_{\text{hf}}^L(T)]$ has the same behavior as the magnetic measurement results (Fig. 1). The temperature dependence of the absorption area of the doublet is well in agreement with the magnetic measurement results. The derived T_C from $B_{\text{hf}}^L(T)$ curves are 195, 245, and 235 K for the first cooling, first warming, and second cooling curves, respectively, which are, within error, the same as the magnetic measurement results. The virgin effect of T_C, confirmed by magnetic measurements and Mössbauer spectros-

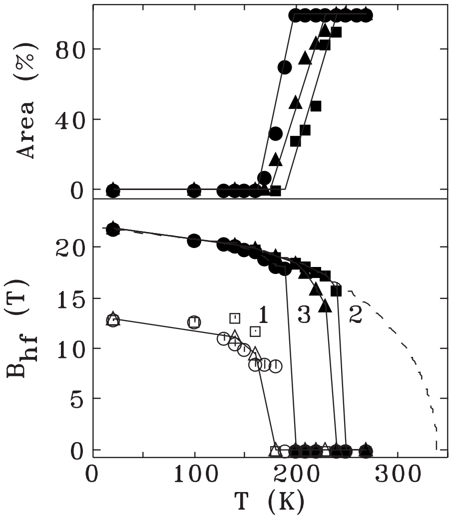

FIG. 4. Temperature dependence of hyperfine field for $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$. The curves 1 (circle), 2 (triangle), and 3 (square) stand for data measured in the cooling, heating, and second cooling processes. Solid and open symbols are for $B_{hf}^{L}(T)$ and $B_{hf}^{G}(T)$, respectively. The dashed line is calculated using BF while the solid line is drawn as a guide to the eyes.

copy, implies the occurrence of an irreversible magnetostructural change during the first cooling process of the as-prepared sample.

It should be noted that $B_{hf}^{G}(T)$ for the Gaussian-broadened magnetic sextet shows no virgin effect with a transition temperature of about 180 K although the sample has an almost single phase with the Fe_2P-type structure except for a small amount of MnO (1 wt %) based on the powder x-ray diffraction results. These results indicate that there may exist complex and competing magnetic exchange interactions. To clarify the magnetic structure in the compound, further works such as neutron diffraction are highly needed.

There is an approximately linear correlation between the mean hyperfine field $B_{hf}(T)$ and the mean magnetic moment. $B_{hf}(T)$ could thus be expressed based on a mean field theory using a Brillouin function (BF) with $J=\frac{1}{2}$, $B_{1/2}(x)=2\coth(2x)-\coth(x)$, and $x=(B_{hf}(T)^{*}T_C)/(B_{hf}(0)^{*}T)$, as

$$B_{hf}(T)=B_{hf}(0)B_{1/2}(x). \tag{1}$$

The BF T_C could be derived by fitting the measured $B_{hf}(T)$, wherein the fitting details have been reported elsewhere.[16]

As shown in Fig. 4. $B_{hf}(T)$ can be fitted very well using the BF relation. However, with increasing temperature, $B_{hf}(T)$ changes more sharply than that predicted by the BF relation near T_C. This behavior confirmed the occurrence of a first-order FM-PM transition. This is also the main reason that $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ has a large magnetic entropy change near T_C.

In summary, $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$ with the hexagonal Fe_2P-type structure shows complex magnetic behavior. Both bulk magnetization measurements and Mössbauer spectroscopy indicate that the as-prepared sample has a significantly lower transition temperature on first cooling ($T_C^1=200$ K) than after it has undergone thermal cycling to 20 K ($T_C^{20\ \mathrm{K}}=240$ K). The temperature dependence of the hyperfine field, $B_{hf}(T)$, is more rapid than that predicted by a simple mean field BF, which is responsible for the large MCE. These results show that the magnetic transition at T_C is definitely first order and suggest that there is an additional irreversible magnetostructural change during the first cooling process of an as-prepared sample. To clarify the magnetic structure in the compound, further works such as neutron diffraction are highly needed.

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