

Neutron diffraction study of the magnetic refrigerant $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$

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Polycrystalline $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ was prepared by mechanical alloying and spark plasma sintering. Neutron diffraction was used to determine the structure of the title compound, and its nuclear and magnetic structures were refined using the Rietveld method. It is found that temperature and magnetic field can induce phase transition between the paramagnetic and the ferromagnetic phases in the material, and the paramagnetic and ferromagnetic phases have very distinct crystal structures and different Ge contents. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3478986]

Key words: neutron diffraction, crystal structure, magnetic refrigerant

I. INTRODUCTION

Magnetic refrigeration discovered by Warburg in 1881 is based on the magnetocaloric effect (MCE). Tegus *et al.* (2002) discovered the hexagonal $\text{MnFe}(\text{PAs})$ compound for room-temperature applications, which has a first-order phase transition and exhibits a huge MCE. However, there are some problems to use $\text{MnFe}(\text{PAs})$ as refrigerant because As is a toxic element. Recently, it was found that by replacing As with Ge and Si in $\text{MnFe}(\text{PAs})$, a large MCE can also be achieved near room temperature (Tegus *et al.*, 2005; Brück *et al.*, 2004; Cam Thanh *et al.*, 2006; Dagula *et al.*, 2006; Ou *et al.*, 2006). Moreover, the Curie temperature can be adjusted by changing the content of Ge or Si. Liu *et al.* (2009) reported that the compound $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.8}\text{Ge}_{0.2}$ has a value of MCE of 75 J/kg K. However, the Curie temperature of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.8}\text{Ge}_{0.2}$ was reported by Yue *et al.* (2009) to be below room temperature at about 253 K. In this study, a $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ sample was prepared by mechanical alloying and spark plasma sintering (SPS) to enhance the Curie temperature to the room-temperature range. The crystal structure of the title compound was investigated by neutron diffraction.

II. EXPERIMENTAL

The starting materials for the polycrystalline sample used in this work, pure Mn (>99.99%), Fe powders (>99.99%), red P (>99.3%), and Ge chips (>99.9999%), were submitted to ball milling, which was carried out under argon atmosphere for 1.5 h in a high-energy pulverisette 4 mill. Then, the milled powders were collected into a graphite mold and consolidated into a $\varnothing 20 \text{ mm} \times 5 \text{ mm}$ wafer at 1203 K under 30 MPa by SPS.

Neutron powder-diffraction (NPD) data were collected at the NIST Center for Neutron Research on a high-resolution powder neutron diffractometer (BT1) with monochromatic neutrons of wavelength 1.5403 Å produced by a Cu (311) monochromator. Data of the nuclear and magnetic structures were refined by the Rietveld method using the General Structure Analysis System (GSAS).

A TA Instrument differential scanning calorimetry (DSC) Q200 was used for calorimetric measurements. Nitrogen gas with a flow rate of 50 ml/min was purged into the cell. The sample with about 30 mg was investigated by heating at the rate of 1 K/min between 190 and 320 K.

III. RESULTS AND DISCUSSION

Neutron diffraction analysis of the $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ compound reveals that the compound is single phase and paramagnetic (PM) at higher temperatures and ferromagnetic (FM) at lower temperatures, and in between the system goes

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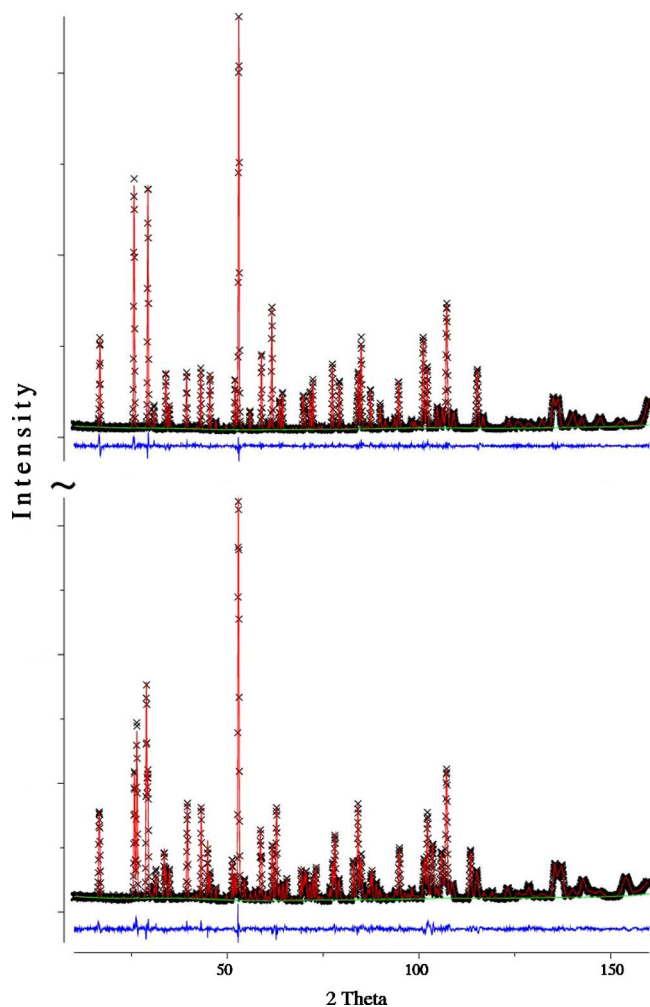


Figure 1. (Color online) Refined NPD patterns for $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ sample collected at room temperature (upper panel) and 267 K (lower panel).

through a strongly first-order phase transition. The transition can be induced by either temperature or applied magnetic field. Both phases have the same symmetry space group ($P\bar{6}2m$).

Figure 1 shows the neutron powder-diffraction patterns for the $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ sample measured at room temperature (upper panel) and 267 K (lower panel). The upper panel displays a fit with only the nuclear structure model of the PM phase. The lower panel depicts a fit by including the PM phase as well as a ferromagnetic phase with its moments in the a - b plane. The refined data are given in Table I.

The crystal structure of the FM phase is shown in Figure 2. It has the Fe_2P -type hexagonal structure with space group $P\bar{6}2m$, and the symmetry of the magnetic structure is $P11m'$. The Mn atoms are coplanar with the P/Ge(1) atoms, and the Fe/Mn atoms are coplanar with P/Ge(2). The Mn atoms are surrounded by four P/Ge(2) atoms located on above and below and by one apical P/Ge(1) atom on the same layer, forming a pyramid. The Fe/Mn site is coordinated by two P/Ge(2) atoms located on the same layer and two P/Ge(1) atoms in the layers above and below, forming a tetrahedron. The tet-

TABLE I. Results on Rietveld-refinement analysis of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$ NPD patterns measured at RT and 267 K (space group $P\bar{6}2m$ and $z=3$).

Atom ^a	Parameters	RT		267 K	
		PMP	PMP	FMP	FMP
		95.45%	42.0(9)%	51.6(3)%	
	a (Å)	6.077 05(5)	6.081 80(8)	6.155 85(7)	
	c (Å)	3.456 13(4)	3.446 56(6)	3.364 04(1)	
	V (Å ³)	110.537(2)	110.40(4)	110.40(0)	
Fe1 (3f site)	x	0.252 709	0.253 790	0.254 358	
	Occupancy	0.921	0.932	0.943	
	B (Å ²)	1.13(3)	0.82(1)	0.82(1)	
	M (μ_B)			1.027	
Mn1 (3f site)	x	0.252 709	0.253 790	0.254 358	
	Occupancy	0.079	0.068	0.057	
	B (Å ²)	0.94(9)	0.82(1)	0.82(1)	
	M (μ_B)			3.020	
Fe2 (3g site)	x	0.592 747	0.592 944	0.596 507	
	Occupancy	0.021	0.001	0.004	
	B (Å ²)	0.77(6)	0.82(1)	0.82(1)	
	M (μ_B)			1.027	
Mn2 (3g site)	x	0.592 747	0.592 944	0.596 507	
	Occupancy	0.979	0.999	0.996	
	B (Å ²)	0.94(9)	0.82(1)	0.82(1)	
	M (μ_B)			3.020	
P1(1b site)	B (Å ²)	0.62(3)	0.55(2)	0.55(2)	
	Occupancy	0.086	0.935	0.85	
Ge1(1b site)	B (Å ²)	0.57(5)	0.55(2)	0.55(2)	
	Occupancy	0.024	0.065	0.15	
P2(2c site)	B (Å ²)	0.48(6)	0.55(2)	0.55(2)	
	Occupancy factor	0.751	0.694	0.703	
Ge2(2c site)	B (Å ²)	0.57(5)	0.55(2)	0.55(2)	
	Occupancy factor	0.249	0.306	0.293	
	R_p (%)	4.26		3.94	
	R_{wp} (%)	5.41		5.13	
	χ^2	1.395		2.513	

^aThe Wyckoff positions for space group ($P\bar{6}2m$) at the 3f site are $(x,0,0)$, $(0,x,0)$, and $(-x,-x,0)$, at the 3g site are $(x,0,1/2)$, $(0,x,1/2)$ and $(-x,-x,1/2)$, at the 2c site are $(1/3,2/3,0)$ and $(2/3,1/3,0)$, and at the 1b site is $(0,0,1/2)$.

rahedra share edges with each other and share corners with the nearest pyramids. The intraplane transition metals form a triangular configuration.

At room temperature the sample is in the PM phase and there is no magnetic order. The Rietveld-refinement results show that the sample contains a small amount of impurity phases (4.54% MnO and $\text{Fe}_3\text{Mn}_4\text{Ge}_6$). The Mn/Fe ratio is

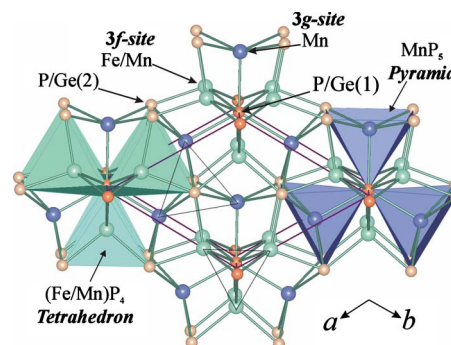


Figure 2. (Color online) Crystal structure of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.76}\text{Ge}_{0.24}$.

1.058/0.942, very close to the nominal value of Mn/Fe = 1.1/0.9. As shown in Table I, the 3*g* site has 97.9% Mn and only 2.1% Fe atoms, while the 3*f* site has 92.1% Fe and 7.9% Mn atoms. The Ge atoms prefer the 2*c* site (24.9% Ge) to the 1*b* site (2.4% Ge).

Refined diffraction data at 267 K show that 42.09% of the PM phase, 51.63% of the FM phase, and 6.28% impurities (MnO and Fe₃Mn₄Ge₆ mainly) coexist. The unit-cell parameters for the PM phase are as follows: $a=b=6.08180$ Å, $c=3.44656$ Å, and $V=110.40$ Å³. For the PM phase, the 3*g* site has 99.9% Mn and only 0.1% Fe atoms, while the 3*f* site has 93.2% Fe and 6.8% Mn atoms. The 2*c* site has 69.4% P and 30.6% Ge atoms, while the 1*b* site has 93.5% P and 6.5% Ge atoms (see Table I). The actual composition of the PM phase was calculated to be Mn_{1.067}Fe_{0.933}P_{0.774}Ge_{0.226}.

The crystal structure of the FM phase is different from that of the PM phase for the Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24} sample at 267 K. The crystal-structure parameters of the PM phase are as follows: $a=b=6.15585$ Å, $c=3.36404$ Å, and $V=110.4$ Å³. The 3*g* site has 99.6% Mn and only 0.4% Fe atoms, while the 3*f* site has 94.3% Fe and 5.7% Mn atoms. The 2*c* site has 70.3% P and 29.7% Ge atoms, while the 1*b* site has 85% P and 15% Ge atoms (see Table I). The actual calculated composition of the FM phase is Mn_{1.053}Fe_{0.947}P_{0.752}Ge_{0.248}. Combining the FM and the PM phases, we have found that the actual composition of the whole sample is Mn_{1.06}Fe_{0.94}P_{0.762}Ge_{0.238}, which is very close to the nominal composition of Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24}. It should be noted the FM phase has a higher Ge content than that of the PM phase. The refined data reveal that the ferromagnetic structure has Mn and Fe moments parallel in the *a-b* plane at 267 K. The ferromagnetic moments are 3.02μ_B and 1.027μ_B for the Mn and the Fe atoms, respectively. The *a* axis of the FM phase is larger, while the *c* axis is smaller than those of the PM phase. However, the unit-cell volumes for these two phases are practically the same.

Figure 3 shows the continuous-heating DSC curve for Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24} alloy. An obvious endothermic peak is shown in the graph, which corresponds to the reaction process from the FM phase to the PM phase. It reveals that the transition from the FM phase to the PM phase is a first-order phase transition and the Curie temperature of Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24} is ~278 K, indicating that Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24} is superior to be used as a room-temperature magnetocaloric material compared to the Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2} compound with a T_C of 253 K reported by Yue *et al.* (2009).

IV. CONCLUSION

Polycrystalline Mn_{1.1}Fe_{0.9}P_{0.76}Ge_{0.24} prepared by mechanical alloying and spark plasma sintering has a T_C at about 278K. The neutron powder-diffraction measurements

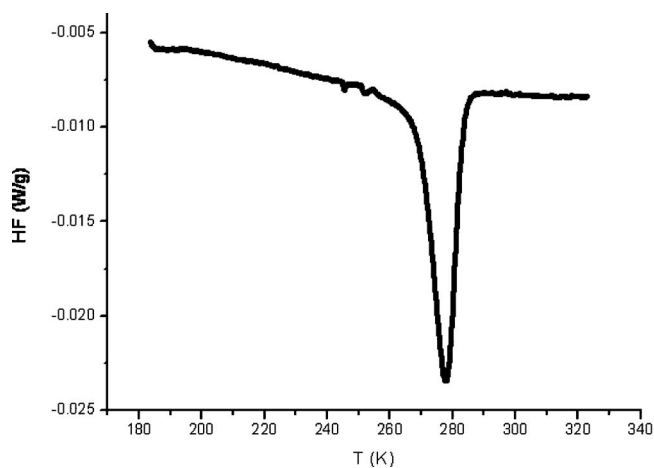


Figure 3. DSC heat flow.

reveal that the FM and the PM phases have two very distinct crystal structures and different Ge contents after a phase change induced by a temperature change. Compared to the PM phase, the *a* axis of the FM phase is relatively larger and the *c* axis is smaller. The volumes of the unit cell for these two phases are practically the same.

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