Magnetic Field Effect on Structural Property of MnFeP$_{0.5}$As$_{0.5}$

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The magnetic field effect on the structural property of a ferromagnetic compound MnFeP$_{0.5}$As$_{0.5}$ was investigated by powder X-ray diffraction measurement in magnetic fields up to 5 T. The compound with the hexagonal Fe$_2$P-type structure shows a field-induced isostructural transformation with a hysteresis by applying magnetic field, accompanied by the metamagnetic transition from the paramagnetic to ferromagnetic state just above the Curie temperature of 284 K. In this transformation, the $a$ parameter expands by 0.5% whereas the $c$ parameter contracts by 1%. However, the cell volume slightly and continuously decreases with increasing magnetic field through the transformation.

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1. Introduction

The phosphide-arsenide compound MnFeP$_{1-x}$As$_x$ ($0.15 \leq x \leq 0.66$) with the hexagonal Fe$_2$P-type structure exhibits unique magnetic and structural properties, which strongly depends on the P/As concentration.$^{1,2}$ The compound with $0.15 \leq x \leq 0.26$ is an antiferromagnet with the Néel temperature of about 180 K. For the As concentration of $0.26 \leq x \leq 0.66$, the compound shows a first-ordered magnetic phase transition from a ferromagnetic (FM) to either a paramagnetic (PM) or an antiferromagnetic (AF) state, accompanied by an isostructural transformation.$^{1,2}$ In this As concentration, this ordering temperature increases from 200 to 350 K with increasing $x$.$^{1,2}$ A neutron diffraction study for MnFeP$_{0.5}$As$_{0.5}$ showed that the Mn atoms occupy the 3g sites and the Fe atoms occupy the 3f sites, but the P and the As atoms are statistically distributed over the 2c and 1b sites in the hexagonal Fe$_2$P-type structure (P-62m) (see Fig. 1). In this structure, the Fe(3f) atom is in the tetrahedral site with four P/As atoms, and the Mn(3g) atom is in the pyramidal site with five P/As atoms as nearest neighbors. However, the results of the neutron diffraction experiment showed that the Fe(3f)–Fe(3f) interatomic distance is the most sensitive to the magnetic phase transition, compared to other interatomic distances among Fe, Mn, P and As.$^{3,4}$

Moreover, recently, MnFeP$_{1-x}$As$_x$ with $x \sim 0.5$ has attracted interest as a magnetic refrigeration materials, because the compound exhibits a large magnetocaloric effect at room temperature, accompanied by the first-order magnetic phase transition.$^{3,4}$ It is considered that magnetic properties of MnFeP$_{1-x}$As$_x$ closely relate to the structural properties, as mentioned above. Therefore, it is very important that we reveal the structural properties in magnetic field, because the magnetic refrigeration materials will be utilized by controlling magnetic field.

In this study, in order to clarify the relationship between the magnetic and the structural properties of MnFeP$_{1-x}$As$_x$ with $x \sim 0.5$ in magnetic field, we have carried out powder X-ray diffraction measurements for MnFeP$_{0.5}$As$_{0.5}$ under magnetic fields up to 5 T in the wide temperature range from 8 to 300 K.

2. Experimental

The polycrystalline sample of MnFeP$_{0.5}$As$_{0.5}$ was prepared by the following procedure. Powders of Mn (99.99%) and Fe (99.99%), and grains of P (99.9999%) and As (99.9999%) were mixed in desired proportion, and sealed in an evacuated silica tube. The mixture was slowly heated up to 1223 K and annealed for 3 days. The reaction product was pulverized, remixed and annealed under the same conditions. Furthermore, the same treatment was repeated twice to obtain a homogenized sample with a single phase. The obtained powder sample was confirmed to be a single phase with the hexagonal Fe$_2$P-type structure by powder X-ray diffraction measurement at room temperature.

The magnetic transition temperature was determined by the temperature dependence of AC initial permeability $\mu$. Magnetization measurement is performed for the powder sample using a vibrating sample magnetometer in the magnetic fields $\mu_0H$ up to 13 T at the temperature $T$ ranging from 4 to 300 K. In this measurement, the powder was fixed in a sample holder using a nonmagnetic wax after measuring.

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the mass. A powder X-ray diffraction experiment with Cu Kα radiation was carried out at 8.6 ≤ T ≤ 293 K in magnetic fields up to 5 T. The powder sample was fixed with vacuum grease on a copper sample holder. The diffraction data was taken at 20° ≤ 2θ ≤ 90° with a step size of 0.01°. We confirmed that the powder sample was not removed by the magnetic force until the measurement in high fields was completed. For determining the X-ray reflection line indexes and the crystal structure at several temperatures, the observed diffraction profiles were analyzed by comparison with simulation profiles using a Rietveld program (RIETAN). The temperature and magnetic field dependences of the lattice parameters were determined from the 300 and the 212 peak positions.

3. Results and Discussion

Figure 2 shows the magnetic moment M vs. H curves of MnFeP0.5As0.5 at the vicinity of Tc and 4 K. From measurement of μ−T curve, Tc is determined to be 284 K for this sample, and the magnetic phase transition is of a first order with a thermal hysteresis, as shown in the inset of Fig. 2. A metamagnetic transition from the PM to field-induced ferromagnetic (FFM) state is clearly seen in the magnetization process at 285 K (just above Tc) and 290 K with a hysteresis. The metamagnetic transition fields are estimated to be μ0Hmi = 1.0 T for increasing the field and μ0Hmd = 0.8 T for decreasing the field at 285 K. The transition fields increase with increasing T from Tc, and the hysteresis was not clearly observed above 300 K. The magnetic properties of MnFeP0.5As0.5 are in good agreement with previous reports.

In Fig. 3, we show the typical results of the X-ray diffraction profiles in 50.5 ≤ 2θ ≤ 54.0° under a zero field and 5 T at several temperatures. Here, hkl_PM, hkl_FM and hkl_FFM denote the Miller indices in the PM, FM and FFM phases, respectively. In this figure, the reflections by Kα1 and Kα2 radiations are detected. Below 270 K in the PM state, we observed the 300_PM, 211_FM and 002_FM reflection peaks. In a zero field, the 002_PM peak shifts to the higher 2θ angle side with decreasing T, indicating the decrease of the c parameter. In contrast, the 300_PM peak does not clearly shift, indicating that the a parameter is almost constant against T in the low temperature region. In addition, by applying a magnetic field, the profiles do not drastically change, but the 002_PM peak slightly shifts to the higher 2θ angle side, indicating that c slightly decreases with increasing H in the FM phase.

On the other hand, the profile at 280 K is deformed compared to that at 270 K, which is probably due to a structural transformation. At 285 K in the PM phase, the profile is different from that for the FM phase. From the detailed measurement in 20° ≤ 2θ ≤ 90° for the PM and the FM phases, we confirmed that the compound exhibits an isostuctural transformation with the Fe2P-type structure at the vicinity of Tc. That is, the 002_PM peak merges with the 111_FM peak at 2θ = 52.4° in the PM phase (T = 285 K) under a zero field. Furthermore, we observed that the profile drastically changes and is similar to the profiles of the FM state by applying fields up to 5 T. This is consistent with the metamagnetic transition from the PM to the FFM state at this temperature.

Figure 4 shows the temperature dependence of a and c and the unit cell volume V under μ0H = 0 and 5 T. With cooling from 300 K in a zero field, a abruptly increases at Tc, and then it seems to be almost constant for T below 150 K. On the contrary, c decreases abruptly at Tc, and then it gradually decreases with decreasing T. At Tc, V also abruptly contracts...
by $\Delta V/V = 0.44\%$, accompanied by the magnetic phase transition from the PM to FM phase. In the FM phase, it seems that $V$ decreases with cooling as a normal thermal contraction but expands abruptly in the PM phase. In contrast, $a$, $c$ and $V$ under 5 T continuously vary from 8 (FM phase) to 290 K (FFM phase), indicating that the FFM state is similar to the FM state.

Figure 5 shows the XRD profiles in 50.5 $\leq 2\theta \leq 54.0^\circ$ at 285 K for increasing and decreasing $H$. With increasing $H$ from 0 T, the intensity of the peaks for the PM phase ($hkl_{PM}$) becomes weaker and is not observed above 3 T. In contrast, the reflection peaks of the FFM phase ($hkl_{FFM}$) appear and develop above 1 T, and then the single phase of the FFM is formed above 3 T. The two-phase coexistence consisting the PM and the FFM phases is observed in 1 $\mu_0 H \leq 3$ T for increasing $H$. In decreasing $H$ from 5 T, the two-phase coexistence is not seen even in 2 T but is observed in 1 T. The profiles show the small hysteresis for magnetic field, which is consistent with the magnetization curve at 285 K. Unfortunately, since the measurement at 285 K is just above $T_C$, the small amount of the FM phase completely disappears in a zero field. However, we clearly see the field-induced isostructural transformation with the small hysteresis, accompanied by the metamagnetic transition.

The magnetic field dependence of $a$, $c$ and $V$ at 285 K is shown in Fig. 6. The field-induced isostructural transformation process is consistent with the metamagnetic transition process on the $M$--$H$ curves, as shown in Figs. 2 and 6. In this study, we found that $a$ and $c$ drastically change by 0.5 and 1%, respectively, but $V$ continuously and slightly contracts with increasing $H$ through the isostructural transformation.

Fig. 4 Temperature dependence of the lattice parameters $a$ and $c$, and the unit cell volume $V$ of MnFeP$_{0.5}$As$_{0.5}$ under a zero field (closed circles) and 5 T (open triangles).

Fig. 5 Powder X-ray diffraction patterns of MnFeP$_{0.5}$As$_{0.5}$ in magnetic fields up to 5 T at 285 K. $hkl_{PM}$, $hkl_{FM}$ and $hkl_{FFM}$ denote the Miller indices for the hexagonal Fe$_2$P-type structure in the PM, FM and FFM phases, respectively.

Fig. 6 Magnetic field dependence of the lattice parameters $a$ and $c$, and the unit cell volume $V$ of MnFeP$_{0.5}$As$_{0.5}$ at 285 K. The closed and open circles indicate the data for the PM phase and the FFM phase, respectively. The solid lines show the results of least squares calculations for the presented data.
from the PM to FFM phase. In addition, we confirm that $c$ slightly decreases with increasing field in both phases, while the field dependence of $a$ is negligibly small. Furthermore, it is noted that $V$ of MnFeP$_{0.5}$As$_{0.5}$ in the FM and FFM phases is smaller than that in the PM phase. This feature is quite different from that of other itinerant-electron metamagnetic compounds such as MnAs$_{1-x}$Sb$_x$\cite{9,11}, La(Fe$_{0.88}$Si$_{0.12}$)$_3$\cite{12}, Y(Co$_{1-x}$Al$_x$)$_2$\cite{13}, Lu(Co$_{1-x}$Ga$_x$)$_2$\cite{13} and so on. These compounds exhibit the volume expansion, accompanied by the magnetic transition from the PM phase to the FM and the FFM phases. For example, MnAs shows a first-ordered structural transformation from the orthorhombic MnP-type structure to the hexagonal NiAs-type structure with the volume expansion of 2.1% accompanied by the metamagnetic transition.\cite{10} On the other hand, MnAs$_{0.9}$Sb$_{0.1}$ exhibits an isosctructural transformation (NiAs-type) with the volume expansion of 1.1%.\cite{11}

Here, we briefly discuss our results on the basis of results of the neutron diffraction\cite{14,15} and the band structural calculations.\cite{14,15} The neutron diffraction study for MnFeP$_{0.5}$As$_{0.5}$ in a zero field showed that the magnetic moment of Mn(3g) ($m_{\text{Mn}}$) is 2.02 $\mu_B$, but the moment of Fe(3f) ($m_{\text{Fe}}$) is suppressed and only 1.48 $\mu_B$ at 200 K (FM phase). In addition, the Fe(3f)–Fe(3f) interatomic distance is markedly expanded with the isosctructural transformation, accompanied by the magnetic transition from the PM to FM phase, suggesting that the extent of the Fe(3f) d-band overlap is the important factor in the magnetic and structural properties.\cite{2} That is, the expansion of the Fe(3f)–Fe(3f) distance (isosctructural transformation) yields a larger $m_{\text{Fe}}$, which stabilizes the FM state. A band structure calculation by Tobala \etal. for MnFeAs with the Fe$_3$P-type structure also supports the small value of $m_{\text{Fe}}$ at the 3f site.\cite{14} Recently, Yamada and Terao pointed out that the effective exchange field $B_{\text{ex}}$(Mn–Fe) created by $m_{\text{Mn}}$ at the 3g-site plays a key role to the induced $m_{\text{Fe}}$ at the 3f-site and stabilization of the FM state.\cite{15} This $B_{\text{ex}}$(Mn–Fe) originates from the hybridization between the Fe(3f)–3d and the Mn(3g)–3d electrons.\cite{15}

Deducing from above reports, the field-induced isosctructural transformation in MnFeP$_{0.5}$As$_{0.5}$ is interpreted qualitatively as follows. At the PM phase, a magnetic field probably suppresses the thermal fluctuation of $m_{\text{Mn}}$, which enhances the static $m_{\text{Fe}}$. When $B_{\text{ex}}$(Mn–Fe) exceeds a critical field, $m_{\text{Fe}}$ appears and the compound shows the metamagnetic transition. As shown in Fig. 1, the crystal structure of MnFeP$_{0.5}$As$_{0.5}$ consists of atomic layers stacked in the sequence of Fe(3f)–[Fe(As)$_2$(P)$_2$] layer and the Mn(3g)–[P$_2$As$_2$(1b)] layer along the $c$-axis. In this structure, it is considered that $m_{\text{Fe}}$ is enhanced and becomes more stable when the interlayer Fe(3f)–Mn(3d) distance decreases and the Fe(3f)–Fe(3f) distance increases in the $c$-plane. That is, the FFM state is stabilized when $c$ decreases and $a$ increases, as shown in Fig. 6. As a result of minimizing the total energy including the magnetic and the elastic energies, we observed the field-induced isosctructural phase transition, accompanied by the metamagnetic transition from the PM to the FFM phase.

4. Summary

We performed the X-ray diffraction measurement for MnFeP$_{0.5}$As$_{0.5}$ in magnetic fields up to 5 T and the magnetization measurement in order to clarify the magnetic field effect on the structural property. The compound with a hexagonal Fe$_3$P-type structure exhibits the field-induced isosctructural phase transformation with the small hysteresis by applying magnetic field, accompanied by the metamagnetic transition from the paramagnetic to ferromagnetic state at just above the Curie temperature of 284 K. In this transformation, the lattice parameters anisotropically change; $a$ expands by 0.5% whereas $c$ contracts by 1%. However, the cell volume slightly and continuously decreases with increasing magnetic field through the transformation. This work shows that “in situ” structural study under magnetic fields is very important and useful for the structural investigation on field-controlled magnetic materials such as magnetic refrigerants.

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