Electronic States of Magnetic Refrigerator Materials
\( \text{Mn}_{0.9}\text{Fe}_{1.1}\text{P}_{0.55}\text{As}_{0.45} \) using Soft X-ray Magnetic Circular Dichroism

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Abstract.

The system of MnFeP\(_{1-x}\)As\(_x\) is a candidate of a magnetic refrigerator material. We have investigated the temperature (\(T\))- and magnetic field (\(H\))-dependence of the magnetic properties of the Mn and Fe ions for Mn\(_{0.9}\)Fe\(_{1.1}\)P\(_{0.55}\)As\(_{0.45}\) using a soft x-ray magnetic circular dichroism (XMCD) in the regions of the Mn and Fe \(L_{2,3}\) absorption edges. In the ferromagnetic states, the magnetic moments of the Mn and Fe ions turn to the same direction. It is considered that the Mn ions are close to divalent (Mn\(^{2+}\)) states and that the Fe ions are a mixture of trivalent (Fe\(^{3+}\)) and divalent (Fe\(^{2+}\)) states. However, we deduce that the ferromagnetic properties of the Fe ions are mainly derived from the Fe\(^{2+}\) states. Using the XMCD sum rules, we have found that the magnitude of the magnetic moment of the Mn ions is larger than that of the Fe ions. The paramagnetic to ferromagnetic transitions are clearly observed by the \(T\)- and \(H\)- dependent XMCD measurements. Since the shapes of the spectra don’t change in all experiment conditions, the electronic configurations of the Mn and Fe ions are not changed by the PM-FM transition.

A magnetic refrigerator material system of MnFeP\(_{1-x}\)As\(_x\) has a remarkable dependence of the As concentration in the magnetic properties and the crystal structures [1]. For the As contents (\(x < 0.15\)), it crystallizes in the orthorhombic Co\(_2\)P-type structure, while the tetragonal Fe\(_2\)As-type structure is stabilized at the As concentration (\(x > 0.66\)). In these As concentrations, the corresponding compounds are nonmagnetic. In the region with \(0.15 \leq x \leq 0.66\), system is transited into the hexagonal Fe\(_2\)P-type structure and shows interesting magnetic properties. For \(0.15 \leq x \leq 0.26\), an antiferromagnet appears with the Néel temperature \(\sim 180\) K. For \(0.26 \leq x \leq 0.66\), it shows a first-ordered magnetic phase transition from a paramagnetic (PM) to antiferromagnetic (0.26 \(\leq x \leq 0.32\)) or ferromagnetic (FM) states (0.32 \(\leq x \leq 0.66\)) as the temperature (\(T\)) decreases [1, 2, 3]. Among the various magnetic properties, the concentration

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with $x \sim 0.5$ exhibits a first-ordered PM-FM magnetic phase transition around room temperature [4, 5]. At the slightly higher temperature than the Curie temperature ($T_C$), the PM-FM transition is also caused by applying an external magnetic field ($H$) with several tesla, generating a large entropy change at the same time. The large magnetocaloric effect is expected for an application as a magnetic refrigerant. The similar behaviors are observed in MnFe$_{1-x}$Ge$_x$, substituting the germanium atom for the arsenic atom [6, 7]. In order to obtain a clue to understanding the unique magnetic properties, it is important to characterize the magnetic properties of the Mn and Fe ions individually. An x-ray magnetic circular dichroism (XMCD), which is an element specific magnetic probe, is a powerful technique to address the above issues. In the present study, we have performed the $T$- and $H$-dependent XMCD experiments for Mn$_{0.9}$Fe$_{1.1}$P$_{0.55}$As$_{0.45}$ in the region of the Mn and Fe $L_{2,3}$ absorption edges.

The sample of Mn$_{0.9}$Fe$_{1.1}$P$_{0.55}$As$_{0.45}$ is a polycrystalline and characterized by electron probe microanalysis and powder x-ray diffraction measurements [8, 9]. The magnetization measurements show that the PM-FM transition is occurred at $T_C \sim 293$ K under $H = 1$ T with a hysteresis about $\Delta T = 1$ K and the metamagnetic PM-FM transition is occurred at between $H = 3$ and 4 T at $T = 300$ K, where is slightly higher than $T_C$, with a hysteresis about $\Delta H = 0.25$ T [9]. The procedure of the sample preparation is described in the Ref [9]. The x-ray absorption spectroscopy (XAS) and XMCD measurements were performed at the beamline BL23SU of SPring-8. The XAS spectra were obtained by the total-electron yield mode. We have measured a set of four XAS spectra by reversing both the external magnetic field and the helicity of light just after an acquisition of a whole XAS spectrum in order to obtain an XMCD spectrum [10]. The clean surfaces were obtained by fractured samples in the ultra-high vacuum.

**Figure 1.** Mn 2$p$ XAS and XMCD spectra of Mn$_{0.9}$Fe$_{1.1}$P$_{0.55}$As$_{0.45}$ taken at $T = 10$ K and $H = 6$ T (a) XAS spectrum $(\mu^+ + \mu^-)/2$ (b) XMCD spectrum $(\mu^+ - \mu^-)$. The intensity of the XAS spectrum is normalized to 1 at 640.5 eV.

**Figure 2.** Fe 2$p$ XAS and XMCD spectra of Mn$_{0.9}$Fe$_{1.1}$P$_{0.55}$As$_{0.45}$ taken at $T = 10$ K and $H = 6$ T (a) XAS spectrum $(\mu^+ + \mu^-)/2$ (b) XMCD spectrum $(\mu^+ - \mu^-)$. The intensity of the XAS spectrum is normalized to 1 at 710.0 eV.

Figures 1 (a) and 2 (a) show the XAS spectra $(\mu^+ + \mu^-)/2$ of the Mn 2$p$ and Fe 2$p$ ($L_{2,3}$) absorption edges, respectively. Figures 1 (b) and 2 (b) show the corresponding XMCD spectra, defined as $(\mu^+ - \mu^-)$. The spectra were obtained at $T = 10$ K and $H = 6$ T. Here, $\mu^+$ ($\mu^-$) refers to the absorption coefficient for the photon helicity parallel (anti-parallel) to the Mn or Fe 3$d$ majority spin direction. The intensities of the XAS spectra are normalized to 1 at 640.5 and 710.0 eV for the Mn 2$p$ and Fe 2$p$ XAS spectra, respectively. We can conclude that the
magnetic moments of the Mn and Fe ions turn to the same direction because the XMCD signals of the Mn and Fe ions exhibit the same sign as shown in Figs 1 (b) and 2 (b). From the shapes of the Mn 2p XAS and XMCD spectra [11, 12], the Mn ions in the compound are close to divalent (Mn$^{2+}$) states. The energy position of a main peak of the XMCD spectrum in the Mn L$_3$ absorption edge is located at 640.5 eV where is the same position of the main peak of the XAS spectrum as shown in Figs. 1 (a) and (b). On the other hand, as for the Fe L$_3$ absorption edge, it is considered that the Fe ions in the compound are a mixture of trivalent (Fe$^{3+}$) and divalent (Fe$^{2+}$) states from comparison with the results from the theoretical calculations and previous experiments [11, 12, 13, 14]. The peak of XAS spectrum at 710.0 eV mainly comes from the component of the Fe$^{3+}$ and the peak at 708.5 eV is ascribed to the contributions of the Fe$^{2+}$ and Fe$^{3+}$ states. It should be noted that the main peak of the XMCD spectrum in the Fe L$_3$ absorption edge is only observed at the energy position of the lower peak of the XAS spectrum and no XMCD peak is observed at 710.0 eV as shown in Fig. 2 (b). Therefore, there is a possibility that the ferromagnetic properties of the Fe ions are dominantly controlled by the Fe$^{2+}$ states [14].

In order to estimate the magnitude of the spin magnetic moment ($M_S$) and the orbital magnetic moment ($M_L$), we have applied the XMCD sum rules [15, 16]. Assuming the number of the 3d electrons $N_d = 5$ for the Mn ions and 6 for the Fe ions, the magnetic moments at $T = 10$ K and $H = 6$ T are estimated to be $M_S = 1.21$ and 0.61, $M_L = 0.05$ and 0.06 ($\mu_B$ per atom) with an error $\pm 0.02$ for the Mn and Fe ions, respectively. Since the magnetic moment from the magnetization measurements is 4.2 ($\mu_B$ per formula unit) at $T = 5$ K and $H = 5$ T [9], the value of $\sim 1.9$ ($\mu_B$ per formula unit) estimated from the XMCD measurement is smaller than that by the magnetization measurement. The small ferromagnetic XMCD signals may be due to magnetically dead surface layers on the sample surface in spite of the sample preparation in the ultra-high vacuum. However, we have found that the $M_S$ of Mn ions is about 2 times larger than that of Fe ions. The tendency that the $M_S$ of Mn ions is larger than that of Fe ions is also observed by the neutron diffraction experiment [2].

![Figure 3](image3.png)

**Figure 3.** The $T$ dependence of the $M_S$ of the Mn and Fe ions under $H = 1$ T. The closed circles and open squares indicate the data for the Mn and Fe ions, respectively. The measurements were done on cooling $T$.

![Figure 4](image4.png)

**Figure 4.** The $H$ dependence of the $M_S$ of the Mn and Fe ions at $T = 300$ K. The closed circles and open squares indicate the data for the Mn and Fe ions, respectively. The measurements were done on increasing $H$.

Next we performed the $T$- and $H$-dependent XMCD experiments in order to investigate the PM-FM transitions. We have applied the XMCD sum rules to these spectra too. Figure 3 shows the $T$ dependence of the $M_S$ of the Mn and Fe ions at $H = 1$ T. The $T$-dependent measurements
were done by cooling $T$ from 310 to 270 K. The PM-FM transition is clearly observed at $T_C \sim 290$ K as $T$ decreases. Figure 4 shows the $H$ dependence of the $M_S$ of the Mn and Fe ions at $T = 300$ K. The $H$-dependent measurements were done by increasing $H$ from 1 to 5.5 T. Although the paramagnetic behaviour is observed below $H = 3$ T, the $H$-induced PM-FM transition is clearly observed at $H_C \sim 3.5$ T as $H$ increases. The $T_C$ and $H_C$ observed in the XMCD experiments are consistent with the results from the magnetization measurements [9]. Although the magnitudes of the $M_S$ between the Mn and Fe ions are different, the $T$ and $H$ dependences of the $M_S$ of the Mn ions are similar to those of the Fe ions within the present experimental conditions. These results indicate that the magnetic behaviour of the Mn ions is strongly correlated with that of Fe ions. Although the intensity of the XMCD depends on the $T$ and $H$ conditions, the shapes of the XAS and XMCD spectra don’t change. This indicates that the electronic configurations of the Mn and Fe ions are not changed by the PM-FM transition.

To summarize, we have performed the XMCD measurements for Mn$_{0.9}$Fe$_{1.1}$P$_{0.55}$As$_{0.45}$ in the regions of the Mn and Fe $L_{2,3}$ absorption edges. In the FM states, it is found that the magnetic moments of the Mn and Fe ions turn to the same direction and the magnitude of $M_S$ of Mn ions is always larger than that of Fe ions using the XMCD sum rules. From the shapes of the XAS and XMCD spectra of the Mn ions, the Mn ions is close to the Mn$^{2+}$ states. As for the Fe ions, it is considered that the Fe ions are a mixture of the Fe$^{2+}$ and Fe$^{3+}$ states. The ferromagnetic properties of the Fe ions, however, are considered to be derived from the Fe$^{2+}$ states. The PM-FM transitions are clearly observed by the $T$- and $H$-dependent XMCD experiments. The $T$ and $H$ dependences of the $M_S$ of the Mn ions are similar to that of the Fe ions, indicating that the magnetic behaviours of the Mn and Fe ions are correlated strongly. Since the spectral shapes don’t change in all experimental conditions, the electronic configurations of the Mn and Fe ions are not changed by the PM-FM transition. In future studies, it is important to study the electronic states theoretically and to compare the magnetic behaviors of MnFe$_{1-x}$As$_x$ with that of MnFe$_{1-x}$Ge$_x$ in order to clarify the mechanism of the PM-FM transition of these compounds.

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