Magnetic properties of Fe$_2$P single-crystal under multi-extreme conditions

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Abstract. $^{57}$Fe nuclear resonant forward scattering experiment has been performed on a single crystalline Fe$_2$P under multi-extreme conditions, which shows a pressure induced ferromagnetic-antiferromagnetic transition and magnetic field induced metamagnetic transition. We present the clear experimental evidence that internal magnetic fields in two Fe sites at 3 K, 25 kOe and 2.5 GPa are comparable with those in a ferromagnetic state at ambient pressure. These internal magnetic fields, which are related to magnetic moments, are not aligned collinearly along the [001] axis by the external magnetic field.

1. Introduction
Iron phosphide, Fe$_2$P, with a hexagonal structure is a ferromagnetic compound accompanied with discontinuous lattice change at the Curie temperature ($T_C$) [1]. In this structure, the Fe atoms have two nonequivalent sites, that is, the tetrahedral (Fe$_{I}$) and pyramidal (Fe$_{II}$) sites surrounded by four and five P atoms, respectively. The magnetic properties of Fe$_2$P under pressure have been studied using the electrical resistivity and magnetization measurements [2, 3, 4]. From these results, $T_C$ decreases as increasing pressure and a new antiferromagnetic state appears above 0.5 GPa. In this antiferromagnetic phase, metamagnetic transition is observed at about 2 kOe under 4.2 K and 1.4 GPa [4]. Meanwhile, the saturation magnetic moment at 4.2 K is not sensitive with pressure up to 1.4 GPa. There is no knowledge of magnetic structures and magnetic moments of Fe atoms in Fe$_2$P under pressure and external magnetic fields.

Mössbauer spectroscopy is a useful method for the study of the electronic state of Fe under high pressure. The conventional Mössbauer absorption spectra have usually been measured using a point source. Under multi-extreme conditions, the γ-ray emitted from the source has a broadening line shape or does not have a single line related to hyperfine splitting levels of the nuclei because of a magnetic interaction and/or external magnetic fields. It is very difficult to obtain spectra of satisfactory quality under such experimental environments. Because of rapid developments in synchrotron based X-ray spectroscopy, a monochromatized X-ray from synchrotron radiation (SR) is a highly dense Mössbauer source. In Mössbauer spectroscopy using SR, the forward scattering from nuclei excited by a pulsed X-ray of SR is observed in the
time domain. The decay rate in the collective excited nuclei is modulated by quantum beats owing to the constructive interferences of photons emitted from the various nuclear levels of different energies. Thus $^{57}\text{Fe}$ nuclear forward scattering (NFS) is a good candidate for the study of the electronic state of Fe under multi-extreme conditions [5].

2. Experimental
Non-enriched high-quality single crystals of Fe$_2$P were synthesized by thermal annealing of ingots which were prepared by melting at about 1460 °C and cooling in air. The Curie temperature of the single-crystal sample was evaluated to be $T_C = 210$ K by magnetization measurement. Fe$_{2-x}$P has a substantial deficiency at the iron site. The $x$ value in the single-crystalline sample is estimated to be less than 0.005 using the empirical relation for the concentration of Fe in the system Fe-P versus $T_C$ [6].

We have measured the temperature dependence of conventional Mössbauer spectra using a constant-acceleration-type spectrometer. The single-crystalline sample was finely ground in order to get a uniform resonant-absorber thickness.

$^{57}\text{Fe}$ NFS experiment under multi-extreme conditions was performed at beamline NE3 in the accumulation ring, High Energy Accelerator Research Organization. The pulsed SR was monochromatized using a high-resolution monochromator. The monochromatized X-ray transmitted through the sample was detected with Si-avalanche photodiodes. Under high pressure, the single-crystalline sample was loaded with ruby crystals into a sample cavity of 0.6 mm diameter in a 0.3-mm-thick Inconel 625 alloy gasket. The use of Fluorinert as a pressure-transmitting medium ensured quasi-hydrostatic conditions. Pressure was calibrated by measuring the wavelength shift of the $R_{1\ell}$ luminescence line of ruby crystals in the clamp-type diamond-anvil cell (DAC). The [001] axis of the single-crystalline sample in DAC was aligned along the propagation vector of SR. External magnetic field ($H_{\text{ex}}$) was applied to the sample in DAC using a superconducting magnet, where the $H_{\text{ex}}$ direction was parallel to the [001] axis of the sample.

3. Results and Discussion
Mössbauer spectrum of Fe$_2$P at 4.2 K and ambient pressure is shown in Fig. 1, where the closed circles represent the measured data. As previously assigned [7, 8], the subspectra with smaller and larger magnetic hyperfine fields, $H_{\text{hf}}$, correspond, respectively, to the Fe$_I$ and Fe$_{II}$ sites. In an analysis of Mössbauer spectra, we assume that the magnetic hyperfine interaction is much larger than the electric quadrupole interaction, and use first-order perturbation theory with an axial symmetry approximation in the magnetic ordered state. As seen in Fig. 1, the spectrum was well fitted with the two subspectra. The refined hyperfine interaction parameters are summarized in Table 1 (a), which are comparable with the previous results [7, 8].

Figure 2 shows $^{57}\text{Fe}$ NFS spectrum of Fe$_2$P at 3 K, 2.5 GPa and 25 kOe. We have observed a clear quantum beat pattern in the $^{57}\text{Fe}$ NFS spectrum. The quantum beat comes from a constructive interference of photons emitted from the various nuclear levels with different energies. Thus, the nuclear levels of $^{57}\text{Fe}$ are split by the hyperfine interaction. Due to a pure $M1$ character of the 14.413 keV $^{57}\text{Fe}$ nuclear resonance, the nuclear transitions with $\Delta m = m_e - m_g = 0, \pm 1$ were directly and collectively excited, where $m_e$ and $m_g$ are the magnetic quantum numbers of nuclear excited and ground states, respectively. These transition probabilities depend on the directions of $H_{\text{hf}}$ and the principle axes of the electric-field-gradient (EFG) tensor because SR is linearly polarized and we have used the single-crystalline sample.

At the Fe$_I$ site, the FeP$_4$ tetrahedron is nearly regular because of small $\Delta E_Q$ value at 300 K and the principle $z$ axis of EFG tensor is assumed to be parallel to the [001] axis. Meanwhile, the Fe$_{II}$ sites are surrounded pyramidal by five P atoms and the direction from the Fe atom to the P atom at the vertex of the nearly square pyramid is parallel to one of the $\langle 110 \rangle$ axes.
Figure 1. Mössbauer spectrum of Fe\textsubscript{2}P at 4.2 K. The closed circles indicate the observed spectrum, the solid line represents the fitting curve obtained by the analysis, and the extracted subspectra are shown by the dotted lines.

Figure 2. $^{57}$Fe nuclear forward scattering spectrum of Fe\textsubscript{2}P at 3K, 2.5 GPa and 25 kOe. The closed circles with error bars indicate the observed spectrum and the solid line represents the fitting curve obtained by MOTIF [9].

Then, we assumed that the principle $z$ axis of EFG tensor at the Fe\textsubscript{II} sites is parallel to one of the (110) axes. In the present experimental conditions, the Fe\textsubscript{II} site gives three subspectra with the intensity ratio of 1:1:1. Hence, the observed $^{57}$Fe NFS spectrum was analyzed with four subspectra, assuming the intensity ratio of 3:1:1:1.

The spectrum analysis was performed with the package MOTIF [9] by using the full dynamical theory of nuclear resonant scattering, including the digitalization of the complete hyperfine Hamiltonian. As shown in Fig. 2, the spectrum was well fitted with the four subspectra and the refined hyperfine interaction parameters are summarized in Table 1 (b). We have evaluated the difference in $\delta_{c3}$ between two Fe sites to be 0.03 mm/s from $^{57}$Fe NFS spectrum because the quantum beat comes from a constructive interference of photons. Since this value is comparable with that estimated from the Mössbauer spectrum at 4.2 K, the electronic states of Fe in the two sites do not change at 3K, 2.5 GPa and 25 kOe. At the Fe\textsubscript{II} site, the refined $\frac{1}{2}eV_{zz}Q$ value is comparable with $\Delta E_{Q}$ at ambient pressure. On the other hand, the refined $\frac{1}{2}eV_{zz}Q$ value at the Fe\textsubscript{I} site is much larger than $\Delta E_{Q}$ at ambient pressure. Recent our X-ray diffraction measurement under pressure at low temperature indicates that there is no structural transition at the pressure-induced ferromagnetic-antiferromagnetic transition. Thus the position of Fe atom changes in the FeP\textsubscript{4} tetrahedron at 3K, 2.5 GPa and 25 kOe.

The refined $H_{in}$ is composed of $H_{ex}$ and an internal magnetic field ($H_{in}$), which is related to a magnetic moment of Fe atom and is usually negative. We have evaluated the values and directions of $H_{in}$ at the Fe\textsubscript{I} and Fe\textsubscript{II} sites from refined $H_{hf}$, $\varphi$, and $H_{ex}$. The obtained $|H_{in}|$ and $\varphi_{in}$ are 118 kOe and 22 deg. for the Fe\textsubscript{I} site and 181 kOe and 16 deg. for the Fe\textsubscript{II} site, where $\varphi_{in}$ is an angle between $H_{in}$ and the [001] axis. Since $|H_{in}|$ at two Fe sites are comparable with those at 4.2 K and ambient pressure, this result suggests that the magnetic moments at these sites do not change at 2.5 GPa. The directions of $|H_{in}|$ at the Fe\textsubscript{I} and Fe\textsubscript{II} sites are not parallel to the [001] axis. Accordingly the magnetic structure at 2.5 GPa above the metamagnetic transition is more complex one than a collinearly aligned structure although the components in the (001) plane of $|H_{in}|$ at the two Fe sites are not determined by $^{57}$Fe NFS. The magnetic
Table 1. Hyperfine interaction parameters in Fe₂P. ∆Ε₀ can be expressed as $\frac{1}{2}eV_{zz}Q(3\cos^2θ - 1)/2$ in the magnetic ordered state and $|\frac{1}{2}eV_{zz}Q(1 - η^{1/2})|$ in the paramagnetic state, where $Q$ is the nuclear electric quadrupole moments, $V_{zz} = \partial^2V/\partial z^2$ the principal component of diagonalized EFG, $θ$ the angle between the direction of principal component of the EFG and the magnetic hyperfine field and $η = (V_{xx} - V_{yy})/V_{zz}$. $ϕ$ is an angle between the direction of $H_{hf}$ and the [001] axis.

(a)

| $T$ (K) | Site | $δ_{CS}$ (mm/s) | $∆E₀$ (mm/s) | $H_{hf}$ (kOe) |
|--------|------|----------------|--------------|----------------|
| 4.2    | Feᴵ  | 0.38           | 0.08         | 114            |
|        | FeᴵІ | 0.65           | 0.20         | 180            |
| 77     | Feᴵ  | 0.39           | 0.08         | 110            |
|        | FeᴵІ | 0.65           | 0.21         | 174            |
| 300    | Feᴵ  | 0.17           | 0.10         |                |
|        | FeᴵІ | 0.59           | 0.42         |                |

(b)

| $T$ (K) | $P$ (GPa) | $H_{ex}$ (kOe) | Site | $\frac{1}{2}eV_{zz}Q$ (mm/s) | $H_{hf}$ (kOe) | $ϕ$ (deg.) |
|--------|-----------|----------------|------|--------------------------|----------------|------------|
| 3      | 2.5       | 25             | Feᴵ  | 0.21                     | 95.6           | 28         |
|        |           |                | FeᴵІ | -0.57                    | 158            | 19         |

moment of Fe₂P along the [001] axis at 25 kOe is estimated to be 2.8 $µ_B$/f.u. from $|H_{in}|$ which is comparable with that obtained by magnetization measurement [4].

In summary, we have observed the satisfactory quality $^{57}$Fe NFS spectrum of the single-crystalline Fe₂P sample under multi-extreme conditions. The result of analysis indicates that $|H_{in}|$s in two Fe sites at 3 K, 25 kOe and 2.5 GPa are comparable with those in the ferromagnetic state at ambient pressure. Furthermore, it was pointed out that the magnetic moments at the two Fe sites under 2.5 GPa above the metamagnetic transition are not aligned collinearly by $H_{ex}$.

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