ANTIFERRO-QUADRUPOLAR ORDERING OF 4f-ELECTRON STATE IN THE FILLED SKUTTERUDITE $PrFe_4P_{12}$* **

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Magnetic field induced antiferromagnetic (AF) Bragg reflections and superlattice reflections due to a crystal-structure modulation have been observed simultaneously by neutron diffraction in the low temperature phase of the filled-skutterudite $PrFe_4P_{12}$. The present result demonstrates that 4f electrons of Pr ions undergo antiferro-quadrupolar (AFQ) ordering accompanied by the structural phase transition. The field induced AF magnetic moment has been evaluated as $0.065\mu_B$ at $H = 5.0$ T.

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The filled skutterudites RT_4X_{12} (R = rare earth, T= transition metal, X = pnictogen) have attracted much attentions due to various unusual properties [1]. Among them $PrFe_4P_{12}$ is especially interesting because it shows very heavy electron mass of $81m_0$ [2] and a mysterious low-temperature phase transition [3]. Electrical resistivity, specific heat and magnetic susceptibility exhibit sharp anomalies at $T_A = 6.5$ K in zero magnetic field, which indicates a clear phase transition. The sharp increase of the electrical resistivity at T_A indicates that a gap opens at the Fermi level in the phase transition. The phase transition is suppressed by external magnetic field and finally disappears above 5.5 T when the magnetic field is applied along the [0, 1, 1] direction [3]. Neutron powder diffraction measurement shows no magnetic long range ordering in the low-temperature phase [4].

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Very recently, we observed superlattice reflections characterised by the wave vector of $\boldsymbol{q} = (1, 0, 0)$ by X-ray diffraction below T_{A} at zero field [5]. It is noticed that the band calculation suggests a possibility of a nesting of Fermi surface with the same wave vector [6]. The scattering pattern has been fully explained by the model of the longitudinal modulation mainly due to the Fe-ion displacement, which gives a space group change from I to P [5]. The model indicates that two kinds of tetragonal configurations of Fe ions appear around the center and corner of Pr-ion sites in the unit cell in the low-temperature phase. Thus an antiferro-quadrupolar (AFQ) ordering of the 4f electrons of Pr ions is expected to occur in the phase below T_{A}. In this paper, we report the first evidence for the AFQ ordering in $\mathrm{PrFe_4P_{12}}$ obtained by neutron diffraction experiments under magnetic fields.

A single-crystal sample with the size of $5 \times 3 \times 3$ mm^3 was prepared by the tin-flux method. Neutron scattering experiments were carried out on the thermal-neutron spectrometer PONTA (5G) installed in the JRR-3M reactor of JAERI, Tokai, Japan, which was operated with double-axis mode with neutron wavelength of 0.235 nm. Magnetic fields up to 5.8 T were applied along the [0, 1, -1] direction, and the temperature range was between 1.5 K and 10.3 K. Scans were performed within the plane perpendicular to the [0, 1, -1] axis.

The intensities of the fundamental Bragg peaks increase with increasing magnetic field at $T = 1.5$ K. It is interpreted as due to the superposition of a field-induced ferromagnetic reflection on the nuclear reflection. The induced ferromagnetic moment value evaluated from the Bragg reflection intensities agrees well with bulk magnetization measurements [3].

Reflections at $\boldsymbol{Q} = (h, k, l)$ with $h + k + l =$ odd which are forbidden in the space group of the high temperature phase (Im$\bar{3}$) were observed at the temperatures below T_{A}. Some results at 1.5 K are shown in Fig. 1(a). These were obtained by subtraction of the data at 10.3 K and at zero field which were confirmed to be due to higher-order reflections of nuclear scattering and background. It can be seen that the intensities at (1, 0, 0) and (3, 0, 0) increase by applying a magnetic field of 4.8 T, and all the intensities disappear at $H = 5.8$ T. The finte peak at (3, 0, 0) at $H = 0$ is regarded as the reflection only due to the lattice modulation. Figure 1(b) shows the peak intensities of some superlattice reflections as functions of magnetic field. With increasing magnetic field up to 5 T, the intensities of the superlattice peaks increase gradually. At the boundary of the low-temperature phase, all the superlattice intensities disappear. These experimental facts clearly demonstrate that the superlattice reflections are characteristic of the unusual low-temperature phase. The intensities induced by magnetic field are considered to be due to the AF magnetic moment induced by the field, because the scattering-angle dependence of intensities is explained by that of a magnetic form factor of a Pr^{3+} ion. They are superimposed on the superlattice intensities by the crystal-lattice modulation.

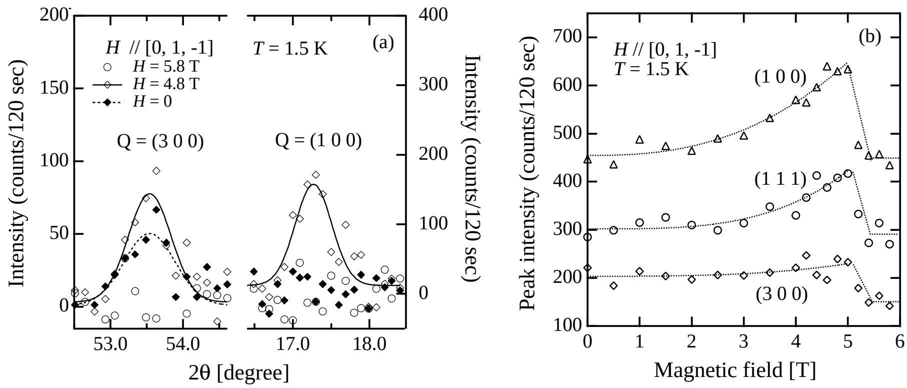

Fig. 1. (a) Scan profiles of superlattice reflections at $\boldsymbol{Q} = (3,0,0)$ and $(1,0,0)$. The intensities are the difference between the measured counts at 1.5 K and those at 10.3 K in zero field. (b) Magnetic-field dependences of superlattice reflections at $\boldsymbol{Q}$ = (1, 0, 0), (1, 1, 1) and (3, 0, 0) at 1.5 K. Lines are guide to eyes.

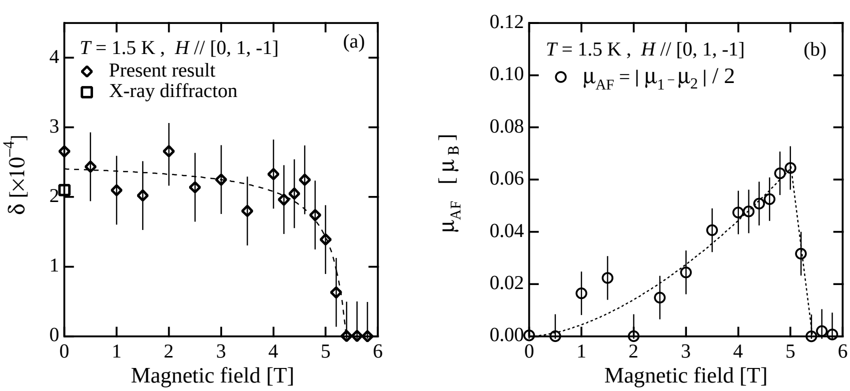

Fig. 2. Magnetic-field dependences of (a) displacement parameter δ for the Fe-ion coordination and of (b) field-induced AF moment μ_{AF}. Lines are guide to eyes.

The superlattice intensities in the low-temperature phase are regarded as a sum of the square of nuclear structure factor $F_{\mathrm{N}}(\boldsymbol{Q})$ for the modulated structure and that of magnetic structure factor $F_{\mathrm{M}}(\boldsymbol{Q})$ for the induced AF component. In the analysis of the data the Fe-ion displacement is assumed to be $(\delta, \delta, -2\delta)$ as proposed theoretically [7]. For the magnetic component, two different magnetic moments μ_1 and μ_2 are assumed to be induced along the magnetic field direction at the center and corner of Pr-ion sites in the unit cell, respectively. Thus, the magnetic intensity for $h + k + l =$ odd is proportional to the square of the structure factor $F_{\mathrm{M}} = 2\mu_{\mathrm{AF}} f_{\mathrm{Pr}}$, where $\mu_{\mathrm{AF}} = (\mu_1 - \mu_2)/2$ is the field induced AF moment and f_{Pr} means the magnetic form factor of a Pr^{3+} ion. We performed a least-squares fitting of the calculated F_{N} and F_{M} with free parameters δ and μ_{AF} to the observed intensities of the seven superlattice reflections at 1.5 K for each magnetic field. The model reproduces well the observation, and we obtained the parameters whose magnetic field dependences as shown in Fig. 2. The value of δ is 2.6×10^{-4} at $H = 0$ coincides with the result of X-ray diffraction within experimental accuracy [5]. The Fe-ion displacement disappears under the magnetic field above about 5.2 T at 1.5 K. The field induced AF moment increases with increasing field and reaches a maximum value of $\mu_{\mathrm{AF}} = 0.065\mu_{\mathrm{B}}$ at $H = 5$ T. Above the upper field, it jumps down to zero.

The origin of the magnetic field induced AF moment can be naturally ascribed to the AFQ ordering of 4f-election state of Pr ions. A possible model for the AFQ ordering is an alternative arrangement of crystal-field state Γ_3^+ and Γ_3^- on the different Pr-ion sites. In this model, the field induced AF component is due to the different mixing effect between each Γ_3 state and excited states under magnetic field [7].

In conclusion, we have observed superlattice reflections owing to the field induced AF moments as well as the crystal-lattice modulation mainly due to the Fe-ion displacement in $\mathrm{PrFe_4P_{12}}$. The present study gives strong evidence for the AFQ ordering in the low temperature phase of $\mathrm{PrFe_4P_{12}}$ which is accompanied by a gap opening as well as a structural modulation.

REFERENCES

[1] M.S. Torikachvili *et al.*, *Phys. Rev.* **B36**, 8660 (1987); H. Sato *et al.*, *Phys. Rev.* **B62**, 15125 (2000).

[2] H. Sugawara *et al.*, *Phys. Rev.* **B66**, 134411 (2002).

[3] T.D. Matsuda *et al.*, *Physica B* **281-282**, 220 (2000); Y. Aoki *et al.*, *Phys. Rev.* **B65**, 064446 (2002).

[4] L. Keller *et al.*, *J. Alloy, Compd.* **323-324**, 516 (2001).

[5] K. Iwasa *et al.*, *Physica B* **312-313**, 834 (2002).

[6] H. Harima *et al.*, *Physica B* **312-313**, 843 (2002).

[7] S.H. Curnoe *et al.*, *Physica B* **312-313**, 837 (2002).