# Resonant x-ray scattering study on the filled skutterudite $PrFe_4P_{12}$

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**Abstract**

Resonant x-ray scattering study was carried out to investigate an anomalous ordered state ($T_A$ = 6.5 K) in the filled skutterudite $PrFe_4P_{12}$. At the Pr-$L_{III}$ absorption edge, we observed resonant features in $h + k + l$ = odd reflections, which are forbidden in the *bcc* structure above $T_A$. Because these reflections contain the difference of anomalous scattering factor between two Pr atoms in the *bcc* unit cell, and the ordered state is attributed to the ordering of two different electronic states of Pr.

*Key words:* filled skutterudite; resonant x-ray scattering

The filled skutterudites $RT_4X_{12}$ (R = rare earth, T = Fe, Ru, and Os, X = P, As, and Sb), which crystallize in a *bcc* structure, exhibit a wide variety of electronic properties, such as superconductivity, magnetic order, and metal-insulator transition. Among them, the interest in $PrFe_4P_{12}$ is an anomalous ordered state at low temperature. The phase transition at $T_A$ = 6.5 K is confirmed by the specific heat measurement [1] and steep increase in resistivity was observed at $T_A$ [2]. No magnetic reflection was observed in neutron powder diffraction [3], and upper bound of Pr magnetic moment was determined to be $0.03\mu_B$/Pr by nuclear Schottkey specific heat of $^{141}$Pr [4]. On the other hand, lattice distortion which is characterized by the modulation wave vector of $\mathbf{q} = [1, 0, 0]$ was observed in recent X-ray diffraction study [5], and magnetic field induced antiferromagnetic moment with the same characteristic wave vector $\mathbf{q}$ as above was observed at the temperatures below $T_A$ by neutron diffraction experiment [6]. These facts strongly suggest that the phase transition below $T_A$ is accompanied by an antiferroquadrupolar ordering. It is noted that a nesting of Fermi surface with the same vector is suggested by band calculation [7]. This ordered state is suppressed by magnetic field, and a heavy-fermion-like behavior appears, which is evidenced by large electronic specific heat coefficient of 1.4 J/K$^2$mol [1], and large cyclotron effective mass of $67m_0$ [8].

Here we report the resonant x-ray scattering (RXS) experiments at the Pr-$L_{III}$ absorption edge to investigate the ordered state of $PrFe_4P_{12}$. RXS is a combined technique of diffraction and spectroscopy, and can elucidate a spatially ordered electronic states, such as magnetic, charge, and orbital order [9,10].

Single crystals of $PrFe_4P_{12}$ were grown by a tin-flux method. The surface normal to the scattering vector was cut and carefully polished. X-ray scattering experiments were carried out at beamline 4C and 16A2 at Photon Factory, KEK.

We measured three reflections, (300), (111), and (210) which are forbidden in the *bcc* structure above $T_A$ and become allowed below $T_A$ due to the lattice distortion. For the measurement of (210) reflection, we used a sample whose surface is parallel to (100) plane.

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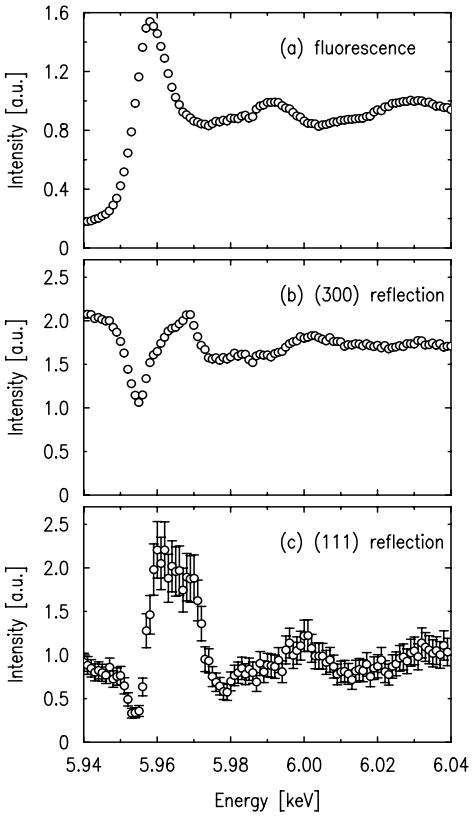


Fig. 1. Energy dependence of (a) fluorescence yield, (b) (300) reflection, and (c) (111) reflection. The temperature is 4.2 K. Absorption effect is corrected for the reflection intensity.

Iwasa *et al.* [5] successfully explained the scattering pattern of the superlattice reflections by the longitudinal modulation of $\mathbf{q} = [1, 0, 0]$ mainly due to the displacement of the Fe atom, which changes the space group from I to P. According to this argument, (300) reflection has large intensity because scattering vector ($\mathbf{Q}$) and displacement ($\mathbf{u}$) of the Fe atom are parallel, while (210) reflection is weak because $\mathbf{Q}$ is closely perpendicular to $\mathbf{u}$. (111) reflection contains no effect from Fe-atom displacement and its intensity is weak.

Figures 1 show fluorescence and scattering intensity of superlattice reflections, (300) and (111), near the Pr-$L_{III}$ absorption edge. We observed two resonant features around 5.965 eV and 6.000 eV in the reflections. The scattering amplitude of the superlattice reflections at the absorption edge of Pr consists of two components, the lattice distortion and the resonant scattering of Pr. If both components are finite, interference term appears in the intensity. As mentioned above, the intensity of (300) reflection is much larger than that of (111). The difference in spectral shape between (300) and (111) reflections may be ascribed to the interference term. Because (210) reflection also has small intensity from the lattice distortion, the spectral shape

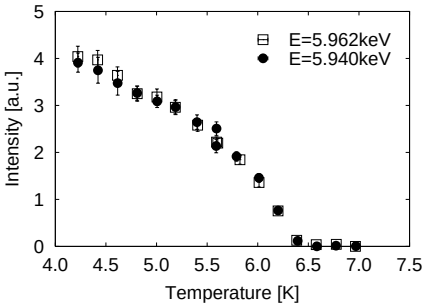


Fig. 2. Temperature dependence of the intensity of (111) reflection at resonant ($E = 6.962$ keV) and non-resonant ($E = 5.940$ keV) x-ray energies.

in x-ray energy dependence is similar to that of (111).

The assumption that Pr atoms do not change the position at the phase transition is reasonable in the structural model proposed experimentally [5] and theoretically [11]. Based on this assumption, resonant scattering term for the odd number of $h+k+l$ corresponds to the difference of anomalous scattering factor between two Pr atoms in the *bcc* unit cell. Anomalous scattering factor is closely related to the electronic states of resonating atom. Therefore our result suggests spatial ordering of two different electronic states of Pr atom, which is probably an antiferroquadrupolar ordering, appears below $T_A$.

Figure 2 shows the temperature dependence of the intensity of (111) reflection at resonant and non-resonant energies. The intensity of the reflection contains in general both components of lattice distortion and orderd electronic state. However, the latter is strongly enhanced in the intensity at the resonant energy due to the anomalous scattering. Quite similar temperature dependence at two energies indicates that the lattice distortion and ordering of electronic state of Pr occur and evolve simultaneously.

## References

[1] T. D. Matsuda *et al.*, Physica B 281&282 (2000) 220.

[2] H. Sato *et al.*, Phys. Rev. B 62 (2000) 15125.

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

[4] Y. Aoki *et al.*, Phys. Rev. B 65 (2002) 064446.

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

[6] L. Hao *et al.*, to be published .

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

[8] H. Sugawara *et al.*, J. Magn. Magn. Matter. 226-230 (2001) 48.

[9] K. Namikawa *et al.*, J. Phys. Soc. Jpn. 54 (1985) 4099.

[10] Y. Murakami *et al.*, Phys. Rev. Lett. 80 (1998) 1932.

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