Investigation of $4f$ electronic state and atomic vibration in rare-earth based compounds by neutron scattering

K. Iwasa[1], K. Saito[1], R. Igarashi[1], H. Kobayashi[1]
Tohoku Univ.[1]

Electronic and vibrational states of filled atoms in cage-like structures have been attractive. Such structure can enhance electronic hybridization between filled ions and surrounding ligands, and the filled ion motion with large amplitude may couple with the electronic state. We have investigated such properties in the rare-earth filled skutterudites. In addition to these studies, we have studied following subjects in FY2009.

(a) Crystal-field excitation and multipolar ordering in $Pr(Ru_{1-x}Rh_x)_4P_{12}$
Spontaneous ordering of higher-rank multipoles of $4f$ electrons has been detected in various rare-earth based materials. $PrRu_4P_{12}$ is one of typical systems, exhibiting the antiferro-type hexadecapolar (rank-4 multipolar) ordering below the metal-nonmetal transition at 63 K (T. Takimoto: J. Phys. Soc. Jpn. 75 (2006) 034714). It should be notable that the ordering is characterized by the crystal field excitations exhibiting the strong temperature dependence in accordance with the evolution of the multipolar order parameter (K. Iwasa *et al.*: Phys. Rev. B 72 (2005) 024414). The substitution of Rh to Ru gives rise to suppress of metal-nonmetal transition (C. Sekine *et al.*: Physica B 378-380 (2006) 211). Thus, a study of the doping effect leads to understand the ordered phase of $PrRu_4P_{12}$. We have carried out inelastic scattering experiments to measure crystal-field excitation of $Pr(Ru_{1-x}Rh_x)_4P_{12}$.

We have performed experiments using the triple-axis spectrometers TOPAN (6G) for polycrystalline sample of $Pr(Ru_{0.99}Rh_{0.01})_4P_{12}$. Previous studies revealed that the Rh doping systems (x = 0.03, 0.05, 0.10 and 0.15) shows the crystal field excitations at 2.4 and 13 meV whose peak positions do not show any temperature dependence, in addition to the strongly temperature dependent ones as observed in $PrRu_4P_{12}$. The most recent measurement for x = 0.01 performed at HER also shows the same temperature-independent excitation peak. The peak appearing in the Rh doped systems indicates that some Pr ions does not contribute to the ordering. We carried out the inelastic measurements in thermal neutron range. The strong temperature-dependent peak was observed around 9 meV, which is identified as that in the pure $PrRu_4P_{12}$. Thus, Rh 1% sample is consistent with the aforementioned separation of ordered and disordered regions in the sample crystals.

(b) Rare-earth atomic vibrations in hexaborides RB_6
RB_6 is composed of a hard frame of boron atoms and rare-earth ions filled inside. Among them, Gd ions in GdB_6 exhibit larger thermal vibration amplitude, so that it can be categorized into the so-called rattling systems. This material has been famous for the simultaneous magnetic and structural phase transition with the distinct two transition temperatures at T_N = 16 K and T_* = 9 K (K. Kuwahara *et al.*: Physica B 359-361 (2005) 965, R. M. Galera *et al.*: J. Appl. Phys. 63 (1988) 3580). At T_N, the magnetic ordering characterized by the wave vector $\mathbf{q_M} = (1/2, 1/4, 1/4)$ and the structural superlattice by $\mathbf{q_1} = (1/2, 0, 0)$ appear. The latter is expected to be given by the displacement of Gd ions, due to magnetoelastic-type interaction (M. Amara *et al.*: Phys. Rev. B 72 (2005) 064447). We performed inelastic x-ray (BL35XU at SPring-8) and neutron (6G TOPAN at JRR-3) scattering experiments for GdB_6 and YbB_6, respectively. The latter compound is nonmetallic and nonmagnetic, in contrast

to the typical RKKY-type magnet GdB_6, so it was measured as a reference material.

The dispersion relation curve of the longitudinal acoustic mode propagating along the simple cubic [100] axis shows the maximum energy around the wave vector $\mathbf{q} = (0.25, 0, 0)$, and it bends down with approaching the Brillouin zone boundary. The lower-energy zone-boundary mode at $\mathbf{q_1} = (1/2, 0, 0)$ corresponds to the structural modulation in the ordered phase. The energy of this mode is 75% of the maximum value on the branch at 300 K and further decreases by 10% with decreasing temperature down to T_N, so that this phonon mode softens considerably far above the transition temperature. On the other hand, the reference material YbB_6 does not show such softening. The observation indicates a strong electron-phonon coupling in GdB_6, which is expected to be magnetoelastic-type interaction between $4f$ states and displacement of Gd ions.

(c) Heavy-electron material with $4f^2$ state in $PrCu_4Au$

Recently, the group of Univsersity of Toyama reported the succeeding synthesis of $PrCu_4Au$ and a characteristic heavy-electron properties (S. Zhang *et al.*: J. Phys.: Condens. Matter 21 (2009) 205601). They also suggest antiferromagnetic ordering below 2 K from the magnetic susceptibility and specific heat measurements. The heavy fermion with f^2 electronic state provided by Pr or U ions have been discussed in terms of quadrupolar Kondo effect, dual nature of itinerant and localized f electrons, and effect of quasi-degeneracy of a crystal-field singlet-triplet scheme. Thus, we started to investigate the microscopic electronic state in $PrCu_4Au$.

A polycrystalline sample was grown by arc-melting method, and neutron scattering experiment was carried out at 6G TOPAN using 1 K and 10 K refrigerators.

We succeeded in detecting the magnetic ordering below about 2 K with a propagation vector $\mathbf{q} = (1/2, 1/2, 1/2)$ in $MgCu_4Sn$-type cubic structure ($F\bar{4}3m$). The suggested antiferromagnetic ordering was confirmed, and the ground state is thought to be magnetic as proposed by previous paper. In inelastic scattering measurement, clear crystal-field excitation peaks are observed. Considering the cubic point symmetry at Pr sites, four eigenstates are expected. The observed results of intensities as well as excitation energies imply that all the states locate in the excitation energy range less than 10 meV. Such small crystal-field level split may support fluctuation of electronic state mediated by hybridization between $4f$ and conduction electrons. In addition, a broad response is also seen in the spectrum. Although its origin has not been clarified yet, $PrCu_4Au$ may take double features of itinerant and localized f electrons.