Experimental report

02/05/2016

Proposal: **4-05-623** **Council:** 4/2015

Title: Magnetic excitations in electron-mass-enhanced semiconductors Ce3Co4Sn13 and Ce3Rh4Sn13

Research area: Physics

This proposal is a new proposal

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Samples: Ce3Rh4Sn13
Ce3Co4Sn13

Instrument	Requested days	Allocated days	From	To
THALES	10	5	18/11/2015	23/11/2015

Abstract:

We propose inelastic cold-neutron scattering experiments to investigate spin fluctuations of Ce3Co4Sn13 and Ce3Rh4Sn13, which show heavy-fermion (HF) states at low temperatures subsequent to charge-density-wave formations at 160 and 352 K, respectively. The semiconducting behaviors are enhanced below approximately 20 K, while the effective electron masses are pointed out to become large due to electronic correlation. The experiments are aimed at investigating characteristics of spin dynamics relevant to the HF state unexpectedly coexisting with the gapped electronic state. This study must reveal a new dual nature between localized and itinerant electrons in the correlated f-electron systems.

Experimental report of 4-05-623 on ThALES
(November 17-23, 2015)
"Magnetic excitations in electron-mass-enhanced semiconductors $Ce_3Co_4Sn_{13}$ and $Ce_3Rh_4Sn_{13}$"

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Scientific background

Electronic properties of materials crystallizing into the $Yb_3Rh_4Sn_{13}$-type cubic structure, which is shown in Fig. 1, are extensively studied. $(Ca_xSr_{1-x})_3Ir_4Sn_{13}$ exhibits superconductivity, whose transition temperature increases with decreasing x corresponding to the approach to the critical point of structural instability (L. E. Klintberg et al., PRL **109**, 237008 (2012)). Superconductivity was also discovered in $R_3T_4Sn_{13}$ (R = La, Sr; T = Rh, Ir) (N. Kase et al.: PRB **83**, 184509 (2011)). $Ce_3Pt_4In_{13}$ is a heavy-fermion (HF) antiferromagnet (AFM) (M. F. Hundley et al., PRB **65**, 024401 (2001)). Thus, the 3-4-13 series is a candidate of strongly correlated electron systems due to hybridized R-ion f electrons with conduction electrons originated from Sn and transition metal atoms. $Ce_3Co_4Sn_{13}$ has been reported to form a charge density wave (CDW) at 160 K (C. S. Lue et al., PRB 85, 205120 (2012)), and the similar phenomena are also suggested for $Ce_3Rh_4Sn_{13}$ (A. Ślebarski et al., PRB **86**, 155122 (2012)). Our group succeeded in synthesizing single-crystalline samples using the Sn self-flux method. We observed structural transitions at 160 and 352 K in $Ce_3Co_4Sn_{13}$ and $Ce_3Rh_4Sn_{13}$, respectively, using an x-ray diffraction technique (Y. Otomo, K. Suyama, and K. Iwasa, under preparation).

Aim of proposal

Below the CDW transition temperatures of $Ce_3Co_4Sn_{13}$ and $Ce_3Rh_4Sn_{13}$, the electrical resistivity values of both compounds are larger than those of the La-based reference materials (no $4f$ electrons). The temperature dependence of electrical resistivity exhibits a steep upturn below approximately 15 K. At much lower temperature, the Sommerfeld coefficient, $\gamma = C/T$, reach approximately 4 J/(mol-Ce K^2) (A. L. Cornelius et al., Physica B 378-380, **113** (2006), A. Ślebarski et al., PRB **86**, 205113 (2012), E. L. Thomas et al., J. Solid State Chem. **179**, 1642 (2006)). This fact indicates that these materials are candidate HF systems with a huge effective electron mass. $Ce_3Co_4Sn_{13}$ does not exhibit any magnetic ordering down to 0.5 K, and $Ce_3Rh_4Sn_{13}$ is suggested to undergo an antiferromagnetic (AFM) ordering below 2 K (Y. Oduchi et al., J. Magn. Magn. Mater. **310**, 249 (2007)). It is interesting to reveal the role of Ce-ion $4f$ electrons in the coexistence of the HF state with the semiconductor or semimetallic state. A similar electronic state was found in $CeOs_4Sb_{12}$, which shows $\gamma = 0.2$ J/(mol-Ce K^2) and a semiconducting behavior (H. Sugawara et al., PRB **71**, 125127 (2005)). The photoemission spectroscopy study on this compound suggests that the symmetry dependent hybridization between f and conduction electrons, which can account for the electronic dual nature based on the anomalous coexistence of the HF state and the low-energy band gap state (M. Matsunami et al., PRL **102**, 036403 (2009)). However, the spin of $CeOs_4Sb_{12}$ is too tiny to be detected by neutron scattering, and the characteristic spin fluctuation remains unsettled (K. Iwasa et al., ILL Experimental Report 4-01-710). Therefore, the aim of this experiment is to reveal characteristic spin fluctuation in the HF state of $Ce_3T_4Sn_{13}$ (T = Co, Rh).

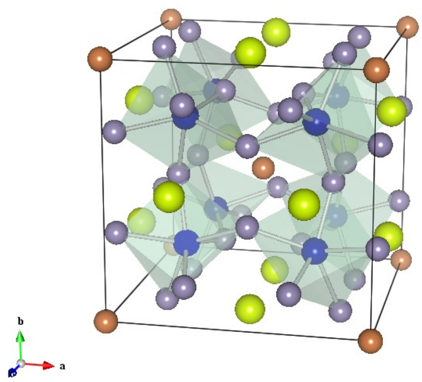

Figure 1: $Yb_3Rh_4Sn_{13}$-type cubic structure. Yellow circles on the surfaces of the cubic unit cell are rare-earth ions. Dark blue circles are transition-metal atoms, and others are Sn atoms.

Experimental procedures

Single crystalline samples of $Ce_3Rh_4Sn_{13}$ were synthesized at Tohoku University by using the molten Sn-flux method as described in the literatures mentioned above. We measured inelastic neutron scattering (INS) from this sample at ThALES. We used FlatCone with $k_f = 1.4$ Å^{-1}, in order to search wave-vector dependent INS signal. The normal triple-axis mode with the fixed $k_f = 1.3$ and 1.5 Å^{-1} was also applied, in order to reveal energy spectral shape at selected scattering vectors. The co-aligned single crystals were installed in a liquid-helium cryostat, and sample temperature was controlled between 1.6 and 40 K. The study on the $Ce_3Co_4Sn_{13}$ was also carried out by using 4F2 at Laboratories Léon Brillouin.

Experimental results and discussions

Figure 2 shows energy spectra at the scattering vector $\mathbf{Q} = (0.75, 0.75, 0.75)$ at measurement temperatures of 1.6 and 40 K. We found temperature dependence in the scattering intensity between 0.1 and 0.5 meV in energy transfer. The neutron-energy-gain side (negative energy region) shows an increase in intensity with decreasing temperature, and vice versa in the neutron-energy-loss side (positive energy region). This behavior indicates that a Lorentzian-like quasielastic spectrum centered at zero-energy transfer is enhanced with decreasing temperature, as expected from the Bose distribution factor. In addition, a shoulder-like inelastic peak is seen at approximately 0.35 meV, which is also enhanced at 1.6 K. These signals are expected to indicate characteristics of the spin fluctuation relevant to the electronic correlation in the low-temperature range. The present result of the energy spectrum is consistent with previously reported result for the polycrystalline sample (D. T. Adroja et al., Physica B **403**, 898 (2008)).

We also attempted measurements of wave-vector dependence of the low-temperature signal. Figure 3 shows scans along the principal crystallographic axes, $[q, 0, 0]$, $[q, q, q]$, and $[0, q, q]$, with the fixed energy transfer of 0.25 meV. Blue open circles, red, ope squares, and black closed diamonds are raw data of the scans at 1.6, 20, and 40 K, respectively. The difference between the intensity at 1.6 and 20 K are shown by blue closed circles, and that between 20 and 40 K by red squares. It is noteworthy that the all of the scan data along the three directions show increases in intensity at 1.6 K, in contrast to no clear change between 20 and 40 K. Within the present statistical certainty, we cannot conclude any dependence of the scattering-intensity enhancement on the wave vector.

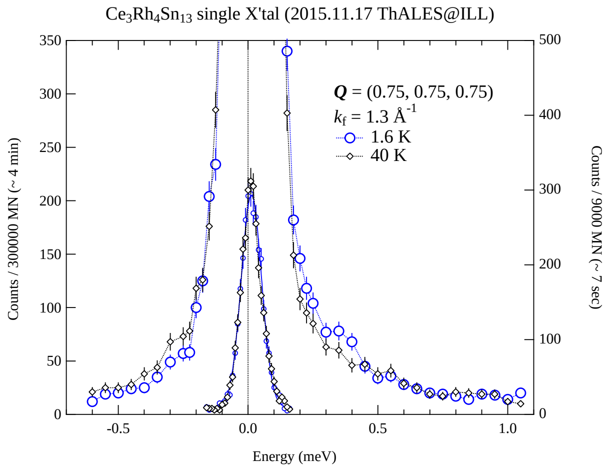

Figure 2: Inelastic neutron scattering spectra of $Ce_3Rh_4Sn_{13}$ at 1.6 and 40 K. The measurement scattering vector is fixed at $\mathbf{Q} = (0.75, 0.75, 0.75)$, and the $k_f = 1.3$ Å^{-1} fixed mode was used.

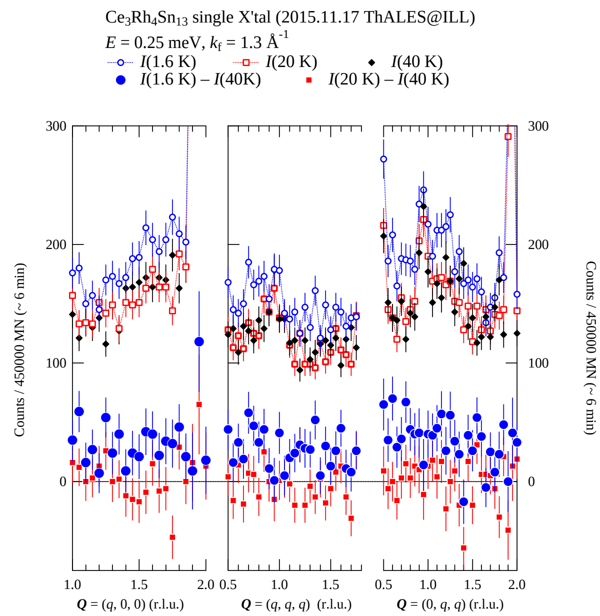

Figure 3: Scans along the principal crystallographic axises, $[q, 0, 0]$, $[q, q, q]$, and $[0, q, q]$, with the fixed energy transfer of 0.25 meV of $Ce_3Rh_4Sn_{13}$. Top panels are data taken at measurement temperatures of 1.6, 20 and 40 K, and a bottom panels are differences of intensity obtained by subtracting the data at 40 K from the lower-temperature data

Summary

According to magnetic susceptibility data at high-temperature range of $Ce_3Rh_4Sn_{13}$, the Ce ion takes a trivalent ionic state with $4f^1$ configuration. Thus, the ground state of the Ce-ion crystalline field splitting is a Kramers doublet. Adroja and co-workers reported that the excited states are located at 9 and 38 meV, so that the spin fluctuation is associated with the lowest-energy doublet. It should be noted that the structural distortion on the CDW transition gives rise to the two independent atomic sites. This fact means that there are at least two inequivalent $4f$-electrons state. We speculate that each of the state correspond to the two components of the present inelastic neutron scattering: the quasielastic response and the inelastic 0.3-meV peak. Each of them is caused by the Kondo effect and the well-localized $4f$ states with clear level splitting. Such duality in the spin dynamics is a key to understand the coexistence of the HF electron state and the high electrical resistivity in $Ce_3Rh_4Sn_{13}$.

We carried out the same inelastic neutron scattering for $Ce_3Co_4Sn_{13}$ by using the triple-axis neutron spectrometer 4F2 at Laboratories Léon Brillouin, in order to compare spin dynamics between these isomorphic compounds. $Ce_3Co_4Sn_{13}$ shows also enhancement of magnetic excitation in the energy range lower than 0.5 meV below approximately 15 K. We obtained characteristic spin dynamics that are relevant to the low-temperature electronic properties of both compounds. However, in contrast to $Ce_3Rh_4Sn_{13}$, $Ce_3Co_4Sn_{13}$ shows a wave-vector-dependent inelastic scattering intensity. Thus, much lower-temperature inelastic neutron scattering experiment is thought to be necessary to investigate whether the spatial correlation in spin dynamics of $Ce_3Rh_4Sn_{13}$ emerges or not.

Acknowledgments

The present study at ILL for $Ce_3Rh_4Sn_{13}$ was performed under the collaboration with Dr. J.-M. Mignot (LLB, CEA-CNRS, CEA-Saclay) for the study on $Ce_3Co_4Sn_{13}$. Sample preparation and measurements of basic properties were supported by Ms. Y. Otomo, Dr. K. Tomiyasu, and Mr. M. Onodera (Tohoku University). Travel expenses for the present experiment were supported by General User Program for Neutron Scattering Experiments, Institute for Solid State Physics, The University of Tokyo (proposal no. 15528), at JRR-3, Japan Atomic Energy Agency, Tokai, Japan.