BL-4C, BL-8A, BL-8B, BL-11B/2012S2-005, 2015G549, 2016P006

Evidence for chiral crystal structure of $RE_3Tr_4Sn_{13}$ (RE = La and Ce, Tr = Co and Rh)

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1 Introduction

Electronic states in chiral and noncentrosymmetric structures are recent attractive issues of condensed-matter physics. For example, magnetic skyrmion [1] and superconductivity associated with the Rashba-type spin-orbit interaction [2] have been investigated extensively.

We have studied the 3–4–13 class of materials crystallizing into the $Yb_3Rh_4Sn_{13}$-type structure, which are categorized under the cubic space group *Pm-3n* (No. 223). $(Ca_xSr_{1-x})_3Ir_4Sn_{13}$ and $(Ca_xSr_{1-x})_3Rh_4Sn_{13}$ exhibit superconductivity below approximately T_c = 5 K, which is enhanced by the Ca substitution suppressing structural phase transition at higher temperatures (~100 K) [3, 4]. The Ce-based compounds are also interesting because of electronic hybridization effect as well as structural instability. $Ce_3Co_4Sn_{13}$ is hypothesized to be a heavy fermion system. The specific heat divided by temperature reaches approximately 4 J/(K^2 mol-Ce) at approximately 1 K [5-8]. The electrical resistivity exhibits a slight kink at $T_D \simeq 160$ K. This behavior at T_D was suggested to be a signature of charge density wave (CDW) formation [9]. Below T_D, the electrical resistivity is insensitive to temperature, and it increases below 15 K. This feature is in marked contrast to metallic $La_3Co_4Sn_{13}$, which becomes a superconductor below 2.85 K [6]. Specific heat data of $Ce_3Co_4Sn_{13}$ shows a broad peak at 0.7 K, and no magnetic ordering has been identified down to 0.4 K [9, 10]. $Ce_3Rh_4Sn_{13}$ and $La_3Rh_4Sn_{13}$ also exhibit similar behaviors as those of $Ce_3Co_4Sn_{13}$ and $La_3Co_4Sn_{13}$, respectively. The electrical resistivity of $Ce_3Rh_4Sn_{13}$ is much higher than that of $La_3Rh_4Sn_{13}$ undergoing a superconducting phase transition at 2-3 K [11, 12]. The specific-heat data of $Ce_3Rh_4Sn_{13}$ show a peak at 1.2 K and 2 K, which had been considered to indicate magnetic ordering phase transitions [11, 13, 14]. On the other hand, from the specific heat divided by temperature, the Sommerfeld coefficient was estimated to be 0.4 J/(K^2 mol-Ce) at 0.1 K. Crystal structure of $Ce_3Rh_4Sn_{13}$ and $La_3Rh_4Sn_{13}$ have not fully solved, despite that x-ray diffraction spots characterized by the wave vector $\boldsymbol{q}$ = (1/2, 1/2, 0) were suggested to appear even at room temperature [15-17].

In order to clarify the structural and electronic properties of $RE_3Tr_4Sn_{13}$ (RE = La and Ce, Tr = Co and Rh), we conducted x-ray scattering measurements using the Photon Factory (PF) instruments. The results were published in several papers [18, 19]. The phase transition from the high-temperature *Pm-3n* structure (phase I) to the low-temperature $I2_13$ (phase I') was evidenced for these 3-4-13 compounds. Complementary x-ray absorption spectra (XAS) and neutron scattering studies were also performed, and the results will also be presented later.

2 Experiment

Single-crystalline samples (dimensions of 7 mm or less) of $RE_3Tr_4Sn_{13}$ (RE = La and Ce, Tr = Co and Rh) were synthesized by the molten Sn-flux method [6]. Starting materials were rare earth elements (3N), Co and Rh (4N), and Sn (5N).

For indentifying the structural transformation, x-ray diffraction experiments were performed using a four-circle single-crystal diffractometer with a rotating anode source of Mo $K\alpha$ radiation, which are installed in the university laboratories. A helium gas closed-cycle refrigerator was used to cool down the samples. Precise structural determination was performed using the imaging-plate x-ray diffractometer installed at BL-8A and 8B of PF, KEK. Incident x-ray energies of 18.0 keV were selected, and a helium-gas-flow cryostat was used to control the sample temperatures. Structural analysis was carried out using softwares: Rigaku Rapid for evaluating the structure factors, Sir2004 for a direct method, and SHELX for refinement analysis in WinGX suite [20]. Measurements of x-ray absorption spectra (XAS) as a function of incident light energy were performed by using the instruments at BL-4C and BL-11B. We adopted a setup of x-ray emission from the 110 surface of the single-crystalline sample. Magnetic susceptibity was measured using a SQUID magnetometer at the Department of Physics, Tohoku University.

3 Results

Figure 1 shows temperature dependencies of superlattice reflections at the scattering vector $\boldsymbol{Q}$ = (6.5, 6.5, 0) from the single-crystal samples of $La_3Co_4Sn_{13}$ and $Ce_3Co_4Sn_{13}$. Below T_D = 160 K, both compounds transform into a superlattice structure characterized by $\boldsymbol{q}$ = (1/2, 1/2, 0), indicating doubling of the unit cell above T_D. Such second-order phase transition was also observed

for $La_3Rh_4Sn_{13}$ and $Ce_3Rh_4Sn_{13}$, the transition temperature of which is 350 K. The common T_D for the La- and Ce-based compounds indicates that the structural instability is associated with electronic states originating from the *Tr* and Sn atoms. According to the band calculation studies, covalent bonding between the neighboring *Tr* and Sn carries relatively large charge density, which might be rearranged across the structural transitions [21]. We also measured magnetic susceptibilities. Even in the less magnetic La-based compounds, the susceptibility increases with decreasing temperature across T_D. This fact supports that the scenario of covalent bonding instability is much favorable than the CDW formation.

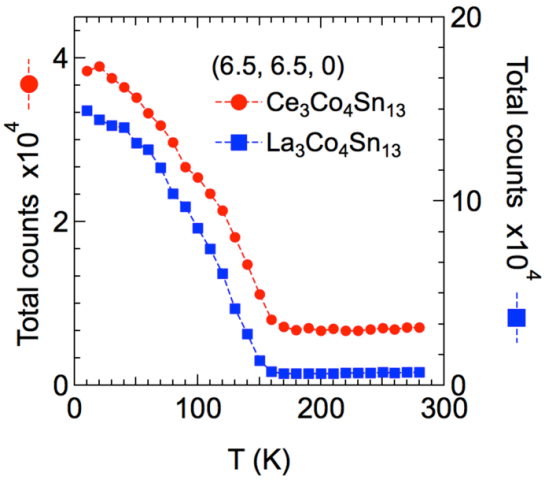

Fig. 1: Temperature dependencies of integrated counts of the superlattice reflections at $\boldsymbol{Q}$ = (6.5, 6.5, 0) of $Ce_3Co_4Sn_{13}$ and $La_3Co_4Sn_{13}$.

We measured x-ray diffraction intensities using imaging plates installed at BL-8A and 8B. The data of $Ce_3Co_4Sn_{13}$ measured at 200 and 30 K are shown in top and bottom panels of Fig. 2, respectively. The low-temperature data clearly show superlattice peaks. As mentioned above, the structural refinement procedures based on the WinGX suite were carried out for these data. The high-temperature phase-I data are reproduced by the *Pm-3n* structure, as proposed in previous studies. The low-temperature phase-I' data do not show any clear peak splitting. Thus, we examined structural models for various cubic space groups that are subgroups of *Pm-3n*, which are allowed for the second-order transition. We concluded that all of the phase-I' structure of $RE_3Tr_4Sn_{13}$ (*RE* = La and Ce, *Tr* = Co and Rh) are well reproduced by the $I2_13$ space group. Schematic view of the determined crystal structures in phases I' is shown in Fig. 3.

XAS spectra were measured using BL-4C and BL-11B in order to investigate electronic states relevant to the structural phase transition. The Co *K* edge spectrum in $Ce_3Co_4Sn_{13}$ and the Rh *L* edge spectra in $Ce_3Rh_4Sn_{13}$ depend on temperature, while the Ce L_3 edge does not show clear temperature dependence. These experimental results are consistent with the charge rearrangement scenario for the structural transformation.

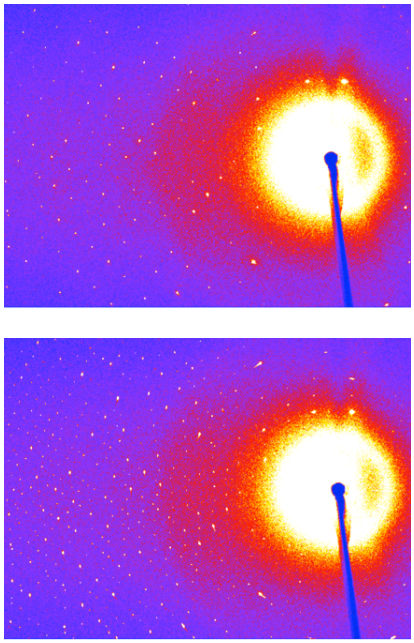

Fig. 2: X-ray diffraction spots on the imaging plates from $Ce_3Co_4Sn_{13}$ at 200 K (top panel) and at 30 K (bottom panel with superlattice reflections).

We also performed neutron diffraction measurement of $Ce_3Rh_4Sn_{13}$ down to 50 mK, in order to reveal whether the magnetic ordering occurs or not [19]. No clear magnetic long-range order was detected. Therefore, $Ce_3Co_4Sn_{13}$ and $Ce_3Rh_4Sn_{13}$ are considered to be paramagnetic semimetal systems in phase I'. In addition, inelastic neutron scattering measurements revealed that two inequivalent crystal-electric-field (CEF) level schemes of the Ce $4f^1$ electron appear in $Ce_3Co_4Sn_{13}$, which are consntent with the inequivalent atomic sites of the Ce ions, Ce1 and Ce2, as shown in Fig. 3 [22]. The CEF ground state doublet mediates spin fluctuation with characteristic energy of 0.5 meV, which emerges with the electrical-resistivity enhancement below 15 K [6].

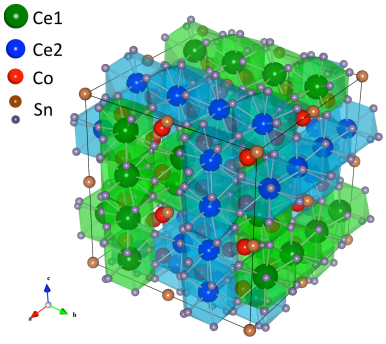

Fig. 3: One of enantiomers of chiral crystal structure of $Ce_3Co_4Sn_{13}$ in phase I' below T_D = 160 K [18]. The same crystal-structure symmetry also appears in phase I' of $La_3Co_4Sn_{13}$ below T_D = 160 K [18] and $RE_3Rh_4Sn_{13}$ (*RE* : La and Ce) below T_D = 350 K [19].

4 Discussion

The low-temperature phase I' of $RE_3Tr_4Sn_{13}$ (*RE* = La and Ce, *Tr* = Co and Rh) is characterized by the chiral structure. It is noteworthy that the chiral symmetry is proposed to protect topologically the Weyl fermion state [23]. Because of a crossing of linear electron band of the Weyl fermion at particular momentum points, a three-dimensional semimetal state can be realized if the Fermi energy is close to the crossing point. Therefore, the paramagnetic semimetal state in the Ce-based compounds is expected to be the Weyl semimetal in which the large band gap is formed by the *c-f* hybridization (Kondo semiconductor), and the topologically protected linear band mediates the semimetal conductivity. In addition, the superconductivity in the La-based compounds occurs in the chiral lattice, which means noncentrosymmetric superconductivity as in the $CePt_3Si$ [2]. Therefore, we conclude that new strongly correlated electron systems are found in the 3-4-13 series.

5 Summary

The present quantum-beam-scattering study including the synchrotron radiations evidences the chiral symmetry phase in $RE_3Tr_4Sn_{13}$ (*RE* = La and Ce, *Tr* = Co and Rh). It is a further issue to search for topological features of electronic state in these materials.

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