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 $Yb_Rh_{3}Sn_{13}$-type structure, which are categorized under the cubic space group $Pm-3n$ (No. 223). ($Ca_{1}Si_{1}$_{$x$)$_{1}Sn_{13}$ and ($Ca_{1}Si_{1}$_{$x$)$_{1}Rh_{1}Sn_{13}$ 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. $Ce_{1}Co_{4}Sn_{13}$ 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 $T_D = 160$ 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 $La_{1}Co_{4}Sn_{13}$, which becomes a superconductor below 2.85 K [6]. Specific heat data of $Ce_{1}Co_{4}Sn_{13}$ shows a broad peak at 0.7 K, and no magnetic ordering has been identified down to 0.4 K [9, 10]. $Ce_{1}Rh_{3}Sn_{13}$ and $La_{1}Rh_{3}Sn_{13}$ also exhibit similar behaviors as those of $Ce_{1}Co_{4}Sn_{13}$ and $La_{1}Co_{4}Sn_{13}$, respectively. The electrical resistivity of $Ce_{1}Rh_{3}Sn_{13}$ is much higher than that of $La_{1}Rh_{3}Sn_{13}$ undergoing a superconducting phase transition at 2-3 K [11, 12]. The specific-heat data of $Ce_{1}Rh_{3}Sn_{13}$ 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 $Ce_{1}Rh_{3}Sn_{13}$ and $La_{1}Rh_{3}Sn_{13}$ have not fully solved, despite that x-ray diffraction spotted characterized by the wave vector $q = (1/2, 1/2, 0)$ 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 $I2_{3}$ (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 identifying 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 SHEXL 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 susceptibility 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 $Q = (6.5, 6.5, 0)$ from the single-crystal samples of $La_{1}Co_{4}Sn_{13}$ and $Ce_{1}Co_{4}Sn_{13}$. Below $T_D = 160$ K, both compounds transform into a superlattice structure characterized by $q = (1/2, 1/2, 0)$, indicating doubling of the unit cell above $T_D$. Such second-order phase transition was also observed.
for La₄Rh₂Sn₁₃ and Ce₄Rh₂Sn₁₃, the transition temperature of which is 350 K. The common \( T_p \) 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 \( T_p \). This fact supports that the scenario of covalent bonding instability is much favorable than the CDW formation.

The high-temperature phase-I 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 \( RE_TrSn_{11} \) (\( RE = \text{La and Ce}, \ Tr = \text{Co and Rh} \)) are well reproduced by the \( I2_3 \) 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 Ce₄Co₂Sn₁₃ and the Rh L edge spectra in Ce₄Rh₂Sn₁₃ depend on temperature, while the Ce L₃ edge does not show clear temperature dependence. These experimental results are consistent with the charge rearrangement scenario for the structural transformation.

We also performed neutron diffraction measurement of Ce₄Rh₂Sn₁₃ 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, Ce₄Co₂Sn₁₃ and Ce₄Rh₂Sn₁₃ 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 4f⁸ electron appear in Ce₄Co₂Sn₁₃, which are consistent 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].

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**Fig. 1:** Temperature dependencies of integrated counts of the superlattice reflections at \( Q = (6.5, 6.5, 0) \) of Ce₄Co₂Sn₁₃ and La₄Co₂Sn₁₃.

**Fig. 2:** X-ray diffraction spots on the imaging plates from Ce₄Co₂Sn₁₃ at 200 K (top panel) and at 30 K (bottom panel with superlattice reflections).

**Fig. 3:** One of enantiomers of chiral crystal structure of Ce₄Co₂Sn₁₃ in phase I’ below \( T_p = 160 \text{ K} \) [18]. The same crystal-structure symmetry also appears in phase I’ of La₄Co₂Sn₁₃ below \( T_p = 160 \text{ K} \) [18] and \( RE_{4}Rh_{2}Sn_{13} \) (\( RE : \text{La and Ce} \)) below \( T_p = 350 \text{ K} \) [19].
4 Discussion
The low-temperature phase 1 of RE$_3$Tr$_2$Sn$_3$ (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 semi-metal state can be realized if the Fermi energy is close to the crossing point. Therefore, the paramagnetic semi-metal state in the Ce-based compounds is expected to be the Weyl semi-metal in which the large band gap is formed by the $c$-$f$ hybridization (Kondo semiconductor), and the topologically protected linear band mediates the semi-metal conductivity. In addition, the superconductivity in the La-based compounds occurs in the chiral lattice, which means noncentrosymmetric superconductivity as in the CePt$_3$Si [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$_3$Tr$_2$Sn$_3$ (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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