Transport and Magnetic Properties of RERuSn₃ (RE: La, Ce, Pr Nd and Sm)

by

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論文名（和文）
RERuSn₃ (RE: La, Ce, Pr, Nd, Sm) の輸送現象及び磁性（英文）

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Transport and Magnetic Properties of
RERuSn$_2$ (RE=La,Ce,Pr,Nd and Sm)

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Abstract

The electrical resistivity, thermoelectric power, Hall effect, magnetoresistivity, magnetic susceptibility, magnetization and specific heat on intermetallic ternary compounds RERuSn₃ (RE=La, Ce, Pr, Nd and Sm) have been investigated. CeRuSn₃ is found to be a new heavy fermion compound with a large coefficient of electronic specific heat \(\gamma=400\text{ mJ/mol.K}^2\) at 0K. In order to gain the deeper insight into the heavy fermion state of CeRuSn₃, non-stoichiometric compounds CeRuSnₓ (2.85\(\leq x\leq 3.15\)), CeRu(Sn₁₋ₓInₓ)₃ and NdRuSn₂.₉₁ have also been investigated. The low temperature resistivity for CeRuSnₓ shows a maximum at \(x=3.0\) as a function of \(x\). Sn deficient samples show three step phase transitions at 33K, 4K and 1.3K.

SmRuSn₃ is a new valence fluctuating compound with an antiferromagnetic ordering at 6K. The valency of Sm ion is estimated to be 2.8~2.9. Both CeRuSn₃ and SmRuSn₃ show unique magnetic features possibly due to their crystal structures as compared to the reported heavy fermion and the valence fluctuation compounds. LaRuSn₃ shows superconducting transition at 1.5K. PrRuSn₃ and NdRuSn₃ do not show any magnetic ordering down to 1.8K.
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§1. Introduction

Recently there has been much work concerning the properties of rare-earth (RE) intermetallic compounds. These compounds are interesting because of anomalous magnetic properties originated from the 4f shells in the RE ions. In particular, the heavy fermion behavior and the valence fluctuation phenomena due to instability of 4f shell are very attractive.

In order to obtain rough idea about the difference between 3d and 4f electrons, we first show the atomic wavefunctions calculation in the one-electron approximation. The radial part of Schrödinger equation becomes

\[
- \frac{\hbar^2}{2m} \frac{d^2}{dr^2} (rR(r)) + \left( - \frac{Z_{\text{eff}}(r)}{r} + \frac{\hbar^2 l(l+1)}{2mr^2} \right) (rR(r)) = E(rR(r))
\]

\[ \tag{1} \]

In case of \( l<2 \), the influence of the centrifugal potential term is nothing \( (l=0) \) or very small \( (l=1) \), so that outer s or p orbitals spread outside of an atomic core region and form wide bands in a crystal. Such s or p electrons can be well described by a band model. Thus s-p metals show no strong magnetism, since they have no partially filled inner shell.

When \( l \) is more than 2, the centrifugal potential becomes so strong that 3d or 4f electrons form a partially filled inner shell responsible for magnetism. Figure 1 shows atomic wavefunctions of Ni and Ce atoms, which are calculated from Eq.(1) [1]. As is shown in figure 1-(a), the 3d wavefunction on
Ni atom has significant amplitude outside the 3s and 3p closed shells. Due to the overlap of the wavefunctions between nearest ions, 3d electrons form a narrow d-band in metals or intermetallic compounds. In this case, one-electron band model is still a good approximation.

In contrast to the 3d electrons, the 4f shell in RE ions lies deep inside the 5s and 5p closed shells (figure 1-(b)), and retains its atomic character. In most RE systems, the occupied 4f levels lie much lower than the Fermi energy $E_F$, so that the 4f electrons are stably localized. It is known from the neutron scattering experiment [2] that the radius of the 4f-electron shell is about 0.35 Å which is sufficiently small compared with the inter-RE atoms distances in metals or intermetallic compounds to preclude any effects due to the direct 4f-4f overlap. In such systems, the well known Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is successful to describe physical properties such as helical ordering in heavy RE metals.

The free lanthanide ions usually occur in the trivalent state, and this can also be said of them in the solid state. Exceptions often occur in Ce, Eu and Yb compounds due to the tendency to adapt a state with either empty, half-full or full 4f-shells. The intermetallic compounds of those RE elements often show anomalous magnetic behaviors originated from the instability of 4f electrons, which is due to hybridization of 4f-electron states with ligand states (c-f hybridization). Recently also in several Sm intermetallic compounds, such hybridization effects have been reported.

The dense Kondo effect in Ce compounds is one of the most attractive phenomenon in the RE intermetallic compounds. In Ce
compounds, c-f hybridization plays an important role in their magnetic properties. Such c-f hybridization causes a Kondo effect at Ce-ion sites, while the intersite exchange RKKY interaction brings about some magnetic order. A ground state of Ce compounds is basically determined by relative strength of the Kondo effect and the RKKY interaction. The dense Kondo Ce intermetallic compounds roughly come under three classification.

(a) magnetically ordered systems
   (CeAl₂ [3], CeB₆ [4], CeCu₂ [5] etc.)

(b) itinerant f-electron systems
   (CeSn₃ [6], CePd₂ [7], CeNi [8])

(c) non-magnetic heavy fermion systems
   (CeAl₃ [9], CeCu₆ [10] CeCu₂Si₂ [11] etc.)

In the compounds which belong to the group (a), the RKKY interaction is stronger than the Kondo effect. In this case, these compounds undergo a transition to a magnetically ordered state at low temperatures. The ordered moments are, however, reduced compared to their free moment due to the Kondo effect. Large part of the dense Kondo compounds found to date are classified into this group.

The group (b) compounds are sometimes called valence fluctuating or mixed valence compounds. The 4f electrons in those compounds are delocalized due to strong c-f hybridization and become itinerant. This itineracy of f-state has been evidenced by the dHvA experiment. For example, the recent dHvA measurement on CeSn₃ [12] shows excellent coincidence with the band structure calculation which treats the 4f electron as an
The compounds which belong to the group (c) show certain anomalous behaviors. The term "non-magnetic" does not mean "non-magnetic moment" but "non-magnetic ordering". In such compounds, the Kondo effect occurs independently on each Ce ion site well above a characteristic temperature $T_\text{K}$. At low temperatures, there is no evidence of a local moment type long range order but is some sign of a heavy fermi liquid state. In such heavy fermion state, a large specific heat coefficient $\gamma$ and a large $T^2$ term in the electrical resistivity are observed, as was observed in CeAl$_3$ [9] and CeCu$_6$ [10]. In CeCu$_2$Si$_2$, a transition into a superconducting state was discovered by Steglich et al. [11]. The work stimulated an intense search for other non-magnetic heavy fermion systems. However, only a limited number of those compounds have been classified into this group. The heavy fermion state arises from complex many body effects which have not been completely solved at present stage. The more experimental and theoretical works are needed.

The anomalous magnetism in Sm compound is also very attractive. In Sm$^{3+}$ ion, the first excited state of spin-orbit coupling multiplet $^6H_{7/2}$ is not so far from the ground state $^6H_{5/2}$, and we can not ignore thermal excitation of 4f electrons to the excited state. Actually in most Sm compounds, the paramagnetic susceptibility does not obey Curie-Weiss law. If we take into account the higher multiplet, magnetic properties of most Sm intermetallic compounds investigated can be understood in terms of stable Sm$^{3+}$ ions under the crystal electric field [14]. Several Sm compounds, however, exhibit still unexplainable anomalous electronic and magnetic properties. Those anomaly can
be roughly classified into two types.

(a) a dense Kondo like behavior, such as SmSn₃ [15],
(b) a valence fluctuation between Sm⁻⁺ and Sm⁺⁺.

(b) is further classified into two classes.

(b-1) SmB₆ type: Sm⁺⁺ state is near the Fermi energy in conduction band (SmB₆ [16], metallic SmS [17]),
(b-2) Sm₃S₄ type: Sm⁺⁺ state is below the bottom of empty conduction band (Sm₃S₄ [18], Sm₄Bi₃ [19]).

The valency of Sm ions for the group (a) compounds is almost tri-valent and the compounds shows the Kondo type anomaly. In diluted Sm compounds La₁₋ₓSmₓSn₃ [20], the magnetic resistivity shows logarithmic increase at low temperature like the dilute Kondo alloy. The theoretical work about the Kondo state in Sm system is still under way [21].

The gap formation at Fermi energy in SmB₆ and metallic SmS is most remarkable characteristics of group (b-1) and have been investigated by many workers [22]. The origin of the gap formation have not been completely understood yet. Concerning the origin of the gap, two mechanisms (the single particle f-d hybridization gap by Mott [23] and the amorphous Wigner crystallization gap by Kasuya [24]) have been proposed.

The situation of group (b-2) is rather special. Almost all SmₓXₙ (X: chalcogen or pnictogen) compounds are not metallic. Since electronic affinity of X atoms is large, the bonding of those compounds are strong. Thus the conduction band becomes empty and the compounds usually becomes an insulator or a semimetal. In case of Sm₃S₄ and Sm₄Bi₃ type compounds, the
The valency of Sm becomes both Sm$^{2+}$ and Sm$^{3+}$ with suitable ratio in order to keep a stable bonding. The valency of Sm ions fluctuates spatially, while no charge ordering has been observed. Recently, the dense Kondo effect in low carrier density valence fluctuating compounds, such as Sm$_4$Bi$_3$ [19], has attracted much attention.

All these anomalies might originate from the c-f hybridization effect, though there is as yet no definite theoretical approach which can well explain the above mentioned anomalies. Experimentally, only a few dense Kondo or valence fluctuating Sm compounds have been reported, while a large number of Ce compounds exhibiting an anomalous hybridization effect have been reported. This fact is possibly due to the deeper 4f-level position of Sm$^{3+}$ compared to that of Ce$^{3+}$.

In order to study anomalous magnetism of Ce and Sm intermetallic compounds, it is fruitful to investigate isostructural Pr and Nd compounds which have stable 4f moments and a La compound which has no 4f electrons as the reference compounds.

In Pr compounds, where Pr$^{3+}$ ion is the non Kramers type, the ratio of the RKKY interaction to the crystal field splitting width between the ground singlet state and the excited state determines whether the system has a magnetic transition or not. For example, PrCu$_6$ shows no magnetic order due to 4f electrons [25], while PrB$_6$ orders antiferromagnetically below 7K [26].

Nd compounds usually exhibit a magnetic ordering of localized moments. A number of Nd compounds have very complex and interesting magnetic structures. For example, NdCu$_6$ is a metamagnetic substance with four discontinuous steps in the
magnetization curve [27].

The separation of the f-electron atoms in heavy fermion compounds is an important parameter, presumably determining the effective width of the hybridized f-band [28]. For a sufficiently small separation of f-electron atoms, the overlap of neighboring f wavefunctions leads to the formation of a broad f-band which behaves like one in a normal metal. Therefore the compounds with small RE-spacing become like a normal metal, and we can not expect any interesting magnetic properties. Actually, the well known heavy fermion compounds have relatively large f-ion spacing: 4.43Å and 4.83Å in CeAl₃ and CeCu₆. In this point of view, we turned our attention to the series of isostructural intermetallic compounds RERuSn₃ which has a large RE-ion spacing of about 4.9Å (RE=La, Ce, Pr, Nd and Sm). Eisenmann and Schäfer [29] first reported the existence of intermetallic compounds with the formula RERuSn₃ which have a cubic structure (Pr₃Rh₄Sn₁₃ structure Pm₃n), though they reported nothing about their physical properties. Figure 2 shows the Pr₃Rh₄Sn₁₃ structure of RERuSn₃.

One of the aim of this work is searching for new Ce and Sm compounds which show the heavy fermion and the valence fluctuating behaviors. In order to deepen the understanding of f-electron system, it is important to search for new interesting materials. RERuSn₃ which has suitably large RE-RE distance seems to be a hopeful candidate for that purpose.

In this thesis, we report the transport and magnetic properties of the RERuSn₃ (RE=La, Ce, Pr, Nd and Sm) and discuss about the behaviors of 4f electrons in each compound. In §2, we describe about the sample preparation and the experimental
techniques. In §3-1, we first give an overview about the experimental results on RERuSn₃ system. The experimental results for CeRuSnₓ (2.85 ≤ x ≤ 3.15), CeRu(Sn₁₋ₓInₓ)₃ (y=0.15 and 0.15) and NdRuSn₂₋₀.₉₁ are presented in §3-2. In §4, the results are discussed. Finally in §5, several conclusion obtained from the present investigation are given.

In appendix, we also report some transport and magnetic properties of new actinide intermetallic compounds U₅T₄Sn₁₃ (T=Ru and Rh) which have same or similar structures with RERuSn₃. The 5f electrons in uranium compounds shows intermediate characters between localized 4f and itinerant 3d electrons, and it is of interest to compare to the magnetic properties of U compounds with RE compounds.
§2. Experiment

The polycrystalline $\text{RERuSn}_3$, $\text{CeRuSn}_x$, $\text{NdRuSn}_y$ and $\text{CeRu(Sn}_{1-y}\text{In}_y)_{13}$ samples were prepared by arc-melting appropriate amounts of the high-purity elements (RE 99.9%, Ru 99.98%, Sn 99.999%) on a water cooled copper hearth. The ingots were wrapped in Ta and Zr foils and were annealed at 950°C for 3 days in evacuated quartz tubes. In ref.[30], single crystals of intermetallic stannides with $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ structure were prepared by the molten tin solution method. In the present work, we grew single crystals with a suitable size for the transport measurements by Czochralski pulling method using SELEC tri-arc furnace [31]. The appropriate amounts of the high-purity elements, usually the total amount is 5~15g, are first melted by a tri-arc furnace on a water cooled copper hearth. A piece of a polycrystal sample or a twisted tungsten wire are used as a seed crystal in the single crystal growth. Weight loss during crystal growth is generally small. It is surprising that the obtained $\text{SmRuSn}_3$ single crystal has good quality in spite of the high vapor pressure of Sm at crystal growth temperature. A photograph of a typical grown crystal is shown in figure 3. The rectangular part of right-hand side of the crystal is a polycrystalline seed. The growth characteristics of the $\text{RERuSn}_3$ are summarized in table I.

The samples obtained were analysed by Cu Kα x-ray powder diffraction. No parasitic phase was detected in stoichiometric $\text{RERuSn}_3$ and $\text{CeRu(Sn}_{1-y}\text{In}_y)_{13}$ (y=0.05 and 0.15), while diffraction patterns of $\text{CeRuSn}_x$ (x≠3) and $\text{NdRuSn}_{2.91}$ indicate very weak additional reflections. We have not identified the impurity
phase yet amount of which estimated from the intensity of additional lines is at most several percent. Lattice constants of RERuSn₃ were determined from the room temperature powder diffraction pattern of crushed single crystalline samples, high purity Si powder as an internal standard.

Single crystalline samples for the transport and magnetic measurements were cut into rectangular rods by a spark cutter after oriented by x-ray Laue diffraction. Typical dimension of the samples is 1x1x5 mm³ with their longitudinal direction parallel to the [100]. The magnetization and the magnetic susceptibility of RERuSn₃ were measured up to 55kOe by a Quantum Design SQUID magnetometer between 1.8K and 300K. The electrical resistivity was measured by the standard four-probe method. The thermoelectric power (TEP) was measured by the conventional differential method with a thin copper wire as a reference. The Hall coefficient at 10kOe was measured by the conventional DC four-probe method or DC five-probe valance method. The high field magnetoresistivity and the Hall resistivity were measured up to 75kOe.
<table>
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<tr>
<th>Compound</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>LaRuSn₃</td>
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<td>5.5</td>
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<td>10</td>
<td>6</td>
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<td>14</td>
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<td>17</td>
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<td>NdRuSn₃</td>
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<td>6.4</td>
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<td>SmRuSn₃</td>
<td>13</td>
<td>5.7</td>
<td>14</td>
<td>5.5</td>
<td>7</td>
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</tbody>
</table>

**Legend:**

A - pulling rate: necking (mm/h)
B - pulling rate: growing (mm/h)
C - seed rotation rate (rpm)
D - crucible rotation rate (rpm)
E - total amount of starting materials (g)

**Table I.**

Characteristics of the crystal growth procedure of RERuSn₃.
§3. Results

3-1 RERuSn₃ (RE=La, Ce, Pr, Nd and Sm)

Figure 4 shows the lattice constant of RERuSn₃ determined by x-ray analysis together with those reported earlier for RERuSn₃ [29] and isostructural compounds RE₃Rh₄Sn₁₃ [30]. The numerical data of lattice constants for RERuSn₃ and RE₃Rh₄Sn₁₃ are shown in table II. The lattice constants of our samples grown by the triarc Czochralski method are in good agreement with those reported in ref.[29]. The lattice constants of RERuSn₃ system show an anomalous expansion at SmRuSn₃, while those for RE₃Rh₄Sn₁₃ system exhibit smooth lanthanoid contraction. The expansion for SmRuSn₃ suggests the valence fluctuating character of this element.

Figure 5 shows the temperature dependence of the reciprocal magnetic susceptibility for RERuSn₃ (RE=Ce, Pr and Nd) between 1.8K and 300K. The susceptibility of all the three compounds follows Curie-Weiss law between 100K and 300K. The paramagnetic Curie temperatures are -66K, -39K and -31K and the effective moments are 2.4, 3.5 and 3.6 μₜ/RE atom for RE=Ce, Pr and Nd, respectively. The effective moment of each compound is close to the value for the tri-valent ion (Ce⁺:2.56μₜ, Pr⁺:3.62μₜ and Nd⁺:3.68μₜ). The departure from Curie-Weiss law below 100K in each compound is due probably to the crystal field effect.

The inset of figure 5 shows the magnetic susceptibility below 20K. For all the three systems, no sign of magnetic ordering was observed down to 1.8K. The susceptibility of CeRuSn₃ and NdRuSn₃ continues to increase strongly with decreasing temperature down to 1.8K, which suggests some enhancement of magnetic correlation.
<table>
<thead>
<tr>
<th>RE</th>
<th>lattice constant [Å]</th>
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<tr>
<td></td>
<td>RERuSn₃</td>
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<tr>
<td></td>
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</tr>
<tr>
<td>La</td>
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<tr>
<td>Ce</td>
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<tr>
<td>Pr</td>
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<td>Nd</td>
<td>9.698</td>
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<td>Sm</td>
<td>9.732</td>
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Table II.
Lattice constant of RERuSn₃ together with those reported earlier for RERuSn₃ (Eisenmann and Scäfer 1985:ref.[29]) and isostructural compound RE₃Rh₄Sn₁₃. (Remeika et al. 1980:ref.[30]).
among 4f electrons at low temperature. Compared to the other two compounds, the increase of the susceptibility of PrRuSn$_3$ at low temperature is slightly weaker. This is possibly due to the gradual freezing out of the singlet ground state.

Figure 6 shows the temperature dependence of the low-temperature AC susceptibility ($\chi_{AC}$) for CeRuSn$_3$ below 1.5K. The $\chi_{AC}$ shows a sharp peak at 0.6K which is attributable to some magnetic correlation. The origin of the peak is discussed later. Since the absolute value of $\chi_{AC}$ has not been calibrated, it is difficult to estimate the peak $\chi_{AC}$ value. By comparing $\chi_{AC}$ to DC $\chi$ value at 1.8K, we estimated it to be the order of 0.1-1 (emu/mol.). This estimated magnitude of $\chi_{AC}$ is larger than that of most of the dense Kondo compounds.

Figure 7 shows the temperature dependence of the magnetic susceptibility for SmRuSn$_3$ between 1.8K and 300K. The susceptibility of SmRuSn$_3$ does not obey Curie-Weiss law between 1.8K and 300K. In the figure the broken curve shows the theoretical susceptibility of Van Vleck-Franck Sm$^{3+}$ [32]. The observed susceptibility does not follow the theoretical model. We calculated a susceptibility in a valence fluctuating state $\chi_{vf}$ by simply assuming

$$\chi_{vf} = (1-a)\chi_{3^+} + a\chi_{2^+},$$

(2)

where $\chi_{3^+}$ and $\chi_{2^+}$ are the susceptibilities of Sm$^{3+}$ and Sm$^{2+}$ respectively. The solid curve, which represents the calculated susceptibility for $a=0.2$, reproduces the experiment near room temperature well. This fact also suggests that Sm ion is in the valence fluctuating state in SmRuSn$_3$. The observed
susceptibility deviates from the calculated value below 150K and exhibits a broad bump around 100K. A similar bump was reported for SmB₆ [33] which is a typical valence fluctuating Sm compound.

The inset of figure 7 shows an enlarged view of the magnetic susceptibility and the electrical resistivity near the magnetic transition. The susceptibility shows a broad maximum around 9K and a drastic decrease at 6K reflecting the transition into antiferromagnetic state. The resistivity increase below 6K implies the formation of an antiferromagnetic gap, which is consistent with the results of the susceptibility.

Figure 8 shows the temperature dependence of the electrical resistivity for single crystalline RERuSn₃ between 1.3K and 300K. The resistivity at 300K of RERuSn₃ (RE=La, Ce, Pr, Nd and Sm) is 320±30, 490±50, 410±40, 480±50 and 400±40 μΩcm, respectively. Except for SmRuSn₃, the resistivity of single crystalline RERuSn₃ increases with decreasing temperature near room temperature. The resistivity of LaRuSn₃ and PrRuSn₃ reaches a broad maximum and then decreases slightly at lower temperatures, while the resistivity of CeRuSn₃ and NdRuSn₃ continues to increase down to 1.3K. Only the resistivity of SmRuSn₃ decreases smoothly with decreasing temperature. We find the superconducting transition at 1.5K for LaRuSn₃, as is shown in the inset of figure 8. Figure 9 shows the resistivity of RERuSn₃ (RE=La, Pr and Nd) as a function of T¹/². For all the three compound, T¹/² dependence can be clearly seen at high temperatures. Judging from the data which are collected by Tsuei [34], most crystalline disordered conductors with the resistivity larger than 400μΩcm tend to exhibit negative temperature coefficient of the resistivity at room temperature. Recently Vodop'yanov et al [35] observed T¹/²...
dependence of the resistivity also on LuRh$_{1.2}$Sn$_4$ which is isostructural with RERuSn$_3$. They suggested that the localization effect is due to random occupation of crystal sites by different type of atoms.

Figure 10 shows the magnetic resistivity $\rho_m$ ($\rho_m = \rho_{CeRuSn_3} - \rho_{LaRuSn_3}$) of CeRuSn$_3$. $\rho_m$ behaves like a dilute Kondo alloy without showing the coherence effect at least down to 0.7K. The resistivity of dilute Kondo system is generally well described by Hamman-Fisher law [36]

$$\rho_m = A + \frac{B}{2} \left[ 1 - \ln(T/T^*) \cdot \frac{\ln(T/T^*)}{\ln^2(T/T^*) + \pi^2 S(S+1)} \right]^{1/2} \quad \text{(3)}$$

where $T^*$ is the Kondo temperature. $A = \rho_u \sin^2 \delta$ and $B = \rho_u \cos^2 \delta$ where $\rho_u$ is the unitarity limit resistivity and $\delta$ is the phase shift. We observed two well-defined successive logarithmic regimes (figure 10). This temperature dependence of resistivity is very similar to those for Ce diluted in La compounds such as La$_{1-x}$Ce$_x$Cu$_6$ [10] or La$_{1-x}$Ce$_x$InCu$_2$ [37]. This behavior is attributable to the fact that the upper crystal field splitted levels also contribute to the Kondo effect at high temperature; the Kondo temperature depends on the degeneracy of f-orbital ($N_f$). The resistivity in each logarithmic regime is expected to be fitted to Eq. (3) as a function of $T/T_k^h$ and $T/T_k$ respectively, where $T_k^h$ is the Kondo temperature at higher temperatures ($N_f = 6$) and $T_k$ is that at lower temperatures ($N_f = 2$). In the figure, two broken curves were calculated with $T_k = 20K$ and $T_k^h = 120K$ for a single value $\rho_u = 310 \mu\Omega cm$. The calculated value of $\rho_m$ well reproduces the experiment in each temperature range. According
to Hanzawa et al. [38], a relation between the Kondo temperature $T_{K}^h$ and $T_K$ is given as

$$T_{K}^h = (T_K \Delta_1 \Delta_2)^{1/3},$$

where $\Delta_1$ and $\Delta_2$ are the energies of the excited levels measured from the lowest level. If we assume $\Delta = \Delta_1 = \Delta_2$, we obtain $\Delta \approx 300K$ which is the same order as those of ordinary Ce compounds.

Figure 11 shows the temperature dependence of the Hall coefficient for LaRuSn$_3$, CeRuSn$_3$, and PrRuSn$_3$. The Hall coefficient of LaRuSn$_3$ is $2 \times 10^{-4}$ cm$^3$/C at 300K and is weakly temperature dependent. The estimated carrier density based on a single carrier model is $3 \times 10^{16}$ electrons/cm$^3$ at 300K. The Hall coefficient of PrRuSn$_3$ is $2 \times 10^{-4}$ cm$^3$/C at 300K and gradually increases with decreasing temperature. The increase is empirically expressed as

$$R_h = R_0 + R_\alpha \chi,$$

where $R_0$ is the normal Hall coefficient, $\chi$ is the magnetic susceptibility and $R_\alpha$ is the anomalous Hall coefficient. This anomalous term $R_\alpha \chi$ originates from a left-right asymmetric scattering due to magnetic ions (a skew scattering). The Hall coefficient of CeRuSn$_3$ ($5 \times 10^{-4}$ cm$^3$/C at 300K) increases monotonously with decreasing temperature to be $6.8 \times 10^{-2}$ cm$^3$/C at 4K. This value is extremely large compared to ordinary heavy fermion compounds. The Hall coefficient of the impurity Kondo system calculated by Fert et al [39] on the basis of the skew scattering by Ce impurities is given as
where \( \gamma = -(15/7)g\mu_B k_B^{-1}\cos \delta \sin \delta \), \( \rho_m \) is the magnetic resistivity and \( \chi \) is the normalized susceptibility. The broken curve in figure 11 was calculated from Eq.(6). For the fitting we have estimated the parameters \( R_0 \) and \( \gamma \) by plotting \( R_H \) as a function of \( \rho_m \chi \) as shown in the inset. The Hall coefficient can be fitted well with the calculated curve down to 4K, which suggests the dominance of the impurity Kondo scattering consistent with the resistivity analysis.

Figure 7.2 shows the temperature dependence of the Hall coefficient for SmRuSn₃ between 1.5K and 300K. In this temperature range, the Hall coefficient is positive. The Hall coefficient rises steadily with decreasing temperature, reaches a flat maximum near 30K, and again starts to increase near 8K. After reaching a maximum at 3K, it decreases steeply. These variations at low temperatures are attributable to the formation of an antiferromagnetic gap, which is consistent with the results of the susceptibility and the electrical resistivity. The Hall coefficient of SmRuSn₃ is enhanced compared to that of PrRuSn₃ (broken curve in figure 12) between 300K and 10K. As shown in the figure 5 and 7, the susceptibility of SmRuSn₃ is far smaller than that of PrRuSn₃. The experimental result of the Hall coefficient means that the anomalous Hall coefficient \( R_H \) in Eq.(5) is far larger in SmRuSn₃ than in PrRuSn₃; the magnetic asymmetric scattering is highly enhanced in SmRuSn₃ compared to the 4f localized PrRuSn₃. If the c-f hybridization is large enough leading to the valence fluctuation, the strong magnetic
scattering of conduction electrons is naturally expected. Therefore the result of the Hall coefficient also supports the valence fluctuation in SmRuSn$_3$. The Hall coefficient of the typical valence fluctuating compound SmB$_6$ also shows similar increase with decreasing temperature between 1000K and 200K [33].

Figure 13 shows the temperature dependence of the thermoelectric power (TEP) for RERuSn$_3$ (RE=La, Ce, Pr, Nd and Sm). TEP of LaRuSn$_3$ at 300K is positive and decreases monotonously with decreasing temperature without change of sign down to T$_c$. TEP of NdRuSn$_3$ is very close to that for LaRuSn$_3$ except for a broad shoulder around 15K. TEP of CeRuSn$_3$ has a negative sharp minimum around 8K and a positive broad maximum around 80K. In dilute Kondo systems, we generally observe a maximum or a minimum around T$_K$, so that we can expect that the temperature gives a rough estimation of the Kondo temperature of this system. The temperature 8K is not so far from 20K estimated from the temperature dependence of resistivity. The high temperature peak is originated from the competition of the Kondo scattering and the conduction electron scattering accompanying crystal field excitation and can be compared with the high temperature Kondo temperature T$_K$$^h$. The peak temperature 80K also agrees roughly with the estimated T$_K$$^h$ 120K. TEP of PrRuSn$_3$ at 300K is positive and decreases with decreasing temperature. At lower temperature TEP has some structures below 20K, where no appreciable structures have been observed in the resistivity and the magnetic susceptibility. Only a possible explanation for the lower temperature TEP structure is the conduction electron scattering accompanying crystal field excitation [40], since we
can not expect to observe the phonon drag effect in such a large residual resistivity sample. TEP of SmRuSn$_3$ shows a large positive maximum of 20$\mu$V/K near 150K. No change of sign is observed down to 1.5K. This behavior is similar to TEP of valence fluctuating compounds such as CeSn$_3$ [41] and again support the valence fluctuation in SmRuSn$_3$. TEP has a small kink corresponding to magnetic phase transition at 6K.

The measurement of specific heat is important for the study of the dense Kondo compounds, since we can estimate the effective mass of a conduction electron directly from the specific heat coefficient $\gamma$. In case of normal metal, the temperature dependence of specific heat obeys well known expression.

$$C=\gamma T+\beta T^3,$$  

(7)

where the first term is the electronic part and the second is the lattice contribution. If we plot the experimental $C/T$ as a function of $T^2$, the electronic specific heat coefficient $\gamma$ is obtained from the intercept. In the Fermi liquid theory, $\gamma$ is related to the density of states at Fermi energy $N(E_F)$ and the effective mass of a conduction electron $m^*$. The relation is given by

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F)$$

(8)

and

$$N(E_F) = \frac{3N_a}{\hbar^2 k_F^2} m^*.$$  

(9)
where \( N_a \) is Avogadro's number and \( k_F \) is Fermi wave vector.

In the heavy fermion compounds, the C/T gradually shows strong upturn below the Kondo temperature, since the mass enhancement of conduction electrons gradually increases. The enhancement of \( \gamma \) can be also explained as a growing up of the electronic density of states near Fermi energy: the Kondo peak. Actually in some valence fluctuation compounds (or high Kondo temperature compounds), such an enhancement of the density of states near Fermi energy has been reported in XPS and BIS measurement [42]. Figure 14 shows the temperature dependence of C/T of CeRuSn_3 between 0.6K and 20K. The C/T has a minimum around 7K. The C/T versus T curve bears a close resemblance to that of CeInCu_2 [43] which is a heavy fermion compound with a cubic crystal structure, although the C/T of CeInCu_2 starts increasing at a somewhat higher temperature and shows rough saturation below 1K. The inset of figure 14 shows the low temperature part of the C/T for CeRuSn_3 between 0.05K and 2.5K. The C/T has a maximum of 1.67 J/mol.K^2 around 0.6K. This maximum is attributable to the magnetic correlation effect observed in the AC susceptibility (figure 6). Even if C/T contains some contribution from magnetic correlation at these temperatures, the C/T value extrapolated to 0 K (400mJ/mol.K^2) is still largely enhanced compared to normal metals. The origin of the peak at 0.6K and the large C/T value at 0K are discussed later.
As shown in §3-1, CeRuSn₃ does not show any coherence effect. In order to investigate the reasons, we have prepared intentionally off-stoichiometric samples CeRuSnₓ (2.85≤ₓ≤3.15).

Figure 15 shows the lattice constants of CeRuSnₓ (2.85≤ₓ≤3.15), CeRu(Sn₁₋ₓInₓ)₁₋₃ (y=0.05 and 0.15) and NdRuSnₓ (x=3.0 and 2.91) determined from x-ray powder diffraction measurement. The lattice constant of CeRuSnₓ (2.91≤ₓ≤3.15) is independent of x within an experimental error, while the lattice constants of CeRuSn₂.₈₅ and NdRuSn₂.₉₁ show some expansion. The expansion has some relation to the lattice distortion induced by Sn deficiency, since the diffraction lines of the Sn deficient samples show broadening of the line width. The lattice constant of CeRu(Sn₁₋ₓInₓ)₁₋₃ (y=0.05 and 0.5) is also independent of y within an experimental error.

Figure 16 shows the temperature dependence of the electrical resistivity for CeRuSnₓ (2.85≤ₓ≤3.15). In the Sn excessive case, the resistivity becomes smaller with increasing x. The temperature dependence of the resistivity for x=3.03 and 3.09 is not much different from the stoichiometric sample, while the excess of 5 at.% of Sn (x=3.15) leads to drastic decrease of the resistivity at low temperature. In this sample, the extraction of pure Sn was confirmed by x-ray diffraction measurement, and the gradual decrease of the resistivity below 3.7K is due to the superconducting transition of the extracted Sn. The temperature dependence of the resistivity for the Sn deficient samples shows three step anomalies. The absolute value of the resistivity decreases with decreasing x. For CeRuSn₂.₉₁, we observe drastic
decreases of resistivity at 33K, 4K and 1.3K. In particular, the amount of resistivity drop near 1.3K reaches 150µΩcm and the resistivity still tends to decrease at 0.8K.

The dramatic change has been observed in the specific heat with decreasing Sn content. Figure 17 shows the temperature dependence of the low temperature specific heat for CeRuSn$_3$ and CeRuSn$_{2.91}$. The specific heat of CeRuSn$_{2.91}$ shows a clear $\lambda$-type anomaly around 1.3K indicating some kind of phase transition. This $\lambda$-type anomaly around 1.3K is corresponding to the resistivity drop at 1.3K. The specific heat of CeRuSn$_3$ does not show any such anomalies. This fact suggests that the phase transition of CeRuSn$_{2.91}$ is induced by the Sn deficiency.

Figure 18 shows the temperature dependence of the specific heat as a function of magnetic field for CeRuSn$_{2.91}$. The $\lambda$-peak at 1.3K under 0kOe is suppressed and becomes a broad peak under 5kOe. Such a sensitive response to the field suggests that the $\lambda$-peak at 1.3K is probably due to some magnetic ordering. The broad peak gradually shifts from 1.3K to 2.5K with increasing field up to 25kOe. These complex behavior of specific heat is similar to that of Ce(Cu$_{0.8}$Ag$_{0.2}$)$_6$ [44].

Figure 19-(a) shows the temperature dependence of TEP for CeRuSn$_x$(2.85≤x≤3.15). TEP of CeRuSn$_x$ are very sensitive to the Sn content. The excess Sn leads to increase of TEP and gradual disappearance of a negative peak around 8K. The deficiency of Sn leads to drastic increase of TEP at high temperature. Figure 19-(b) shows the low temperature part of TEP for the Sn deficient CeRuSn$_x$ (2.85≤x≤2.97). At lower temperatures (< 40K), TEP of the Sn deficient sample has a negative peak around 8K and a positive peak around 28K which gradually grow with decreasing x.
These TEP peaks correlate with the drastic decreases of the resistivity. The sign of TEP at 1.6K changes from negative to positive with decreasing Sn content. TEP of the stoichiometric compound approaches zero with decreasing temperature after passing through the negative peak. For x=2.91 and x=2.85, TEP changes sign from negative to positive near 3K. Below 3K, we expect one more positive peak possibly related to the magnetic transition at 1.3K, since TEP must be zero at 0K.

As to x dependence of the low temperature resistivity, a maximum was observed at x=0. In the same way, the high temperature TEP has a minimum at x=0. These facts suggest that the absence of the coherence effect in CeRuSn₃ is not due to deviation from stoichiometry.

In order to know magnetic properties of Sn deficient Ce compounds, magnetic susceptibility, magnetization, Hall coefficient and field dependence of Hall resistivity and magnetoresistivity have been investigated on CeRuSnₓ (x=2.91 and 2.85).

Figure 20 shows the temperature dependence of the magnetic susceptibility for CeRuSnₓ (x=3.0, 2.91 and 2.85). The susceptibility follows Curie-Weiss law between 100K and 300K with the paramagnetic Curie temperatures of -39K, -38K and -34K for x=3.0, 2.91 and 2.85. The susceptibility of the Sn deficient samples is gradually enhanced below 50K. There is no anomaly near 30K corresponding to those observed in the resistivity and TEP. The susceptibility of CeRuSn₂.₉₁ increases smoothly down to 1.8K, while the susceptibility for CeRuSn₂.₈₅ shows small bump around 4K. At the present stage, it is not clear whether this bump is intrinsic or not.
The inset of figure 20 shows the field dependence of the magnetization at 1.8K. The magnetization of the Sn deficient samples is enhanced compared to the stoichiometric sample. The magnetization of the Sn deficient samples at 55kOe reaches 0.7μB/Ce which is close to the full moment 0.7μB of a Ω7-doublet. The magnetization of CeRuSn2.85 shows a metamagnetic like behavior around 6kOe below 4K. This metamagnetic transition is related to the bump of susceptibility at 4K.

Figure 21 shows the field dependence of the longitudinal magnetoresistivity (IMR) for CeRuSnx (x=3.0, 2.91 and 2.85) at 4.2K and 1.5K. IMR of CeRuSn3 is very small and shows anomalous positive contribution at low field. This behavior is possibly explained by the competition between a negative contribution from the Kondo effect and a positive one from the localization effect. IMRs of the Sn deficient samples show large negative values. In particular, IMR of CeRuSn2.91 at 1.5K amounts to about -200μΩcm comparable with the temperature dependent resistivity decrease below the magnetic ordering temperature 1.3K (figure 15). This fact demonstrates that the applied magnetic field enhances the ordering of magnetic moments just above the transition temperature.

Figure 22 shows the temperature dependence of the Hall coefficient for CeRuSnx (x=3.0, 2.91 and 2.85). The Hall coefficient of the Sn deficient samples shows monotonous increase down to 2K with decreasing temperature. There is no anomaly near 30K where the resistivity shows drastic decrease and TEP shows a maximum. Hall coefficient maximum characteristic of the coherent state of heavy fermion compounds has not been observed at least down to 2K. This means that the resistivity decrease of the Sn
deficient samples near 30K is not due to the coherence effect. As shown in figure 11, the Hall coefficient of the stoichiometric sample can be well fitted to the expression based on the skew scattering by independent Ce impurities. From Eq. (6), we can estimate \( R_a \) using \( \rho_{\text{H}} \) vs. \( R_m \) plot. The inset of figure 22 shows \( \rho_{\text{H}} \) vs. \( R_m \) plots for the three compounds. \( R_m \) of the stoichiometric sample shows linear \( \rho_{\text{H}} \) dependence between 300K and 4K, while \( R_m \) of the Sn deficient samples depends linearly on \( \rho_{\text{H}} \) only above 100K. We estimated \( R_a \) for these compounds using least square fitting to Eq. (6). The estimated \( R_a \) are -2, -0.3 and 2 \( (10^{-4} \text{ cm}^3/\text{C}) \) for \( x=3.0, 2.91 \) and 2.85, respectively. This successive increase of \( R_a \) with decreasing \( x \) suggests that the Sn deficiency induces some change in carrier concentration.

Figure 23 shows the field dependence of the Hall resistivity \( \rho_{\text{H}} \) for CeRuSn\(_{2.91}\) up to 75kΩ at both 4.2K and 1.5K. The anomalous part of the Hall coefficient becomes larger with decreasing temperature. In the figure, the broken curve shows the best fitted curve at 4.2K to a conventional expression of the Hall resistivity in magnetic materials

\[
\rho_{\text{H}} = R_a H + R_m M
\]

(10)

where \( R_a \) is the anomalous Hall coefficient and \( M \) is the magnetization. In Eq. (10), we first assumed that \( R_a \) is not dependent on field. \( R_a \) was adjusted so as to get best fit to Eq. (10). We obtain \( R_a = -7 \times 10^{-4} \) \( (\text{cm}^3/\text{C}) \) from this fitting. The normal part of the Hall resistivity thus estimated is less than ten percent of the Hall resistivity measured at 10kΩ, suggesting the dominance of the anomalous Hall part. \( R_a \) values thus
determined is more than an order of magnitude larger than the high temperature limit value \(-0.3 \times 10^{-4}\) (cm\(^3\)/C) determined from the plot in figure 22. We cannot, however, rule out the possibility of the field dependence of \(R_a\).

In order to clarify the effect of carrier concentration change in CeRuSn, we have prepared CeRu(Sn\(_y\)In\(_{1-y}\))\(_3\) (\(y=0.05\) and 0.15). Figure 24 shows the temperature dependence of electrical resistivity and magnetic susceptibility for CeRu(Sn\(_y\)In\(_{1-y}\))\(_3\) (\(y=0, 0.05\) and 0.15). The resistivity decreases successively with increasing \(y\). As to the effect on the carrier concentration, we expect that the 15 at% substitution of In for Sn gives rise to the same contribution as 5 at% Sn deficiency. The room temperature resistivities for CeRuSn\(_{2.85}\) and CeRu(Sn\(_{0.85}\)In\(_{0.15}\))\(_3\) have a same value 360±40\(\mu\)\(\Omega\)cm within the experimental error as expected. The temperature dependence of the resistivity of CeRu(Sn\(_y\)In\(_{1-y}\))\(_3\) (\(y=0.05\) and 0.15) is monotonous, however, and any anomalies which were observed in the Sn deficient samples have not been observed. In contrast to the enhanced susceptibility of the Sn deficient samples, the magnetic susceptibility of the In alloy is reduced compared to the stoichiometric sample. These facts imply that some effects other than carrier concentration change play much important role in the Sn deficient samples.

In order to know the effect of the Sn deficiency on a non-Kondo system, we have also prepared NdRuSn\(_{2.91}\). Figure 25 shows the temperature dependence of the magnetic susceptibility and the electrical resistivity for NdRuSn\(_x\) (\(x=3.0\) and 2.91). The susceptibility of NdRuSn\(_{2.91}\) obeys Curie-Weiss law between 30K and 300K with an effective moment of 3.6 \(\mu_B\)/Nd and a paramagnetic Curie temperature \(\Theta_c\) of -13K. The effective moment is close to
the value for the tri-valent ion (3.68μ$_B$) similar to the stoichiometric compound, while the absolute value of $\Theta$ is smaller than that of the stoichiometric compound. This fact suggests that the magnetic correlation is altered by the Sn deficiency. An obvious cusp-like peak of susceptibility was observed at 3K, suggesting antiferromagnetic transition. Both in CeRuSn$_3$ and NdRuSn$_3$ systems, Sn deficiency induces magnetic transitions and simultaneously leads to the resistivity decrease. These facts suggest that the low magnetic phase transition temperature (possibly the absence of magnetic transition) has some correlation with the large residual resistivities in these compounds.
4. Discussion

4-1 CeRuSn$_3$

At low temperatures, the specific heat $C$ of the free electron Fermigas is proportional to $T$: $C=\gamma T$. The coefficient $\gamma$ is given by Eq. (8). The free electron model gives the expression of a paramagnetic susceptibility for the Fermi gas at $T \to 0$ as

$$\chi(0) = \frac{g^2\mu_B^2J(J+1)}{3N(E_F)}$$  \hspace{1cm} (11)

where $J$ is the spin of an electron. From (8) and (11), we can calculate the ratio of $\chi(0)$ to $\gamma$ as

$$\frac{\chi(0)}{\gamma} = \frac{g^2\mu_B^2J(J+1)}{\pi^2k_B^2}.$$  \hspace{1cm} (12)

Since the spin of a free electron is 1/2, thus the ratio $\chi(0)$ to $\gamma$ has a constant value for every Fermi gas systems. From the analogy to this situation, we expect the constant ratio $\chi(0)$ to $\gamma$ for the Fermi liquid state in every non-magnetic heavy fermion compounds. So-called "Wilson ratio" $R$ is derived from the Fermi liquid approach. It is given by

$$R = \frac{\pi^2k_B^2}{\mu_{\text{EFF}}^2} \frac{\chi(0)}{\gamma}.$$  \hspace{1cm} (13)

where $\mu_{\text{EFF}}^2 = g^2\mu_B^2J(J+1)$. This quantity is a good parameter for qualifying the heavy fermion systems. Since the $R$ values suffer from uncertainty in $\mu_{\text{EFF}}$, we consistently use $\mu_{\text{EFF}}=2.54\mu_B$ which is the value for free Ce$^{3+}$ ion, in this discussion. Under the condition, non interacting Fermi gas of $S=1/2$ have $R=0.47$. Table III shows the $\chi(0)$, $\gamma$ and $R$ for three typical dense Kondo compounds together with those of CeRuSn$_3$.  

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\begin{tabular}{|c|c|c|c|}
\hline
$\chi(0)$ [emu/mol.] & $\gamma$ [mJ/mol.K$^2$] & R \\
\hline
CeAl$_3$ & 0.036 & 1620 & 0.75 \\
CeCu$_6$ & 0.034 & 1600 & 0.72 \\
CeAl$_2$ & 0.043 & 135 & 10.8 \\
\hline
CeRuSn$_3$ & 0.116 & 400 & 9.8 \\
\hline
\end{tabular}

**Table III.**

$\chi(0)$, $\gamma$ and Wilson ratio R of typical dense Kondo compounds and CeRuSn$_3$.

The R value of the non-magnetic heavy fermion compounds CeAl$_3$ and CeCu$_6$ are close to that of non interacting Fermi gas due to the normal metallic behavior at low temperatures. On the other hand, R value of magnetically ordered dense Kondo system CeAl$_2$ is more than ten times larger than those of CeAl$_3$ and CeCu$_6$. In CeAl$_2$, the recent dHvA experiment [45] has confirmed that the 4f electron is not itinerant in the antiferromagnetically ordered state. The large R value is attributable to the enhancement of $\chi(0)$ due to the magnetic interaction between localized moments. The $\gamma$ value of CeAl$_2$ is considerably large as compared with those of non-Kondo systems at T=0K. Such large $\gamma$ value of CeAl$_2$ originates from the mass enhancement of conduction electrons due to the c-f hybridization.
In order to discuss the ground state of CeRuSn$_3$, we must estimate $R$ value of CeRuSn$_3$. One of the problems in estimating $R$ value is $\chi(0)$ value used in Eq.(13), because our $\chi_{ac}$ measurement only gives the relative dependence on temperature. We use the DC $\chi$ value at 1.8K as $\chi(0)$ (figure 5), because $\chi_{ac}(T=0) \approx \chi_{ac}$ (extrapolated to $T=1.8K$) as shown in figure 6. The $\gamma$ is obtained from C/T curve by extrapolation to OK. Thus calculated $R$ value of CeRuSn$_3$ which is also listed in the table III is comparable in size with that of CeAl$_2$. This fact implies that the ground state of CeRuSn$_3$ is magnetic. The magnetic moment in CeRuSn$_3$ probably remains down to OK, though it is reduced by the Kondo effect. The large $\gamma$ value (400 mJ/mole.K$^2$) originates from the mass enhancement of conduction electrons due to the c-f hybridization, as was also observed in CeAl$_2$. There is, however, clear difference between the magnetic state of CeRuSn$_3$ and those of the known magnetic heavy fermion compounds such as CeAl$_2$.

The peak at 0.6K in $\chi_{ac}$ of CeRuSn$_3$ (figure 6) could arise from an antiferromagnetic transition, but the absence of a $\lambda$-type peak characteristic of an antiferromagnetic transition in the specific heat (figure 17) rules out such possibility. In addition, CeRuSn$_3$ does not exhibit a linear temperature variation of the specific heat below 0.6K as was found in both metallic and insulating spin glasses [46]. Recently Gschneidner et al. claimed the existence of a spin glass like magnetic order in several Ce intermetallic compounds [47]. They suggest that some disorder of ambient non magnetic atoms induces a random variation of Ce-Ce exchange interactions, even if Ce atoms occupy a periodic lattice. Such interactions give rise to the spin glass behavior, as observed in CePd$_{3}$B$_{0.3}$ [46] or CeCu$_{6.5}$Al$_{6.5}$ [48].
They called this phenomenon as a non magnetic atom disorder (NMAD) spin glass. The anomalous magnetic behaviors in CeRuSn₃ are similar to those of NMAD spin glasses, but the large $\gamma$ value in CeRuSn₃ can not be explained by a NMAD spin glass model. The c-f hybridization effect plays an important role in magnetic properties of CeRuSn₃ at low temperatures. In the off stoichiometric Ce compounds, 3% deficiency of Sn induces some kind of magnetic order, as is observed in the specific heat (figure 17) and the electrical resistivity (figure 16). This fact suggests that the competition between the RKKY interaction and the Kondo effect is very critical in CeRuSn₃. The strong competition between the spin glass order and the Kondo effect might exist in stoichiometric CeRuSn₃. It can be said that CeRuSn₃ is a new heavy fermion compound with a unique low temperature magnetic ground state.
As briefly discussed in §3-1, the valence fluctuation of SmRuSn$_3$ is clearly shown by the lattice constant (figure 4), the magnetic susceptibility (figure 7) and the Hall coefficient (figure 12). The large absolute value and the characteristic temperature dependence of TEP (figure 13) also support the possibility. As shown in figure 7, the valency of Sm ion can be estimated to be about 2.8 by the fitting of the magnetic susceptibility to Eq. (2). The valency of RE ion in intermetallic compounds can also be estimated by the core spectra of x-ray photoemission spectroscopy (XPS). In SmRuSn$_3$, the valency of Sm obtained by 3d and 4d XPS measurement was estimated by Ishii et al. to be about 2.9 [49]. In many Sm intermetallic compounds, spectra of Sm$^{\pm}$ is observed in XPS measurements, while the magnetic susceptibility of the same compound does not show any valence fluctuating behavior. In SmRuSn$_3$, the fraction of Sm$^{\pm}$ estimated from XPS is the same order as that estimated from susceptibility.

As mentioned in §1, the anomalous hybridization effects in Sm intermetallic compounds can be roughly classified into three classes (a), (b-1) and (b-2). Here we discuss about the classification of SmRuSn$_3$. The possibility of the dense Kondo type (a) is easily excluded. Sm ion in the dense Kondo type Sm is close to trivalent, while SmRuSn$_3$ obviously contain Sm$^{\pm}$; the hybridization is too large. The (b-2) type situation also hardly occurs in SmRuSn$_3$. In case of (b-2) type, the compound usually becomes an insulator or a semimetal as mentioned in §1. However, the experimental results of Hall coefficient on SmRuSn$_3$ (figure...
12) and the other RERuSn$_3$ compounds (figure 11) suggest that they are normal metallic compounds with certain amount of conduction electrons. Judging from our experimental results, the valence fluctuating state in SmRuSn$_3$ is rather close to that of (b-2) group. SmRuSn$_3$ has, however, an interesting and unique point. It does not show any sign of the SmB$_6$ type gap formation. Such behavior is a rare case in hitherto reported Sm intermetallic compounds.
Transport and magnetic properties of new isostructural RE intermetallic compounds RERuSn$_3$ (RE=La, Ce, Pr, Nd and Sm) have been investigated in order to study anomalous magnetism originated from instability of 4f electrons.

RERuSn$_3$ have a cubic structure (Pr$_3$Rh$_4$Sn$_{13}$ structure: Pm$\bar{3}$m) with a large f-atomic distance of about 4.9Å. We have succeeded in growing large and high quality single crystals of RERuSn$_3$ by the Czochralski pulling method using a tri-arc furnace.

CeRuSn$_3$ shows impurity Kondo like behaviors between 300K and 1.5K. Below 1.5K, the magnetic correlation between the localized moments becomes strong. The $\chi_{ac}$ and the C/T reaches a maximum at 0.6K due to the magnetic correlation. Both C/T at T=0 and $\chi(0)$ are large compared to ordinary metals. The large "Wilson ratio" suggests some complex magnetic correlations. The critical competition between the spin-glass like state and the Kondo state may be essential in this substance. CeRuSn$_3$ is a new heavy fermion compound with an unique magnetic ground state.

SmRuSn$_3$ shows the valence fluctuation. The magnetic susceptibility $\chi$ does not obey both Curie-Weiss and Van Vleck-Franck susceptibilities for Sm$^{3+}$. From the $\chi$ value near room temperatures, valency of Sm ion is estimated to be 2.8. This estimation is in good agreement with the XPS core-spectra results by Ishii et al. [49]. SmRuSn$_3$ also shows antiferromagnetic transition at 6K. SmRuSn$_3$ is found to be a rare example which show such a "normal" type valence fluctuation in metallic Sm compound. It is not yet clear why SmRuSn$_3$ does not show SmB$_6$ type gap formation.
The other three RERuSn$_3$ (RE=La, Pr and Nd) show rather ordinary normal metallic behaviors. LaRuSn$_3$ shows superconducting transition at 1.5K. Both PrRuSn$_3$ and NdRuSn$_3$ have stable moments due to trivalent RE ion, and do not show any magnetic order down to 1.8K.
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Appendix

As mentioned in §1, as to their itineracy, 3d electrons show a sharp contrast to 4f electrons. In an uranium atom, 5f electrons have moderate amplitude outside the 6s and 6p closed shells. Therefore, uranium intermetallic compounds show wealth of different magnetic and electrical behaviors from complete Pauli itinerant to localized magnetic moment including heavy fermion state [50]. It is believed that the direct 5f-5f overlap and the 5f-ligand hybridization are the most important factors. In this thesis, we have described about properties of a large 4f-4f distance RE system RERuSn₃ which includes a heavy fermion compound CeRuSn₃ and a valence fluctuating compound SmRuSn₃. In order to see the difference between 4f electrons and 5f electrons, it is interesting to study the magnetic properties of uranium compounds which have the same or similar structures to RERuSn₃.

In this appendix, we report our trial to make uranium compounds which have Pr₂Ru₄Sn₁₃ type structure or a similar structure. We also report the transport, magnetic and thermal properties of obtained U₃Ru₄Sn₁₃ and U₅Rh₄Sn₁₃ compounds.
A. Sample preparation and analysis

The crystal structure of $\text{RE}_3\text{Rh}_4\text{Sn}_{13}$ (RE=La–Gd and Yb) compounds is first determined by Vandenberg [51]. The $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ structure has four crystallographic positions in $\text{Pm}3\text{m}$ symmetry, as shown in figure 2. In case of $\text{REE}_3\text{Ru}_3\text{Sn}_3$, since 2a positions are occupied by RE ions, the composition of RE-Ru-Sn is 1-1-3. If 2a positions are occupied by Sn atoms, the composition becomes 3-4-13 such as $\text{RE}_3\text{Rh}_4\text{Sn}_{13}$. In the hand book of crystal structure for intermetallic compounds [52], 1-1-4 composition compounds are also reported in the column of $\text{Pr}_3\text{Ru}_4\text{Sn}_{13}$ structure. Since there has been no report about uranium compounds which have $\text{Pr}_3\text{Ru}_4\text{Sn}_{13}$ structure, we have tried to make polycrystalline $\text{URuSn}_3$, $\text{URuSn}_4$ and $\text{U}_3\text{Ru}_4\text{Sn}_{13}$ and to grow a single crystalline sample pulling from 1-1-3 composition. The polycrystals were prepared by arc melting appropriate amount of the constituent elements (99.9% U, 99.99% Ru and 99.999% Sn), and were turned over and remelted several times to ensure homogeneity. A single crystal was grown by Czochralski method using a tri-arc furnace. They were wrapped in Ta foils and Zr foils and sealed in a evacuated quartz tube, and annealed at 950°C for three days. After annealing they were analysed by x-ray powder diffraction. Results of x-ray analysis are shown in table A-1. The crystal structure of the phase III is reported to be close to $\text{Pr}_3\text{Ru}_4\text{Sn}_{13}$ (phase I) type [51], while the precise determination of the structure has not been succeeded. Figure A-1 shows a trial structure of phase III structure given by Vandenberg in ref.[51]. The x-ray analysis reveals the existence of several percent of ferromagnetic impurity $\text{URuSn}$ ($T_c=53K$ [53]) in $\text{URuSn}_3$ and $\text{URuSn}_4$, which was
also confirmed by magnetic susceptibility measurements. Both the polycrystalline $U_3Ru_4Sn_{13}$ and the single crystalline samples are almost single phase of the phase III structure except for small amount of impurities $Ru_3Sn_7$ and Sn. The powder diffraction patterns of both samples are shown in figure A-2. The physical properties of both samples agree each other. For example, figure A-3 shows the temperature dependence of electrical resistivities for the polycrystalline $U_3Ru_4Sn_{13}$ and the single crystalline sample between 4K and 300K. The behavior of each electrical resistivity is quite similar. These facts suggest the composition of the single crystalline sample is close to 3-4-13. The electrical resistivity of the grown single crystalline sample shows superconducting transition at 3.7K probably due to impurity Sn, though no Sn line has been detected in x-ray diffraction analysis.

In case of Rh compound, we prepared only 3-4-13 compound. The x-ray powder diffraction analysis reveals that as cast 3-4-13 sample is not single phase. It becomes a single phase of $Pr_3Rh_4Sn_{13}$ (phase 1) structure after annealed at 950° C. Those x-ray powder patterns are shown in figure A-4.

The $U_3Ru_4Sn_{13}$ and the $U_3Rh_4Sn_{13}$ samples were cut into suitable forms by a spark cutter for the electrical, magnetic and thermal measurement.
<table>
<thead>
<tr>
<th>sample name</th>
<th>structure of main phase</th>
<th>impurity phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>URuSn₃</td>
<td></td>
<td>URuSn</td>
</tr>
<tr>
<td>URuSn₄</td>
<td></td>
<td>URuSn, Sn</td>
</tr>
<tr>
<td>U₃Ru₄Sn₁₃ (poly.)</td>
<td>Phase III (F43m; FCC)</td>
<td>Ru₃Sn₁₇, Sn</td>
</tr>
<tr>
<td>U₃Ru₄Sn₁₃ (single)</td>
<td></td>
<td>Ru₃Sn₁₇, (Sn)</td>
</tr>
<tr>
<td>U₃Rh₄Sn₁₃</td>
<td>Phase I (Pm₃n)</td>
<td>Pr₃Rh₄Sn₁₃</td>
</tr>
</tbody>
</table>

Table A-I.

Results of qualitative analysis for U-T-Sn series using x-ray powder diffraction.
B. Results on U₃Ru₄Sn₁₃

As shown in figure A-3, the temperature dependence of the electrical resistivity for U₃Ru₄Sn₁₃ shows a type of curve that is characteristic for many uranium compounds: a sharp rise at low temperature and tendency to saturate near room temperature. These behaviors are ascribed to the strong conduction electrons scattering by spin fluctuations. The residual resistivity of U₃Ru₄Sn₁₃ (85μΩcm) is rather small as compared with those of RERuSn₃.

Figure A-5 shows the temperature dependence of the magnetic susceptibility for U₃Ru₄Sn₁₃. From the higher temperature slope of χ⁻¹-T curve, we obtained ϕₜ=-76K and μₑₑₑ=3.4μB which is close to the value of the trivalent uranium ion (3.62μB). There is no clear sign of magnetic order down to 1.8K. The magnetic susceptibility shows considerable enhancement at low temperatures, while the magnetization curve at 1.8K dose not show any sign of ferromagnetic order as shown in figure A-6. One of the characteristics of this system is the large magnetic susceptibility at low temperatures. This suggests the possibility of some magnetic order at lower temperatures. Such a magnetic behavior is similar to those of CeRuSn₃. A step like anomaly suggesting some phase transition is observed near 120K. The origin of this structure is not yet clear. We only notice the similarity of this structure to that observed in UPd₃In [54].

Figure A-7 shows the temperature dependence of TEP for U₃Ru₄Sn₁₃. The sign of TEP is negative between 300K and 1.5K. TEP is proportional to temperature between 300K and 150K and extrapolated to zero at 0K as expected from the ordinary
diffusion TEP. The absolute value of the slope for the diffusion TEP is several times larger than those of Cu or Ag suggesting the steeper energy dependence of N(E) near E_F compared to normal metal. A negative peak is observed near 23K. As an origin of this peak, we hardly expect such a large phonon drag contribution, since the residual resistivity is considerably large. The more reasonable origin is in the spin fluctuation scattering of conduction electrons. Actually the temperature dependence of electrical resistivity in these temperature region also suggests the spin fluctuation scattering. In order to obtain the deeper insight into the ground state of U₃Ru₄Sn₁₃, the specific heat measurement is necessary.
C. Results on $U_3Rh_4Sn_{1.3}$

Figure A-8 shows $C/T$ of $U_3Rh_4Sn_{1.3}$ as a function of $T^2$ between 0.7K and 13K measured at Hokkaido University of Education. In this temperature range, $C/T$ does not show any anomaly suggesting any phase transitions or Schottky anomaly. By extrapolating to 0K, we observed $\gamma=260$ mJ/mol$\cdot$K$^2$. The linear dependence of $C/T$ on $T^2$ suggests the simple combination of a constant electronic part and phonon contribution. The absence of upturn of $C/T$ at low temperatures exclude the possibility of the magnetic correlation such as Non Magnetic Atomic Disorder spin glass as mentioned in §4-1. It also suggests that the effective $T_c$ is higher than the ordinary heavy fermion compounds such as CeAl$_3$ and CeCu$_6$.

Figure A-9 shows the temperature dependence of the magnetic susceptibility and the electrical resistivity between 1.3K and 350K. The inverse magnetic susceptibility $\chi^{-1}$ shows the modified Curie-Weiss type behavior. From the slope of $\chi^{-1}$-$T$ curve above 300K, we obtained $\Theta_F=-77$K and $\mu_{eff}=3.3\mu_B$ which is close to the value of the trivalent uranium ion ($3.62\mu_B$). The electrical resistivity increases monotonously with decreasing temperature. As shown in figure A-10, we observed logarithmic temperature dependence between 100K and 300K, suggesting Kondo type scattering. The sharp increase of resistivity near 18K suggests some phase transition. A similar behavior has been often observed in antiferromagnetic ordering process. In order to get more information about this transition, we measured magnetic susceptibility under the several different conditions. The temperature dependence of magnetic susceptibility for several
values of magnetic field is shown in figure A-11. The open and close circles are for field-cooled (FC) susceptibility and zero-field-cooled (ZFC) one. The FC susceptibility at 50O shows a bend around 18K. The bend shifts to the lower temperature with increasing field, which suggests some magnetic order at this temperature. The difference between the FC susceptibility and the ZFC one at 50O is similar to the case of the micromagnetic materials. The origin of a drastic change of the ZFC susceptibility near 4K is not yet clear. The anomaly is not due to the bulk magnetic order, since the specific heat does not show any anomaly near 4K as shown in figure A-8. One of a possible origins is in a ferromagnetic domain effect, because the magnetisation measurement reveals the existence of weak spontaneous magnetisation at 1.8K as shown in figure A-12.

Figure A-13 shows the temperature dependence of TEP. Between 1.5K and 300K, sign of TEP is negative, which is a common feature between U3Rh4Sn13 and U3Ru4Sn13 in contrast to positive sign of TEP for RERuSn3. TEP of U3Rh4Sn13 shows a broad negative peak of -10μV/K near 100K as is often observed in the dense Kondo compound. TEP also has a small kink corresponding to magnetic order at 18K. The behavior of TEP of uranium systems is, however, not so simple as compared to Ce and Yb compounds as is also reported in ref.[55].
D. Summary on U-system

We have succeeded in making new $U_3T_4Sn_{13}$ (T:Ru and Rh) intermetallic compounds with reasonably good quality. The interesting physical properties of these compounds obtained in our experiments are summarized as follows.

(1) $U_3Ru_4Sn_{13}$ has the phase III ($F43m$) structure which has a structure close to that of $RERuSn_3$. The magnetic susceptibility does not show any clear magnetic order, but has considerable magnitude at low temperatures. The effective moment estimated from the high temperature slope of inverse susceptibility is $3.3\mu_B$. The electrical resistivity does not show any Kondo type anomaly, but a type of curve for the spin fluctuation scattering. Such behavior is observed in many uranium intermetallic compounds.

(2) $U_3Rh_4Sn_{13}$ has the phase I ($Pr_3Rh_4Sn_{13}$) structure which is same as that of $RERuSn_3$. $U_3Rh_4Sn_{13}$ is a heavy fermion compound with $\gamma=260$ mJ/mol.U$^\circ$K$^2$. It shows some kind of magnetic order below $18K$. The effective moment estimated from the high temperature slope of inverse susceptibility is $3.3\mu_B$. The electrical resistivity and TEP show Kondo like behaviors.

Above mentioned anomalous magnetic behaviors of $U_3T_4Sn_{13}$ compounds are more complex and seems to be difficult to understand on a simple model as compared to $RERuSn_3$, such as the impurity Kondo model for CeRuSn$_3$. The same tendency has been reported in many uranium and RE intermetallic compounds. It might reflect the stronger hybridization effects in 5f electrons system that in 4f electrons system.
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Figure 1.
Atomic wavefunctions of Ni and Ce atoms. (Kasuya1987; ref.[1])
Figure 2.

The $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ structure of $\text{RERuSn}_3$. 

The $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$ structure of $\text{RERuSn}_3$. 

Wyckoff position

- RE
  - 2a
  - 6d
- Ru
  - 8e
- Sn
  - 24k
Figure 3.
Photograph of a typical grown single crystal.
Figure 4.
Lattice constant of $\text{RE}_3\text{Ru}_3\text{Sn}_3$ together with those reported earlier for $\text{RE}_3\text{Sn}_3$ (Eisenmann and Schäfer 1985; ref.[29]) and isostructural compound $\text{RE}_3\text{Rh}_4\text{Sn}_{13}$ (Remeika et al.1980; ref.[30]).
Figure 5.
Temperature dependence of reciprocal magnetic susceptibility for RERuSn$_3$ (RE=Ce, Pr and Nd). The inset shows magnetic susceptibility below 20K.
Figure 6.
Temperature dependence of AC susceptibility for CeRuSn$_3$. 
Figure 7.
Temperature dependence of magnetic susceptibility for SmRuSn$_3$. The broken curve shows the theoretical magnetic susceptibility of Van Vleck-Franck Sm$^{3+}$. The solid curve shows the susceptibility calculated simply assuming $\chi = (1-a)\chi^{3+} + ax^{2+}$ with $a=0.2$. The inset shows an enlarged view of magnetic susceptibility and electrical resistivity near the magnetic transition.
Figure 8.
Temperature dependence of electrical resistivity for RERuSn$_3$ (RE=La,Ce,Pr,Nd and Sm). The inset shows an enlarged view of electrical resistivity for LaRuSn$_3$ near a superconducting transition.
Figure 9.
Electrical resistivity of RERuSn$_3$ (RE=La, Pr and Nd) as a function of $T^{1/2}$. 
Figure 10.
Temperature dependence of magnetic resistivity for CeRuSn₃. The broken curves are the best fitted curves to the Hamman-Fisher law with \( T_{k}=20\text{K} \) and \( T_{k}^{''}=120\text{K} \).
Figure 11.
Temperature dependence of Hall coefficient for RERuSn₃ (RE=La, Ce and Pr) at 10k⁺. The broken curve is best fitted to Eq. (6). The inset shows Hall coefficient as a function of $\rho_m \chi$ where $\rho_m$ is magnetic resistivity and $\chi$ is normalized susceptibility.
Figure 12.
Temperature dependence of Hall coefficient for SmRuSn$_3$ at 10kø.
The broken curve is Hall coefficient for PrRuSn$_3$. 
Figure 13.
Temperature dependence of thermoelectric power for RERuSn$_3$ (RE=La, Ce, Pr, Nd and Sm).
Figure 14.
Temperature dependence of specific heat coefficient for CeRuSn$_3$ between 0.6K and 20K. The inset shows the low temperature part in an extended temperature scale.
Figure 15.
Lattice constant for the non-stoichiometric compounds CeRuSn$_x$ (2.85 $\leq x \leq$ 3.15) and NdRuSn$_x$ (x=2.91 and 3.0), and In alloys CeRu(Sn$_{1-y}$In$_y$)$_3$ (y=0.15 and 0.05).
Figure 16.
Temperature dependence of electrical resistivity for CeRuSn$_x$ ($2.85 \leq x \leq 3.15$).
Figure 17.
Temperature dependence of low temperature specific heat for CeRuSn$_{x}$ and CeRuSn$_{2.91}$.
Figure 18.

Temperature dependence of low temperature specific heat for CeRuSn$_{2.91}$ under several magnetic fields.
Temperature dependence of thermoelectric power for CeRuSn,
(2.85 ≤ x ≤ 3.15).

Figure 19-(a).
Figure 19-(b).
Thermoelectric power of Sn deficient CeRuSn$_x$ ($x=2.85$, 2.91 and 2.97) below 60K.
Figure 20.
Temperature dependence of magnetic susceptibility for CeRuSn$_x$ (x=2.85, 2.91 and 3.0). The inset shows magnetization as a function of magnetic field at 1.8K.
Figure 21.

Field dependence of longitudinal magnetoresistivity for CeRuSn,
(x=2.85, 2.91 and 3.0) at 4.2K and 1.5K.
Figure 22.
Temperature dependence of Hall coefficient for CeRuSn$_x$ (x=2.85, 2.91 and 3.0). The inset shows Hall coefficient as a function of $\rho_m \tilde{X}$. 
Figure 23.
Field dependence of Hall resistivity for CeRuSn$_{2.91}$ at 4.2K and 1.5K. The broken curve shows the best fitted curve to Eq.(8) at 4.2K.
Figure 24.
Temperature dependence of electrical resistivity and magnetic susceptibility for CeRu(Sn$_{1-y}$In$_y$)$_3$ ($y$=0.15 and 0.05).
Figure 25.
Temperature dependence of electrical resistivity and magnetic susceptibility for NdRuSn$_x$ (x=2.91 and 3.0). The inset shows an enlarged view of electrical resistivity of NdRuSn$_{2.91}$ near $T_H$=6K.
Figure A-1.

One octant of the phase III structure (Vandenberg 1980:ref.[50])
Figure A-2.

Cu Kα x-ray powder diffraction pattern of the annealed $U_3Ru_4Sn_{13}$ polycrystalline sample and the single crystalline sample pulling from 1-1-3 composition.
Figure A-3.
Temperature dependence of electrical resistivity for the annealed U$_3$Ru$_4$Sn$_{13}$ polycrystalline sample and the single crystalline sample pulling from 1-1-3 composition.
Figure A-4.

Cu Kα x-ray powder diffraction pattern of U₃Rh₄Sn₁₃ for (a) as cast sample and (b) sample annealed at 950°C for 3 days along with calculated one (c).
Figure A-5.
Temperature dependence of magnetic susceptibility for $U_3Ru_4Sn_{13}$. 
Figure A-6.
Field dependence of magnetization for $U_3Ru_4Sn_{13}$ at 1.8 K and 5 K.
Figure A-7.

Temperature dependence of TEP for $\text{U}_3\text{Ru}_4\text{Sn}_{\text{13}}$. 
Figure A-8.
Specific heat coefficient of $U_3Rh_4Sn_{13}$, $C(T)$ divided by temperature as a function of $T^2$ between 0.7K and 13K.
Figure A-9.
Temperature dependence of magnetic susceptibility and electrical resistivity for $U_3 Rh_4 Sn_{13}$. 
Figure A-10.

Electrical resistivity of $U_3Rh_4Sn_{13}$ as a function of $\log T$. 
Figure A-11.
Temperature dependence of magnetic susceptibility for U₃Rh₄Sn₁₃ measured at 50ø, 500ø, 1kø and 55kø. The open and close circles are for field-cooled (FC) susceptibility and zero-field-cooled (ZFC) one respectively.
Figure A-12.
Field dependence of magnetization for U₃Rh₄Sn₁₃ at 1.8K, 5K, 10K and 20K. The inset shows the low field part at 1.8K.
Figure A-13.

Temperature dependence of thermoelectric power for $U_3\text{Rh}_4\text{Sn}_{13}$. 
Supplement
LETTER TO THE EDITOR

Electronic and magnetic properties of a new heavy-fermion compound, CeRuSn$_3$

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Abstract. Measurements of electrical resistivity, Hall coefficient, thermoelectric power, magnetic susceptibility and specific heat have been made on CeRuSn$_3$, with cubic Pm$_3$n structure. The results indicate that CeRuSn$_3$ is a new heavy-fermion compound with a specific heat coefficient of 1.4 J mol$^{-1}$ K$^{-2}$ at 0.6 K. Above 0.6 K, it shows no magnetic ordering.

The properties of heavy-fermion Ce compounds with non-magnetic ground states have been studied extensively in recent years. Their common features are: an enhanced electronic specific heat coefficient, a large Pauli paramagnetic susceptibility at low temperature, a resistivity drop below the Kondo temperature and a large positive thermoelectric power at high temperature.

Heavy-fermion compounds have relatively large Ce spacing: 4.43 Å and 4.83 Å in CeAl$_3$ and CeCu$_6$, respectively [1, 2]. The spacing of f-electron atoms in heavy-fermion compounds is an important parameter, presumably describing the effective width of the hybridised f band [3, 4]. Almost all the cubic Kondo compounds, such as CeB$_6$ and CeAl$_2$ [5, 6], order magnetically at low temperatures, except CeInCu$_2$ which has recently been reported to be a heavy-fermion compound [7]. CeInCu$_2$ also has a large Ce spacing of 4.80 Å, which is close to that of CeCu$_6$.

The existence of compounds with the formula RRRuSn$_3$ (R = La, Ce, Pr, Nd) was reported by Eisenmann and Schäfer [8]. CeRuSn$_3$ crystallises in a cubic structure (with Pr$_3$Rh$_4$Sn$_{13}$ structure Pm3n) and with a Ce spacing of 4.86 Å. It is of interest to know physical properties of CeRuSn$_3$. In this Letter we report the first experimental studies of resistivity, magnetic susceptibility, Hall coefficient, thermoelectric power and specific heat on this compound.

Polycrystals of CeRuSn$_3$ and LaRuSn$_3$ were obtained under argon atmosphere by arc melting stoichiometric amounts of 99.9% purity Ce and La, 99.98% purity Ru and 99.999% purity Sn. To ensure homogeneity, the ingots were turned over and remelted several times. The samples obtained were analysed by x-ray diffraction. No parasitic phase was detected even in as-cast samples. The lattice constants obtained by x-ray analysis agree with literature values, namely 9.73 Å and 9.77 Å for CeRuSn$_3$ and LaRuSn$_3$, respectively. Single-crystal samples were grown by the Czochralski pulling
Figure 1. Temperature dependence of electrical resistivity $\rho(T)$ of CeRuSn$_3$ (curve A) and LaRuSn$_3$: as-grown (curve B), annealed (curve C). Inset shows temperature dependence of magnetic resistivity $\rho_m = \rho(\text{CeRuSn}_3) - \rho(\text{LaRuSn}_3)$.

method using a tri-arc furnace. Samples were annealed at 950°C for three days. For transport measurements, samples were cut into rectangular rods by a spark cutter.

Figure 1 shows the temperature dependence of the electrical resistivity for CeRuSn$_3$ and LaRuSn$_3$. For CeRuSn$_3$, the resistivity increases at least down to 1.3 K. All CeRuSn$_3$ samples measured have almost the same resistivity of about 470 ± 40 $\mu$Ω cm at 300 K and about 670 ± 50 $\mu$Ω cm at 1.3 K. We have plotted the magnetic resistivity $\rho_m (\rho_m = \rho(\text{CeRuSn}_3) - \rho(\text{LaRuSn}_3))$ in the inset of figure 1. The $\rho_m$ is proportional to $-\log T$ between 300 K and 70 K. At the present stage, it is not clear why we do not see a decrease in resistivity due to the coherence effect at low temperatures.

In order to study the dependence of the resistivity on heat treatments, we repeated the measurement after annealing CeRuSn$_3$ under different conditions: 1000 °C for three days; 950 °C for three days; 600 °C for two weeks. There is no detectable change of the resistivity. In the case of LaRuSn$_3$, the effect of annealing on the temperature dependence of the resistivity is larger than that on CeRuSn$_3$. The resistivity of an as-grown sample increases with decreasing temperature, reaches a broad maximum and then decreases at lower temperatures. For a sample annealed at 950 °C for three days, the resistivity shows normal metallic behaviour. LaRuSn$_3$ shows a transition to a superconducting state at $T_c \approx 1.5$ K.

Figure 2 shows the temperature dependence of the inverse magnetic susceptibility $\chi^{-1}$ of CeRuSn$_3$ between 1.7 and 300 K. The susceptibility follows the Curie–Weiss law above 100 K. The paramagnetic Curie temperature and the effective Bohr magneton $\mu_{\text{eff}}$ are about $-38$ K and 2.5$\mu_B$ mol$^{-1}$ respectively. $\mu_{\text{eff}}$ is close to the value for Ce$^{3+}$ (2.56$\mu_B$). The susceptibility shows a large value of about $1.5 \times 10^{-1}$ emu mol$^{-1}$ at 1.7 K, which is about five times as large as the values that have been observed for CeCu$_6$, CeAl$_3$ and CeInCu$_2$. The preliminary $\text{AC}$ susceptibility measurement below 1.7 K reveals a sharp maximum around 0.5 K suggesting some magnetic ordering. The susceptibility of
LaRuSn₃ is $1.6 \times 10^{-4}$ emu mol$^{-1}$ at 300 K and is almost independent of temperature down to 1.5 K.

Figure 3 shows the temperature dependence of the Hall coefficient $R_H$. The Hall coefficient of LaRuSn₃ is $2 \times 10^{-10}$ m$^3$ C$^{-1}$ at 300 K and is weakly temperature dependent. The estimated carrier density based on a single carrier model is normal metallic ($3 \times 10^{28}$ electrons m$^{-3}$ at 300 K). The Hall coefficient of CeRuSn₃ increases with decreasing temperature and has a large value of $6.8 \times 10^{-8}$ m$^3$ C$^{-1}$ at 2 K. The Hall coefficient of this f-electron system is still increasing at 2 K. According to Coleman and co-workers [9], the Hall coefficient due to skew scattering by independent Ce impurities is given by

$$R_H \sim g \mu_B \rho_m \chi(1 - \tilde{\chi} T)$$  \hspace{1cm} (1)
\( \hat{\chi} = \chi/C \) (\( C \) being the Curie constant). In figure 3 the broken curve shows \( R_H \) calculated by equation (1). In order to obtain a good fit, we multiplied \( \rho_m \) by a factor of 3.3. All these experimental features are characteristic of Ce dense Kondo compounds.

Figure 4 shows the temperature dependence of the thermoelectric power. Compared to the other properties, the dependence of thermoelectric power on the sample is larger. The temperature dependencies measured on different samples, however, have common characteristics. In figure 4, two examples of the temperature dependence of CeRuSn\(_3\) are shown. We observe a negative sharp minimum around 6 K, and a positive broad maximum around 80 K. The sign of thermoelectric power is positive at 300 K, though the positive value is somewhat smaller compared to general Ce Kondo compounds. Maekawa and co-workers analysed the thermoelectric power of the Ce Kondo system theoretically [10]. They obtained positive thermoelectric power in all the temperature range, unless they take into account the potential scattering and/or coherence effect of electron scattering by Ce ions. Since in CeRuSn\(_3\) the coherence effect is not clearly seen in resistivity or Hall effect in this temperature range, the effect of potential scattering is the possible origin of the negative peak near 6 K. For LaRuSn\(_3\), thermoelectric power at 300 K is positive and decreases monotonically with lowering temperature without change of sign down to \( T_c \).

Figure 5 shows the temperature dependence of the specific heat coefficient divided by temperature, \( C/T \), of CeRuSn\(_3\) between 0.6 and 20 K. The \( C/T \) has a minimum around 7 K then increases at lower temperatures without any sign of phase transition down to 0.6 K. At 0.6 K, it reaches 1.40 J mol\(^{-1}\) K\(^{-2}\), which is comparable with those of CeCu\(_6\), CeAl\(_3\) and CeInCu\(_2\). The \( C/T \) versus \( T \) curve bears a close resemblance to that of CeInCu\(_2\), although \( C/T \) starts increasing at a somewhat higher temperature and shows saturation below 1 K in CeInCu\(_2\).

To summarise, the present experimental results suggest that CeRuSn\(_3\) is a new heavy-fermion compound. It shows no magnetic ordering down to 0.6 K. There still remain several questions to be answered in order to clarify the low-temperature behaviour. To this end, measurements on samples with controlled stoichiometry and at lower temperature are now in progress.
Figure 5. Temperature dependence of specific heat coefficient of CeRuSn, $C(T)/T$ divided by temperature.

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References

CRITICAL MAGNETIC BEHAVIORS IN CeRuSn, (2.85≤x≤3.15)

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CeRuSn4 is reported to be a heavy fermion compound with an enormous coefficient of electronic specific heat γ=1.4 J/mole·K². In order to gain a deeper insight into the heavy fermion state of CeRuSn4, we have measured resistivity, magnetization, magnetic susceptibility, Hall effect and thermopower on CeRuSn4 (2.85≤x≤3.15). The low temperature resistivity shows a maximum at x=0, as a function of x. Sn deficient samples exhibit two phase transitions at 30K and 4K.

1. INTRODUCTION

The intermetallic ternary compound CeRuSn4 crystallize in the cubic Pr₃Rh₂Sn₃ structure (1) (Pu3Sn type group). Our recent experiments (2) suggest that CeRuSn4 is a new heavy fermion compound. According to Takayamagi et al. (3), the heat capacity exhibits only a small bump around 0.5K. The electronic specific heat coefficient reaches a maximum of about 1.4 J/mole·K² at 0.6K.

Transport properties of CeRuSn4 show anomalous behaviors. As temperature decreases the electrical resistivity (ρ) increases continuously down to 0.7K without showing coherence effect. The Hall coefficient (R_H) also increases down to 1.7K as expected from the skew scattering by independent Ce impurities. We suspect that the coherence is destroyed by the random occupation of original Sn site (24k in Wyckoff notation). According to our study, the Pr₃Rh₂Sn₃ structure is stable over a wide range of nonstoichiometric compounds. In order to get a better understanding about the heavy fermion state in CeRuSn4, we have performed transport and magnetic measurements in the series CeRuSn4, where 2.85≤x≤3.15.

2. EXPERIMENT

The polycrystalline CeRuSn4 samples were prepared by arc-melting appropriate amounts of the constituent elements (Ce 99.9%, Ru 99.98%, Sn 99.999%) on a water cooled copper hearth. The ingots were wrapped in Ta and Zr foils and annealed at 950°C for 3 days in a evacuated quartz tube. The samples obtained were analysed by X-ray diffraction. No parasitic phase was detected in the sample of x=3, while X-ray diffraction patterns for x=2 indicate very weak additional reflections. Single crystals of CeRuSn4 have been grown using the Czochralski method in a SELEC triarc furnace. We have not observed any significant difference in bulk properties between single crystals and polycrystals.

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of ρ for CeRuSn4 (2.85≤x≤3.15). Between 80K and 300K, ρ(x=3.0) exhibits a logarithmic increase with decreasing temperature due to the incoherent Kondo scattering.

In the Sn excessive cases, the absolute value of ρ becomes smaller with increasing x, while the temperature dependence of ρ for x=3.03 and 3.09 is not so much different from that for x=3.0. The excess of 5 at% Sn (x=3.15) leads to drastic decrease of ρ at low temperature. In this sample the extraction of pure Sn was confirmed by X-ray diffraction, and the abrupt drop of ρ(x=3.15) at 3.7K is due to the superconducting transition of Sn impurity. In the Sn deficient cases, ρ becomes smaller with decreasing x, and exhibits two step anomalies reflecting some kind of phase transitions near 33K and 4K. As to x dependence of the low temperature resistivity, a maximum was observed at x=3.0. This fact partly supports that the low temperature increase of ρ for CeRuSn4 is not due to the random occupancy of Sn site as opposed to the above-mentioned suspicion.

Figure 2 shows the magnetic susceptibility χ of CeRuSn4, (x=3.0, 2.91 and 2.85) down to 1.8K.
The absolute value of $\chi(x=3)$ at 1.8K is large in comparison with those of typical heavy fermion compounds, and is rather close to those of Kondo compounds with magnetic order (such as CeRu or CeCu$_2$). It suggests that the possibility of some magnetic order at lower temperature in CeRuSn$_3$. In the Sn deficient samples, $\chi$ is clearly enhanced compared to $x=3.0$ sample. The enhancement is especially evident below 30K, but no significant kink or bend can be seen around 30K. Corresponding to the lower temperature anomaly in $\rho$, the bump at 4K in $\chi$-$T$ curve gives a clear evidence of a magnetic transition for $x=2.85$. For $x=2.91$, $\chi$-$T$ curve only shows a small change in slope around 4K.

The inset in figure 2 shows the field dependence of magnetization ($M$) at 2K. $M$ becomes larger with decreasing Sn content. $M(x=2.85)$ also shows a metamagnetic behavior at about 6 KG. This fact together with the small bump in $\chi$-$T$ curve suggest that an antiferromagnetic long range order develops below 4K in CeRuSn$_{2.95}$.

Figure 3 shows the temperature dependence of the Hall coefficient $R_H$ of CeRuSn$_{2.9}$ and CeRuSn$_{3.0}$ at 10KG. The broken curve is calculated from the skew scattering model.

The similar upturn is also seen at 30K, though it is not so clear as low temperature one. Even at 300K, $R_H(x=2.91)$ is about 60% larger than $R_H(x=3.0)$. This fact implies some change of carrier concentration, since the estimated anomalous part $\rho_{\alpha}\chi$ can not explain the difference. It is reasonable to expect that a deficiency of Sn will cause a change of the number of electrons in the conduction band.

To summarize, the competition between RKKY interaction and Kondo effect is very critical in CeRuSn$_3$. The deficiency of Sn induces two step phase transitions at 4K and 33K. The lower temperature one is an antiferromagnetic ordering, while the higher temperature one is not clear at present stage. The microscopic measurements, such as neutron scattering, are necessary to clean up its origin.

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HEAVY FERMION BEHAVIOUR IN CeRuSn₃ COMPOUND

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The electrical resistivity under pressure (up to 23 kbar), magnetic susceptibility and specific heat of CeRuSn₃ with cubic Pm₃n structure were measured between 30 mK and 300 K. The magnetic scattering of the resistivity behaves like a dilute Kondo type. Below 1 K, the ratio C/T remarkably increases and reaches a broad maximum around 0.5 K. The magnetic susceptibility also shows a maximum at the same temperature. These results indicate an antiferromagnetic-type ordering induced by the RKKY-interaction between 4f-electrons below 0.5 K. CeRuSn₃ is a new heavy fermion compound with specific heat coefficient of 1.67 J/K²·mol at 0.6 K.

1. INTRODUCTION

The f-atom spacing in heavy fermion systems is an important parameter, presumably dominated the effective width of the hybridized f band. Heavy fermion compounds have f-f distance greater than 4 Å beyond which Hill point out that f-f overlap ceases and magnetism occurs. For example, CeAl₃ and CeCu₆ have relatively large Ce-Ce distance of 4.43 Å and 4.83 Å respectively. Almost all the cubic Kondo compounds, such as CeB₁₂ and CeAl₁₃, order magnetically at low temperatures except CeInCu₆ which have been recently reported to be a heavy fermion compound (1). CeInCu₆ also has large Ce spacing 4.80 Å which is close to that of CeCu₆.

The existence of compounds with the formula RRRuSn₃ (R=La, Ce, Pr, Nd) was reported by Eisenmann and Schaefer (2). CeRuSn₃ crystallize in cubic structure (Pr₃RuSn₁₃ structure: Pm₃n), and Ce spacing is 4.86 Å. Recently, we have found this compound to be a new heavy fermion system with a large electronic specific heat coefficient (3) such as that of CeCu₆. It is of interest to know the ground state properties of CeRuSn₃ in detail. In this letter we report the extensive experimental studies of resistivity, magnetic susceptibility and specific heat.

2. EXPERIMENTAL

Polycrystals of CeRuSn₃ and LaRuSn₃ were obtained under argon atmosphere by arc melting stoichiometric amounts of 99.9%-Ce, -La and 99.9%-Ru. The lattice constants obtained by x-ray analysis agree with literature values CeRuSn₃: 9.73 Å, LaRuSn₃: 9.77 Å. Single crystal samples were grown by the Czochralski pulling method using a tri-arc furnace. Samples were annealed at 950°C for 3 days. The electrical resistivity was measured under hydrostatic pressures up to 23 kbar using a standard four-lead method. The pressure was generated by means of a Cu-Be clamp type piston-cylinder apparatus. The specific heat measurements were carried out between 50 mK and 50 K using two adiabatic calorimeters; one was for 2-50 K measurements and the other was mounted in a dilution-refrigerator for low temperature measurements (50 mK-2 K).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the temperature dependence of the electrical resistivity for CeRuSn₃ and仕

![Figure 1](image-url)
LaRuSn₃. We plotted magnetic resistivity, which looks like a dilute Kondo type, in the inset of figure 1. The $\sigma$ is proportional to $-\log T$ between 300 K and 70 K. LaRuSn₃ shows a transition into a superconducting state at $T_c=1.5$ K.

We discuss why the magnetic resistivity of CeRuSn₃ does not show a decrease due to the coherence effect at low temperatures. For heavy fermion systems, the coherence effect is destroyed easily by the existence of atomic disorder (1) and impurity. For example, in the case of CeLaAlC₁₅ system, the Kondo lattice is formed above $x=0.8$. Figure 2 shows the pressure dependence of the resistivity of CeRuSn₃ between 1.7 K and 200 K. This behavior is similar to the result for amorphous system. It may indicates the existence of atomic disorder for CeRuSn₃ compound.

The $C/T$ of CeRuSn₃ has a minimum around 7 K then increases at lower temperatures without any sign of phase transition down to 0.6 K (3). But, at 5 K, as shown in figure 3, the specific heat coefficient $C/T$ reaches a maximum of 1.67 J/K·mol which is comparable with those of CeCu₂, CeAl₃, and CeInCu₂. The $C/T$ vs T curve has close resemblance to that of CeInCu₂, though $C/T$ shows saturation below 1 K in CeInCu₂.

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**Figure 2.** Temperature dependence of electrical resistivity under the hydrostatic pressure.

**Figure 3.** Temperature dependence of specific heat coefficient $C(T)/T$ of CeRuSn₃.

**Figure 4.** Temperature dependence of the ac-magnetic susceptibility below 1.5 K.

The susceptibility follows the Curie-Weiss law above 100 K. The paramagnetic Curie temperature is $-38$ K and the effective Bohr magneton is $2.3 \mu_B$/mole which is close to the value of Ce₃. The susceptibility shows a large value of $1.5 \times 10^{-3}$ emu/mole at 1.7 K, which is about five times as large as the values that have observed for CeCu₂ and CeAl₃ and CeInCu₂.

The ac-susceptibility measurement, as shown in fig. 4, below 1.5 K reveals a sharp maximum around 0.5 K suggesting some antiferromagnetic ordering. But, the behaviour is very similar to the formation of a spin glass ordering. This is presumably caused by the presence of the atomic disorder of Ce-ions.

To summarize, the present experimental results suggest CeRuSn₃ is a new fermion compound which displays some (antiferromagnetic or spin glass ) ordering below 0.6 K. Also it indicates that the atomic disorder plays an important role in the magnetic property of the heavy fermion CeRuSn₃ at lower temperature. For the purpose, measurements on samples with controlled stoichiometry and under the lower temperature are now in progress.

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MAGNETIC AND TRANSPORT PROPERTIES OF NEW URANIUM COMPOUNDS $U_3Sn_5$ AND $URuSn_x^+$

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The electrical resistivity, the thermoelectric power, and the magnetization have been measured below 300K. $U_3Sn_5$ shows ferromagnetic transitions near 70K, while $URuSn_x$ shows no magnetic transition down to 1.8K. Above the transition temperature, the resistivity of $U_3Sn_5$ increases with decreasing temperature reflecting Kondo scattering. At low temperatures, $U_3Sn_5$ shows peculiar magnetic behaviors.

1. INTRODUCTION

Recently uranium intermetallic compounds have attracted much attention because of their wealth of different magnetic and electrical behaviors from the complete Pauli itinerant to the localized magnetic moment including heavy fermion state (1). It is believed that the direct 5f-5f overlap and 5f-ligand hybridization are the most important factors. We recently investigated a large 4f-4f distance Ce compound $CeRuSn_3$ (2), which was found to show heavy fermion characters.

In this paper we report our trial to make URuSn$_x$ type compound. We also report the transport and the magnetic properties of $U_3Sn_5$, since we believe it important when we explore uranium ternary stannides. The physical properties of $U_3Sn_5$ has not been reported because of the pyrophoric nature of Sn-U alloys at intermediate compositions, though its existence is settled (3).

2. EXPERIMENT

The samples were prepared by arc melting appropriate amount of the constituent elements (99.9% U, 99.99% Ru and 99.999% Sn), and were turned over and remelted several times to ensure homogeneity. In case of URuSn$_x$, a single crystal was grown by SEELE triarc furnace. They were wrapped in Ta foil plus Zr foil and sealed in evacuated quartz tubes, and annealed at 950 C for three days. As to $U_3Sn_5$, a sample annealed for three weeks and an as cast one are also prepared. In a single crystal URuSn$_x$, only sharp X-ray diffraction peaks for the type III structure reported by Vandenberg (4) for $Rb_3Sn_5$ (R=rare earth) were observed except very weak Sn reflections, though small amount of Sn and URuSn was generally inevitable as impurity phase in polycrystals. We have not succeeded in obtaining reasonable X-ray diffraction pattern for $U_3Sn_5$ because of its pyrophoric nature. Electrical resistivity ($\rho$) was measured using a standard four probe dc technique and the magnetization (M) measurements were performed with a SQUID magnetometer.

3. RESULTS AND DISCUSSION

3.1 $U_3Sn_5$

Figure 1 shows the temperature dependences of $\rho$ for $U_3Sn_5$. The temperature dependencies of $\rho$ on the samples annealed for three days and for three weeks are fundamentally same. It increases with decreasing temperatures down to near 70K ($T_d$) where it drops sharply. The higher temperature part of curve is reminiscent of the single ion Kondo effect. In the as cast sample, the temperature dependence is largely different. $d\rho/dT$ at higher temperature is positive, and the residual resistivity is an order of magnitude larger. $T_d$ is, however, unaffected by the heat treatment. The smallness of the residual resistivity on the annealed samples (4.8 to 13 $\mu\Omega$cm) implys good crystalinity of these samples. Below about 20K

![Fig. 1](image)

The temperature dependence of resistivity for $U_3Sn_5$.
If Sato, T. Fukuhara, I. Sakamoto, Y. Onuki

The temperature dependence of susceptibility, and magnetization at 4K.

The magnetic susceptibility $\chi$ and $\chi'$ are shown in figure 2. Above 180K, $\chi$ follows Curie-Weiss law, and effective magnetic moment $\mu_{eff}$ and Curie temperature $\Theta_p$ are estimated to be $3.06\mu_B$ and $-30K$ respectively. At lower temperatures, $\chi-T$ curve has two shoulders near 100K and 70K, and the latter position agrees with $T_d$. Above 70K, M-H curve is linear up to 55KOe. $\chi-T$ curve have a bend also near 60K below which the remnant magnetization starts to grow. These facts suggest that $U_3Sn_5$ is ferromagnetic at least below 50K.

At the lower temperatures, M-H curve shows interesting behaviors. As is shown in figure 2, M shows a sharp knick in the hysteresis curve at 4K. At 1.8K, M shows more complex metamagnetic like dependence below 10KOe and near 40KOe (Fig. 3). One possible explanation at present stage is that $U_3Sn_5$ is a very anisotropic ferromagnet and all the moments in a grain flip spin in a group. A single crystal study is necessary in order to clear up its origin.

The magnetic hysteresis on $U_3Sn_5$ at 1.8K.

In polycrystalline samples, we always observed some sign of ferromagnetic ordering at 53K due to the impurity phase $U_3Sn_5$.

The temperature dependence of $\rho$ for a single crystal (Fig. 4) shows a type of curve that is characteristic for many actinide compounds: a sharp rise at low temperature and tendency to saturate at large values near room temperature, which is ascribed to strong conduction electron scattering by the spin fluctuations. There is no sign of magnetic phase transition at least down to 3.7K where $\rho$ shows superconductivity due to impurity Sn.

From the higher temperature slope of $\chi^{-1}-T$ curve (Fig. 4), $\chi_{eff}=2.77\mu_B$ and $\Theta_p=-45K$. There is also no clear sign of magnetic ordering down to 1.8K. One of the characteristics of this system is the large magnetic moment at low temperatures. This suggests the possibility of some magnetic order at the lower temperature. In order to clarify the low temperature ground state, the study on the lower temperature specific heat is necessary.

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Some Characteristics of the Thermoelectric Power in Uranium Intermetallic Compounds

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The temperature dependences of thermoelectric power for various type of uranium compounds of Pauli itinerant UIr, and U₆Fe, spin fluctuating USn₅, heavy fermion URu₂Si₂ and UCu₅, and 5f localized UPd₁₃, are measured. We found that various kinds of phase transitions in these materials are well reflected in the thermoelectric effect.

thermoelectric power, U compound, heavy fermion

In the past few years, there has been considerable interest in unusual properties of actinide intermetallic compounds, since they show a wide variety of behaviors in the physical properties. Transport properties including the electrical resistivity and the Hall effect have been widely investigated. The thermoelectric power (TEP) of Ce intermetallic compounds has been intensely investigated, and several peculiar features were discovered. For uranium compounds, however, only limited materials have been investigated.

In this paper, we report the temperature dependence of TEP of UPd₁₃, URu₂Si₂, UCu₅, USn₅, U₆Fe and U₁Ir. Among these materials, the difference in the itinerancy of 5f electrons gives a wide variety to their physical properties. UPd₁₃ is the only one uranium intermetallic compound which has well localized 5f electrons. URu₂Si₂ and UCu₅ are heavy fermion materials with antiferromagnetic order near 17 K and 15 K respectively. USn₅ shows no magnetic order and is known to be a typical spin fluctuation compound. In U₆Fe, the hybridization of 5f electrons with conduction electrons is stronger but it still exhibits anomalous low-temperature properties including superconductivity at 3.8 K. In U₁Ir, the hybridization is even stronger and the 5f electrons behaves as band electrons.

All the samples are polycrystals which are cut from the same batch used for the Hall effect measurements in ref. 2.

Figure 1 shows the temperature dependences of TEP for URu₂Si₂ and UCu₅ which have already been reported in the conference proceedings. If we compare the results with those of the resistivity and the Hall coefficient, we notice both systems have some resemblance. The temperature

![Graph](file)

Fig. 1. The absolute thermoelectric power of UCu₅ and URu₂Si₂. The arrows show the reported Neel temperatures. The dashed curves are the temperature dependences of resistivity for both compounds.
dependence of resistivity in UCu₅ and UR₆S₁₂ has a peak near 100 K and 70 K respectively above which the resistivity decreases smoothly. Above about 100 K and 70 K, TEP also depends on temperature approximately linearly like the normal diffusion term, although the linear temperature dependence can not be extrapolated to zero at 0 K in case of UCu₅. At the resistivity maximum, TEP shows a bend in both compounds.

In both systems, the most striking features reflecting their magnetic transition are found at low temperatures. In UR₆S₁₂, TEP shows a sharp bend to negative direction at 17.5 K which was reported to be the Neel temperature of this compound. After showing a deep minimum near 13 K, TEP tends to be zero with decreasing temperature.

In case of UCu₅, TEP also shows a sharp bend at Neel temperature of 15 K to positive direction, and changes sign near 10 K. After a positive peak near 7 K, it approaches to zero with decreasing temperature. The bends found in these materials reflect destruction of some part of the Fermi surface due to the formation of antiferromagnetic spin density wave. Also in the Hall effect measurement, sharp changes at the same temperatures were reported in both systems. For UCu₅ no sign change in the Hall coefficient was observed contrary to the result of TEP. At least from TEP measurement, these two compounds seem to give a common character of heavy fermion compounds with antiferromagnetic ordering. The antiferromagnetic transition appears more drastically compared to usual antiferromagnetic materials, which might reflect the enhanced density of state at Fermi level.

In Fig. 2, the temperature dependences of TEP of the other four compounds are shown. Although these compounds have a wide variety of characters of 5f electrons from localized to itinerant, the overall temperature dependence of TEP are not much different at first sight. TEP is positive at room temperature, decreases with decreasing temperature and changes sign. After showing a negative peak, TEP approaches to zero. None of the measured materials exhibits the simple linear temperature dependence through zero.

The absolute value of TEP in USn₃ is some-

what larger than the other three compounds. Among the spin fluctuating uranium compounds of USn₃, UA₁₂ and UP₃₃, we notice some similarity in their temperature dependence of TEP. Especially those of USn₃ and UA₁₂ have close resemblance; TEP have positive large values at room temperature. Near 30 K they change sign from positive to negative and have a negative peak. In case of UP₃₃, the sign of TEP is opposite but the temperature dependence resembles to those of USn₃ and UA₁₂. Recently Sakurai et al. have showed empirically that TEP of spin fluctuation compounds like MnSi above the spin fluctuation temperature can be represented as,

\[ S(T) = AT + B, \]

where \( B \) is a constant term reflecting spin fluctuation effect. The above mentioned three compounds obey this equation. In order to ascertain the validity of the rule for the general spin fluctuation materials, theoretical support and more experimental investigation are necessary. As an origin of the minimum at low temperature, we can not discard the possibility of phonon drag contribution. The temperature at the minimum is within the expected temperature ranges; \( T_{\text{min}} < T_D/5 \) (\( = 39 \) K) where \( T_D \) is the Debye temperature.\(^{12}\)
In case of U₆Fe and U₁ᵣ₃, the absolute values are rather small, reflecting the wide band character. Also in the Hall effect measurement, small absolute values with a little temperature dependence are reported for both compounds.² For U₁ᵣ₃, the minimum in TEP at a lower temperature is possibly due to phonon drag effect, since \( T_{\text{min}} < T_D/5 \) (\( T_D \) is 293 K). In the sample of U₁ᵣ₃ with such a small residual resistivity, we can naturally expect clear phonon drag effect. In case of U₆Fe, the broad minimum cannot be explained by the phonon drag effect, since \( T_D/5 = 25 \text{ K} \) of this material is too low. The temperature 100 K near which TEP starts to deviate from the high temperature linear dependence is close to the temperature where some phonon anomaly have been reported in Mössbauer effect and neutron-diffraction experiments.²⁰ That was attributed to a change in the electronic structure of the Fe atom.²⁰ Such a change can be expected to appear also in TEP experiment.

In case of UPd₃, it is interesting to see whether the influence of the inelastic scattering among crystalline-electric field (CEF) levels shows up in TEP. A strong neutron energy loss line near 14 mV (=165 K) due to the inelastic scattering between CEF levels was reported in this compound.⁹ According to Takayama and Fulde,²¹ we can expect a TEP peak at 1/3 of CEF splitting energy. The temperature 50 K of the minimum is just close to the value.

The low temperature data of U₆Fe and UPd₃ are shown in Fig. 3, where we see significant changes in TEP reflecting some phase transitions in the low temperature region. In UPd₃, the bend near 6.5 K is thought to be due to a quadrupolar ordering.²² In U₆Fe, TEP becomes zero below the superconducting transition temperature. As is also shown in Fig. 3, the transition temperature decreases about 0.35 K under magnetic field of 1 T, which agrees with the reported \( T_e \) decrease.²³

To summarize, TEP of all the measured compounds can not be described by the combination of the simple diffusion term and the phonon drag term. Irrespective of the different itinerancy of 5f electrons, we observed a minimum below 100 K in all the studies compounds. The possible origins for each compound were discussed. Compared to the ordinary antiferromagnet, the heavy fermion systems such as UC₃ and URu₂Si₂ show much drastic changes in TEP at the antiferromagnetic transitions.

Acknowledgments

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MAGNETORESISTANCE OF THE SECOND-STAGE NiCl₂−, CoCl₂−
AND CuCl₂−-GRAPHITE INTERCALATION COMPOUNDS

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Abstract

The magnetoresistance of the second-stage graphite intercalation compounds of MC₇Cl₂ has been measured in the temperature range 1.4 - 30 K and in magnetic fields up to 10 kOe. Here, M is one of Ni, Co or Cu, and the host material is single-crystal (KISH) graphite. All the compounds showed a negative magnetoresistance, whose minimum is distributed around a few hundred Oe. The existence of negative magnetoresistance suggests a considerable contribution of the magnetic scattering from the intercalants to the conduction electrons. It has been concluded that the dominant origins of the negative magnetoresistance come from the suppression of magnon or spin disorder scattering by the magnetic field, and/or from the spin flop process. The competition between the different anisotropy of effective fields, the different transition temperatures and the different spin flop fields gives rise to a variety of behaviours in different samples.

Introduction

Since the early work by Karimov [1 - 3], the magnetic properties of graphite intercalation compounds (GIC) of 3d transition metal dichlorides have been studied by many authors [4 - 14]. Because of the sandwich-like structure of magnetic and non-magnetic layers, the magnetic properties in those compounds are highly anisotropic. The magnetic layers in those compounds are known to have an island structure with mean island diameters of the order of 100 Å. The filling coefficients usually range between 0.9 and

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0.7 when the host materials are single crystals [4]. Such an in-plane structure gives a characteristic magnetic behaviour. It has been observed that NiCl$_2$- and CoCl$_2$-GICs show a magnetic phase transition at two successive temperatures, which are described as $T_{\text{Cu}}$ and $T_{\text{Cl}}$, respectively. The higher temperature phase at $T > T_{\text{Cu}}$ is paramagnetic. The intermediate phase between $T_{\text{Cu}}$ and $T_{\text{Cl}}$ is two dimensional (2D). It has no spontaneous magnetization as a whole, but is unstable and changes to a ferromagnetic state in an applied magnetic field. The low temperature phase below $T_{\text{Cl}}$ has three-dimensional (3D) order. The metal ions in the intercalant are ferromagnetically coupled along the c-plane of the crystal, and the layers are antiferromagnetically coupled along the c-axis. The antiferromagnetic spin flop field, $H_F$, is also anisotropic and is much reduced compared with the pristine transition metal dichloride.

Suzuki et al. [5, 6] measured the magnetic susceptibility of NiCl$_2$- and CoCl$_2$-GICs in fields along the two independent crystal axes. They determined $T_{\text{Cu}}$ and $T_{\text{Cl}}$, and estimated anisotropy parameters including the spin flop critical fields parallel and perpendicular to the c-axis, $H_{F||}$ and $H_{F\perp}$. Suematsu et al. [7] measured the magnetization of well-staged samples of NiCl$_2$-GIC prepared from synthetic single crystals (KISH) of graphite, and determined $T_{\text{Cu}}$ and $T_{\text{Cl}}$ and magnetic parameters in fields along the hexagonal plane (c-plane). Oguro et al. [8] measured the field dependence of magnetization at 4.2 K in NiCl$_2$- and CoCl$_2$-GICs in fields parallel and perpendicular to the c-axis. They observed a strong magnetic anisotropy in CoCl$_2$-GIC, while the anisotropy in NiCl$_2$-GIC was rather weak.

In CuCl$_2$-GIC, on the other hand, the intraplane interaction is two-dimensionally [10] or one-dimensionally [11] antiferromagnetic. Rancourt et al. [10] measured the magnetic susceptibility of the second-stage compounds of CuCl$_2$ intercalated into four types of host materials: natural graphite crystals, HOPG and pitch-based fibres with two different orientations. They suggested that three-dimensional ordering did not occur down to 1.9 K at least. The spin flop field was predicted to be higher than 41 kOe, which is attributed to the pristine CuCl$_2$. The c-plane was the easy plane of magnetization below 16 K. They also showed that the temperature dependence of the magnetic properties depends on the size of islands and on the filling parameter. Nishihara et al. [11] measured the temperature and the stage dependences of the magnetic susceptibility in CuCl$_2$-GIC in fields along the c-axis. In the first-stage compounds with single crystal KISH graphite, they suggested the possibility of the two successive magnetic transitions similar to those in NiCl$_2$- and CoCl$_2$-GICs, but the occurrence in the second-stage compounds has not been established. Summaries of the magnetic properties in this kind of compound are given by Ikeda [12] and Matsuura et al. [13, 14]. Several parameters obtained previously are summarized in Table 1.

If the conduction electrons move under any magnetic interaction with the intercalants, the transport properties should reflect the above magnetic structure in addition to the spatial anisotropy of the crystal. In some of the
Parameters in the second-stage NiCl$_2$-, CoCl$_2$- and CuCl$_2$-graphite intercalation compounds. $T_{C1}$ and $T_{Cu}$ are the lower and upper magnetic transition temperatures, respectively. $H_{F\parallel}$ and $H_{F\perp}$ are the spin flop fields in the antiferromagnetic phase of every material, where $\parallel$ and $\perp$ refer to the crystal c-axis.

<table>
<thead>
<tr>
<th>Intercalant</th>
<th>Host material</th>
<th>Spin flop fields (Oe)</th>
<th>Transition temperatures (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$H_{F\parallel}$</td>
<td>$H_{F\perp}$</td>
<td>$T_{C1}$</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>HOPG</td>
<td>$&gt;300^*$</td>
<td>$-10$</td>
<td>17.3</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>KISH</td>
<td>$-$</td>
<td>$-10$</td>
<td>17.5</td>
</tr>
<tr>
<td>CoCl$_2$</td>
<td>KISH</td>
<td>$&gt;130$</td>
<td>10 - 20</td>
<td>8.0</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>natural crystal,</td>
<td>$&gt;41 \times 10^3$</td>
<td></td>
<td>$T_N = 23.9$ in pristine CuCl$_2$</td>
</tr>
<tr>
<td></td>
<td>HOPG, fibres</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* [5] states that the external field reduces $T_{C1}$, and the value mentioned was interpreted as the para- to ferromagnetic transition field.

Present samples, the critical fields of spin flop, $H_F$, are as low as a few hundred Oe, or less. The spin flop transition also affects the conduction process when the applied field increases through $H_F$. The present research has been concerned with the behaviour in the lower field region.

**Experimental**

Samples used are based on single crystals of KISH graphite, which were prepared by a vapour reaction method and were confirmed by X-ray diffraction to be pure second-stage phases [12]. Every sample has the approximate thickness and area of 1 mm and $3 \times 5$ mm$^2$, respectively. As the samples have irregular shapes, d.c. leads of copper wire were attached on four successive points of their circumference. A typical arrangement of the sample and the electrical and magnetic fields for magneto-resistance measurement are shown in Fig. 1. According to van der Pauw [15], the absolute value of resistivity is determined by the measurement on two different pairs of current and/or

![Fig. 1. A typical configuration for the magnetoresistance measurement. The magnetic field is rotatable from parallel ($\theta = 0^\circ$) to normal ($\theta = 90^\circ$) to the hexagonal axis of the crystal. The rotation axis coincides with the direction of the sample current.](image)
voltage leads. However, we used only the fixed pairs of leads, because it is enough to know the change of resistance relative to the zero-field value in the magnetoresistance measurement. This configuration was needed to keep the flow line of current always normal to the magnetic field, when it was rotated from parallel to normal directions of the crystal c-axis.

The Hall effect was also measured on every sample in order to check if any anomalous Hall effect was seen or not. No anomalous part was observed in fields parallel and perpendicular to the c-axis of the crystal.

In most cases, the samples were cooled to 1.4 K out of the magnetic field, then were heated to the desired temperature, and the resistivity was measured in an increasing field at a fixed temperature. The voltage drop between a pair of probes was counted and analysed by a Fujitsu Micro-8 (FM8) microcomputer through a Keithley type-181 nanovoltmeter. In the field range 0 - 10 kOe, no notable hysteresis on the transport effect was detected during cycles of increasing and decreasing fields.

Results and discussion

Figures 2(a), (b) and (c) show the anisotropy of magnetoresistance, $\Delta \rho/\rho_0$, at around liquid helium temperature in CoCl$_2$-, CuCl$_2$- and NiCl$_2$-GICs respectively.

![Graphs showing anisotropy of magnetoresistance](image_url)

Fig. 2. The magnetoresistance as a function of magnetic fields up to 10 kOe. (a) CoCl$_2$-GIC; (b) CuCl$_2$-GIC; (c) NiCl$_2$-GIC. All were measured at low temperatures, where the systems are in the three-dimensional antiferromagnetic phase. The values of the angle shown as a parameter mean the directions of magnetic fields measured from the c-axis of the crystal.
In the higher field region, the dependence on the direction of field shows some common behaviour in the three kinds of compounds. At 10 kOe, for example, $\Delta \rho/\rho_0$ is always positive through the direction of the magnetic fields. It is biggest when the field is parallel to the c-axis of the crystal, decreases when it is tilted, and reaches a minimum value when the field is in the hexagonal plane (c-plane). $\Delta \rho/\rho_0$ behaves like the square of the cosine of the angle, $\theta$, between the field and the c-axis except when $\theta$ is near $\pi/2$. This is reasonable if the Fermi surface of the conduction electrons is cylindrical, reflecting the two-dimensional crystal structure. Here most of $\Delta \rho/\rho_0$ seems to come from the normal Lorentz force. The fact that a finite $\Delta \rho/\rho_0$ is observed even in fields along the c-plane suggests some finite current component is carried along the c-axis. The conduction is not perfectly two dimensional.

Figures 3 (a) - (c) show the enlarged pictures of $\Delta \rho/\rho_0$ in the region up to fields of 2 or 4 kOe for the three kinds of compounds. In all cases we can see that $\Delta \rho/\rho_0$ has some negative value around zero field, which passes through a minimum at a few hundred Oe and then becomes positive with increasing field. We will concentrate on the low field region hereafter.
The scattering process of conduction electrons by magnetic ions is made up of the following two contributions:

1. The spatial disorder of the s–d direct exchange interaction (magnon or spin disorder; we will describe it as 'spin disorder scattering' in short).

2. The phonon-connected interband transition.

The second process is a resistive effect caused by the temporary stay of conduction electrons in the virtual bound state on a magnetic ion. This is more effective in a paramagnetic phase than in a magnetically-ordered one, because scattering into a down-spin state in the latter is forbidden by Pauli's exclusion principle [16]. Even in a paramagnetic phase, the scattering probability decreases under an external field, when the down-spin state hides under the Fermi surface through the Zeeman splitting. The reduction of scattering probability brings in the negative magnetoresistance, which is more remarkable at lower temperatures. When the temperature is sufficiently high, the scattering is always probable independent of the fields, because the effect of magnetic field may be smeared out by the distribution function tail of the order of $k_B T$.

The first process is essential in a ferromagnetically ordered system. The periodic configuration of spins is disturbed by the influence of temperature, and the aperiodicity makes a resistive contribution [17]. At sufficiently low temperatures, where spins are ordered without an external field, conduction electrons move in a good periodicity of internal fields. The zero-field resistivity is low there, and the magnetic fields only make a resistive contribution by the Lorentz force, which increases with increasing field. Now we may observe a positive magnetoresistance. When the spin disorder increases with increasing temperature, the zero-field resistivity increases too. The process whereby the external field aligns the ionic spins reduces the resistivity, where the negative magnetoresistance is caused and is kept till the order is recovered. Then the magnetoresistance goes through a minimum, and increases toward positive values by the Lorentz force. The minimum is deeper at higher temperature, and is deepest in the paramagnetic state. This process saturates when the system reaches the paramagnetic limit at a far higher temperature, and the negative contribution is masked by the positive behaviour from the Lorentz force. The comparison between the contributions of the above two processes to the temperature- and field-dependent behaviour of resistivity is schematically shown in Fig. 5.

If the interband transition has a major effect on the resistivity, some anomalous Hall effect under the spin–orbit coupling should be observed. Hall resistivity measured on all the present samples did not show any detectable anomalous part. It will also be described later that the negative tendency of magnetoresistance is more remarkable at higher temperature. These facts suggest that the dominant contribution may come from the spin disorder scattering, at low temperature at least.

CoCl₂-GIC in the field parallel to the c-plane shows a typical behaviour in a ferromagnetically-ordered system. The easy axis of magnetization of this compound lies in the c-plane and the spin flop field is only about ten Oe [6].
In Fig. 3(a), for example, the curve in $H\perp c$ (at 1.4 K) shows a positive ferromagnet-like behaviour over the whole region of fields in the present experiment. In Fig. 4(a) the negative magnetoresistance is initiated with increasing temperature, and is remarkable at around $T_Cu$, where the magnetic order is almost destroyed. At high temperature (30 K), where the magnetic disorder is complete, the magnetoresistance increases monotonically, reflecting only the effect of Lorentz force.

When the spins interact antiferromagnetically with each other, the spin disorder scattering may decrease till they reach a new ferromagnetic order passing through a finite spin flop field. When this effect overcomes the

![Graphs showing temperature dependence of magnetoresistance](image)

Fig. 4. The temperature dependence of $\Delta\rho/\rho_0$ under a magnetic field in the c-plane. (a) CoCl$_2$-GIC; (b) NiCl$_2$-GIC. Parameters on the lines show the measured temperatures. $T_{CI}$ is the critical temperature where the 3D antiferromagnetic to 2D intermediate phase transition occurs. $T_{Cu}$ is the paramagnetic transition temperature.

![Graphs showing magnetic contributions to resistivity](image)

Fig. 5. The magnetic contributions to the resistivity of (a) the spin disorder scattering, and (b) the interband transition. In (a), the alignment of spins by the field reduces the scattering probability. The zero-field resistivity is higher at higher temperature and its reduction by the field is bigger there. In (b), the decrease of scattering probability by the field arises from the exclusion principle. The effect is more remarkable at lower temperature, where $k_B T < g\mu_B H$ (the $g$ factor is attributed to the ionic spin).
Lorentz part, it brings in another possibility of negative magnetoresistance. The behaviour of CoCl$_2$-GIC in fields parallel to the c-axis seen in Fig. 3(a) is typical of an antiferromagnet with a finite spin flop field. There is another example in Fig. 3(b), showing the behaviour of CuCl$_2$-GIC. The intraplanar coupling between spins in CuCl$_2$-GIC is antiferromagnetic, and the spin flop fields are much higher than the field region in the present experiment [10]. Then the resistivity decreases with increasing field, and reaches a minimum before the scattering is taken over by the Lorentz part. The c-plane is the easy plane of magnetization at 1.4 K, and the contribution from the Lorentz part in the field dependence may be delayed in $H \perp c$. The field where the magnetoresistance is minimized is thus lowest in $H \parallel c$. It is seen in Fig. 3(b) that the position of the minimum shifts towards the high field when the field is tilted from the c-axis.

As seen in Fig. 3(c), the dependence of $\Delta \rho/\rho_0$ in NiCl$_2$-GIC on the field direction is opposite to that in CoCl$_2$-GIC, while the values and anisotropy of the spin flop field are similar in both compounds. According to Oguro et al. [8], the anisotropy constant is as small as 0.01 K in this compound. The saturation field of magnetization is less than 10 kOe both parallel to and perpendicular to the c-axis. This might be reflected in the fact that the magnetoresistance in NiCl$_2$-GIC shifts to the Lorentz-like $\cos^2 \theta$ dependent behaviour at a rather low field (around a few hundred Oe). The origin of the negative magnetoresistance is not clear. The island structure in the intercalant layers, which is common in the present three kinds of materials, can introduce some ambiguity. There are a few percent of free magnetic ions contributing paramagnetically, which may negatively affect $\Delta \rho/\rho_0$ through the spin disorder scattering. Ions inside an island are ferromagnetically coupled below $T_{Cu}$ and behave as ferromagnets under an applied field. This may act positively on $\Delta \rho/\rho_0$, at low temperature at least. It is difficult at the present stage to explain how the competition between the above two kinds of magnetic ions contributes to the anisotropy at low temperature. The temperature dependence is seen in Fig. 4(b), which is an example in fields parallel to the crystal layers. The behaviours in Fig. 4(a) and (b) are consistent with each other. Both show that the negative trend of magnetoresistance becomes more remarkable, since the magnetic order is destroyed at the two successive phase transition temperatures. The depth of the minimum and the field value at the magnetoresistance minimum are both biggest around the two critical temperatures, $T_{Cu}$ and $T_{Cl}$, and $\Delta \rho/\rho_0$ also goes to a positive value at sufficiently higher temperatures than $T_{Cu}$ in NiCl$_2$-GIC.

The effect of a cooling field was also examined for some samples. When a sample was measured as soon as it was cooled to 1.4 K in a field of 5 kOe normal to the c-axis, the negative trend of the magnetoresistance in CuCl$_2$-GIC around 1 kOe disappeared (the dashed line in Fig. 3(b)), and the curve in CoCl$_2$-GIC showed a slight shift towards the positive side. This supports the above suggestion that the negative contribution to the magnetoresistance mainly comes from the spin flop process. Such behaviours were unstable, and samples kept in a field-free state for about half an hour recovered a similar behaviour to that in the zero-field cooled one.
Conclusion

In NiCl₂-, CoCl₂- and CuCl₂-GICs, the major effect of scattering on the electronic conduction comes from the magnetic moments on the intercalants, at least near $T_{Cu}$ and lower temperatures. As the origin of this scattering, the disorder of spins (spin wave and/or spin disorder) and the interband transition were taken into consideration. The temperature dependence of magnetoresistance is well explained with the assumption that the former is dominant. The disturbance of periodicity of the alignment of spins induced by phonons scatters the conduction electrons. The scattering probability decreases in an applied field and negative magnetoresistance is induced. The effect is most remarkable around the paramagnetic transition temperature, $T_{Cu}$. The field-dependent behaviours of the three-dimensional ordered phase below $T_{Cl}$ are understood by the idea of the spin flop process, in CoCl₂-GIC and CuCl₂-GIC at least. Even if the phonon excitation is negligible, the system starting from antiferromagnetic order also shows a negative magnetoresistance through the spin flop process with increasing field.

The difference between the different intercalants is understood as being the result of different critical temperatures, of different spin flop fields and of different anisotropy of the internal fields. The temperature- and field-dependent behaviours in NiCl₂-GIC particularly, are complicated by the island structure, though such a structure is common in this kind of compound.

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