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Thermopower of several ternary compounds of cerium and uranium: CeTX and UTX (T \equiv Ni, Pd or Pt; X \equiv In or Sn)

Y Yamaguchi[†], J Sakurai[†], F Teshima[‡], H Kawanaka[‡], T Takabatake[‡] and H Fujii[‡]

[†] Faculty of Science, Hiroshima University, Higashi-Senda-Machi, Naka-ku, Hiroshima 730, Japan

[‡] Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Senda-Machi, Naka-ku, Hiroshima 730, Japan

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Abstract. We have measured the thermopower S , from 2 to 300 K, of several ternary compounds of cerium and uranium: CeTX and UTX with T \equiv transition metals Ni, Pd or Pt and with X \equiv In or Sn. The behaviour of S for these cerium compounds seems to be capable of interpretation as due to the strength of the hybridisation of the Ce 4f electron with conduction electrons. On the other hand, the behaviour of S for the uranium compounds changes enormously for each compound. Prominently sharp peaks of S as a function of temperature were observed both for UNiSn near its semiconductor-to-metal transition temperature and for CeNiSn near its metal-to-semiconductor transition temperature.

1. Introduction

A large number of new compounds of cerium and uranium have been studied recently to determine the wide variety of their unusual properties (see, e.g., [1]). Systematic studies of the physical properties of cerium or uranium compounds are especially interesting. For example, a group of the equiatomic ternary compounds of cerium, CeNiIn, CePdIn and CePtIn, the transition metals being from the same column in the periodic table, have mostly been studied by us at Hiroshima University. The crystal structure of the compounds is of a hexagonal Fe₂P type. CeNiIn turned out to be an intermediate-valence compound, CePdIn to be a Kondo antiferromagnet with moderately heavy electrons and CePtIn to be a typical heavy-electron system [2–6].

A second group of equiatomic ternary compounds of cerium with tin, CeNiSn, CePdSn and CePtSn, having the same transition metals as the first group, has also been studied by us. Their crystal structure is an orthorhombic TiNiSi type. CeNiSn was found to be a singular compound with an energy gap at low temperature [7–9]. CePdSn and CePtSn were found to be Kondo antiferromagnets [10].

On the other hand, recent studies have shown that uranium compounds have an even wider variety of physical properties than do cerium compounds [11]. Several equiatomic ternary compounds of uranium, e.g. UPdIn, UNiSn and UPtSn, have been studied by

us. UPdIn has a hexagonal Fe_2P -type crystal, and the other two have a cubic MgAgAs-type crystal. UPdIn was found to be an antiferromagnet with a Néel temperature of 20 K and to become a ferrimagnet below 8 K [12]. UNiSn was found to have an interesting phase transition at 47 K from a paramagnetic and semiconducting state to an antiferromagnetic and metallic state [13].

In this paper, the results of our measurements of the thermopower S on all these compounds are reported and discussed. S is a sensitive quantity to which many contributions contribute (see, e.g., [14]), and data for S alone are sometimes difficult to interpret. However, for the compounds in the present study, we have already ample data for the magnetic properties, the electrical resistivity, the specific heat and others. Therefore, when the characteristic features of the thermopower of the compounds are discussed in connection with these other data, we believe that unique and subtle information can be usefully drawn from the thermopower. The thermopower data on some of the samples in the present study have preliminarily been reported already [2, 4, 13].

2. Experiments

The sample preparations have already been reported in [2–9, 13].

The thermopower was measured by a standard stationary technique of detecting a small electrical potential difference due to a small and variable temperature gradient across a sample. The measurements were fully controlled and recorded by a computer. The temperature range of the measurements was from 2 K, the temperature of liquid helium under vacuum, to 300 K. The samples were in the shape of rods with typical dimensions of $1 \times 1 \times 10 \text{ mm}^3$.

3. Results and discussions

3.1. CeNiIn, CePdIn and CePtIn

In figure 1 the thermopower S for a group of three compounds, CeNiIn, CePdIn and CePtIn, is plotted as a function of temperature T . Very large and broad positive peaks of S are observed at 130, 85 and 60 K for the above three compounds, respectively. In addition, a shoulder is observed in S at around 30 K for CeNiIn and at around 10 K for CePtIn. We assume on the basis of Mott's equation $S = (\pi^2 k^2/3|e|)T [\partial (\ln \sigma)/\partial E]$ [14] that S extrapolates linearly to zero at $T = 0$. Then the temperature range of this proportionality is estimated to be below 10 K and below 5 K for CeNiIn and CePtIn, respectively, and the constant of the proportionality will be rather large, especially for CePtIn.

In table 1 are summarised the values of some of crystal, magnetic and thermal data which have been obtained in our previous work [2–6]. Among them, the values of the Kondo temperature T_K and the electronic specific heat constant γ are indicative of the hybridisation strength of Ce 4f electron with conduction electrons. This hybridisation is considered to give rise to a state density peak near the Fermi energy E_F for temperatures below T_K [15]. Hence the thermopower, being sensitive to the energy dependence of the density of states through its involvement in E , may give rise to structure at or near T_K .

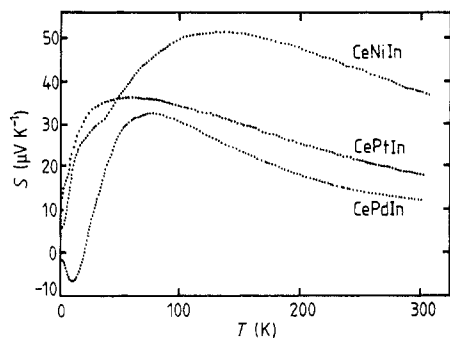


Figure 1. Thermopowers for CeNiIn, CePdIn and CePtIn.

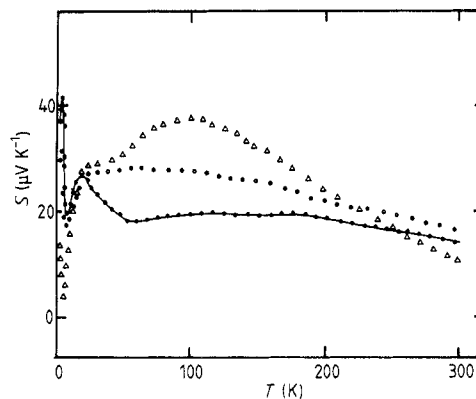


Figure 2. Thermopowers for CeNiSn single crystals along the *a* axis (○), the *b* axis (△) and the *c* axis (●).

Table 1. The crystal type, the constant *a* of the unit cell, T_K , T_N and the electronic specific heat constant γ of CeNiIn, CePdIn and CePtIn [2–4].

Compound	Crystal type	<i>a</i> (K)	T_K (K)	T_N (K)	γ (mJ mol ⁻¹ K ⁻²)
CeNiIn	Fe ₂ P	7.503	124		70
CePdIn	Fe ₂ P	7.690	5.1	1.7	700
CePtIn	Fe ₂ P	7.640	17		500

For CeNiIn, this hybridisation peak at an energy slightly above the Fermi energy E_F is considered to give rise to a large, broad and positive peak of S at a temperature near T_K . The shoulder in S at around 30 K probably indicates a further minor change in the hybridisation structure at around this temperature.

In the case of CePtIn, the sharp hybridisation peak is considered to be reached at an energy above and very near to E_F . The large value of proportionality of S to T below 5 K may be related to the sharpness of this hybridisation peak and hence to the large value of the specific heat constant γ .

On the other hand, CePdIn is antiferromagnetic and Ce 4f electrons of the compound have a more localised character than those of other two compounds. A negative peak of S for the temperature range above and below T_N is a common experimental feature in many antiferromagnetic cerium compounds with a dense Kondo effect [16]. We would like to interpret this negative sign of S as being due to the hybridisation peak appearing near but below E_F so that Ce atoms have atomic moments. On the other hand, the large positive peak at 80 K may be due to the Kondo effect in the presence of a crystal-field splitting of the Ce 4f electron.

Among the above three compounds, CeNiIn has the smallest value of crystal lattice parameter *a* of the Fe₂P structure, and CePdIn has the largest value of *a*, while the parameters *c* of the compounds do not change so much. A small lattice size favours an intermediate-valence state, and a large lattice size favours a well localised Ce 4f electron.

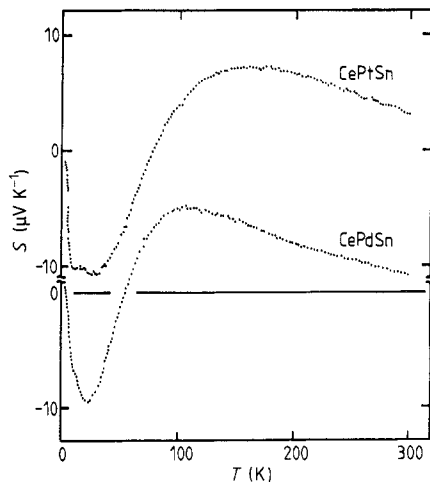


Figure 3. Thermopowers for CePdSn and CePtSn.

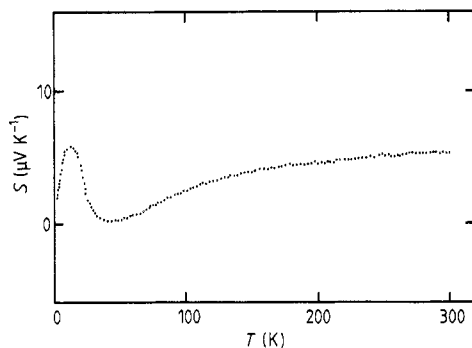


Figure 4. Thermopowers for UPdIn.

Table 2. The crystal type, the unit cell volume, T_N , Θ_p and γ for CeNiSn, CePdSn and CePtSn [7–10].

Compound	Crystal type	Atomic volume (\AA^3)	T_N (K)	Θ_p (K)	γ ($\text{mJ mol}^{-1} \text{K}^{-2}$)
CeNiSn	TiNiSi	258.2			200 ($T > 8 \text{ K}$)
CePdSn	TiNiSi	282.7	7	-40	
CePtSn	TiNiSi	276.5	7	-40	

At an intermediate size between the two, a heavy-electron state is often realised. This is what we observed for the above three compounds [17].

3.2. CeNiSn, CePdSn and CePtSn

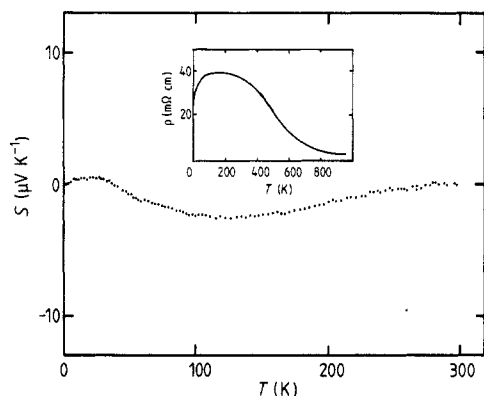
CeNiSn was found to be an intermediate-valence compound with a band-gap formation below 8 K [7, 8].

In figure 2, the thermopower S for a CeNiSn single crystal along the three axes of its orthorhombic crystal is plotted as a function of temperature T . The anisotropy in S can be seen to be rather large. Below 8 K, the S -values along all directions start to increase steeply. S along the a and c axes manifests very sharp peaks at around 3 K. More details will be published later in a separate paper [9]. Above 20 K, the S -values along the a and c axes are rather flat, while S along the b axis shows a broad peak at 100 K. The average of S along the three axes gives rise to a broad peak, which resembles that of CeNiIn as a whole.

Figure 3 shows S for CePdSn and CePtSn crystals plotted as a function of temperature T . Both curves of S have a positive peak at 100 or 150 K and a negative peak at around 20 K and resemble each other and also the curve of S for CePdIn, having characteristic features of an antiferromagnetic Kondo compound of Ce. Table 2 lists the crystallographic as well as magnetic data for the three compounds.

Table 3. The crystal type, the constant a of the unit cell, T_N , θ_p and γ for UPdIn, UNiSn and UPtSn [12, 13].

Compound	Crystal type	a (Å)	T_N (K)	Θ_p (K)	γ (mJ mol ⁻¹ K ⁻²)
UPdIn	Fe ₂ P		20 ($T_C = 8$)	-54	280
UNiSn	MgAgAs	6.385	47	-58	28
UPtSn	MgAgAs	6.617		-120	11

**Figure 5.** Thermopower for UPtSn. The inset shows the electrical resistivity of the sample.

3.3. UPdIn, UPtSn and UNiSn

In figure 4, S for UPdIn is plotted as a function of temperature T . It is noted that S is rather small and has no structure above 30 K. It starts to increase below 30 K and gives rise to a peak at about 10 K. However, the origin of the peak is not known. UPdIn is an antiferromagnet with $T_N = 20$ K and it transforms to a state having a ferromagnetic component below $T_C = 8$ K. However, the curve of S in figure 4 shows no effect of these magnetic transitions.

The crystallographic and magnetic data as well as other physical properties for the three compounds are listed in table 3.

S of UPtSn shown in figure 5 is amazingly small and without any notable structure throughout the temperature range of the measurements, although ρ drops progressively below 100 K as shown in the inset. The curve of S looks as if it were for a compound of La or Y. From a semiconductive behaviour of ρ above 300 K, an energy gap of 0.34 eV for the compound was estimated [18].

In contrast, S for UNiSn is surprisingly large and has much structure. In figures 6(a) and 6(b), ρ and S , respectively, for the compounds are plotted. Moreover, the duration of the annealing of the sample is found to have a strong effect on their absolute value and on the sharpness of their structures, although their qualitative features do not change. For a sample which had been annealed for 3 months, the curve of S has three maxima at 17, 43 and 100 K in addition to two minima at 35 and 60 K. It tends to a large negative value of $-45 \mu\text{V K}^{-1}$ at 300 K. On the other hand, S for a sample which had been annealed for 1 month is smaller than that of the sample which had been annealed

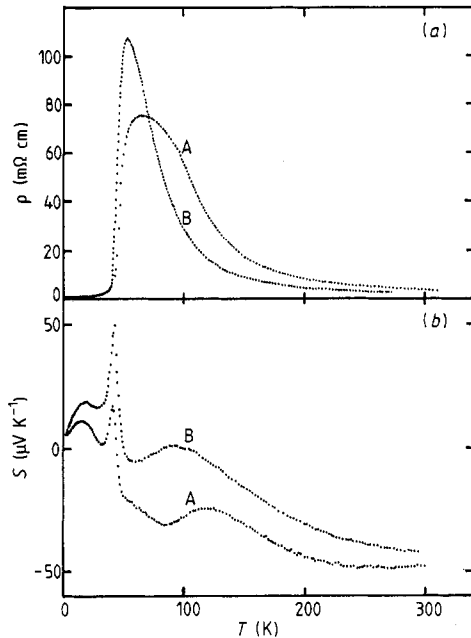


Figure 6. (a) Electrical resistivities and (b) thermopowers for two samples of UNiSn annealed for 1 month (curves A) and for 3 months (curves B).

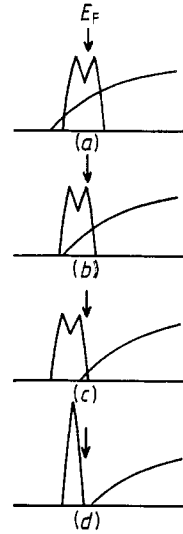


Figure 7. Changes in the band structure for UNiSn around the antiferromagnetic transition temperature T_N : (a) $T > T_N$; (b) $T = T_N$; (c) $T = 43 \text{ K}$; (d) $T < 43 \text{ K}$.

for 3 months. The maximum and the minimum S for the former sample at high temperatures are displaced in comparison with those of the latter sample. The very sharp peak in S appears for both samples at the same temperature of 43 K. A notable decrease in ρ takes place at around 50 K and definitely above 43 K, the temperature of the sharp maximum of S .

The sample was extensively studied by magnetic susceptibility, neutron diffraction and other measurements in addition to the electrical resistivity, and the sample was established as undergoing a phase transition from a paramagnetic semiconductive state to an antiferromagnetic and conductive state with the transition temperature T_N at 45–47 K [13, 18].

To explain these significant behaviours of S and ρ for the compound at around its transition, we assume the very qualitative electron band picture shown in figure 7, which consists of a narrow band of U 5f electrons and a wide conduction band. Above T_N , there is an energy gap between these two bands and the Fermi energy E_F is in this gap (figure 7(a)), so that the compound is semiconductive. At around T_N , an antiferromagnetic splitting of the 5f band takes place. As a result, this band touches the conduction band and the compound becomes metallic (figure 7(b)). At the same time, S starts to increase sharply. With a further decrease in the temperature, the 5f band splitting becomes larger. At 43 K, E_F is at the top of the 5f band, and hence S is at the maximum (figure 7(c)). Below 43 K, E_F passes the top of the 5f band, and S starts to decrease sharply (figure 7(d)). Our model, although it is oversimplified and arbitrary, succeeds in explaining qualitatively the prominent features of S and ρ around the

transition and in particular how the peak of S appears at a temperature lower than that of ρ .

It should be recalled that, for CeNiSn, band-gap formation occurs below 8 K and that very sharp peaks of S along its a and c axes are found at 3 K. Therefore, both the band-gap formation and the band-gap annihilation seem to give rise to sharp peaks in S . It should be noted that the temperature of the peak of S is slightly lower than the temperature of the band formation or annihilation.

Finally, we can see that the curves of S for these uranium compounds have quite different behaviours with no systematic or common feature like those for Ce compounds. This may be interpreted to indicate that the character of U 5f electron states in uranium compounds varies more widely than that of the Ce 4f electron states in the Ce compounds.

4. Conclusions

The behaviour of the thermopower S of two groups of cerium compounds, CeTIn and CeTSn ($T \equiv \text{Ni, Pd or Pt}$) was found to be very different from that of a group of uranium compounds, UPdIn, UPtSn and UNiSn. This seems to indicate the different nature of the hybridisation of the Ce 4f electron and of the U 5f electrons with conduction electrons. The appearance of a very sharp peak of S for UNiSn was observed slightly but definitely below T_N , and a band model which successfully interprets the observations was proposed.

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