

Anisotropic Thermopower of the Kondo Insulator CeRu₄Sn₆

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The intermetallic compound CeRu₄Sn₆ has been tentatively classified as Kondo insulator. This class of material, especially non-cubic representatives, is not yet fully understood. Here we report thermopower measurements on single-crystalline CeRu₄Sn₆ between 2 K and 650 K, along the main crystallographic directions. Large positive thermopower is observed in the directions along which the hybridization is strong and a Kondo insulating gap forms. A negative contribution to the thermopower dominates for the crystallographic *c* axis where hybridization is weak and metallicity prevails.

Key words: Kondo insulator, thermopower, power factor, anisotropic hybridization

INTRODUCTION

Thermoelectric materials can convert (waste) heat directly into electricity or, alternatively, can be used to pump heat. They are, thus, promising candidates for electricity generation and thermoelectric cooling without environment pollution. However, the search for efficient thermoelectric materials is a challenge because large thermopower and electrical conductivity have to be combined with low thermal conductivity. These are generally conflicting requirements. In Kondo insulators, the position of the Fermi level inside the narrow hybridization gap leads to a strong enhancement of the thermopower. In addition, formation of cerium containing cages in the crystal structure of CeRu₄Sn₆ might reduce the thermal conductivity.

In Kondo insulators an energy gap in the electronic density of states (DOS) opens at the Fermi level as a consequence of strong electronic correlations. The gap arises from a half-filled conduction band hybridized with the almost localized *f* levels (*c*-*f* hybridization). The gap width of Kondo insulators is typically of the order of 1–10 meV.¹ A particularly interesting situation arises when the *c*-*f* hybridization is strongly anisotropic or develops nodes along specific directions in *k* space.^{2,3}

The cage compound CeRu₄Sn₆ crystallizes in a tetragonal crystal structure with the space group *I42m*⁴ and lattice parameters *a* = 6.8810 Å and *c* = 9.7520 Å.⁵ Interestingly, the diagonal of the tetragonal plane, *c*' = √2*a* = 9.7312 Å, differs from *c* by only 0.2%, forming a “quasi-cubic” unit cell.

Electrical resistivity measurements on CeRu₄Sn₆ revealed pronounced anisotropy between the crystallographic *c* axis and the directions within the tetragonal plane (*a* and *c*' directions).⁶ These data cannot be explained solely on the basis of a gapped electronic band structure as found in conventional semiconductors, and Kondo scattering processes affected by the crystal electric field (CEF) must be taken into account.

More recently, optical conductivity measurements together with the local density approximation (LDA) plus dynamic mean-field theory (DMFT) calculations have explained the anisotropic behaviour of this compound.⁷ Whereas along the *c* direction metal-like features can be seen at low temperatures, within the tetragonal plane semiconductor-like behaviour is observed. This is visible in the LDA + DMFT band structure as the development of a gap at the Fermi energy at low temperatures for the in-plane directions.

Here we report investigation of the electronic properties of single-crystalline CeRu₄Sn₆ by use of thermopower measurements. Our purpose was to

gain better understanding of the anisotropic gap in the electronic DOS and the involvement of the CEF.

EXPERIMENTAL

The polycrystalline starting material for the crystal growth was synthesized by first melting Ce and Ru, then melting the resulting Ce/Ru alloy with Sn, in a horizontal water-cooled copper boat, by use of high-frequency heating. The purity of the starting materials was 99.99% for Ce and Ru, and 99.9999% for Sn. Single crystal growth was achieved by use of the floating zone melting technique, by using optical heating in a four-mirror furnace. All steps were performed under Ar 99.9999% as protective atmosphere after several purgings with Ar. Because CeRu₄Sn₆ melts incongruently we used a self-flux technique.⁸ X-ray diffraction and scanning electron microscopy/energy dispersive x-ray spectroscopy investigations revealed that the crystals are single-phase and have the correct stoichiometric composition.

The low-temperature (2–300 K) thermopower was measured by means of a toggled heating method. By use of two different heaters, a heat gradient was applied along one direction of the sample and subsequently in the opposite direction to eliminate spurious background voltage signals. High-temperature (300–650 K) thermopower measurements were performed on a commercial system.

PHYSICAL PROPERTIES

The temperature variation of the thermopower ($S(T)$) of CeRu₄Sn₆ is shown in Fig. 1 for the different crystallographic directions. $S(T)$ is strongly anisotropic. The in-plane directions are maximum and minimum at the temperatures $T_{max} \approx 110$ K and $T_{min} \approx 15$ K, respectively. Along the c direction only a minimum is clearly seen at $T_{min}^c \approx 25$ K, somewhat higher than T_{min} for the in-plane directions. Thermopower data on polycrystalline CeRu₄Sn₆ were published by Brüning et al.⁹ They are included in Fig. 1 for comparison.

We have estimated T_{max} and T_{min} as the temperatures at which the first derivative of the thermopower (dS/dT) intersects zero (Fig. 2).

It is interesting to note that, even though there is no maximum in $S(T)$ along the c direction, dS/dT in Fig. 2 shows a clear upturn below the same T_{max} . This can be related to the relevant effect of CEF splitting on the Kondo scattering process, as we explain below.

The positive thermopower values for the c direction are much smaller than those along a and c' . The negative thermopower values, on the other hand, are larger in absolute value for the c direction than for a and c' . Within the interpretation proposed in Ref. 7 we conclude that a large, positive, peaked thermopower is because of the strong hybridization and the resulting Kondo insulator gap formation within the tetragonal plane, and that the negative

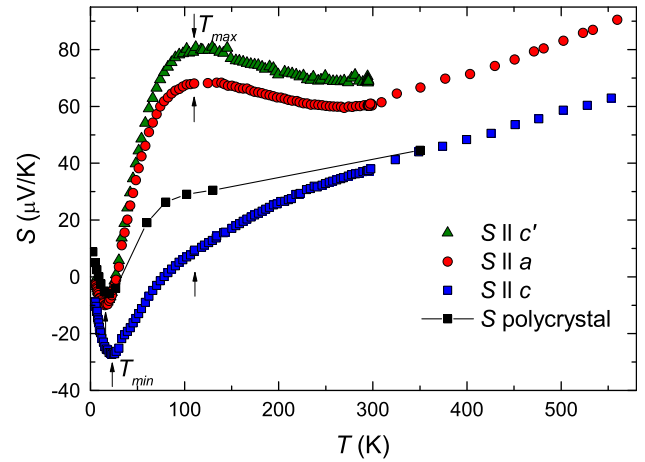


Fig. 1. Temperature dependence of the thermopower S of CeRu₄Sn₆ along three different crystallographic directions. For comparison, data for polycrystalline CeRu₄Sn₆ are shown.

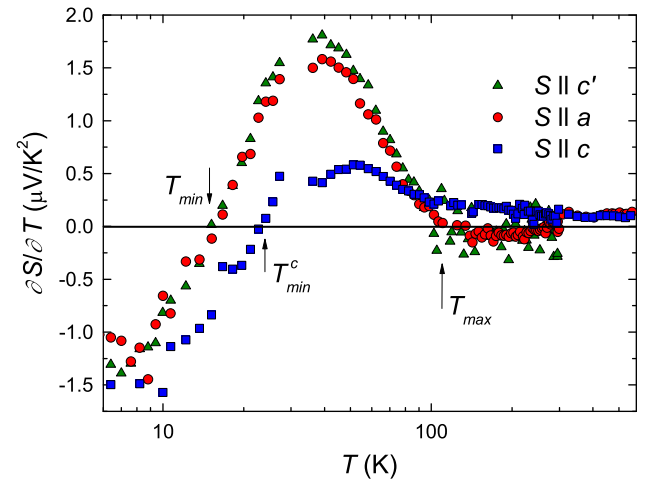


Fig. 2. Temperature dependence of the first derivative of the thermopower $\frac{dS}{dT}$ of CeRu₄Sn₆ along three different crystallographic directions.

contribution to the thermopower dominating along c is the signature of weak hybridization and a prevailing weakly metallic state.

In fact, the maximum of $S(T)$ observed at T_{max} in Fig. 1 is a characteristic feature observed in the thermopower of many Ce-based Kondo lattice systems, as shown in Fig. 3.

In general, $S(T)$ for Kondo lattice systems arises from two mechanisms that involve two different energy scales. One mechanism is the Kondo scattering on the CEF ground state level of the system. It gives rise to a maximum at a low temperature approximately equal to the single-ion Kondo temperature T_K . Another mechanism is incoherent Kondo scattering from excited CEF levels¹⁰ which appears in $S(T)$ as a broad high-temperature anomaly at $T_{max} \approx (\frac{1}{3} - \frac{1}{6})\Delta_{CEF}/k_B$, where Δ_{CEF} is the overall CEF splitting. Using this model and T_{max} observed in Fig. 1 for the in-plane directions,

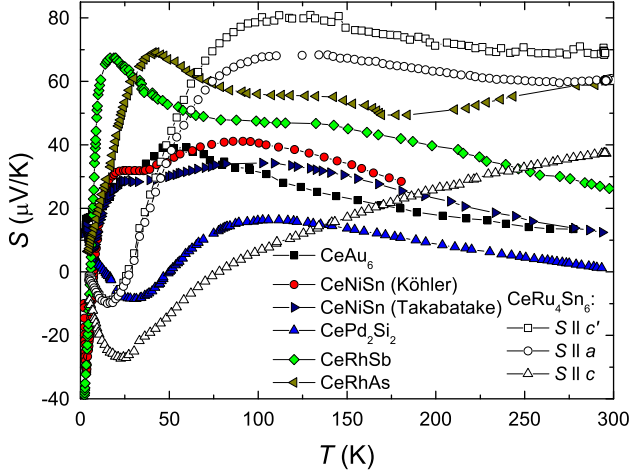


Fig. 3. Temperature dependence of the thermopower of the Kondo lattice systems CeAu_6 ,¹¹ CeNiSn ,^{12,13} CePd_2Si_2 ,¹⁴ CeRhSb ¹³ and CeRhAs ,¹³ compared with our data for CeRu_4Sn_6 (open symbols).

Δ_{CEF}/k_B of CeRu_4Sn_6 might be located between 330 K and 660 K. Because our $S(T)$ data show only one maximum we assume it originates from the combined Kondo scattering at the ground state doublet and at the excited doublets of the Ce^{3+} ion.

Figure 3 shows the temperature variation of the thermopower for some polycrystalline Kondo lattice systems with different crystal structures: orthorhombic (CeAu_6 ,¹¹ CeNiSn ,^{12,13} CeRhSb ¹³ and CeRhAs ¹³) and tetragonal (CePd_2Si_2 ¹⁴). The presence of two maxima at high temperatures is only observed for systems with orthorhombic crystal structure. These two maxima arise from the fact that T_K and Δ_{CEF}/k_B are well separated. In CeRu_4Sn_6 , which is tetragonal, similar to CePd_2Si_2 ,¹⁴ the Kondo temperature $T_K \approx 290$ K was reported.⁷ Therefore, the observation of only one maximum at T_{max} could indicate that T_K and Δ_{CEF}/k_B are close to each other, leading to an estimated Δ_{CEF}/k_B close to 330 K for CeRu_4Sn_6 .

Figure 4 shows the temperature dependence of the thermoelectric power factor $S^2(T)/\rho(T)$, where $\rho(T)$ is the electrical resistivity previously in Ref. 6.

At the highest temperatures of approximately 600 K, $S^2(T)/\rho(T)$ reaches values of $15 \mu\text{W}/\text{cm K}^2$ and $9 \mu\text{W}/\text{cm K}^2$ for the a and c direction, respectively. In the intermediate temperature region $120 \text{ K} < T < 300 \text{ K}$ the in-plane direction $a(c')$ has a plateau of approximately $6.5(8) \mu\text{W}/\text{cm K}^2$. These values are comparable with, e.g., those for the type-I clathrates $(\text{Ce}, \text{Ba})_8\text{Au}_x\text{Si}_{46-x}$ and $(\text{La}, \text{Ba})_8\text{Au}_x\text{Si}_{46-x}$ which have power factors of approximately $6 \mu\text{W}/\text{cm K}^2$ and $11 \mu\text{W}/\text{cm K}^2$,¹⁵ respectively. Of course the record values of $S^2(T)/\rho(T) \approx 8000 \mu\text{W}/\text{cm K}^2$ reported for the correlated semiconductor FeSb_2 ¹⁶ are well beyond our values. At temperatures below 75 K, clear enhancement of the power factor to $1 \mu\text{W}/\text{cm K}^2$ is seen for the c axis at approximately $T_{\text{min}}^c \approx 25$ K, the temperature of the pronounced minimum in $S(T)$.

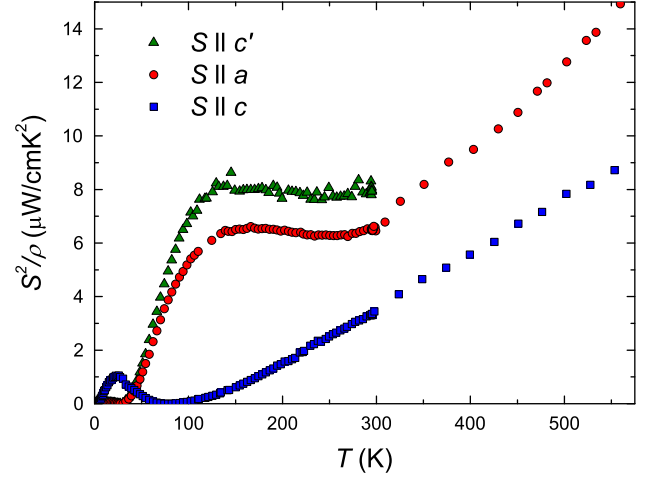


Fig. 4. Temperature dependence of the power factor $PF = \frac{S^2}{\rho}$ of CeRu_4Sn_6 along three different crystallographic directions.

CONCLUSION

We have presented thermopower data for single crystalline CeRu_4Sn_6 in a wide temperature range (2–650 K), for the three crystallographic directions a , c' , and c . The anisotropy between the in-plane (a , c') and out-of-plane (c) directions previously reported^{6,7} is also seen in the thermopower. The thermopower has a single maximum at high temperatures for the a and c' directions indicating that the overall CEF splitting and the Kondo temperature are of similar magnitude. The negative thermopower with no maximum for the c direction is attributed to the quasi-metallicity along this direction.

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REFERENCES

1. G. Aeppli and Z. Fisk, *Comments Condens. Matter Phys.* 16, 155 (1992).
2. H. Ikeda and K. Miyake, *J. Phys. Soc. Jpn.* 65, 1769 (1996).
3. J. Moreno and P. Coleman, *Physica B* 259–261, 190 (1999).
4. I. Das and E.V. Sampathkumaran, *Phys. Rev. B* 46, 4250 (1992).

5. R. Pöttgen, R.-D. Hoffmann, E.V. Sampathkumaran, I. Das, B.D. Mosel, and R. Müllmann, *J. Solid State Chem.* 134, 326 (1997).
6. H. Winkler, K.-A. Lorenzer, A. Prokofiev, and S. Paschen, *J. Phys. Conf. Ser.* 391, 012077 (2012).
7. V. Guritanu, P. Wissgott, T. Weig, H. Winkler, J. Sichelschmidt, M. Scheffler, A. Prokofiev, S. Kimura, T. Iizuka, A.M. Strydom, M. Dressel, F. Steglich, K. Held, and S. Paschen, *Phys. Rev. B* 87, 115129 (2013).
8. S. Paschen, H. Winkler, T. Nezu, M. Kriegisch, G. Hilscher, J. Custers, A. Prokofiev, and A. Strydom, *J. Phys. Conf. Ser.* 200, 012156 (2010).
9. E.M. Brüning, M. Brando, M. Baenitz, A. Bentien, A.M. Strydom, R.E. Walstedt, and F. Steglich, *Phys. Rev. B* 82, 125115 (2010).
10. A.K. Bhattacharjee and B. Coqblin, *Phys. Rev. B* 13, 3441 (1976).
11. M.R. Lees, B.R. Coles, E. Bauer, and N. Pillmayr, *J. Phys. Condens. Matter* 2, 6403 (1990).
12. U. Koehler, P. Sun, N. Oeschler, T. Takabatake, S. Paschen, and F. Steglich, *J. Phys. Conf. Ser.* 150, 042096 (2009).
13. T. Takabatake, T. Sasakawa, J. Kitagawa, T. Suemitsu, Y. Echizen, K. Umeo, M. Sera, and Y. Bando, *Physica B* 328, 53 (2003).
14. D. Huo, J. Sakurai, O. Maruyama, T. Kuwai, and Y. Isikawa, *J. Magn. Magn. Mater.* 226–230, 202 (2001).
15. A. Prokofiev, A. Sidorenko, K. Hradil, M. Ikeda, R. Svagera, M. Waas, H. Winkler, K. Neumaier, and S. Paschen, *Nat. Mater.* 12, 1096 (2013).
16. Q. Jie, R. Hu, E. Bozin, A. Llobet, I. Zaliznyak, C. Petrovic, and Q. Li, *Phys. Rev. B* 86, 115121 (2012).