Anisotropy of the Kondo insulator CeRu$_4$Sn$_6$

S. Paschen, H. Winkler, T. Nezu, M. Kriegisch, G. Hilscher, J. Custers, and A. Prokofiev
Institute of Solid State Physics, Vienna University of Technology, Wiedner Hauptstr. 8-10, 1040 Vienna, Austria

A. Strydom
Physics Department, University of Johannesburg, P.O. Box 524, Auckland Park 2006, South Africa
E-mail: paschen@ifp.tuwien.ac.at

Abstract. The intermetallic compound CeRu$_4$Sn$_6$ has tentatively been classified as Kondo insulator. Its tetragonal crystal structure places it inbetween the archetypal Kondo insulators like YbB$_{12}$ or Ce$_3$Bi$_4$Pt$_3$, which are cubic, and the orthorhombic “Kondo semimetals” CeNiSn and CeRhSb. It is of great interest to investigate possible anisotropies – or even nodes – of the Kondo insulating gap in CeRu$_4$Sn$_6$. We have succeeded, for the first time, to grow single crystals of this compound. Interestingly, we could not only reveal anisotropy between the tetragonal c direction and the tetragonal a-a plane but even within a quasi-cubic cell which happens to be formed in CeRu$_4$Sn$_6$ because the length of the diagonal of the tetragonal plane $c' = \sqrt{2}a$ differs from c by only 0.2%.

1. Introduction
In Kondo insulators or heavy fermion semiconductors a narrow gap (or pseudo gap) develops at low temperatures in the electronic density of states at the Fermi level [1]. While most Kondo insulators known to date adopt a cubic crystal structure (e.g., YbB$_{12}$, SmB$_6$, FeSi, Ce$_3$Bi$_4$Pt$_3$) a few compounds (e.g., CeNiSn, CeRhSb) are orthorhombic. These latter show anisotropic properties which have been interpreted as indications for nodes of the energy gap along certain directions in k-space [2, 3].

CeRu$_4$Sn$_6$, first synthesized by Das and Sampathkumaran [4], crystallizes in a tetragonal structure of space group I42m ($a = 6.8810$ Å, $c = 9.7520$ Å, $c/a = 1.4172$) [5]. A peculiarity of this compound is that, in addition to the tetragonal (body-centered) cell with lattice parameters $a$ and $c$ there exists a quasi cubic (face-centered) cell with lattice parameters $c'$ and $c$, where $c'$ is the diagonal of the tetragonal plane which differs by only 0.2% from $c$. This makes it very difficult to orient single crystals in an unambiguous way. On the other hand it allows us to study a “tetragonal” and a “quasi-cubic” Kondo insulator within the same material which is very appealing.

2. Experimental
The polycrystalline starting material for crystal growth was synthesized by melting first Ce and Ru, and subsequently the Ce/Ru alloy with Sn in a horizontal water cooled copper boat using...
HF heating. The purity of the starting materials was 99.99% for Ce (Ames Lab) and Ru, and 99.9999% for Sn. Single crystal growth was performed by the floating zone melting technique using optical heating (Crystal Corporation four mirror furnace). All steps were done under Ar 6.0 protective atmosphere after several purgings with Ar. Since CeRu$_4$Sn$_6$ melts incongruently we used a self-flux technique. X-ray diffraction and SEM/EDX investigations revealed that the crystals are single phased and have the correct stoichiometric composition, which is uniform along the growth direction.

Electrical resistivity measurements were done by a standard 4-point technique, with alternating dc current in a physical property measurement system (PPMS) from Quantum Design between room temperature and 2 K, and with low-frequency ac current in a $^3$He/$^4$He dilution refrigerator from Oxford Instruments at temperatures below 2 K. The magnetization was measured in a SQUID magnetometer of Cryogenic Ltd., the specific heat in a PPMS by the relaxation technique.

3. Physical properties

Figure 1 shows the temperature dependence of the electrical resistivity, $\rho(T)$, of CeRu$_4$Sn$_6$ on a semi-logarithmic scale. The current was applied along $c$ or $c'$ which cannot be distinguished by our Laue diffractograms. With decreasing temperature $\rho$ first increases steeply (range 1), then passes over a maximum at about 10 K, increases again, albeit less steeply (range 2), and finally tends to saturate at the lowest temperatures. A possible explanation of this behaviour is a double-gap structure frequently encountered in simple semiconductors: a larger intrinsic gap visible at high temperatures and a smaller extrinsic gap between impurity states and the band edge that dominates the low-temperature behaviour. Approximating $\rho(T)$ between 120 and 300 K with exponential behaviour ($\rho = \rho_0 e^{\Delta_1/(2k_BT)}$, Arrhenius law) yields an energy gap $\Delta_1/k_B = 125$ K, sizeably larger than previously reported [4, 6]. Fitting the data between 0.8 and 1.8 K with the same function yields $\Delta_2/k_B = 0.1$ K (see full red lines in Fig. 1 for both fits). Since this temperature is sizably smaller than the lower boundary of the fitting range weaker than exponential temperature dependencies are no longer negligible and a more complete fitting function would be needed for a reliable determination of $\Delta_2$.

Alternatively, one may approximate the temperature dependence of $\rho$ in the two ranges by a $-\ln T$ law, which is characteristic of incoherent Kondo scattering or quantum critical behaviour in metallic heavy fermion compounds. While in range 1 the $-\ln T$ law holds only between 40 and 80 K, in range 2 it describes the data well over a rather extended temperature range (cf. green dashed lines in Fig. 1). From resistivity data alone no unambiguous interpretation is possible.
The magnetic susceptibility (not shown) was measured on an oriented single crystal in two mutually perpendicular directions (magnetic field $H$ within the tetragonal plane and perpendicular to it). A pronounced difference is seen, with clear Curie-Weiss behaviour only for $H$ within the tetragonal plane.

In order to test whether anisotropy also exists within the quasi-cubic cell we oriented a single crystal along three mutually perpendicular directions: two of these directions are $c'$, one is $c$. As explained above, our Laue diffractograms cannot identify which orientation is which. The magnetization measurements, however, allow to clearly identify the $c$- and $c'$-orientations (Fig. 2). The magnetization is essentially identical for two orientations which thus correspond to $H \parallel c'$ but drastically reduced for the third one ($H \parallel c$). Thus, strong anisotropy persists even in the quasi-cubic cell.

This behavior is confirmed by our specific heat measurements on small single crystalline platelets (with geometries which allowed for specific heat measurements only) cut from one

![Figure 2. Magnetic field dependence of the magnetization, $M(\mu_0H)$, of CeRu$_4$Sn$_6$, taken at 3 K for fields applied along the crystallographic $c$ or $c'$ axes.](image)

![Figure 3. Temperature dependence of the specific heat, $c_p(T)$, of three CeRu$_4$Sn$_6$ platelets with mutually perpendicular normals ($c$ and $c'$, see text).](image)
single crystal in such a way that three mutually perpendicular directions were obtained: for two samples a \( c' \) axis is perpendicular to the platelet plane, for one sample it is \( c \). Again, before the measurement we do not know which sample is which but the specific heat measurements allow to clearly identify the \( c \)- and \( c' \)-oriented samples. While the zero field data are very similar for all three samples a magnetic field applied perpendicular to the platelet planes induces sizable anisotropy (Fig. 3). Two samples (sc1 and sc2) show very similar behaviour and must thus be \( c' \)-oriented while sc3 shows distinctly different behaviour and is thus identified as the \( c \)-oriented sample.

The difference is best seen by plotting the relative difference in specific heat induced by a magnetic field, \( (c_p(\mu_0H) - c_p(0))/c_p(0) \), which reaches a maximum of more than 70% at 3.5 K for \( H \parallel c' \) but is below 15% for \( H \parallel c \) at this temperature. This is a strong indication for an anisotropic ground state of the Kondo insulator CeRu\(_4\)Sn\(_6\). A more detailed analysis of the data will require bandstructure information. Also, more experiments in wider temperature and magnetic field ranges are needed to fully analyse and understand the anisotropy of CeRu\(_4\)Sn\(_6\).

4. Conclusions
Pronounced magnetic anisotropies revealed in this work in the magnetic-field dependent magnetization and specific heat of CeRu\(_4\)Sn\(_6\) present the opportunity to advance our understanding of the enigmatic hybridization-induced energy gap formation in strongly correlated electron systems. A nodal or directional gap in the case presented here is especially attractive. Further work is in progress to assess the double-gap structure of this compound, as well as the extent to which the gapped state may be modified by applied magnetic fields.

Acknowledgements We gratefully acknowledge financial support from the Austrian Science Fund (project P19458-N16). AMS thanks the Science Faculty of the University of Johannesburg and the SA-NRF (2072956) for support.

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