Sn-NMR Study on the Correlated Semimetals U_2Ru_2Sn and $CeRu_4Sn_6$

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Up to now all Kondo insulators have either a cubic symmetry ($Ce_3Bi_4Pt_3$ for example) or are orthorhombic systems. i. e. CeNiSn, CeRhSb and CeRhAs [1,2]. It would be straightforward to speculate that tetragonal systems also might exist in this class of materials. One of the key features of Kondo insulators is the formation of a narrow gap at the Fermi level at low temperatures, frequently related to the hybridization of 4*f* (or 5*f*) and conduction electrons [1,2]. The signature of the gap formation is usually found in transport (resistivity, thermopower) and specific-heat measurements. Strong experimental evidence often comes from magnetic resonance techniques (NMR and NQR) on various nuclei. To overcome problems in the determination of the gap due to the magnetic anisotropy and/or granularity in polycrystalline samples, this local probe is very suitable.

The first ^{119}Sn-NMR results on U_2Ru_2Sn presented in the last report were obtained from polycrystalline material and, therefore, they are averaged over all orientations. Furthermore, the conventional Fourier-transform NMR technique (in a fixed field of 7.05 T, MSL300 Bruker) was used. This method is powerful for narrow NMR lines, where the complete line could be excited by a single pulse in the spin echo experiment. Broad lines, like in U_2Ru_2Sn, could be investigated solely by the time consuming "point by point" method (manual frequency sweep). To overcome this difficulty, the field sweep NMR technique was established at the MPI-CPfS in the last two years (s. "*Broad Line Solid State NMR: New Equipment and Techniques, First Results*").

In the following section highlights of a detailed ^{119}Sn-NMR study on random powder (RP), oriented powder (OP), single crystals (SC) and oriented single crystals (OSC) of the system are presented, together with very recent results on the new tetragonal system $CeRu_4Sn_6$, which is semimetallic, with correlations becoming apparent below 10 K. After more than three years of research on U_2Ru_2Sn, the system can consistently be classified as a Kondo insulator with a gap of about 230 K, the smallest gap ever found among all U-based Kondo insulators.

U_2Ru_2Sn

U_2Ru_2Sn belongs to the 221 family of compounds U_2T_2X (*T*: transition metal Fe, Co, Ni, Ru, Rh, Pt and *X*: = In or Sn) which form in an ordered version of the tetragonal U_3Si_2 lattice [3]. First investigations indicated itinerant paramagnetism [4], whereas more recent investigations of Menon et al. [5] and du Plessis et al. [6] assign U_2Ru_2Sn as a Kondo insulator due to its semiconducting behaviour of the resistivity accompanied by a loss of the local moment at low temperatures. Triggered by this, NMR investigations on polycrystalline samples were initiated [7,8,9].

^{119}Sn field sweep NMR spectra, Knight shift and hyperfine coupling

Typical ^{119}Sn field sweep NMR spectra on poly- and single-crystalline samples at different temperatures are shown in Fig. 1. The anisotropic shift values $^{119}K_{\|}(T)$ and $^{119}K_{\perp}(T)$ are obtained by either modeling the rather broad powder spectra taken from the polycrystal or by fitting a symmetrical Lorenzian line shape to the single lines obtained from the single crystals oriented in different directions. Fig. 2 shows $^{119}K(T)$ in the parallel ($H \| c$) and perpendicular ($H \perp c$) directions. $^{119}K(T)$ is anisotropic in the entire measured range of temperature. However, below 150 K, $^{119}K_{\|}(T)$ exhibits a rapid decrease as indicated by the $\Delta K(T)$ plot. We assume that the dominant contribution to ^{119}K(T) and to the hyperfine field is the *s–f* exchange interaction (polarization of conduction electrons via strong correlations to U-5*f* moments). Therefore, such a $^{119}K(T)$ might be attributed to opening of a gap in the quasi-particle density of states. From the anisotropy of $^{119}K(T)$ one can speculate that such a gap opening is more prominent in the parallel direction. However, it is

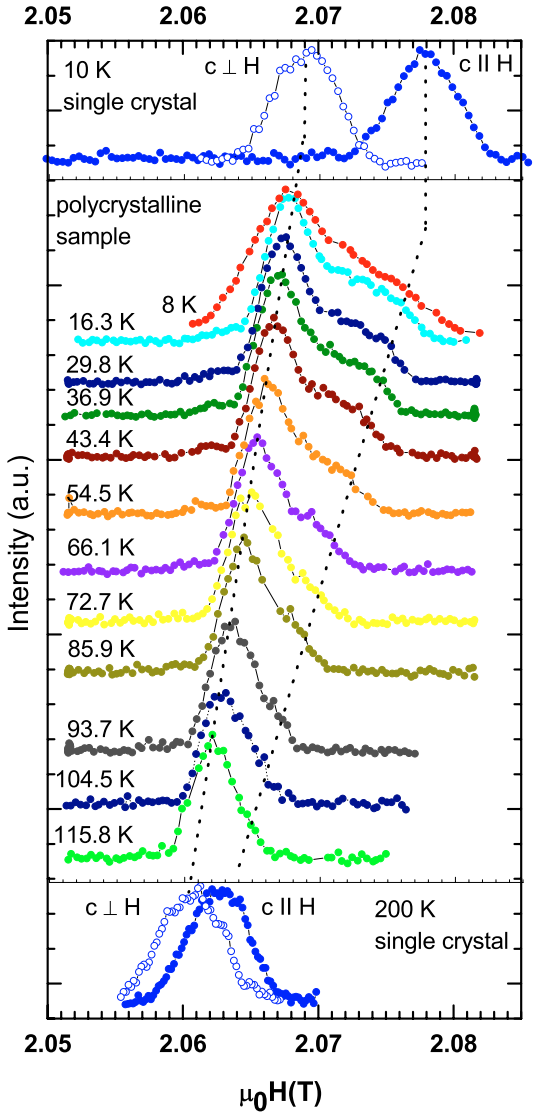

Fig. 1: ^{119}Sn field sweep NMR spectra of U_2Ru_2Sn single crystals (top/bottom) and random oriented powder (middle) at various temperatures (NMR frequency was 33.26 MHz, Larmor field is $\mu_0 H_L$ = 2.096 T). Dashed lines indicate the temperature dependent anisotropic shift in the powder pattern.

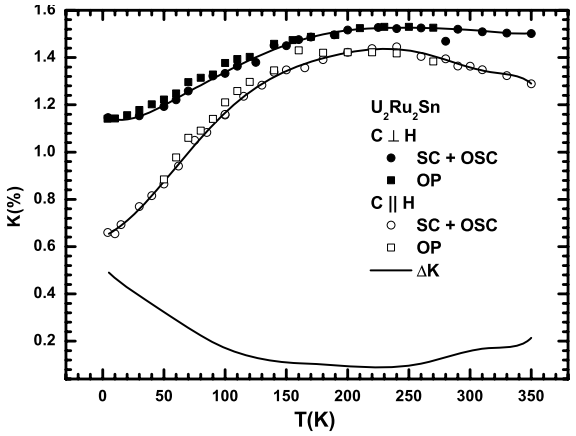

Fig. 2: Temperature dependence of the Knight shift $^{119}K(T)$ for fields parallel and perpendicular to the c direction. Data obtained from NMR investigations on single crystals (SC), oriented single crystals (OSC) and oriented powder (OP). Solid lines are guides to the eye by using a polynomial fit. ΔK(T) is obtained by subtracting the two polynomials from each other [14].

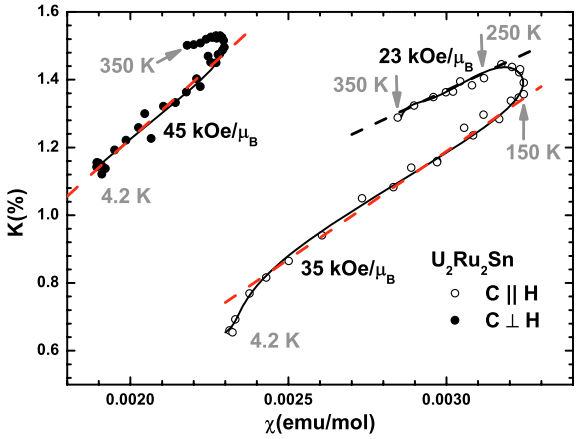

Fig. 3: $^{119}K(T)$ vs. $\chi(T)$ plot with temperature as an implicit parameter. Dotted lines are fits of the linear relation $^{119}K(T) = (A_{hf}/\mu_B N_A)\chi(T)$ to the data in the temperature range between 4 K and 150 K and 250 K and 350 K, respectively. The A_{hf} values estimated from the fit are given in the plot [14].

also possible that the anisotropy in $^{119}K(T)$ comes from an anisotropy of the residual density of states [10] or due to an anisotropic residual U-5*f* magnetism. The values of the hyperfine coupling constant A_{hf} obtained from the slope of $^{119}K(T)$ vs. $\chi(T)$ plot (Fig. 3) are comparable in magnitude with those obtained for CeNiSn [11]. The anomalous "turn-over" observed in $^{119}K(T)$ vs. $\chi(T)$ between 150 K and 250 K is a general feature observed in many Kondo systems and the turn-over point is often attributed to the Kondo (or coherence) temperature where correlations set in. [12,13]. Furthermore, NMR investigations on metallic Th_2Ru_2Sn, iso-electronic (assuming U-5f^2) and iso-structural to U_2Ru_2Sn are performed. ^{119}K in Th_2Ru_2Sn, is isotropic and temperature independent ($^{119}K(Th) \sim$ 0.1 %), whereas in $^{119}1/T_1(T)$ a linear T-dependence was found. This confirms nicely the Korringa relation where $(T_1TK^2) = const.$ is valid. A hyperfine field coupling constant of approximately 6 Oe/μ_B is estimated from the susceptibility [8,9] assuming negligible diamagnetic contributions.

Nuclear spin lattice relaxation rate $^{119}1/T_1$

The spin lattice relaxation rate $^{119}(1/T_1)$ of U_2Ru_2Sn as a function of temperature obtained by applying a standard inversion recovery pulse sequence is plotted in Fig. 4 together with the results on Th_2Ru_2Sn. The rate of U_2Ru_2Sn decreases drastically over three orders of magnitude by lowering the temperature. A simple explanation of this behavior is that $^{119}R = 1/T_1(T)$ could be divided into two independent contributions: one is the spin component arising from the *5f* moments, $^{119}R_{5f}(\propto \chi_{5f}(T))$, the other one is the charge component from the conduction electrons at the Fermi level, $^{119}R_{CE}$ ($\propto N(E_F)^2$). The total rate is the sum of both, $^{119}R(T) = {}^{119}R_{5f} + {}^{119}R_{CE}$. The conduction electron part is given by the Th reference, $^{119}R_{CE}(U) = {}^{119}R_{CE}(Th)$. Our finding that $^{119}R(U)$ first decays to the value of the Th reference, ^{119}R(Th), indicates the loss of the spin component, consistent with susceptibility results. The further decay of $^{119}R(U)$ towards lower temperatures indicates the evolution of a gap in the electronic density of states around the Fermi level. So, roughly spoken, signatures of spin and charge gap formation are evidenced by the relaxation rate measurements. It should be mentioned that this scenario is an oversimplified approach, because the interaction between the nuclear and the electron spin is mediated via the (*s*-like) conduction electrons at the Fermi level (the so called Fermi contact interaction) and, therefore, the assumption of independent contributions $^{119}R_{CE}$ and $^{119}R_{5f}$ is strictly not valid.

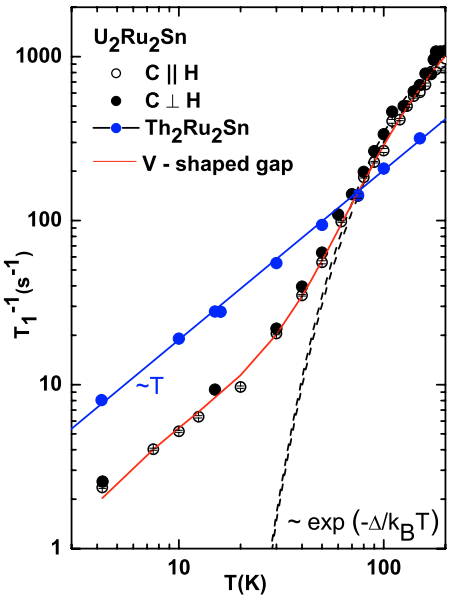

Fig. 4: Temperature dependence of the spin lattice relaxation rate $^{119}(1/T_1)$ of U_2Ru_2Sn for fields parallel and perpendicular to the c axis. Data for the Th- homologue are obtained from a polycrystalline sample. The red solid curve represents the "V-shaped" gap model as described in Ref. [15], whereas the dashed curves are simple exponential fits to the different directions (Δ/k_B = 180 K).

In order to model our rate in the entire temperature range we tried to fit the data by assuming a single particle excitation spectrum with a gapped density of states. As a first approach we fitted the rate with an exponential curve ($1/T_1 \sim exp\{-\Delta/k_BT\}$), known from Spin-Peierls systems or conventional superconductors. The striking deviation from the exponential curve observed at low temperatures has been ascribed to a "V-shaped" gap in *N(E)* around E_F. Residual states in the gap are responsible for the Korringa-like linear behavior in $^{119}R(T)$ for $T \rightarrow 0$. Our data could be nicely fitted within the "V-shaped" gap model described in Ref [15]. The gap value of Δ/k_B = 230 K is in a good agreement with recent neutron scattering results [16]. Furthermore, the fitting yields a bandwidth of D/k_B = 2500 K and a fraction of residual density of states of (N_{res}/N_0) at the Fermi level $E = E_F$ of about 3 %, where N_0 holds at $T \gg \Delta/k_B$.

In conclusion, we have shown that U_2Ru_2Sn is the first Kondo insulator with tetragonal lattice structure. Coherence sets in at around 230 K, experimentally evidenced by the loop in the $^{119}K(T)$ vs. $\chi(T)$ plot and the decay of the spin lattice relaxation rate $^{119}(1/T_1)$.

$CeRu_4Sn_6$

Triggered by investigations of the electrical resistivity and the specific heat identifying $CeRu_4Sn_6$ as a dense Kondo system [17-20], we performed a ^{119}Sn-NMR study on the tetragonal compound $CeRu_4Sn_6$ (hereafter referred to as Ce-146) and its non-magnetic reference compound $LaRu_4Sn_6$ (La-146). Here we report on temperature-dependent NMR investigations on the ^{119}Sn nuclei, Knight shift $^{119}K(T)$ and spin lattice relaxation rate $^{119}(1/T_1)$ of polycrystalline powder samples of Ce-146 and La-146. The temperature dependent field sweep spectra at ν = 47 MHz of Ce-146 are shown in Fig. 5. The line width for the Ce-146 compound is broadened in comparison to U_2Ru_2Sn the only tetragonal Kondo insulator known so far [14]. This

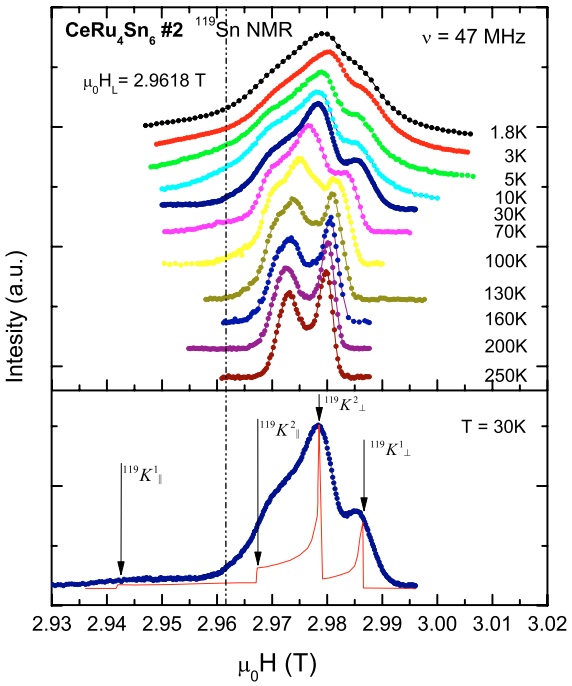

Fig. 5: ^{119}Sn field sweep spectra of $CeRu_4Sn_6$ (at different temperatures, NMR frequency is ν= 47 MHz). The spectra show a broadening towards lower temperature plus a definite splitting at higher temperatures (due to the two different Sn sites in the tetragonal structure). The powder pattern could be simulated with two sites with anisotropic shift values $^{119}K_{\parallel}(T)$ and $^{119}K_{\perp}(T)$ (bottom).

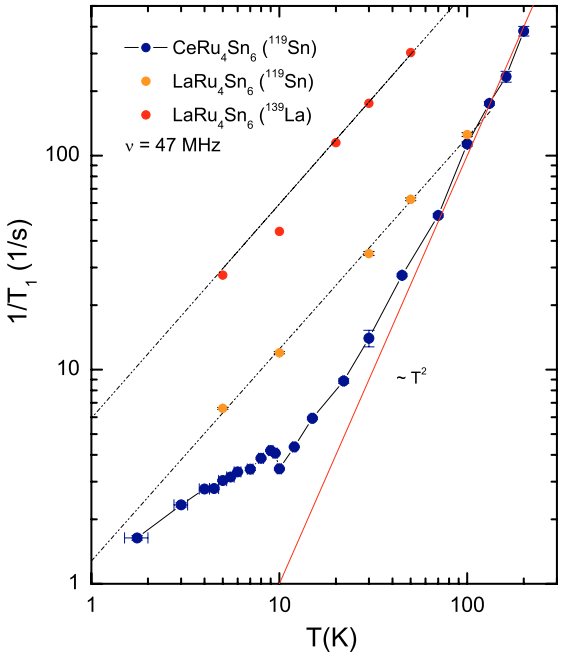

Fig. 6. Temperature dependence of the spin lattice relaxation rate $^{119}(1/T_1)$ of $CeRu_4Sn_6$ and the non-magnetic reference compound $LaRu_4Sn_6$. In addition, ^{139}La NMR on La-146 was performed to get $^{139}(1/T_1)$. The values shown here are averaged because polycrystalline samples with random orientations were used. For Ce-146, the temperature dependence of $1/T_1$ is close to T^2 at higher temperatures and below approximately T = 10 K an upturn is observed. The rates of ^{139}La (red points) and ^{119}Sn (orange points) obtained from La-146 show linear behaviour, nicely confirming the Korringa relation.

broadening is due to the two different Sn sites in the Ce-146 structure. Above T = 100 K, a definite splitting in the spectrum becomes apparent which indicates the intrinsic presence of two overlapping Sn lines. The spectra could be simulated with a superposition of two broadened anisotropic $S = 1/2$ lines. The ^{119}Sn field sweep spectra of Ce-146 show a small and nearly constant negative Knight shift (K = –0.33%). This indicates a small hyperfine coupling (powder averaged hyperfine field H_{Hf} of about 100 Oe for Ce-146 at 100 K). Fig. 6 shows the temperature dependences of $^{119}(1/T_1)$ for the polycrystalline powder sample Ce-146 (blue) as well as for ^{139}La (red points) and ^{119}Sn in La-146 sample (orange points).

At higher temperatures, the temperature dependence of $1/T_1$ is close to T^2, while below approximately T = 10 K an upturn is observed. Here, the formation of correlations becomes apparent. This is consistent with specific heat results in the framework of the Korringa model, where $1/T_1T \sim K^2 \sim N^2_{EF} \sim (C/T)^2$ is valid. The rates of ^{139}La and ^{119}Sn obtained from the La-146 sample show Korringa behaviour. The reason for this might be that the shift also bears contributions other than the Fermi-contact interaction (chemical shift). Investigations of $1/T_1$ at higher fields are currently under progress and preliminary results show the suppression of the low temperature upturn. In conclusion, the results for $CeRu_4Sn_6$ suggest the formation of a ground state of strongly correlated quasiparticles within a charge carrier system of low density.

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