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Towards strongly correlated semimetals: U_2Ru_2Sn and $Eu_8Ga_{16}Ge_{30}$

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Abstract

We present results of transport, magnetic, and calorimetric measurements on two f-electron based compounds: U_2Ru_2Sn and $Eu_8Ga_{16}Ge_{30}$. We show that U_2Ru_2Sn shares several properties with the strongly correlated semimetal CeNiSn. These analogies suggest that in U_2Ru_2Sn a narrow energy gap (or pseudogap) opens which is one order of magnitude larger than the one of CeNiSn. The two modifications of the clathrate $Eu_8Ga_{16}Ge_{30}$ behave as local-moment ferromagnetic metals with relatively low Curie temperatures and small charge-carrier concentrations. The thermal conductivity is low and glass-like, as expected for 'filled-cage' systems. If, by modification of the Ga–Ge cages, a 'Kondo insulating' ground state could be realized, a high thermoelectric figure of merit associated with the (pseudo)gap opening would be expected.

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1. Introduction

Heavy fermion semiconductors or semimetals, usually referred to as 'Kondo insulators' [1], are an intriguing set of materials. A narrow gap or pseudogap at the Fermi energy develops at low temperatures, but the origin of the gap formation is unclear. The local moments steming from partially filled f (or d) shells, present on regular lattice sites in all these compounds, appear to be at least partially compensated at low temperatures, without the occurrence of long-range order. The extreme sensitivity of the low-temperature properties of these materials to impurities makes it difficult to identify intrinsic properties. The best example in this respect is CeNiSn. It was first identified as a Kondo insulator because of the thermally activated temperature dependence of the electrical resistivity observed in early samples [2]. Samples of improved quality, however, lacked this characteristic of a semiconductor and showed a metal-like temperature dependence of the electrical resistivity instead [2]. That in spite of this metal-like behavior a gap (or pseudogap) opens is, for example, evidenced by the temperature dependence of the spin lattice relaxation rate [3].

Kondo insulators are not only a challenging fundamental research topic but might also find an application as thermoelectric materials. This is due to the huge thermopower observed in the temperature range where the gap opens. For CeNiSn, for example, the thermopower along the *a*-axis is as large as 50 μV/K at 4 K [4]. So far, the thermoelectric figure of merit, $Z = S^2\sigma/\kappa$, of a material in a Peltier cooling device is, however, not competitive for Kondo insulators. To further improve it, the ratio of the electrical to the thermal conductivity, σ/κ, must be increased. This appears to be realized in so-called 'filled-cage' systems like filled skutterudites [5] or clathrates [6], where (guest) atoms are loosely bound in oversized atomic cages (host). These systems are believed to behave as 'phonon glasses and electron crystals' [7]: The guest atoms undergo large local anharmonic vibrations. This 'rattling' may resonantly scatter acoustic-mode, heat-carrying phonons and thus lead to very

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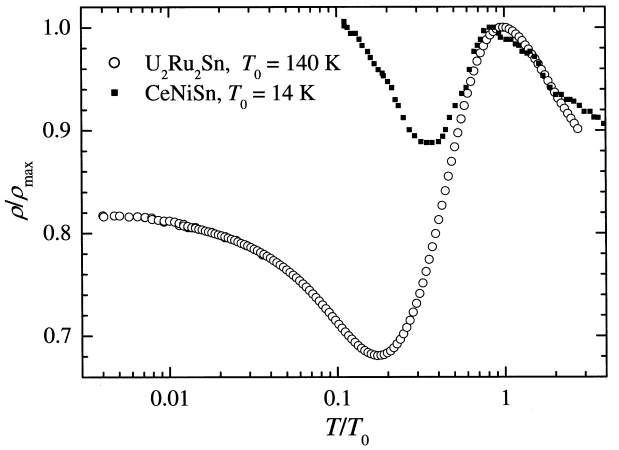

Fig. 1. Normalized electrical resistivity, ρ/ρ_{max}, of U_2Ru_2Sn and of CeNiSn [2] as a function of the reduced temperature T/T_0.

low and 'glass-like' (phonon-dominated) thermal conductivities ('phonon glasses'). The charge carriers (and therefore also the electrical conductivity) are less affected by the rattling and thus behave as electrons in an ordinary crystalline lattice ('electron crystals').

We present here comprehensive results on a potential new strongly correlated semimetal, U_2Ru_2Sn [8], and on two modifications of the clathrate $Eu_8Ga_{16}Ge_{30}$ [9]. In U_2Ru_2Sn we have evidence for a narrow gap of the order of 140 K. Both $Eu_8Ga_{16}Ge_{30}$ modifications, which are the only clathrates known so far where the guest positions are fully occupied by a rare-earth element, behave as local-moment ferromagnets with relatively low Curie temperatures (10.5 and 36 K) and small charge-carrier concentrations (3.8 and 12.5×10^{20} cm^{-3} at 2 K). To transform them into Kondo insulators the host will have to be modified such that Eu becomes intermediate valent.

2. U_2Ru_2Sn

U_2Ru_2Sn belongs to a series of compounds, U_2T_2X with T = Fe, Co, Ni, Ru, Rh, Pd, Pt and X = Sn, In which crystallize in an ordered version of the tetragonal U_3Si_2-type structure (*P4/mbm*). U_2Ru_2Sn was first classified as a weak paramagnet [10] and more recently as a possible Kondo insulator [11]. This latter assignment was based on the observation that the electrical resistivity increases upon cooling below 30 K, which was taken as evidence for a (pseudo)gap formation. Triggered by this observation we have measured the electrical resistivity, Hall coefficient, ^{119}Sn NMR, magnetic susceptibility, specific heat, thermopower, and thermal conductivity of polycrystalline samples of U_2Ru_2Sn [8]. All these measurements suggest indeed that there is a narrow energy gap. However, similar to the case of early samples of CeNiSn, the earlier described increase of the electrical resistivity appears not to be directly related to the gap opening.

To emphasize the similarities with CeNiSn, we show in Figs. 1–3 the electrical resistivity, ρ, the Hall coefficient, R_H, and the spin lattice relaxation rate, $1/T_1$, respectively, of U_2Ru_2Sn together with literature data of CeNiSn [2,3], as a function of the normalized temperature, T/T_0. T_0 was taken as 14 K for CeNiSn, which corresponds to the value of the energy gap k_BT_0 determined from the $1/T_1(T)$ measurement of Ref. [3]. For U_2Ru_2Sn, T_0 was determined by shifting the $1/T_1(T/T_0)$ data of U_2Ru_2Sn on top of the ones of CeNiSn, giving 140 K. The same T_0 values were used for $\rho(T/T_0)$ and $R_H(T/T_0)$. The features related to the gap opening are surprisingly similar in all three plots, as will be further outlined later. Thus, U_2Ru_2Sn behaves as CeNiSn, but with a gap energy k_BT_0 which is one order of magnitude larger than for CeNiSn.

The transport data of CeNiSn used earlier [2] were taken on a medium quality single crystal with the current, I, along the c-axis for $\rho(T)$, and with I along the b-axis and the magnetic field along the c-axis for $R_H(T)$. The upturn of ρ below $T/T_0 = 0.3$ is sample and direction dependent and was shown to be extrinsic [2]. We believe that the same may be true for U_2Ru_2Sn. In fact, a comparison of two U_2Ru_2Sn samples of different purity [11] showed that the upturn in $\rho(T)$ is less pronounced for the cleaner sample. Also the precise shape of $R_H(T)$ is sample and direction dependent for CeNiSn [2]. For cleaner samples the absolute value of R_H increases steeply towards the lowest temperatures. Assuming that the gap extracted from $1/T_1(T)$ is also the relevant gap for the electronic transport properties, gap related features in $\rho(T/T_0)$ and $R_H(T/T_0)$ are expected below $T/T_0 = 1$. For both U_2Ru_2Sn and CeNiSn, $\rho(T/T_0)$ assumes a maximum at $T/T_0 = 1$ and decreases steeply towards lower temperatures (Fig. 1). Thus, the decrease of ρ, rather than the thermally activated increase observed in cubic Kondo insulators, seems to be the $\rho(T)$ characteristic of the gap (or pseudogap) opening in strongly correlated semimetals. The absolute value of R_H of both U_2Ru_2Sn and CeNiSn increases

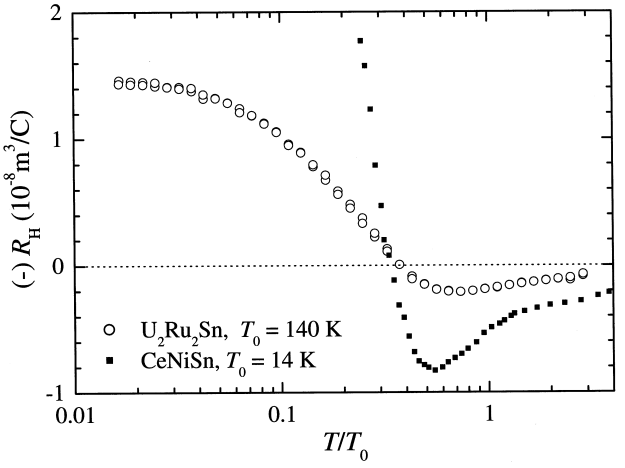

Fig. 2. Hall coefficient, R_H, of U_2Ru_2Sn and negative Hall coefficient, $-R_H$, of CeNiSn [2] as a function of the reduced temperature T/T_0.

below $T/T_0 = 1$ (Fig. 2). This corresponds, in a one-band model, to a decrease of the charge-carrier concentration, which appears to be the $R_H(T)$ characteristic of the gap opening. The fact that, upon further lowering the temperature, $R_H(T/T_0)$ assumes an extremum and then changes its sign must be due to a small concentration of residual charge carriers having the opposite sign to the one of the majority carriers at high temperatures, which are electrons for U_2Ru_2Sn and holes for CeNiSn. $1/T_1(T/T_0)$ of both U_2Ru_2Sn and CeNiSn may, at $T/T_0 > 0.3$, be well approximated by $A\exp(-T_0/T)$, where A is a constant (Fig. 3). This relation is well known for spin-Peierls systems like $CuGeO_3$ or conventional superconductors like Al. A deviation from this simple law at low temperatures is observed, e.g., for unconventional superconductors like the cuprates and heavy-fermion superconductors, as well as for Kondo insulators like CeNiSn. In the latter case, this is ascribed to a so-called V-shaped gap and to the presence of residual charge carriers within the gap [3].

For the other properties investigated here the similarities with CeNiSn are less obvious. While, similar to several cubic Kondo insulators, the magnetic susceptibility of U_2Ru_2Sn assumes a maximum somewhat above T_0 and decreases strongly below this temperature, the situation is more complex for CeNiSn [2]. In the absence of a good 'phonon-reference' sample (e.g. Th_2Ru_2Sn), the gap related contribution to the specific heat of U_2Ru_2Sn cannot be determined unambigously. Therefore, a comparison with CeNiSn cannot be made at this point. What is, however, obvious from the specific-heat data is that no cooperative (antiferromagnetic) phase transition takes place. Thus, the earlier described reduction of the magnetic susceptibility might have the same origin as in other Kondo insulators, namely the opening of a narrow spin gap. The thermopower of CeNiSn [4] being extremely anisotropic makes a comparison with the data on polycrystalline U_2Ru_2Sn difficult. Nevertheless, the maximum of almost 30 μV/K observed for U_2Ru_2Sn slightly below T_0 is a feature typical for Kondo insulators. Finally, the thermal conductivity of U_2Ru_2Sn displays an anomalous enhancement somewhat below T_0, similar to the case of CeNiSn [4]. The dimensionless thermoelectric figure of merit, ZT, of U_2Ru_2Sn reaches a maximum value of 0.004 at 140 K, while the one of a single crystal of CeNiSn measured along the a-axis [4] reaches 0.006 at 4 K.

In conclusion, the close analogy in several physical properties between the recently discovered compound U_2Ru_2Sn and the well-known compound CeNiSn suggests that also U_2Ru_2Sn may be classified as a strongly correlated semimetal. Obviously, more detailed studies will be needed to verify that these analogies have indeed the same physical origin. All Kondo insulators known to date have cubic symmetry, except for the orthorhombic systems CeNiSn, CeRhSb, and CeRhAs [12]. It is straightforward to suspect that the new potential member U_2Ru_2Sn sharing more properties with CeNiSn than with the cubic systems might be due to its tetragonal structure.

3. $Eu_8Ga_{16}Ge_{30}$

We studied both, the well-known $Eu_8Ga_{16}Ge_{30}$ (β-) modification with clathrate-I structure, and the new $Eu_8Ga_{16}Ge_{30}$ (α-)modification with clathrate-VIII structure (Fig. 4), by measuring the magnetization, specific heat, electrical resistivity, Hall coefficient, thermopower, and thermal conductivity [9].

Upon cooling in zero magnetic field, a spontaneous magnetization builds up at 10.5 and 36 K for the α- and β-phase sample, respectively. This behavior is typical for ferromagnetic phase transitions with Curie temperatures of 10.5 and 36 K. The specific-heat data display pronounced λ-type anomalies in the temperature ranges of the ferromagnetic phase transitions. The entropies below these anomalies

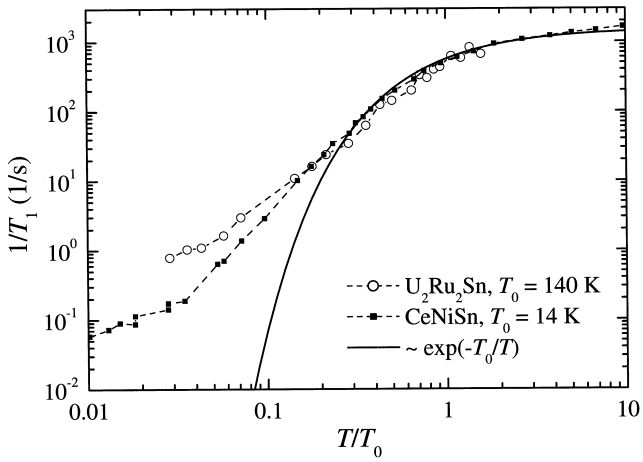

Fig. 3. Spin lattice relaxation rate, $1/T_1$, of the ^{119}Sn nuclei of U_2Ru_2Sn and of CeNiSn [3] as a function of the reduced temperature T/T_0. The solid line is a best fit to the CeNiSn data at $T/T_0 > 0.3$.

confirm the bulk nature of the transitions. Well above the phase transitions, the magnetic susceptibilities have Curie–Weiss-type temperature dependences with effective magnetic moments close to the moment expected for a free Eu^{2+} ion. Also the magnetization vs field curves at 2 K saturate at 5 T to the value expected for a free Eu^{2+} ion.

The temperature dependence of the electrical resistivity, $\rho(T)$, of both $Eu_8Ga_{16}Ge_{30}$ modifications is metallic in nature

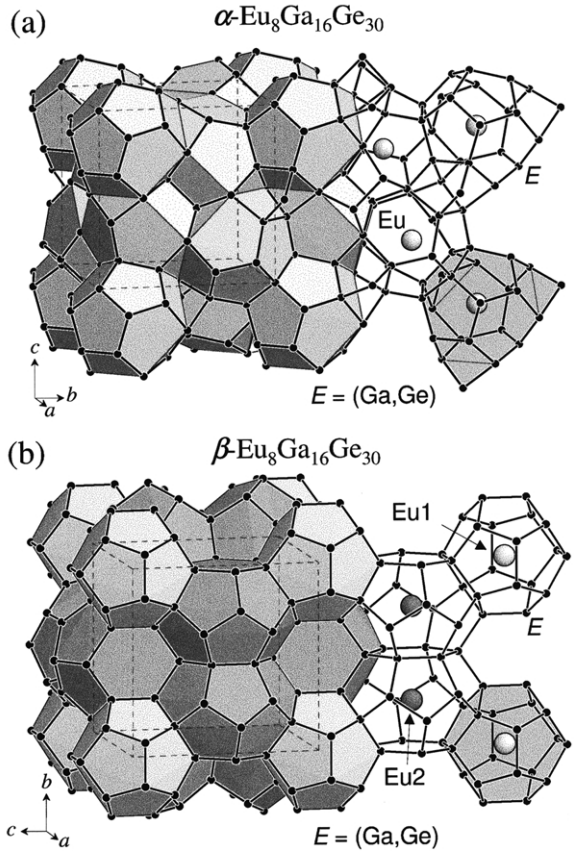

Fig. 4. Crystal structures of α- and β-$Eu_8Ga_{16}Ge_{30}$ in (a) and (b), respectively.

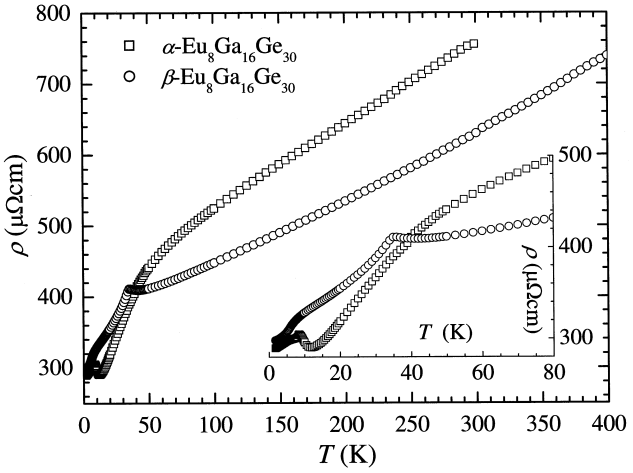

Fig. 5. Temperature dependences of the electrical resistivity, $\rho(T)$, of α- and β-$Eu_8Ga_{16}Ge_{30}$. The inset shows a blow-up of the low-temperature data.

(Fig. 5). Only in the vicinity of the phase transitions $d\rho/dT$ is negative which may be due to scattering from critical fluctuations. The Hall coefficient of both $Eu_8Ga_{16}Ge_{30}$ modifications is only weakly temperature dependent. At 2 K it corresponds to an electron concentration of 3.8×10^{20} cm^{-3} (12.5×10^{20} cm^{-3}) or to 0.46 (1.5) electrons per $Eu_8Ga_{16}Ge_{30}$ formula unit for the α-phase sample (β-phase sample). These small carrier concentrations are in agreement with the occurrence of ferromagnetism in the RKKY formalism [9].

The thermopower of both $Eu_8Ga_{16}Ge_{30}$ modifications, shown in Fig. 6, is relatively large and negative in agreement with the small concentration of electron-like charge carriers. The straight lines shown in Fig. 6 are estimates of the diffusion thermopower in a free-electron model, using the charge-carrier concentrations determined in the Hall-effect measurements at 2 and 300 K. Apparently, it is an important contribution to the total thermopower. The temperature dependence of the lattice thermal conductivity, $\kappa_L(T)$, obtained by subtracting the electronic contribution, $\kappa_e(T)$, from the raw data, is shown for both $Eu_8Ga_{16}Ge_{30}$ modifications in Fig. 7. $\kappa_e(T)$ estimated from the electrical resistivity using the Wiedemann–Franz law is, below 100 K, less than 20% of the total thermal conductivity for α-$Eu_8Ga_{16}Ge_{30}$ and less than 60% for β-$Eu_8Ga_{16}Ge_{30}$. As expected for filled-cage compounds, [13], $\kappa_L(T)$ is typical of highly disordered solids. In fact, $\kappa_L(T)$ of both $Eu_8Ga_{16}Ge_{30}$ modifications may be well described by a model [14] in which, in addition to mass–density scattering, two scattering mechanisms related to the filled-cage structure are taken into account: Resonant scattering which is related to the rattling of the guest atoms in the oversized cages and scattering from tunneling states which may be associated with cage atoms tunneling between different

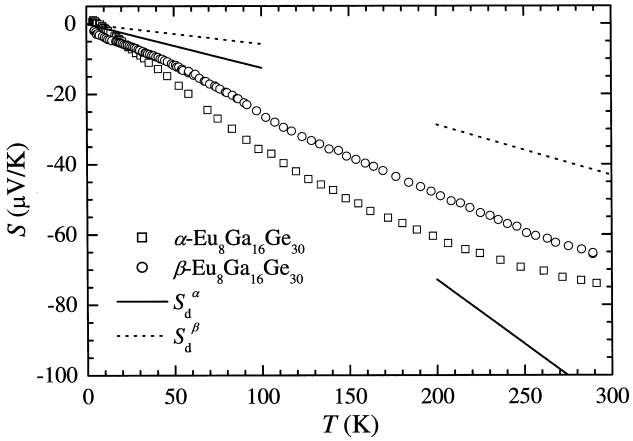

Fig. 6. Temperature dependences of the thermopower, $S(T)$, of α- and β-$Eu_8Ga_{16}Ge_{30}$. The low- and high-temperature limits of the free-electron diffusion thermopower, S_d, are plotted as straight lines (cf. text).

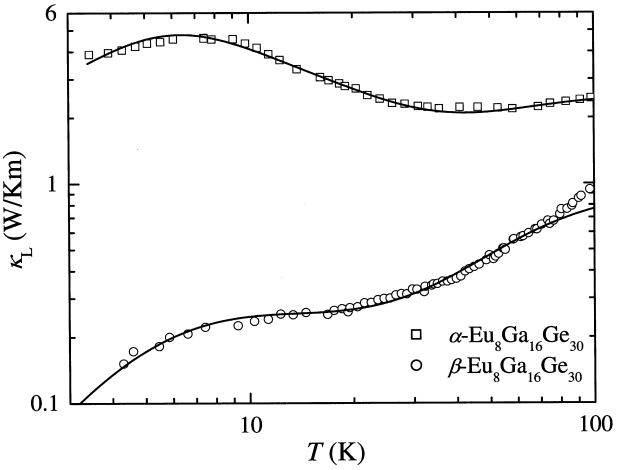

Fig. 7. Temperature dependences of the lattice thermal conductivity, $\kappa_L(T)$, of α- and β-$Eu_8Ga_{16}Ge_{30}$. The lines are fits of a model [14] for filled-cage systems to the data.

split sites [9]. The dimensionless thermoelectric figure of merit increases monotonously with temperature. At room temperature, ZT is estimated to be approximately 0.1, which is one order of magnitude smaller than for commercially used materials on the basis of Bi_2Te_3 [15].

Summing up, both $Eu_8Ga_{16}Ge_{30}$ modifications may be classified as local-moment ferromagnets, with Eu being in its Eu^{2+} state in the entire temperature range. This stable valence of Eu inhibits the formation of a Kondo insulating ground state. However, the Curie temperatures being relatively small may indicate that the RKKY ferromagnetism is not very robust and might lose against the Kondo screening if the hybridization of Eu with the host could be increased. The thermal conductivity of both $Eu_8Ga_{16}Ge_{30}$ modifications is indeed low and glass-like as expected for filled-cage compounds. Thus, a high thermoelectric figure of merit should result corresponding to the opening of a narrow (pseudo)gap, if $Eu_8Ga_{16}Ge_{30}$ could be turned into a Kondo insulator.

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