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Transport and magnetic properties of new ternary $Ce_2T_3X_9$-compounds (T=Rh, Ir, X=Al, Ga)

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Abstract

Measurements of thermoelectric power, electrical resistivity, and magnetic susceptibility on new $Ce_2T_3X_9$-compounds (T=Rh, Ir; X=Al, Ga) are presented. These compounds crystallize in the orthorhombic $Y_2Co_3Ga_9$-structure. The transport data show for each compound two characteristic anomalies, around 100 K and around 20 K, respectively. In contrast to many Ce-systems, where such anomalies can be ascribed to crystalline-field and Kondo effects, respectively, for these systems the temperature dependence of the susceptibility and the specific heat suggest an intermediate valent Ce-state which shows additional low energy interactions. © 1998 Elsevier Science S.A.

Keywords: Heavy-fermion systems; Mixed-valency; Thermopower; Susceptibility

1. Introduction

Recently, a new class of compounds with the stoichiometry $R_2T_3X_9$ (R=Ce, U, T=Rh, Ir, X=Al, Ga) has been reported to crystallize in a rather complicated orthorhombic (Cmcm) $Y_2Co_3Ga_9$-structure [1], with only one R-site. Whilst the U-based compounds order magnetically at temperatures below 30 K, the Ce-counterparts are all non-magnetic, at least down to 2 K. However, the first investigations give evidence that the latter compounds have properties both of typical intermediate-valent compounds such as $CeSn_3$, but also of heavy-fermion compounds such as $CeRu_2Si_2$.

We have now investigated the low temperature transport and magnetic properties in more detail. The results will be discussed in comparison with other Ce-based heavy-fermion and mixed-valent systems.

2. Experimental

All samples investigated were polycrystals obtained by repeated argon arc-melting of the constituting elements. Except for $Ce_2Ir_3Al_9$, which exists as a high-temperature phase only, all samples were annealed at 1000°C in high vacuum for 120 h. By means of X-ray powder diffraction, all samples were confirmed to properly crystallize in the $Y_2Co_3Ga_9$-structure. Within the resolution of our diffractometer, no traces of impurity phases could be detected. Therefore, the maximum impurity content is below 2%. However, in the case of $Ce_2Ir_3Al_9$, a small amount of impurities might well be present since this compound exists at high-temperatures only and is found to decompose to binary and ternary compounds (e.g. CeIrAl, Ce_3Al_{11}, and $CeAl_2$) during annealing. Details on the preparation and lattice parameters can be found in [1].

Thermoelectric power (TEP) was measured on bars of approx. 10×1.5×1.5 mm size for all samples using a steady-state method with one end of the samples thermally anchored to the cold plate of a commercial ^{4}He-cryostat. Small temperature gradients (typically 50 mK) were provided by a heater fixed to the other end of the samples and were measured using AuFe vs. Chromel thermocouples. The DC-resistivities ρ were measured in the same run. Magnetic susceptibilities were measured in the temperature range 2 K–350 K using a MPMS SQUID magnetometer. In addition, magnetization of $Ce_2Ir_3Ga_9$ at low temperatures was determined in magnetic fields $B<5.5$ T.

3. Transport properties

The TEP of all compounds (Fig. 1) reaches very high

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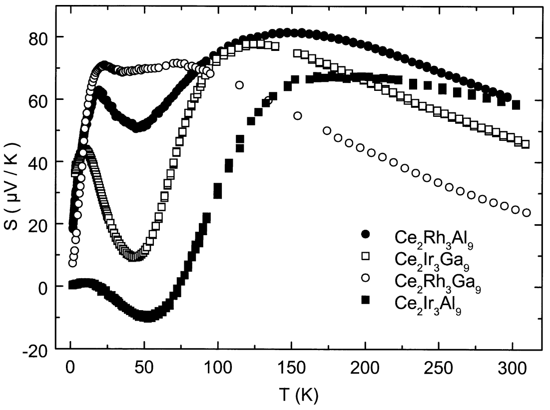

Fig. 1. TEP data in the temperature range 1.5 K$<T<$310 K.

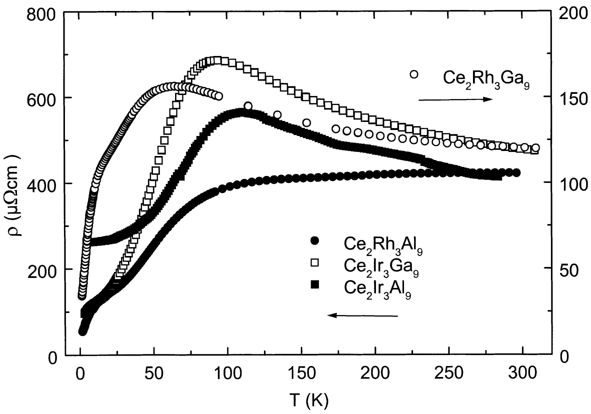

Fig. 2. Resistivity data in the temperature range 1.5 K$<T<$310 K. Note the different scaling for $Ce_2Rh_3Ga_9$ (right scale).

values of the order of 80 μV K^{-1} as common to Ce-based compounds with Ce-valency slightly deviating from 3^+. The temperature dependence is rather similar for all compounds with a broad maximum around 150 K, a minimum below around 50 K, and a sharp peak below 20 K. In the case of $Ce_2Ir_3Al_9$, the low-T peak is strongly reduced, probably due to lower sample quality. The positions of the maxima are summarized in Table 1. A systematic trend in the TEP is clearly visible: Whilst the minimum is only weakly pronounced for $Ce_2Rh_3Ga_9$, it gets much deeper for $Ce_2Rh_3Al_9$ and $Ce_2Ir_3Ga_9$. Finally, the TEP of $Ce_2Ir_3Al_9$ has a negative minimum. In addition, the temperatures of the low-T maxima are also shifted towards lower temperatures in the same sequence, whilst the high-T maxima get shifted towards higher temperatures.

At low temperatures, the TEP rises linearly in T for all compounds (with the exception of $Ce_2Ir_3Al_9$) with a giant slope in the order of 10 μV K^{-2}. Since in the Fermi liquid scenario the linear contributions to both the TEP and the specific heat scale with the effective thermal carrier masses [2], such giant slopes in the TEP are commonly observed in heavy-fermion systems such as $CeCu_6$ [3] with Sommerfeld coefficients of the specific heat around 1 J mol K^{-2}. The observed Sommerfeld coefficient of the specific heat of 0.2 J mol_{Ce}^{-1} K^{-2} found for $Ce_2Rh_3Al_9$ [1] in 8 T-field is unexpectedly small in this respect. Furthermore, in smaller external fields the specific heat C/T diverges as common to Non-Fermi-Liquid systems close to magnetic instability, reaching 0.4 J mol_{Ce}^{-1} K^{-2} at 0.5 K [4]. Specific heat measurements are also underway on the other Ce-compounds, but from the similarity of the TEP-data one might expect all compounds to be heavy-fermion systems close to magnetic ordering.

The resistivity curves (Fig. 2) also show two distinct features pointing to two characteristic temperatures for each compound: a maximum in the T-range 100–200 K and a clear hump in the T-range 15–25 K. The large discrepancy between the absolute resistivity values of $Ce_2Rh_3Ga_9$ and that of the other compounds most presumably results from errors in determining the geometry factor of the brittle samples, but might also indicate strong anisotropy even in polycrystalline materials. The characteristic temperatures are also summarized in Table 1. The temperature of the high-T maximum follows the same tendency as that of the high-T peak in the TEP, i.e. the temperature is the lowest in $Ce_2Ir_3Al_9$ and the highest in $Ce_2Rh_3Ga_9$.

Taking only the transport data together, one could attribute a Kondo-temperature T_K of approx. 20 K to all compounds. Crystalline-field effects would then be most likely to cause the high-T anomalies around 150 K.

4. Magnetic properties

The temperature dependence of the susceptibility (Fig. 3) is again rather similar for all compounds. All compounds show a rather small absolute value of the suscep-

Table 1
Characteristic temperatures from TEP and resistivity data

Compound	$Ce_2Ir_3Al_9$	$Ce_2Ir_3Ga_9$	$Ce_2Rh_3Al_9$	$Ce_2Rh_3Ga_9$
High-T maximum in TEP (K)	185	125	150	75
High-T maximum in ρ (K)	110	95	90	62
Low-T peak in TEP (K)	10.5	9.5	18.7	22.5
Low-T anomaly in ρ (K)	25	13.3	23	14.3

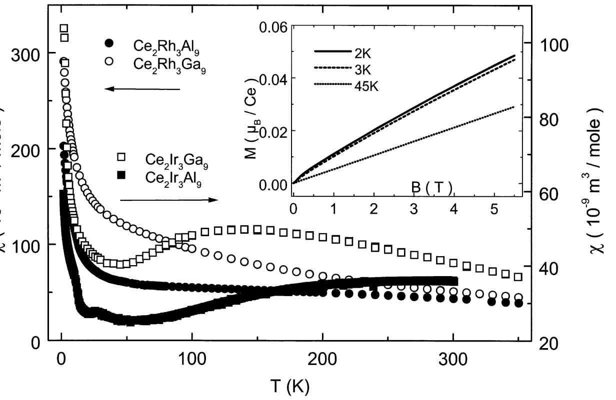

Fig. 3. Magnetic susceptibility in 0.1 T field and at temperatures 2 K$<T<$350 K. Note the different scaling for the Rh-based compounds (left scale) and the Ir-based compounds (right scale). The small anomaly in the susceptibility of $Ce_2Ir_3Al_9$ around 25 K is most probably due impurity contributions. Inset shows magnetization of $Ce_2Ir_3Ga_9$ at $T=2$, 3, and 45 K in field up to 5.5 T.

tibility at room temperature and a broad maximum around 150–200 K as common to mixed-valent compounds such as $CeSn_3$ [5], which is clearly pronounced for the Ir-based compounds. For the Rh-based compounds, the low-temperature tails have to be subtracted from the data to reveal the maxima. At low temperatures, pronounced tails are obvious for all compounds. These tails can be modeled with a Curie-like temperature dependence incorporating an effective moment of 0.6–1.0 μ_B per Ce-ion, which is far to large to be due to impurities alone. As one example, magnetization curves at different temperatures of $Ce_2Ir_3Ga_9$ are shown in the inset of Fig. 3. At 2 K and 3 K the magnetization is almost linear in B except for a very small curvature which might be due to the saturation of a tiny fraction (1%) of free Ce^{3+}-ions. Thus, the low-temperature tail is intrinsic to these compounds.

The susceptibility maxima around 150 K cannot be explained by crystalline-field effects. In an orthorhombic crystal field symmetry with large anisotropy, a susceptibility maximum can be obtained in the magnetic hard direction, whilst the susceptibility along the easy and intermediate axes will monotonously rise upon lowering the temperature. Since the susceptibilities along these axes are much larger than that along the hard axis, the weighted sum over all directions in a polycrystalline sample can never show a maximum. To clarify this statement, it is useful to compare the observed susceptibilities with those of orthorhombic (Imma) $CeCu_2$ [6]: In this system, the susceptibility has a clear maximum around 150 K along the magnetically hard b-axis followed by a minimum around 60 K, but monotonously diverges along the a- and c- axes. However, the hard axis susceptibility is much smaller than that along the other axes, resulting in a polycrystalline susceptibility that monotonously increases with decreasing temperature [7]. Thus, the temperature dependence of the susceptibility and the rather low values of χ in the T range 30–100 K can only be accounted for by an intermediate valent Ce state, with a higher characteristic energy in the Ir-based compounds than in the Rh-based counterparts.

5. Discussion

The newly discovered compounds of $Ce_2T_3X_9$-stoichiometry show a rather ambiguous behavior: Regarding the transport properties with the two clear anomalies around 20 and around 150 K alone, they must be classified as systems close to magnetic ordering, and with characteristic energies in the order of 20 K. In contrast to this, the temperature dependence of the susceptibility can only be understood with a much higher characteristic energy: The high-T maxima in the susceptibility cannot be explained by crystalline-field effects and must therefore be attributed to an intermediate valent behavior of the Ce-ions. Thus, an energy of approx. 150 Kelvin is the hybridization energy in these systems. This is also in agreement with the γ-value of 0.2 J mol_{Ce}^{-1} K^{-2} observed in $Ce_2Rh_3Al_9$ in applied field of 8 T, since such a value corresponds to a T_K between 40 K and 200 K, depending on the lifting of degeneracy of the involved J-multiplet of the Ce-ion [8]. However, the well-pronounced low-T anomalies in the transport properties and the large paramagnetic moments close to 1 μ_B per Ce clearly show the existence of a second energy scale. Therefore, two different energy scales which differ by one order of magnitude must be attributed to the Cerium-ions. Since the crystal structure has only one equivalent Ce-site, both localized and itinerant f-electrons can be found on the same Ce-ion. This scenario resembles the two-band model proposed to explain the superconducting and magnetic properties of the heavy-fermion superconductor UPd_2Al_3 [9].

6. Summary

The temperature dependence of the thermoelectric power, the electrical resistivity, and the magnetic susceptibility of the new compounds $Ce_2Rh_3Al_9$, $Ce_2Ir_3Al_9$, $Ce_2Rh_3Ga_9$, and $Ce_2Ir_3Ga_9$ has been measured in the temperature range 1.5 K–300 K. All compounds were found to show two pronounced anomalies in the transport data as common to heavy-fermion systems close to magnetic ordering. Commonly, such transport data are observed for heavy-fermion systems with Kondo-temperatures around 20 K and crystal field excitations around 150 K. However, the magnetic susceptibilities cannot be explained in terms of crystalline field effects, but instead show maxima as common to intermediate valent compounds around 150 K, and also low-T tails with large paramagnetic moments. A satisfactory explanation is still missing, but a description will have to invoke two different energy scales attributed to the same 4f-electrons.

Acknowledgements

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