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Electrical and magnetic properties of semiconducting ternary U compounds: UTSn and UTSb

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We have measured the electrical-transport and magnetic properties of several intermetallic compounds UTSn and UTSb, where T is a transition metal. The electrical resistivity is up to three orders of magnitude larger than usually found for U-based compounds. This is ascribed to the occurrence of a spin polarized energy gap related to the MgAgAs-type crystal structure. For UNiSn at least one spin band closes at low temperature, resulting in half-metallic behavior. Interestingly, the magnetic properties exhibit Kondo-lattice character and weak-moment ordering.

I. INTRODUCTION

Since the discovery of the half-metallic ferromagnets¹ there is a growing interest in the Heusler compounds of the MgAgAs-type structure. This activity stems from the remarkable fact that 100% spin polarization occurs at the Fermi surface, resulting from a semiconducting energy gap in the minority-spin band at the Fermi level, whereas the majority-spin band exhibits normal metallic behavior. This phenomenon was studied first for 3d-band compounds, like NiMnSb. Because of our general interest in the magnetic and electrical transport properties of U-based compounds, we have investigated whether such behavior could also be established for 5f-band compounds.

For that purpose we have prepared the systems UTSn and UTSb, with T being a transition metal. Most compounds crystallize in the hexagonal Fe₂P- or CaIn₂-type structure, which are characterized by normal metallic conduction and local moment behavior, as has been discussed extensively elsewhere.² Still, a few compounds adopt the desired MgAgAs-type (C1_b) crystal structure, like UNiSn, URhSb, and UPtSn. Interestingly, these compounds exhibit semiconducting-like behavior in the transport properties, and a magnetic behavior reminiscent of Kondo-lattice systems. Since this combination is highly anomalous we have extended our studies of the magnetic and transport properties by measuring and comparing the electrical resistivity, Hall resistivity, magnetization and specific heat of these compounds, and their nonmagnetic (Th, Hf, Zr, Ti) T (Sn, Sb) reference materials.

II. EXPERIMENTAL PROCEDURES AND RESULTS

For sample preparation and experimental procedures we refer to Ref. 2. In Fig. 1 we show the electrical resistivity of the three U-based compounds UNiSn, URhSb, and UPtSn. These compounds exhibit a low-temperature resistivity increase, beyond which an exponential decrease is observed. Fitting the data in the temperature interval

$500 < T < 1000$ °C (not shown) to the formula appropriate for semiconductors $\rho \sim \exp(E_{\text{gap}}/2k_B T)$, we obtain a value of $E_{\text{gap}} = 0.12, 0.44$, and 0.34 eV for UNiSn, URhSb, and UPtSn, respectively. Note that the absolute value of the resistivity is up to three orders of magnitude larger than usually found for intermetallic compounds. In addition the resistivity of the nonmagnetic materials is very high. The highest value was observed for TiPtSn, which has a residual resistivity of $6.3 \times 10^{-5} \mu\Omega \text{ cm}$.

Figure 2 shows the temperature dependence of the magnetization of the U-based compounds. At high-temperature Curie-Weiss behavior is observed with effective moments of 3.08, 3.25, and $3.55 \mu_B/\text{f.u.}$ and large negative Curie-Weiss temperatures of -75 , -111 , and -100 K for UNiSn, URhSb, and UPtSn, respectively. In spite of these effective moments with large antiferromagnetic interactions, no clear antiferromagnetic ordering is observed at low temperature. UNiSn has a change of slope in the M - T curve at 47 K, URhSb exhibits a broad maximum with an inflection point at 37 K and UPtSn only shows a leveling off of the Curie-Weiss increase of the magnetic susceptibility below about 75 K. The two small steplike anomalies in the M - T curve of UPtSn at about 5 and 25 K can probably be ascribed to the presence of 0.3% of the binary compound UPt, which is

FIG. 1. Temperature dependence of the electrical resistivity of (U, Th) NiSn, (U, Th) PtSn and (U, Hf, Zr) RhSb.

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FIG. 2. Temperature dependence of the dc susceptibility of UNiSn, URhSb, and UPtSn.

ferromagnetic ($T_c = 27$ K).

In Fig. 3 we show the specific heat of several compounds plotted as C/T vs T^2 . For the U-based compounds a λ -like anomaly is clearly observable at 48 K for UNiSn and at 35 K for URhSb and UPtSn. The nonmagnetic materials exhibit low values for the specific-heat coefficient $\gamma < 2$ mJ/mol f.u. K², and Debye temperatures (calculated for $T < 10$ K) ranging from 185 to 310 K.

We plotted in Fig. 4 the Hall resistivity R_H of UNiSn, URhSb, and UPtSn. For UNiSn the λ -like anomaly in the specific heat and resistivity peak at 48 K is reflected in a sharp wedge-shaped maximum of R_H at 40 K. However, for URhSb and UPtSn not such pronounced anomalies are present at the temperature at which the specific-heat anomaly is observed. Nevertheless, the specific-heat anomalies are still reflected in the field-dependence of the transport properties for these compounds. In the inset of Fig. 4 we plotted the (transverse) magnetoresistivity coefficient, $a(T)$, defined as

$$[\rho(H) - \rho(0)]/\rho(0) = a(T)H^2.$$

Here an abrupt increase of the coefficient $a(T)$ occurs below 60 K for UNiSn and below 30 K for URhSb.

III. DISCUSSION

A salient feature of our experimental results is the extremely high electrical resistivity of these compounds, being up to 3 orders of magnitude larger than usually found for intermetallic compounds. The exponential decrease of the resistivity at high temperature indicates that these com-

FIG. 3. Temperature dependence of the specific heat of (U, Th) NiSn, (U, Th) PtSn, and URhSb plotted as C/T vs T^2 .

FIG. 4. Temperature dependence of the Hall resistivity of UNiSn, URhSb, and UPtSn. The inset shows the temperature dependence of the magnetoresistivity coefficient a (see text).

pounds are semiconductors. This is confirmed by the relatively large values of the Hall resistivity, which is inversely proportional to the carrier concentration. The semiconducting properties cannot be ascribed to ionic or covalent bonds, but rather to the fact that the valence band is completely filled. This property seems to be closely related to the band structure of the MgAgAs-type crystal structure,³ since high resistivity values were also observed for binary Mg₂(Si,Ge,Sn,Pb) (Ref. 4) and ternary AsAgMg and SbAgMg,⁵ all crystallizing in the MgAgAs-type crystal structure or the related CaF₂-structure.

Still, the exponential decrease of the resistivity with increasing temperature is only observed at high temperature, whereas the resistivity remains rather constant below room temperature. This must probably be ascribed to impurity band conduction. However, for the U-based compounds the resistivity even decreases with decreasing temperature at lower temperature. For UNiSn a dramatic decrease of the resistivity is observed below 55 K and a residual resistivity of 413 $\mu\Omega$ cm is attained, comparable to typical values for other intermetallic compounds. We believe that this decrease in the resistivity of the U-based compounds is caused by a decrease in the size of the energy gap, probably induced by magnetic interactions and ordering. For UNiSn the energy gap in (at least) one of the spin bands disappears below 55 K, resulting in metallic conduction.

This interpretation is in keeping with recent band structure calculations,⁶ which show (at $T = 0$) that UNiSn belongs to the class of half metallic ferromagnets, i.e., the majority spin band exhibits metallic conduction, whereas the minority spin band has an energy gap at the Fermi level. It should be mentioned that these band structure calculations give no information about the type of magnetic interactions (ferro- or antiferromagnetic), although it was clearly established that the magnetic properties are related to the U bands, as the Ni d bands are almost completely filled. This means that with UNiSn we have found an analogue for NiMnSb, where the conduction band is 100% spin polarized. Furthermore, this interpretation requires that the conduction band is strongly hybridized with the 5f band. This has also been suggested from recent XPS measurements,⁷ which show that the 5f band is very near the Fermi level. For URhSb and UPtSn a much larger energy gap is present at high temperature and consequently the band gap fails to completely close at lower temperature. Nevertheless for UPtSn some closure of the band begins below 100 K and results in a resistivity decrease of a factor two.

A second remarkable property of these compounds is the magnetic behavior. Magnetization measurements at high temperature reveal effective moments of $3.0\text{--}3.5\mu_B/\text{f.u.}$, which agree with typical values of local U moments. Local-moment magnetism is in keeping with the Hill criterion, which predicts local moment magnetism for U-U spacings larger than $3.6\text{ \AA}$ as is the case for these compounds.² Also the band structure calculations⁶ show that the magnetism in these compounds originates from the U 5f electrons. Yet, in spite of the high-temperature moments and large antiferromagnetic interactions, no standard local moment magnetic ordering is observed. Instead, weak anomalies are observed in the magnetization measurements (Fig. 2), with corresponding anomalies in the specific heat (Fig. 3), indicating some sort of phase transition and/or crystal field effects.

The overall behavior of the magnetization is reminiscent of spin-fluctuation behavior, as observed for heavy-electron systems.⁸ Here also large effective moments with large negative Curie-Weiss temperatures were observed at high temperature, turning to weakly magnetic systems at low temperature. This correspondence is most remarkable because of the greatly reduced number of conduction electrons in the cases of URhSb and UPtSn. Still, the linear specific heat coefficient, γ , has a value comparable to values of metallic systems, e.g., $\gamma = 10.9\text{ mJ/mol K}^2$, whereas the residual resistivity, $\rho_0 = 19\,000\text{ }\mu\Omega\text{ cm}$, is orders of magnitude higher than in metallic systems. Speculatively, we suggest that this γ -value results from a hybridization of the impurity band with the nearby lying 5f band. This could result in an enhancement of the γ value with respect to the low-temperature density of states value expected from the residual resistivity. Accordingly, ThPtSn has a six times smaller γ value, in spite of a seven times higher conductivity.

IV. CONCLUSION

The electrical transport properties of the compounds UTSn, UTSb, and their nonmagnetic reference materials are governed by an energy gap at the Fermi level, resulting in semiconducting behavior. At lower temperature the gap is strongly influenced by the magnetic behavior and for UNiSn one spin band gap closes below 55 K. Hence, this compound belongs to the class of half-metallic magnets, due to the presence of the 5f electrons of U. The magnetic ground state is highly complex and a complete understanding requires further study, including the optical behavior. If the spin-orbit coupling is important, then a large magneto-optical (Kerr) effect should be observed.

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