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# HEAVY ELECTRON BEHAVIOR IN A NEW URANIUM-BASED TERNARY COMPOUND: $UPd_2Sn$

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Electrical resistivity, magnetic susceptibility and specific heat measurements on a new compound, $UPd_2Sn$, reveal that this material exhibits valence fluctuation or Kondo lattice phenomena below a characteristic temperature ~10 K. In particular, the electronic specific heat coefficient appears to be strongly temperature dependent with a maximum of ~ 270 mJ/mole U-$K^2$ at 9.7 K and an extrapolated value of ~70 mJ/mole U-$K^2$ at 0 K. The compound $UPd_2Sn$ was expected to crystallize in the same structure as the family of cubic Heusler alloys, but instead, crystallized in a more complicated structure which appears to be orthorhombic. The compound can be characterized as a nonmagnetic, nonsuperconducting heavy electron material.

## Introduction

The recent observation of superconductivity in Heusler alloys (cubic $L2_1$ structure) such as $YPd_2M$ (M = Sn, Pb, In, Sb)[1], $YAu_2Sn$[2] and $RPd_2Sn$ (R = Sc, Y, Tm, Yb, Lu)[3] has stimulated new interest in these materials. Moreover, $YbPd_2Sn$[1,3] has also been found to exhibit the coexistence of superconductivity and antiferromagnetism, a behavior that, to our knowledge, has only been observed for compounds belonging to the ternary rare earth (R) molybdenum chalcogenides $RMo_6S_8$ and $RMo_6Se_8$, the rare earth rhodium borides $RRh_4B_4$, and the rare earth transition metal (T) stannides $RT_xSn_y$.[4] In a search for new U-based compounds with possible heavy electron properties, we have studied the particular family of compounds $UT_2M$ with T = Pd, Au and M = In, Si, Ge, Sn, Sb. In this paper, we report measurements of the electrical resistivity $\rho$, the dc magnetic susceptibility $\chi_{dc}$ and the specific heat C on $UPd_2Sn$, the most interesting sample we have found within this group of materials. Although data on the other $UT_2M$ compounds will be presented elsewhere, it is worth mentioning that none of the $UT_2M$ materials that were studied exhibits superconductivity down to 80 mK.

## Experimental Details

The polycrystalline $UPd_2Sn$ samples were prepared by arc-melting stoichiometric amounts of the constituents, U (3N), Pd (3N7) and Sn (5N), together on a copper hearth in an atmosphere of ultra-high purity argon gas. The resultant ingots were then wrapped in tantalum foil, sealed in vacuum, and annealed at 800°C for 4 days. The quality of the samples was assessed by means of powder X-ray diffraction and metallographic analyses. Low frequency four lead ac electrical resistivity measurements were carried out between 1.2 K and 300 K using an ac impedance bridge operating at a frequency of 16 Hz. The dc magnetic susceptibility was measured with an SHE SQUID magnetometer between 2 K and 300 K in a magnetic field of 1 tesla. The specific heat was determined between 0.5 K and 22 K with a semi-adiabatic $He^3$ calorimeter using a standard heat pulse method.

## Results and Discussion

### Crystal Structure

Among the $UT_2M$ compounds that we investigated, only the ones with M = In form with a cubic Heusler structure. The X-ray diffraction patterns of the other $UT_2M$ compounds (i.e., M ≠ In) reveal a more complicated structure. We believe that $UPd_2Sn$ crystallizes in the $Fe_3C$ orthorhombic structure (space group Pnma, Z = 4) as reported previously for $YPd_2Si$[5] and $YPd_2Ge$.[6] Although we were unable to index properly the large number of lines present in the X-ray diffraction pattern and to determine precise values for the lattice parameters, metallographic analysis showed that the

material contains less than ~ 5 vol. % of impurity phase. The stability of the cubic phase in the Heusler alloys $RT_2M$ (here, R is a rare earth element or one of the actinide elements U or Th) appears to depend strongly on the atomic sizes of the R and M elements. In fact, structural transformations have been reported in the rare earth compounds $RPd_2Sn$,[7] as well as in the related materials $XTh_2Sn$ where X = V, Cr, Fe, Co.[8]

## Electrical Resistivity

The electrical resistivity of $UPd_2Sn$, which is displayed in Fig. 1, shows very little temperature dependence down to ~140 K and then decreases rapidly below ~100 K. At low temperatures, in the range 1.2 K - 10 K, $\rho(T)$ approximately follows a $T^2$ law which is characteristic of spin fluctuations or a Fermi liquid [specifically, $\rho = \rho_o + AT^n$ with $\rho_o = 14\ \mu\Omega$-cm, $A = 0.2\ \mu\Omega$-cm$(K)^{-2.3}$, and $n = 2.3$]. The general behavior of $\rho(T)$ for $UPd_2Sn$ is very similar to that of $UPt_3$[9] and many other actinide compounds.[10] The electrical resistivity of $UPd_2Sn$ at room temperature is ~190 $\mu\Omega$-cm, and the residual resistivity ratio $\rho$(295 K)/$\rho$(1.2 K) is ~13.

In order to estimate the contribution $\delta\rho(T)$ to $\rho(T)$ due to the U 5f electrons, the electrical resistivity of the isostructural compound $ThPd_2Sn$ was also measured; $\delta\rho(T)$ was defined by subtracting $\rho(T)$ for the Th-based compound from $\rho(T)$ for the U-based compound. The contribution $\delta\rho(T)$ increases by ~30% from room temperature down to 96 K, where it attains a maximum and then decreases rapidly at lower temperatures. The high temperature part of the curve is reminiscent of the single ion Kondo effect. The abrupt drop in $\rho(T)$ at 1.42 K of the isostructural $ThPd_2Sn$ compound reveals that it becomes superconducting, a result that was also confirmed by specific heat measurements (see below). A systematic trend of the $\rho(T)$ curves has been observed for the non-cubic $UPd_2M$ and $UAu_2M$ compounds (M = Si, Ge, Sn); the Pd-based samples display a resistivity behavior similar to that described here for $UPd_2Sn$, whereas the resistivity of the Au-based materials increases by less than ~15% from room temperature down to approximately 20-40 K where it attains a maximum before reaching a constant value slightly larger than $\rho$(300 K). This systematic difference in $\rho(T)$ for the $UPd_2M$ and $UAu_2M$ compounds illustrates the strong influence of the T element on the scattering mechanisms governing the electrical resistivity of these materials.

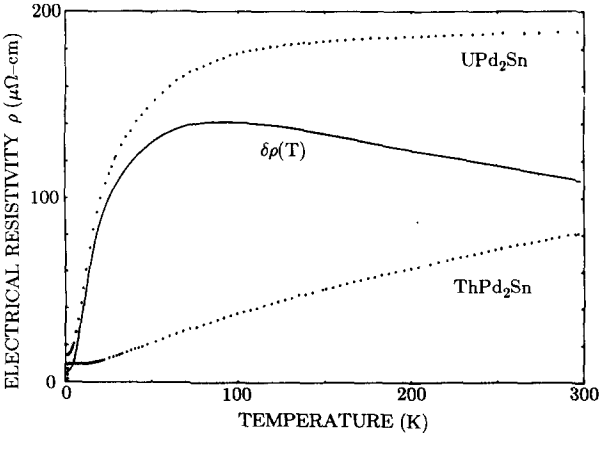


Fig. 1: Electrical resistivity $\rho(T)$ of $UPd_2Sn$ and its isostructural counterpart $ThPd_2Sn$ as a function of temperature T. The solid line is the U 5f electron contribution defined by $\delta\rho(T) \equiv \rho(UPd_2Sn) - \rho(ThPd_2Sn)$.

## Magnetic Susceptibility

The magnetic susceptibility $\chi$ and its inverse $\chi^{-1}$ are plotted versus temperature in Fig. 2. The $\chi(T)$ data can be described by a Curie-Weiss law $\chi = N\mu_{eff}^2/3\,k_B(T-\theta)$ with an effective moment $\mu_{eff} = 3.18\ \mu_B$ and a Curie-Weiss temperature $\theta = -77$ K between ~10 K and room temperature; below 10 K, $\chi(T)$ tends to saturate to a constant value of $\chi(0) = 1.4 \times 10^{-2}$ cm$^3$/mole U as $T \to 0$, which is slightly larger than the value observed for the heavy electron compound $UBe_{13}$. Assuming that the low temperature saturation of $\chi$ is representative of a Pauli-like susceptibility, we can estimate the electronic specific heat coefficient $\gamma$ from $\gamma = \pi^2 k_B^2 \chi(0)/3\,\mu_B^2$ which yields a value of ~1 J/mole U-K$^2$. The value of the effective moment $\mu_{eff}$ is close to the values of 3.62 $\mu_B$ and 3.54 $\mu_B$ expected for the free ion $U^{3+}$ ($5f^3$ configuration, J = 9/2) and $U^{4+}$ ($5f^2$ configuration, J = 4) valence states, respectively. At 5 K, the magnetization M of $UPd_2Sn$ varies

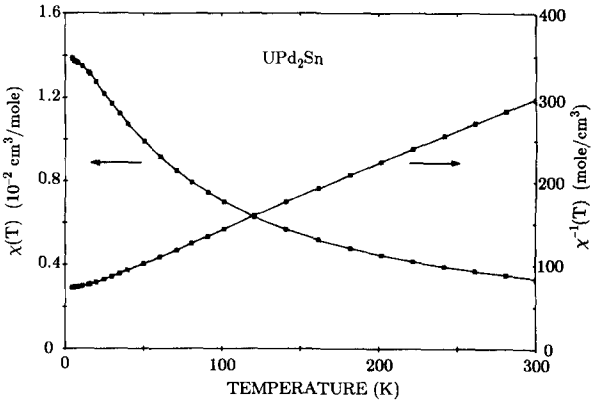


Fig. 2: Magnetic susceptibility $\chi$ and its inverse $\chi^{-1}$ versus temperature T for $UPd_2Sn$.

linearly with H between 0 and 5 tesla, with no indication of any saturation. The magnetic susceptibility of $ThPd_2Sn$, which was also measured between 300 K and 4.2 K in a field of 1 tesla, never exceeds $7.1 \times 10^{-5}$ $cm^3$/mole and is negligible compared to that of $UPd_2Sn$. This result shows that the U 5f electrons are the dominant contribution to the density of states $N(E_F)$ at the Fermi level $E_F$ in $UPd_2Sn$.

Specific Heat

As discussed above, the large value of $\chi(0)$ suggests that there will be a corresponding large value for $N(E_F)$, or equivalently, a large electronic specific heat coefficient $\gamma$. Shown in Fig. 3 are C/T versus $T^2$ data for $UPd_2Sn$ between 0 and ~22 K, which are approximately linear between 0.5 and 5 K and show strong negative curvature in the vicinity of 10 K. In the linear region below 5 K, the data can be described by the relation $C/T = \gamma + \beta T^2$ where $\gamma \approx 80$ mJ/mole U-$K^2$ and $\beta = 5.4$ mJ/mole U-$K^4$ (corresponding to a Debye temperature $\theta_D = 71$ K). Also shown in Fig. 3 are C/T versus $T^2$ data for the isostructural reference compound $ThPd_2Sn$, which display weak negative curvature around 16 K. A superconducting jump $\Delta C$ is observed at 1.35 K with $\Delta C/\gamma T_c = 0.9$ which is ~65% of the BCS value. The value of $\gamma$ for $ThPd_2Sn$ is about 8.5 mJ/mole-$K^2$ (see inset of Fig. 3). Assuming that the phonon spectra of $UPd_2Sn$ and $ThPd_2Sn$ are similar, the excess specific heat $\delta C$ which can be attributed to the localized U 5f electrons can be estimated by subtracting the C(T) data for $ThPd_2Sn$ from the data for $UPd_2Sn$. The excess specific heat data are plotted in the form of $\delta C/T$ versus $T^2$ in Fig. 3 and $\delta C/T$ versus T in Fig. 4. The curve of $\delta C/T$ versus T exhibits a large peak at ~9.7 K with a value of 272 mJ/mole U-$K^2$. The value of C/T extrapolated to T = 0 K gives $\gamma$ = 70 mJ/mole U-$K^2$ which corresponds to an effective mass $m^* \sim 29\, m_e$, where $m_e$ is the free electron mass. The effective mass $m^*$ was calculated from the formula

$$m^* = \hbar^2 k_F^2 \gamma / \pi^2 k_B^2 (Z/\Omega)$$

where $k_F = (3\pi^2 Z/\Omega)^{1/3}$, $\Omega$ is the volume of the unit cell which is taken to be approximately the same as for $YPd_2Si$,[5] and Z = 12, assuming that the number of "heavy electrons" is 3 per U atom. The entropy S associated with the excess specific heat, assuming a linear increase of $\delta C/T$ from 0 K to the first data point, is small and attains values of 0.3 R $\ell n$ 2 at the temperature of the maximum in $\delta C/T$ (9.7 K) and 0.67 R $\ell n$ 2 at 21 K.

Peaks in $\delta C(T)/T$ have also been reported for the heavy Fermion materials $CeAl_3$,[11] $CeCu_2Si_2$,[12] and $CeCu_4Al_8$,[13] at ~0.4 K in the former two compounds and at ~1 K in the latter compound; however, the decrease in $\delta C/T$ of ~70% below the maximum as well as the temperature of the maximum of 9.7 K for $UPd_2Sn$ are much larger than for these compounds. The peaks in $\delta C/T$ for $CeAl_3$, $CeCu_2Si_2$ and $CeCu_4Al_8$ have been attributed to fine structure in the heavy Fermion quasiparticle density of states due to the formation of the coherent Kondo lattice ground state. (For the single ion Kondo effect, no maximum in

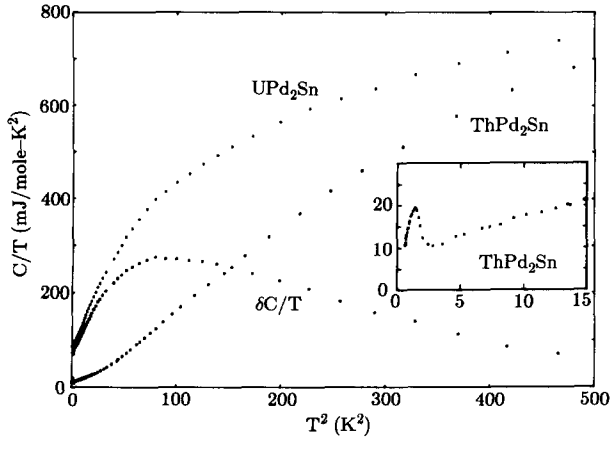


Fig. 3: Specific heat C divided by temperature T versus $T^2$ for $UPd_2Sn$ and $ThPd_2Sn$. Also shown in the figure is the estimated excess specific heat $\delta C \equiv C(UPd_2Sn) - C(ThPd_2Sn)$ due to the U 5f electrons. The superconducting specific heat anomaly at $T_c = 1.35$ K for $ThPd_2Sn$, plotted as C/T versus $T^2$, is displayed in the inset.

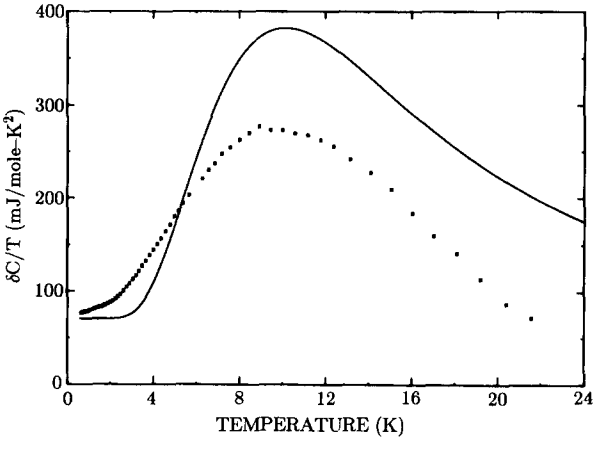


Fig. 4: Excess specific heat $\delta C \equiv C(UPd_2Sn) - C(ThPd_2Sn)$ divided by temperature T as a function of temperature T. The $C(ThPd_2Sn)$ data below 1.5 K are for the normal state and were obtained from a linear extrapolation of the C/T versus $T^2$ data for $UPd_2Sn$ above 1.5 K. The solid line is a $\delta C/T$ versus T plot of a Schottky anomaly calculated for two singlet states separated by 33 K (see text).

$\delta C/T$, where $\delta C$ is the contribution from the transition metal, rare earth or actinide impurity ion, has been observed experimentally nor is expected on theoretical grounds.) This interpretation seems reasonable for $UPd_2Sn$, although the depth and width of the pseudogap structure in the density of states must therefore be significantly larger than in the other heavy Fermion materials cited above.

The temperature scale for the development of the nonmagnetic Fermi liquid ground state in $UPd_2Sn$ is roughly given by the Kondo temperature $T_K$ which can be estimated from the zero temperature value of the magnetic susceptibility $\chi(0) = W_J \mu_{eff}^2/3 k_B T_K$, where $W_J$ is the Wilson number, $\mu_{eff} = g_J[J(J+1)]^{1/2}\mu_B$ is the effective magnetic moment, and $g_J$ and J are, respectively, the Landé g-factor and total angular momentum of the Hund's rule ground state for U. As noted above, the value of $\mu_{eff}$ determined from the Curie-Weiss behavior of $\chi(T)$ above $\sim$10 K is consistent with both J = 4 for $U^{4+}$ ($5f^2$ configuration) and J = 9/2 for $U^{3+}$ ($5f^3$ configuration). Hewson and Rasul[14] have given a formula

$$F(J) = \beta\gamma \exp[-3(J+1)/(2J+1)]/\Gamma[2(J+1)/(2J+1)]$$

where $\beta = 1.94$, $\ln\gamma = 0.577$ is Euler's constant, and $\Gamma$ is the gamma function, which reproduces to within 0.5% the values of $W_J$ calculated from the Bethe ansatz solution of the Coqblin-Schrieffer model for various values of J from 1/2 to 7/2. From this formula, we obtain $W_J \approx 0.7$ for both J = 4 and J = 9/2. Since $\mu_{eff} \approx 3.6\,\mu_B$ for both J = 4 and J = 9/2, we estimate that $T_K \approx 81$ K. The value of $T_K$ is comparable to the temperature below which $\rho$ starts to drop rapidly, which signals the onset of the coherent Fermi liquid ground state.

It is also of interest to estimate the Wilson ratio $R_W = \pi^2 k_B^2 \chi(0)/\mu_{eff}^2 \gamma(0)$ which, according to calculations based on Fermi liquid theory[15] and the Coqblin-Schrieffer model, diagonalized by the Bethe ansatz,[14] should be equal to (2J+1)/2J. Using the value of $\chi(0)$, the value of $\gamma_{max}$ (the maximum of the $\delta C/T$ versus T curve at 9.7 K) as an approximation of $\gamma(0)$ in the single ion limit, and $\mu_{eff} \approx 3.6\,\mu_B$, we obtain $R_W \approx 0.87$, which is comparable to the values of (2J+1)/2J of 1.125 for J = 4 and 1.11 for J = 9/2. It is noteworthy that the general temperature scale in $UPd_2Sn$ is larger than in $CeAl_3$, $CeCu_2Si_2$ and $CeCu_4Al_8$. This is evident in the positions of the peak in C/T versus T, and in the comparison of $T_K$ = 81 K for $UPd_2Sn$ with the values of $T_K$ = 9.2 K for $CeAl_3$, 13.4 K for $CeCu_2Si_2$ and 15.5 K for $CeCu_4Al_8$. The values of $T_K$ for the Ce compounds were estimated from the relation $T_K = W_J \pi^2 k_B/3R_W \gamma_{max}$ using J = 5/2 for $Ce^{3+}$ and the appropriate values of $\gamma_{max}$.[11-13]

On the other hand, an alternative interpretation of the peak in $\delta C/T$ is that it is an electronic Schottky anomaly, due to the crystalline electric field (CEF) which partially lifts the degeneracy of either a $U^{3+}$ J = 7/2 ($5f^3$), or $U^{4+}$ J = 4 ($5f^2$) Hund's rule multiplet. Whereas isolated U ions in a CEF can have magnetic ground states for both the $5f^3$ and $5f^2$ configurations, nonmagnetic ground states are possible for the $5f^2$ configuration. For example, in a cubic CEF, the $5f^2$ J = 4 multiplet splits into a $\Gamma_1$ singlet, a $\Gamma_3$ nonmagnetic doublet, and two magnetic $\Gamma_4$ and $\Gamma_5$ triplets. Thus, the nonmagnetic character of the U ions in $UPd_2Sn$ could be associated with a nonmagnetic $\Gamma_1$ or $\Gamma_3$ ionic ground state for the $5f^2$ configuration, rather than the formation of a nonmagnetic Kondo lattice or intermediate valence ground state due to the hybridization of the U 5f states with conduction electron states. In this case, the entropy associated with the excess specific heat $\delta C$ should be corrected for the contribution due to the conduction electrons which we would estimate to be

$$S_e = \int_0^T (C/T')\,dT' = \int_0^T \gamma\,dT'$$

with $\gamma \approx 70$ mJ/mole-$K^2$. This yields entropy values of S = 0.183 R $\ln$ 2 at 9.7 K and 0.415 R $\ln$ 2 at 21 K. In order to compare the $\delta C/T$ versus T data with the behavior expected for a Schottky anomaly, the specific heat was calculated for two singlets with a splitting $\Delta$ = 33 K which was chosen to give a peak in $\delta C/T$ at 9.7 K, in agreement with the data. The solid line in Fig. 4 is the calculated Schottky anomaly plotted as $\delta C/T$ versus T and shifted upwards by 70 mJ/mole-$K^2$ to take into account the background contribution of the conduction electrons. The discrepancy between the $\delta C/T$ versus T data and the calculated Schottky anomaly is quite large, especially at low temperature where the data show a much faster increase with temperature than predicted from the Schottky formula. Although the calculated entropy associated with the Schottky anomaly is of the order of 0.66 R $\ln$ 2 at 21 K, a value close to the measured one, the poor agreement between the shapes of the measured and calculated curves in Fig. 4 suggests that it is more reasonable to attribute the existence of the peak in $\delta C/T$ to the onset of a coherent Kondo lattice regime below 10 K.

## Concluding Remarks

We have investigated several new U-based ternary compounds with the formula $UT_2M$ and found that $UPd_2Sn$ exhibits certain properties that are typical of heavy electron systems. In particular, the compound behaves like a Fermi liquid below $\sim$10 K, according to the approximately $T^2$ contribution to the electrical resistivity between 1.2 and 10 K, the deviation of the

magnetic susceptibility from a Curie-Weiss law below 10 K, and the maximum in the $\delta C/T$ vs T curve near 10 K. The large difference between the shapes of the $\delta C/T$ versus T curve and the calculated Schottky anomaly suggests that the CEF is not the dominant factor in determining the observed properties of $UPd_2Sn$.

Further effort is being made to definitively establish the crystal structure of these compounds, and other measurements are underway in order to characterize the electronic structure and to better understand the role of the CEF in these materials.

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