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UHg_3: A heavy-fermion antiferromagnet similar to U_2Zn_{17} and UCd_{11}

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Heavy-fermion physics deals with the ground state formation and interactions in f-electron materials where the electron effective masses are extremely large, more than 100 times the rest mass of an electron. The details of how the f electrons correlate at low temperature to become so massive lacks a coherent theory, partially because so few materials display this "heavy" behavior and thus global trends remain unclear. UHg_3 is now found experimentally to be a heavy-fermion antiferromagnet—just as are *all* the other U_xM_y compounds with the metal M being in column IIB (filled d-electron shells) in the periodic table (Zn/Cd/Hg) and the spacing between uranium ions $d_{\text{U-U}}$ being greater than the Hill limit of 3.5 Å. This result, that—independent of the structure of these U_xM_y, $M =$ Zn/Cd/Hg, compounds and independent of the value of their $d_{\text{U-U}}$ (ranging from 4.39 to 6.56 Å)—all exhibit heavy-fermion antiferromagnetism, is a clear narrowing of the parameters important for understanding the formation of this ground state. The sequence of antiferromagnetic transition temperatures T_N of 9.7, 5.0, and 2.6 K for U_xM_y as the metal M varies down column IIB (Zn/Cd/Hg) indicates an interesting regularity for the antiferromagnetic coupling strength.

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The study of "heavy-fermion" physics became [1] a recognized subfield of condensed matter physics starting with the discovery in 1979 of superconductivity at $T_c = 0.6$ K in $CeCu_2Si_2$, a material with a large ("heavy") effective mass m^* of the paired electrons—greater than 100 times that of a regular superconducting metal such as Sn or Al. By 1984, two additional superconductors, two nonordering compounds, and three antiferromagnets had been added to the list of heavy-fermion systems.

The present Rapid Communication focuses on a discovery that may help to explain the subclass represented by the two antiferromagnets, U_2Zn_{17} and UCd_{11}, whose correlated density of states at the Fermi energy [proportional to the linear term γ coefficient in the specific heat $C/T\,(T \to 0) = \gamma + \beta T^2$, where $m^* \propto \gamma$] is *independent* of temperature at low temperature. This is in contrast with the other six compounds, which show specific heat γ's rising between 50% and 500% with decreasing temperature below 10 K. Thus, these six strongly correlated electron systems do not reenter the renormalized Fermi-liquid state (where γ would be constant) at even very low temperature, i.e., they remain "non-Fermi-liquid"-like in the sense that the strong correlations responsible for the γ values are still temperature dependent as $T \to 0$.

Using phenomenological arguments involving the Hill limit [2] and the known behavior of U_2Zn_{17} and UCd_{11} as the basis for prediction, we report the third large (defined in Ref. [1] as $\gamma > 400$ mJ/mol K^2) *constant*-γ heavy-fermion compound (again an antiferromagnet), UHg_3. This prediction and experimental work is an example of successful "materials by design," and provides focused input into the theory of understanding heavy-fermion ground state formation, at least in the case where γ is a constant at low temperature.

The choice of UHg_3 for the investigation of possible heavy-fermion antiferromagnetic behavior involved the following considerations. The first two elements in column IIB of the periodic table, Zn and Cd, form [1] binary heavy-fermion antiferromagnetic compounds with U (U_2Zn_{17}, $T_N = 9.7$ K, with the spacing between the U atoms, $d_{\text{U-U}} = 4.39$ Å, and UCd_{11}, $T_N = 5.0$ K, $d_{\text{U-U}} = 6.56$ Å, $\gamma = 535$ and 840 mJ/U mol K^2, respectively). These γ values imply effective electron masses greater than 100 that of a normal metal and are proportional to the correlated density of states at the Fermi energy $N(\varepsilon_F)(1+\lambda)$. Since γ at low temperatures in U_2Zn_{17} and UCd_{11} is constant with temperature at low temperatures, this implies that the mass renormalization due to the $(1+\lambda)$ factor is also temperature independent at low temperatures, i.e., the samples have entered into a new, renormalized Fermi-liquid ground state upon cooling. Such a simplifying assumption—that the mass renormalization is constant at low temperatures in these two systems—is an important input for any theory explaining this highly correlated ground state. Thus, if a third such system could be found, this could serve to provide useful input to theory for understanding highly correlated metals physics.

In order to put the rarity of materials known to have such large γ values in perspective, prior to the present work, U_2Zn_{17} and UCd_{11} were the only two known systems with constant-γ values >400 mJ/mol K^2 at low temperatures. If we consider all known systems with two, three, or four constituent elements and including superconductors, magnets, and nonordered systems such as $CeCu_6$ and $CeAl_3$, there are less [1,3] than 15 known with temperature-*dependent* γ values (i.e., where the γ is due to temperature-dependent spin fluctuations, perhaps from a quantum critical point [4,5]) above 400 mJ/mol K^2. Since the definition of how large a γ has to be to be named a "heavy" fermion is arbitrary (although note that simple d-electron materials such as β-manganese have [6] γ values of 60 mJ/mol K^2), if the range is extended down to 200 mJ/mol K^2, there are still only approximately 30 systems, including the antiferromagnets $NpIr_2$ ($\gamma = 230$ mJ/mol K^2) [7], UZn_{12} ($\gamma = 200$ mJ/mol K^2) [8], and UMn_2Al_{20} ($\gamma = 200$ mJ/mol K^2) [9]. The normal state ($T > T_N$) γ values in these three materials are, although a factor of 2.5–4 smaller than in U_2Zn_{17} and UCd_{11}, also temperature independent at low temperatures.

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It is important to note here that there *must* be hybridization taking place between the U $5f$ electrons and the ligand electrons in the column IIB atoms Zn and Cd in the heavy-fermion antiferromagnets U_2Zn_{17} and UCd_{11}. This U $5f$–Zn/Cd ligand electron hybridization has to be present since the distance between neighboring U atoms in both cases is larger than the Hill limit [2] of 3.5 Å. Below the Hill limit, the $5f$ electron orbitals can overlap and form conduction bands such as in a regular metal. Beyond the 3.5 Å limit the $5f$ orbitals are either localized [where localized electrons are not available to contribute to the enhanced density of states at the Fermi energy $N(\varepsilon_F)(1+\lambda)$] *or* are at least partially itinerant due to hybridization with intervening ligand atom electrons. There are no heavy-fermion compounds where the f-electron orbitals overlap—the mechanism for forming a highly correlated, highly effective mass ground state depends on the f-electron–ligand electron hybridization. The theory of how this hybridization functions in detail needs further development, since U_2Zn_{17} and UCd_{11} have differing structures and symmetries (rhombohedral and cubic, respectively) and differing $d_{\text{U-U}}$, but yet rather similar (in the sense of similar size γ and T_N values and both with temperature-independent γ values) heavy-fermion antiferromagnetism.

The present work investigated whether this quasiunique hybridization between U $5f$ electrons and the column IIB ligand Zn and Cd electrons would translate into a heavy-fermion antiferromagnet if a U_xHg_y compound could be found with $d_{\text{U-U}} > 3.5$ Å, where Hg is the third element after Zn and Cd in column IIB. In support of this premise, the only other compound present in the U-Zn phase diagram besides the heavy-fermion antiferromagnet U_2Zn_{17} is UZn_{12} (an antiferromagnet with $d_{\text{U-U}} \geq 4.45$ Å and an intermediate size γ of 200 mJ/mol K^2) [8] and there is only the UCd_{11} compound in the U-Cd phase diagram. Thus, based on these two members of the possible column IIB ligands with U, the idea that U_xHg_y will be a heavy-fermion antiferromagnet if a U_xHg_y compound with $d_{\text{U-U}} > 3.5$ Å can be found served as the phenomenological basis for the present work.

In the U-Hg phase diagram, preparation and characterization of the samples is difficult since [10] all the compounds "oxidize with great rapidity." This difficulty explains the dearth of characterizations of U_xH_y compounds: Magnetic susceptibility χ data on [11] UHg_2 exist and resistivity data have been measured on UHg_3 to infer [12] "some kind of ordering" near 50 K. The known U_xHg_y compounds have the following structures and $d_{\text{U-U}}$ values. UHg_2 is a regular metal with overlapping f orbitals, $d_{\text{U-U}} = 3.22$ Å, antiferromagnetic [11] at ~70 K with a hexagonal unit cell with three atoms. UHg_3 has been determined [12] to have a hexagonal structure which is, however, "unrefined," with therefore an unknown $d_{\text{U-U}}$. Reference [10] discusses the placement of the U atoms in UHg_3 as randomly distributed over the position of hexagonal closest packing. There are a number of MHg_3 compounds (with, e.g., M = Ce, La, Lu, Sc, Y, Yb) which occur in the hexagonal structure (called "DO19") in which two well-known heavy-fermion compounds (UPt_3 and $CeAl_3$) also form, with eight atoms per unit cell. If the $d_{\text{U-U}}$ in UHg_3 were to be calculated using the placement of atoms in this DO19 hexagonal structure, then $d_{\text{U-U}} \sim 4.54$ Å. In any case, if heavy-fermion behavior is found in UHg_3, this would be a proof that $d_{\text{U-U}} > 3.5$ Å, the Hill limit. The third compound in the binary U-Hg phase diagram is $U_{11}Hg_{45}$, which has $d_{\text{U-U}} =$ 5.3 Å and a cubic face centered unit cell with 448 atoms.

Thus, below, we discuss the preparation and characterization of UHg_3. Just as in the U-Zn phase diagram where both U_2Zn_{17} and UZn_{12} have large γ values (535 and 200 mJ/U mol K^2, respectively), $U_{11}Hg_{45}$ may also be of interest. However, in the constrained vapor ($P \sim 100$ atm) phase diagram UHg_3 is stable up to 735 °C, where it forms in a peritectic reaction, while $U_{11}Hg_{45}$, which also forms peritectically, is only stable up to 455 °C. Thus, UHg_3 should form more readily and characterization thereof will provide a test of our prediction.

Samples of UHg_3 were prepared [13] using 60 mesh U powder, 99.7% pure, which has been deoxidized using 1:1 HNO_3 and water. The Hg used was 99.999 995% pure. Stoichiometric amounts of the U and Hg were placed in a preoutgassed alumina crucible with a lid, which was sealed in a Nb cylinder with a bottom and top Nb lid welded on. This was then placed in a tube furnace through which Ar flowed to prevent the Nb from oxidizing, heated to 900 °C, held for 10 h, and cooled at 5 °C/h to 250 °C, followed by 75 °C/h cooling to room temperature. The amount of Hg in the approximately 6 cm^3 volume Nb containment was kept below about 200 mg. Even so, the pressure generated inside was sufficient to bow the flat endcaps outwards slightly during the reaction sequence. There was no reaction between the Hg and the containment. In addition, all of the Hg was reacted with the U powder, with no excess remaining. X-ray diffraction characterization revealed less than 5% of any possible second phase (e.g., UHg_2, $U_{11}Hg_{45}$, or U metal). The x-ray diffraction peaks of the prepared UHg_3 are similar to those of the DO19 hexagonal structure, but with several weak peaks (e.g., [102] and [103]) in the DO19 pattern either extinct or much reduced in intensity. As has been pointed out [10], U and Hg have very similar ionic radii which could lead to site switching. However, the Z values (92 and 80 of U and Hg, respectively) and scattering factors are rather similar. Thus, our calculations of the x-ray diffraction pattern using the program POWDER CELL indicate that such site switching cannot explain the disagreement between a calculated DO19 x-ray pattern and that measured in the present work for UHg_3. Thus, UHg_3 appears not to have a disordered DO19 hexagonal structure.

The magnetic susceptibility χ of UHg_3 is shown in Fig. 1. As will be seen below when the specific heat data are presented, there are two bulk anomalies at 2.6 and 4.8 K, respectively. Magnetization versus field up to 5 T (not shown) is essentially linear up to 5 T for the sample of UHg_3 presented here, implying no magnetic impurities present to exhibit saturation behavior. This linearity of M vs H, combined with the rather large value of χ (2 K) (13 memu/mol), is consistent [14] with heavy-fermion behavior. χ at low temperatures for U_2Zn_{17} is 4.5 memu/U mol and for UCd_{11} is 38 memu/mol [1].

The specific heat of UHg_3 at low temperatures down to 0.4 K is presented in Fig. 2. The zero field data are plotted by themselves in Fig. 2(a) to accentuate the good linearity of C/T plotted versus T^2, i.e., the extrapolation shown is clearly convincing evidence for a γ value that is constant at these low temperatures.. The peak in χ at 2.7 K shown in Fig. 1 clearly

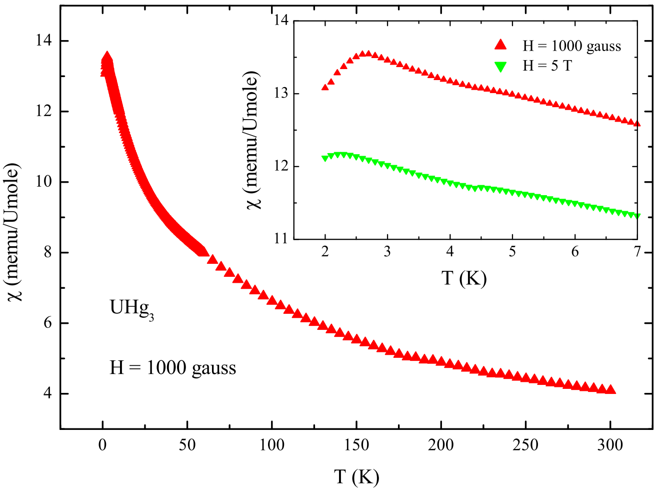

FIG. 1. (Color online) The dc magnetic susceptibility of polycrystalline UHg_3 both on an expanded low temperature scale at two applied fields and over the whole 2–300 K measurement range in 1000 G. Note that the peak in χ at 2.7 K and its shift downwards with a 5 T field are both consistent with an antiferromagnetic transition. There is also a slight ($\approx$2%) anomaly at 4.5 K (see the specific heat in Fig. 2). This slight anomaly shows no field dependence in χ up to 5 T. The small change in slope of χ around 45 K may correspond to the anomaly observed in the resistivity in Ref. [12]. If a constant term (2.2 memu/U mol) is subtracted from these χ data, a plot (not shown) of $1/\chi$ vs T is linear and implies an effective moment of $2.3\mu_B$ per U atom, consistent with an f^1 state for the U ion.

correlates with the large, sharp peak in the specific heat at 2.35 K (onset at 2.8 K) in Fig. 2. Also, the field suppression of the ordering temperature measured by the field specific heat data is further consistent with this anomaly indeed being an antiferromagnetic transition.

The anomaly in the specific heat starting at around 5.3 K, on the other hand, shows no field dependence up to the highest field of measurement, 12 T. This anomaly, as well as the antiferromagnetic transition at $T_N^{\rm mid} = 2.6$ K, was present in all seven of the UHg_3 samples measured, including those made from small chunks (similar to the method in Ref. [16] for preparing $CeHg_3$) of U rather than from U powder, and is clearly an intrinsic feature.

Without low temperature x-ray characterization or neutron scattering data the nature of the ~5 K, field-independent transition in the specific heat is presently uncertain. It is worthwhile to note, however, that the upper transition looks very similar to the structural transition (cubic → tetragonal upon cooling) observed [17,18] in the specific heat in the A-15 structure superconductors Nb_3Sn and V_3Si. In V_3Si the depression with field of this structural transition (at 21.3 K, while the superconducting transition is at 16.9 K) was found [17] to be quite small, 0.26 K in 9 T. Also, there is [19] a 6% decrease in χ as Nb_3Sn is cooled through its structural transition at 45 K (versus 2% in the data for UHg_3 shown in Fig. 1) due to a change in the electronic density of states at the Fermi energy caused by the change in structure.

Finally, the size of the specific heat γ (where C/T is fit to $\gamma + \beta T^2$) extrapolated from above 5.9 K is, as shown in Fig. 2, approximately 420 mJ/U mol K^2. This value is—together with the presence of antiferromagnetism at 2.6 K—validation of the prediction of heavy-fermion antiferromagnetism in U_xHg_y. Although there are certainly differences (e.g., the decrease in γ below the antiferromagnetic transitions in U_2Zn_{17} and UCd_{11} is 63% and 70%, respectively [1], versus 92% in UHg_3—i.e., the antiferromagnetic transition's reconstruction of the Fermi surface is much more severe in UHg_3), the series of

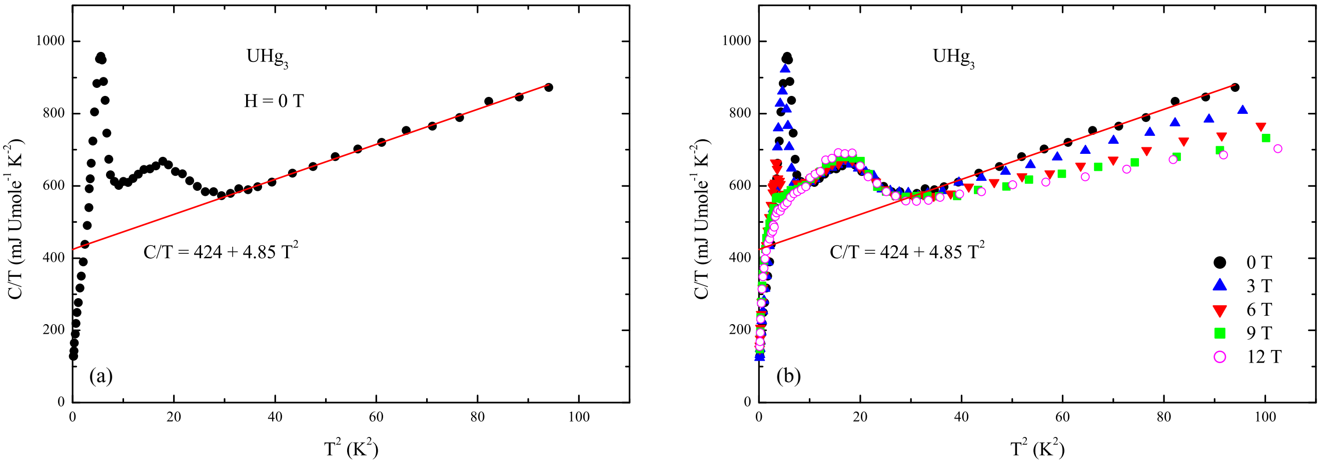

FIG. 2. (Color online) Specific heat C divided by temperature T vs T^2 in zero and applied field up to 12 T between 0.4 and 10 K of pressed pellets of polycrystalline UHg_3. The peak in C/T is at 2.35 K, while the onset of this transition is about 2.8 K, giving a midpoint of about 2.6 K. The shoulder in the specific heat starts at around 5.3 K and peaks at 4.3 K. The zero field T^2 coefficient for C/T (4.85 mJ/mol K^2) gives a Debye temperature θ_D of 117 K, indicating a rather soft lattice. The extrapolation of the C/T data from above (starting at $T = 5.9$ K) the upper transition—which are quite linear when plotted vs T^2—gives a value for γ of over 400 mJ/mol K^2. This value is robust, varying by <3% if a different starting temperature (6.9 vs 5.9 K) is chosen for the fit of C/T to $\gamma + \beta T^2$. The low temperature extrapolation of the C/T data in the antiferromagnetic ordered state is only 35 mJ/mol K^2, a large reduction from the high temperature extrapolated value. Note that the applied magnetic field data in (b) imply an increase of γ with field, consistent with the results [15] of the specific heat in field of UPt_3, where spin fluctuations are present.

heavy-fermion antiferromagnets U_2Zn_{17} ($T_N = 9.7$ K), UCd_{11} ($T_N = 5.0$ K), and UHg_3 ($T_N = 2.6$ K) must be considered to belong to a related family of compounds. Certainly, if one looks at a log-log plot of γ vs χ as put forward by Fisk and also by Jones (see Ref. [20]), the points for these three materials cluster rather closely together.

The question for which new theory is now needed is as follows: How does the hybridization of the U $5f$ electrons with the electrons in the column IIB elements Zn, Cd, and Hg cause this quasiunique, constant-γ heavy-fermion antiferromagnetism? The details of this outer shell ligand electron hybridization of the column IIB elements with the U $5f$ electrons need to be addressed theoretically. Also, is the decreasing magnitude of T_N as M in U_xM_y shifts down the column IIB elements (approximately a factor of 2 between each member, with a second value for $M =$ Zn of $T_N = 5.0$ K for UZn_{12}) accidental, or also understandable through a proper theoretical explanation?

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