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**P-T-H phase diagram of heavy-electron UCD_{11}**

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At ambient pressure UCD_{11} undergoes a phase transition near 5 K that is believed to arise from antiferromagnetic order within a strongly correlated electron system. Under moderate hydrostatic pressures, two new phase transitions appear below 5 K that are manifested by anomalies in the temperature-dependent electrical resistivity. We present the evolution of these transitions with pressure, temperature, and magnetic field and discuss possible interpretations of their origin given the pressure dependence of the resistivity and magnetic susceptibility.

**INTRODUCTION**

The observation that superconductivity can appear within a system of strongly correlated electrons having huge effective electron masses has stimulated the search for additional examples of heavy-electron behavior.\(^1\) Such searches have led to the discovery of two uranium-based heavy-electron materials that order magnetically at low temperatures. Characteristic of the strong electronic correlations in each of these is a very large value of the electronic specific-heat parameter \(\gamma\). Of the two \([\text{U}_2\text{Zn}_{17}\) (Ref. 2) and UCD_{11} (Ref. 3)], UCD_{11} has the largest \(\gamma\) value, 840 mJ/mole K\(^2\), obtained by extrapolating \(C/T\) versus \(T^2\) from above the phase transition to \(T=0\) K. Clear evidence\(^3\) for a phase transition in UCD_{11} comes from a large peak both in the specific-heat and thermal-expansion coefficient at 5.05 K, as well as from a sharp drop in the electrical resistivity at the same temperature. Both the specific-heat and thermal-expansion anomalies are of a magnitude comparable to those observed\(^4\) in \([\text{U}_2\text{Zn}_{17}\), the ordering in which recently has been established by neutron diffraction to be antiferromagnetic with a much reduced ordered moment and a simple ordered structure.\(^5\) However, the precise nature of the phase transition in UCD_{11} is considerably less well understood; although, muon spin rotation experiments\(^6\) indicate antiferromagnetic order. Unlike the sharply defined phase transition in \([\text{U}_2\text{Zn}_{17}\), the specific-heat \(C\) and thermal-expansion features near 5 K in UCD_{11} are characterized by rather broad high-temperature “tails” and a shoulder in \(C/T\) versus \(T^2\) near 3.5 K. Because the U-U nearest neighbors are well separated (6.56 Å) in UCD_{11}, it might be expected that the uranium ions carry well-defined 5f-electron moments. The large \(\gamma\) value, however, indicates the formation of a narrow band by hybridization.\(^3\) In analogy with the speculation\(^1\) that superconductivity in heavy-electron materials is of an unusual type, the nature of magnetic ordering in comparable systems may be similarly atypical in comparison with conventional \(f\)-electron magnetic systems.

By viewing the heavy-electron system in UCD_{11} as a Fermi liquid with a large effective mass of the quasiparticles, it is possible from the electronic specific-heat coefficient to estimate a corresponding characteristic degeneracy temperature \(T^*\) to be on the order of 10 K.\(^7\) Therefore, the phase-transition temperature and \(T^*\) are of comparable magnitudes. Given this observation, one expects the phase transition to be sensitive to slight perturbations of the electronic system, such as can be accomplished by the application of moderate hydrostatic pressures. With this in mind, we have studied the temperature-dependent electrical resistance and magnetic susceptibility of UCD_{11} subjected to hydrostatic pressures exceeding 17 kbar and 7 kbar, respectively.

**EXPERIMENTAL DETAILS**

The electrical resistance was measured using a standard four-lead ac technique from room temperature to typically 1.3 K. Experiments were performed on a small single crystal of UCD_{11} which was grown from excess molten cadmium. X-ray analysis performed on crystals grown at the same time as the one employed in this work confirmed the cubic BaHg_{11} crystal structure and gave a lattice parameter of 9.283 Å. There was no evidence from the x-ray study for the presence of second phases. Hydrostatic pressures were produced in a self-clamping Be-Cu pressure cell, with a mixture of 1:1 isooamyl alcohol and \(n\) pentane as the pressure-transmitting medium. Pressures within the cell were determined at low temperature from the inductively measured superconducting transition of lead. These measurements provide a relative accuracy in pressure determinations of better than ±0.5 kbar. Additional details of the pressure cell and measurement procedures have been given elsewhere.\(^8\)

A similar, though significantly miniaturized, pressure cell made of binary beryllium-copper was used for susceptibility \(\chi\) measurements in a Faraday magnetometer. The susceptibility of UCD_{11} single crystals from the same batch as the resistivity sample was determined by sub-
trating the susceptibility of the empty cell from that of the cell containing crystals. In order to minimize systematic errors associated with measurements near $\chi=0$, the diamagnetism of beryllium-copper was compensated by wrapping Pt foil around the cell body. All measurements were performed in a dc field of 1 T and in the temperature range $2 < T < 300$ K for pressures up to 7.6 kbar.

RESULTS

In Fig. 1 we show the electrical resistance of UCd$_{11}$ at four different pressures. The detailed shape of the zero-pressure curve agrees with that published previously, including a distinct break in the curve at 5.04 K (see Fig. 1 inset) that signals the phase transition. With increasing pressure the broad resistance maximum centered at $T_{\text{max}} = 84$ K (for $P=0$) shifts approximately linearly to lower temperatures at a rate of $-1.6$ K/kbar and becomes more prominent. We also observe in Fig. 1 a rather large, systematic increase in the overall resistance with applied pressure. Near room temperature the resistance increases linearly with pressure at the relative rate $(1/R_0)\partial R/\partial P = 0.01$/kbar. Although we cannot disregard the possibility that the resistance rise might be due to the formation of microcracks, we note that the measurements were performed on a single crystal and that, after an initial pressure increment, there was no detectable hysteresis in the room temperature resistance with repeated pressure cycling.

The occurrence of a phase transition is observed most clearly in plots of the temperature derivative of the resistance $\partial R/\partial T$ versus temperature [see Fig. 2(a)]. In the vicinity of the phase transition, this curve appears similar to that of $C_p/T$ versus $T$ measured at ambient pressure. With increasing pressure [Figs. 2(b) and 2(c)] there is a significant change in the temperature dependence of $R$ below 4 K that culminates in the appearance of a new phase transition near 3 K at 2.8 kbar. Concurrent with the evolution of the new transition $T_3$ is a gradual shift of the original phase transition $T_1$ at temperature $T_{1c}$ to higher temperatures and a diminution of its $\partial R/\partial T$ signature, i.e., an apparent decrease in the spin-disorder scattering removed by the phase transition. (In the following we refer to phase transitions $T_i$ which are defined by their respective pressure- and field-dependent critical temperatures $T_{ic}$.) $T_{2c}$ falls rapidly toward $T=0$ K [Figs. 2(d)–2(f)] as the pressure is raised above $\sim 5$ kbar. At the highest pressures [Fig. 2(i)], a third transition $T_3$ appears whose signature is characterized by a negative-going peak in $\partial R/\partial T$. Both $T_2$ and $T_3$ are also clearly discernible in plots of $R$ versus $T$.

Specific-heat measurements at ambient pressure show that $T_{1c}$ is depressed somewhat over 1 K by an 11 T magnetic field. We also have studied the influence of magnetic fields to 4 T on the transitions $T_2$ and $T_3$ at pressures of 3.8 and 17.3 kbar, respectively. These measurements were performed, with the pressure cell immersed in liquid helium, by fixing the magnetic field and slowly sweeping the temperature through the transition. Starting conditions for each measurement cycle were $T=4$ K, $H=0$ T. Both $T_{2c}$ and $T_{3c}$ were found to be nonlinear functions of $H$ with $T_{2c}$ (3.8 kbar) decreasing by nearly 1.5 K in 4 T and $T_{3c}$ (17.3 kbar) increasing by over 0.5 K at 3 T. The $P$-$T$-$H$ phase diagram for UCd$_{11}$ resulting from these studies is shown in Fig. 3.

The dependence of $T_{1c}$ on pressure is unusual, increasing initially at a rate of $\sim 70$ mK/kbar, reaching a plateau between 8 and 13 kbar, and finally increasing again at a rate of about 100 mK/kbar. The initial rate of increase in $T_{1c}$ can be compared to that expected on the basis of Ehrenfest’s equation$^9$ appropriate for second-order phase transitions

$$\partial T_{1c}/\partial P = 3VT_{1c}\Delta \alpha/\Delta c_p,$$

where $\Delta \alpha$ and $\Delta c_p$ are the thermal-expansion and specific-heat changes, respectively, at $T_{1c}(P=0)$ and $V$ is the molar volume. From the measurements of Fisk et al.,$^3$ we estimate $\Delta \alpha = 20 \times 10^{-7}$/K and $\Delta c_p = 8$ J/mole K, which give $\partial T_{1c}/\partial P \approx 60$ mK/kbar, a value in reasonable agreement with that determined directly.

A most striking feature in this work is the observation of two new phase transitions in UCd$_{11}$ that are separated by only about 14 kbar. The $P$-$T$-$H$ diagram suggests a possible inter-relationship between phases $T_1$ and $T_2$ as well as between $T_1$ and $T_3$. We see in Fig. 3 that $T_2$ disappears near the pressure where $T_{1c}$ becomes independent of pressure and $T_3$ appears when $T_{1c}$ once again depends on pressure. This correspondence is supported further by the systematics in the resistivity data of Fig. 2. At the same time it is clear from the sign difference in field derivatives of $T_{2c}$ and $T_{3c}$ that these transitions are quite different. There is some indication from specific-heat measurements that perhaps the second transition is beginning to form already at ambient pressure. As mentioned earlier an unexplained shoulder occurs near 3.5 K in a plot of $C/T$ versus $T^2$. This temperature agrees well with that obtained by smoothly extrapolating the phase boundary $T_{2c}(P)$ to $P=0$. Despite attempts to observe an unambiguous signature for the second transition at pressures less than 3 kbar, no evidence for $T_2$ could be

![Fig. 1](image)

FIG. 1. The electrical resistance of single crystal UCd$_{11}$ as a function of temperature at four pressures. We estimate the room temperature resistivity to be about 100 $\mu$A-cm at $P=0$. 

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FIG. 2. Temperature derivative of the electrical resistance $\partial R/\partial T$ as a function of temperature at fixed pressures and zero-applied magnetic field. Arrows denote the temperature at which a phase transition appears. For transitions induced by pressure, two arrows are shown corresponding to different criteria applied to define the transition.

found. However, as shown in Figs. 2 (a)–2(c), there is a systematic development in $\partial R/\partial T$ leading up to the phase transition. This trend could be interpreted as arising from an increase in magnetic scattering at temperatures less than $T_1(P)$, corresponding to a progressive decrease in spin-spin correlations below $T_1$ as pressure is applied.

Figure 4 shows the temperature dependence of the inverse molar susceptibility of UCd$_{11}$ at the two extremes
of our pressure measurements. Slopes of these curves
give effective moments $\mu_{\text{eff}}$ of 3.60±0.02 and 3.57±0.02
$\mu_B/U$ for $P = 0.6$ and 7.6 kbar, respectively, values con-
sistent with either 5$f^3$ or 5$f^2$ configurations at both pres-
ures. The intercepts provide negative paramagnetic Cu-
rie temperatures whose magnitudes increase with pressure
from 39.4±0.3 to 41.7±0.3 K. Although it is
difficult to determine from these measurements the pre-
cise pressure dependence of $T_{1c}$, a clearly positive trend
is observed, as displayed in the inset of Fig. 4. Because of
the limited temperature range over which these measure-
ments could be made and the fact that a 1 T field was ap-
plied to the sample, no distinct evidence for phase transi-
tion $T_2$ could be detected. However, the system-
atic change in the temperature dependence of $\chi$ below $T_{1c}$
might hint of a pressure-induced suppression of $T_{2c}$. We
also note a progressive broadening of the susceptibility
maximum near $T_{1c}$ that is consistent with the trends in
$\partial R/\partial T$ shown in Figs. 2(a)–2(e).

**DISCUSSION**

As mentioned, muon spin-rotation and relaxation ex-
periments indicate that the phase transition $T_1$ is due to
antiferromagnetic order. This has not yet been confirmed
by neutron scattering but only an upper limit of 1.5$\mu_B/U$
on the ordered moment has been established. Such a re-
cued ordered moment is consistent with neutron mea-
surements on related systems U$_2$Zn$_{17}$ (Ref. 5) and UCd$_4$
(Ref. 12) and with the ratio of the electronic specific-heat
contributions above and below the Neel temperature. That
the ordered moment is significantly less than $\mu_{\text{eff}}$ in-
fected from susceptibility measurements at temperatures
higher than $T_{1c}$ suggests the presence of Kondo-like in-
teractions leading to partial compensation of the local
moment at reduced temperatures. Such interactions, to-
gether with Ruderman-Kittel-Kasuya-Yoshida (RKKY)
interactions, also appear important for determining the
temperature dependence of transport and magnetic prop-
erties.

Many Ce- and U-based heavy-electron compounds
have a maximum in their electrical resistivity at some
moderately low temperature $T_{\text{max}}$, as is also the case in
UCd$_{11}$ (Fig. 1). Pressure measurements show that, un-
lke UCd$_{11}$, in almost all of these cases $dT_{\text{max}}/dP > 0$;
however, for Yb-based systems with a low-temperature
resistivity maximum, $dT_{\text{max}}/dP < 0$. This behavior
also has been attributed to the pressure-dependent in-
teraction between intrasite Kondo-like interactions and
intersite RKKY-type interactions. Presumably in most
Ce- and U-based compounds, pressure ostensibly favors a
less-magnetic ground state due to the relatively more rap-
id increase in Kondo spin compensation than the en-
hancement of RKKY interactions. The heavy-electron
superconductor UBe$_{13}$, however, appears to provide a
case in which a more-magnetic-like ground state is
favored by pressure even though $dT_{\text{max}}/dP > 0$. On the
other hand, in Yb systems, the low volume state is more
magnetic and hence generally promoted by applied pres-
sure.

A different example of the behavior described is found
in CeAl$_3$ in which the resistivity maximum near 100 K
moves to lower temperatures with increasing pressure. Here,
however, $T_{\text{max}}$ has been attributed to Kondo-like
scattering off thermally populated crystalline-electric field
levels whose splitting from the ground state decreases
with pressure. Although the presence of crystal fields has
been established in a number of Ce compounds, including
CeAl$_3$, this is not true of U compounds, with the excep-
tion of UPd$_3$. The 1/$\chi$ versus $T$ data shown in Fig. 4
would suggest that crystal fields are not well-defined and
certainly not manifested clearly in UCd$_{11}$. Even in the
absence of crystal-field splittings, we would expect to find
an entropy of Rln2 below $T_{1c}$ in UCd$_{11}$, characteristic of
the strongly interacting Fermi liquid ground state in-
furred from the large $\gamma$ value. Our analysis of the specific
heat data for UCd$_{11}$ up to $T_{1c}$ does give an entropy
slightly less than Rln2 consistent with this expectation.
It is also not obvious that pressure effects in UCd$_{11}$
and Yb compounds $(dT_{\text{max}}/dP < 0)$ can be interpreted simi-
larly. This is made particularly difficult because the two
possible 5$f$ configurations have nearly identical effective
moments.

UCd$_{11}$, therefore, appears to be somewhat pathological
in the sense that it is not straightforwardly analogous to
previously studied systems. However, we believe that our
observations are generally consistent with the concept of
competing intra- and intersite interactions. In this perspec-
tive, the large electronic specific-heat coefficient $\gamma$
is determined primarily by the intrasite energy scale $T_K$. For
$T_K > T_R$, where $T_R$ is a measure of the intersite cou-
pling scale determined by the $q$-dependent exchange $J$,
the ground state is paramagnetic. However, when
$J(q)/T_K = 1$ a magnetic instability occurs and the spin-
system Ordering. Because UCd$_{11}$ has the largest $\gamma$ of any
known U-based heavy-electron magnet, this viewpoint
suggests that $T_K$ must be small, certainly smaller than
$T_R$. In this regime we expect the magnetic ground state
to be favored initially as $J$ is enhanced by pressure, pro-
ducing $dT_{1c}/dP > 0$. At much higher pressures, when
$T_K$ and $T_R$ become comparable, Kondo spin compensa-
tion dominates and we would expect $dT_{1c}/dP < 0$. Evi-
dence for this trend is found from pressure measure-
ments of the Neel temperature $T_N$ in U$_2$Zn$_{17}$ in which $T_R$
and $T_N$ have been argued to be more comparable. Again
because of the large ratio $T_R/T_N$ in UCd$_{11}$, RKKY inter-
actions will dominate with initial increments in pres-
sure, producing $dT_{\text{max}}/dP < 0$ even though the ratio
$T_R/T_N$ becomes smaller. (For simplicity this argument
ignores $q$-dependent effects which may be important. See
below.) Similar arguments can be used to predict the be-
havior of Yb-based heavy-electron materials under pres-
sure. Although the point of view developed here would
suggest that at sufficiently high pressures $dT_{\text{max}}/dP$
should reverse sign, as well as $dT_{1c}/dP$, in UCd$_{11}$, for Yb
systems this should not occur within a comparable pres-
sure range since the low volume, magnetic state will al-
ways be favored. Such a distinction could be tested
straightforwardly.

This simple picture is also consistent with the pressure
dependence of the susceptibility. The dc magnetic sus-
susceptibility detects the $q \to 0$ limit of the generalized susceptibility measured in quasi-elastic scattering. At low temperatures $\chi \sim 1/\Theta$, where $\Theta$ is the paramagnetic Curie temperature, which for a single Kondo impurity system is proportional to $T_K$. However, in the case of a lattice of Kondo impurities, $\Theta$ is not so simply described because of the existence of intersite correlations. Unfortunately, no simple expression for $\Theta$ exists in this case; however, the data of Fig. 4 indicate $d(\Theta)/dP > 0$, consistent with the expected increase in $T_K$ with pressure. If we assume that spectral weight lost at $q = 0$ by the application of pressure reappears at some $q > 0$, then a second magnetic instability $[J(q)/T_K = 1]$ could occur. We suggest that this may be the mechanism responsible for the additional phase transition $T_2$. Its extremely strong suppression with pressure, however, is not understood.

As mentioned above, the phase diagram presented in Fig. 3 clearly suggests an inter-relationship between phase transitions $T_1$ and $T_2$ as well as $T_1$ and $T_3$. Although a plausible argument has been given for the origin of $T_3$ and the pressure dependence of $T_1$ at low pressures, the source of $T_3$ remains a mystery. Certainly additional experiments, e.g. specific heat, magnetic susceptibility at higher pressures and lower temperatures, as well as neutron scattering under pressure, are required to clarify our understanding of the most interesting $P$-$T$-$H$ behavior of UCD$_{11}$.

**SUMMARY**

Electrical-resistivity and magnetic-susceptibility measurements on UCD$_{11}$ as functions of pressure reveal two new phase transitions that are both strongly volume dependent and couple to an applied magnetic field. The pressure dependences of $T_{1c}$ and $T_{max}$, as well as the large electronic specific heat coefficient and reduced ordered moment of UCD$_{11}$, are consistent with the competition between intersite (RKKY-like) and intrasite (Kondo-like) interactions in which at low pressures intersite interactions dominate. We suggest that the phase transition first induced by pressure ($T_3$) arises from a volume-dependent change in the $q$-dependent susceptibility. At present, no explanation exists for the source of the second pressure-induced transition ($T_3$) except to note that it appears to be coupled to the magnetic transition $T_1$, which itself may have been modified in a subtle way by pressure sufficiently large to give $T_3$.

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5Two other U-based compounds, UCu$_3$ and UAgCu$_4$, order magnetically and may be considered to belong to the class of heavy-electron compounds but their $\gamma$ is less than 400 mJ/mole K$^2$. See Ott and Fisk (Ref. 1) for additional details.


