Unusual Ground-State Properties of UPd_2Al_3: Implications for the Coexistence of Heavy-Fermion Superconductivity and Local-Moment Antiferromagnetism

R. Caspary, P. Hellmann, M. Keller, G. Sparn, C. Wassilew, R. Köhler, C. Geibel, C. Schank, and F. Steglich

Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-64289 Darmstadt, Germany

N. E. Phillips

Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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We report measurements of the resistivity and the specific heat, performed as a function of temperature, magnetic field, and hydrostatic pressure on the antiferromagnetic ($T_N = 14$ K) heavy-fermion superconductor ($T_c = 2$ K) UPd_2Al_3. Our results suggest a coexistence of two subsystems with more localized $5f$ states responsible for the magnetic properties and less localized states responsible for the superconducting properties. The latter are compatible with an order parameter of octagonal d-wave symmetry.

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The coexistence of heavy-fermion (HF) superconductivity and antiferromagnetic (AF) ordering with extremely small staggered moments in certain U-based compounds has recently created much excitement [1–3]. In UPt_3, a splitting of the superconducting transition at T_c has been observed [4] and was ascribed [5] to an interaction between the superconducting and AF order parameters. While these findings are often analyzed in terms of unconventional superconductivity [5], the smallness of the ordered moment has been ascribed either to strong Kondo-type local magnetic fluctuations [6] or to itinerant HF magnetism [7] and is also involved in arguments for an unconventional, i.e., non-Néel type, nature of AF order [8]. A common feature of HF superconductors of this kind, i.e., UPt_3, URu_2Si_2 (Ref. [1]), and UNi_2Al_3 (Ref. [3]), is the fact that their (superconducting/AF) phase transitions occur out of an (incipient) coherent Fermi-liquid phase. This is in contrast to the behavior of the majority of HF compounds (or "Kondo lattice" systems), which undergo a magnetic phase transition *before* coherence among the electronic quasiparticles can develop and for which the local f-derived magnetic moments are retained. In contrast to the *stable* $4f$ moments in Gd metal and Chevrel phases (e.g., $DyMo_6S_8$), however, the magnetic moments in Kondo lattices are usually reduced by the Kondo effect to $\mu_S \simeq (0.5\text{–}1)\mu_B$, although they still exceed the small moments found in the AF ordered superconductors by up to 2 orders of magnitude [1–3]. As was first demonstrated [9] for the prototypical "local-moment magnet" (LMM) $CeAl_2$, the Kondo reduction of μ_S is accompanied by an enhancement of the electronic specific heat, $\gamma_0 T$, in the AF ordered state. This is also found in many other LMM systems, e.g., CeB_6, U_2Zn_{17}, and UCd_{11} [7], and reflects [7,10] the formation of itinerant electronic degrees of freedom at the cost of local magnetic ones near the magnetic instability that derives from the competition between RKKY and Kondo couplings [11]. By introducing the "Kondo-lattice temperature" T^*, measuring the energy gain associated with the formation of a Kondo singlet, we can classify the two respective groups of HF compounds by T_c, $T_N \ll T^*$ (UPt_3-type) and $T^* \lesssim T_N$ ($CeAl_2$-type) [7].

In this Letter we report a novel, completely unexpected variant of the ground-state properties mentioned above: The HF compound UPd_2Al_3 (Ref. [12]) appears to be *both* an LMM system and a superconductor. The properties of AF ordered UPd_2Al_3 are quite similar to the type-II AF state of $CeAl_2$; and the superconducting transition, taking place at the record-high T_c of 2 K out of this LMM state, shows all the signatures of HF superconductivity [12] which homogeneously coexists with AF order for $T \leq T_c$ [13]. This implies that the $5f$ electrons are responsible for these different kinds of cooperative order [14]. Most surprisingly, however, UPd_2Al_3 shows a unique behavior under pressure (p), namely, a strong suppression of the AF phase-transition anomaly in the specific heat, accompanied by an increase of both T_N and the electronic specific heat $\gamma_0 T$. This is in contrast to all other (magnetic and nonmagnetic) HF compounds. Following a brief description of some experimental details, the rest of this Letter includes (i) a discussion of the magnetic ordering based primarily on the zero-pressure resistivity and specific-heat data, and emphasizing the identification of UPd_2Al_3 as an LMM system; (ii) results on the p dependence of the specific heat that suggest the division of the $5f$-quasiparticle states into two nearly separate subsystems, one strongly pressure dependent in which the magnetic ordering occurs, and one nearly pressure independent in which superconductivity occurs; (iii) new conclusions relevant to the nature of the superconducting state derived from the specific-heat data.

Polycrystalline samples (1,2) were prepared by arc melting the appropriate amounts of pure elements. A single crystal was grown in a tri-arc furnace using the Czo-

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chralski technique. All samples were annealed for 120 h at 900 °C. Both the large T_c values (2 K) and small transition widths (0.1 K) characterize samples 1 and 2 as high-quality samples. The resistivity of the single crystal ($T_c = 1.55$ K) was measured in a Cu-Be pressure cell with glycerin as pressure-transmitting medium with the current parallel to the *ab* plane. Utilizing a "compensated heat-pulse method" [15] in order to compensate for the self-heating of uranium without losing quasiadiabatic conditions, we measured the specific heat (i) at $p = 0$ kbar on sample 1 in a dilution refrigerator between 0.18 and 4 K in magnetic fields up to $B = 8$ T, and (ii) at $0 < p \leq 10.8$ kbar in a ^{3}He cryostat ($T = 0.4$–25 K) by using another Cu-Be cell loaded with sample 2 and AgCl as pressure-transmitting medium. In that case the precision from run to run is better than 0.2%, though the accuracy for higher temperature ($T > 8$ K) is limited due to the decreasing heat capacity of the sample relative to that of the cell (cf. error bars in Fig. 2). The pressure was determined from the superconducting transitions of In and Sn pieces mounted at the top and the bottom of the sample, respectively.

Evidence for local moments in UPd_2Al_3 includes pronounced crystal-field (CF) splitting effects which were ascribed to a U^{4+} ($5f^2$) configuration with a singlet CF ground state [16], and the onset of AF order between induced moments at $T_N = 14.2$ K. Further insight into the nature of the AF ordering is provided by the resistivity [$\rho(T)$] and specific-heat [$C(T)$] data at zero pressure in the vicinity of T_N; see Figs. 1(a) and 2. An increase in slope of $\rho(T)$ upon cooling through T_N indicates the freezing out of *spin-disorder scattering,* also pointing to the existence of local moments. Note that no discontinuity in slope can be resolved at T_N—in contrast to URu_2Si_2 (Ref. [17]) and UNi_2Al_3 (Ref. [18])—which makes an itinerant AF phase transition of the spin-density-wave type unlikely. At $p = 0$ bar, a substantial fraction of the local Zeeman entropy ($0.65R\ln 2$) is recovered by the ordering temperature [12]. For $T_c < T \leq T_N/2$, the specific heat is well represented by $C = \gamma_0 T + \beta T^3$, where $\gamma_0 \simeq 140$ mJ/K^{2}mole is very similar to the enhanced Sommerfeld coefficient of $CeAl_2$ [9]. The coefficient of the cubic term $\beta = \beta_m + \beta_p = 2.1$ mJ/K^{4}mole is dominated by long-wavelength acoustic magnons with $\beta_m = 1.6$ mJ/K^{4}mole ($\beta_p = 0.5$ mJ/K^{4}mole is the phonon contribution [19]) implying a magnetic Debye temperature $\Theta_m \approx 100$ K. This $C(T)$ dependence is consistent with the temperature dependence of the resistivity, which can be represented by either $\rho - \rho_0 = aT^2 + bT^5$ [$T < 13$ K, dash-dotted curve in Fig. 1(a)] or, more precisely, $\rho - \rho_0 = aT^2 + \rho_i(T/\Theta_m)$ ($T < 14$ K, dashed curve) [20]. The Grüneisen function $\rho_i(T/\Theta_m)$ implies $\Theta_m \approx 90$ K, close to the value derived from the specific-heat results. These expressions (using three and four parameters, respectively) fit the data in the stated temperature intervals as well as one with four parameters and exponential terms [18,21]: The existence of a gap in either the electronic density of states or the magnon spectrum is not necessary to explain the data in this temperature range ($2 < T \leq 13$ K). Thus, our $p = 0$ kbar results characterize UPd_2Al_3 as a *long-range ordered LMM system* (like $CeAl_2$), with no measurable gap in the magnetic excitation spectrum. It contains itinerant strongly correlated electronic states, most probably of $5f$ symmetry, and coexisting with AF order. These states are manifested by considerably enhanced $\gamma_0 T$ and aT^2 terms in $C(T)$ and $\rho(T)$ well below T_N. The pressure dependence of T_N provides additional evidence for LMM properties of UPd_2Al_3: As Figs. 1(a) and 2(b) show, a slight positive shift of $T_N(p)$ with increasing p, $dT_N/dp = 40$–100 mK/kbar, can be deduced from our data [22], similar to that observed for the type-II phase of $CeAl_2$ (Ref. [24]) and for other U-based HF magnets [25].

Figure 2 shows that, with increasing pressure, there is a

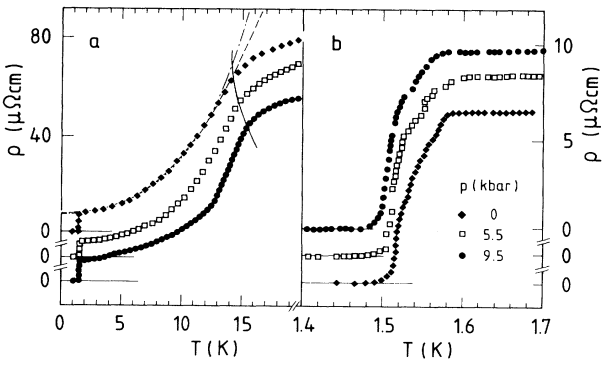

FIG. 1. Resistivity (ρ) vs temperature (T) for $p = 0$, 5.5, and 9.5 kbar, $T \leq 20$ K (a) and $1.4 \leq T \leq 1.7$ K (b). Solid, dash-dotted, and dashed lines in (a) indicate the p dependence of T_N, a three-parameter fit, $\rho - \rho_0 = aT^2 + bT^5$ for $T < 13$ K, as well as $\rho - \rho_0 = aT^2 + \rho_i(T/\Theta_m)$ for $T < 14$ K (see text).

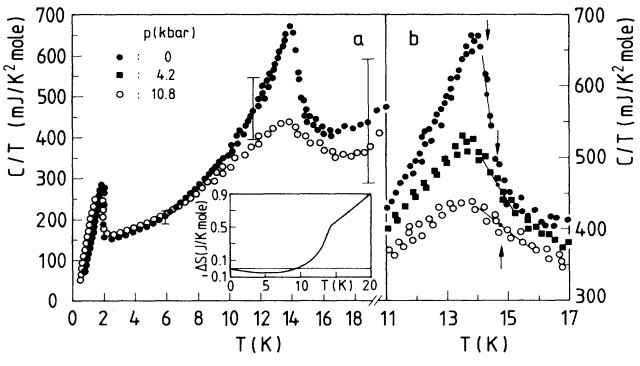

FIG. 2. Specific heat of UPd_2Al_3 at $p = 0$, 4.2, and 10.8 kbar as C/T vs T for $T \leq 20$ K (a) and $11 \leq T \leq 17$ K (b). Error bars in (a) indicate uncertainty in accuracy due to the heat capacity of the Cu-Be cell (see text). Inset shows entropy difference $S(0) - S(10.8\ \text{kbar})$ vs T. Arrows in (b) mark T_N.

dramatic suppression of the specific-heat anomaly at T_N—a much stronger effect than in, e.g., URu_2Si_2 (Ref. [26]). Even more surprising than the *magnitude of the reduction* of the entropy associated with AF ordering, is the *increase* in entropy at lower temperatures with increasing pressure. For $T < 9$ K, except for a small interval at T_c, $C(10.8\ \text{kbar})$ is significantly greater than $C(p=0\ \text{kbar})$, as shown in Figs. 2(a) and 3. One measure of this increase is given by the change in γ_0, $\Delta\gamma_0 = \gamma_0(10.8\ \text{kbar}) - \gamma_0(p=0\ \text{kbar}) = 16\ \text{mJ/K}^2\text{mole}$ for the normal (n)-state data of Fig. 3. Such a $\Delta\gamma_0$ is *not* in accord with published specific-heat data on $CeAl_2$ [24]. For $CeAl_2$, as had generally been found for *all* other magnetic and nonmagnetic Ce- and U-based HF compounds, the electronic-specific-heat coefficient γ_0 is reduced by increasing pressure [23]. In the inset of Fig. 2(a), the anomalous $\Delta\gamma_0(p) > 0$ is reflected by a negative entropy difference $\Delta S = S(p=0\ \text{kbar}) - S(p=10.8\ \text{kbar})$ vs T, which changes sign near $T=9$ K. Since $\Delta S(T)$ has to vanish at sufficiently high temperatures, it has to assume a maximum in between. The most surprising negative sign of $\Delta S(T)$ at low T (in connection with a positive sign of dT_N/dp) cannot be understood in the frame of the Kondo-lattice model [11] alone. In addition to the Kondo reduction of the ordered moment, the CF-level splitting, being very likely increased under pressure, will result in an additional reduction of the induced moment. This will cause an anomalous transfer of local Zeeman into itinerant electronic degrees of freedom.

We now turn to the effect of pressure on the specific heat in the superconducting state, $C_S(T)$. The most accurate characterization of $C_S(T)$ at $p=0$ kbar is based on our measurements with the dilution refrigerator ($T_{\min}=0.18$ K). The $B=0$ T data, for $T \leq 1$ K, are well represented by $C_S = \gamma_r T + AT^3$, where $\gamma_r = 24$ mJ/K mole

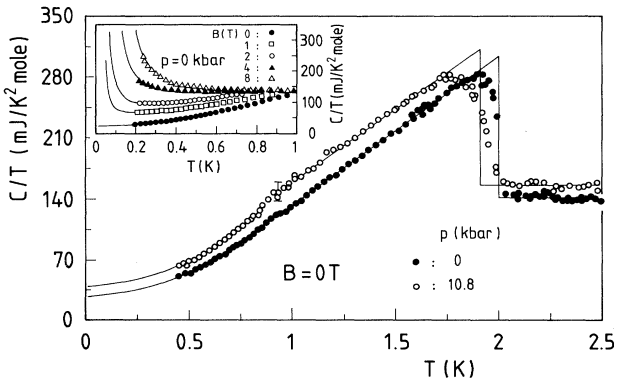

FIG. 3. Specific heat of UPd_2Al_3 as C/T vs T at and below $T_c = 2$ K for $P=0$ and 10.8 kbar at $B=0$ T (sample 2) and for $B=0$, 1, 2, 4, and 8 T at $P=0$ kbar (sample 1); see inset. Solid lines represent idealized jumps to determine T_c or a fit to the data by $C = a/T^2 + \gamma_r T + AT^3$ (note that γ_r varies by only 10% among samples 1 and 2). The small structure at $T=0.8$ K is ascribed to hydrogen in copper [27] of the addenda.

is the coefficient of a "residual" linear term in the superconducting state (inset of Fig. 3). The data taken in the pressure cell are well represented (above $T_{\min} = 0.4$ K) by the same temperature dependence, but the derived values of γ_r are uncertain by $\approx 10\%$. To that accuracy, however, *the p-induced increase in* γ_r *is the same as that in* γ_0: $\Delta\gamma_r = \gamma_r(10.8\ \text{kbar}) - \gamma_r(p=0\ \text{kbar}) = 15 \pm 4\ \text{mJ/K}^2\text{mole}$, to be compared with $\Delta\gamma_0 = 16\ \text{mJ/K}^2\text{mole}$. This surprising result, that the p-induced increase of γ_0 (for $T > T_c$) is the same as that of γ_r (for $T \ll T_c$), suggests a separation of the electronic low-temperature n-state specific heat, $\gamma_0(p)T$, into a pressure-dependent term, $\gamma_r(p)T$, and an almost pressure-independent term, $\gamma_1 T$, where $\gamma_1 = \gamma_0(p) - \gamma_r(p)$. It is tempting to relate $\gamma_r(p)$ and γ_1 to different subsystems of more or less localized quasiparticles of $5f$ symmetry, respectively: The more localized quasiparticles, generated by both the Kondo reduction (at $p=0$ kbar) and the p-induced reduction of the U moments, appear related to the LMM state. For that subsystem, the analogy to prototypical LMM systems like $CeAl_2$ [9], $CeAg_2Si_2$, or $CeAu_2Si_2$ (Ref. [28]) suggests a Kondo-lattice temperature $T^*_{\text{low}} \leq T_N \simeq 14$ K. These more localized $5f$ states do not seem to participate in forming the HF-superconducting phase. The latter appears due to a subsystem of less localized $5f$ states, characterized by $\gamma_1 \simeq 115\ \text{mJ/K}^2\text{mole}$ [29]. This implies that the corresponding T^* value, T^*_{high}, exceeds $T^*_{\text{low}} \leq 14$ K: First, we estimate the fraction of "superconducting" $5f$ states as $f \geq \gamma_1 T_N / S(T_N) \approx 50\%$, which leads to $T^*_{\text{high}} (\approx T_K) \approx 25$ K, if the simple relation [7] $\gamma_1/f = 0.68R/T_K$ is used to estimate the "single-ion Kondo temperature" T_K [30]. The weak sensitivity of γ_1 to p for $p < 11$ kbar manifests itself in a p-induced depression of T_c (Ref. [32]) and a corresponding reduction of the specific-heat-jump height $\Delta C(p)$, which are remarkably small compared to what is found, e.g., in URu_2Si_2 [26]. Such a division of the electronic quasiparticles into two independent subsets is no doubt an oversimplification. Straightforwardly, a weak interaction between them should, in fact, be responsible for the weak depression of both T_c and ΔC under pressure.

Concerning the parity and the shape of the superconducting order parameter, we recall (i) a strong (and nearly isotropic) paramagnetic limiting of $B_{C2}(T)$, the upper critical field, strongly pointing to even-parity pairing [14], and (ii) a quasiparticle mean free path being large compared to the coherence length, which makes UPd_2Al_3 a candidate for unconventional pairing [12]. In fact, the T^3 law found in $C_S(T)$, which corroborates previous results for the thermal expansion [31], is compatible with the recently proposed [33] octagonal d-wave state (Γ_3, A_{1g}), characterized by eight zeros in the order parameter on symmetric points at the Fermi surface. Despite this non-BCS type of $C_S(T)$ dependence, the reduced jump height, $\Delta C/\gamma_1 T_C \approx 1.48$, is close to the BCS prediction, similar to earlier findings on certain $CeCu_2Si_2$

samples (Ref. [7]). A more conventional behavior is also deduced from an analysis of the $C(T)$ data obtained in the mixed state (1,2 T) and plotted in the inset of Fig. 3 along with n-state results ($B=4,8$ T). These data can be fitted by a polynomial $C_S(T,B)=\alpha(B)T^{-2}+\gamma_r(B)T+A(B)T^3$. The hyperfine term $\alpha(B)T^{-2}$ vanishes for $B=0$ T, indicating [14] a cancellation of internal fields transferred from the local $5f$ moments to the high-symmetry ^{27}Al sites, and is fully explained by the Zeeman splitting due to the applied B field. The $\gamma_r T$ term increases with applied field. This is explained by normal excitations in the vortex cores, $d\gamma_r/dB \simeq 40\,\mathrm{mJ/K^2 mole\,T}$, being close to the theoretical prediction [34] for a BCS superconductor in the clean limit, when using $B'_{c2}(T_c)=-4.3$ T/K (Ref. [14]) and the related part of the n-state electronic specific heat, $\gamma_1 T$, with $\gamma_1=115$ mJ/K^{2}mole.

In conclusion, UPd_2Al_3 combines the signatures of a "magnetic superconductor" (coexistence of superconductivity and AF of *local f* moments) and a HF superconductor (Cooper pairs formed by *weakly delocalized f* electrons). In contrast to the Chevrel-phase superconductors containing superconducting ($4d$) and magnetic ($4f$) electrons nearly separated in real space [35], however, in UPd_2Al_3 two nearly disjunct subsystems with different energy scales k_BT^* seem to coexist in k space. Thus, both subsystems represent the $CeAl_2$ and UPt_3 types of HF systems on either side of the magnetic instability [11], respectively. Such a scenario may be more general among HF compounds: Both UCu_5 (Ref. [36]) and Ni poor $Ce(Cu_{1-x}Ni_x)_2Ge_2$ (Ref. [37]) show a phase transition, perhaps of itinerant magnetic origin, that takes place out of a local-moment type of AF ordered state.

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