Tetravalency and magnetic phase diagram in the heavy-fermion superconductor UPd_2Al_3

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Measurements of the dc susceptibility $\chi(T)$, dc magnetization, magnetoresistivity, and magnetostriction are utilized to delineate the magnetic B-T phase diagram of the antiferromagnetically ordered ($T_N = 14$ K) heavy-fermion superconductor ($T_c = 2$ K) UPd_2Al_3. The single-crystal data reveal three antiferromagnetic phases for $B\perp c$, but only one for $B\|c$. The anisotropic $\chi(T)$ in the paramagnetic state suggests a tetravalent configuration of uranium.

One of the essential open questions in heavy-fermion physics concerns the interference of antiferromagnetism and superconductivity of strongly renormalized carriers,[1] this question being related to the potential role of magnetic fluctuations in the Cooper pairing in heavy-fermion superconductors (HFS's).[2] Coexistence between HFS's and antiferromagnetism with extremely small ordered moments, $\mu_s \sim (2-3) \times 10^{-2} \mu_B$, was reported for URu_2Si_2[3] as well as UPt_3,[4] whereas this issue is still controversial for both $CeCu_2Si_2$ (Ref. 5) and UBe_{13} (Ref. 6). The discovery of the two homologs UM_2Al_3, which are antiferromagnetically ordered HFS's (Refs. 7–10) with $T_N = 4.6$ K and 14 K as well as $T_c = 1$ K and 2 K for $M = $ Ni and Pd, respectively, has increased the number of these interesting materials. Whereas the ordered moment of UNi_2Al_3, $\mu_s = 0.1$ μ_B,[9] exceeds μ_s of URu_2Si_2 and UPt_3 by a factor of 3–5 only, a μ_s value as large as 0.85 μ_B was reported[10] for UPd_2Al_3. This latter value is of the same order as μ_s of U_2Zn_{17} (Ref. 11) and Th- (and Pd-) doped UPt_3 (Ref. 4). Both systems share with UPd_2Al_3 (Refs. 12, 13, and 10) an easy magnetic, i.e., the hexagonal, plane. On the other hand, for both UNi_2Al_3 (Ref. 9) and tetragonal URu_2Si_2 (Ref. 3) an easy c axis was reported.

In this paper, we address the magnetic phase diagram of UPd_2Al_3, based upon dc susceptibility, dc magnetization, transverse magnetoresistivity, and magnetostriction measurements on single crystals. Three different antiferromagnetic phases are found if the magnetic field is applied within the hexagonal plane ($B\perp c$), whereas only one magnetic transition at $T = T_N$ can be resolved if $B\|c$. A combination of susceptibility measurements on polycrystalline samples up to $T = 650$ K and on single crystals ($T \le 300$ K) was used to get information about the ionic configuration of uranium in UPd_2Al_3. A tetravalent ($5f^2$, $J = 4$) state is found to be the most likely one, similar to earlier conclusions drawn for the Ni homolog.[14]

The polycrystalline sample ($T_c = 2$ K) was prepared and characterized as reported in Ref. 8. Three single crystals (with $T_c = 1.4$, 1.6, and 1.85 K) were grown by the Czochralski method.[13] All samples had the proper

CaCu₅-derived $PrNi_2Al_3$ structure and did not show secondary phases within the resolution of x-ray powder diffractometry and microprobe analysis (a few at. %). The single crystals (typically $1.5 \times 1.5 \times 6$ mm³) were oriented along the [210], [110], and [100] axes, respectively. Measurements of the dc susceptibility and dc magnetization at low fields ($B \le 0.01$ T) were carried out in a SQUID magnetometer designed to exhibit a very low remnant field ($\le 10^{-7}$ T). For the high-field ($B \le 5.5$ T) measurements, a commercial SQUID magnetometer (Quantum design) was utilized. Measurements of the isothermal magnetoresistivity $\Delta\rho(B)/\rho = [\rho(B) - \rho(0)]/\rho(0)$ ($T \ge 1.5$ K, $B \le 8$ T), and of the isothermal magnetostriction, $\Delta l(B)/l = [l(B) - l(0)]/l(0)$ ($T \ge 0.05$ K, $B \le 8$ T), were done using standard techniques.[15] From an angular-dependent single-crystal measurement of the susceptibility $\chi_\perp(\varphi)(B\perp c)$, no a/b anisotropy could be resolved within less than 5%.
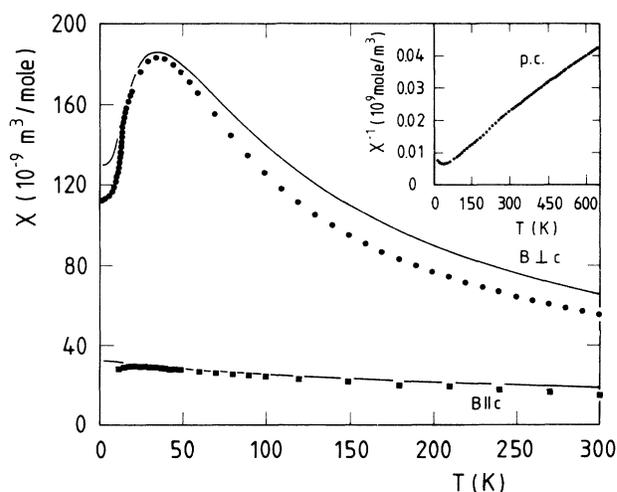
In Fig. 1 we show the results[12] of the paramagnetic sus-

FIG. 1. dc susceptibility at $B = 10^{-2}$ T vs temperature for UPd_2Al_3 single crystal: $B\|c$ (■) and $B\perp c$ (●), whereas the two solid lines are CF calculations. Inset: Inverse susceptibility vs T for a polycrystalline UPd_2Al_3 sample up to 650 K.

TETRAVALENCY AND MAGNETIC PHASE DIAGRAM IN THE . . .

ceptibility, $\chi_\perp(T)$ and $\chi_\parallel(T)$ (**B**$\parallel c$). Apart from a distinct anisotropy, indicating a magnetically easy basal plane, we mention the Curie-Weiss (CW) behavior found above $T \geq 100$ K for both $\chi_\perp(T)$ and $\chi_\parallel(T)$. At lower temperatures, the former exhibits a pronounced peak near $T = 35$ K, while the latter is of van Vleck type. The measurements on the polycrystalline sample reveal two linear regions in a plot χ^{-1} vs T, the i.e., for 100 K $\leq T \leq 300$ K and 350 K $\leq T \leq 650$ K; see the inset of Fig. 1. Fitting CW laws to these data, one finds an effective moment $\mu_{\text{eff}}^{\text{low}} \simeq 3.2\mu_B$ and a Weiss temperature $\Theta_W^{\text{low}} = -36$ K for the low-T region, while $\mu_{\text{eff}}^{\text{high}} \simeq 3.4\mu_B$ and $\Theta_W^{\text{high}} = -123$ K are derived at higher T.

We ascribe these observations to the dominating effect of crystal-field (CF) splitting of the localized $5f$ state of uranium, in accord with previous specific-heat results[14] and the single-crystalline susceptibility data, $\chi_\perp(T)$ and $\chi_\parallel(T)$. To understand the latter, we have assumed Russel-Saunders coupling and calculated $\chi_\perp(T)$ and $\chi_\parallel(T)$ for various CF splittings either of the $U^{4+}(5f^2, \mu_{\text{eff}}=3.58\mu_B)$ or the $U^{3+}(5f^3, \mu_{\text{eff}}=3.62\mu_B)$ configuration. The $5f^1$ state is discarded because of its small effective moment, $\mu_{\text{eff}}=2.54\mu_B$. Assuming trivalent uranium, we are able to describe qualitatively the pronounced maximum in $\chi_\perp(T)$, while $\chi_\parallel(T)$ is found to diverge as $T \rightarrow 0$, in contrast to the measured $\chi_\parallel(T)$. On the other hand, our data strongly suggest a tetravalent uranium state. This is not surprising in view of the strikingly similar anisotropy of the susceptibilities of UPd$_2$Al$_3$ and PrNi$_5$.[16] In the latter compound, which crystallizes in the CaCu$_5$ structure, the Pr^{3+} ($4f^2$) ions exhibit the same site symmetry as the U ions in UPd$_2$Al$_3$. The best fit to the single-crystal data in Fig. 1 was achieved with the CF-level scheme for U^{4+} displayed in Fig. 2. In these fits (solid lines in Fig. 1), intersite correlations have been accounted for by the following mean-field parameters, defined through $\chi^{-1}=\chi_{\text{CF}}^{-1}+a^{\text{mf}}$: $a_\parallel^{\text{mf}}=2\times10^7$ mole/m^3 and $a_\perp^{\text{mf}}=2.5\times10^6$ mole/m^3, respectively. Within this CF-level scheme, the pronounced maximum of $\chi_\perp(T)$ at $T=35$ K is explained by different van Vleck contributions due to the two low-lying singlets and the thermal population of the excited Γ_1 and Γ_6 states. Similar $\chi(T)$ maxima measured along the easy-plane/axis have also been observed for U$_2$Zn$_{17}$ (Ref. 17) and URu$_2$Si$_2$ (Ref. 18) and, for the latter compound, have likewise been attributed to a low-lying singlet belonging to the CF split $J=4$ multiplet of U^{4+} (Ref. 19).

The present single-crystal study reveals three different

$$1006\,K \; ==== \; |\Gamma_5\rangle = 0.2597\;|\mp2\rangle + 0.9657\;|\pm4\rangle$$
$$562\,K \; ---- \; |\Gamma_3\rangle = 1/\sqrt{2}\;(|+3\rangle + |-3\rangle)$$
$$152\,K \; ==== \; |\Gamma_5\rangle = 0.9657\;|\mp2\rangle - 0.2597\;|\pm4\rangle$$
$$102\,K \; ==== \; |\Gamma_6\rangle = |\pm1\rangle$$
$$33\,K \; ---- \; |\Gamma_1\rangle = |0\rangle$$
$$0\,K \; ---- \; |\Gamma_4\rangle = 1/\sqrt{2}\;(|+3\rangle - |-3\rangle)$$

FIG. 2. Crystal-field level scheme for U$^{4+}(5f^2)$ in UPd$_2$Al$_3$ used to calculate the anisotropic susceptibility $\chi(T)$ curves in Fig. 1.
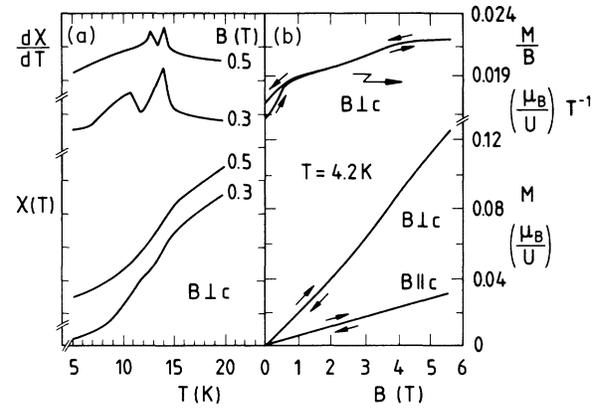

FIG. 3. (a) Susceptibility $\chi(T)$ vs T for **B**$\perp c$ at $B=0.3$ T and 0.5 T. Top: $d\chi/dT$ vs T at the same magnetic fields. (b) Magnetization curves at $T=4.2$ K for **B**$\parallel c$ and **B**$\perp c$. Top curve: $M(B)/B$ for **B**$\perp c$. The hysteresis loop at $B<1$ T is lacking any remnant magnetization.

antiferromagnetic regimes (I, II, and III) in the B-T diagram, if the magnetic field is applied parallel to the easy plane (**B**$\perp c$). The corresponding I-II and II-III transitions, which are *absent* for **B**$\parallel c$, manifest themselves in the results of the susceptibility, magnetization, magnetoresistivity and magnetostriction [Figs. 3(a) and 3(b), and 4(a) and 4(b)] and can be used to construct the phase diagram of Fig. 5(a). The critical field for antiferromagnetic ordering, $B_{\text{AFM}}(T)$, i.e., the boundary between phase III and the paramagnetic state, is obtained from the Néel temperatures, $T_N(B)$, read off either the break slope in $\chi_\perp(T)$ or the λ-type peak in $d\chi_\perp(T)/dT$ near 14 K displayed in Fig. 3(a). For $B \leq 5T$, $B_{\text{AFM}}(T)$ exhibits a vertical slope. At low temperatures it assumes a value of $\simeq 18$ T as recently shown by high-field magnetization measurements of de Visser et al.;[20] cf. Fig. 5(b).

The transition between phases II and III is reflected by (i) a second peak, at $T<T_N$, in $d\chi_\perp(T)/dT$ for fields $B>0.3$ T [Fig. 3(a)], (ii) an inflection point in the magnetization curve, e.g., near $B=4$ T for $T=4.2$ K [Fig. 3(b)], (iii) a break of slope in the transverse magnetoresistivity
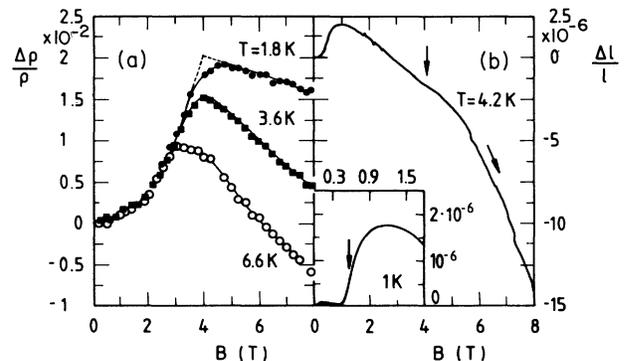

FIG. 4. (a) Isothermal transverse magnetoresistivity, $\Delta\rho/\rho$ vs B, for different temperatures $T<T_N$. (b) Isothermal magnetostriction, $\Delta l/l$ vs B at $T=4.2$ K upon increasing field. Inset: low-field results at $T=1$ K. Arrows mark phase transitions I-II and II-III; see text.

A. GRAUEL *et al.*

[Fig. 4(a)], and (iv) a very shallow "shoulder" in the magnetostriction [Fig. 4(b)]. No hysteresis effects are resolved for the II-III transition indicating that it is of second (or weakly first) order. Clearly, the transition line II-III hits (as $B \rightarrow 0$) the Néel temperature, which thus behaves as a "tricritical" point in the B-T plane.

Evidence for the transition from phase I to phase II (which sets in at $T_l = 12$ K for magnetic fields 0.01 T $< B \leq 0.3$T) stems from shallow maxima in $\chi_{\perp}(T)$, respectively, sharp ones in $d\chi_{\perp}(T)/dT$ [see Fig 3(a)] as well as from a distinct increase in both $M(B)/B$ [see the upper part of Fig. 3(b)] and $\Delta l(B)/l$ measured along [110] [see Fig. 4(b)]. The hysteresis found for the anomaly in $M(B)/B$ suggests that the I-II transition is of first order. The absence of a remnant magnetization seems to rule out domain-ordering effects (implying weakly ferromagnetic domain walls).[21] Strangely enough, no maximum can be resolved in $\chi(T)$ for fields smaller than 0.01 T. This suggests that, for such low fields, the transition at $T_l \simeq 12$ K is of higher than second order or removed by thermal fluctuations (hinting at a critical point on the I-II phase boundary). According to the magnetostriction results, the I-II transition persists in the superconducting state [cf. the inset of Fig. 4(b)].

Our measurements prove a complex magnetization process with the easy (a,b) plane of UPd_2Al_3, involving up to three steps depending on the temperature. According to the neutron-powder-diffraction results done at zero magnetic field by Krimmel *et al.*,[10] the antiferromagnetic structure of UPd_2Al_3 consists of ferromagnetically ordered planes alternating along the c axis, as described by the propagation vector $\mathbf{q} = (0,0,1/2)$ in reciprocal units of the chemical unit cell $(4\pi/(\sqrt{3}a), 4\pi/(\sqrt{3}a), 2\pi/c)$. In this structure, the U moments are aligned in the basal plane. In addition, an incommensurate structure was found to coexist with the $\mathbf{q} = (0,0,1/2)$ ordering at temperatures slightly below T_N and to disappear only upon heating the sample up to approximately $T = 20$ K.[10] No phase transition near 20 K can, however, be detected in the bulk measurements discussed in this paper. Instead, these measurements highlight a change in the magnetic structure below $T_l \simeq 12$ K (for $B > 0.01$ T). Future neutron-diffraction experiments on single crystals have to resolve the discrepancy to the powder-diffraction data. Concerning the existence of three different "in-plane structures" as suggested by Fig. 5(a), we refer to the $T = 0$ results of a recent local-density approximation (LDA) calculation by Sticht and Kübler:[22] apart from the $\mathbf{q} = (0,0,1/2)$ structure, two nearly degenerate additional types of moment arrangements in the basal planes, being energetically even more favorable than the former, have been obtained. One of them is a collinear structure with $\mathbf{q} = (1/\sqrt{3}, 0, 1/2)$ (the L point of the Brillouin zone), whereas the other one is noncollinear with $\mathbf{q} = (1/\sqrt{3}, 1/3, 1/2)$ (the H point of the Brillouin zone). Based upon the available experimental and theoretical results, we propose that phases I, II, and III correspond to the $\mathbf{q} = (0,0,1/2)$, $(1/\sqrt{3},0,1/2)$, and $(1/\sqrt{3},1/3,1/2)$ structures, respectively. Partial support for this assignment derives from the field dependence of the transverse magnetoresistivity [Fig. 4(a)]: a B^2 dependence of $\Delta\rho(B)$
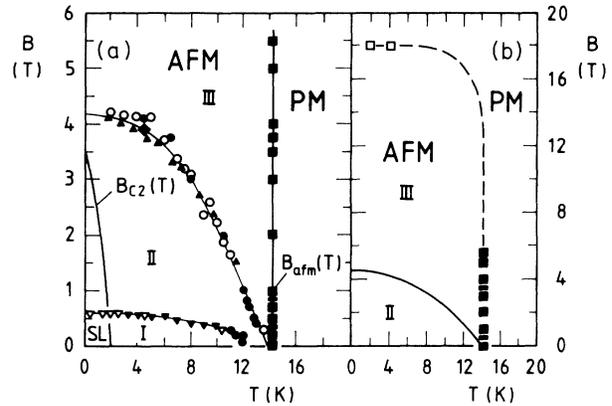

FIG. 5. (a) Magnetic phase diagram of UPd_2Al_3 for $B \perp c$ as constructed from results of dc susceptibility $\chi(T)$ ($\bullet$,$\blacksquare$), magnetization $M(B)$ ($\circ$,$\blacktriangledown$) magnetostriction $\Delta l(B)/l(\triangledown,\blacklozenge)$ and transverse magnetoresistivity ($\blacktriangle$). The transition I-II exists above and below $B_{c2}(T)$. (b) Partial phase diagram including the metamagnetic transition found (Ref. 20) for $T \leq 4.2$ K at $B = 18$ T ($\square$).

as observed in phase II is, in fact, expected for a collinear antiferromagnetic moment arrangement along the direction of the applied field.[23] Also, the field-induced transition to a noncollinear "in-plane" structure should cause a break in the slope of $\Delta\rho(B)$,[23] as found at the II-III transformation. The low-T magnetization demonstrates only small changes at the two low-lying transitions [Fig. 2(b)], which is not surprising for reorientation processes with the antiferromagnetic structure. By contrast, for the transition from phase III into the paramagnetic state, which takes place at $B = 18$ T for $T \leq 4.2$ K, a factor of 3 increase in the $M(B)/B$ data was reported.[20] Neutron-diffraction experiments on single crystals are necessary to check the assignments anticipated from the present results. In particular, the existence or nonexistence of a critical point near $T = 12$ K and $B = 0.01$ T remains to be clarified.

In conclusion, the anisotropy of the temperature dependence of the susceptibility in the paramagnetic state of UPd_2Al_3 supports strongly a tetravalent ground-state configuration of uranium. Like URu_2Si_2,[19] UPd_2Al_3 is identified as another heavy-fermion compound showing a singlet CF ground state within a tetravalent ionic configuration of uranium. This may imply that the ordinary (one-channel) Kondo mechanism is not sufficient to explain heavy-fermion formation in UPd_2Al_3 and, therefore, more general models have to be applied.[24] The magnetization process within the easy magnetic plane of UPd_2Al_3 passes through three phase transitions whose natures have to be unraveled by future neutron-diffraction work. Since the transition at the lowest field, $B < 0.5$ T, remains unchanged in the superconducting state, we conclude that antiferromagnetic ordering, i.e., in both phase I and phase II, coexists with heavy-fermion superconductivity down to, at least, $T = 50$ mK. Further on, no substantial superconductivity-induced changes in

the antiferromagnetic order are expected on the basis of the experiments presented in this paper.

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