U_2PtC_2 and Systematics of Heavy Fermions

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Our results for superconducting U_2PtC_2 place it intermediate to heavy-fermion (UBe_{13}, UPt_3) and less anomalous (U_6Fe) superconductors. Heavy-fermion behavior represented by the electronic specific heat correlates well with spacing between f-electron atoms in U, Np, and Ce materials. Two regimes of spacing are evident and arise from direct and indirect interactions between f-electron atoms. We suggest that this correlation provides a reasonable criterion for heavy-fermion behavior and a test for theories.

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The highly unusual low-temperature properties of heavy fermions exhibited by certain compounds formed with cerium, uranium, neptunium, and perhaps plutonium originate with nearly localized f electrons. Strong electron correlations dominate the low-temperature properties and lead to enormous electronic specific heats and heavy effective masses on the order of 200 times the free electron mass. This extreme electronic ground state is compatible with a broad spectrum of phenomena[1] that includes superconductivity ($CeCu_2Si_2$,[2] UBe_{13},[3] UPt_3[4]), itinerant magnetism ($NpBe_{13}$,[5] U_2Zn_{17},[6] UCd_{11}[7]), Kondo-type behavior ($PuBe_{13}$[5]), coexistence of superconductivity with spin fluctuations (UPt_3[4]), and neither superconductivity nor magnetism ($CeAl_3$,[8] $CeCu_6$[9]). Moreover, the low-temperature properties of UBe_{13} and UPt_3 are so anomalous[1] that they have prompted claims that these compounds may be examples of p-state rather than s-state superconductivity.[10–13] While much emphasis has been placed on this question of unconventional superconductivity, little progress has yet been made toward an understanding of the development of the heavy-fermion state itself[14] although evidence suggests that heavy-fermion behavior exists independently from the occurrence of superconductivity or magnetism.[15,16] The superconductor[17] U_6Fe also has unusual low-temperature properties compared to more ordinary (i.e. non-f-band) superconductors,[18] but is considerably less anomalous than the heavy-fermion materials. In this Letter we report a characterization of another uranium superconductor, U_2PtC_2, and find it to have properties intermediate between those of U_6Fe and those of the heavy-fermion systems UBe_{13} and UPt_3. This compound now allows the systematics of the properties of itinerant f-electron systems to be examined more continuously over the complete range of electron masses. The evidence we present suggests that the spacing between f-electron atoms is an important parameter relating the electronic specific heat to nearly localized f-band formation.

The occurrence of superconductivity at 1.47 K for U_2PtC_2 has been known for fifteen years.[19] Its crystal structure is body-centered tetragonal with lattice parameters $a_0 = 3.52$ Å and $c_0 = 12.54$ Å.[19] We prepared samples of U_2PtC_2 by arc melting and then annealing in vacuum at 1300 °C for 3 h. Metallographic examination revealed large-scale inhomogeneous distributions of secondary phases, and the measurements reported below were performed on selected pieces that were at least 95% single-phase U_2PtC_2. Our x-ray and superconductivity measurements were in good agreement with the previous work.[19,20]

The electrical resistivity of U_2PtC_2 shown in Fig. 1 is very similar to that of U_6Fe[21] and UPt_3.[4] We

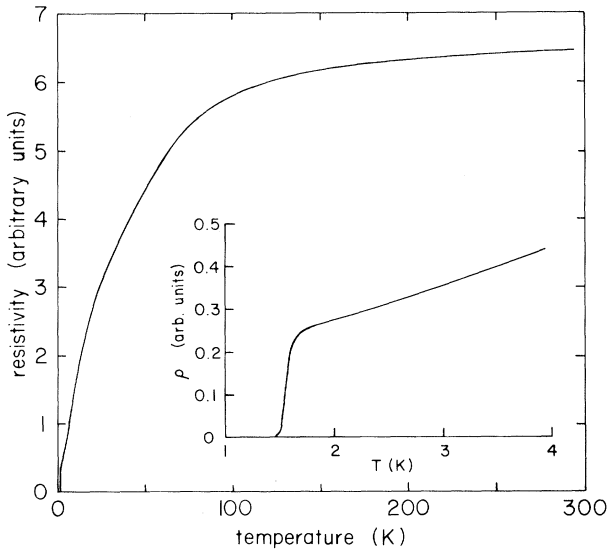

FIG. 1. The electrical resistivity of U_2PtC_2. At room temperature the absolute resistivity is 254 $\mu\Omega$ cm, and the residual resistance ratio is ~25. The low-temperature resistivity and the superconducting transition are shown in the inset.

observe that the anomalous curvature present in *s-d* superconductors[21] is even more anomalous for these materials, developing ultimately into a peak at low temperatures for the extreme cases of UBe_{13}, $CeCu_2Si_2$, $CeAl_3$, and $CeCu_6$.[1] Our specific-heat measurements on U_2PtC_2 confirm bulk superconductivity at 1.47 K and yield an electronic specific-heat coefficient of $\gamma = 75$ mJ/(mole *f*-atom)$\cdot$K^2 and a Debye temperature of $\theta_D = 273$ K. The initial slope dH_{c2}/dT of the upper critical field H_{c2} measured resistively in fields up to 4 kOe is -90 kOe/K. The magnetic susceptibility χ of U_2PtC_2 determined from the slope dM/dH of the magnetization M at fields H between 12 and 30 kOe was found to be very weakly temperature dependent, increasing from 1.5×10^{-3} emu/(mole *f*-atom) at 150 K to 2.2×10^{-3} emu/(mole *f*-atom) at 4 K. The expected magnetic susceptibility from the measured specific heat is given by

$$\chi_{calc} = 3\mu_B^2\gamma/\pi^2 k_B^2,$$

where μ_B is the Bohr magneton and k_B is Boltzmann's constant. The ratio of the measured to calculated susceptibility, which reflects the degree of exchange enhancement, is at most 2.1, if we use the low-temperature value of χ, and is about 1.6 if we use the value of χ at 150 K.

Our results for U_2PtC_2 are summarized in Table I together with the results for the other uranium superconductors. The compounds are listed in the order of decreasing γ, and we note that the superconducting-state properties T_c and dH_{c2}/dT do not correlate with γ, nor with each other. This is not unexpected since superconductivity is very sensitive to many factors besides γ (viz., crystal structure, anisotropy, phonons). The normal-state properties γ and χ are both proportional to the density of states at the Fermi energy and do correlate well with each other. For the compound UBe_{13}, χ/χ_{calc} is unity and is interpreted as a demonstration that its enormous low-temperature specific heat is indeed of electronic origin.[3] Although the susceptibilities of the other uranium superconductors show a small exchange enhancement ($\chi/\chi_{calc} > 1$) which tends to be larger for smaller γ's, the relationship between γ and χ is that expected for a purely itinerant-electron system. The lower value of $\chi = 1.5\times10^{-3}$ emu/(mole *f*-atom) for U_2PtC_2 is more consistent with this trend, and may contain a small impurity contribution.

Most systems of nearly localized *f* electrons favor magnetism rather than superconductivity. A general criterion for superconducting versus magnetic *f* electrons put forward by Hill[26] is based on the systematic occurrence of these two phenomena as a function of the spacing between the *f*-electron atoms. At sufficiently short spacings ($\lesssim 3.4$ Å for uranium), the direct *f*-atom interactions lead to the formation of *f* bands that are too broad to support magnetism. As the spacing increases, the interaction cuts off at a characteristic spacing determined by Hill (~ 3.6 Å for uranium) beyond which the *f* electrons tend to localize, and thereby become magnetic. This describes the basic features of the Hill plots of uranium, cerium, neptunium, and plutonium materials.[26] In the presence of strong hybridization of the *f* electrons with electrons on neighboring non-*f*-electron atoms, a competition can exist between localized *f* electrons and itinerant hybridized *f* bands even when no direct overlap between *f*-electron atoms is present. The compounds UBe_{13} and UPt_3, for example, fall well into the magnetic region of the Hill plot and yet are superconductors.

Table I lists the U-U spacings for the uranium su-

TABLE I. Selected physical properties of uranium superconductors.

Compounds	T_c[a] (K)	$-dH_{c2}/dT$ (kOe/K)	γ [mJ/(mole *f*-atom)$\cdot$K^2]	$\chi\times10^4$ [emu/(mole *f*-atom)]	χ/χ_{calc}[b]	U-U spacing (Å)	Refs.
UBe_{13}	0.8	440	1100	151	1.0	5.13	3,22
UPt_3	0.5	63	450	89	1.4	4.1	4,23,24
U_2PtC_2	1.47	90	75	15–22	1.6–2.1	3.52	c
U_6Fe	3.8	34	25	5.0	1.5	3.2	18
α-U	2.1	?	12	3.7	2.3	3.12	25

[a]Superconducting transition temprature.
[b]See text for definition of χ_{calc}.
[c]This work.

perconductors, which clearly correlate with γ and χ. This implies that the separation of the f-electron atoms in heavy-fermion systems remains an important parameter, even at large spacings, presumably describing the effective width of the hybridized f band. In Fig. 2 the quantity γ is plotted as a function of f-atom spacing, and the superconductors (filled circles) exhibit a smooth variation of γ with spacing. To show how this correlation extends to itinerant f-electron systems in general, the results for other uranium, neptunium, and cerium compounds are also plotted in Fig. 2, including all such materials having γ's larger than 300 mJ/(mole f-atom)$\cdot$K^2.[1] The large-γ magnets U_2Zn_{17} and UCd_{11} follow the same correlation as the uranium superconductors. The downturn at very large spacings is expected since γ must vanish for completely localized f electrons in the limit of infinite separation. The properties of materials having smaller γ's are less dominated by the narrow f bands, and there are obviously many low-γ materials with relatively large f-atom spacings.[1] Thus the existence of large γ's is a distinguishing feature, and hence the curves in Fig. 2 are based on those materials having the largest γ's we found for a given spacing. Two regimes can be distinguished in both the $4f$ (open symbols, dashed curves) and $5f$ (filled symbols, solid curves) systems. At sufficiently short spacings, *direct* f-atom interactions prevail, leading to roughly an exponential dependence of γ on spacing. We note that compounds of ytterbium appear to follow this trend as well. The displacement of the $4f$'s to the right of the $5f$'s in this regime is a consequence of the larger metallic size[28] of the $4f$ elements. At large spacings, the delocalization of the f electrons must be accomplished by intervening atoms. In this *indirect* f-atom interaction regime, where the metallic size of the f atoms becomes unimportant, the intrinsically narrower $4f$ bands lead to larger γ's but follow the same dependence on spacing as the $5f$'s. When the indirect hybridization yields insufficient delocalization of the f electrons, the development of the heavy-fermion state is inhibited; hence the existence of low-γ materials with large f-atom spacings. Thus, an extreme or special condition of f-electron delocalization and band formation is represented by the curves in Fig. 2 by virtue of the occurrence of superconductivity.

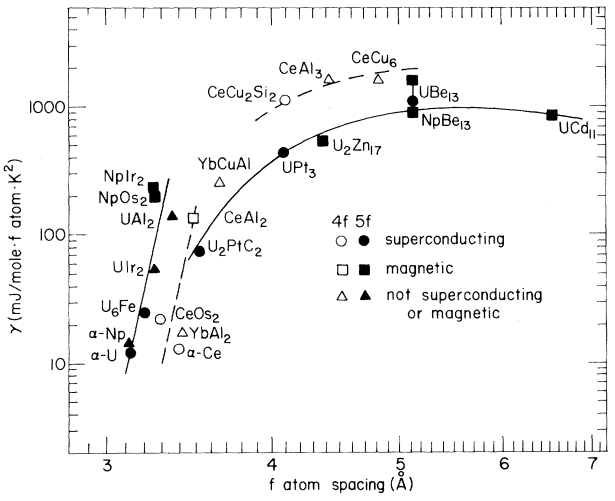

FIG. 2. The electronic specific-heat coefficient γ vs f-atom spacing plotted on logarithmic scales for $4f$ (open symbols, dashed lines) and $5f$ (filled symbols, solid lines) atoms in superconducting (circles), magnetic (squares), and neither superconducting nor magnetic (triangles) materials. The values for γ (Ref. 27) are extrapolated from above the superconducting or magnetic transitions except for $NpBe_{13}$ where the upturn in the specific heat accompanying the development of the heavy-fermion state is obscured by the magnetic ordering.

We have presented new results on the superconductor U_2PtC_2 that place it intermediate between the heavy-fermion materials, such as UBe_{13} and UPt_3, and the less anomalous materials, such as U_6Fe and α-U. The systematic occurrence of heavy-fermion behavior represented by the specific-heat coefficient γ as a function of the spacing between f atoms holds for uranium, neptunium, and cerium systems. We believe this correlation for heavy-fermion systems of γ with spacing in the regime of indirect f-atom interaction may constitute a reasonable criterion for heavy-fermion behavior. Ytterbium-based heavy-fermion systems are thus not yet known to exist even though ytterbium and cerium behave similarly in the direct f-atom interaction regime. The f-atom spacing not only is important for distinguishing the two regimes of f-atom interaction, but also plays a role in determining crucial parameters of the nearly localized f bands that lead to heavy-fermion behavior. We therefore suggest that the correlation of γ with spacing for heavy-fermion systems provides a test for theoretical descriptions of the heavy-fermion state.

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