Modification of the Fermi-Surface Instability in UPt_3 by Th Substitution

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(Received 21 March 1986)

The magnetic susceptibility, specific heat, and electrical resistance of $U_{1-x}Th_xPt_3$ have been studied for x between 0.01 and 0.10 at temperatures between 1.5 and 20 K. In addition to the well known heavy-fermion behavior, at 6.5 K a Fermi-surface instability is observed and it is concluded that the superconducting ground state in UPt_3 is replaced by a spin-density wave. This result demonstrates the delicate balance between superconductivity and magnetism in UPt_3.

PACS numbers: 72.15.Nj, 75.20.Hr

Heavy-fermion (HF) compounds are interesting because they display a rich variety of unusual ground states, in addition to their strongly renormalized electronic properties.[1] These ground states include superconductivity with extreme gap anisotropies, and itinerant-electron magnetism, which can both be described by Fermi-surface (FS) instabilities. Among the HF compounds, superconducting UPt_3 is unique since its resistivity decreases monotonically upon cooling—in contrast to the "Kondo lattice" resistance rise normally observed—and since its low-temperature specific heat provides good evidence for spin fluctuations in a Fermi liquid.[2] It seems likely that the uniqueness of UPt_3 is partly rooted in a peculiar Fermi surface, which in turn is the result of a well-defined quasiparticle band structure. If this view is correct, then one would expect that the superconducting ground state in UPt_3 would be quite sensitive to impurity doping, since impurities modify the band structure via distortions of the lattice. To test this idea we have studied the low-temperature thermodynamic behavior of the dilution series $U_{1-x}Th_xPt_3$ for small x (< 0.10).

The results show that the superconducting transition is rapidly suppressed by substitution of nonmagnetic Th and is replaced at $T_0 = 6.5$ K by a new spin-density-wave (SDW) instability, involving only a small portion of the FS. This supports the idea that the spin fluctuations in UPt_3 can lead to either a superconducting or a magnetic ground state, depending on FS details, which can be easily modified.

The samples were prepared from high-purity uranium starting material by arc melting in argon atmosphere. The polycrystalline product consists of several macroscopic needlelike crystals (typical for UPt_3) which are well oriented with respect to each other. Diffractograms were obtained in a Gandolfi camera to avoid any strain induced by powdering. Both lattice parameters of the hexagonal $P6_3/mmc$ structure were found to increase from their $x=0$ values of $a_0 = 5.750(2)$ Å and $c_0 = 4.897(2)$ Å as the percentage of the (larger) Th ions is increased. The unit-cell volume change $\Delta V/V$ is 3.8×10^{-4} per 1% Th substitution and the c/a ratio decreases slightly from 0.8517(5) at $x=0$ to 0.8511(5) at $x=0.10$. No broadening of the lines can be detected up to 20% Th concentration, but it is clearly visible for specimens exceeding 40% Th. The smooth variation of the lattice parameters, the sharpness of the diffraction lines, and the absence of any additional reflections is evidence for phase purity up to at least $x=0.10$, the region of interest in this investigation.

The susceptibility was measured with a S.H.E. squid magnetometer. A standard adiabatic heat-pulse technique was used to measure the specific heat, and the electrical resistance was measured with a four-probe technique at 93 Hz.

Figure 1 shows the magnetic susceptibility as a function of temperature for several samples with varying dopant concentrations. We find the expected maximum in χ at ~ 17 K for the pure UPt_3. As the Th concentration is increased, the $\chi(T)$ curves change in two ways. First, for the lower Th concentrations, the temperature of the maximum decreases until, at 2.7%, it becomes a poorly defined plateau, centered at 10 K. Second, for the higher Th concentrations, up to 10%, a peak develops at $T_0 \approx 7$ K and remains remarkably constant in temperature. It disappears, however, at $x = 20\%$. (The two samples denoted by dashed lines were made in a different series from the others, with different starting materials and in different size melts.) Figure 2 shows the specific heat of the 3%, 5%, 7%, and 19% Th-doped samples. We note the appearance of pronounced peaks, corresponding in temperature to the susceptibility anomalies, superimposed on a background very similar to that of pure UPt_3. In all of the doped samples studied, superconductivity was suppressed at least down to 50 mK. This is to be contrasted with the case of UBe_{13}, where T_c is rather weakly suppressed by doping. Particularly, for Th doping,[3-5] a second order parameter, possessing magnetic signatures, develops within the superconducting state.

The temperature dependence of the resistance for $T > 100$ K is the same as for pure UPt_3, but the disorder caused by the Th results in a higher residual resistance at low T. The most significant difference, how-

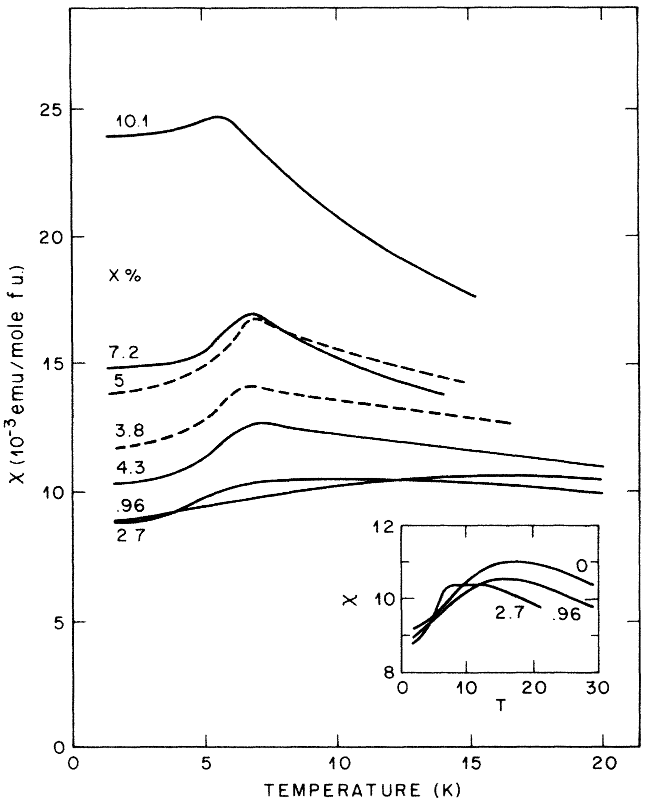

FIG. 1. The susceptibility of $U_{1-x}Th_xPt_3$ as a function of temperature for several different dopant concentrations. The dashed lines correspond to samples grown from different starting materials and in different size melts from the rest. Inset: Comparison between the pure UPt_3 and the two lowest concentration samples, on a reduced scale.

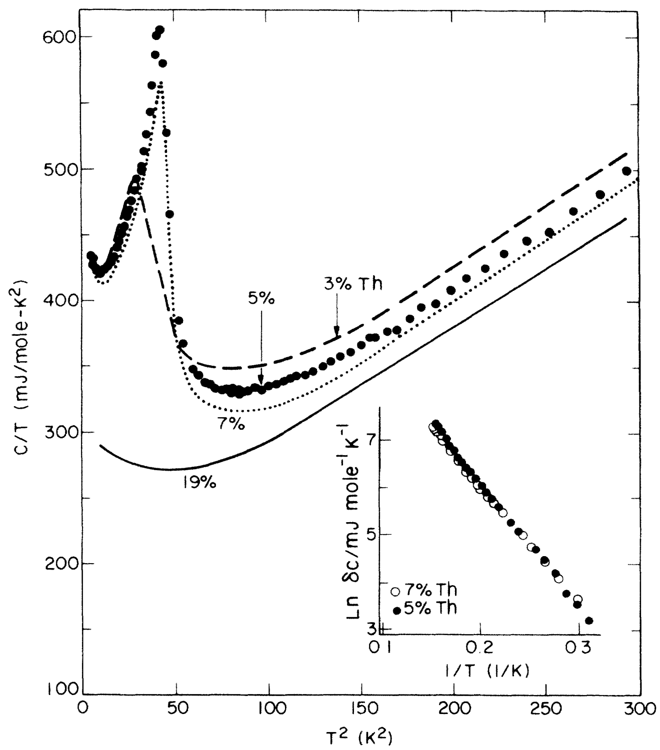

FIG. 2. C/T for $U_{1-x}Th_xPt_3$ for 3%, 5%, 7%, and 19% Th concentration, as a function of T^2. Only the raw data for the 5% sample are shown, with the other data represented by lines for the sake of clarity. Inset: Arrhenius plot of the impurity-related contribution for the 5% and 7% samples. The activation energy Δ is 26 ± 2 K, and $\Delta/T_0 = 4$.

ever, is given in Fig. 3 for a 5% sample in the temperature interval up to 12 K, with applied fields of 0 and 5 T. Superimposed on the sloping background is an additional contribution, indicated by hatching in the diagram. Conventional ideas about local-moment magnetic ordering cannot explain this upswing of the resistance, which is magnified in the inset. This type of effect is, rather, a well-established hallmark of a transition that removes part of the FS. (The formation of a SDW in chromium is a prototype for such a transition.) Furthermore, the small suppression of T_0 by only 0.25 K in a 5-T field is much smaller than expected for local-moment antiferromagnetic ordering. It is, however, within factors of 2, the same as found for other heavy-fermion compounds which undergo FS-instability transitions.[6] We thus conclude that the electrons involved in the transition in (U,Th)Pt_3 are of an itinerant nature.

To illustrate further the relationship among the anomalies associated with this phase transition, we have plotted in Fig. 4, for the 5% sample, the susceptibility, dR/dT, and the specific heat, adjacently. Here we see that the minimum in dR/dT coincides exactly with both the inflection point in the susceptibility and the maximum in the specific heat. This behavior (though clearly not indicative of local-moment order-

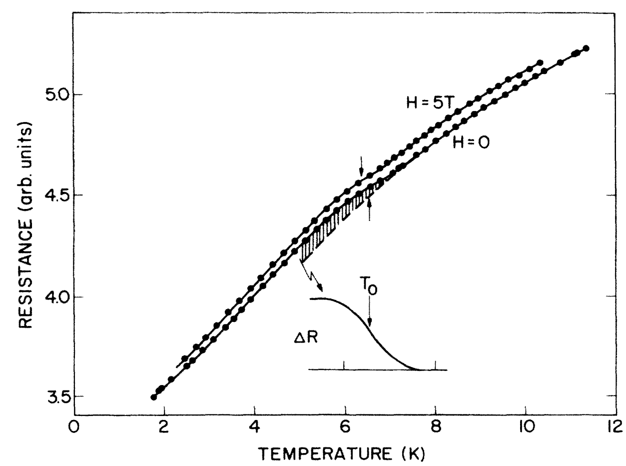

FIG. 3. The resistance of $U_{0.95}Th_{0.05}Pt_3$ as a function of temperature for 0 and 5 T, with the minima in dr/dT denoted by arrows. Inset: Growth of the hatched region for the zero-field curve, obtained by subtracting off the expected behavior for pure UPt_3.

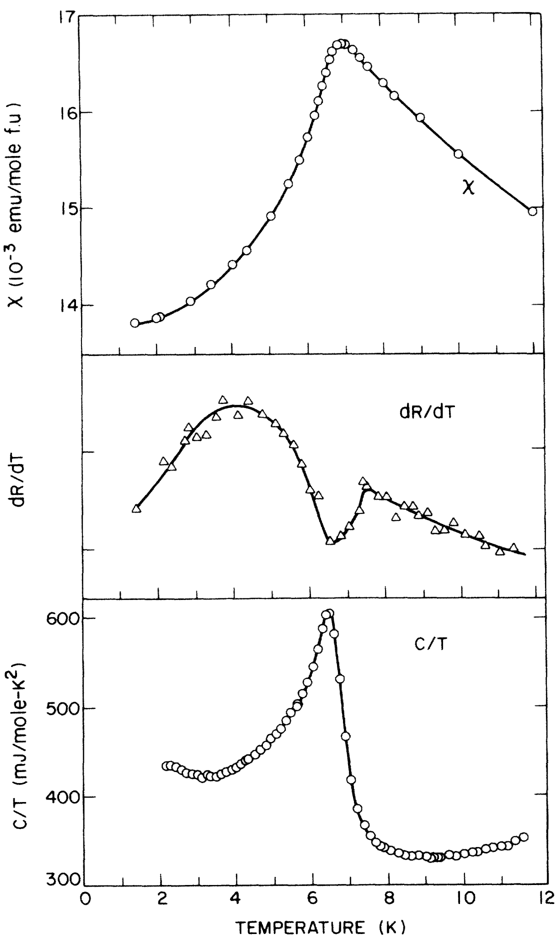

FIG. 4. Comparison of the susceptibility, dR/dT, and C/T for the 5% Th-doped sample. Note that the peak in the specific heat, the local minimum in dR/dT, and the inflection point in the susceptibility all coincide, indicating an itinerant-electron antiferromagneticlike transition.

ing) is characteristic of a spin- or charge-density-wave (CDW) transition, in which a gap in the electronic excitation spectrum is developed for certain regions in reciprocal space. Below the transition temperature T_0, the quasiparticles excited across the gap contribute to the specific heat, and their contribution, δC, grows exponentially with T, provided that the gap extends over regions of the Fermi surface larger than lines or points. To show that the specific-heat anomaly in Th-doped UPt_3 falls into this category of phase transition, we analyzed the associated specific-heat change, δC, by subtracting from the values below T_0 a background characteristic of pure UPt_3. In Fig. 2 we show an Arrhennius plot of this excess specific-heat peak, which indeed follows an activation law of the form $\delta C = A\exp(-\Delta/T)$, with an activation energy of $\Delta = 26 \pm 2$K, and $A = 110$ J/mole-K. The ratio $\Delta/T_0 = 4.0$ is substantially larger than the BCS weak-coupling value of 1.73. *The exponential behavior of the excess specific heat, in addition to the resistance slope change, provides the main evidence for the development of a gap on the FS.* We determined the fraction of the FS involved in the transition by estimating the excess entropy developed and comparing it to the entropy of pure UPt_3. Accordingly, (10 ± 2)% of the FS is removed by the transition, on the assumption that the mass enhancement (m^*) of the affected FS part is the same as the average. This is reasonable only for a rough estimate because one has to keep in mind that the mass enhancement due to quasiparticle band structure as well as due to spin fluctuations is expected to be highly anisotropic.

Two additional observations allow one to speculate about the nature of the ordered state. First, one knows that when a gap opens because of SDW or CDW formation, the magnetic susceptibility is reduced. Although the fractional change in χ can be estimated only rather imprecisely since the behavior in the ordered phase is not known, a simple extrapolation of the $\chi(T)$ curve below T_0 suggests a decrease in χ by roughly $\frac{1}{4}$ to $\frac{1}{3}$. Keeping the limitations in mind, one concludes that the susceptibility associated with the gapping part of the FS is larger than the FS average, thus supporting the existence of a SDW instead of a CDW. Second, recent neutron-scattering measurements on pure UPt_3 single crystals[7] reveal an enhancement of spin fluctuations at the Brillouin-zone boundary. Assuming that Th substitution leads to a stabilization of these antiferromagnetic fluctuations, one would again expect a SDW rather than a CDW.

Any attempt to explain the microscopic mechanism behind the formation of a SDW in (UTh)Pt_3 will be highly speculative at this stage: Even for the pure system the band structure of the fully renormalized quasiparticles is not known experimentally.[8] However, conventional band-structure calculations[9] indicate a complicated FS for the unrenormalized electrons and one would expect the related anisotropies to persist into the HF regime. Nevertheless, as a starting point for an empirical understanding, one can ask what Th substitution does to the lattice. An important investigation in this regard is the recent study of the dilution series U(Pt,Pd)$_3$ by deVisser *et al.*,[10] where ordering phenomena quite similar to that in (U,Th)Pt_3 were observed with the replacement of Pt by ~ 5% Pd (though these samples were not characterized by their resistance and were not analyzed in terms of a FS instability). Both Th and Pd substitution lead to a smaller c/a ratio, and we believe this to be an important factor for the observed transitions.

The main point of this study is not only to establish the existence of a SDW or CDW in a HF system —other compounds such as U_2Zn_{17},[11] UCd_{11},[12] UCu_5,[13] and URu_2Si_2[14] also undergo transitions which remove part of the Fermi surface. The main point is, however, to demonstrate the remarkable result that substitution of only a few percent of a nonmagnetic species in UPt_3 destroys superconductivity and brings about a new, magnetic ground state, supporting the view that superconductivity in UPt_3 is not the conventional phonon-mediated type, but rather results from an interaction involving spin-carrying excitations. Of particular relevance to theory is the fact that the present results, in addition to those obtained from neutron scattering, imply that the spin fluctuations in UPt_3 are dominantly antiferromagnetic $[\chi(q)_{max} = \chi(k_{BZ})]$ as opposed to ferromagnetic $[\chi(q)_{max} = \chi(0)]$, as is commonly inferred from a $T^3 \ln T$ term in the specific heat. The q dependence of the effective potential arising from spin fluctuations places severe constraints on the symmetry of the superconducting pair wave function, and recent calculations[15] indicate that, in particular, antiferromagnetic fluctuations enhance anisotropic even-parity pairing, while suppressing odd-parity pairing.

We wish to acknowledge useful discussions with E. Abrahams, G. Aeppli, D. J. Bishop, C. M. Varma, and R. G. Wheeler. We also acknowledge the hospitality of W. P. Wolf and thank D. Face for technical help with the specific-heat measurements which were done at Yale University and supported in part there by the National Science Foundation under Grant No. DMR 821622.

Note added.—While drafting this Letter, we received a preprint by Stewart *et al.*[16] which contained a similar investigation of the dilution series of both $(U,Th)Pt_3$ and $U(Pt,Pd)_3$, and results which support our main conclusions.

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