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Superconducting and Magnetic Transitions in the Heavy-Fermion System URu_2Si_2

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The intermetallic compound URu_2Si_2 can be classified as a heavy-fermion system because of its large linear specific-heat coefficient $\gamma = 180$ mJ/mol·K^2. Susceptibility, magnetization, and specific-heat measurements on single-crystal samples indicate *both* a magnetic phase transition at 17.5 K and a superconducting transition at 0.8 K. The magnetic and superconducting properties are highly anisotropic.

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Despite an intense theoretical interest in heavy-fermion systems,[1,2] there are no predictions as to which ground state will develop at low temperatures. Experimentally, three possibilities have been demonstrated: (i) the "bare" heavy-fermion materials characterized by their very large γ coefficients, e.g., $CeAl_3$[3] and $CeCu_6$,[4] (ii) the heavy-fermion superconductors such as $CeCu_2Si_2$,[5] UBe_{13},[6] and UPt_3,[7] (iii) the antiferromagnetically ordered heavy-fermion systems like U_2Zn_{17}[8] and UCd_{11}.[9] A fourth possibility exists, namely systems with both magnetic and superconducting order.[10]

During a systematic study of the magnetic properties of CeT_2Si_2 and UT_2Si_2 compounds[11] (T is a transition metal) we have found that one particular system, URu_2Si_2, exhibited a magnetic transition at 17.5 K and a very sharp superconducting one at 0.8 K. Our measurements included susceptibility, magnetization, and specific heat and were performed on high-quality, single-crystal samples. Both the magnetic and superconducting properties were observed to be highly anisotropic. Previously, indications for superconductivity in polycrystalline material were given by Schlabitz *et al.*[12] In this Letter we present our experimental evidence for the existence of anisotropic magnetic and superconducting order in URu_2Si_2. We limit our interpretation to a phenomenological description of the experimental effects.

We have prepared and studied one polycrystalline and two single-crystalline samples of URu_2Si_2. The purity of the elements was better than 99.8% for U, 99.96% for Ru, and 99.9999+% for Si. The polycrystalline sample (≈ 6 g) was fabricated by arc melting and was vacuum annealed for 7 d at 1000 °C. The single crystals (≈ 5 and 10 g) were grown with a specially adopted Czochralski "tri-arc" method[13] and no further heat treatment was performed. The high quality of our samples was established by x-ray analysis—*only* lines corresponding to the $ThCr_2Si_2$-crystal structure were observed—and microprobe and metallograph: *No* indications for inhomogenities or second phases were found. The lattice parameters were $a = 4.121$ Å, $c = 9.681$ Å for the polycrystal at 294 K; $a = 4.1279(1)$ Å, $c = 9.5918(7)$ Å at 294 K; and $a = 4.1239(2)$ Å, $c = 9.5817(8)$ Å at 4.2 K for the single crystals. Consequently, there are no distortions or changes in symmetry between 300 and 4.2 K.

Specific heat was measured on the polycrystalline sample with an adiabatic heat-pulse method, using a sapphire substrate, an evaporated heater, and a bare-element glass-carbon thermometer. Magnetization was measured with a Foner vibrating-sample magnetometer in magnetic fields up to 5 T and from 1.4 up to 300 K on two oriented single-crystalline cylinders, shaped by spark erosion. ac susceptibility was measured on an oriented sphere, shaped by spark erosion, down to 0.33 K with a standard mutual-inductance bridge operating at a frequency of 87 Hz. The ac driving field was 0.5 Oe and a dc magnetic field parallel to the driving field could be applied up to 3 T. Experiments in the different orientations were performed by cementing the sphere, after fixing the orientation, to an epoxy cylinder which fitted exactly into the primary coils. The Meissner effect and magnetization below 1 K were determined exactly in the same manner as described earlier.[14]

In Fig. 1 we show the specific heat of annealed polycrystalline URu_2Si_2 plotted as C/T vs T and C/T vs T^2. The magnetic transition (see below) is clearly discerned by a λ-like anomaly at 17.5 K. The superconducting transition exhibits a peak at 1.1 K. Extrapolation of the high-temperature regime yields a value for $\gamma = 180$ mJ/mol·(formula unit)·K^2 and a Debye temperature $\Theta_D = 312$ K. Use of these values in the entropy plot (C/T vs T) results in a negative entropy balance of $-0.166R$. This value is comparable to the values obtained for U_2Zn_{17} and UCd_{11}, $-0.165R$ and $+0.196R$, respectively.[15] In addition the relative change in γ between the extrapolated and observed values at 0 K, $(\gamma_{ext} - \gamma_{obs})/\gamma_{ext} = 72\%$ for URu_2Si_2, is very similar to the 70% for U_2Zn_{17} and the 63% for UCd_{11}.[15]

Figure 2 shows the dc magnetizations measured in a magnetic field $\mu_0 H = 2$ T ($\chi_{dc} = M/\mu_0 H$) parallel to

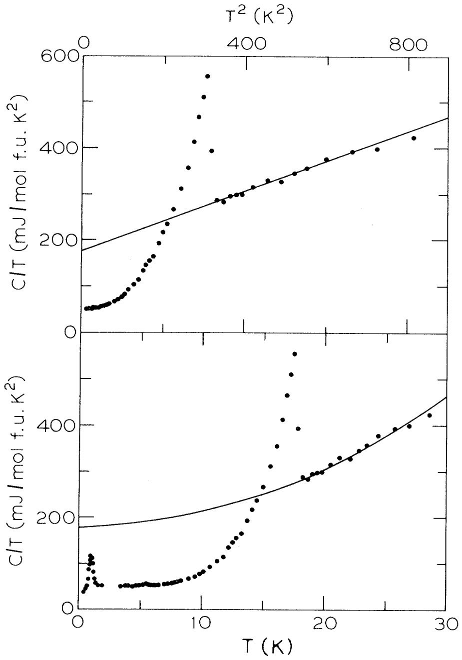

FIG. 1. Specific heat of URu_2Si_2 plotted as C/T vs T^2 (above) yielding γ and Θ_D, and as C/T vs T (below) showing the entropy balance.

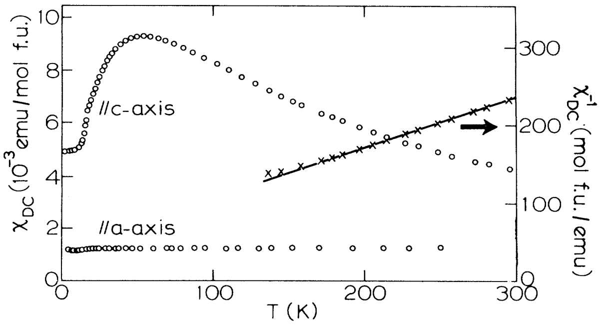

FIG. 2. dc susceptibility χ_{dc} and inverse susceptibility of URu_2Si_2, measured in a field of 2 T, parallel to the a and c axes. The crosses represent the inverse susceptibility along the c axis and yield $\theta_{CW} = -65$ K.

the a and c axes. The magnetization is clearly very anisotropic and the c axis is the easy axis with very little magnetization parallel to the a axis. The Néel temperature, if the transition is considered to be antiferromagneticlike, can be defined as the maximum of $d(\chi T)/dT$ and occurs at 17.5 K.[16] This value corresponds exactly with the anomaly in the specific heat. The high-temperature data along the c axis yield an effective moment $\mu_{eff} = 3.51\mu_B$/(formula unit) and a Curie-Weiss temperature $\Theta_{CW} = -65$ K. Note, however, the deviations from Curie-Weiss and the reduced μ_{eff} already beginning at ≈ 150 K.[17] The room-temperature dc susceptibility of URu_2Si_2 is about 30 times larger than for $ThRu_2Si_2$.[18]

In Fig. 3 we plot the superconducting transition temperature, defined as the 50% point of the transition in the ac susceptibility (see inset of Fig. 3), as a function of the magnetic field, parallel to the a axis and parallel to the c axis. For strong-pinning, type-II superconductors this represents a determination of H_{c2}. No corrections were made for the demagnetizing effects $[D(\text{sphere}) = \frac{1}{3}]$ for both directions. The transitions are all very sharp: ΔT between the 10% and 90% points is 0.015 K. This further demonstrates the homogeneity of our samples. We have very carefully corrected for the magnetic field dependence of the thermometer. The initial slope $-\mu_0\, dH_{c2}/dT$ as $T \rightarrow T_c$ is the same in both directions, viz. 4 T/K. However, as T is reduced the slope decreases parallel to the c axis (as is usual), but it increases strongly reaching 14 T/K parallel to the a axis. Note that it is the hard-magnetic a axis which exhibits the largest and most atypical $H_{c2}(T)$ behavior.

Figure 4 displays one of a series of curves of magnetization (M) versus magnetic field (H) in the superconducting state. The initial slope represents a superconducting volume fraction of more than 80%. This, we argue below, is convincing evidence that the superconductivity must be ascribed to the bulk. The $\mu_0 H_{c1}$ value (1.4 mT) obtained from this magnetization loop compared with the $\mu_0 H_{c2} = 0.86$ T determined from the ac susceptibility in the same direction yields a very large Ginzburg-Landau parameter $\kappa \approx 33$. Note in Fig. 4 the typical "type-II" shape of the M vs H curves which are fully reproducible upon cycling and independent of the reversing field amplitude. Other standard features are the nice overlap of the virgin

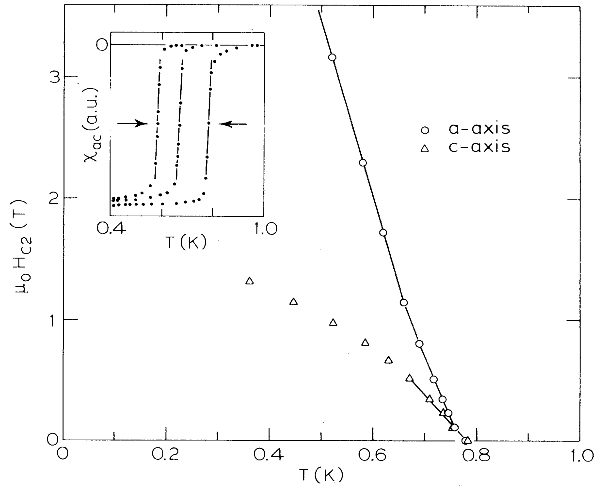

FIG. 3. Upper critical field $\mu_0 H_{c2}$ of URu_2Si_2 vs temperature parallel to the a and c axes. The inset shows three ac-susceptibility superconducting transitions measured parallel to the c axis in applied magnetic fields of 0, 0.52, and 0.81 T.

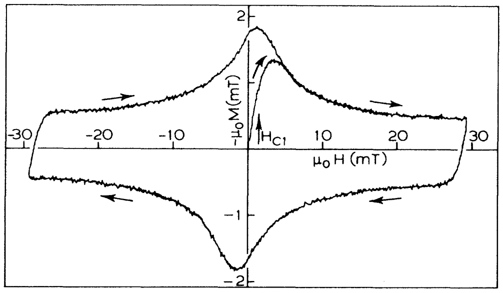

FIG. 4. Recorder trace of a magnetization loop (M vs H) with virgin curve at 657 mK. The field H was applied in an arbitrary direction.

curve with the field-cycled curves and that the initial and maximum- and minimum-field slopes are all equal.

Although the magnetization and specific-heat experiments indicate a magnetic phase transition at 17.5 K, nevertheless the exact mechanism for magnetism is not clear. The magnetization curve in 2 T shows a broad transition indicative of an antiferromagnetic ground state.[16] In contrast, we observe a very sharp transition in the specific heat which cannot be explained simply by a standard type of magnetic phase transition. The negative entropy balance and the large relative change in γ suggest that the transition must be accompanied by other effects of electronic or magnetostrictive origin. Neutron-scattering measurements are required to resolve this problem.

Very similar features have been observed for the heavy-fermion system U_2Zn_{17}.[8] Here also a broad magnetization curve was found accompanied by a λ-like anomaly in the specific heat, a similar relative change in γ, and a small, negative entropy balance. Although an ordinary magnetic phase transition cannot alone explain all these observations, yet neutron scattering[19] has verified the existence of a long-range ordered antiferromagnetic state. The close similarities in the specific heat of U_2Zn_{17} and URu_2Si_2 suggest that the magnetic phase transition should be of the same origin.

Additional information about the magnetism in URu_2Si_2 is obtained from our systematic study[11] of the CeT_2Si_2 and UT_2Si_2 compounds. Here we have determined a trend from antiferromagnetism to Pauli paramagnetism with decreasing number of d electrons. This trend was explained by an increasing Kondo-type compensation of the U moments as the number of d electrons is decreased and it eventually leads to a disappearance of the moment. Two systems, namely $CeCu_2Si_2$ and $CeRu_2Si_2$, lie on the borderline between antiferromagnetism and Pauli paramagnetism and they are usually described with a Kondo lattice model. As URu_2Si_2 also lies close to this border, the general trend suggests a "confined-moment" behavior,[2] although less severe than in $CeCu_2Si_2$ where the moments completely disappear. Still for URu_2Si_2 it is not clear to what extent this moment confinement proceeds at low temperatures before the superconductivity sets in or whether the superconductivity coexists with the magnetic order. Again, neutron scattering should be able to illuminate these questions.

We now will establish from our observations that the superconductivity must necessarily be a bulk property. The magnetization measurements were performed on a high-quality single crystal, with no contaminations or precipitations observable on the scale of light microscopy and microprobe analysis (10 μm). Besides being a bulk property, the superconductivity might be ascribed to very small filaments or a thin surface layer. Superconducting filaments can be ruled out immediately because of the large initial slope of M vs H (Fig. 4). In the case of a superconducting surface layer there are two possibilities[20]: (i) If the applied field is large enough to penetrate through the layer, then the magnetization would collapse at that field by an amount $H - H_{c1}$ for very strong flux pinning or to a value corresponding to the superconducting volume fraction of the surface for the case of weak pinning. (ii) If the applied field is not large enough, no observable drop in the magnetization would be detected. Both possibilities are clearly in contradiction with our observation in Fig. 4. Thus the superconductivity must be a bulk property. Moreover, the specific-heat data below 2 K on the annealed polycrystal, shown in Fig. 1, confirm bulk superconductivity. Here, we observe a discontinuity at 1.1 K with $(C_s - C_n)/C_n \approx 1.3$. The normal-state specific heat between 2 and 17 K can accurately be fitted with $C = \gamma T + \alpha T^3 + \delta e^{-\Delta/T}$ where $\Delta \approx 115$ K. This exceptional behavior suggests the opening of an energy gap at 17.5 K over at least part of the Fermi surface.

The anisotropy in H_{c2} is different from that observed for $CeCu_2Si_2$ and UPt_3.[15] Now the initial slope $(-\mu_0\, dH_{c2}/dT)$ is, within our measuring accuracy, the same for the a and c axes. However, whereas the c axis has the usual convex behavior, the a axis displays a very anomalous, concave dependence of $H_{c2}(T)$. Nevertheless, the $H_{c2}(T)$ behavior shows some resemblance to the H_{c2} diagrams calculated by Fisher[21] for superconductors with local magnetic moments.

In conclusion, we have demonstrated the existence of most unusual magnetic and superconducting transitions in URu_2Si_2. The magnetism is related to a confined-moment type of antiferromagnetism, while the superconductivity is bulk and exhibits abnormal critical-field behavior. The experimental properties are highly anisotropic with the c axis strongly magnetic and the a axis favorable for superconductivity. A full theoretical description of these results is certainly warranted.

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[17] The electrical resistivity ρ is highly anisotropic in magnitude and temperature dependence. In general, there is a negative temperature coefficient ($d\rho/dT < 0$) above 70 K followed by a rapid falloff at lower temperatures. A "Cr-like anomaly" in $\rho(T)$ occurs around 17.5 K; T. T. M. Palstra *et al.*, to be published.

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