Low-Temperature State of UCu_5: Formation of Heavy Electrons in a Magnetically Ordered Material

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The formation of a heavy-electron state in a magnetically ordered material is established by measurements of the low-temperature specific heat of UCu_5 and $UAgCu_4$. In UCu_5 this state undergoes a continuous but hysteretic phase transition which removes parts of the Fermi surface with a high density of electronic states and leads to a resistivity increase of almost an order of magnitude.

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In two previous publications,[1,2] UCu_5 was identified as ordering antiferromagnetically at 15 K. This conclusion was based on data from measurements of the magnetic susceptibility[1] and from neutron-diffraction experiments.[2] Later measurements[3] of the specific heat and the electrical resistivity confirmed the phase transition but also led to the conclusion, in the course of a more general investigation of $UNi_{5-x}Cu_x$ compounds, that UCu_5 is, in fact, an intermediate-valent compound.[3] It was argued that the drastic change in the properties of the compounds in this series implies that for $4 < x < 5$ the uranium ions adopt an electronic configuration that is intermediate between U^{4+} and U^{3+}, fluctuating in time. Among other indications, the abrupt increase of the low-temperature electronic specific heat for x exceeding 4 was a major argument for this conclusion. The electronic specific-heat parameter γ was obtained from data in the temperature range between 1.5 and 30 K by extrapolation of a c_p/T vs T^2 plot to $T=0$ K. An anomalous increase of c_p/T with decreasing temperature below 4 K was ascribed to the onset of a Schottky-type contribution to the specific heat due to the spontaneous splitting of nuclear levels in the magnetically ordered matrix.

In this Letter we demonstrate that this increase in c_p/T is due to many-body effects that are now a familiar feature of heavy-electron materials and that UCu_5 undergoes another phase transition around 1 K which is, so far, of unknown origin but, more important, involves the heavy-mass quasiparticles that lead to the enhanced low-temperature specific heat. To our knowledge, this is the first example of such a distinct enhancement effect that occurs in a magnetically ordered material.

Our reasoning is based on data obtained from measurements of the specific heat and the electrical resistivity that were made on well-annealed polycrystalline samples of UCu_5 and $UAgCu_4$. The specific heat was measured between 0.15 and 21 K. Specimens that were cut from the same respective buttons were used for measurements of the electrical resistivity below room temperature, extending to 0.4 K in the case of UCu_5 and to 1.2 K for $UAgCu_4$.

In UCu_5 the distance between adjacent U atoms of 4.96 Å is quite large.[4] In principle, one would therefore expect an integral occupancy of the $5f$-electron shell of the U ions. As mentioned above this was first put in question by van Daal *et al.*[3] who concluded that although U in UNi_5, with a U-U distance of 4.80 Å,[4] adopts the $5f^2$ configuration, no integral valence can be assumed for U in UCu_5. In the work of Schneider *et al.*,[5] however, photoemission data indicate that the $5f$-electron-state occupation barely changes between UNi_5 and UCu_5 and these authors concluded that in both cases, hybridization effects between U $5f$ and Ni or Cu $3d$ electrons were important. There was also no evidence for two different final-state $5f$ multiplets in the valence-band spectrum of UCu_5 that would indicate valence fluctuations between U^{4+} and U^{3+} states. The experimental results that we present below also rather indicate itinerant-$5f$-electron behavior that is most likely due to hybridization with $3d$ electrons.

In Fig. 1 we show the results of our measurements of the specific heat c_p of UCu_5 and $UAgCu_4$ between 0.15 and 21 K. For temperatures above 1.5 K we plot c_p/T vs T^2 and in the insets we display c_p vs T for temperatures below 0.6 K. For UCu_5 we confirm the data of van Daal *et al.*[3] obtained for $T > 1.5$ K with the main features of an anomaly induced by magnetic ordering around 15 K and the upturn of c_p/T with decreasing temperature below 4 K. Replacement of Cu by Ag obviously results in quite different changes of

the low-temperature properties than when Ni is replacing Cu. While 20% of Ni completely suppresses the magnetic phase transition and also lowers the electronic specific heat by at least a factor of 3,[3] the same amount of Ag leads to an increase of the magnetic ordering temperature but leaves c_p/T almost unchanged between 1.5 and 4 K.

For both compounds the temperature dependence of $c_p(T)$ below 0.6 K already shows that the c_p/T upturn below 4 K is not due to nuclear specific heat.[3] The linear dependence of c_p on T indicates that we observe an electronic specific heat which is quite large. We note that the electronic specific-heat parameter $\gamma(0)$ is almost 4 times larger for $UAgCu_4$ than for UCu_5, although the c_p/T values at 1.5 K are almost identical for both compounds. This implies that UCu_5 must undergo a phase transition between 0.5 and 1.5 K, removing parts of the Fermi surface which contribute to the electronic density of states and, hence, the electronic specific heat. In Fig. 2 we show $c_p(T)$ for UCu_5 between 0.15 and 2.5 K. Obviously the specific-heat anomalies indicating the anticipated phase transition occur at slightly different temperatures ($\Delta T = 0.17$ K) depending on whether the data are taken upon cooling or heating the sample through the transition. In spite of various special efforts we did not observe any latent heat associated with the transition. Measurements where the temperature range between 0.8 and 2 K, or vice versa, was traversed either in 4 min or else in 3 h gave the same results. Therefore, the observed hysteresis is certainly not due to a low internal thermal conductivity of the specimen but rather is an intrinsic property of UCu_5. The observation of a hysteresis but of no latent heat opens the question of how the transition should be characterized. It is interesting to note that similar problems arise in the description of transitions between commensurate and incommensurate charge-density-wave states.[6]

For comparison we also show $c_p(T)$ of $UAgCu_4$ between 0.3 and 2.5 K. It is obvious that substitution of one Ag atom for one Cu atom per formula unit is fatal for the new phase transition, and therefore the electronic specific-heat parameter of $UAgCu_4$ for T approaching 0 K is still about 310 mJ/mole K^2, sizably larger than 86 mJ/mole K^2 as observed for UCu_5. It is also evident from Fig. 2 that for $UAgCu_4$, c_p/T must pass over a maximum when the temperature is raised from 0.5 to 2 K. It reaches 340 mJ/mole K^2 at 1.4 K.

From these data we conclude that in UCu_5 the electronic subsystem has similar properties to those of well-established heavy-electron materials like UBe_{13},[7] UPt_3,[8] $CeAl_3$,[7,9] or $CeCu_2Si_2$.[10] In all of them a pronounced increase of the c_p/T ratio is observed with decreasing temperature below about 10 K.

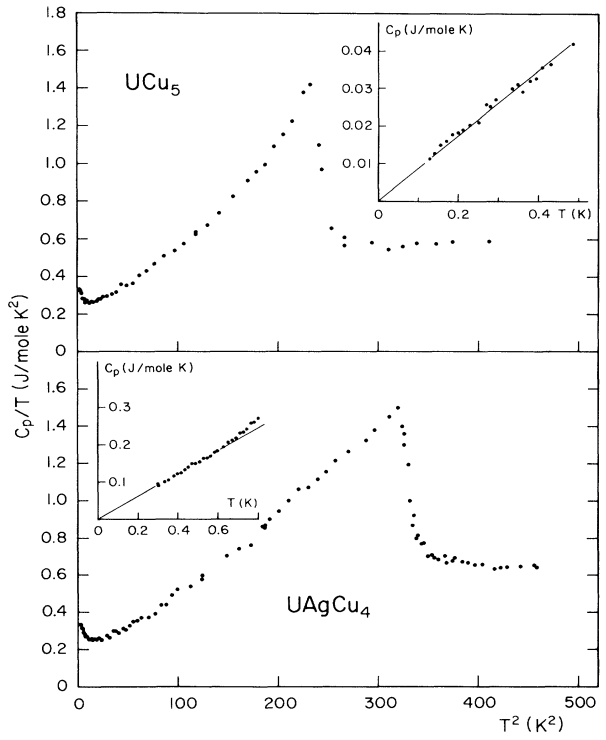

FIG. 1. Low-temperature specific heats of UCu_5 and $UAgCu_4$ between 0.15 and 21 K.

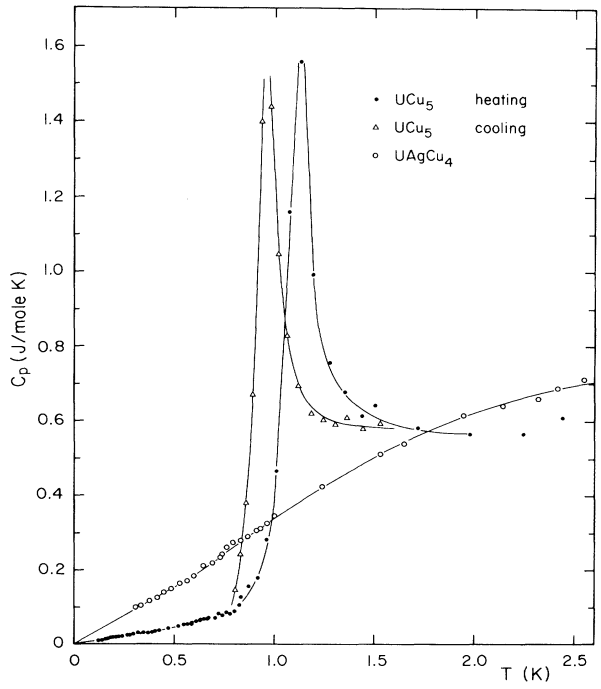

FIG. 2. Specific heat of UCu_5 and $UAgCu_4$ between 0.15 and 2.5 K.

Previous experiments have shown that the heavy-electron state itself may be unstable with respect to phase transitions and superconductivity or magnetic order have been observed.[8,10,11] What in our opinion is special about UCu_5 is the formation of a heavy-electron state, as manifested by the enhancement of the specific heat, in a magnetically ordered material, with the subsequent newly discovered phase transition itself showing unusual features. That the enhancement of the specific heat is not simply a precursor to the quoted phase transition is demonstrated by the behavior of $UAgCu_4$. Because it is known that phase transitions in the heavy-electron state can easily be suppressed by impurities,[12,13] we deliberately chose this composition to prevent the phase transition but to keep the large electronic specific heat.

Previous[3] and our own specific-heat data reveal that the molar entropy associated with the upper magnetic phase transition is only about $0.6R$ ln2, considerably less than expected for magnetic ordering that induces a spontaneous splitting of an at least doubly degenerate magnetic $5f$-electron ground state. van Daal *et al.*[3] also found a distinct anomaly in the temperature dependence of the electrical resistivity ρ that is associated with the magnetic ordering. We repeated and extended these measurements and show our results for $\rho(T)$ of UCu_5 between 0.4 and 30 K in Fig. 3. Our data above 30 K up to room temperature confirm the results of Ref. 3 and therefore we concentrate on the low-temperature part. This upper transition clearly influences the electronic structure giving rise to a local maximum in $\rho(T)$ about 2 K below the transition temperature. Such $\rho(T)$ curves have been observed for itinerant antiferromagnets with Cr as the most prominent example[14] and they are ascribed to the formation of gaps on the Fermi surface.[15]

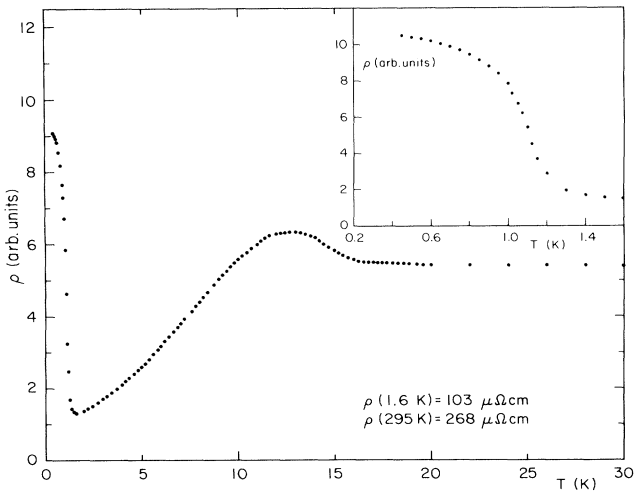

FIG. 3. Temperature dependence of the electrical resistivity of UCu_5 between 0.4 and 30 K.

What is of more interest here, however, is the influence of the lower transition on $\rho(T)$. The inset in Fig. 3 shows the low-temperature part of $\rho(T)$ on an expanded temperature scale. After a steady decrease with decreasing temperature $\rho(T)$ passes through a minimum at 1.6 K with a ρ value that is roughly 5 times less than the preceding maximum and subsequently smoothly increases by a factor of 7 through the transition. Although some increase in $\rho(T)$ might be expected considering the appreciable loss of Fermi surface as indicated by $c_p(T)$, it does not necessarily have to occur as was recently shown for U_2Zn_{17},[16] for example. The behavior of $\rho(T)$ of UCu_5 below the new phase transition certainly adds more questions as to the nature of the low-temperature phase and will be a topic of future investigations. As expected, we find no minimum in $\rho(T)$ for $UAgCu_4$, where all other features of $\rho(T)$ of UCu_5 below 300 K are retained, however.

Our results imply the following conclusions. The formation of a heavy-electron state characterized by an increasing enhancement of the electronic specific heat with decreasing temperature is also possible in a magnetically ordered material. This observation in a way supports recent discussions[17] of the mutual influence of Kondo or Ruderman-Kittel-Kasuya-Yoshida interactions. As in other cases, this state in UCu_5 undergoes a phase transition, whose origin remains to be established, but which opens gaps in the excitation spectrum of the heavy quasiparticles. Impurities in the sense of replacing part of the Cu by Ag remove the phase transition, and all parts of the electronic spectrum with high densities of states survive down to low temperatures. New aspects of this phase transition under these circumstances are its thermal hysteresis without its being discontinuous, and the very high electrical resistivity in the state below the transition. Up to now the general trend of all heavy-electron systems went towards very low values of $\rho(T)$ for T approaching 0 K, irrespective of the nature of the finally adopted ground state. It is clear that further experiments, especially involving microscopic methods, will have to clarify the situation.

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