Formation and destruction of the heavy-electron ground state in U compounds with AuBe$_5$ crystal structure

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The strong influence of changes of the chemical composition on the formation of a heavy-electron ground state is demonstrated in uranium intermetallic compounds crystallizing in the cubic AuBe$_5$ structure. The most spectacular effect is the large enhancement of the low-temperature electronic specific heat in UPt$_5$ when one Pt atom per formula unit is replaced by Au. UAuPt$_4$ may be a heavy-electron superconductor.

The formation of a heavy-electron ground state in uranium intermetallic compounds is, so far, observed exclusively in materials where the nearest distance d_{U-U} between uranium atoms in the crystal lattice exceeds 4 Å. The most prominent examples are UBe$_{13}$ (Ref. 1) and UPt$_3$,[2] both heavy-electron superconductors, and U$_2$Zn$_{17}$ (Ref. 3) and UCd$_{11}$,[4] which order magnetically out of a heavy-electron state. Among these examples the largest electronic contributions to the molar low-temperature specific heat c_p are observed in UBe$_{13}$ and UCd$_{11}$, for which d_{U-U} exceeds 5 and 6 Å, respectively. More recently, the formation of a heavy-electron state, indicated by a c_p/T ratio which increases with decreasing temperature, in an already magnetically ordered material was observed in UCu$_5$,[5] another uranium compound where d_{U-U} is close to 5 Å. While these observations suggest that a large separation between 5f-electron-carrying atoms is favorable for the formation of a heavy-electron state it seems *a priori* questionable that this condition alone is sufficient, because, as we shall see below, other compounds with U-U separations close to or more than 5 Å do not show heavy-electron characteristics at low temperatures. In a discussion of the low-temperature behavior of uranium compounds with the Cu$_3$Au crystal structure, Koelling, Dunlap, and Crabtree[6] have already noted that d_{U-U} alone is not a reliable parameter for predictions of the magnetic properties and that hybridization effects play a crucial role.

Clear indications that even more subtle details of the electronic structure are essential were obtained from investigations of the effect of impurities on the low-temperature properties of UBe$_{13}$ and UPt$_3$. Small amounts of impurity atoms replacing U in UBe$_{13}$ lead to sizeable changes of the c_p/T ratio of UBe$_{13}$ at very low temperatures[7] and similar effects were observed by introducing either Pd on the Pt sites[8] or Th on the U sites[9] of UPt$_3$.

Further evidence was obtained from drastic reductions of the low-temperature specific heat of CeAl$_3$,[10] UBe$_{13}$,[11] and UPt$_3$ (Ref. 12) under rather moderate external pres-

sures and from the formation and destruction of a heavy-electron state in the U(Sn$_{1-x}$In$_x$)$_3$ series upon varying x.[13] As we shall see below, small amounts of impurities can also influence the above-mentioned formation of the state with enhanced specific heat in magnetically ordered UCu$_5$.

In this work we will give distinct examples of how changes of chemical compositions in isostructural compounds may influence their low-temperature properties, with particular emphasis on the formation or destruction of a heavy-electron ground state. For this purpose we choose uranium compounds crystallizing in the cubic AuBe$_5$ structure[14] shown in Fig. 1. Within the Be sublattice we recognize two inequivalent sites forming large and small tetrahedra as emphasized in Fig. 1. Its obvious simplicity makes this structure attractive for the investigations we have in mind; in addition, in these compounds the above-mentioned requirement of a large separation of the
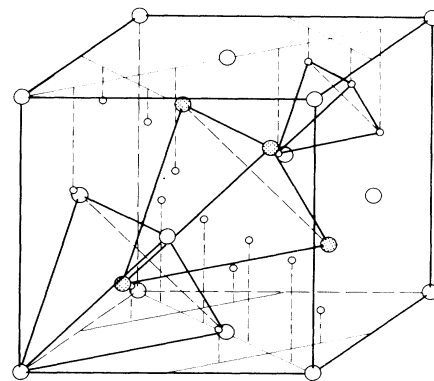

FIG. 1. The AuBe$_5$ crystal structure. The large open circles denote the Au sites; the large dotted circles and the small open circles denote the Be sites. The lines are drawn to visualize the individual positions.

uranium atoms is fulfilled.

Both UNi_5 and UCu_5 crystallize in the structure shown in Fig. 1. In the original work of van Daal, Buschow, van Aken, and van Maaren[15] on $UNi_{5-x}Cu_x$, it was pointed out that replacing Ni by Cu leads to dramatic changes in the low-temperature behavior of these substances. While UNi_5 has an essentially temperature-independent magnetic susceptibility below room temperature and stays paramagnetic, $\chi(T)$ of UCu_5 increases substantially with decreasing temperature and antiferromagnetic order is observed below 15 K. Moreover, the c_p/T ratio at helium temperatures is about one order of magnitidue smaller in UNi_5 than in UCu_5. For UNi_5 and UCu_5 the nearest U-U distances are 4.796 and 4.973 Å, respectively, and it might be argued that the difference in this separation alone is responsible for the observed different behavior. In our first example we demonstrate that this is only partially true, particularly with respect to the behavior below 4 K, disregarding, however, in this discussion the recently discovered phase transition around 1 K in UCu_5.

In Fig. 2 we show the temperature dependence of the low-temperature specific heat of UCu_5 and $UCu_{4.95}Ni_{0.05}$ in the form of c_p/T vs T^2 plots. It is evident that 1% Ni impurities on the Cu sites do not greatly affect the overall specific heat, but they are sufficient to suppress the c_p enhancement below 4 K. We recall that this enhancement, however, persists when 20% of the Cu sites are occupied by Ag atoms.[5] Therefore, it seems difficult to ascribe the change of the c_p/T ratio displayed in Fig. 2 to a simple size effect in the sense mentioned above. It is rather the electronic part of the above-mentioned background specific heat which changes upon larger variations of d_{U-U}, as was shown in Ref. 15, and which is most likely due to band-structure effects. Our measurements of the electrical resistivity ρ in this temperature range reveal that $\rho(T)$ is also quite different in UCu_5 and $UCu_{4.95}Ni_{0.05}$. At 1.5 K, ρ of the Ni-doped material is at least a factor of 2 larger than that of pure UCu_5. In contrast, $\rho(T)$ of $UAgCu_4$ is almost identical to that of UCu_5 between 1.5 and 10 K.[5]
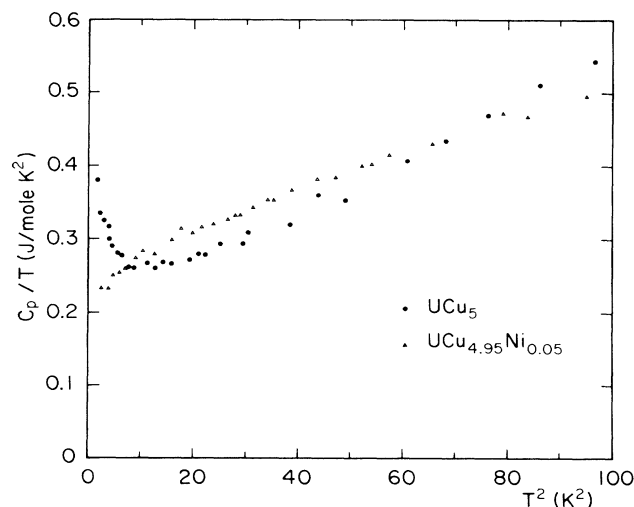
In another example we show that changing the chemical composition of $AuBe_5$-type uranium compound may lead to drastic changes in the opposite direction, i.e., to the formation of a heavy-electron state, rather than its destruction as demonstrated above. For this purpose we consider UPt_5 and $UAuPt_4$. The physical properties of UPt_5 have been investigated before. $\chi(T)$ below 300 K and the room-temperature valence-band photoemission spectrum were reported by Schneider and Laubschat,[16] $c_p(T)$ was measured by Frings[17] between 1.5 and 15 K, and $\rho(T)$ data between 1.5 and 300 K were published by de Visser, Franse, and Menovsky.[18] Although in UPt_5 the U-U separation is 5.25 Å and hence favorable for the formation of a heavy-electron state, the properties mentioned above indicate a much weaker trend to it than is observed in UPt_3, where the nearest U-U distance is aproximately 1 Å less. It is mainly the temperature dependences of c_p and ρ below 6 K which suggest the presence of spin fluctuations in UPt_5. As Frings points out, a $T^3 \ln T$ term is needed to properly describe $c_p(T)$ below 6 K, and de Visser and co-workers note a T^2 dependence of ρ below 5 K.

Some of the properties we just described change considerably when one Pt atom per formula unit is replaced by Au. Below, we demonstrate this by reporting results of measurements of $\rho(T)$ and $\chi(T)$ of $UAuPt_4$ between 1.5 and 300 K and of $c_p(T)$ between 0.15 and 15 K, and by displaying them in comparison with available data on UPt_5.

In Fig. 3 we show $\chi(T)$ for $UAuPt_4$ and UPt_5 below room temperature, where the latter data are those of Ref. 16. It may be seen that this change in chemical composition enhances the susceptibility by at least a factor of 2 at all temperatures. Above 60 K, $\chi(T)$ of $UAuPt_4$ may be described by a Curie-Weiss-type straight line corresponding to an effective moment $p_{eff} = 3.21\mu_B$/(U ion) and a paramagnetic Curie temperature Θ_p of -135 K. However, this simple interpretation is questionable because, in spite of the large negative value of Θ_p, $UAuPt_4$ does not order magnetically down to 0.15 K. Quite obvious is also the change in electrical resistivity as is shown in Fig. 4, where
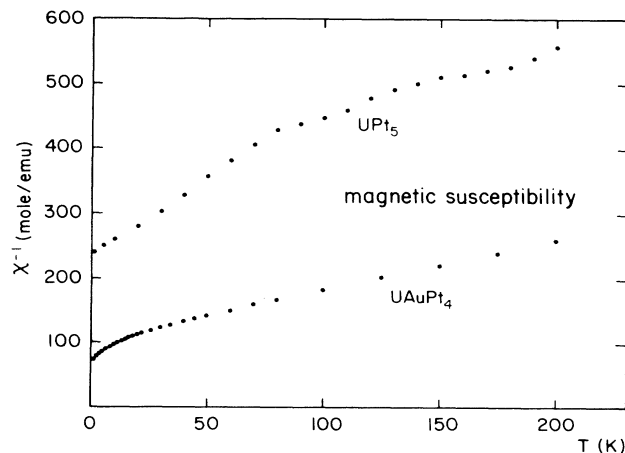

FIG. 2. c_p/T vs T^2 for UCu_5 and $UCu_{4.95}Ni_{0.05}$ between 1.5 and 10 K.

FIG. 3. Inverse magnetic susceptibility $\chi^{-1}(T)$ of UPt_5 and $UAuPt_5$ between 1.5 and 220 K. The data for UPt_5 were taken from Ref. 14.
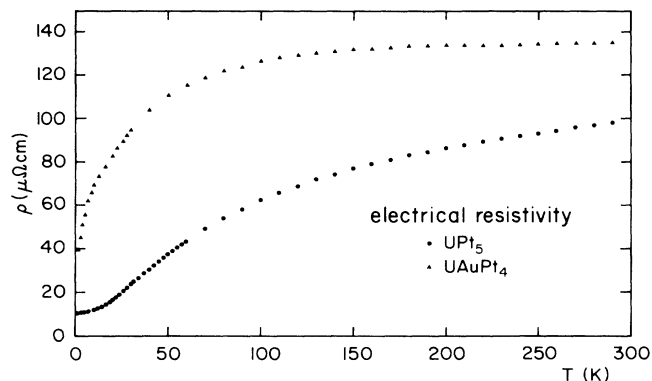
FIG. 4. Temperature dependence of the electrical resistivity $\rho(T)$ of UPt$_5$ and UAuPt$_4$ between 1.2 and 300 K.

FIG. 5. c_p/T vs T^2 for UPt$_5$ and UAuPt$_4$ below 15 K. The data for UPt$_5$ (above 1.5 K) are those of Ref. 15. The data for UAuPt$_4$ extend down to 0.15 K.

we present $\rho(T)$ between 1.5 and 300 K for both UAuPt$_4$ and UPt$_5$. Both sets of data were obtained in this work and our results for UPt$_5$ are somewhat at variance with those reported by de Visser et al.,[18] the main difference being the sizeably lower values of ρ obtained in our measurements. $\rho(T)$ of UAuPt$_4$ is clearly enhanced with respect to that of UPt$_5$ and the enhancement increases with decreasing temperature. The temperature dependence of ρ of UAuPt$_4$ approaches that of the heavy-electron uranium compounds UCd$_{11}$ (Ref. 4) and U$_2$Zn$_{17}$.[3]

The most dramatic change is observed in the temperature dependence of the low-temperature specific heat. This may be seen from the c_p/T vs T^2 plots for both UAuPt$_4$ and UPt$_5$ shown in Fig. 5. The data for UPt$_5$ are those of Frings.[17] The slight enhancement of c_p of UAuPt$_4$ with respect to UPt$_5$ observed at 15 K, increases steadily with decreasing temperature and below 5 K; c_p/T of UAuPt$_4$ shows the characteristic upturn of heavy-electron materials. From our measurements down to 0.15 K we extrapolate a c_p/T ratio at $T=0$ K of 725 mJ/mole K^2, indicating that the zero-temperature electronic-specific-heat parameter γ is eight times larger in UAuPt$_4$ than in UPt$_5$. Below 1 K, the specific heat of UAuPt$_4$ can be described very accurately by considering c_p due to electrons, the lattice, and a spin-fluctuation-type term of the form $T^3\ln T$. The resulting fit, however, clearly deviates from the experimental data above 2 K and therefore we have not much faith in that sort of interpretation, especially also because the resulting fit parameter of the spin-fluctuation temperature $T_{SF}=9.5$ K is equal to T_{SF} in UPt$_5$.[17] The separation of the U atoms d_{U-U} in UPt$_5$ and UAuPt$_4$ is 5.25 and 5.285 Å, respectively. Although the change of about 0.7% is quite remarkable we tend to ascribe the large enhancement of c_p/T below 5 K again to a many-body effect and not to a size-induced band-structure effect which may, however, cause the specific-heat increase in UAuPt$_4$ above 7 K.

From the temperature dependence of ρ we suspect, without definite proof yet, that UAuPt$_4$ will ideally form an ordered compound with all the Au atoms occupying those Be sites of the AuBe$_5$ structure that form large tetrahedra (see Fig. 1). Remaining deviations from the
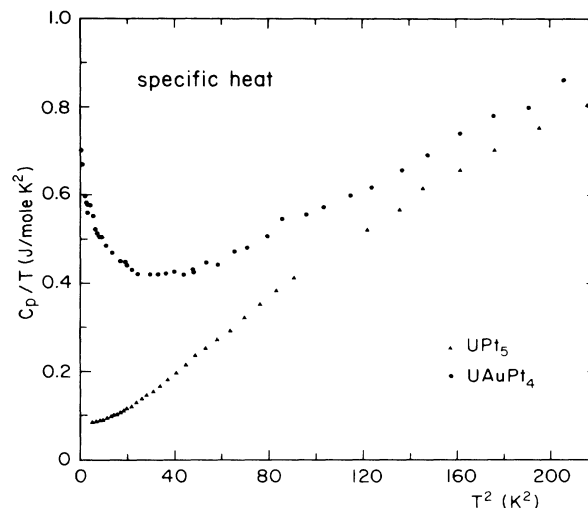
ideal distribution of the atoms on different lattice sites are most likely the cause for the absence of any phase transition in our samples. This statement is supported by the fact that all known heavy-electron uranium compounds undergo a phase transition at low temperatures unless it is suppressed by impurities or other imperfections of the crystal lattice. In other words, we may also state that we doubt that UAuPt$_4$ is a uranium analogue to CeAl$_3$ or CeCu$_6$, two heavy-electron Ce compounds that show no phase transition down to 20 mK. It is thus of interest to speculate what kind of phase transition is the most likely to occur in perfect UAuPt$_4$. In a previous comparison of low-temperature properties of heavy-electron U compounds[19] it became apparent that the superconductors UBe$_{13}$ and UPt$_3$ have distinctly larger electronic specific heats per unit volume γ_v than all other compounds which order antiferromagnetically. For UAuPt$_4$ we calculate a γ_v value of 11.5 mJ/cm^{3}K^2, very close to those obtained for UPt$_3$ and UBe$_{13}$, respectively. Hence, we conjecture that UAuPt$_4$ may be a heavy-electron superconductor once it can be prepared in perfect enough form. This conjecture is also supported by the fact that the renormalized ratio of the values of the low-temperature magnetic susceptibility and specific heat $(\pi^2 k_B^2/3\mu_B^2)(\chi/\gamma)$ for UAuPt$_4$ is 1.43, close to the values found for the three known heavy-electron superconductors. This value is also near a phenomenological boundary separating magnets and superconductors, which was recently proposed by DeLong.[20]

Our last point is of general and fundamental interest. It should be possible to perform band-structure calculations for both UPt$_5$ and UAuPt$_4$.[21] This would then allow one to test the significance of such calculations in conjunction with heavy-electron behavior because the large difference in the low-temperature specific heat of these two compounds should reflect itself in the calculated energy dependence of the electronic density of states, if band-structure effects were indeed responsible for the obviously different behavior.

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