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Superconductivity and magnetism in heavy-electron U intermetallics (invited)

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Recent work intended to investigate a Fermi-liquid-type low-temperature state in uranium intermetallic compounds is reviewed. In form of a comparison of physical properties with those of CeAl_3 , the prototype heavy-electron system, some details concerning the occurrence of this heavy-electron state are discussed. Special attention is then given to experimental data giving evidence for superconductivity or magnetic order, both involving these heavy electrons. The possibility of unconventional superconductivity in these systems is supported by increasing experimental evidence.

I. INTRODUCTION

The discovery of peculiar low-temperature properties of CeAl_3 , namely a large electronic specific heat,¹ a temperature-independent magnetic susceptibility¹ and a temperature dependence of the electrical resistivity proportional to T^2 ,¹ which are preceded at higher temperatures by a strongly temperature-dependent c_p/T ratio,² a Curie-Weiss-type magnetic susceptibility³ and an electrical resistivity which, below room temperature, increases with decreasing temperature and only after passing through a maximum varies with a positive slope $\partial\rho/\partial T$,⁴ gave a first indication for the occurrence of an unusual electronic state in metals which appeared to be best described as a Fermi liquid of quasiparticles with very large effective masses. After very similar behavior, at least above 1 K, was found in the ternary compound CeCu_2Si_2 ⁵—its spectacular low-temperature properties will be discussed in detail in another contribution to this volume⁶—it was for some time thought that only Ce-based intermetallics would show these unusual features. Quite recently, indeed another cerium compound, CeCu_6 , was found to be an analog to CeAl_3 .⁷⁻⁹

What we intend to present and discuss below is recently obtained evidence that the same transition from a state at elevated temperatures which thermodynamically is best described by classical or Boltzmann statistic, to a low-temperature, Fermi-liquid-type behavior, may also be observed in uranium-based intermetallic compounds. One of the major problems with respect to these observations is, of course, to find a convincing description for this smooth transition between the two characteristically different, high- and low-temperature properties. After a short description of experimental results to visualize this problem we wish to concentrate, however, on other experimental data with regard to phase transitions within this Fermi-liquid state and to show examples for the occurrence of superconductivity or magnetic order in such systems.

II. NORMAL STATE OF HEAVY-ELECTRON U INTERMETALLICS

As mentioned in the Introduction, an outstanding feature of the considered materials is the unusual and for a metal atypical temperature dependence of the electrical resistivity. In Fig. 1 we show $\rho(T)$ between 1.5 and 300 K of three compounds which represent the class of substances we have in mind, UBe_{13} , U_2Zn_{17} , and UPt_3 . For all three compounds, the room temperature resistivity is of the order of $100 \mu\Omega \text{ cm}$. Clearly the most anomalous behavior is observed in UBe_{13} , where at low temperatures a rather narrow peak precedes the decrease of $\rho(T)$ down to 1 K.¹⁰ In U_2Zn_{17} , $\rho(T)$ increases with decreasing temperature below 300 K and a low-resistive state is formed below 10 K with a drop in resistivity of almost two orders of magnitude.¹¹ For UPt_3 , the resistivity has been measured along different crystallographic directions,^{12,13} giving evidence for some anisotropy effects. The temperature dependences, however, are quite similar for all directions and we show $\rho(T)$ measured parallel to the c direction of the crystal lattice.¹³ Although $\partial\rho/\partial T$ is positive over the whole temperature range shown, the main

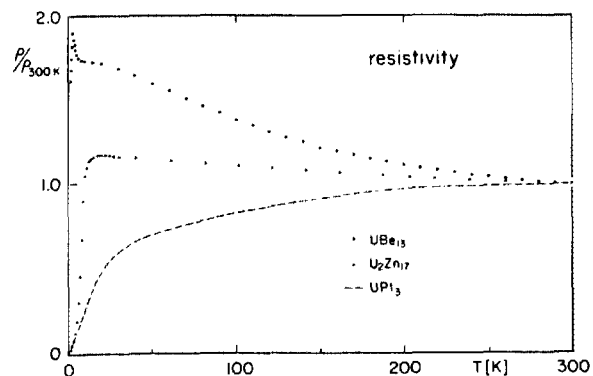


FIG. 1. Temperature dependences of the electrical resistivities of UBe_{13} (Ref. 2), U_2Zn_{17} (Ref. 11), and UPt_3 (Ref. 13), between 1.5 and 300 K.

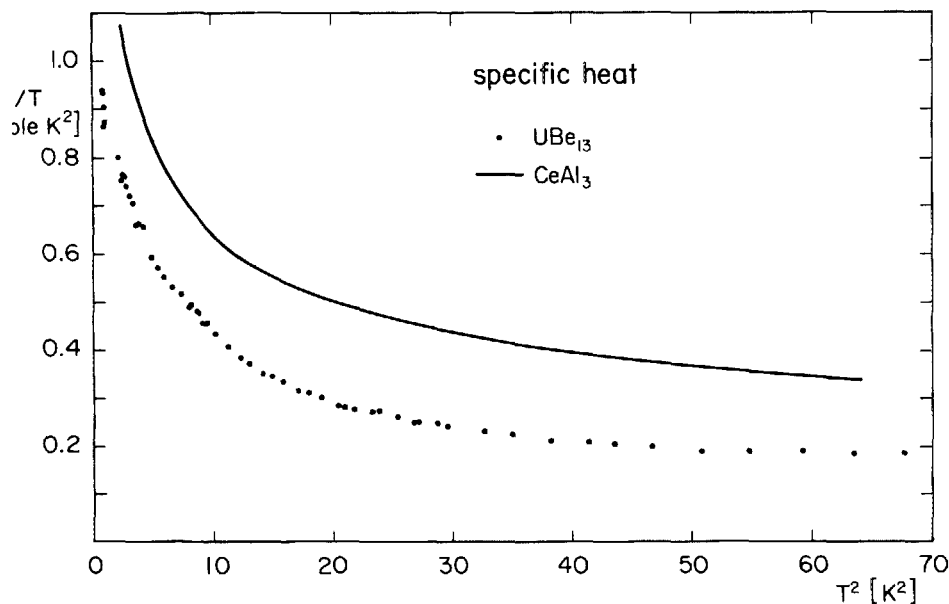


FIG. 2. c_p/T vs T^2 for CeAl_3 and UBe_{13} between 1.5 and 8 K. In both cases a T^3 lattice contribution was subtracted from the total specific heat.

decrease of ρ is again observed below 25 K. Apart from certainly important details, especially in the case of UBe_{13} , we therefore consider the resistive behavior of these three compounds as characteristically similar. Not shown here is another example for this $\rho(T)$ behavior that was recently observed in UCd_{11} .¹⁴ In that case $\rho(T)$ is more or less constant down to 50 K and decreases with increasing slope below that temperature. For completeness we should like to mention that also other actinide compounds show characteristically similar $\rho(T)$ curves.¹⁵

For all the above mentioned compounds, the magnetic susceptibility is strongly temperature dependent below room temperature. At least for UBe_{13} , UPt_3 , and UCd_{11} a Curie-Weiss-type behavior with effective moments of $3.08 \mu_B/\text{U ion}$,² $2.9 \mu_B/\text{U ion}$ ¹⁶ and $3.45 \mu_B/\text{U ion}$,¹⁴ respectively, may be identified in different temperature ranges. Deviations from this simple temperature dependence are observed in all three cases at low temperatures. Somewhat less clear is the situation for U_2Zn_{17} , where no simple T^{-1} dependence of χ is apparent over a wide enough temperature range.¹¹ Again in UPt_3 , χ is found to be anisotropic¹³ as may also be expected for U_2Zn_{17} , but has not been investigated as yet.

To illustrate the characteristics of the low-temperature specific heat and to demonstrate the similarities between different compounds we show c_p^{el}/T for CeAl_3 and UBe_{13} between 1 and 8 K^2 in Fig. 2. c_p^{el} was in both cases obtained from the total specific heat by subtracting the lattice part which is, however, virtually negligible in this temperature range. It may be seen that the main increase towards the limiting low-temperature value of the electronic specific-heat parameter occurs in the shown temperature interval. A similar upturn of c_p/T was reported for UPt_3 .¹² In this latter case the data could be fitted over an extended temperature range by including a $T^3 \ln T$ term besides the electronic and the lattice specific heats, which is believed to be characteristic for spin-fluctuation contributions. Attempts to fit the results for CeAl_3 and UBe_{13} in the same way were less successful. However, Rice and co-workers¹⁷ suggested another possibility to be the cause for the enhancement of the elec-

tronic specific heat. Extending the Brinkman-Rice model¹⁸ for almost localized electrons to finite temperatures by proposing an ansatz for the entropy of such a system, they were able to fit the experimental data for UBe_{13} reasonably well using the effective mass of the itinerant electrons and the unrenormalized Fermi temperature as fit parameters. At this point we should mention that the c_p^{el}/T ratios for CeAl_3 and, somewhat less pronounced for CeCu_2Si_2 , show a maximum below 1 K. This feature has recently been interpreted as being due to coherence effects in a Kondo lattice.¹⁹ There is, however, no experimental evidence as yet for similar effects in the U compounds discussed here.

Somewhat different is the situation found for U_2Zn_{17} and UCd_{11} , where the c_p^{el}/T ratio is large and constant in temperature already above 10 K.^{11,14} Specific-heat measurements at temperatures above 15 K are certainly needed to clarify the transition to the low-temperature state in these cases. It should be mentioned that the observations on these two compounds suggest that the formation of that state is not drastically influenced by the interatomic U-U distance. For U_2Zn_{17} , the nearest U-U distance is about 4.4 Å,²⁰ considerably smaller than in UCd_{11} where a 6.5 Å²¹ separation between adjacent U atoms was established.

III. SUPERCONDUCTIVITY

Until 1983 only few substances containing U as a regular constituent were known to be superconductors. Therefore the discovery of bulk superconductivity below 0.9 K in UBe_{13} ¹⁰ was rather surprising and it is understandable that first magnetic indications for superconductivity in UBe_{13} were discarded and ascribed to precipitated U filaments.²² The large specific-heat anomaly associated with the superconducting transition, which is displayed in Fig. 3, not only confirmed the bulk character of the transition but also demonstrated both the electronic nature of the large specific heat just above T_c and the participation of these "heavy" electrons in the formation of the superconducting state. The results of these measurements also confirmed that the previously claimed superconductivity of CeCu_2Si_2 ²³ was indeed

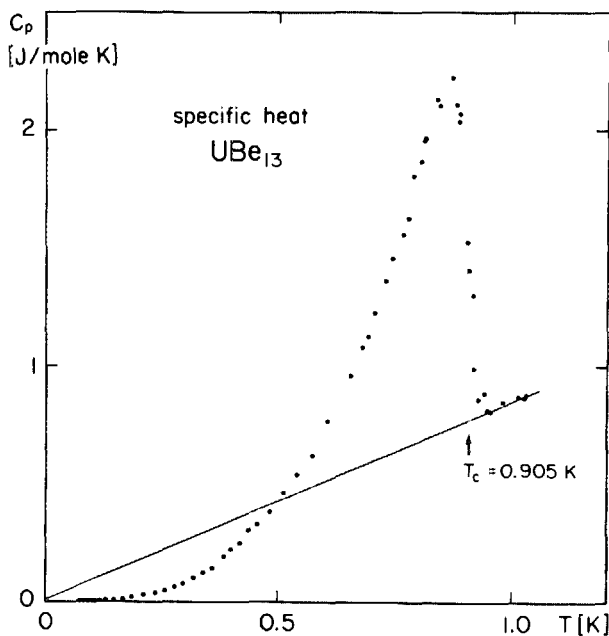


FIG. 3. Specific heat of UBe_{13} between 0.1 and 1 K. The solid line is an extrapolation of the normal state specific heat, linear in T to 0 K.

an intrinsic effect of this material, although often questioned because of initial material problems in that case. Subsequently also UPt_3 was found to be a superconductor below 0.5 K,¹² again out of a normal state with high electronic specific heat.

The occurrence of superconductivity under seemingly unfavorable conditions soon gave rise to speculations concerning the mechanism providing the transition and also concerning the characterization of the adopted superconducting state.²⁴ Evidence for an anisotropic superconducting state with zeroes of the energy gap on the Fermi surface and hence an $l \neq 0$ pairing of the electrons was obtained from specific heat²⁵ and NMR spin-lattice relaxation time experiments²⁶ below T_c for UBe_{13} and also from critical-field anisotropy²⁷ and especially the temperature dependence of ultrasound absorption²⁸ in the superconducting state of UPt_3 . Theoretical work dealt with suggestions for treating the problems of both the occurrence of heavy electrons and also their superconducting state²⁹ and furthermore with investigations concerning the existence of possible anisotropic superconducting states in real metals by involving group-theoretical methods.^{30,31} Moreover some predictions concerning the anisotropy of critical fields for such states were made.^{27,32} For completeness it should be mentioned that a somewhat different view is expressed in work attempting to describe the behavior of CeCu_2Si_2 and which is based on calculations assuming a Kondo-lattice situation and conventional superconductivity.³³⁻³⁵

The most often raised argument against the possibility of $l \neq 0$ pairing is the claim that such a state would never survive the potential pair breaking in substances that are considered here. It should be noted therefore, that superconductivity may indeed easily be suppressed in these materials, either by deviations in the chemical composition (CeCu_2Si_2),³⁶ or by mechanical damage (UPt_3)¹² or by adding certain species of impurities (UBe_{13}).³⁷ A detailed study revealed that substituting a nonmagnetic impurity like Th for

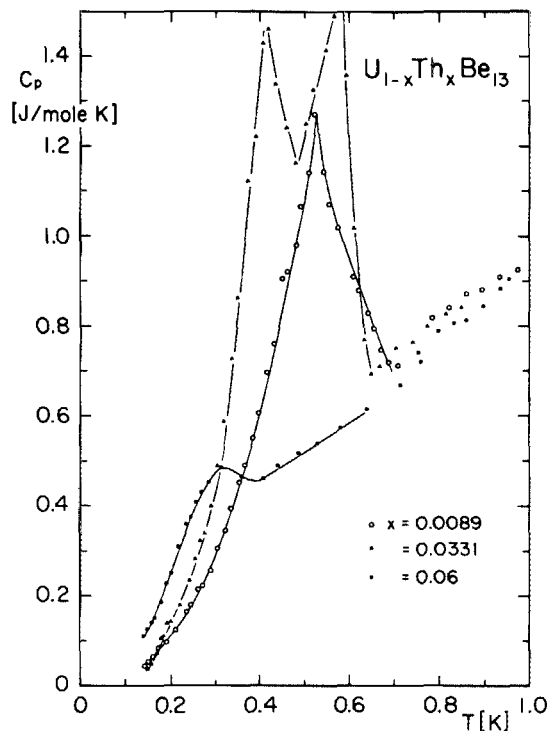


FIG. 4. Specific heat of various $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ compounds below 1 K for $x = 0.0089, 0.0331,$ and 0.06 .

U in UBe_{13} not only affects the superconducting state but also and quite considerably the transport properties in the normal state of this material.³⁸ The most spectacular feature, however, is the appearance of a second phase transition in the superconducting state of $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ compounds in a limited range of x values.³⁹ In Fig. 4 we show the temperature dependence of c_p below 1 K for three values of x . These curves should be compared with Fig. 3. The second anomaly appears for values of $x > 0.02$ and disappears when $x \sim 0.06$. From other experiments it is obvious that the second transition does not destroy the superconducting state which is formed at the discontinuity of c_p at a slightly higher temperature. The above mentioned NMR experiments²⁶ made on a sample with 3.3% Th content set an upper limit for an ordered moment in case of a magnetic transition to $0.01 \mu_B/\text{U}$ ion. This leads us to the conclusion that this transition is not to a magnetically ordered state. It is also quite unlikely that a structural transition is induced by adding impurities, rather the opposite might be expected. Hence we are left with the possibility of a transition from one superconducting state to another, a feature which is certainly not expected in a conventional superconductor but might occur for $l \neq 0$ paired states.⁴⁰

As a final comment regarding the superconducting properties of heavy-electron U intermetallics we should like to mention the very unusual temperature dependence of the upper critical field of UBe_{13} . After starting with a slope $\partial H_{c2}/\partial T$ of nearly -0.5 MOe/K at T_c , H_{c2} increases linearly with a slope of -91 KOe/K above about 20 KOe.⁴¹ This slope appears to increase again at temperatures below 0.4 K resulting in an H_{c2} value of about 120 KOe at 0.1 K.⁴² This temperature dependence is clearly different from that observed for the upper critical fields of CeCu_2Si_2 and UPt_3

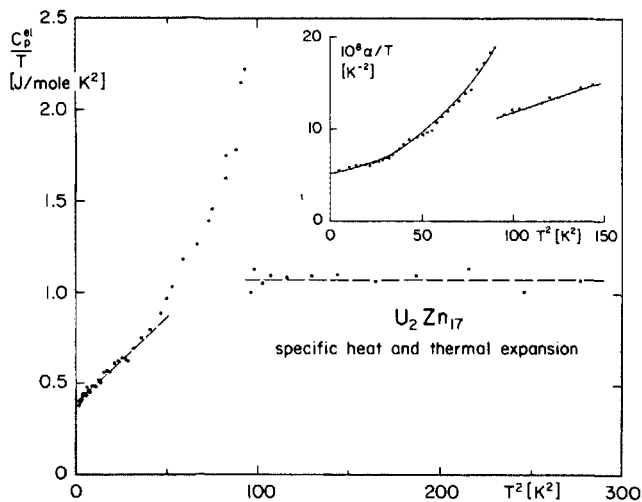


FIG. 5. Specific heat c_p^{el}/T and linear thermal expansion coefficient α/T vs T^2 through the phase transition of U_2Zn_{17} . The electronic specific heat c_p^{el} was obtained by subtracting the lattice contribution from the total specific heat (Ref. 11). α is the total expansion coefficient.

where saturation of H_{c2} is discernible around $T = T_c/2$.^{43,44}

IV. MAGNETIC ORDER

The possibility of phase transitions in the low-temperature, heavy-electron state automatically raises the question whether other phenomena than superconductivity may be observed. If suggestions that magnetic interactions are responsible for triggering superconductivity in these systems^{25,29} are taken seriously, it does not seem impossible that, for another weight distribution of the interactions, magnetically ordered ground states might be more favorable.

From measurements of magnetic susceptibility, electrical resistivity, and especially specific heat and thermal expansion it may be concluded that U_2Zn_{17} undergoes a phase transition at 9.7 K to, as indicated by the results of $\chi(T)$, a most likely antiferromagnetically ordered state involving the heavy electrons.¹¹ Both the specific heat and the thermal-expansion coefficient (both shown in Fig. 5) show a sharp discontinuity at the critical temperature, indicating the mean-field character of the transition. As mentioned above and shown in Fig. 5, the electronic specific heat parameter, given by c_p^{el}/T , is constant and large above T_N . The phase transition obviously removes only parts of the Fermi surface with a high density of states as is exemplified by the persistence of a still considerable intercept on the vertical axis for $T = 0$ K. A sizable T^3 contribution at the lowest temperatures and which certainly does not originate from the lattice, suggests the existence of low-lying spin-wave excitations. It is interesting to note that also this phase transition leaves behind an anisotropic electron excitation spectrum.

A similar transition but with somewhat different features in the physical properties is observed at 5.05 K for UCd_{11} . Again the large electronic specific heat above the transition is reduced by a factor of about 2 as T approaches 0 K. A transition of this kind was reported previously for another actinide compound, namely NpSn_3 ,⁴⁵ where, however, the specific heats above and below the transition are consid-

erably lower than in the mentioned U compounds. For another Np compound, NpBe_{13} , a fairly large specific heat with the characteristic c_p/T increase with decreasing temperature and a subsequent magnetic phase transition at 3.4 K have been reported.¹⁵ This offers the unique opportunity of investigating the transition from superconductivity in UBe_{13} to magnetic order in NpBe_{13} in two heavy-electron systems by changing only the atoms on the actinide sublattice of the crystal structure. From presently available data it appears that not only is superconductivity fairly rapidly suppressed by replacing U by Np in UBe_{13} ,³⁸ but also magnetic order can be quenched rather easily by replacing Np by U in NpBe_{13} .¹⁵ No doubt that further experimental efforts using this compound series will provide valuable information concerning superconductivity and magnetism and their possible relationship in heavy-electron systems.

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