

# Heavy electrons in metals

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## HEAVY ELECTRONS IN METALS

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Abstract : Characteristic properties of heavy-electron metals are demonstrated using  $\text{CeAl}_3$  as an example. The occurrence of superconductivity involving heavy electrons and some unconventional features of this superconducting state are outlined using data on  $\text{UPb}_3$ . Finally, an example of a heavy-electron state in a magnetically-ordered material,  $\text{UCu}_5$ , is discussed.

### 1. Introduction

The low-temperature physical properties of ordinary metals have some qualitative characteristics that are well known. Examples that we have in mind are the decreasing electrical resistivity with decreasing temperature, the nearly temperature-independent magnetic susceptibility and a contribution to the specific heat that varies linearly with temperature and originates of possible thermal excitations of electrons. For a description of these and other properties one needs to consider the energy excitation spectra of the conduction electrons and of the possible vibrations of the atomic lattice, the phonons. In the simplest approximations the conduction electrons are treated as a gas of non-interacting particles obeying Fermi-Dirac statistics and the lattice vibrations are described using the model of Debye. In both these models, characteristic temperatures enter as important parameters. These are the Fermi temperature  $T_F$ , determining the energy up to which all states of the conduction electrons are occupied at  $T = 0$  K, and  $\theta_D$ , the Debye temperature, giving a measure for the energy cut-off of the phonon spectrum. In ordinary metals,  $T_F$  is of the order of  $10^4$  to  $10^5$  K while  $\theta_D$  ranges from  $10^2$  to  $10^3$  K. At temperatures that are low with respect to both  $T_F$  and  $\theta_D$  and assuming that no interactions occur between electrons and phonons, the predictions of the above mentioned models are particularly simple for the specific heat  $c_p$  and the magnetic susceptibility  $\chi$  and they agree qualitatively with the experimentally observed behaviour that was partially mentioned above. We should note, however, that con-

siderable deviations may occur in transition metals and their alloys. To consider those, the difficult problem of taking into account possible interactions of conduction electrons among themselves or with core electrons of the atoms forming the crystal lattice has to be treated. Interactions of electrons with the crystal lattice have to be considered when attempting to describe the temperature dependence of the electrical resistivity  $\rho(T)$  and a result of the simplest approximation is the  $T^5$  law of Bloch and Grüneisen.

At this point we should like to mention that even without taking into account interactions within the assumed electron gas, temperature-dependent deviations from the simple behaviour of the electronic part of  $c_p$  and of  $\chi$ , which become increasingly important as  $T$  approaches  $T_F$  are predicted by theory. Since in most cases  $T_F$  is, as mentioned above, very large, these corrections can be neglected below room temperature but it should be remembered that in the high-temperature limit, the electronic subsystem could be described using classical statistical mechanics if not the melting points of metals were usually considerably lower than  $T_F$ .

In this paper we should like to describe the properties of certain intermetallic compounds that indicate that the electronic states of these materials have a characteristic energy  $kT_F$  that is orders of magnitude smaller than in ordinary metals. Accordingly the transition from classical to quantum-statistical behaviour is shifted to below room temperature. Writing the electronic energies  $\epsilon(k)$  in a free-electron form, we obtain for the Fermi energy

$$\epsilon_F = \frac{\hbar^2}{2m^*} k_F^2 \quad (1)$$

Since  $k_F$  is still determined by the interatomic spacing and the number of electrons, hence not much different from ordinary metals, the effective mass  $m^*$  must be orders of magnitude larger than the free-electron value. Hence these substances are usually called "heavy-electron" - or "heavy-Fermion" systems.

So far this phenomenon has been observed in intermetallic compounds where one of the constituents is a rare-earth or actinide atom with a partially filled 4f -or 5f-electron shell. At elevated temperatures these materials behave as if these f electrons were localized and classical thermodynamic behaviour is indicated by the observation of a Curie-Weiss-type temperature dependence of  $\chi$ . At low temperatures, some of these f electrons

seem to become itinerant, forming a metallic state with the characteristics mentioned above. Experimentally this is indicated by a large but temperature-independent magnetic susceptibility and a correspondingly large specific heat varying linearly with temperature. The two relevant expressions, in the spirit of eq. 1 also in simple form, are:

$$\chi = 2\mu_B^2 N(\epsilon_F) \quad (2)$$

and

$$c_p^{el} = \frac{2}{3} k_B^2 \pi^2 N(\epsilon_F) \cdot T = \gamma T \quad (3)$$

where  $\mu_B$  is the Bohr magneton,  $k_B$  the Boltzmann constant and  $N(\epsilon_F)$  the density of electron states at  $\epsilon_F$ .  $\gamma$  is usually denoted as the electronic specific heat.  $N(\epsilon_F)$  is proportional to  $m^*$  and therefore it may also be stated that these materials adopt a low-temperature state that is dominated by a large electronic density of states.

Recently the exciting discovery was made that in some of these materials the heavy electrons may form a superconducting state at very low temperatures. Since this superconductivity occurs under conventionally-viewed unfavourable conditions it was soon speculated that both the superconducting state and the mechanism inducing it might be different from those known in all conventional superconductors and indeed, as we shall see below, various features of this superconducting state were found to be unusual.

The heavy-electron state may also be unstable with respect to magnetic ordering, a topic that we shall not cover in this short review. However, we shall mention the formation of a heavy-electron state in an already magnetically ordered matrix, an observation that is particularly important in view of general considerations dealing with the question under which conditions such a state forms at all.

In the next section we shall demonstrate some of the outstanding properties of heavy-electron materials, taking the first-recognized substance of this kind,  $\text{CeAl}_3$ , as an example. Next we discuss the occurrence of superconductivity in such a material with  $\text{UBe}_{13}$  serving as the show piece and mention various facts that underline the peculiarities of this superconducting state. Finally we mention the unusual low-temperature behaviour of  $\text{UCu}_5$  which is characterized by a heavy-electron state in a magnetically ordered matrix. This state is unstable against a phase transition of as yet unknown character which removes a large part of the Fermi surface. The layout of the



paper is intended to give also the non-specialists some idea of the significance of recent developments in this branch of physics.

## 2. Typical features of heavy-electron materials ( $\text{CeAl}_3$ )

As was mentioned above,  $\text{CeAl}_3$  is the prototype heavy-electron material and it shows no phase transition down to 10 mK, the lowest temperature that was reached when investigating its properties. It is therefore very well suited to demonstrate the different behaviour compared to ordinary metals.

In fig. 1 we show the temperature dependence of the electrical resistivity of  $\text{CeAl}_3$  below room temperature [1,2]. Unlike in ordinary metals,  $\rho(T)$  goes through a minimum just below 300 K and increases with decreasing temperature reaching a maximum at  $35 \pm 1$  K. At still lower temperatures,  $\rho(T)$  decreases with increasing slope and drops by two orders of magnitude without, however, going through a phase transition. The inset in fig. 1 demonstrates that at temperatures below 0.1 K,  $\rho(T)$  can be approximated very well by [3]

$$\rho(T) = \rho_0 + AT^2 \quad (4)$$

where  $\rho_0$  is the residual resistivity of less than  $1 \mu\Omega\text{cm}$  and  $A=35\mu\Omega\text{cm}/\text{K}^2$ .

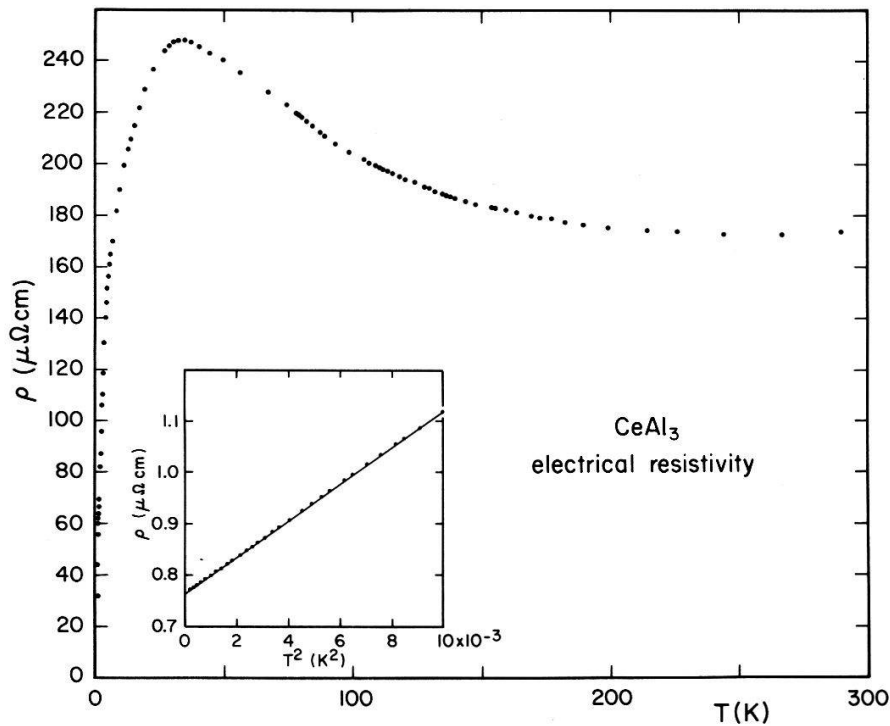


Figure 1 -  $\rho(T)$  of  $\text{CeAl}_3$  between 1.5 and 300 K and below 0.1 K. Data from refs. [2] and [3].

This latter term indicates a very effective temperature-dependent scattering in a temperature range where in ordinary metals only the temperature-independent impurity scattering determines the residual resistivity. Other Ce compounds with very similar  $\rho(T)$  curves are  $\text{CeCu}_2\text{Si}_2$  [4] and  $\text{CeCu}_6$  [5].

In fig. 2 we show the temperature dependence of the inverse magnetic susceptibility  $\chi^{-1}(T)$  below 300 K. At high temperatures,  $\chi^{-1}(T)$  clearly follows a Curie-Weiss-like behaviour [6] and the effective moment  $\mu_{\text{eff}}$  that is given by the slope of  $\chi^{-1}(T)$  is  $2.55 \mu_B/\text{Ce ion}$ , virtually identical with the expected moment of a free trivalent Ce ion with one electron occupying the 4-f shell. The inset of fig. 2 makes clear that there is a sudden break in the  $\chi^{-1}(T)$  curve and  $\chi(T)$  is almost temperature independent below 1.5 K [3]. This break occurs, again, without a phase transition and this is particularly surprising because conventionally it must be expected that the degeneracy of the crystal-field-split  $J = 5/2$  Hund's rule ground state of  $\text{Ce}^{3+}$  ions is split further upon a magnetic phase transition. Hence  $\chi(T)$  below 1.5 K is reminiscent of a Pauli susceptibility but  $\chi(T = 0 \text{ K})$  is  $3.6 \cdot 10^{-2} \text{ emu/mole}$ , a large susceptibility, orders of magnitude larger than paramagnetic susceptibilities observed in ordinary metals. Assuming for the moment that this interpretation is correct, eq. (2) would then indicate a very large density of electronic states at  $\epsilon_F$  for  $\text{CeAl}_3$ .

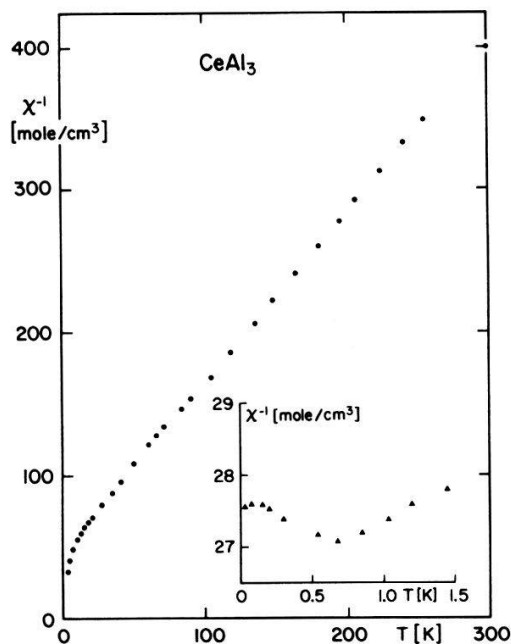


Figure 2  
 $\chi^{-1}(T)$  of  $\text{CeAl}_3$ . Data between 4.2 and 300 K are from ref. [6], data below 1.5 are from ref. [3].

In fig. 3 we have plotted the low-temperature specific heat of  $\text{CeAl}_3$  in the form  $c_p/T$  versus  $T$ . For an ordinary metal such a plot would result in a curve with slightly increasing positive slope with increasing  $T$  and a finite ordinate intercept at  $T = 0$  K. This intercept which, according to eq. (3) is a measure of the electronic contribution to the specific heat, would be of the order of a few  $\text{mJ/mole K}^2$  or less. Here we observe a distinctly different behaviour.  $c_p/T$  increases with decreasing temperature [7]. The inset shows that for  $T$  approaching 0 K, this ratio adopts a value of roughly  $1.6 \text{ J/mole K}^2$  [3], after having passed over a maximum of still higher value at temperature between 0.3 and 1 K [8]. While the interpretation of this maximum, is still not quite clear [9], it is obvious that the magnitude of this  $c_p/T$  ratio is 2000 times larger than that of copper, for example and, using eq. (3) in this case, we may again conclude that this points to a very large  $N(\epsilon_F)$ . That these large values of  $N(\epsilon_F)$  apparent in both  $\chi$  and  $c_p$  are indeed of the same origin is apparent by considering that the ratio  $\chi/\gamma$  as defined by eqs. (2) and (3) is given by known numerical quantities and may be compared with the experimental value for  $\chi/\gamma$  at  $T = 0$  K. In c.g.s. units the theoretical value of  $\chi/\gamma$  is  $1.372 \times 10^{-9}$  whereas the experimental value for  $\text{CeAl}_3$  amounts to  $2.22 \times 10^{-9}$ . In view of the simple-minded expressions for  $\chi$  and  $c_p$  a surprising and intriguing result alike.

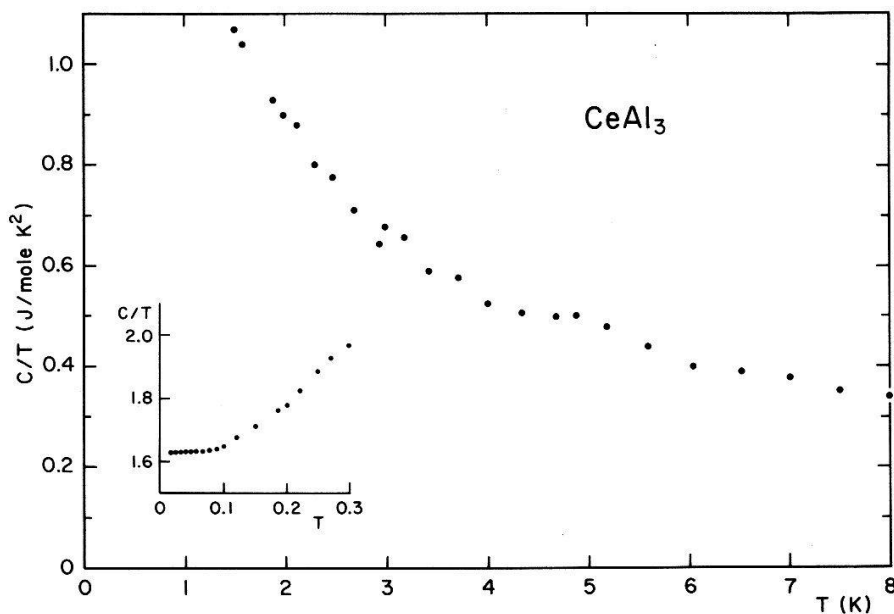


Figure 3 -  $c_p/T$  versus  $T$  for  $\text{CeAl}_3$  at low temperatures. The data for  $T < 0.3$  K are from ref. [3].

This very short display of some important physical properties of  $\text{CeAl}_3$  leads us to the following conclusions. At higher temperatures,  $\text{CeAl}_3$  may be viewed as a system with one localized 4-f electron per Ce atom. Upon cooling the atomic moments due to the f electrons, against all expectations, do not order spontaneously. Instead it appears that some of the f electrons become itinerant at low temperatures and form a metallic state. This state may be viewed as a Fermi liquid in the sense of Landau [10] where part of the interactions are taken into account by assigning an effective mass to the quasiparticles of the system. In our case this effective mass turns out to be several hundred times the free electron mass. Another way of stating the same thing is to view these heavy electrons as quasiparticles of a Fermi system with a very low Fermi temperature  $T_F$  of some 10 K. This leaves us with the very unusual situation that  $T_F < \theta_D$ , quite opposite to what is true for other metals.

### 3. Superconductivity of $\text{UBe}_{13}$

The discovery, that heavy-electron materials may be superconductors by involving these heavy quasiparticles was first made in  $\text{CeCu}_2\text{Si}_2$  [11]. It was certainly an unexpected event because before it was believed that local moments on the Ce atoms, as evidenced by  $\chi(T)$ , always strongly depress superconductivity by breaking the Cooper electron pairs. Here we should like to demonstrate this superconductivity in another compound, where the heavy electrons have their origin in an unfilled 5-f shell, namely  $\text{UBe}_{13}$ . The discovery of bulk superconductivity in this material [12] not only supported and confirmed the often debated results on  $\text{CeCu}_2\text{Si}_2$  but showed that this phenomenon is not limited to materials containing 4-f electrons.

In fig. 4 we show  $\rho(T)$  of  $\text{UBe}_{13}$  between 1.2 and 300 K. The general feature is, as shown in section 2, an increasing resistivity with decreasing temperature and an, as yet unexplained, narrow feature at low temperatures peaking at 2.5 K. The inset displays the superconducting transition by the discontinuous loss of resistivity at  $T_c$  below 1 K [12]. Measurements of the magnetic susceptibility [7] indicate a Curie-Weiss-type  $\chi(T)$  between 1.6 and 300 K with an effective moment of  $3.1 \mu_B/\text{U ion}$ . The characteristic up-turn of  $c_p/T$  with decreasing temperature below 7 K is shown in fig. 5.

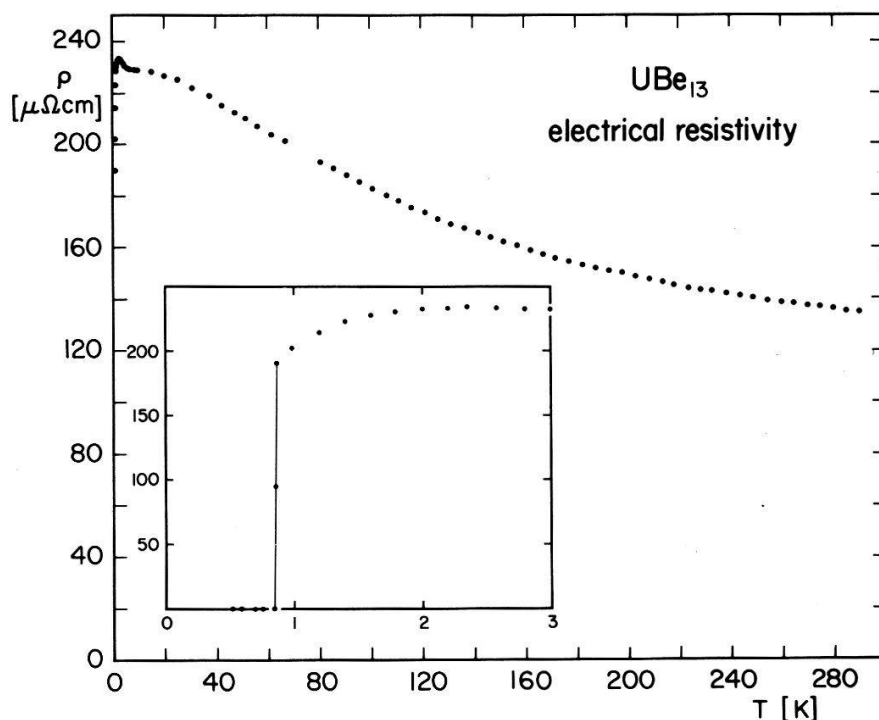


Figure 4 -  $\rho(T)$  for  $\text{UBe}_{13}$  between 1.2 and 300 K. The inset shows the superconducting transition on an extended temperature scale.

Also shown is the discontinuity of  $c_p$  at the superconducting transition and the temperature dependence of  $c_p$  below  $T_c$  down to 0.15 K. In this figure the lattice contribution to  $c_p$  has already been subtracted from the measured specific heat [7]. The solid line indicates the expected behaviour of  $c_p^{\text{el}}/T$  in the superconducting state as predicted by the theory of Bardeen, Cooper and Schrieffer [13]. This experiment is important in various ways. It demonstrates the bulk character of the superconducting state and it confirms the electronic nature of the large specific heat in the normal state at  $T_c$ , because the gap formation in the electronic excitation spectrum due to superconductivity obviously removes  $c_p$ , as expected.

An important quantity of any superconductor is its critical magnetic field above which the material returns to its normal state. The temperature dependence of the upper critical magnetic field  $H_{c2}$  ( $\text{UBe}_{13}$  is a type-II superconductor) is shown for both single-crystalline and polycrystalline  $\text{UBe}_{13}$  in fig. 6 [14]. What surprises immediately is the magnitude of  $H_{c2}$ . A zero-temperature critical field of about 100 kOe for a superconductor with  $T_c$  less than 1 K is extraordinary, to say the least. Also quite unusual is

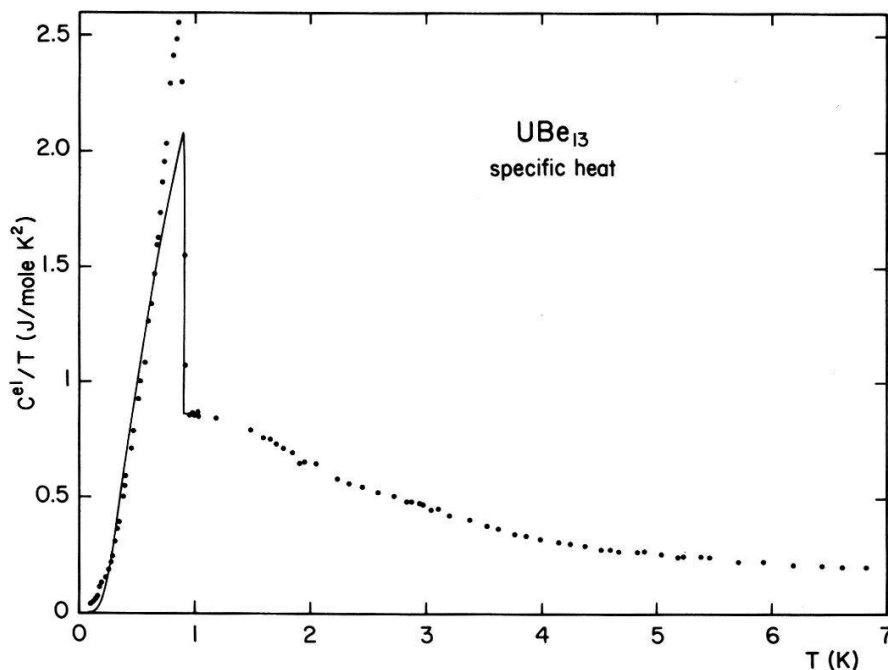


Figure 5 - Electronic specific heat of  $\text{UBe}_{13}$  plotted as  $c_p^{\text{el}}/T$  versus  $T$  between 0.15 and 7 K. The solid line marks the prediction of the BCS-theory.

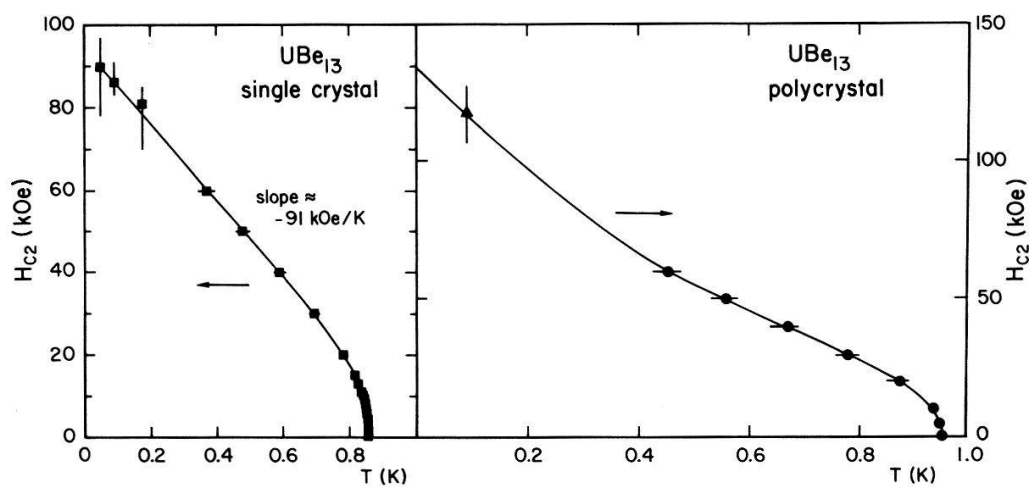


Figure 6 -  $H_{c2}(T)$  for single-crystalline and polycrystalline  $\text{UBe}_{13}$ . Data are from ref. [14].

the temperature derivative  $\partial H_{c2}/\partial T$  at  $T_c$  which is at least of the order of 0.5 MOe/K, but a vertical slope cannot be ruled out from presently available experimental data. The obvious difference in  $H_{c2}(T)$  at low temperatures may be due to an anisotropy of  $H_{c2}$  which leads to the peculiar upturn below 0.3 K in the polycrystal. For the single crystal the direction of the applied external magnetic field was parallel to  $[100]$  of the cubic crystal lattice.

The occurrence of superconductivity under seemingly unfavourable conditions soon raised the question whether it might be unconventional in the sense that no longer is the electron-phonon interaction the essential ingredient to trigger the phase transition. Under such circumstances it seems also possible that the superconducting state is characterized by unconventional pairing of the electrons or, as Anderson pointed out first [15], no longer is it a state of even but rather odd parity. This immediately raises the question about the existence of analogies, but clearly also differences, to the case of superfluid  $^3\text{He}$ , where it is fairly well established that the superfluid phase is due to triplet pairing leading to an intrinsically anisotropic phase [16]. In the case of superconductivity in metals, such anisotropies would manifest themselves by points or lines of zeroes of the superconducting energy gap which in turn would distinctly influence thermal and transport properties of the investigated material below  $T_c$ . An overall finite gap leads to exponential temperature dependences of these properties as  $T \rightarrow 0$  K, whereas in the case of an above mentioned anisotropy one would expect non-exponential  $T$  dependences in experimental measurements such as the specific heat, ultrasound attenuation, thermal conductivity or NMR relaxation rates, to mention a few examples.

In fig. 7 we show that such an observation is made for the specific heat in the superconducting state of  $\text{UPb}_{13}$ , where the renormalized specific heat  $C_s/C_n(T_c)$  is plotted versus  $T_c/T$ . We recognize immediately the distinct deviations from the BCS curve, representing an exponential  $T$  dependence for large values of  $T_c/T$ . Deviations are observed both close to the critical temperature and also well below  $T_c$ . The deviations close to  $T_c$  indicate so called strong-coupling effects. The curves labelled ABM indicate the temperature dependence of the specific heat in a state that corresponds to the anisotropic A phase of superfluid  $^3\text{He}$  (Anderson-Brinkman-Morel state) and is characterized by points of zeroes of the energy gap, often denoted as axial



state. Calculations for the weak-coupling (w.c.) and strong-coupling (s.c.) case are presented in ref. [17].

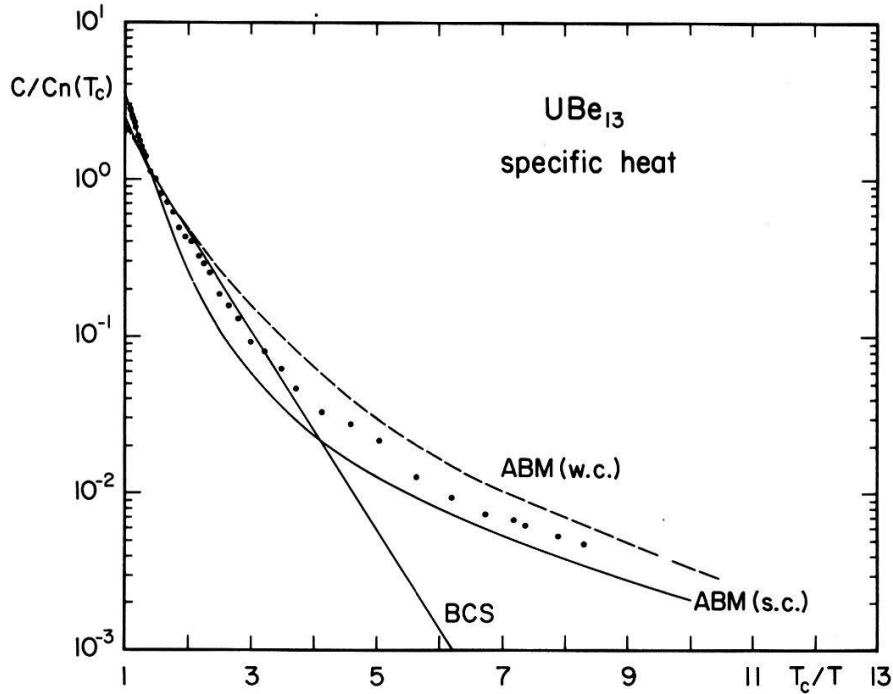


Figure 7 -  $C/C_n(T_c)$  for superconducting  $UBe_{13}$ . Dashed line: weak-coupling ABM state; solid lines: BCS and strong-coupling ABM state.

Subsequently, analogous non-exponential temperature dependences were also found in other experiments. In fig. 8 we show another example, namely the attenuation of ultrasound in superconducting  $UBe_{13}$  [18]. Clearly as  $T$  approaches 0 K, the decay is not governed by an exponential, as expected from BCS, but rather a  $T^2$  dependence is observed. Unfortunately it is much more difficult to make reliable theoretical predictions in this case and therefore it is not clear yet whether this result is also compatible with an axial (ABM) state of superconductivity. Similar power laws in  $T$  were found for the thermal conductivity [19] and the nuclear-spin-lattice relaxation rate [10] of  $UBe_{13}$  below  $T_c$ .

Another unusual feature is the anomalous peak in the ultrasound attenuation just below  $T_c$  of  $UBe_{13}$ , as shown in fig. 9. It has been argued that it might be due to collective modes of the order parameter in an anisotropic superconductor [18] but the final word has not been said in this case. The shift of the anomaly in an external magnetic field demonstrates

that it is related with the superconducting transition. It is surprising that the anomaly increases with increasing field.

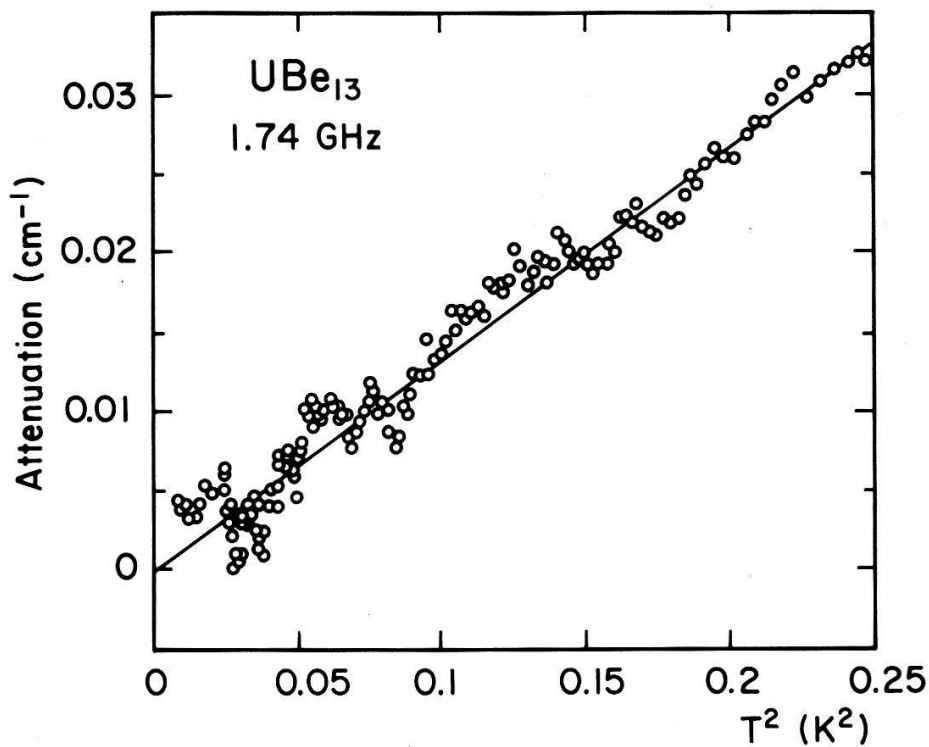


Figure 8 - Temperature dependence of the attenuation of ultra-sound in superconducting  $\text{UBe}_{13}$  between 0.1 and 0.5 K.

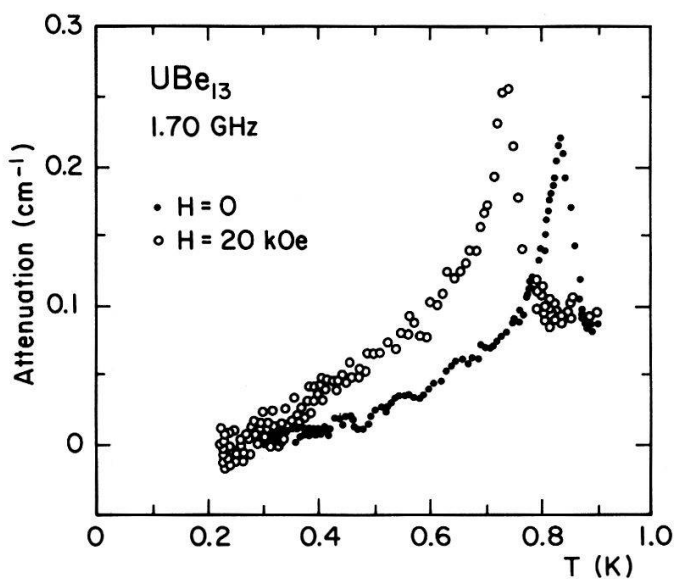


Figure 9

Acoustic attenuation peak in superconducting  $\text{UBe}_{13}$  below  $T_c$ . The peak shifts to lower temperatures with increasing magnetic field.

It is, of course, also of interest to probe the temperature dependence of a quantity that is related exclusively to the superconducting phase. In principle this is possible by measuring the penetration depth of a magnetic field into the superconductor, the so called London penetration depth, because it is given by

$$\lambda_L^2 = \frac{m^* c^2}{4\pi n_s e^2} \quad (5)$$

where  $n_s$  is the renormalized density of superconducting particles, i.e.  $n_s = 1$  at  $T = 0$  K and  $n_s = 0$  for  $T > T_c$ . This has recently been done by Einzel and co-workers [21] and we show their result for  $UBe_{13}$  in fig. 10. Since the technique employed in these measurements did not allow for an absolute measurement, only the temperature dependence of  $\lambda_L$  can be shown. For comparison, fig. 10 also displays the result of the same experimental method for tin in the same region of reduced temperature  $T/T_c$ .  $\lambda_L$  of tin is known to follow the temperature dependence given by the BCS theory rather well and it is obvious that this is not the case for  $\lambda_L$  of  $UBe_{13}$ . Elaborate calculations and comparison with the experimental data lead to the conclusion [21,22] that  $\lambda_L$  of  $UBe_{13}$  is most compatible with expectations assuming an axial superconducting state. Without going into details, we mention here that this same assumption fixes the temperature dependence of  $\lambda_L$  and hence an estimate of the absolute value of  $\lambda_L$  can be made using the data shown in fig. 10. As expected,  $\lambda_L(0)$  turns out to be a few thousand Å, compatible with a large effective mass  $m^*$  which enters eq. (5).

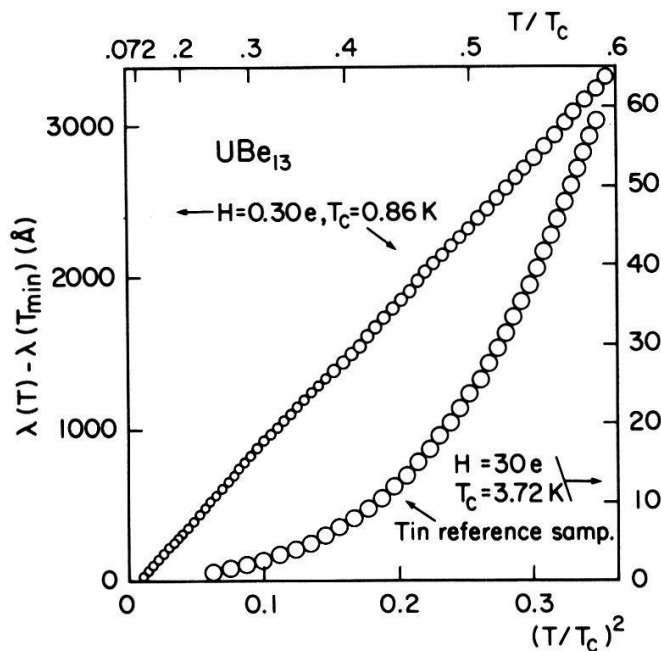


Figure 10  
Incremental magnetic-field penetration depth of  $UBe_{13}$ . Also shown, for comparison, are the data for a tin reference sample.

Since it is expected that superconductivity with  $\ell \neq 0$  pairing is extremely susceptible to any kind of impurities, it is often argued that an anisotropic superconducting state is not possible in any real metal. Since many other experimental facts, some of which we mentioned above, suggest the possibility of such a state, it is of some interest to investigate the influence of deliberately introduced impurities which will do again for the case of  $\text{UBe}_{13}$ . Before concentrating on the superconducting state we show in fig. 11 that small amounts of non-magnetic impurities have a remarkable influence on the low-temperature specific heat of the normal state. While Th impurities on U sites enhance the  $c_p/T$  ratio just above  $T_c$ , the same amount of Lu replacing U reduces it considerably [23]. Similarly drastic effects are observed in the temperature dependence of the electrical resistivity. Th impurities reduce the resistivity at  $T_c$  whereas Lu impurities lead to a negative temperature derivative  $\partial\rho/\partial T$  down to  $T = 0$  K [24].

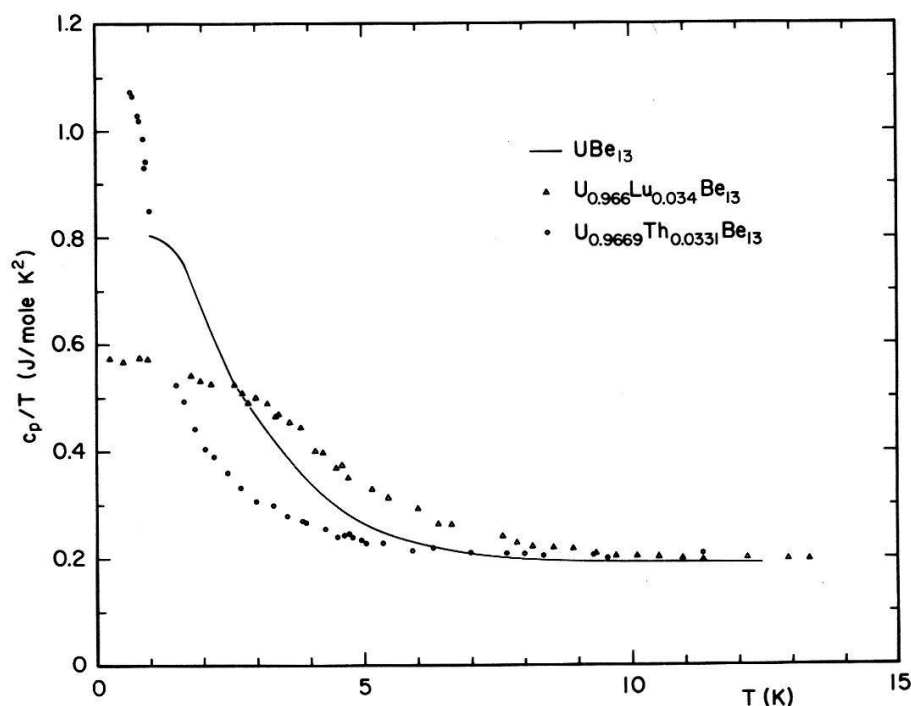


Figure 11 - Comparison of the influence of different impurities on the low-temperature normal-state specific heat of  $\text{UBe}_{13}$ .

Quite spectacular is the influence of Th atoms on U sites on the superconducting state of  $\text{UBe}_{13}$ . In fig. 12 we show the concentration dependence of  $T_c$  of  $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$  for small values of  $x$ . First,  $T_c$  is reduced quite

strongly, considering that Th is a non-magnetic impurity. When  $x$  exceeds about 0.017,  $T_c$  starts to rise again and passes over a broad maximum centered around  $x \approx 0.03$ . For still higher values of  $x$ ,  $T_c$  decreases again. What is most surprising, however, is the second phase transition that occurs

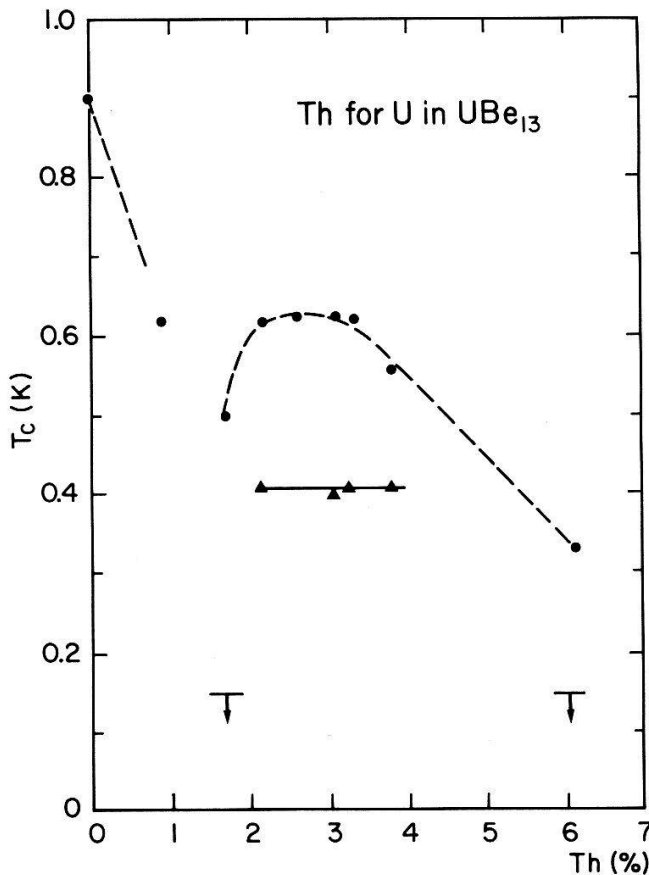


Figure 12

Critical temperatures for  $U_{1-x}Th_xBe_{13}$  from  $c_p$  measurements. Dots indicate the superconducting transition, triangles the second transition at  $T_{c2}$ . At 1.7 and 6% Th, no second transition was observed above 0.15 K.

in the superconducting state of  $U_{1-x}Th_xBe_{13}$  when  $x$  has values between about 0.02 and 0.04. The temperatures  $T_{c2}$  at which these second transitions occur, as first observed with specific heat measurements [25], are indicated by solid triangles in fig. 12, and it appears that they do not depend very much on  $x$ . An example of the temperature dependence of  $c_p$  below 1 K for such a case is shown in fig. 13. Other manifestations of the second transition were subsequently observed by measurements of the thermal expansion [23] and the ultrasound attenuation [26]. There is still some uncertainty with respect to the interpretation of the transition at  $T_{c2}$ . It definitely does not destroy the superconducting state. Microscopic measurements employing nuclear-magnetic-resonance (NMR) [20] and muon-spin-rotation ( $\mu$ SR) [27] techniques suggest that no ordered moments of size bigger than  $0.01 \mu_B/U$  exist below  $T_c$ . A structural transition cannot be ruled out completely but

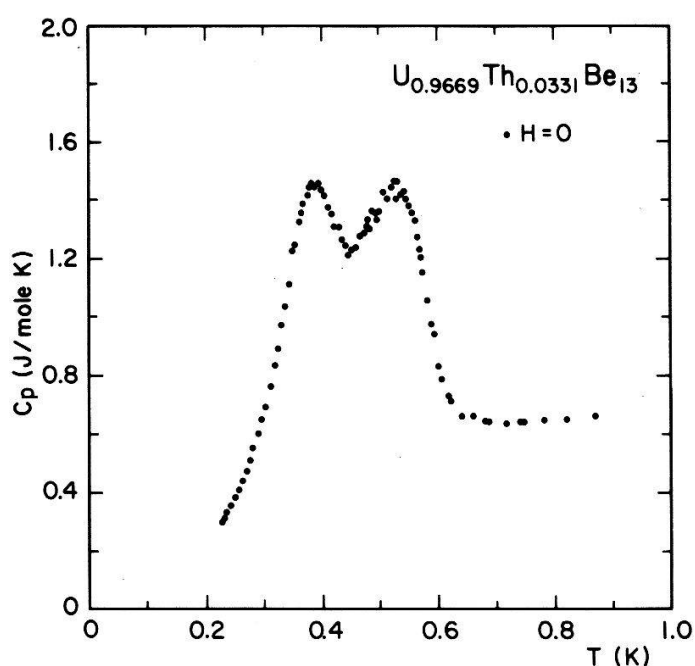


Table 13

Specific-heat anomalies for  
Th doped  $\text{UBe}_{13}$  below 1 K.

it is very unlikely because the lower transition is shifted in a magnetic field to lower temperature very similar as is the superconducting transition. This may be seen in fig. 14. where we show the specific heat of Th doped  $\text{UBe}_{13}$  for some values of an external magnetic field [23]. Currently it is considered that this lower transition leads from one anisotropic superconducting state to another [28]. This could, of course, only happen with some unconventional type of superconductivity. Another interesting aspect that is revealed by fig. 14 is the continuous increase of the  $c_p/T$  ratio in the magnetic-field induced normal state, tending to a value at  $T = 0$  K that is more than twice as big as that of pure  $\text{UBe}_{13}$ .

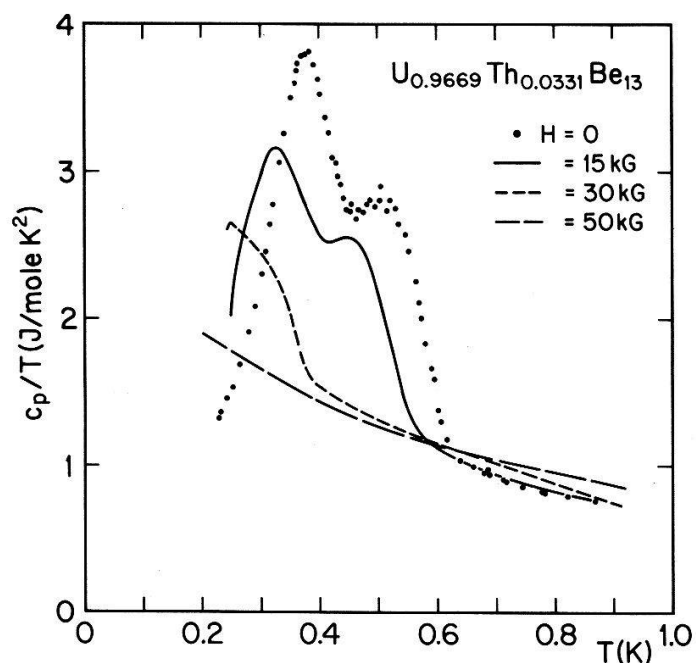


Table 14

Influence of external magnetic fields on the specific heat of Th-doped  $\text{UBe}_{13}$  below 1 K.

In fig. 15 we show that various other non-magnetic impurities replacing U are indeed harmful for the superconductivity of  $\text{UBe}_{13}$ . Amounts of less than 2% of Lu, Y and Zr reduce  $T_c$  and the specific-heat anomaly very effectively. For 1.5% Zr,  $T_c$  is still 0.7 K but, as may be seen in fig. 15,  $c_p(T)$  is quite different from that of pure  $\text{UBe}_{13}$  or of a similarly doped (U,Th) $\text{Be}_{13}$  sample. It is, in fact, reminiscent of  $c_p(T)$  of  $\text{UPt}_3$ , another heavy-electron superconductor with  $T_c \approx 0.5$  K [29]. For Lu and Y impurities of similar concentration,  $T_c$  is shifted to below 0.3K and the corresponding  $c_p$  anomalies have virtually vanished. This implies that these impurities very rapidly lead to a gapless state in the sense that the superconducting energy gap is zero on most parts of the Fermi surface. That this happens with non-magnetic impurities is suggestive for an extension of the intrinsic gap-zeroes of an anisotropic superconducting state by normal impurity scattering as was discussed by Ueda and Rice [30]. This would again be compatible with the view that we are dealing with some kind of unconventional superconductivity.

At this point it can, of course, not be claimed that the occurrence of unconventional superconductivity in heavy-electron metals has been proven beyond any doubt. But it is true that the mere possibility and growing experimental evidence for it has initiated a new activity among theorists to in-

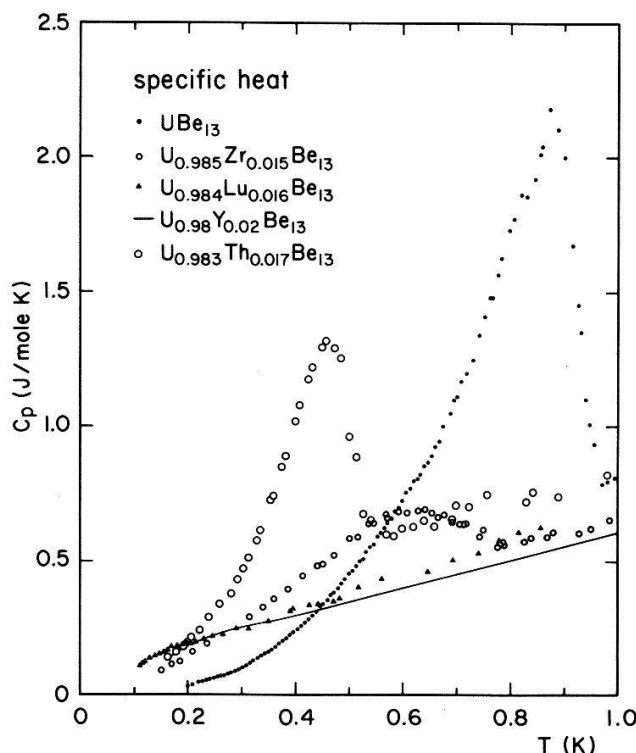


Figure 15  
Influence of various impurities  
on the specific heat of UBe  
below 1 K.



investigate various possibility of such superconducting states and their expected properties [31]. Not much has been done yet concerning possible mechanisms that would be responsible for inducing this superconductivity. No doubt many of these questions still have to be settled, opening a vast field for fruitful collaborations between experimentalists and theorists.

#### 4. Heavy electrons in a magnetically-ordered material, $\text{UCu}_5$

For some time the formation of a heavy-electron state was viewed as a result of suppressed magnetic order. This seems plausible because the slow loss of entropy  $S$  with decreasing temperature as opposed to a rapid reduction of  $S(T)$  upon a phase transition inevitably leads to large specific heats at low temperatures [32]. Two well known interactions of conduction electrons with atomic moments are thought to be responsible for the general low-temperature behaviour of potentially magnetic metals. These are the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction which favours parallel or antiparallel alignment of atomic moments mediated by conduction electrons and may provide spontaneous magnetic ordering, and the Kondo interaction which tends to compensate atomic moments by antiparallel alignment of nearby conduction electrons and hence suppresses magnetic order. Theoretically it is still investigated, whether these two interactions influence each other and, if yes, how [33]? It is of some significance in connection with these questions that recently it was demonstrated that the formation of a heavy-electron state is also possible in a magnetically ordered material, namely  $\text{UCu}_5$  [34].

The antiferromagnetic ordering of  $\text{UCu}_5$  had been investigated by various authors [35-37]. Recent specific-heat measurements from 0.15 to 21 K have revealed [34] that at temperatures well below the magnetic transition, a distinct enhancement of the  $c_p/T$  ratio indicates the formation of a heavy-electron state. We show these results in fig. 16. The inset demonstrates the linear  $T$  variation of  $c_p(T)$  at the lowest temperatures but it should be noted that the slope of  $c_p(T)$  is only about 1/4 of the value of  $c_p/T$  obtained at 1.5 K. In fig. 17 we show the cause of this sizeable reduction, namely the occurrence of another phase transition in  $\text{UCu}_5$  in the vicinity of 1 K, which appears to open gaps in the excitation spectrum of the heavy quasiparticles. This phase transition can be suppressed by replacing one Cu atom per formula unit by Ag and in that case, the heavy-electron state is unaffected down to 0.2 K, as is indicated by corresponding  $c_p$  data also

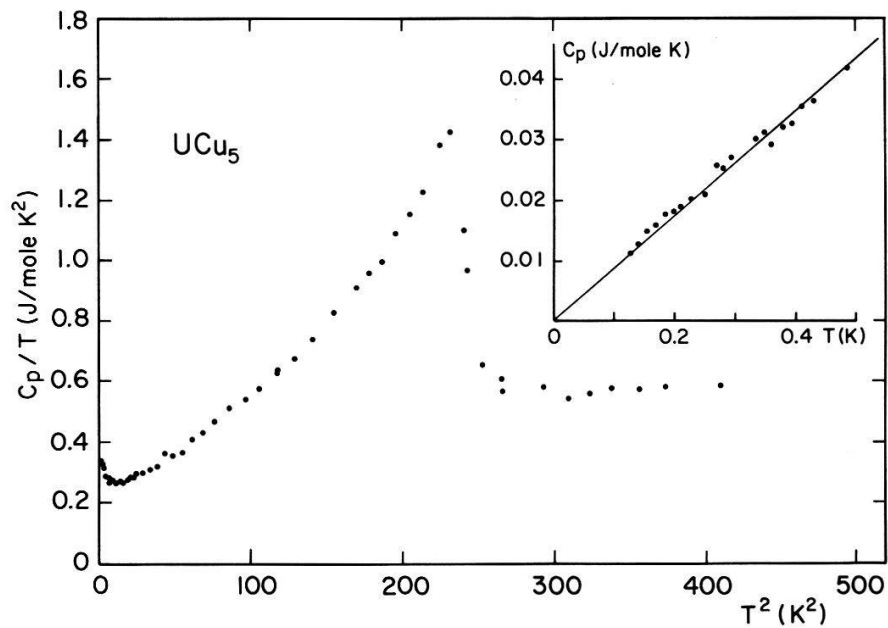


Figure 16 - Low-temperature specific heat of  $\text{UCu}_5$  between 0.15 and 21 K.

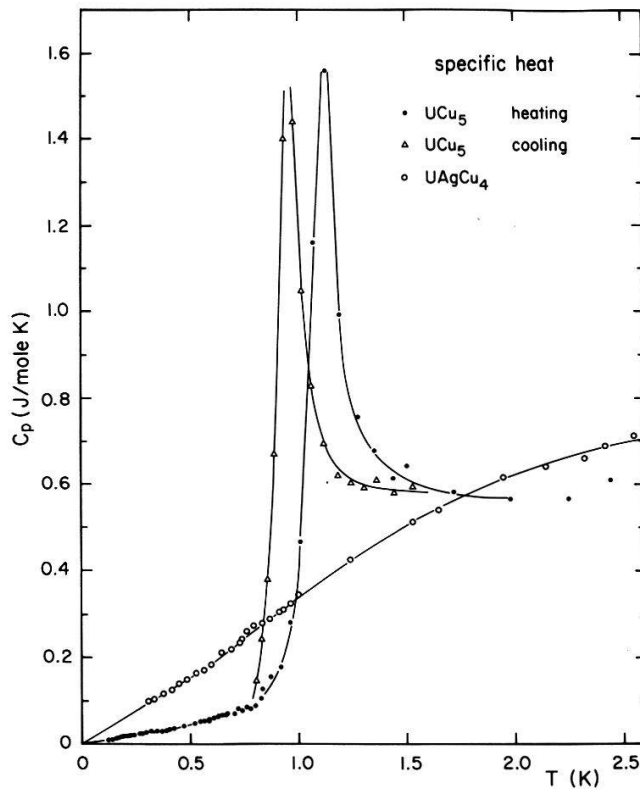


Table 17

Specific heat of  $\text{UCu}_5$  and  $\text{UAgCu}_4$  between 0.15 and 2.5 K.

shown in fig. 17. Of additional interest are the particular features of the  $c_p$  anomalies related with this new phase transition in  $\text{UCu}_5$ , whose nature has not firmly been established yet. Depending on whether the  $c_p$  measure-

ments are made upon cooling or warming the sample, the anomalies appear at slightly different temperatures. In spite of some efforts, no latent heat associated with the transition was found. The observation of a hysteresis but of no latent heat rises some questions with regards to the classification of this transition and further investigations have to be made.

In connection with this phase transition a new aspect concerning the electrical resistivity of heavy-electrons states arised. The formation of the heavy-electron state is usually accompanied by a strong reduction of the electrical resistivity as demonstrated above with the example of  $\text{CeAl}_3$  or seen, only as an onset which is intercepted by the superconducting transition, in the case of  $\text{UBe}_{13}$ . In  $\text{UCu}_5$ ,  $\rho(T)$  decreases steadily below 10 K, passes through a minimum at 1.6 K and subsequently increases by a factor of 7 with decreasing temperature through the transition. In contrast to all other known heavy-electron ground states, the low-temperature state of  $\text{UCu}_5$  is thus characterized by a large value of  $\rho$  as verified to about 0.02 K.

As we have outlined above, partial replacement of Cu by Ag only affects the phase transition in but not the formation of the heavy-electron state. Quite different is the influence of other impurities in  $\text{UCu}_5$ . As may be seen from fig. 18, 1% Ni on the Cu sites is sufficient to suppress

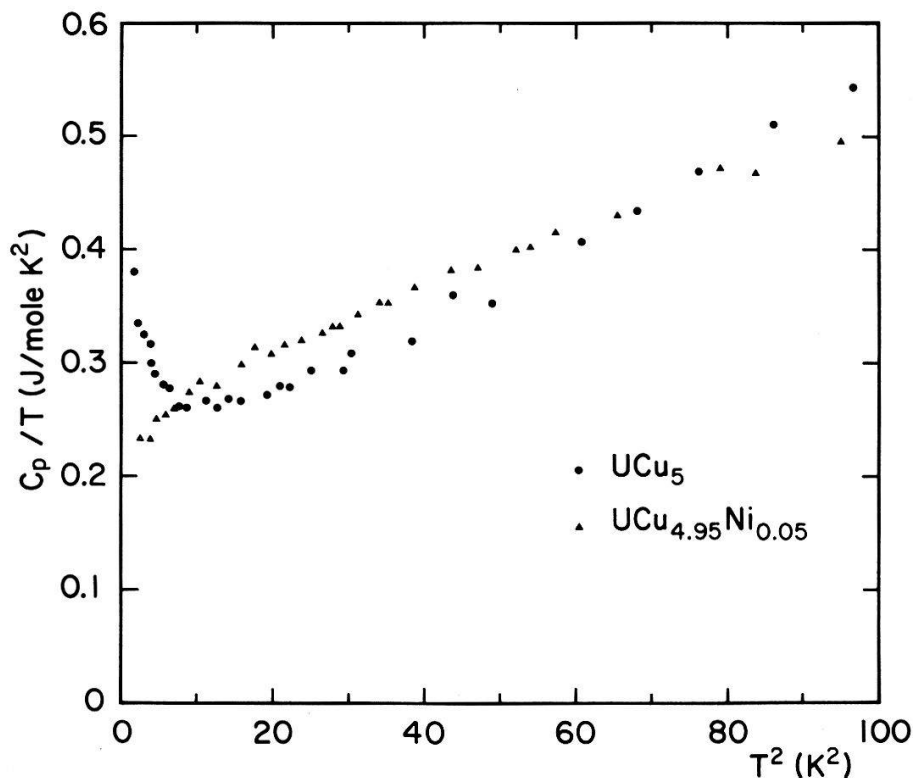


Figure 18 -  $c/T$  versus  $T^2$  for  $\text{UCu}_5$  and  $\text{UCu}_{4.95}\text{Ni}_{0.05}$  between 1.5 and 10 K.

completely the specific-heat enhancement that is observed in the pure case. In addition it has been found [38] that in this case the electrical resistivity at 1.5 K is enhanced by a factor of 2 and the temperature derivative is negative at all temperatures. This again demonstrates that the formation of such a state may easily be influenced by small amounts of impurities. As in the case of  $\text{UBe}_{13}$ , that was demonstrated above (see fig. 11), it is not yet established whether simple impurity scattering or the influence of a, whatever small, lattice-constant change, or both, are responsible for these changes.

In fig. 16 it may be seen that the antiferromagnetic phase transition in  $\text{UCu}_5$  occurs at about 15 K and microscopic investigations [36,39] indicate that it is a fairly conventional type of ordering. It is therefore rather surprising that, again, small amounts of Ni atoms on the Cu sites may influence the magnitude of the  $c_p$  anomaly as drastically as is shown in fig. 19. Although the ordering temperature is not shifted, the amount of entropy that is released by the phase transition is drastically reduced upon Ni doping [40]. Again quite in contrast to it is a Cu replacement by Ag where  $T_N$  is enhanced by about 20% and the  $c_p$  anomaly is correspondingly large [34].

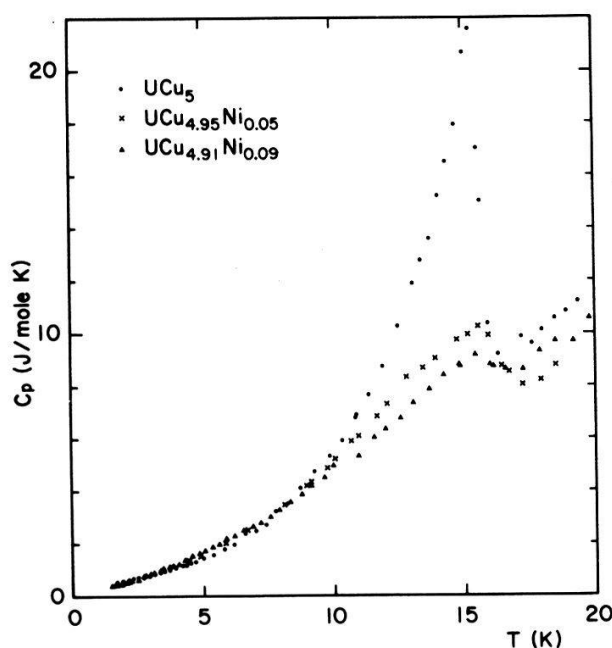


Figure 19

Influence of small amounts of Ni impurities on the anomaly of the specific heat at the antiferromagnetic transition of  $\text{UCu}_5$ .

## 5. Summary

All the data shown above are intended to demonstrate the vast amount of interesting physics that rewards any investigation on heavy-electron materials. Of general interest, hopefully also for non-solid-state physicist, are the aspect of many-body effects among conduction electrons in metals which are clearly a prominent feature here, the possibility of a new kind of superconductivity and finally the materials-science aspects as evidenced by the strong influence of small amounts of impurities on physical properties of these solids.

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