HEAVY ELECTRONS IN METALS

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After recognizing the occurrence of heavy electrons in metals at low temperatures it was found that they may undergo transitions to a superconducting state. Details of one of these materials, UBe₁₃, are shown and discussed. A comparison of experimental data of the specific heat and theoretical calculations suggests that the superconducting state is the electronic analogue of the A phase of superfluid ³He. The influence of impurities on the superconducting state of UBe₁₃ and properties of similar compounds which are not superconductors but order magnetically instead support these ideas.

1. Introduction

Although Sommerfeld's free electron model [1] is surprisingly successful in describing the salient features of the electronic system in metals it is clear that it must fail when electronic properties of real metals are considered qualitatively. Since many of these properties depend on the mass m of the electrons it has become customary to choose this mass as a free parameter and to introduce effective masses m* in order to approximate theoretical results to experimental data. A more scientific basis to this heuristic point of view was then given by Landau in his famous Fermi-liquid theory [2].

In most metals, the ratio m*/m lies in the range of 0.1 < m*/m < 10, whereby the extremal values are attained in singular cases only. Here we should like to consider cases, where m*/m is of the order of 100 or more. The low-temperature behaviour of metals whose electronic system is characterized by these extraordinary values is apparently quite well described by using Landau's Fermi-liquid approach. Since liquid ³He is the standard example for a Fermi liquid it seems natural to look for analogies between these above mentioned metallic solids and liquid ³He, especially with respect to ground-state properties. Therefore these aspects will also be discussed to some extent below.

2. Normal-state properties

The occurrence of electrons in metals with Fermi-liquid behaviour was first recognized from the low-temperature properties of CeAl₃ by measurements of the specific heat cₚ, the magnetic susceptibility χ and the electrical resistivity ρ at temperatures well below 1 K [3]. In this temperature range, the specific heat has a linear T dependence with an enormous slope of about 1.6 J/mole K²; the magnetic susceptibility varies very little with temperature and ρ may be expressed as ρ = ρ₀ + AT², where ρ₀ is the residual resistivity and A = 35 μΩ cm/K², a rather large value. Very recently it was found [4] that the thermal conductivity λ shows roughly, as displayed in fig. 1, the expected corresponding behaviour, namely λ⁻¹ = BT + CT⁻¹, leading to a maximum of λ at about 0.25 K where, with decreasing temperature, impurity scattering becomes dominant. The solid line in fig. 1 was obtained from λ = (L₀/ρ)T, where L₀ is the Lorenz number and ρ the experimentally measured electrical resistivity. Deviations from this idealized behaviour are, however, quite likely.

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especially if one considers the temperature dependence of $\lambda$ in liquid $^3$He, as shortly discussed below. It should also be mentioned that all these properties are very little affected by external magnetic fields.

This low-temperature behaviour of CeAl$_3$ is all the more surprising, since the temperature dependences of both $\chi$ and $\rho$ at higher temperatures do not give any indication that it might be expected. $\chi(T)$ follows a Curie-Weiss law and the slope of $\chi^{-1}(T)$ is consistent with an effective moment of 2.55 $\mu_B$/Ce ion as expected for free Ce$^{3+}$ ions [5]. $\rho(T)$ is quite anomalous for a metal, as may be seen in fig. 2. Below room temperature $\rho$ increases steadily with decreasing temperature and, after a well-defined maximum at 35 K, drops from values of the order of 100 $\mu\Omega$ cm to below 1 $\mu\Omega$ cm at $T = 0$ K. In an attempt to interpret early measurements of Buschow and co-workers [6], Cornut and Coqblin [7] were able to account for the high temperature behaviour of $\rho$ by considering the influence of the Kondo effect and a crystal-field splitting of the $J = 5/2$ ground state of the Ce$^{3+}$

**Fig. 1.** Thermal Conductivity of CeAl$_3$ between 0.06 and 1.6 K. The solid line is calculated from $\lambda = (L_0/\rho)T$, where $L_0$ is the Lorenz number and $\rho$ the experimental electrical resistivity. At 1.6 K, the lattice contribution equals the electronic contribution.

**Fig. 2.** Temperature dependence of the electrical resistivity of CeAl$_3$ between 1 and 300 K.
ions. This approach, however, fails completely and, in retrospect naturally, at very low temperatures, because it is based on a one-impurity concept.

All the low-temperature properties of CeAl₃ mentioned above indicate an effective Fermi temperature $T_F^*$ for its electronic subsystem at low temperatures of the order of 10 K, thereby suggesting a large effective mass $m^*$ since $T_F^*$ is proportional to $m^*^{-1}$. We recall that for the classical Fermi liquid, namely $^3$He, $T_F^*$ is an order of magnitude lower, a few tenths of a Kelvin [8]. It seems therefore instructive to look for similarities between the two systems for temperatures $T < T_F^*$. This is demonstrated in fig. 3 where the electronic specific heat of CeAl₃ [9] is plotted in the form $c_p/T$ versus $T$ and compared with $c_p/T$ versus $T$ of liquid $^3$He [10]. In both cases the variation is reminiscent to that of a system of non-interacting particles obeying Fermi-Dirac statistics in the range $T < T_F$, where $T_F$ is the normal Fermi temperature. As a further analogy we may mention the increase of the thermal conductivity with decreasing temperature that was also observed in $^3$He below its $T_F$ [11] where, however, the need for a correction term to the $T^{-1}$ dependence was established experimentally [11] and subsequently also explained theoretically [12]. Discussions attempting to demonstrate the similarities between CeAl₃ and liquid $^3$He have been given by other authors [13] by using similar arguments.

The recent discovery of superconductivity in materials whose normal-state properties are similar to those of CeAl₃, naturally lead to speculations whether the analogy to $^3$He extends also to the superconducting state of these metals with the superfluid state of $^3$He and, moreover, also with the mechanisms leading to the respective ground states.

3. Superconducting ground state

Superconductivity in a material which has normal-state properties that are very similar to
those of CeAl₃ was first observed and identified in CeCu₂Si₂ [14]. The bulk character of the superconducting state was most clearly established by specific-heat measurements which also revealed that this state was formed with the heavy electrons which give rise to the enormous electronic specific heat in the normal state. It was also recognized that the initial slope of the upper critical field \( dH_c/dT \) at \( T_c \) was anomalously large and of the order of \(-10 \ T/K\) [15]. Materials problems with this substance for some time concealed the significance of these observations. Therefore the discovery of bulk superconductivity in another system with heavy electrons, namely UBe₁₃ [16], was most welcome not only because it proved to be free of serious problems with the synthesis of this substance but also because it confirmed that heavy-electron systems may indeed undergo phase transitions at very low temperatures.

UBe₁₃ is a cubic intermetallic compound with a nearest U–U distance of 5.15 Å [17]. Therefore a more or less complete localization of the three 5f electrons per U ion is expected. Early measurements of the magnetic susceptibility seemed to confirm this conjecture but neither magnetic order nor, as in the case of a 5f⁰ configuration, an also possible Van Vleck-type paramagnetic behaviour was observed at the lowest temperatures [18]. Strong diamagnetic signals below 1 K were attributed to precipitated U filaments becoming superconducting [19].

Recent specific-heat measurements, however, demonstrated a bulk transition into a superconducting state at 0.9 K, accompanied by a diamagnetic susceptibility and a zero electrical resistivity below that same temperature [16]. In fig. 4 we show the electronic specific heat of UBe₁₃ in the form \( c_{el}/T \) versus \( T \) below 7 K. To obtain \( c_{el} \), the lattice contribution as deduced from the slope of a \( c/T \) versus \( T^2 \) plot was subtracted from the measured specific heat \( c \).

Above the critical temperature \( T_c \), the same characteristic behaviour as shown for CeAl₃ and \(^3\)He in fig. 3 is observed. Between 1.0 and 1.5 K \( c_{el}/T \) is almost temperature independent. The

![UBe₁₃ specific heat](image)

Fig. 4. Electronic specific heat of UBe₁₃ between 0.06 and 7 K. The discontinuity indicates the superconducting transition. The solid line is the universal BCS curve for \( c_{el}/T \) considering the experimental \( c_{el}/T \) value at \( T_c \) in the normal state.
discontinuity of the specific heat at the superconducting transition is clearly larger than that expected from BCS theory \[20\] in the weak-coupling limit and which is displayed as solid line in fig. 4. It is in fact the magnitude of this discontinuity and the entropy loss due to the transition which definitely prove that the enhanced specific heat just above \(T_c\) is really electronic in nature and that the superconducting state is formed by these heavy-mass electrons.

Measurements of the electrical resistivity of UBe\(_{13}\) in external magnetic fields have shown, that the superconducting state of this material is extremely stable with respect to magnetic fields. In low fields, \(T_c\) is hardly suppressed at all and for \((dH_{c2}/dT)_{T_c}\) an enormous value of the order of \(-1\,\text{MOe/K}\) is observed \[21\]. The slope of \(dH_{c2}/dT\) decreases rapidly around 20 kOe and then stays constant with a value of about \(-100\,\text{kOe/K}\). UBe\(_{13}\) is still superconducting in a field of 60 kOe at 0.37 K \[21\]. As a second main result we note a considerable negative magnetoresistance in the normal state below 1 K \[21\].

The low-temperature properties of UBe\(_{13}\) are considerably influenced by replacing U atoms with Th, even in small amounts of a few percent. As an example we show in fig. 5 the changes of the electrical resistivity when Th is introduced as an impurity. In pure UBe\(_{13}\), \(\rho(T)\) (not shown in fig. 5) also steadily increases with decreasing temperature below 300 K, saturating as a should

![Fig. 5. Temperature dependence of the electrical resistivity of U\(_{1-x}\)Th\(_x\)Be\(_{13}\) compounds between 1 and 300 K for small values of \(x\). Note the rather drastic change for a small variation of \(x\).](image)

![Fig. 6. Temperature dependence of the specific heat of U\(_{0.9669}\)Th\(_{0.0331}\)Be\(_{13}\) between 0.15 and 1 K. The upper discontinuity is the superconducting transition.](image)
possible reasons for their observation would exceed the allotted space. Further work will clarify this.

The extraordinary normal-state and superconducting properties of UBe$_{13}$ at low temperatures naturally lead to speculations that the similarities between $^3$He and CeAl$_3$ might be extended to UBe$_{13}$, especially with respect to what causes the superconducting state and how this state may be characterized. First attempts in this direction have been made by discussing the specific heat $c_s$ of UBe$_{13}$ in the superconducting state [22]. As may be seen from fig. 4, $c_s$ does not follow the universal BCS behaviour. The deviations are most pronounced close to $T_c$ and at very low temperatures. The work presented in ref. 22 suggests that UBe$_{13}$ enters a superconducting state analogous to the A-phase of liquid $^3$He, denoted as the Anderson-Brinkman-Morel (ABM) state [23] which in $^3$He is stabilized by strong spin fluctuations. The strong-coupling parameter deduced from fitting the appropriate expressions to experiment for UBe$_{13}$ [22] is consistent with the ABM state being stable at all temperatures below $T_c$. This would also imply that interactions other than electron-phonon interactions are stabilizing the superconducting ground state of UBe$_{13}$.

4. Magnetic ground state

If, as suggested above, magnetic interactions are important for the low temperature properties of UBe$_{13}$, it is conceivable that in other similar materials, magnetically ordered ground states of the electron system may be observed. This was first suggested to occur in antiferromagnetic Ni$_3$Sn$_3$ [24], and more recently an analogous behaviour at low temperatures, as evidenced by measurements of the specific heat, the magnetic susceptibility and the electrical resistivity, was discovered in U$_2$Zn$_7$ [25]. To illustrate this, we show the low-temperature specific heat of U$_2$Zn$_7$ in fig. 7 where $c^e/T$ is plotted versus $T^2$. $c^e(T)$ denotes the experimental specific heat

\[ c_p = c_{\text{specific heat}} - c_{\text{contribution}}(\text{Th}_2\text{Zn}_7) \]

\[ = \frac{c^e(T)}{T} \]

Fig. 7. $c^e/T$ versus $T^2$ for U$_2$Zn$_7$ between 1.5 and 17 K. $\gamma_6$ and $\gamma_0$ denote the electronic specific heat parameter above and below the magnetic phase transition at 9.70 K. The broken line at low temperatures indicates a non-lattice $T^3$ contribution to $c_p$. 

\[ \text{specific heat} \]

\[ U_2\text{Zn}_7 \]

\[ c_p = c_{\text{specific heat}} - c_{\text{contribution}}(\text{Th}_2\text{Zn}_7) \]

\[ = \frac{c^e(T)}{T} \]
minus the lattice contribution which was obtained from analogous measurements on isostructural \text{Th}_2\text{Zn}_{17}. Again, an anomalously large specific heat linear in \( T \) suggests a high density of electronic states at \( E_F \). The phase transition obviously does not affect the entire Fermi surface since a still quite considerable \( c_{\text{fl}} \) linear in \( T \) is observed as \( T \rightarrow 0 \). Moreover, a non-lattice \( T^3 \) contribution is important at the lowest temperatures which may be attributed to spin waves in the antiferromagnetically ordered state.

5. Conclusions

The shown and mentioned experimental facts reveal unusual and, at least partly, novel effects to occur in metals where electrons adopt a state with a very large density of states at \( E_F \). This state seems to emerge out of an almost localized state at higher temperatures when \( T \) is lowered towards 0 K.

References