### Title
Heavy electrons in metals




### Journal
Physica B+C, 127(1-3)

### ISSN
0378-4363



### Authors
Ott, HR
Rudigier, H
Fisk, Z
et al.



### Publication Date
1984-12-01

### DOI
10.1016/s0378-4363(84)80058-3

Physica 127B (1984) 359–365
North-Holland, Amsterdam

# HEAVY ELECTRONS IN METALS

H.R. OTT* and H. RUDIGIER*
*Laboratorium für Festkörperphysik, ETH-Hönggerberg, 8093 Zürich, Switzerland*

Z. FISK† and J.L. SMITH†
*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

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, $UBe_{13}$ 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 $UBe_{13}$ 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 $CeAl_3$ by measurements of the specific heat $c_p$, the magnetic susceptibility $\chi$ and the electrical resistivity $\rho$ 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 K$^2$; the magnetic susceptibility varies very little with temperature and $\rho$ may be expressed as $\rho = \rho_0 + AT^2$, where $\rho_0$ is the residual resistivity and $A = 35\ \mu\Omega$ cm/K$^2$, a rather large value. Very recently it was found [4] that the thermal conductivity $\lambda$ shows roughly, as displayed in fig. 1, the expected corresponding behaviour, namely $\lambda^{-1} = BT + CT^{-1}$, leading to a maximum of $\lambda$ at about 0.25 K where, with decreasing temperature, impurity scattering becomes dominant. The solid line in fig. 1 was obtained from $\lambda = (L_0/\rho)T$, where $L_0$ is the Lorenz number and $\rho$ the experimentally measured electrical resistivity. Deviations from this idealized behaviour are, however, quite likely,

* Work supported in part by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung.
† Work done under the auspices of the U.S. Department of Energy.

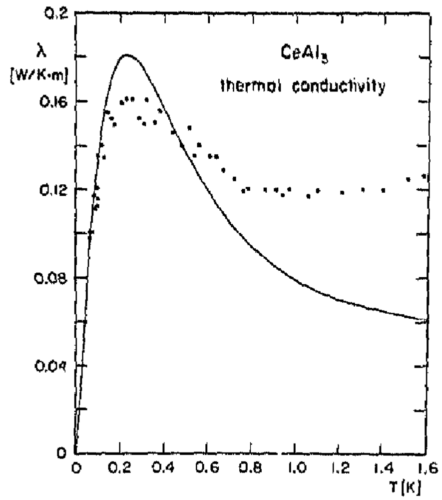


Fig. 1. Thermal Conductivity of $CeAl_3$ between 0.06 and 1.6 K. The solid line is calculated from $\lambda = (L_0/\rho)T$, where $L_0$ is the Lorenz number and $\rho$ the experimental electrical resistivity. At 1.6 K, the lattice contribution equals the electronic contribution.

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 $Ce^{3+}$

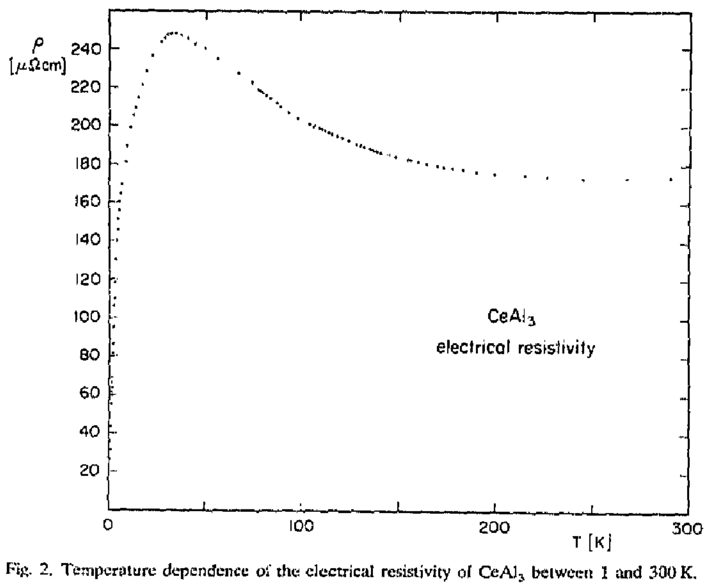


Fig. 2. Temperature dependence of the electrical resistivity of $CeAl_3$ between 1 and 300 K.

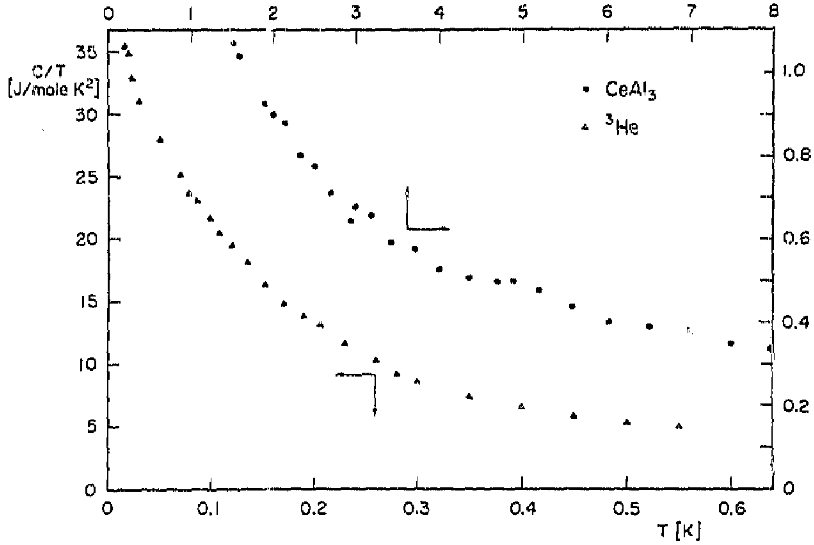


Fig. 3. Comparison of the low-temperature specific heats of $CeAl_3$ and $^3He$, plotted as $c/T$ versus $T$. Note the different scales for both materials. The data for $^3He$ were taken from ref. 10.

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 $CeAl_3$ 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 $^3He$, $T_F^*$ 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 $CeAl_3$ [9] is plotted in the form $c_p^{el}/T$ versus $T$ and compared with $c_p/T$ versus $T$ of liquid $^3He$ [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 $^3He$ 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 $CeAl_3$ and liquid $^3He$ 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 $CeAl_3$, naturally lead to speculations whether the analogy to $^3He$ extends also to the superconducting state of these metals with the superfluid state of $^3He$ 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 $CeAl_3$ was first observed and identified in $CeCu_2Si_2$ [14]. The bulk character of he 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 $dH_{c2}/dT$ 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 $UBe_{13}$ [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.

$UBe_{13}$ is a cubic intermetallic compound with a nearest U–U distance of 5.13 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 $5f^2$ 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 $UBe_{13}$ 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 $c_p/T$ versus $T^2$ plot was subtracted from the measured specific heat $c_p$. Above the critical temperature $T_c$, the same characteristic behaviour as shown for $CeAl_3$ and $^3He$ in fig. 3 is observed. Between 1.0 and 1.5 K $c^{el}/T$ is almost temperature independent. The

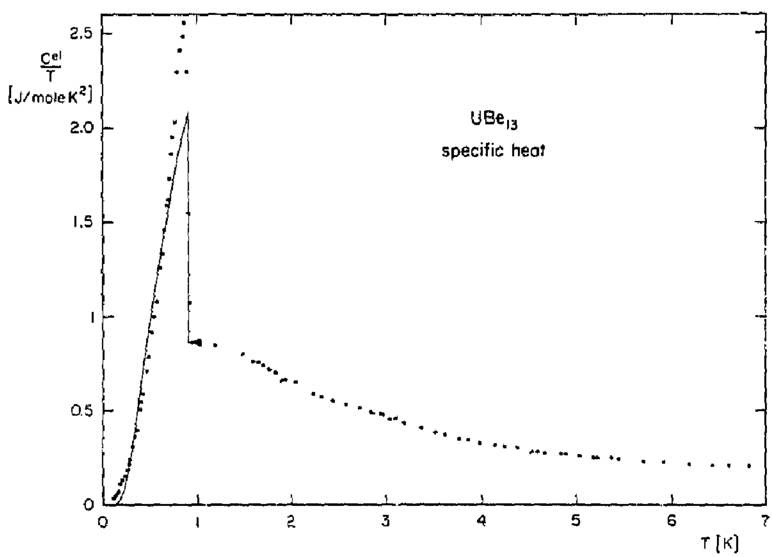


Fig. 4. Electronic specific heat of $UBe_{13}$ between 0.06 and 7 K. The discontinuity indicates the superconducting transition. The solid line is the universal BCS curve for $c^{el}/T$ considering the experimental $c^{el}/T$ value at $T_c$ in the normal state.

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 $-1$ 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 $-100$ 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 shoulder at about 10 K. Below 7 K, $\rho(T)$ again increases more rapidly, going through a distinct maximum at 2.5 K and then decreasing towards the superconducting transition [9]. As may be seen in fig. 5, Th impurities with a concentration of less than 1% shift the pronounced maximum to about 1 K and move the shoulder to about 20 K. With increasing Th content, the low temperature resistivity maximum is shifted to below 1 K. With 0.89% Th content, the superconducting transition temperature is depressed from 0.9 to about 0.6 K and the transition is smeared to a width of about 0.15 K. A further increase of Th content up to about 3.3% leaves $T_c$ unaltered and the transition width reduces again to less than 0.1 K. However, a second transition of hitherto unknown origin develops below $T_c$ as may be seen from specific heat measurements as shown in fig. 6. We show these data without any further comment because speculations on all

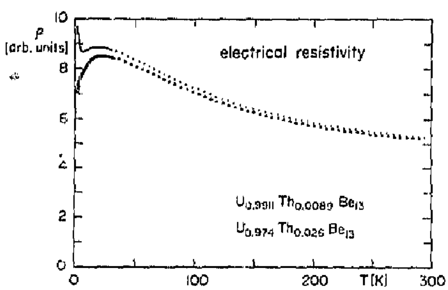


Fig. 5. Temperature dependence of the electrical resistivity of $U_{1-x}Th_xBe_{13}$ compounds between 1 and 300 K for small values of $x$. Note the rather drastic change for a small variation of $x$.

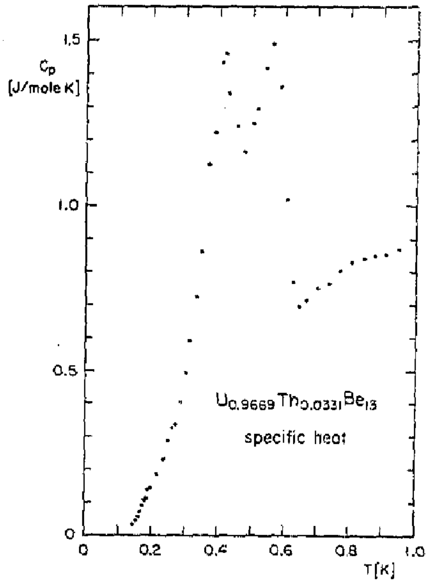


Fig. 6. Temperature dependence of the specific heat of $U_{0.9669}Th_{0.0331}Be_{13}$ between 0.15 and 1 K. The upper discontinuity is the superconducting transition.

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 $^3He$ 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 $^3He$, denoted as the Anderson–Brinkman–Morel (ABM) state [23] which in $^3He$ 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 $NpSn_3$ [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 $U_2Zn_{17}$ [25]. To illustrate this, we show the low-temperature specific heat of $U_2Zn_{17}$ in fig. 7 where $c^{el}/T$ is plotted versus $T^2$. $c^{el}(T)$ denotes the experimental specific heat

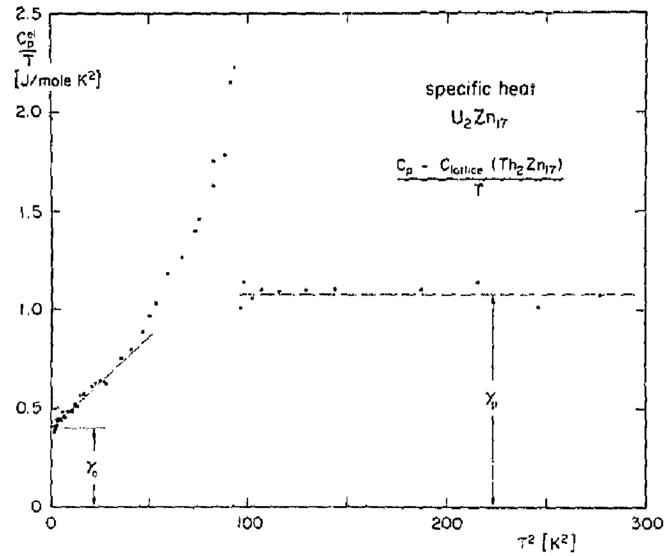


Fig. 7. $c/T$ versus $T^2$ for $U_2Zn_{17}$ between 1.5 and 17 K. $\gamma_p$ and $\gamma_0$ denote the electronic specific heat parameter above and below the magnetic phase transition at 9.70 K. The broken line at low temperatures indicates a non-lattice $T^3$ contribution to $c_p$.

minus the lattice contribution which was obtained from analogous measurements on isostructural $Th_2Zn_{17}$. 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 $c^{el}$ linear in $T$ is observed as $T \to 0$. 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

[1] A. Sommerfeld and H. Bethe, Elektronentheorie der Metalle, in: Heidelberger Taschenbücher (Springer, Berlin, 1967).
[2] L.D. Landau, Zh. Eksperim. Teor. Fiz. 32 (1957) 59 (Sov. Phys. JETP 5 (1957) 101.)
[3] K. Andres, J.E. Graebner and H.R. Ott, Phys. Rev. Lett. 35 (1975) 1779.
[4] H.R. Ott, O. Marti and F. Hulliger, Solid State Comm. 49 (1984) 1129.
[5] K.H. Mader and W.M. Swift, J. Phys. Chem. Solids 29 (1968) 1759.
[6] K.H.J. Buschow, H.J. van Daal, F.E. Maranzana and P.B. van Aken, Phys. Rev. B3 (1971) 1662.
[7] B. Cornut and B. Coqblin, Phys. Rev. B5 (1972) 4541.
[8] S. Doniach and S. Engelsberg, Phys. Rev. Lett. 17 (1966) 750.
[9] H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, in: Moment Formation in Solids, W.J.L. Buyers, ed. (Plenum, New York, 1984) p. 305.
[10] D.F. Brewer, J.G. Daunt and A.K. Sreedhar, Phys. Rev. 115 (1959) 836. A.C. Anderson, W. Reese and J.C. Wheatley, Phys. Rev. 130 (1963) 495.
[11] W.R. Abel, R.T. Johnson, J.C. Wheatley and W. Zimmermann, Phys. Rev. Lett. 18 (1967) 737.
[12] M.J. Rice, Phys. Rev. 159 (1967) 153.
[13] J. Flouquet, J.C. Lasjaunias, J. Peyrard and M. Ribault, J. Appl. Phys. 53 (1982) 2127.
[14] F. Steglich, J. Aarts, C.D. Bredl, W. Lieke, D. Meschede, W. Franz and H. Schäfer, Phys. Rev. Lett. 43 (1979) 1892.
[15] U. Rauchschwalbe, W. Lieke, C.D. Bredl, F. Steglich, J. Aarts, K.M. Martini and A.C. Mota, Phys. Rev. Lett. 49 (1982) 1448.
[16] H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, Phys. Rev. Lett. 50 (1983) 1595.
[17] N.C. Bänziger and R.E. Rundle, Acta Cryst. 2 (1949) 258.
[18] R. Troć, W. Trzebiatowski and K. Piprek, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 19 (1971) 427.
[19] E. Bucher, J.P. Maita, G.W. Hull, R.C. Fulton and A.S. Cooper, Phys. Rev. B11 (1973) 440.
[20] J. Bardeen, L.N. Cooper and J.R. Schrieffer, Phys. Rev. 108 (1957) 1175.
[21] M.B. Maple, J.W. Chen, S.E. Lambert, Z. Fisk, J.L. Smith and H.R. Ott, unpublished results.
[22] H.R. Ott, H. Rudigier, T.M. Rice, K. Ueda, Z. Fisk and J.L. Smith, Phys. Rev. Lett. 52 (1984) 1915.
[23] P.W. Anderson and W.F. Brinkman, in: The Physics of Liquid and Solid He, vol. II, K.H. Bennemann and J.B. Ketterson, eds. (Wiley, New York 1978) p. 177.
[24] R.J. Trainor, M.B. Brodsky, B.D. Dunlap and G.K. Shenoy, Phys. Rev. Lett. 37 (1976) 1511.
[25] H.R. Ott, H. Rudigier, P. Delsing and Z. Fisk, Phys. Rev. Lett. 52 (1984) 1551.