

## Spectroscopic Evidence for Unconventional Superconductivity in UBe<sub>13</sub>

Ch. Wälti and H. R. Ott

*Laboratorium für Festkörperphysik, ETH-Hönggerberg, 8093 Zürich, Switzerland*

Z. Fisk

*National High Magnetic Field Laboratory, Tallahassee, Florida 32306-4005*

J. L. Smith

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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We report on measurements of the differential conductivity  $G$  of UBe<sub>13</sub>-Au contacts, which reveal the existence of low-energy Andreev surface bound states. These bound states are identified via huge conductance peaks at zero bias that may form only in superconductors with nontrivial energy-gap functions. From the voltage dependence of  $G$  at  $T < T_c$  we also establish a lower limit of the normalized energy gap, such that  $\frac{2\Delta(0)}{k_B T_c} > 6.7$ , much in excess of the weak coupling BCS value of 3.5, and directly indicating strong coupling effects in superconducting UBe<sub>13</sub>.

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Several experiments probing the superconducting state of UBe<sub>13</sub> [1], such as measurements of the specific heat [2], the NMR spin-lattice relaxation rate [3], or the London penetration depth [4], revealed anomalous features which were interpreted as evidence for unconventional superconductivity in UBe<sub>13</sub>. In unconventional superconductors, the electrons are considered to form Cooper pairs with either a spin-singlet or a spin-triplet configuration, where the former is established with an even angular momentum  $l$  of the pairs, and the latter requires an odd value of  $l$ . The simplest case, which is realized in conventional superconductors, is a spin-singlet configuration with  $l = 0$ . As a consequence of the more complicated pairing configurations, the energy-gap functions of many of these unconventional superconducting states exhibit point or line nodes, distinctly different from the overall nonzero gap function of conventional superconductors.

The problem of quasiparticle transfer between an unconventional superconductor and a normal metal has theoretically first been investigated in detail by Bruder, considering the effects of Andreev reflections [5]. More recent theoretical work has shown that in unconventional superconductors low-energy Andreev bound states may exist at the interface of a superconductor-normal metal contact [6–8]. Such bound states are expected to drastically enhance the differential conductivity through the contact at zero bias and thus to cause a zero-bias conductance peak (ZBCP). Therefore measurements of the differential conductivity of such contacts provide a powerful tool to investigate the pairing state of a superconductor. Previously, contacts between various heavy electron superconductors and normal metals have been investigated by several groups [9–14]. Very recently, the existence of a Josephson supercurrent through a Nb-UBe<sub>13</sub> contact has been demonstrated [15].

In this Letter, we report on measurements of the voltage dependence of the differential conductivity  $G(V)$  of a superconductor-normal metal contact, where the superconductor is the heavy electron superconductor UBe<sub>13</sub>, in polycrystalline form, and the normal metal electrode is pure Au. The observation of very pronounced ZBCPs provides strong evidence for an unconventional energy-gap function in the cubic heavy electron superconductor UBe<sub>13</sub>.

The sharp Au tip touched, with only tiny pressure, the cleaned surface of the UBe<sub>13</sub> sample. Neither the sample surface nor the Au tip was visibly deformed during the experiment, ruling out the possibility of strong pressure effects being involved [16]. The tip radii of the Au tips were typically of the order of 10–50  $\mu\text{m}$ , much larger than the average grain size of the polycrystal. Several different contacts with different normal-state conductances and at various places on our sample, as well as on other UBe<sub>13</sub> specimens, were formed and investigated. All the results were qualitatively similar, and therefore only one set of measurements is presented and discussed in this Letter. The differential conductivity was measured in a <sup>3</sup>He cryostat using a standard four-point ac-modulation technique.

Figure 1 shows the measured differential conductivity  $G(V) = \frac{dI}{dV}(V)$  of a UBe<sub>13</sub>-Au contact as a function of the energy  $E = eV$  at various temperatures. In the inset, the differential conductivity at zero bias  $G(0)$  is plotted as a function of temperature. The distinct change of slope  $\partial G(0)/\partial T$  at  $T = 0.905$  K provides an accurate measurement of the transition temperature  $T_c$  into the superconducting state of UBe<sub>13</sub>.

At the lowest temperatures, we note a very pronounced ZBCP in  $G(E)$ . The height of the peak decreases with increasing temperature up to  $T = T_c$ , where it vanishes. Therefore, we conclude that the ZBCP, which is observed

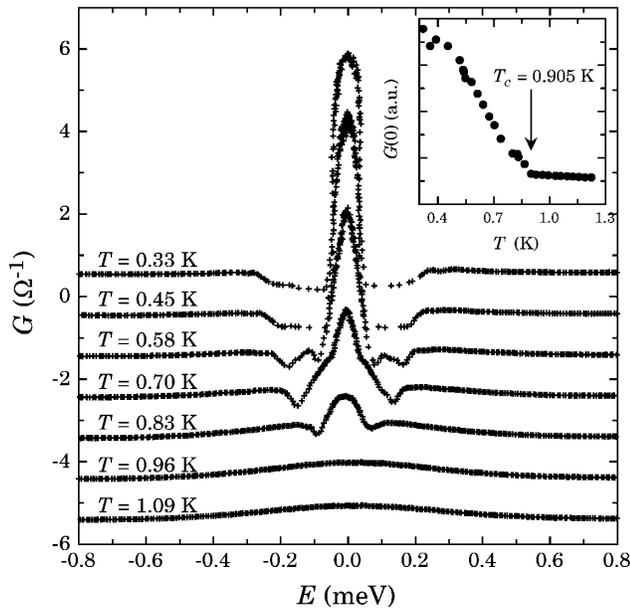


FIG. 1. The differential conductivity of a  $\text{UBe}_{13}$ -Au contact measured vs energy at various temperatures. The curves are vertically shifted for clarity. The curves for  $|E| > 0.6$  meV are identical within experimental errors at all temperatures. The inset shows the measured differential conductivity at zero energy  $G(0)$  vs  $T$ . The sharp raise of  $G(0)$  was used to identify the superconducting transition temperature as  $T_c = 0.905$  K.

only for  $T < T_c$ , must be related to the superconductivity of the heavy electron compound  $\text{UBe}_{13}$ . At temperatures above  $T_c$ , the conductivity at zero bias is still enhanced if compared with the conductivity at large energies, but this broad anomaly is much less pronounced than the feature observed at temperatures below  $T_c$ . The zero-bias anomaly at  $T > T_c$  is, as will be shown below, of different origin than the ZBCP, and is not directly related with the superconductivity of  $\text{UBe}_{13}$ .

At temperatures above  $T_c$ , the measured differential conductivity  $G(V)$  may be separated into a  $T$ -independent term  $G_0$  and a temperature dependent term  $\Delta G(V)$ , which is enhanced around zero bias and given by  $\Delta G(V, T) = G(V, T) - G_0(V)$ . Such zero-bias anomalies were first reported for metal-metal tunnel junctions [17] and were interpreted as being due to a Kondo-type exchange scattering at the interface [18–20]. It was argued that the differential zero-bias conductivity due to this effect,  $\Delta G(0, T)$ , should vary as  $-\ln(T)$ . The measured  $G(0)$  data are plotted vs  $\ln(T)$  in the inset of Fig. 2. The solid line represents a linear fit to the data which reproduces the data rather well. It has also been shown experimentally [17] and subsequently confirmed theoretically [20] that the normalized Kondo term  $G_n(V, T) = [\Delta G(V) - \Delta G(0)]/G_0(0)$  is given by a universal function  $F(eV/k_B T)$ . In the limit  $eV/k_B T \gg 1$ , i.e.,  $E/T \gg 8.6 \times 10^{-5}$  eV/K in our case, this universal function  $F(x)$  can be approximated by  $-\ln(x)$  [18–20]. Above a certain limit of  $E/T$ , this universality fails [17]. In Fig. 2, we show  $G_n(V, T)$  as

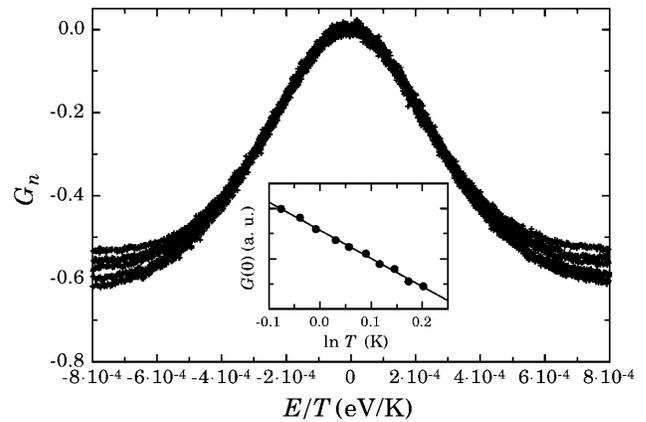


FIG. 2. The normalized conductivity  $G_n$  (see text) vs  $E/T$ , where  $E = eV$ , at  $T = 0.96, 0.99, 1.03, 1.06, 1.10,$  and  $1.12$  K starting from below. The inset shows the differential conductivity at zero energy,  $G(0)$  vs  $\ln(T)$  at  $T > T_c$ . The solid line is a linear fit to the data.

a function of  $eV/T$  for various temperatures  $T > T_c$ . It may be seen that the curves indeed collapse onto a single curve, as expected for Kondo-type exchange scattering at the interface of a metal-metal contact. We thus argue that the zero-bias anomaly in  $G(V)$  observed in our experiments at  $T > T_c$  is of similar origin.

This analysis allows us to estimate a possible contribution to  $G(V)$  due to Kondo-type exchange scattering at the interface at  $T < T_c$ , where the above-mentioned large ZBCP has been observed. In Fig. 3, we show the measured data of  $G(V)$  at the lowest temperature reached in this study. The solid line indicates the calculated estimate of the Kondo-type exchange scattering term, extrapolated from the data above  $T_c$ . The zero-bias anomaly due to this term is much smaller than the observed ZBCP, and its height as well as its shape differs substantially from the measured data. Although it is not *a priori* clear how the Kondo-type exchange scattering term influences  $G(V)$  at low temperatures, we nevertheless note that a possible influence would be small and would not significantly influence the results of our discussion below. In conventional

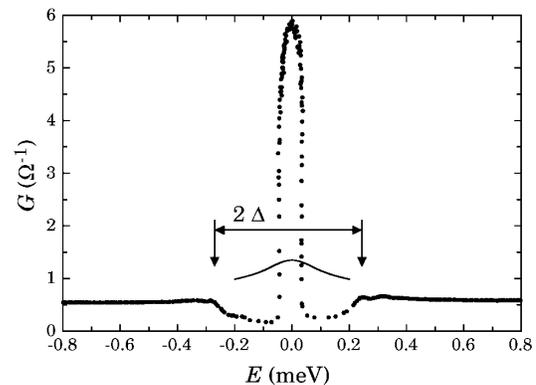


FIG. 3. Differential conductivity of a  $\text{UBe}_{13}$ -Au contact at  $T = 330$  mK. The solid line shows the estimated Kondo contribution to  $G(V)$  as discussed in the text.

*s*-wave superconductors, the enhancement of the conductivity at zero bias, compared to the normal-state conductivity of the contact, never exceeds a factor of 2 and is realized only in a highly transparent junction at  $T \ll T_c$  [21]. The ZBCP observed in our experiment (Fig. 3) is, with  $G(0)/G(E \gg \Delta) \approx 10$ , clearly much more pronounced. We are not aware that enhancements of the differential conductivity at zero bias of comparable size have been observed in any superconductor before. Unfortunately, no theoretical calculations of the differential conductivity in cubic systems have been reported, but, considering previous theoretical calculations for various types of order parameters belonging to different irreducible representations of other crystal symmetries [6–8], this very pronounced ZBCP clearly indicates the existence of low-energy bound states at the surface, forming only if the symmetry of the energy-gap function is nontrivial.

Another feature indicating the unconventional nature of superconductivity in UBe<sub>13</sub> is the sharp drop of  $G(E)$  at an energy  $E_{\text{drop}}$ , marked by vertical arrows in Fig. 3. The occurrence of this sharp feature does not depend on the measuring conditions, ruling out the possibility of local heating effects being involved [14]. Again, a sharp drop followed by a steep increase of  $G(V)$  towards small energies cannot be explained by assuming conventional superconductivity [21]. As indicated above, our experimental data are reminiscent of the results of calculations for several unconventional pairing states [6–8], but a more detailed analysis requires additional numerical work.

Depending on the exact symmetry of the gap function and the current direction, the sharp drop of  $G(E)$  occurs at different energies, but  $E_{\text{drop}}/\Delta \leq 1$  in all cases [6–8]. Hence, we may use the observed sharp drop of  $G(E)$  to establish a lower limit for the energy gap  $\Delta(T)$  of UBe<sub>13</sub>. In Fig. 4, we show the calculated ratio  $[2\Delta(T)]/(k_B T_c)$  vs  $T$  as circles. In the BCS weak-coupling limit, the energy gap at  $T = 0$  is  $[2\Delta(T)]/(k_B T_c) \approx 3.5$ . From  $\Delta(T = 0.33 \text{ K})$  we conclude that  $[2\Delta(T)]/(k_B T_c) > 6.7$  for UBe<sub>13</sub>. Since this ratio is a measure for the strength of the coupling in the pair formation, we argue that our observation gives additional support for unusual strong coupling effects in UBe<sub>13</sub>. This has already been concluded from specific heat measurements [2] and, more recently, from measurements of the pressure dependence of  $H_{c2}$  [22]. The temperature dependence of the BCS gap function is shown by the triangles in Fig. 4. We note that  $\Delta_{\text{BCS}}(T)$ , even if scaled up, does not match our experimentally established  $\Delta(T)$  for UBe<sub>13</sub>.

In conclusion, our experiment clearly indicates the existence of low-energy Andreev surface bound states in UBe<sub>13</sub>, manifest in huge ZBCPs observed in the  $G(V)$  measurements. Such bound states are a new and significant indication of a non-*s*-wave symmetry of the gap function of UBe<sub>13</sub>. The evaluation of a lower limit for the superconducting energy gap leads to the conclusion that the superconducting state in the heavy electron superconductor UBe<sub>13</sub> is related with substantial strong coupling effects.

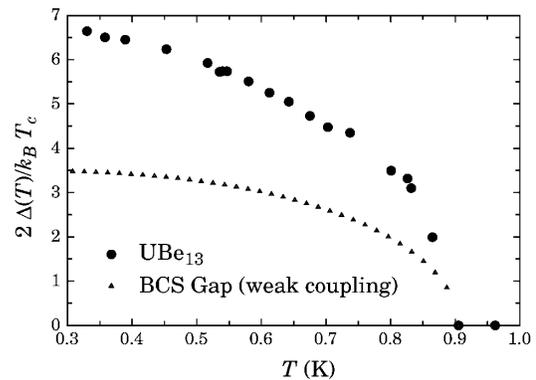


FIG. 4. The circles show the normalized superconducting energy gap of the heavy electron superconductor UBe<sub>13</sub> (see text) and the triangles indicate the BCS weak coupling expectation for  $\Delta(T)$ .

Finally, our experiments provide the first decent data on the amplitude and temperature dependence of the energy-gap in superconducting UBe<sub>13</sub>.

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