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Point-contact spectroscopy of superconducting URu_2Si_2

K. Hasselbach and J. R. Kirtley
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

P. Lejay
Centre de Recherches sur les Tres Basses Temperatures, C.N.R.S., Boite Postal 166X, 38042 Grenoble CEDEX, France
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We present point-contact measurements of the antiferromagnetic heavy-fermion superconductor URu_2Si_2. Our data in the superconducting state agree remarkably well with the theory of Blonder, Tinkham, and Klapwijk (BTK), and are consistent with a gap with *d*-wave symmetry. In the normal state a "gap" in the conductance develops as the temperature is lowered below the Néel temperature. The persistence of this gap into the superconducting state supports the view that magnetically correlated electrons participate in the superconductivity.

The nature of the superconducting state in such highly correlated electron systems as $CeCu_2Si_2$, UPt_3, UBe_{13},and URu_2Si_2, is an active topic of research.[1–5] These compounds show formation of heavy quasiparticles as the conduction electrons hybridize with the uranium (U) localized $5f$ electrons. The hybridization leads to spin fluctuations on the U sites. The heavy quasiparticles constitute the Cooper pairs, as is shown by the large anomaly in the specific heat at the superconducting transition. Whether phonons or spin fluctuations mediate the Cooper pairing is an unresolved question. The close relationship between magnetic correlations and the superconducting state, combined with the nonexponential temperature dependence of, e.g., specific heat and ultrasonic attenuation, has lead to speculation on the symmetry of the order parameter. The experimentally observed power-law behavior in all quantities that probe the single-particle density of states at the Fermi surface suggests superconducting gaps Δ, which have lines or points of zero gap. Recently these speculations were supported by the discovery of a rich phase diagram (H,T) in superconducting UPt_3,[6–9] possibly due to the lifting of degeneracy of the two-dimensional superconducting order parameter through weak in-plane antiferromagnetic ordering. Modeling of this phase diagram implies a gap with nodes, of either *p* (uneven) of *d* (even) wave symmetry.

URu_2Si_2 is particularly well suited for the study of the interplay of magnetism and superconductivity, as it is the only heavy-fermion compound with superconducting and antiferromagnetic phase transitions that are well substantiated in both thermodynamic and transport measurements. The magnetic transition takes place at $T_N = 17.5$ K and the compound becomes superconducting at $T_c = 1.2$ K, slightly less than 1/10 of T_N. In contrast with UPt_3, the superconducting phase diagram (H,T) of URu_2Si_2 is single phased. Although the order parameter may be multidimensional, no mechanism is known to lift its degeneracy.

The antiferromagnetic transition at 17.5 K is associated with spin-density-wave formation.[10] Specific heat,[10,11] ultrasonic attenuation,[12] and resistivity all[13] decrease exponentially with temperature, indicating that a gap opens over parts of the Fermi surface. Spectroscopic studies of the magnetic ordering process with neutron diffraction,[14] infrared reflectance,[15] and synchrotron radiation[16] have established the existence of a gap of about 7.5 meV in both the optical conductivity and the magnetic spin density of states, which disappears above T_N. This fact is evidence for the hybridization of the conduction electrons with the localized $5f$ electrons.

We chose point-contact spectroscopy (PCS) to study the interplay of superconductivity, magnetic order, and magnetic excitations in URu_2Si_2. Point-contact spectroscopy has been a successful tool in studying the phonon spectra of simple metals[17,18] and is well established both theoretically[19] and experimentally in the study of superconductivity. The most prominent uranium-based heavy-fermion superconductors UPt_3, UBe_{13}, and URu_2Si_2 have been studied by PCS.[20–24] Although all of these studies showed "gaplike" features in the superconducting state, the shapes of the structures observed did not agree with theory, and most studies showed irreproducible and often unphysically large "gap sizes." In contrast, here we report results on a high-quality, highly annealed sample, which were quite reproducible, fit conventional theory extremely well, and gave reasonable values for the size of the gap parameter. We therefore believe them to be more reliable than previous studies.

For the present study we used an annealed Czochralski-grown single crystal of URu_2Si_2, of a similar quality[25] to sample 3 in Ref. 26. The sample was cleaved along the *ab* plane at room temperature and mounted in a scanning tunneling microscope.[27] For subsequent runs a weak chemical etch was applied before cooldown. Electrical contact between the sample and the tip was made at 0.5 K with the sample immersed in liquid ^3He. As was often found for the high-T_c ceramic superconductors,[28] it was difficult to attain reproducible results in the high resistance (tunneling) regime, so measurements were made with the tip pressed firmly against the sample, in the low resistance (point-contact) regime. The tip and the applied magnetic field were parallel to the crystal's *c*

axis, with the surface of the crystal in the *ab* plane. The resistance of the contact between sample and tip was between 2 and 10 Ω. We used four terminal measurements and standard modulation techniques to obtain the differential resistance (dV/dI) as a function of the bias voltage. The voltages we report are sample voltages, with the tip at ground. For consistency and ease of comparison with theory we present all of our results as differential conductance dI/dV.

The *c*-axis resistivity of annealed URu_2Si_2 varies between 10–140 $\mu\Omega$ cm in the temperature range 1–20 K. Taking a typical contact resistance of 5 Ω, resistivity $\rho = 10$ $\mu\Omega$ cm, and inelastic mean free path $l_i \sim 100$ Å,[29] the theoretical contact radius is $a \sim 100$ Å using either the Sharvin formula[18] $R_s = 4\rho l_i/3\pi a^2$, or the Maxwell formula $R_M = \rho/2a$. The contacts were therefore not in the Knudsen regime $l_i \gg a$ usually assumed for PCS in metallic contacts. Nevertheless, the increase of the resistivity of the contacts with bias (<40%) was much less than the change of the bulk resistivity of URu_2Si_2 with temperature (more than a factor of 20), so that the contacts did not heat up to the classical Maxwell dirty limit.[30] This means that the maximum energy available for excitations in the contact region was approximately equal to the voltage bias, and the resistance-voltage characteristics retained their spectroscopic information.[31]

Figure 1 shows the conductance $G = dI/dV$ as a function of bias voltage and temperature for a URu_2Si_2-Mo point contact. At high temperatures the conductance of the point contact decreased roughly linearly away from zero bias until saturating above 25 mV. The analogy between this behavior and the linear conduction background often seen in tunnel junctions,[32] will be pursued elsewhere.[24] As the temperature was lowered through the magnetic transition this conductance peak split and a "gap" formed. The characteristic energy scale of this gap ~10 meV is consistent with other spectroscopy measures.[15,16] The total integrated conductance between ±25 mV was nearly constant through the antiferromagnetic transition. Our picture of the mechanism of this gap formation is the following: In the point contact injected electrons probe the change in the scattering amplitude of the hybridized heavy quasiparticles as these undergo the magnetic transition. Strong magnetic elastic scattering has been previously observed in low-energy electron diffraction from antiferromagnetic NiO.[33,34] The inset in Fig. 1 shows the temperature dependence of the amplitude of the structure near zero bias. It undergoes the fastest rise at about $T_N = 17.5$ K, and then increases nearly linearly as the temperature is lowered further. This is quite similar to the behavior of the antiferromagnetic Bragg-peak intensity[14] presented in the inset. We attribute the shift of the gap with respect to zero bias to a small band bending at the interface. Since this shift is three times larger for unannealed samples[24] than for the annealed sample reported here, we consider this effect interesting but irrelevant to the main thrust of this article.

In Fig. 2 we present results for the superconducting state, taken at 0.45 K. Although the overall shape is identical with the 5.5-K data from Fig. 1, a new conductance increase centered around zero bias has appeared. This feature, while not always present, especially in high-resistance contacts, was reproducible in shape and voltage width when present. Similar results were obtained using either a W or Mo tip. The insets show that this conductance increase was associated with the superconducting transition: Fig. 2(a) shows that the conductance peak (symmetrized and with a linear background subtracted) disappeared at the T_c of the bulk material. Figure 2(b) shows that the conductance peak disappeared at H_{c2} of URu_2Si_2 ($H \| c$). We modeled this conductance peak in terms of Andreev scattering using the theory of Blonder, Tinkham, and Klapwijk (BTK).[19] This theory

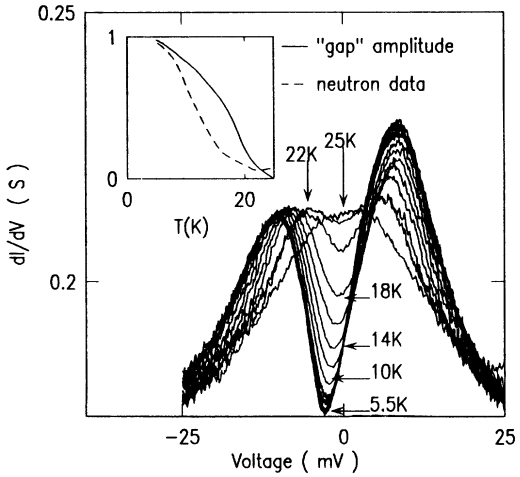

FIG. 1. Dynamic conductance dI/dV vs voltage for a URu_2Si_2-Mo point contact as a function of temperature. The full line in the inset shows the gap amplitude as a function of temperature, the dashed line shows the antiferromagnetic Bragg-peak intensity from neutron experiments (Ref. 14).

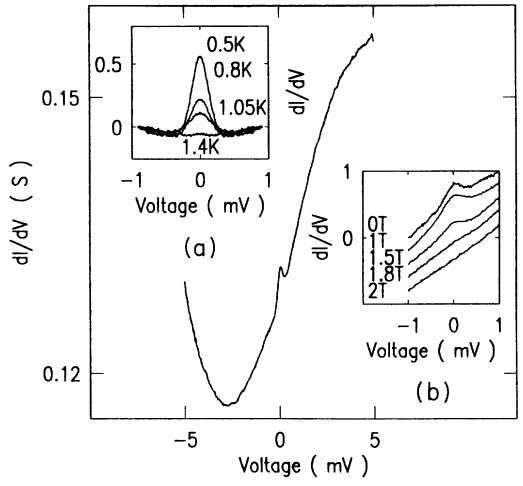

FIG. 2. The dynamic conductance dI/dV of URu_2Si_2 at 0.45 K. Inset (a) shows the temperature dependence of the conductance increase for a URu_2Si_2-W point contact. The peak has been symmetrized and a conductance background subtracted. Inset (b) shows the magnetic-field dependence of the conduction increase of a URu_2Si_2-Mo point contact. The characteristics have been normalized and shifted for the sake of clarity.

predicts the current-voltage characteristic of a normal-superconducting (NS) junction as a function of the barrier strength Z and the superconducting gap Δ. In the limit $Z=0$ there is a peak in conductance for voltages smaller than the gap value due to Andreev scattering. BTK theory reduces to conventional NS tunneling theory in the limit of large Z. For comparison we have fit our experimental data to BTK theory using two forms for the gap—the first a conventional isotropic gap $\Delta(\hat{k})=\Delta_0$, and the second $\Delta(\hat{k})=2\Delta_0 k_x k_y/|k|^2$. The latter case has d-wave symmetry and is among the gap functions proposed by theoretical workers for URu_2Si_2.[5] The analysis of Andreev scattering in anisotropic superconductors is quite complex.[35,36] We have taken the simplest possible approach: BTK theory predicts the current-voltage characteristic $I_{BTK}(V,\Delta)$ for a given Z and temperature T. We substitute into this expression a momentum-dependent gap $\Delta(\hat{k})$ and numerically average over an assumed spherical Fermi surface. In doing so we make the questionable assumption that the transport between the tip and sample averages over all sample crystalline momenta. However, since the tip-sample geometry is poorly defined in this technique, it would be futile to do more sophisticated modeling at this stage. As shown in Fig. 3(a), s-wave BTK theory gives rise to a square topped conductance peak for $Z\sim 0$, which drops abruptly to the ohmic value for voltages above the gap value. The d-wave gap allows for low-energy excitations at the nodes in the gap; therefore the d-wave BTK conductance peak is more triangular in shape. All of the non-s-wave gap symmetries we have tried share this "sharp-peaked" character for $Z\sim 0$. This qualitative difference offers a means to test for non-s-wave gap symmetries using PCS.

In Fig. 3(b) we show the s- and d-wave fits to our data at $T=0.45$ K, using the modified BTK theory described above, with appropriate thermal smearing. The only adjustable parameters to this fit, after the symmetric part of the data was taken and a linear conductance background was subtracted out, were the amplitude of the conductance increase and the gap size. The barrier strength was set at $Z=0$. Both models fit the data remarkably well. The ratio of conductance inside vs outside the gap voltage predicted by BTK is a factor of 2. Our fit values gave much smaller ratios, corresponding to a change of 3–4 %. This reduction in the Andreev feature amplitude is expected, since our point contacts are in the diffusive, as opposed to the ballistic, regime for which BTK theory was developed. Similar amplitude reductions have been observed in phonon point-contact experiments of short mean-free-path materials.[17] The large mismatch between the effective masses of the carriers in the heavy-fermion material and the metal probe should result in effective Z's larger than 0, even in the absence of an interface barrier. It is surprising, therefore, that BTK theory fits our data only for values of the barrier strength $Z\leq 0.3$. This may be indicative of a more complicated interface then envisioned by BTK, e.g., metal-normal heavy-fermion-superconducting heavy fermion. In the lower part of Fig. 3(b) we show difference curves between experiment and the two types of fit. The s-wave fit was always somewhat flatter on top and steeper on the sides of the fits than experiment, resulting in the difference curve shown as the dashed line in Fig. 3(b). The d-wave fit shows no systematic deviation from the data.

Figure 4 shows the temperature dependence of the fitting parameter Δ_0 for the two different kinds of fits. For low temperatures Z was set equal to 0. There was a slight tip change for temperatures above $T=0.7$ K, and a more consistent fit was obtained by setting $Z=0.3$. This small change in Z resulted in changes in the values of Δ_0 within the error bars shown in Fig. 4. The error bars in Fig. 4 correspond to the gap values, where the standard deviation has twice its minimum value, with the amplitude parameter optimized. At high temperatures the uncertainty in Δ became too large to allow for any conclusions about the way the gap disappears at T_c. The solid lines in Fig. 4 are theoretical predictions for $\Delta(T)$: BCS for s wave and weak-coupling theory following a prescription by Tachiki, Nakahara, and Teshima[37] for d wave. The d-wave fits are in better agreement with theory in that the s-wave Δ_0's are about 33% low, whereas the d-wave fits are only about 20% low.

We have shown that there are simultaneous antiferro-

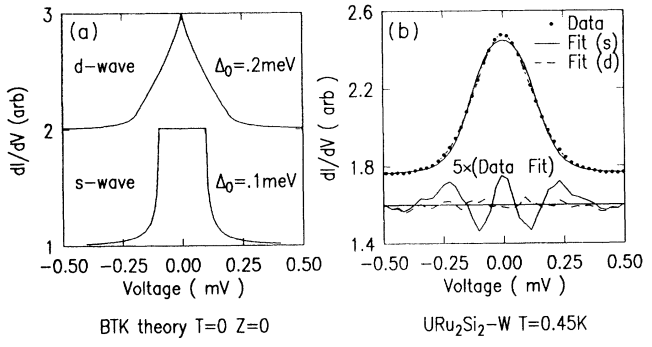

FIG. 3. (a) The predictions of BTK theory, suitably modified as described in the text for an anisotropic gap, for s-wave and a particular d-wave gap symmetry ($\Delta=2\Delta_0 k_x k_y/|k|^2$). (b) The dotted points are the experimental data for a point contact URu_2Si_2-W at 0.45 K. The dashed line is the fit with a gap of d-wave symmetry; the full line corresponds to a fit with an isotropic (s-wave) gap. The lower part of the figure shows the difference curve between the fits and the data.

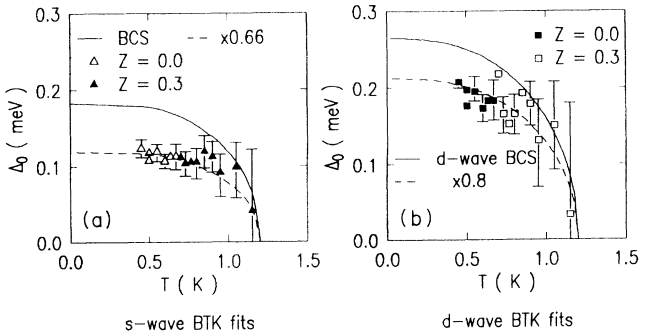

FIG. 4. Temperature dependence of the gap-fitting parameter Δ_0 for (a) an isotropic gap and (b) a gap with $\Delta=2\Delta_0 k_x k_y/|k|^2$ d-wave symmetry. The full lines represent the weak coupling prediction for a T_c of 1.2 K. The dashed line is scaled down by 33% in (a) and 20% in (b).

magnetic and superconducting spectroscopic features in point-contact measurements of URu_2Si_2. This implies that antiferromagnetism and superconductivity are both present[38] within a coherence length ξ, since $\xi \sim 100$ Å is of order the characteristic length of the point contact. There is surprisingly good agreement between experiment and BTK theory for the conductance peak that develops below T_c. Our modeling is clearly oversimplified, and could be refined in allowing for, e.g., proximity effects, pairbreaking, a k-dependent pairing potential and possibly strong-coupling effects. Although both the quality of the line-shape fits and the agreement of the derived gap parameters Δ_0 slightly favored a non-s-wave symmetry for the gap, a conclusive distinction between s-wave and non-s-wave superconductivity could not be made. Lower temperature measurements might draw a sharper distinction. Nevertheless, we have presented reliable gap measurements in a heavy-fermion superconductor that are compatible with a d-wave model.

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[1]F. Steglich, J. Magn. Magn. Mater. **100**, 186 (1991).
[2]A. de Visser and J. J. Franse, J. Magn. Magn. Mater. **100**, 204 (1991).
[3]P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Conds. Mater. Phys. **12**, 99 (1986).
[4]P. Fulde, J. Keller, and G. Zwicknagel, Solid State Phys. **41**, 1 (1989).
[5]L. P. Gorkov, Sov. Sci. Rev. A **91**, (1987).
[6]K. Hasselbach, L. Taillefer, and J. Flouquet, Phys. Rev. Lett. **63**, 93 (1989).
[7]R. N. Kleiman, P. L. Gammel, E. Bucher, and D. J. Bishop, Phys. Rev. Lett. **62**, 328 (1989).
[8]S. Adenwalla *et al.* Phys. Rev. Lett. **65**, 2298 (1990).
[9]G. Bruls, D. Weber, B. Wolf, P. Thalmeier, and B. Lutni, Phys. Rev. Lett. **65**, 2294 (1990).
[10]M. B. Maple *et al.*, Phys. Rev. Lett. **56**, 185 (1986).
[11]W. Schlabitz *et al.*, Z. Phys. B **62**, 171 (1986).
[12]T. Fukase *et al.*, Jpn. J. Appl. Phys. **26-3**, 1249 (1987).
[13]T. T. M. Palstra *et al.*, Phys. Rev. Lett. **55**, 2727 (1985).
[14]C. Broholm *et al.* Phys. Rev. B **43**, 12 809 (1991).
[15]D. A. Bonn, J. D. Garrett, and T. Timusk, Phys. Rev. Lett. **61**, 1305 (1988).
[16]E. D. Isaacs *et al.*, Phys. Rev. Lett. **65**, 3185 (1990).
[17]I. K. Yanson, Fiz. Nizk. Temp. **9**, 676 (1983) [Sov. J. Low Temp. Phys. **9**, 343 (1983)].
[18]A. G. M. Jansen, A. P. van Gelder, and P. Wyder, J. Phys. C **13**, 6073 (1980).
[19]G. E. Blonder, M. Tinkham, and T. M. Klapwijk, Phys. Rev. B **25**, 4515 (1982).
[20]A. Nowack *et al.*, Phys. Rev. B **36**, 2436 (1987).
[21]S. Han *et al.*, Phys. Rev. Lett. **57**, 157 (1985).
[22]S. Kunii, J. Magn. Magn. Mater. **63&64**, 673 (1987).
[23]A. Nowack, Yu. G. Naidyuk, P. N. Chubov, I. K. Yanson, and A. Menovsky, Fiz. Nizk. Temp. **17**, 1170 (1991) [Sov. J. Low Temp. Phys. **17**, 614 (1991)].
[24]K. Hasselbach and J. R. Kirtley (unpublished).
[25]J. P. Brison (private communications).
[26]K. Hasselbach, P. Lejay, and J. Floquet, Phys. Lett. A **156**, 313 (1991).
[27]A. P. Fein, J. R. Kirtley, and R. M. Feenstra, Rev. Sci. Instrum. **58**, 1806 (1987).
[28]J. R. Kirtley, Int. J. Mod. Phys. B **4**, 201 (1990).
[29]U. Rauchschwalbe, Physica B **147**, 1 (1987).
[30]B. Bussian, I. Frankowski, and D. Wohlleben, Phys. Rev. Lett. **49**, 1026 (1982).
[31]I. K. Yanson (private communications).
[32]J. R. Kirtley and D. J. Scalapino, Phys. Rev. Lett. **45**, 336 (1992).
[33]T. Wolfrom and R. E. De Wames, Prog. Surf. Sci. **2**, 233 (1972).
[34]P. W. Palmberg, R. E. De Wames, L. A. Vredevoe, and T. Wolfram, J. Appl. Phys. **40**, 1158 (1969).
[35]Chr. Bruder, Phys. Rev. B **41**, 4017 (1990).
[36]A. Millis, D. Rainer, and J. A. Sauls, Phys. Rev. B **38**, 4504 (1988).
[37]M. Tachiki, M. Nakahara, and R. Teshima, J. Magn. Magn. Mater. **52**, 161 (1985).
[38]R. Konno and K. Ueda, Phys. Rev. B **40**, 4329 (1989).