PHYSICAL REVIEW B **69**, 060504(R) (2004)

Very-low-temperature tunneling spectroscopy in the heavy-fermion superconductor $PrOs_4Sb_{12}$

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(Received 22 December 2003; published 27 February 2004)

We present scanning tunneling spectroscopy measurements on the heavy-fermion superconductor $PrOs_4Sb_{12}$. Our results show that the superconducting gap opens over a large part of the Fermi surface. The deviations from isotropic BCS *s*-wave behavior are discussed in terms of a finite distribution of values of the superconducting gap.

DOI: 10.1103/PhysRevB.69.060504 PACS number(s): 74.70.Tx, 07.79.Cz, 74.50.+r

The intriguing magnetic and superconducting properties of most heavy-fermion metals, which include, e.g., coexistence of superconductivity with ferromagnetism, non-Fermi-liquid behaviors, or multiple superconducting phases, represent a challenge to our current understanding of condensed matter physics.[1–3] The route towards the discovery of heavy fermions is to synthesize materials that maintain degrees of freedom (e.g., local magnetic or electric moments), which do not undergo a phase transition upon cooling and are coupled to the electron bath. A large entropy can then be preserved down to low temperatures, and transferred over to the electrons. Pr^{3+} ions offer this possibility if the Pr is in a cubic point symmetry, where the crystal electric-field ground state can be a nonmagnetic, non-Kramers Γ_3 doublet, which can provide the entropy needed to create a heavy-fermion ground state if a cooperative Jahn-Teller transition can be avoided.[4,5] $PrInAg_2$ meets these criteria, and it was shown to be the first possible example of a Pr-based heavy fermion with a very large linear specific-heat coefficient of 6.5 J/mol K^2.[4] Unfortunately $PrInAg_2$ did not superconduct down to 50 mK, making it hard to independently ascertain that the large linear specific-heat term was indeed of electronic origin. Recently superconductivity has been found with $T_c = 1.85$ K in another Pr based heavy fermion,[6] $PrOs_4Sb_{12}$, where large electronic specific-heat coefficients γ between 300 and 500 mJ/mol K^2 have been reported.[6,7,9–11] The height of the jump of the specific heat at the superconducting transition, which compares well with the BCS theory, shows that the large γ is indeed associated with the conduction electrons, and that, in addition, the heavy electronic bath superconducts.[6,7,9,10] Moreover, two superconducting transitions have been clearly resolved in the specific heat at 1.6 and 1.85 K in high quality single crystalline samples, giving strong indications for the presence of multiple superconducting phases.[7,9,10] The situation seems analogous to the only other known stoichiometric superconductor that presents multiple superconducting phases, UPt_3.[3,12] In that case, most present theoretical and experimental scenarios associate the Cooper pairing mechanism that leads to multiple phase superconductivity to magnetic fluctuations.[12] Instead, in $PrOs_4Sb_{12}$, interactions with fluctuating quadrupolar (electric) moments seem the most likely mechanism that drives the system to an unconventional, multiple phase superconducting state.[6,7,9–11,13–15] Note also that the isostructural compound $LaOs_4Sb_{12}$, which does not show heavy-fermion behavior,[16] superconducts with a lower critical temperature [1 K Ref. (9)].

The determination of the most fundamental superconducting properties of $PrOs_4Sb_{12}$ is clearly needed to understand the formation of unconventional, multiple phase superconductivity. One of the first and most important points is to try to resolve the structure of the superconducting gap in the low temperature, low magnetic-field phase, which occupies the largest part of the phase diagram.[7,8] Indirect information can be obtained by thermodynamic, transport, magnetic, or NMR measurements, but the experiments that have been done up to now lead to contradictory results, and are therefore not conclusive. Specific heat does not seem adequate to study the superconducting gap, because it shows a high Schottky peak at low temperatures.[6,7,9–11] Nuclear quadrupole resonance measurements show an exponential decrease of $1/T_1T$ at low temperatures[13] associated with a well-developed gap. The London penetration depth, as measured with muon spin relaxation, also appears to decrease exponentially at low temperatures.[14] On the other hand, the angular dependent thermal conductivity under magnetic fields appears to be strongly modulated due to significant changes in the superconducting gap over the Fermi surface. This result has been associated with the presence of point nodes.[15]

Here we present direct measurements of the superconducting gap in $PrOs_4Sb_{12}$, done with high-resolution tunneling spectroscopy studies in the superconducting phase with a scanning tunneling microscope (STM). We find a superconducting density of states with no low-energy excitations and a well-developed superconducting gap.

We use a home built STM unit and electronics installed in a partially home built dilution refrigerator and tested by measuring the superconducting properties of Al, which is possibly the best known superconducting material with a critical temperature (1.2 K) of the same order of magnitude as $PrOs_4Sb_{12}$ (1.85 K). The spectra between a gold tip and an Al sample are perfectly fitted to conventional isotropic BCS *s*-wave theory.[17] The lowest measuring temperature of our setup is $T = 190$ mK. Single crystals of $PrOs_4Sb_{12}$ were grown out of a ternary melt that was rich in both Os and Sb. A starting composition of $Pr_2Os_{16}Sb_{82}$ was heated to 1200 °C and cooled over 100 h to 725 °C and then decanted, reveal-

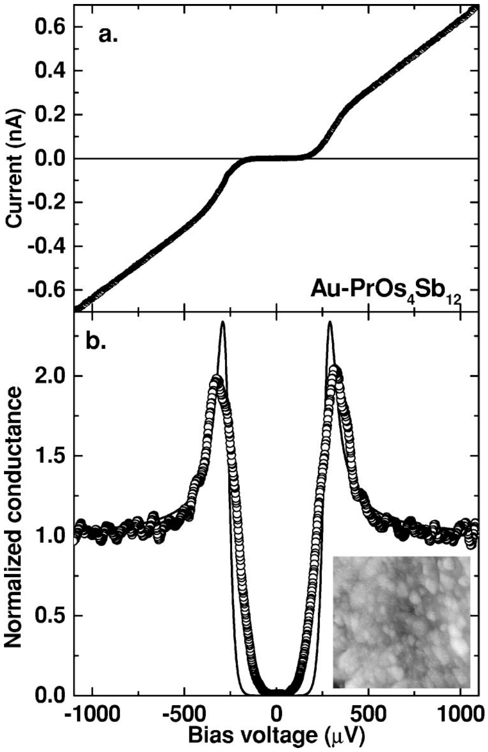

FIG. 1. Current-voltage characteristics (a) and tunneling conductance (b) between PrOs$_4$Sb$_{12}$ and a tip of Au at 0.19 K. The superconducting gap is well developed with no low-energy excitations. The line in (b) is the prediction from conventional isotropic BCS *s*-wave theory using $\Delta = 270\ \mu$ eV and $T = 0.19$ K. The inset in (b) shows a typical topographic image of the surface, representing an area of 50×50 nm^2, with a corrugation of about 4 nm.

ing small cubic crystals. We measured three samples in eight different cool downs by placing a Au tip on optically neat and flat faces of the single crystals. Within a given cool down, we changed the macroscopic position of the Au tip on the surface and measured many (more than 50 in total) different scanning windows (100×100 nm^2), using the positioning capabilities of our *xy* table, as in previous work.[18] The measured work functions were always of several eV's and the topography was reproducible upon changes of the tunneling current. It consists of inclined planes and bumps, with typical corrugations of about 4 nm (inset of Fig. 1), indicating that the crystallographic direction of the surface is not well defined at the nanoscopic length scales relevant for this experiment.

Typical spectra (Fig. 1) show a clean density of states with no low-energy excitations, demonstrating that the superconducting gap is well developed over a large part of the Fermi surface. The best fit with isotropic BCS *s*-wave theory is shown by the line in Fig. 1. Using $T = 0.19$ K we obtain a value for the superconducting gap $\Delta = 270\ \mu$eV, which gives $2\Delta/k_B T_c = 3.4$, very close to the BCS value 3.53. Note that differences between the experiment and the fit are clearly resolved, thanks to the high resolution in voltage of our experiment.[17]

The tunneling current depends on the overlap of the electron wave functions of tip and sample near the surface, being therefore a sum of the contributions from electrons coming from different sheets of the Fermi surface having *k* vectors with distinct orientations. If the superconducting gap is anisotropic in a given sheet, or if it does not have the same value in different sheets of the Fermi surface, or both, the tunneling spectra reflect this distribution of values of the superconducting gap by showing more broadened coherence peaks, which produce a deviation from isotropic BCS s-wave behavior (Fig. 1 and, e.g., Ref. 19). Defects, grain boundaries, or other perturbations that one can figure out to occur near the surface can lead to two effects: either a decrease of the observed anisotropy through the mixing of the electronic wave functions from different parts of the Fermi surface caused by strong interband and/or intraband electronic scattering,[20–23] resulting in less broadened coherence peaks; or to pair breaking effects, resulting in an increased residual density of states at the Fermi level. The former was not observed, and the latter has been observed in some locations of the surface, as discussed further on. Therefore, the deviations between the experiment and the fit shown in Fig. 1 must be intrinsic to the superconducting density of states in this compound.

Note that the conductance begins to increase at about 120 μV, and the highest point of the coherence peak is located at 325 μV. As a matter of fact, the shape of the tunneling spectra we find is similar to the form of the spectra taken in the much studied material NbSe$_2$,[19] where a distribution of values of the superconducting gap over the Fermi surface was deduced from first experiments.[19] Subsequent work have identified this distribution as coming from different gap values in different sheets of the Fermi surface in that compound (multiband superconductivity).[24,25] Whereas more work is clearly needed to understand the origin of the gap distribution in PrOs$_4$Sb$_{12}$, it is noteworthy to remark that strong changes in the mass renormalization in different sheets has been found in the de Haas van Alphen experiments of Ref. 16. These changes may also lead to the distribution of values of the superconducting gap measured in our experiment. This strengthens the idea that both the mass renormalization and superconductivity are of the same origin, i.e., the quadrupolar fluctuations favor superconducting correlations, as well as the possible multiband character of superconductivity in this compound.

The spectra are smeared when we increase the temperature, as shown in Fig. 2(a), and become flat above the bulk critical temperature (1.85 K). The mean value of the superconducting gap, determined as in Refs. 23 and 26, is shown in Fig. 2(b). Using BCS prediction for the temperature dependence of the gap [line in Fig. 2(b)], we can extrapolate the data and obtain a critical temperature of 1.8 K, which is the bulk T_c (1.85 K) value within our experimental error (10%).

The superconducting properties in this compound clearly differ from the ones in magnetically mediated Ce or U heavy fermions. Although we could not find any published STM measurements in the tunneling regime and in the superconducting phase in these materials, there is compelling evidence from many different techniques sensitive to the superconducting density of states that a large amount of low-

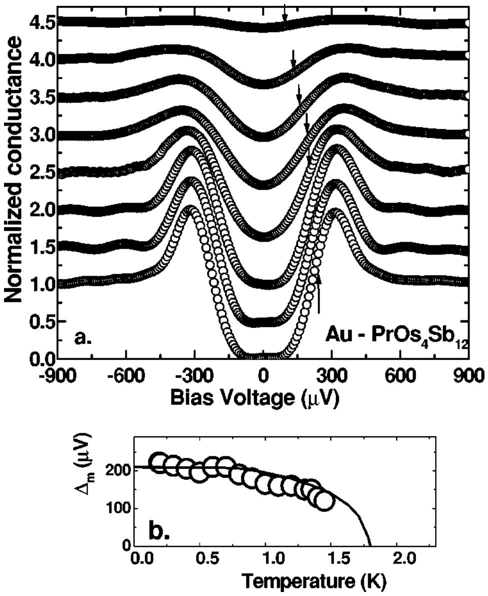

FIG. 2. In (a) we show the temperature dependence of the tunnelling conductance between superconducting $PrOs_4Sb_{12}$ and a normal tip of Au. The curves have been displaced by 0.5 units in the y axis for clarity. The data were taken at 0.2,0.3,0.4,0.6,0.8,1,1.2,1.4 K from bottom to top. In b. the mean value of the superconducting gap [from arrows in (a), see Refs. 23 and 26 for more details] is shown as a function of temperature, together with the prediction of the BCS theory (line). The extrapolated critical temperature coincides with the value found in the bulk.

energy excitations due to a strongly anisotropic superconducting gap is found in most cases. For instance, many experiments show now that the multiphase superconductor UPt_3 presents a line node along the basal plane and nodes along the c axis of its hexagonal crystalline structure, with a superconducting gap that decreases by more than an order of magnitude at the nodes.[12,27] In the case of $PrOs_4Sb_{12}$, there are at present no data pointing towards extended gapless regions on the Fermi surface, as the one caused by a line of nodes, so that the superconducting gap appears to be opened in a much larger part of the Fermi surface than in UPt_3.

The observed behavior has been reproduced in different places, but it is not found over the whole surface. In general, regions with no residual density of states, as shown in Figs. 3(a) and 3(b), have typical sizes of several times the coherence length ($\xi_0 = 12$ nm Ref. 6) and are surrounded by regions where a finite density of states appears at the Fermi level, shown in Figs. 3(c) and 3(d). We can also easily find regions with much less well-defined superconducting features (not shown in the figure). When we find a finite density of states at the Fermi level, the superconducting features also disappear at a temperature smaller than critical temperature of the bulk, indicating that the physical origin for the residual density of states at the Fermi level is some kind of strong pair breaking effect appearing near the surface, easily detected with our technique.

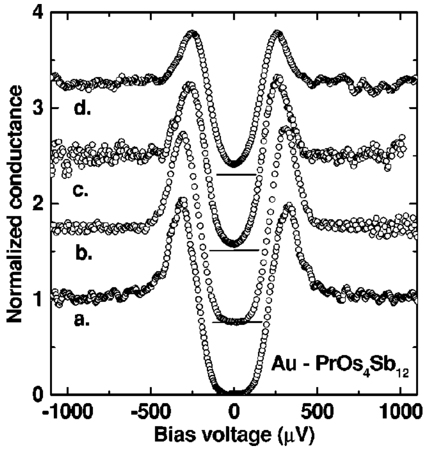

FIG. 3. Set of tunneling conductance curves taken in different positions on the surface of $PrOs_4Sb_{12}$ at 0.19 K with a tip of Au. The curves have been displaced by 0.75 units in the y axis for clarity, and the lines show the location of zero conductance for each curve. The finite density of states at the Fermi level measured in some positions (c,d) shows that pair breaking effects can appear at the surface of this compound.

In conclusion, we performed a direct measurement of the superconducting gap through high-resolution local tunneling spectroscopy measurements in the heavy-fermion superconductor $PrOs_4Sb_{12}$. Typical spectra demonstrate that the superconducting gap is well developed over a large part of the Fermi surface. The presence of a finite distribution of values of the superconducting gap over the Fermi surface can be inferred from deviations between the experiment and isotropic BCS s-wave behavior.

We acknowledge discussions with J. P. Brison, M. Crespo, J. Flouquet, F. Guinea, K. Izawa, Y. Kitaoka, A. Levanyuk, and J. G. Rodrigo and support from the ESF program VORTEX, from the MCyT (Spain, Grant No. MAT-2001-1281-C02-0), and from the Comunidad Autónoma de Madrid (Grant No. 07N/0053/2002, Spain). The Laboratorio de Bajas Temperaturas is associated to the ICMM of the CSIC. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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