Gap opening with ordering in PrFe$_4$P$_{12}$ studied by local tunneling spectroscopy

H. Suderow, K. Behnia, I. Guillamon, V. Crespo, S. Vieira, D. Kikuchi, Y. Aoki, H. Sugawara, and H. Sato

$^1$Laboratorio de Bajanas Temperaturas, Departamento de Física de la Materia Condensada
Instituto de Ciencia de Materiales Nicolás Cabrera, Facultad de Ciencias
Universidad Autónoma de Madrid, 28049 Madrid, Spain

$^2$Laboratoire Photons et Matière (UPR5-CNRS), ESPCI, 10 Rue de Vauquelin, 75231 Paris, France

$^3$Department of Physics, Tokyo Metropolitan University, Tokyo 192-0397, Japan

$^4$Faculty of Integrated Arts and Science, University of Tokushima, Tokushima 770-8502, Japan

(Dated: April 15, 2008)

We present measurements of the local tunneling density of states in the low temperature ordered state of PrFe$_4$P$_{12}$. The temperature dependencies of the Fermi level density of states, and of the integrated density of states at low bias voltages, show anomalies at $T \approx 6.5 K$, the onset of multipolar ordering as detected by specific heat and other macroscopic measurements. In the ordered phase, we find a local density of states with a V-shape form, indicating partial gap opening over the Fermi surface. The size of the gap according to the tunneling spectra is about 2 meV.

PACS numbers: 71.27. a+, 71.30 +h, 73.20.-r

Recently, a new family of heavy fermion f-electron intermetallic compounds with the filled skutterudite structure RT$_4$X$_2$ (R is a rare earth, T a transition metal and X a pnictogen) has been found to show many attractive phenomena, most of them appearing at low temperatures. Among others, metal-insulator transition, heavy fermion behavior, and superconductivity have been found in (R=Pr) systems.

In particular, in PrFe$_4$P$_{12}$, a peculiar phase transition occurs at $T_A = 6.5 K$, with distinct anomalies in both resistivity and specific heat. The intriguing order below $T_A$ is widely believed to be associated with orbital degrees of freedom. A recent NMR study has put severe restrictions on the symmetry of the order parameter. According to it, the ordering involves non-magnetic multipoles, which do not break the point symmetry of the crystal at the Pr sites. The scalar order with $\Gamma_{15}$ is currently the most promising candidate to represent the order parameter. On the other hand, according to transport studies, the itinerant electrons are profoundly affected by this phase transition. The multifold increase in the Hall, Seebeck and Nernst coefficients all suggest a drastic decrease in the number of charge carriers. This is compatible with the results of a de Haas van Alphen study, which found a small Fermi surface (0.0015 of the Brillouin zone) with a moderate effective mass ($\sim 10 m_e$) in the ordered state. In higher magnetic fields, the same study resolved several larger Fermi surfaces with heavier masses up to 81$m_e$. The consequences of the ordering on transport properties recall the case of URu$_2$Si$_2$. In both cases, the ordering leads to an enhanced lattice thermal conductivity, a large Hall coefficient and anomalously large Nernst and Seebeck coefficients due to an incomplete metal-insulator transition, producing a heavy-Fermion semi-metal. In the case of URu$_2$Si$_2$, a partial gap opening has been observed using different techniques.

On the other hand, scanning tunneling microscopy and spectroscopy (STM/S) techniques have been widely applied to systems where some kind of energy gap appears in the quasiparticle spectrum. The superconducting gap is certainly one of the most studied kinds of energy gaps viewed using this technique, although different kinds of charge ordered, and semimetallic or semiconducting compounds, have also received attention. Any features in the density of states at energies of the order of the meV are relatively easy to resolve using STM/S, because the tip density of states remains featureless and temperature independent below several tens of meV. Therefore, when a tip is scanned over a surface, the bias dependence of the local tunneling conductance, below some tens of meV, is simply the temperature smeared local density of states of the sample. Examples of STM/S experiments showing a temperature dependent gapped density of states include e.g. the intriguing pseudogap of the High $T_c$ superconductors, the charge density wave gap in the di-chalchogenides, or the peculiar low energy electronic features appearing in graphite. Here we present local tunneling conductance measurements at low temperatures made with STM/S that evidence the appearance of a gap in the quasiparticle spectrum of the heavy fermion material PrFe$_4$P$_{12}$.

We use a home built STM/S system in a $^4$He refrigerator that goes down to 1.5 K, and has been used for several previous work in superconducting materials. The STM/S has a scanning range of about 2 x 2 $\mu m$ at low temperatures, and a sample holder that allows to move in-situ the tip over the whole area of the sample. When needed, the tip is prepared and cleaned in-situ following the methods discussed in Refs. We took a small single crystalline sample broken at ambient conditions and mounted into the STM sample holder, and used tips of Au. The tip tunnels into the (100) direction.
FIG. 1: In a., we show a 90 nm x 90 nm region with small irregular terraces, and in b., an image of 7 nm x 7 nm, where lines at distances of around 0.2 nm, i.e. of the same order as interatomic distances of the unit cell, are observed. Grey scale of the images accounts for height differences of, respectively, 13 nm in a. and 0.5 nm in b. The corrugation of the terraces and steps observed in a. is of about 2 nm, and the corrugation of the linear structures observed in b. is of about 0.1 nm. A plane has been subtracted from both images. They have been acquired at 1.5 K, on a sample of PrFe$_4$P$_{12}$ with the surface perpendicular to the (100) direction. The tunneling density of states is reproducible over the whole surface, always showing the behavior presented in the Figs. 2 and 3.

of the single crystalline sample. The sample showed large surface areas where clean tunneling conditions could be achieved, with tunneling conductance curves that were reproducible over the whole surface. Moreover, the current-distance characteristics signalled work functions of several eV, and the topography and spectroscopy was independent of the tunneling resistance.

Typical images (Figs 1) consist of irregular terraces or small nanoscopic size granular structures, very similar to the ones observed on the surface of several superconducting materials [5, 19, 20]. In some surface regions, we could observe regular terraces with characteristic distances of the order of the unit cell (Fig.1b). Over the whole surface, we reproducibly observe a gapped local density of states. The curves shown in Fig.2 are obtained in large images of the surface, above and below the ordering temperatures. Above $T_A$, the tunneling conductance shows no significant temperature dependence, besides temperature smearing. The curves are usually slightly parabolic, with a density of states, which has a small bias dependence around the Fermi level. Typically, in this voltage range, metals show a flat density of states. Here, the small decrease of the density of states may signal a band structure with a peculiar form at energies very close to the Fermi level, that may preclude the opening of the gap in the ordered phase. When ordering sets in, a new energy scale appears in the tunneling conductance curves, which show a steep decrease for voltages below about 2 mV. At the lowest temperatures (1.5 K), the decrease is sharpest. The local density of states shows then closely a linear behavior at very low energies, with a characteristic V shape and a density of states at the Fermi level that remains relatively high.

Note that the decrease is not a simple consequence of the reduced temperature smearing of the data above $T_A$. To see this, we have plotted as the dashed line in Fig.3a the zero bias conductance calculated by reducing temperature smearing from the tunneling conductance above $T_A$, and normalized the result to one at 10 K. The conductance is of 1 $\mu$S, and the data have been normalized to 10 mV and displaced by 0.05 in the y axis for clarity (temperature for each curve is given on the right). We find a steep decrease of the density of states below about 2 mV that develops below 7 K. The size of the low temperature gap is estimated from the onset of the decrease in the conductance at low temperatures, as schematically described by the dashed lines.
30% smaller than in the high temperature phase. Furthermore, the integral over the local density of states measured at low energies (Fig.3a) also changes strongly below $T_A$. Indeed, the integral of tunneling conductance curves obtained from a temperature independent density of states also remains temperature independent. Here we observe instead a strong drop below $T_A$, evidencing the loss of charge carriers associated with the ordered state. Actually, the integral rapidly falls down to about 70% its value in the high temperature phase, and remains roughly constant, even on crossing the transition $T_x$. So below $T_x$, the decrease of the local Fermi level density of states (Fig.3a), is compensated by a slight increase at the shoulders of the conductance curves around 2mV.

![Graph](image-url)

**FIG. 3:** In a, we show the zero bias conductance as a function of temperature. Vertical lines represent the temperatures of onset of ordering $T_A$ and $T_x$, obtained in macroscopic measurements (see text). Dashed line represents the extrapolation of the zero bias conductance from the data above $T_A$ down to lower temperatures, calculated by gradually eliminating thermal smearing. The Fermi level density of states shows, at each one of both ordering temperatures, a clear decrease. In b, we show the integral over the tunneling conductance normalized to 1 above $T_A$.

The gap edge can be obtained from the voltage position of the onset of the decrease of the tunneling conductance curves down to the V shape observed at low temperatures (dashed lines in Fig.2). We find $\Delta = 2$ meV, which gives about $2\Delta/k_BT_A\approx 7$, a value that is significantly larger than the mean field BCS result ($2\Delta/k_BT_A = 3.7$) previously used in the discussion of charge or spin density wave phenomena\[17, 23, 24\].

On the other hand, the origin of the V-shape density of states and the significance of the high density of states obtained at the Fermi level and at low temperatures have to be discussed more carefully. As it is well known, in a local tunneling spectroscopy experiment, the obtained local density of states is formed by contributions coming from very different parts of the Fermi surface\[13\]. There is no selectivity in the direction perpendicular to the surface of the sample, as in a planar junction, and, in principle, many in-plane and out of plane momenta are probed\[13, 16\]. However, precise information of the actual electrons taking part in the tunneling process is very difficult to obtain without atomic resolution and comparison with theoretical calculations\[22\]. For instance, note that in the well studied superconducting material MgB$_2$, where until now no STM/S experiment has been made with atomic resolution, nearly all STM/S data show the opening of the superconducting gap on only part of the Fermi surface, namely the so called $\pi$ band gap\[21\]. Data from the rest of the Fermi surface, the so called $\sigma$ bands, where the electron phonon coupling is larger, are more difficult to obtain using STM/S. Actually, STM/S experiments in this compound have never unambiguously shown tunneling features close to what one would expect taking into account the opening of the gap over the whole Fermi surface\[25, 26, 27\]. In general, it is reasonable to assume that lighter electrons couple better with the states of the tip, so that local tunneling may preferentially reflect the properties of the Fermi surface with less mass renormalization, as possibly occurs in MgB$_2$.

In the case of PrFe$_4$P$_{12}$, the magnitude of decrease in the conductance integral indicates that about one third of the electrons participating in the tunneling process come from the gapped part of the Fermi surface. The rest, i.e. the vast majority, must come from part of the Fermi surface where there is no gap at all, or it is vanishingly small. The de Haas van Alphen data\[6\] have detected a small and almost spherical Fermi surface in the center of the Brillouin zone. The size of this Fermi surface is in very good agreement with the carrier density extracted from the low-temperature positive Hall coefficient. Therefore, it is reasonable to assume that this is a hole-like band with a large electronic mobility dominating the Hall response of the system. However, other Fermi surfaces, electron-like, with a larger mass and a lower mobility may have remained undetected by dHvA. They would account for the relatively large magnitude of the linear specific heat\[6\] and thermopower\[11\]. According to band structure calculations\[28\], in addition to a small hole-like spherical surface at the $\Gamma$-point, there is a large quasi-cubic Fermi surface subject to strong a nest-
ing instability. Nesting would lead to a quasi-complete destruction of this larger Fermi surface, leading to small surviving portions (with unknown shape and energy dispersion) coexisting with the small spherical Fermi surface at the center of the Brillouin zone.

Thus, it is tempting to assume that local tunneling spectroscopy experiments preferentially probe the small Fermi surface barely affected by the ordering. The large Fermi level conductance found at low temperatures may result from this Fermi surface. On the other hand, the opening of the gap and the V-shape structure of the curves, may be a signature of the other (that is the larger, nested and undetected) Fermi surface. This would explain the non-observation of a fully developed gap in our experiments, as may be naively expected taking into account the reduction of charge carriers in the ordered phase observed here is generated by the bulk and the measured tunneling density of states reproduces the behavior found in part of the Fermi surface. In particular, we find a gap is of 2 meV, which gives $2\Delta/k_B T_c \approx 7$, and that there are still parts of the Fermi surface that remain ungapped. This shows that the peculiar ordering in this compound leads to a largely frustrated metal insulator transition, and shapes the electronic band structure in such a way as to produce further peculiar properties.

ACKNOWLEDGMENTS.

We acknowledge discussions with J. Flouquet and J.P. Brison, and support from COST P-16 and from NES. The Laboratorio de Bajas Temperaturas is associated to the ICMM of the CSIC. This work was supported by the spanish MEC (Consolider Ingenio 2010 and grant FIS-2004-02897), and by the Comunidad de Madrid through program "Science and technology at the millikelvin" (S-0505/ESP/0337).

[1] Y. Aoki, H. Sugawara, H. Harima, and H. Sato, Journal of the Physical Society of Japan 74, 209 (2005).