Fermi surface instability at the hidden-order transition of URu$_2$Si$_2$.

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Solids with strong electron correlations generally develop exotic phases of electron matter at low temperatures [1, 2, 3, 4, 5]. Among such systems, the heavy-fermion semi-metal URu$_2$Si$_2$ presents an enigmatic transition at $T_o = 17.5$ K to a ‘hidden order’ state whose order parameter remains unknown after 23 years of intense research [6, 7]. Various experiments point to the reconstruction and partial gapping of the Fermi surface when the hidden-order establishes [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. However, up to now, the question of how this transition affects the electronic spectrum at the Fermi surface has not been directly addressed by a spectroscopic probe. Here we show, using angle-resolved photoemission spectroscopy, that a band of heavy quasi-particles drops below the Fermi level upon the transition to the hidden-order state. Our data provide the first direct evidence of a large reorganization of the electronic structure across the Fermi surface of URu$_2$Si$_2$ occurring during this transition, and unveil a new kind of Fermi-surface instability in correlated electron systems.

Earlier angle-resolved photoemission spectroscopy (ARPES) experiments mapped the basic band structure of URu$_2$Si$_2$ in the paramagnetic state (above $T_o$), establishing the existence of hole-pockets at the Γ, Z and X points of the Brillouin zone [19, 20, 21]. These experiments revealed strong disagreements with the calculations for the electronic structure and Fermi surface of URu$_2$Si$_2$. It was speculated that this was due to the presence of narrow features from the U-5$f$ states, not taken into account by the calculations, and difficult to characterize experimentally with the resolutions available at the time [21]. To date, no reports exist of high-resolution ARPES experiments below or across $T_o$. The pressing question is to determine experimentally the electronic structure near the Fermi level ($E_F$), including the heavy 5$f$ states, above and below $T_o$.

Figure 1 summarizes our findings for the temperature evolution of the electronic structure near $E_F$. Figure 1a shows the angle-integrated spectra of electrons with $k_\parallel$, the momentum component parallel to the sample surface, along the (110) direction at two temperatures across the transition. At $T = 26$ K, the only apparent feature is a surface state (SS) at binding energies $E_B < -35$ meV, observed at all the investigated temperatures (see Supplementary Material). In contrast, at 13 K a narrow peak at $E_B \approx -7$ meV appears, signaling the presence of a quasi-particle (QP) band. The temperature dependence of this QP band was systematically studied, and is shown in Figures 1b-d. In these figures we normalized
the spectra by the Fermi-Dirac distribution, following a well established procedure \[22\], to reveal the thermally occupied part of the spectral function up to energies $\sim 5k_B T$ above $E_F$. The angle-integrated data of Fig.\[1\]b shows that at 26 K the QP band lies at $E_B \approx 5$ meV, at 18 K $\approx T_o$ it appears right at $E_F$, and below $T_o$ the band shifts to energies below $E_F$. At 10 K the QP peak is located at $E_B \approx -7$ meV. Figure\[1\]c presents a quantitative evaluation of the QP peak energy as a function of $T/T_o$ from several spectra taken along the (110) and (100) directions, implying that the shift of this QP band occurs over an extended region of momentum space. Figure\[1\]d displays the angle-resolved data at the same temperatures as in Fig.\[1\]b. The data at 26 K and 18 K show, respectively, a flat band (within resolution) above $E_F$ and at $E_F$. These correspond to the peaks observed in the angle-integrated data of Fig.\[1\]b at those temperatures. Interestingly, the spectral weight of this flat band appears to be confined to a momentum region within $k_{\parallel} = \pm 0.2$ Å$^{-1}$, momenta at which there is a clear hint of a Fermi-level crossing. In the spectra at 13 K and 10 K, i.e. below $T_o$, the QP band displays a narrow dispersion, showing that it is a band of itinerant heavy quasi-particles. We will discuss all these observations in detail.

The data of Figure\[1\] show explicitly that the transition to the HO state is accompanied by a significant reorganization of the portions of the Fermi surface involving heavy quasiparticles. Such a transfer of spectral weight across the Fermi surface implies dramatic modifications of the macroscopic properties of the system, strongly suggesting that this is the microscopic origin of the observed abrupt changes in the thermal and transport properties of URu$_2$Si$_2$ during the HO transition \[6, 8, 10, 11, 13\].

Figure\[2\] shows the angle-resolved data at $T = 13$ K, along the (110) direction. The ARPES intensity map (Fig.\[2\]a) shows the narrow quasi-particle band dispersing down to $W \approx -7$ meV, where $|W|$ is the width of the band. Figure\[2\]b shows energy distribution (EDCs) curves in the region close to $E_F$ of this intensity map. The EDCs having the leading edge (LE) closest to $E_F$ are plotted in bold, corresponding to momenta $k_{LE} = 0.2$ Å$^{-1}$. For $|k| < |k_{LE}|$ distinct QP peaks of resolution-limited width ($\sim 5$ meV) are observed. From the values of $W$ and $k_{LE}$, an estimate of the effective mass ($m^*$) of these QPs can be obtained from the relation $W = -\hbar^2 k_{LE}^2/2m^*$. This yields $m^* \approx 22m_e$ ($m_e$ is the bare electron mass), confirming that this band corresponds to heavy quasi-particles. This value of $m^*$ is among the largest values ever measured by ARPES in any material. The values of $m^*$ and $k_{LE}$ agree well with values given by specific heat data \[8\] and de Haas-
van Alphen measurements \cite{9}. The group velocity \( v_{QP} \) of the observed heavy-QPs can also be estimated from \( v_{QP} \approx W/k_{LE} \), yielding \( |v_{QP}| \approx 35 \text{ meV } \AA \), comparable to values obtained from thermal transport data \cite{11}. Notice also from Fig. 2b that for \( |k| > |k_{LE}| \) the leading edge of the spectra shifts to larger binding energies. This suggests that the spectral weight of the heavy-QP band spreads over a large momentum window, as best seen in data along the (100) direction (see Fig. 3). Figure 2c shows momentum distribution curves (MDCs) from the intensity map in Fig. 2a. Besides the peaks corresponding to the hole-like surface state, two lateral shoulders are observed (shown by the dashed lines). They correspond to a light hole-like conduction band with \( m^* \approx -1.4 m_e \), dispersing through \( E_F \) at Fermi momenta \( k_F = \pm 0.2 \text{ Å}^{-1} \), i.e., \( k_F = k_{LE} \) within experimental resolution. Fig. 2d shows the average of the energy and momentum second derivatives of the intensity map in Fig. 2a. This allows to visualize clearly the conduction band and the spectral weight of the heavy-QP band spreading beyond \( |k_{LE}| \).

Figure 3 summarizes the data along the (100) direction at \( T < T_o \). The raw map (Fig. 3a) clearly displays the band of itinerant heavy QPs approaching \( E_F \) at \( k_{LE} = \pm 0.15 \text{ Å}^{-1} \), the light hole-like conduction band dispersing through \( E_F \) at the same momenta, and the tails of spectral weight extending beyond \( |k_{LE}| \). The latter have a clear quasi-particle peak structure, with a hole-like dispersion of velocity \( \sim 12 \text{ meV } \AA \), as seen in the corresponding EDCs (Fig. 3b).

An interesting observation from Figs. 2 and 3 is that the momenta where the conduction band and heavy-QP coincide correspond to the momenta where the heavy-QP band bends back from \( E_F \). This suggests that the whole structure arises from the hybridization of the light conduction band and a band of localized states, though due to the finite experimental resolution, we cannot observe a hybridization gap directly. From our angle-resolved data at 26 K and 18 K in Fig. 11, it appears that these these bands hybridize already above \( T_o \), when the band of localized states is at \( E_B > E_F \). The transition to the hidden-order state shifts the heavy-QP part of the resulting spectral function to \( E_B < E_F \). There, it is clearly observed as a dispersing band of heavy quasi-particles, creating –together with the light conduction band– a heavy Fermi surface. Indeed, previous ARPES experiments in URu$_2$Si$_2$ above \( T_o \) showed strong evidence for the presence of \( f-d \) hybridization \cite{21}.

Note also that along the (100) direction \( k_F \) is lower than along the (110) direction. This provides direct experimental evidence that anisotropic small-sized Fermi-surface pockets
exist around the Γ point in URu$_2$Si$_2$, as indirectly suggested by other techniques [9].

Summarizing, our results explicitly show that the hidden-order transition of URu$_2$Si$_2$ results in a large transfer of spectral weight across the Fermi surface. Below the ordering temperature, our data reveal the existence of a band of heavy quasi-particles dispersing over a narrow energy scale of the order of 7 meV below $E_F$. The observations suggest that this heavy-QP band arises from the hybridization of a $d$-conduction band with a band of localized states, probably of $5f$ character [21]. As temperature rises above $T_o$, the heavy-QP band moves to unoccupied states above $E_F$. These results, which cannot be understood in terms of band-nesting alone, demonstrate that the interplay of localized-itinerant behaviors of the electrons in URu$_2$Si$_2$ is important to understand the hidden-order transition. Moreover, these findings emphasize the fundamental role of heavy quasi-particles during the transition, as it is their spectral weight that shifts to below $E_F$ when the ordered state sets in. This remarkable phenomenon, which is in itself a novel kind of Fermi-surface instability in solids, has to be taken into account in theories of the hidden-order transition in URu$_2$Si$_2$.

One way of interpreting our data is that the hidden-order transition massively re-organizes the spectral function of this strongly-interacting many-electron system. The observed spectral-weight shift of the heavy quasi-particle band would then be a consequence of this many-body effect. A proof of principle of this possibility, that does not need to invoke band-nesting, has been recently given for the case of the magnetic order-disorder transition in the two-dimensional doped Kondo-lattice model [23]. As the small magnetic moment observed in the HO state of URu$_2$Si$_2$ seems to have an extrinsic origin [24] and appears anyway insufficient to explain the large entropy loss due to the transition [12], material-specific calculations for the case of URu$_2$Si$_2$ would be needed to test this idea.

We anticipate that our results will be an invigorating trigger for more, high-resolution studies of the angular-resolved electronic structure of URu$_2$Si$_2$, and for theoretical developments exploring how the competition between itinerant and localized electron behavior can describe the fascinating behaviour of this material. Our observations will provide new insight not only to the theoretical approaches of the hidden-order, but also to the understanding of exotic phases in systems with strong electron interactions and competing ground states.
METHODS

Sample preparation and measurement technique

The high-quality URu$_2$Si$_2$ single crystals were grown in a tri-arc furnace equipped with a Czochralski puller, and subsequently annealed at 900°C under ultra high vacuum for 10 days [25]. The high-resolution ARPES experiments were performed with a Gammadata R4000 analyzer and a monochromatized VUV-lamp at $h\nu = 21.2$ eV (He I$_\alpha$). The energy resolution for the used analyzer settings was 5.18 meV, determined similar to previous experiments [26]. The temperature during each measurement was found by fitting a Fermi-Dirac distribution to the Fermi edge of polycrystalline Ag, mounted next to each URu$_2$Si$_2$ crystal on the same sample holder, and taking into account the above energy resolution. The base pressure in the chamber was $1 \times 10^{-10}$ mbar, increasing to $8 \times 10^{-10}$ mbar during the measurement due to the He leakage from the discharge lamp. The crystals were oriented using Laue diffraction, and cleaved in situ just before the measurement, already at the measurement temperature. Highly ordered surfaces were confirmed by sharp low-energy electron diffraction patterns measured on each sample after the measurements. Because of the observed high-surface reactivity (the quasi-particle peaks below $T_o$ broaden and lose amplitude within 2 hours after cleaveage), the duration of each measurement was kept below 15 minutes immediately after cleaving, at constant temperature.

Procedure of second-derivative rendering

The raw photoemission intensity maps were convoluted with a two-dimensional gaussian of widths $\sigma_E = 7$ meV and $\sigma_k = 0.07$ Å$^{-1}$. Second derivatives along the $E_B$ and $k_\parallel$ axes were normalized to the maximum intensity peak in the surface-state, then averaged. Only negative intensity values are shown to trace the peaks of the raw data.

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COMPETING INTERESTS

The authors declare that they have no competing financial interests.

ADDITIONAL INFORMATION

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[1] van Harlingen, D. J. Phase-sensitive tests of the symmetry of the pairing state in the high-temperature superconductors. Rev. Mod. Phys. 67, 515 (1995).
[2] Mackenzie, A. P. & Maeno, Y. The superconductivity of Sr$_2$RuO$_4$ and the physics of spin-triplet pairing. Rev. Mod. Phys. 75, 657 (2003).
[3] Dagotto, E. & Rice, T. M. Surprises on the way from one- to two-dimensional quantum magnets: the ladder materials. Science 271, 618 (1996).
[4] Hotta, T. Orbital ordering phenomena in $d$- and $f$-electron systems. Rep. Prog. Phys. 69, 2061 (2006).
[5] Mostovoy, M. Helicoidal ordering in iron perovskites. Phys. Rev. Lett. 94, 137205 (2005).
[6] Palstra, T. M. et al. Superconducting and magnetic transitions in the heavy-fermion system URu$_2$Si$_2$. Phys. Rev. Lett. 55, 2727 (1985).
[7] Tripathi, V., Chandra, P. & Coleman, P. Sleuthing hidden-order. Nature Physics 3, 76 (2007).
[8] Maple, M. B. et al. Partially gapped Fermi surface in the heavy-electron superconductor URu$_2$Si$_2$. Phys. Rev. Lett. 56, 185 (1986).
[9] Ohkuni, H. et al. Fermi surface properties and de Haas-van Alphen oscillation in both the normal and superconducting mixed states of URu$_2$Si$_2$. Philosophical Magazine B 79, 1045 (1999).
[10] Palstra, T. M. et al. Anisotropic electrical resistivity of the magnetic heavy-fermion superconductor URu$_2$Si$_2$. Phys. Rev. B 33, 6527 (1986).
[11] Behnia, K. et al. Thermal transport in the hidden-order state of URu$_2$Si$_2$. Phys. Rev. Lett. 94, 156405 (2005).
[12] Wiebe, C. R. et al. Gapped itinerant spin excitations account for missing entropy in the hidden order state of URu$_2$Si$_2$. Nature Physics 3, 96 (2007).
[13] Schoenes, J., Schönenberger, C., Franse, J. J. M. & Menovsky, A. A. Hall-effect and resistivity study of the heavy-fermion system URu$_2$Si$_2$. Phys. Rev. B 35, 5375 (1987).
[14] Hasselbach, K., Kirtley, J. R. & Lejay, P. Point-contact spectroscopy of superconducting URu$_2$Si$_2$. Phys. Rev. B 46, 5826 (1992).
[15] Escudero, R., Morales, F. & Lejay, P. Temperature dependence of the antiferromagnetic state in URu$_2$Si$_2$ by point-contact spectroscopy. Phys. Rev. B 49, 15271 (1994).
[16] Bonn, D. A., Garret, J. D. & Timusk, T. Far-infrared properties of URu$_2$Si$_2$. Phys. Rev. Lett. 61, 1305 (1988).
[17] Broholm, C. et al. Magnetic excitations and ordering in the heavy-electron superconductor URu$_2$Si$_2$. Phys. Rev. Lett. 58, 1467 (1987).
[18] Villaume, A. et al. A signature of hidden order in URu$_2$Si$_2$: the excitation at the wavevector $Q_0 = (100)$. Phys. Rev. B 78, 012504 (2008).
[19] Ito, T. et al. Band structure and Fermi surface of URu$_2$Si$_2$ studied by high-resolution angle-resolved photoemission spectroscopy. Phys. Rev. B 60, 13390 (1999).
[20] Denlinger, J. D. et al. Advances in photoemission spectroscopy of f-electron materials. Physica B 281-282, 716 (2000).
[21] Denlinger, J. D. et al. Comparative study of the electronic structure of XRu$_2$Si$_2$: probing the Anderson lattice. J. Electron Spectrosc. Relat. Phenom. 117-118, 347 (2001).
[22] Ehm, D., Hübner, S., Reinert, F. et al. High-resolution photoemission study on low-$T_K$ Ce systems: Kondo resonance, crystal field structures, and their temperature dependence. Phys. Rev. B 76, 045117 (2007).
[23] Martin, L.C. & Assaad, F. F. Evolution of the Fermi surface across a magnetic order-disorder transition in the two-dimensional kondo-lattice model: A dynamical cluster approach. Phys. Rev. Lett. 101, 066404 (2008).
[24] Amitsuka, H. et al. Pressure-temperature phase diagram of the heavy-electron superconductor URu$_2$Si$_2$. J. Magn. Magn. Mater. 310, 214 (2007).
[25] Lejay, P., Muller, J. & Argoud, R. Crystal growth and stoichiometry study of the ternary...
silicides CeRu$_2$Si$_2$ and Ce$_{1-x}$La$_x$Ru$_2$Si$_2$. *Journal of Crystal Growth* **130**, 238-244 (1993).

[26] Reinert, F., Nicolay, G., Eltner, B. *et al.* Observation of a BCS spectral function in a conventional superconductor by photoelectron spectroscopies. *Phys. Rev. Lett.* **85**, 3930 (2000).
FIG. 1: Temperature dependence of the quasi-particle band in URu$_2$Si$_2$. a, Raw photoemission spectra integrated within $\pm 0.2$ Å$^{-1}$ along the (110) direction at 13 K (blue) and 26 K (red). Below $T_o = 17.5$ K, a quasi-particle (QP) peak appears below $E_F$. For all temperatures, a surface state (SS) at $E_B < -35$ meV is observed. b, Spectra integrated within $\pm 0.2$ Å$^{-1}$ along the (110) direction and normalized by the Fermi-Dirac distribution, at various temperatures around $T_o$: 26 K (red), 18 K (green), 13 K (blue) and 10 K (black). The zero-intensity level of each spectrum is indicated by the color bars in the right axis. The triangle markers give the peak position. c, Energy of the QP peak in the integrated spectra (with respect to $E_F$) as a function of $T/T_o$ for cuts along the (110) (triangles) and (100) (circles) directions. The error bars in $T$ are due to thermal instabilities during the experiment. The error bars in the peak energy are calculated from the peak positions in spectra integrated over different momenta windows around $k_\parallel = 0$. d, Angle-resolved spectra along the (110) direction for the same temperatures as in b, over an extended energy range. The intense hole-like feature dispersing below $E_B \sim -35$ meV is the surface state displayed in panel a.
FIG. 2: **Heavy quasi-particle band in the hidden-order state and hybridisation with a conduction band along the (110) direction.** a, ARPES intensity map along the (110) direction at 13 K. The map shows a heavy quasi-particle band dispersing down to $\sim 7$ meV below $E_F$. b, EDCs of the intensity map in (a) in the region close to $E_F$. The EDCs whose leading edge is closest to $E_F$ are drawn in bold. c, MDCs from the intensity map in (a). Each MDC is normalized to its area. The two central peaks correspond to the hole-like surface state, and two lateral shoulders to a light conduction band that disperses through $E_F$. d, Average of second derivatives along the energy and momentum axes (see methods), showing the heavy-QP band, the surface state, and the hole-like conduction band. In all panels, the dashed lines are guides to the eye for the dispersions of the different bands.
FIG. 3: **Heavy quasi-particle band in the hidden-order state and hybridisation with a conduction band along the (100) direction.**

**a,** ARPES intensity map along the (100) direction at 15 K, with the heavy-QP band dispersing down to $\sim$ 4 meV below $E_F$. The dashed white lines show conduction bands dispersing through $E_F$, clearly visible in the raw map.

**b,** EDCs of the intensity map in (a) in the region close to $E_F$. The EDCs whose leading edge is closest to $E_F$ are drawn in bold. As a guide to the eye, the dispersion of the heavy-QP band is shown by the dashed line. This band, clearly extending beyond the Fermi momenta, is also visible in the raw data map of panel **a**.
SUPPLEMENTARY MATERIAL

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Abstract

The photoemission data of URu$_2$Si$_2$ show an intense hole-like feature with a minimal binding energy of $E_0 \approx -35$ meV right after cleaving the crystal in situ. We briefly present here the evidence that it is a surface state.
Figure SF 1: EDCs at normal emission obtained at different times after cleaving the crystal. The intense feature's energy shifts with time due to adsorption of residual gases in the UHV chamber, characteristic of a surface state. The heavy quasi-particle (QP) feature right below $E_F$ remains at constant energy, indicative of a bulk feature.

Measuring at different times after the cleavage results in an energy shift of such feature. Figure SF 1 shows a measurement series with energy distribution curves (EDCs) at normal emission obtained in time intervals of about 10 min. The peak positions are marked by arrows. This energy shift with time is due to the adsorption by the sample’s surface of residual gas, mainly originating from leakage of the He discharge lamp, to which the states located at the surface are highly sensitive. A similar behavior of noble metal surface states has been observed by Nicolay and coworkers [SR1]. By contrast, note that the heavy-quasi-particle (QP) feature right below $E_F$ remains at a constant energy position, indicating a bulk-like character.

Figure SF 2 shows EDCs at normal emission measured with different excitation energies right after cleaving. In this case the position in energy of the surface related feature is constant. This means that such a state shows no dispersion in the $k_z$ direction and hence
Figure SF 2: EDCs at normal emission measured with different excitation energies. The marked feature stays at a constant energy position showing no dispersion in $k_z$. This indicates a two-dimensional state, which in our case is a surface state.

has a two-dimensional character. This fully confirms that the intense feature below $E_0 \approx -35$ meV is a surface state.

[SR1] G. Nicolay, F. Reinert, F. Forster, D. Ehm, S. Schmidt, B. Eltner and S. H"ufner. Surf. Sci. 543, 47 (2003).