

QUANTUM MATERIALS

Orbital-selective metals

The metallic state of an iron chalcogenide superconductor is demonstrated to be characterized by the simultaneous presence of itinerant carriers with different degrees of correlation. This orbital-selective metal arises from a sizeable Hund's coupling.

Massimo Capone

One of the milestones of solid-state physics is the Landau theory of normal Fermi liquids, which describes why the electrons in metals behave in many respects like non-interacting particles despite the Coulomb interaction. The Fermi-liquid theory is also a pillar of the Bardeen–Cooper–Schrieffer theory, which explains the origin and the properties of the superconducting state, in which the electrons in a solid form Cooper pairs and give rise to a quantum state with zero electrical resistance that expels magnetic fields. Yet these theoretical frameworks are often challenged by the discovery of new materials, such as the discovery of high critical temperature (T_c) superconductivity in Fe-based materials ten years ago. In their recent study of the metallic state of the iron chalcogenide superconductor FeSe, published in *Nature Materials*, Andrey Kostin and colleagues¹ have found clear evidence for a single quantum fluid in which electrons belonging to different orbitals have completely different quasiparticle properties. This is a direct observation of a Hund's metal — a system where the electronic correlations are strongly influenced by the Hund's exchange coupling^{2,3} — whose orbital-selective properties have been proposed as a key to understand the whole family of iron-based superconductors⁴.

While the theoretical framework for the parent state of the iron-based superconductors built on orbital selectivity has been well developed over the past decade and is consistent with many observations, a 'smoking gun' experiment was still lacking. Measuring quasiparticle interference in a scanning tunnelling spectroscopy experiment, Kostin et al. directly image the orbital-selective 'Hund's metal' in FeSe (ref. ⁸), clearly demonstrating that the metallic state from which superconductivity and other broken-symmetry phases emerge has a strong orbital-selective character (Fig. 1b). In this approach, the authors can track the coherence of the low-energy quasiparticles throughout the Brillouin zone and they have been able to show that the regions with d_{xy} orbital character show a very weak

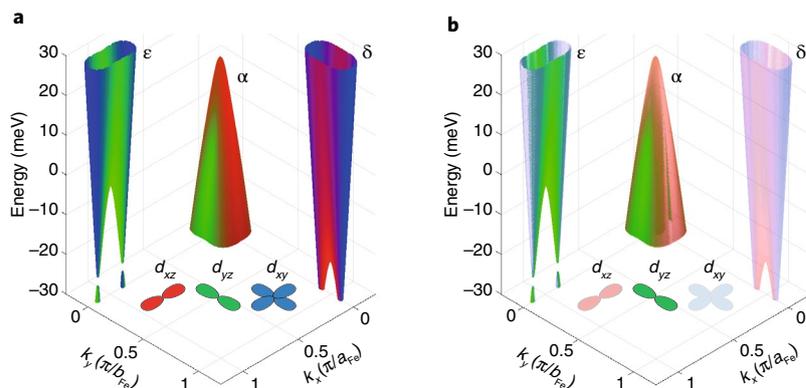


Fig. 1 | Electronic band structure of FeSe. a, Map of the low-energy bands in the two-dimensional Brillouin zone corresponding to the FeSe planes resolved according to the orbital character. Red marks the d_{xz} orbital, green the d_{yz} and blue the d_{xy} . **b**, Same plot including the orbital-dependent quasiparticle renormalization. Faint and pale colours denote the regions where the electron–electron interactions reduce the quasiparticle coherence. In particular, d_{xy} and d_{xz} are more affected by electronic correlations. Reproduced from ref. ¹, Springer Nature Ltd.

coherent signal, as predicted by theoretical calculations based on multi-orbital Hubbard models. Furthermore, their experiment demonstrates a significant difference between the quasiparticle weights of d_{xz} and d_{yz} orbitals, an observation connected to the nematic properties of the material.

The reason why we are so interested in the role of electronic correlations in superconductors is deeply rooted in the discovery of high- T_c superconductivity in copper oxide materials — the cuprates — in 1986. All previously known superconductors were metals, where the coupling of the electrons with the lattice provided the attractive interaction or 'glue' to form the Cooper pairs. By contrast, in the cuprates superconductivity appears through doping a Mott insulator, a quantum state in which the electrons are localized and the electrical conduction is lost because of strong repulsive interactions⁵. This finding gave rise to the bustling field of high- T_c superconductivity, the main goals of which include understanding how this phenomenon — which ultimately boils down to attractive interactions — finds

its most spectacular realization in systems dominated by a very large repulsion. We have made substantial advances in this direction, and a variety of theoretical approaches have provided convincing evidence that simple models with purely repulsive interactions (Hubbard models and relatives) are indeed characterized by superconductivity and are able to reproduce all the qualitative features of the cuprates⁶.

Since the discovery of high- T_c superconductivity with the second highest critical temperatures in iron pnictide superconductors in 2008⁷, it has been natural to compare and contrast this new class of materials with their elder cuprate relatives. In both cases we have layered structures containing ligand and transition-metal atoms, and, importantly, superconductivity appears upon doping a magnetic compound with a maximum critical temperature at an intermediate optimal doping. On the other hand, the parent compound of the iron-based superconductors is not a Mott insulator, but a metal with a spin-density-wave ordering, and the Fermi surfaces are reasonably well described by density

functional theory. Last, but not least, there is overwhelming evidence that the low-energy bands of these materials have a multi-orbital character involving all the iron 3*d* orbitals⁹.

This comparison might simply suggest that the degree of correlation of the iron-based superconductors is significant, but not sufficient to localize the electrons as it does in the cuprates. In this sense the new family would be simply a 'light' version of the most popular one. A more careful analysis suggested the richer scenario where different 'fractions' of the fermionic fluid with varying degrees of correlation coexist in a single quantum state⁴. More precisely, the carriers in iron-based superconductors have a different degree of correlation, as measured by their effective mass renormalization or quasiparticle weight, according to their orbital character. This is a direct result of the Hund's exchange coupling^{2,3}, which favours high-spin configurations. It has been proposed that, among other effects, the Hund's coupling leads to an 'orbital decoupling' that makes the orbitals independent from each other, so that some orbitals can acquire a remarkably larger mass enhancement with respect to the others⁴.

The work of Kostin et al. remarkably validates this orbital-selective picture for the metallic state of an iron chalcogenide superconductor. This result, combined with the previous observation of orbital-selective pairing in the superconducting state of the same material¹⁰, strongly confirms that orbital selectivity can be considered as an organizing principle of the complex fermiology of these materials⁴. Thus, orbital selectivity and electron–electron correlations should be regarded as necessary building blocks of any theory of superconductivity and of the whole phase diagram of this intriguing class of materials.

Several questions are revived by the new evidence presented in the work of Kostin and colleagues. The most natural and compelling issue is the connection between the orbital-selective correlations and superconductivity. Future investigations should tell us whether the selective correlations are also the source of the pairing glue, strengthening the similarity with the cuprates, or rather a companion or booster of a superconducting instability arising from a more conventional mechanism based on the exchange of bosons — for example, spin fluctuations.

Another crucial question that will require further investigation is whether the orbital-selective metal can be considered a Fermi liquid with extreme parameters, or if it features finite-temperature deviations from the Fermi-liquid picture. □

Massimo Capone

International School for Advanced Studies (SISSA) and CNR-IOM Democritos, Trieste, Italy.
e-mail: capone@sissa.it

Published online: 3 September 2018
<https://doi.org/10.1038/s41563-018-0173-7>

References

1. Kostin, A. et al. *Nat. Mater.* <https://doi.org/10.1038/s41563-018-0151-0> (2018).
2. Haule, K. & Kotliar, G. *New J. Phys.* **11**, 025021 (2009).
3. Georges, A., de' Medici, L. & Mravlje, J. *Annu. Rev. Condens. Matter Phys.* **4**, 137–178 (2013).
4. de' Medici, L., Giovannetti, G. & Capone, M. *Phys. Rev. Lett.* **112**, 177001 (2014).
5. Anderson, P. W. *Science* **235**, 1196–1198 (1987).
6. Lee, P. A., Nagaosa, N. & Wen, X.-G. *Rev. Mod. Phys.* **78**, 17–85 (2006).
7. Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. *J. Am. Chem. Soc.* **130**, 3296–3297 (2008).
8. Hsu, F.-C. et al. *Proc. Natl Acad. Sci. USA* **105**, 14262 (2008).
9. For a recent review see, Yi, M., Zhang, Y., Shen, Z.-X. & Li, D. *npj Quant. Mater.* **2**, 57 (2017).
10. Sprau, P. O. et al. *Science* **357**, 75–80 (2017).

TITANIUM DIOXIDE

Shedding light on black titania

Multiscale modelling provides atomic-level insights into how oxygen vacancy defect nucleation leads to the formation of the visible light photocatalyst black titania.

Vassiliki-Alexandra Glezakou and Roger Rousseau

Metal oxides are ubiquitous in everyday life and titania, arguably, has received the most scrutiny from materials scientists due to its functionality for applications such as photocatalytic water splitting, chemical sensors and nanomedicine^{1–3}. What makes this material a daunting challenge to understand is that many of its desirable properties result from imperfections. Titania, formally TiO₂ in its stoichiometric form, consists of Ti⁴⁺ cations and O²⁻ anions, which both have closed electronic shells, such that a perfect crystal would be transparent and non-conductive (Fig. 1a). However, many defects common to TiO₂, such as oxygen vacancies, OH groups or interstitial titanium atoms,

not only disrupt the crystallinity but also create charge carriers that modify optical properties and electrical conductivity (Fig. 1b). Material scientists have spent decades trying to create the right defects to increase visible light optical absorption and electrical conductivity for photocatalytic applications. One example that has recently garnered interest is black TiO₂, which contains substantial numbers of defects (Fig. 1c) and can absorb light in the visible range for water splitting, a holy grail for renewable energy^{4–6}. How it forms, and what its structural composition is, are critical questions.

In the past decade, theory and modelling^{7–9} has been able to address the

nature of these charge carriers and how they move through the TiO₂ lattice. The current belief is that defects create localized Ti³⁺ centres instead of Ti⁴⁺ cations, where titanium atoms are reduced by an electron; this is known as a polaron (Fig. 1b). These polarons can hop from Ti to Ti sites, giving rise to electrical conductivity, while the change in their electronic state creates colour centres that leads to light absorption. When these polaronic defects form close to the surface, they enable chemical reactions by electron/hole exchange with adsorbed molecules. This is why TiO₂ is prevalent in photocatalysis and many other applications that rely on chemistry driven by light and/or electricity.