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Direct Observation of Nodes and Twofold Symmetry in FeSe Superconductor

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Abstract
We investigated the electron-pairing mechanism in an iron-based superconductor, iron selenide (FeSe), using scanning tunneling microscopy and spectroscopy. Tunneling conductance spectra of stoichiometric FeSe crystalline films in their superconducting state revealed evidence for a gap function with nodal lines. Electron pairing with twofold symmetry was demonstrated by direct imaging of quasiparticle excitations in the vicinity of magnetic vortex cores, Fe adatoms, and Se vacancies. The twofold pairing symmetry was further supported by the observation of striped electronic nanostructures in the slightly Se-doped samples. The anisotropy can be explained in terms of the orbital-dependent reconstruction of electronic structure in FeSe.

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responses in dependence on $H$. When $H$ decreases, resonances I and II show opposite spectral behavior, and the transmittance intensities of the two resonance branches cross one another. In particular, resonance I evolves from a broad profile to a narrower and suppressed resonance, whereas resonance II grows in strength and becomes more and more pronounced. This is due to the fact that when the middle rod is successively shifted toward the bottom shorter rod pair and therefore couples more strongly to it, resonance II is enhanced. Simultaneously, resonance I is reduced because the middle rod is shifted gradually away from the top longer rod pair and therefore couples less strongly to it. It is noteworthy that the spectral positions of the two quadrupolar resonances can also provide information on the spatial structure change. Figure 4C shows the calculated spectral positions of the two quadrupolar resonances in dependence of $H$. When the middle rod is shifted downward (see the gray region), the position of resonance I stays nearly the same, whereas resonance II shifts to lower energies. In contrast, when the middle rod is shifted upward (see the white region), resonance II does not show a prominent position change, whereas resonance I shifts to significantly lower energies. Figure 4 clearly demonstrates how the full spectral behavior of the 3D plasmonic structure is correlated to the structural changes in space and will allow for evaluation of the magnitudes as well as the directions of structural changes. Differential spectra that evaluate 3D conformational changes from topological-like spectroscopy from different directions. The realization of 3D plasmon rulers using nanoparticles and biochemical linkers is challenging, but 3D nanoparticle assemblies with desired symmetries and configurations have been successfully demonstrated very recently (24, 25, 27–30). These exciting experimental achievements will pave the road toward the realization of 3D plasmon rulers in biological and soft-matter systems.

References and Notes
17. See Supporting Material on Science Online.

Direct Observation of Nodes and Twofold Symmetry in FeSe Superconductor

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We investigated the electron-pairing mechanism in an iron-based superconductor, iron selenide (FeSe), using scanning tunneling microscopy and spectroscopy. Tunneling conductance spectra of stoichiometric FeSe crystalline films in their superconducting state revealed evidence for a gap function with nodal lines. Electron pairing with twofold symmetry was demonstrated by direct imaging of quasiparticle excitations in the vicinity of magnetic vortex cores, Fe adatoms, and Se vacancies. The twofold pairing symmetry was further supported by the observation of striped electronic nanostructures in the slightly Se-doped samples. The anisotropy can be explained in terms of the orbital-dependent reconstruction of electronic structure in FeSe.

Despite intense experimental investigation, the pairing symmetry in the recently discovered iron (Fe)–based superconductors remains elusive (1–3). Phonon-mediated pairing in conventional superconductors is typically isotropic, leading to $s$-wave symmetry. Unconventional pairing mechanisms, such as spin fluctuations, may give rise to an order parameter with its sign change over the Fermi surfaces and a pairing symmetry such as $s^\pm$ (4, 5). The $s^\pm$ scenario is supported by the phase-sensitive “Josephson tunneling” (6, 7) and angle-resolved photoemission spectroscopy (8) experiments. If the sign change occurs on a single electron or

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hole conducting gap function \( T_c \approx 8 \text{ K} \) that can increase to 37 K at a pressure of 8.9 GPa \((1, 2)\). However, the uncertainty in the stoichiometry of Fe(Se,Te) samples \((1\text{--}3)\) has made it challenging to understand the superconducting and normal states in the materials. To avoid this complexity, we grew the stoichiometric FeSe single-crystalline films on the SiC(0001) substrate with molecular beam epitaxy (MBE) in ultra-high vacuum (UHV) \((13)\) and performed the STM experiment on the films in the same UHV system. The MBE growth of the FeSe films is characterized by a typical layer-by-layer mode, as demonstrated in fig. S1. The STM topographic images (Fig. 1, A and B, and fig. S1) revealed atomically flat and defect-free Se-terminated (001) surfaces with large terraces. The selenium atom spacing of the \((1 \times 1)\)-Se lattice (Fig. 1B) in the topmost layer was 3.8 Å, which is in good agreement with a previous report \((1)\). The synchrotron x-ray power diffraction exhibited a structural transition from tetragonal to orthorhombic symmetry at 90 K for FeSe \((14)\). In the low-temperature orthorhombic phase, the Fe-Fe lattice’s constant difference between the two close-packed directions was 0.012 Å at 20 K. This difference is too small to be resolved with STM, so Fig. 1B appears as a square lattice.

The scanning tunneling spectroscopy (STS) probes the quasiparticle density of states and measures the superconducting gap at the Fermi energy \( E_F \) \((15)\). In Fig. 1C, we show the tunneling spectra on the sample in Fig. 1A at various temperatures. The spatial homogeneity of the STS spectra (fig. S2) further demonstrates the high quality of the MBE samples. At a temperature below \( T_c \), the spectra exhibit two conductance peaks and a gap centered at the Fermi energy. The maximum of the superconducting gap \( \Delta_0 \approx 2.2 \text{ meV} \) is half of the energy between the two conductance peaks. The most striking feature of the spectra at 0.4 K, analogous to the cuprate high-\( T_c \) superconductors \((15)\), is the V-shaped \( dI/dV \) and the linear dependence of the quasiparticle density of states on energy near \( E_F \). This feature explicitly reveals the existence of line nodes in the superconducting gap function. At elevated temperatures, the V-shaped spectra in Fig. 1C smear out as the superconducting gap disappears above \( T_c \).

We suggest that the nodal superconductivity exists only in FeSe with a composition close to stoichiometry. By introducing Te into the compound, the ternary Fe(Se,Te) becomes a nodeless \( s\text{-wave} \) superconductor, which is characterized by a fully gapped tunneling spectrum in the low-temperature limit \((16)\). The nodes are intrinsic to the superconducting gap function of the stoichiometric FeSe. The scattering-induced extrinsic origin of the V-shaped spectrum in FeSe is quite unlikely. If the scattering strength is too weak, the gap is not closed; if it is too strong, there is a finite residual density of states at the Fermi level. In this extrinsic scenario, the V-shaped spectrum without residual density of states at the Fermi level is only possible in an accidental case in which scattering strength exactly matches a specific value \((17)\).

Examination of the electronic structure in the Brillouin zone (BZ) reveals the origin of the nodes as well as the symmetry of the order parameter. In the unfolded BZ of FeSe (Fig. 1D),
the hole and electron pockets are centered at the 
\[ \Gamma = (0, 0) \] and \( M = (0, \pm \pi) \) and \((\pm \pi, 0)\) 
points, respectively (18). The five-band model
(19) suggests that the electron pockets at \((0, \pm \pi)\)
are mainly derived from the \(d_{xz}\) and \(d_{yz}\) orbitals of
Fe and those at \((\pm \pi, 0)\) from the \(d_{xz}\) and \(d_{yz}\) orbitals.
The hole pockets at \((0, 0)\) are derived from the \(d_{xz}\) and \(d_{yz}\) orbitals. In real space, the
nodeless and nodal \(s^\pm\)-wave gap correspond to the
pairing between electrons on the next-nearest-
neighbor (NNN) and nearest-neighbor (NN) Fe
atoms, respectively. For the nodeless \(s^\pm\) pairing, the
Se-mediated exchange interaction \(J_2\) between
the NNN Fe sites dominates, giving rise to the for-
mation of spin-density wave (SDW) and the full
sign reversal between the superconducting gap
functions on the hole and electron pockets. How-
ever, if the exchange interaction \(J_1\) between the
NN Fe sites is comparable with \(J_2\) then nodes
may develop on the electron pockets (the nodal
\(s^\pm\)-wave) to minimize the total energy of the
system (5).

In the extended \(s^\pm\)-wave model, the gap func-
tion is given by
\[
\Delta_{s^\pm} = \Delta_1 \cos k_x \cos k_y + \Delta_2 (\cos k_x + \cos k_y)
\]
(1)
The nodal lines of both \(\cos k_x \cos k_y\) and \((\cos k_x + \cos k_y)\)
are shown in Fig. 1D. According to the local
density approximation calculation (18), the ra-
dius of the pockets at \(M\) points is not large enough
to intercept with the nodal lines of \(\cos k_x \cos k_y\)
wheras \((\cos k_x + \cos k_y)\) naturally lead to the
nodes of superconducting gap on the electron
pockets in the two orthogonal Fe-Fe directions.
The gap function of FeSe is expected to contain
the main features of \(\cos k_x \cos k_y\), implying a
stronger exchange interaction between NN than
NNN. This scenario is also consistent with the ab-


\[ \begin{align*}
\text{Fig. 3.} & \quad \text{Impurity-induced bound states in superconducting gap. (A to C) STM}
\text{topography (10 mV, 0.1 nA, 3 by 3 nm\textsuperscript{2}), }\frac{d\Delta I}{dV}
\text{ spectrum (0.4 K; setpoint, 10 mV, 0.1 nA), and density of states map (0.4 mV, 0.1 nA,}
\text{1.5 by 1.5 nm\textsuperscript{2}) of a single Fe adatom. (D to F) STM}
\text{topography (10 mV, 0.1 nA, 3 by 3 nm\textsuperscript{2}), }\frac{d\Delta I}{dV}
\text{ spectrum (0.4 K; setpoint, 10 mV, 0.1 nA), and density of states map (1.0 mV, 0.1 nA, 3 by 3 nm\textsuperscript{2})}
\text{of a single Se vacancy. The white dots indicate the topmost Se atoms. For each impurity type, at least five impurities were measured, and the energies of the bound states were found to be reproducible within an error of 0.1 meV.}
\end{align*} \]

\[ \begin{align*}
\text{Fig. 4.} & \quad \text{Unidirectional electronic nanostructure induced by extra Se dop-
ing. (A) STM topography (10 mV, 0.1 nA, 40 by}
\text{40 nm\textsuperscript{2}) of a Se-rich sample. The unidirectional}
\text{stripes are along the } a \text{ axis. The bright features, which are elongated along the diagonal directions of } a \text{ and } b \text{ axes, are due to the extra Se atoms. (B) Autocorrelation analysis of the STM image in (A).}
\end{align*} \]

The reason why the Cooper pairing is nodal in FeSe but nodeless in Fe(Se,Te) remains a theo-
retical challenge. A possible mechanism involves
the different chalcogen-height \(h_{ch}\) measured from
the Fe plane in FeSe and Fe(Se,Te). Previous
studies have shown that in pnictide superconduc-
tors, the pnictogen height \(h_{ch}\) may develop on the electron
pockets at \((0, 0)\) (for example, LaFeAsO) to the low-

\[ \begin{align*}
\text{Fig. 5.} & \quad \text{Superconducting states (10 mV, 0.1 nA, 3 by 3 nm\textsuperscript{2})}
\text{showed two } d\Delta I/dV \text{ peaks at zero bias in the vicinity of a single vortex (Fig. 2B).}
\text{This resonance state elongates along the } a \text{ axis (presumably a direction}
\text{with nodes). Intuitively, anisotropic distribution of the core state can be understood by the}
\text{difference between coherence lengths \(\xi\) along the } a \text{ and } b \text{ directions, which mainly stems from the}
\text{twofold symmetry of the gap function. Away from the center of a vortex core, the}
\text{resonance peak splits into two symmetric branches in energy (Fig. 2, C and D). Although the peaks along}
\text{the } b \text{ axis eventually merge into the gap edges at a distance of 20 nm from the center (Fig. 2D),}
\text{the energy of the peaks along the } a \text{ axis approaches to } \pm 0.6 \text{ meV instead of } \Delta_0 = 2.2 \text{ meV (Fig. 2C).}
\end{align*} \]

The above features are rather similar to the con-
ventional \(s\)-wave superconductor NbSe\(_2\) (22),
in which the observed sixfold star-shaped local
density of states of a single vortex and the direction-
dependent spectra are attributed to the anisotropic
\(s\)-wave pairing with hexagonal symmetry (24).
Further theoretical analysis is needed to fully
understand the direction-dependent behavior of the resonance peaks in a nodal superconductor. Not all of the vortex cores orientate along the same direction. Twin boundaries occurred in the crystalline films, and the magnetic vortices were easily pinned at these boundaries. As shown in fig. S4, two sides of a twin boundary exhibited different orientations of the vortex cores. Across the boundary (fig. S4, red arrows), the elongation direction of the core states was rotated by 90°. If a sample is composed of twinned domains, the twofold pairing symmetry cannot be revealed by macroscopic probes.

The response of a superconductor to impurities provides another method for uncovering the nature of superconducting pairing symmetry (15). The twofold symmetry of the FeSe gap function is further supported by the impurity-induced resonance states inside the superconducting gap. We deposited Fe atoms (Fig. 3A) on FeSe surface at low temperature (50 K). Single Fe adatoms formed and occupied hollow sites of the surface Se lattice. On a Fe adatom, two resonance states (at −1.4 meV and −0.4 meV) were clearly observed in STS in Fig. 3B. The density of states map in Fig. 3C again shows the twofold symmetry, but the state is more visible in the direction perpendicular to the long axis of a vortex core. Similar spectra and density of states maps were also observed on Se vacancies (Fig. 3, D to F) (15). Similar spectra and density of states maps were perpendicular to the long axis of a vortex core. The density of states is shown in Fig. 4A. The unidirectional stripes deposited on the surface (Fig. 4A and fig. S5B). A

Thermal Structure and Dynamics of Saturn’s Northern Springtime Disturbance

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Thermal Structure and Dynamics of Saturn’s Northern Springtime Disturbance

Saturn’s slow seasonal evolution was disrupted in 2010–2011 by the eruption of a bright storm in its northern spring hemisphere. Thermal infrared spectroscopy showed that within a month, the resulting planetary-scale disturbance had generated intense perturbations of atmospheric temperatures, winds, and composition between 20° and 50°N over an entire hemisphere (140,000 kilometers). The tropospheric storm cell produced effects that penetrated hundreds of kilometers into Saturn’s stratosphere (to the 1-millibar region). Stratospheric subsidence at the edges of the disturbance produced “beacons” of infrared emission and longitudinal temperature contrasts of 16 kelvin. The disturbance substantially altered atmospheric circulation, transporting material vertically over great distances, modifying stratospheric zonal jets, exciting wave activity and turbulence, and generating a new cold anticyclonic oval in the center of the disturbance at 41°N.

I n contrast to Jupiter’s frequent large-scale storms and vortices (1), Saturn typically appears less active, with short-lived white spots occurring infrequently at mid-latitudes (2–5). Saturn’s temperatures, winds, and circulation patterns above the visible cloud decks evolve slowly in response to the changing levels of sunlight (6), and eruptions of planetary-scale disturbances are extremely rare (7, 8), even though convective processes and eddy mixing are thought to play a key role in transporting Saturn’s internal heat and maintaining the zonal jets (2). This slow evolution was disrupted on 5 December 2010 by a convective plume of bright cloud material near 40°N (planetographic latitude) in Saturn’s northern springtime hemisphere, which created

References and Notes


Supporting Online Material

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Materials and Methods

Figs. S1 to S6

References

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References and Notes

13. Materials and methods are available as supporting material on Science Online.

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