The pairing mechanism underlying unconventional superconductivity is often related to the quantum fluctuations of nearby orders. In most Fe-based superconductors, both magnetic and nematic orders appear simultaneously near the superconducting state. Accordingly, both spin-fluctuation-mediated and orbital-fluctuation-mediated superconducting pairing mechanisms have been proposed \[1–5\]. Although intense experimental studies have been conducted \[6–13\], the exact pairing mechanism of Fe-based superconductors is still under heated debate.

FeSe is a unique material with a novel superconducting state. Orbital order develops in the nematic state of FeSe without breaking the translational symmetry as shown by angle-resolved photoemission spectroscopy (ARPES) studies \[14,15\]. The superconductivity coexists with the nematic order without any long range magnetic order \[16\], thus disentangling the magnetic and orbital orders. Moreover, recent results suggest that FeSe is a quantum paramagnet \[4\] with coexisting Néel and stripe antiferromagnetic interactions \[17,18\]. The novel ground state in FeSe provides a fresh perspective for studying the effect of nematic order on the superconducting gap structure in the absence of the Fermi surface reconstruction induced by magnetic order, which helps to reveal the roles of spin and orbital degrees of freedom in unconventional superconductivity. A nodeless superconducting gap structure in FeSe was suggested by previous reports on specific heat \[19\], Andreev reflection spectroscopy \[20\], and thermal conductivity measurements \[21\]. In contrast, scanning tunnelling spectroscopy (STS) studies on FeSe films \[22\] and transport measurements on bulk FeSe/FeSe_{1−x}S_x crystals with improved quality \[23,24\] all demonstrate a nodal gap structure. However, due to the low \(T_c\) and small gap size of FeSe/FeSe_{1−x}S_x single crystals, the gap distribution in momentum-space is still unknown.

In this work, we studied the superconducting gap structure of high-quality FeSe_{0.93}S_{0.07} single crystals \((T_c = 10 \, \text{K})\) with high resolution ARPES \[25\]. At 6.3 K, both the nematic electronic structure and the superconducting gap are observed. The gap amplitude at the hole pocket is 2.5 meV, similar to that measured by STS \[23\]. The superconducting gap shows 2-fold anisotropy around the \(Z\) point, and is undetectable around the hole Fermi surface near the zone center and the electron pockets at the zone corners. We find that the unique gap structure observed here cannot be resonably fitted by most known theoretical gap structures and their simple combinations, which suggest that the effects of nematicity on the superconductivity are substantial.

FeSe_{0.93}S_{0.07} single crystals were grown using AlCl_3/KCl flux in a temperature gradient (from 400 °C to ~50 °C) for 45 days \[25,26\]. The ARPES measurements were conducted at the I05 beamline at the Diamond Light Source. The data were taken at the temperature of 6.3 K unless otherwise specified. The single crystals were cleaved in-situ and measured under ultra-high vacuum of 1x10^{-10} mbar. For data collection with 23 eV (37 eV) photons, the energy resolution was 3 meV (5 meV). Empirically, this allows resolving a superconducting gap of 0.6 meV (1 meV).

Figure 1(a) illustrates the Fermi surfaces of FeSe/FeSe_{1−x}S_x in the nematic state, which consist of one hole pocket at the zone center and one electron pocket at the zone corner of the 2-Fe Brillouin zone \[14,28\]. There is another electron pocket \((\delta)\) around \(A_1/A_2\) according to the calculation and quantum oscillation measurements \[14,28\], but it has not been detected by ARPES probably due to its small matrix element \[14\]. In our data, the elliptical hole pocket \(\alpha\) around the \(Z\) point is resolved in Fig. 1(b). Another elliptical hole pocket \(\alpha'\), with weaker spectral intensity, is contributed by 90°-rotated twin domains. The distribution of spectral weight is nearly iden-
FIG. 1: (color online). (a) Fermi surface topology in the 2-Fe Brillouin zone of FeSe in the nematic state according to Refs. [14]. (b) Fermi surface mapping around the Z point with linear-horizontal (LH) polarized photons. The corresponding momenta are indicated by the purple square in panel (a). (c) Orbital contents of pocket α (solid ellipse) and its counterpart from another twin domain (α′, dashed ellipses) according to ref. [15]. (d) Same as (b) but around the A point with circular-right (CR) polarized photons. (e) Photoemission intensity along Z-A1. The band splitting $E'_{nematic}$ due to nematic orbital ordering is indicated. (f) Symmetrized photoemission intensity along cut #1 as indicated in panel (c). (g) Energy distribution curves (EDCs) above and below $E_F$ at the momentum points of pocket $\alpha$. Sharp quasiparticle peaks are observed near the major axis endpoints of pocket $\alpha'$. As shown by the symmetrized EDCs in Fig. 2(c), the superconducting gap is reduced around the major axis endpoints of the elliptical Fermi surface $\alpha (\theta \approx 90^\circ$ and $270^\circ$). Around the minor axis endpoints of pocket $\alpha'$, the gap size remains constant [Fig. 2(d)]. By the empirical fitting to a superconducting spectral function [30], the sizes of superconducting gap as a function of polar angle $\theta$ are summarized in one single polar plot [Fig. 2(e)], noting that the $\alpha$ and $\alpha'$ are identical bands from twin domains. The superconducting gap on band $\alpha$ shows anisotropy with 2-fold symmetry. The gap size decreases from about 2.5 meV at the minor axis endpoints of the ellipse, to less than 0.6 meV around the major axis endpoints, which is at the experimental resolution limit.

The photoemission spectra at the Fermi crossing of band $\epsilon'$ show sharp quasiparticle peaks in the superconducting state [Fig. 2(f)]. However, no superconducting gap is detected along the electron pockets $\epsilon$ or $\epsilon'$ [Fig. 2(g)]. The absence of a superconducting gap at these momenta indicates nodes or a small gap size below the experimental resolution limit.

Figure 3(a) illustrates the photoemission cuts through bands $\alpha$ and $\alpha'$ around the $\Gamma$ point with 37 eV photons. The bands $\alpha$ and $\alpha'$ are resolved along cut #3 [Fig. 3(b)], showing sharp quasiparticle peaks at the Fermi crossings [Fig. 3(c)]. Along the elliptical Fermi surface $\alpha'$, the symmetrized EDCs show no detectable superconducting gap [Fig. 3(d)], indicating nodes or a small gap size below the experimental resolution limit. For band $\alpha$, the Fermi crossings with polar angles 264.0° and 275.0° show no observable gap either [Fig. 3(e)].
The quasiparticle peaks at ~ ±4 meV for θ = 80.6° and 95.0° are contributed by band α′, which gives false signatures of gap opening in Fig. 3(e). Actually as shown in Figs. 3(f) and 3(g), the EDCs divided by the resolution-convolved Fermi-Dirac function are flat within 2-3 meV of the Fermi crossings of band α, indicating no detectable gap opening. As shown in the Supplementary Material [29], the gap amplitude decreases from Z to Γ until it diminishes, which is intrinsically opposite to those observed in BaFe2(As1−xPx)2 and Ba1−xKxFe2As2 [30, 31], where the gap of the α band decreases from Γ to Z.

Our results confine the nodes to the vicinity of the two endpoints on the elliptical α pocket around Z, the α pocket around Γ, and the electron pockets. Considering that the STS spectra on superconducting FeSe1−xSx [23] show finite but small density of states at the Fermi energy at 0.4 K, the nodes can only occur on a small portion of the Fermi surface, while most of the momenta without a detectable gap in our data must exhibit a finite gap at much lower temperatures. Though the precise positions of nodes in these regions will have to be determined with better resolution in future studies, the momentum dependent gap structure, especially the large gap anisotropy at the α pocket showing remarkable component of cos 2θ with 2-fold symmetry [Fig. 4(a)], put constraints on current theories of superconductivity in FeSe. The observed gap structure can be used to scrutinize four types of current scenarios:

First, in the case of superconductivity with dominant s++ pairing mediated by orbital fluctuations, the gap form is nearly isotropic and nodeless [3]. The large anisotropy and nodal behavior of the gap in FeSe suggest that the superconducting pairing in FeSe is not mediated by pure orbital fluctuations.

Second, in s± pairing mediated by magnetic interactions, the sign-changing gap form may lead to gap anisotropy and nodes [32, 33]. Since both Néel and stripe spin fluctuations exist in FeSe [18], if the s± superconducting pairing were generated either by the (π,π) interaction with gap form cos k + cos k, or by the (π,0) interaction with gap form (cos k + cos k)/2 [33], the anisotropy of the superconducting gap on the elliptical α pocket would be 3% and 6% for these two gap forms, respectively. These cannot account for
the large anisotropy of at least 78% observed in our data.

If there were static stripe antiferromagnetic order with wave vector \((\pi, 0)\), the electron pockets would have been folded to the zone center and intersect with the \(\alpha\) pocket around the major axis endpoints in FeSe [Fig. 4(b)]. Theory suggests that gap nodes would emerge at the reconstructed Fermi surfaces, major axis endpoints in FeSe [Fig. 4(b)]. Theory suggests that the orbital anisotropy cannot be explained by this scenario.

Third, a composite form of superconducting pairing may arise from the quantum paramagnet ground state with Néel and stripe spin fluctuations [4, 18]. In Fig. 4(a), we fit the gap anisotropy of the \(\alpha\) pocket by [22]

\[
\Delta_{\pi x, x z} = \Delta_1 \cos k_x \cos k_y + \Delta_2 (\cos k_x + \cos k_y)/2,
\]

which gives superconducting gap sizes \(\Delta_1 = 58.2\pm 8.8\) meV and \(\Delta_2 = 62.2\pm 9.2\) meV for \(s\pm\) pairing mediated by the two kinds of spin fluctuations. Moreover, the combination of Néel spin fluctuation mediated \(d\)-wave pairing and stripe spin fluctuation mediated \(s\pm\) pairing with the gap form

\[
\Delta_{d, s \pm} = \Delta_d (\cos k_x - \cos k_y)/2 + \Delta_3 \cos k_x + \cos k_y)/2,
\]

also gives good fitting with \(\Delta_1 = 30.3\pm 2.8\) meV and \(\Delta_2 = 2.24\pm 0.09\) meV [Fig. 4(a)]. Alternatively, by combining the spin-fluctuation-mediated \(s\pm\) pairing and orbital-fluctuation-mediated \(s\pm\) pairing [5], the gap anisotropy at pocket \(\alpha\) can be fitted by

\[
\Delta_{sz, z_\pm} = \Delta_y \cos k_x + \cos k_y)/2 + \Delta_y,
\]

with \(\Delta_2 = 32.8\pm 4.8\) meV and \(\Delta_y = 28.7\pm 4.4\) meV for \(s\pm\) and \(s\pm\) pairing, respectively [Fig. 4(a)]. All three fittings contain gap amplitudes over 30 meV, which are nonphysical compared with the low \(T_c\) of FeSe. Moreover, the obtained gap forms would give a large gap at the \(\epsilon\) pocket [Figs. 4(c), 4(e)], in contrast to the undetectable superconducting gap in our data. Therefore, these simple combinations of gap forms cannot account for the large gap anisotropy on pocket \(\alpha\).

Fourth, we consider an orbital-dependent superconducting pairing symmetry. The orbital anti-phase pairing cannot explain the gap anisotropy on pocket \(\alpha\) [5, 6], because the orbital composition changes around \(\theta = \pm 45^\circ\) and \(\pm 135^\circ\) [Fig. 4(c)], rather than at the major axis endpoints where the gap minima appear. On the pocket \(\alpha\), the Fermi surface sections showing gap minima and gap maxima coincide with those with \(d_{yx}\) and \(d_{xy}\) orbital characters, respectively, indicating that the orbital ordering may lead to weaker superconducting pairing of \(d_{yx}\) orbital than that of \(d_{xy}\) orbital. Alternatively, it was shown that the orbital ordering may mix different pairing symmetries and give rise to pairs of accidental nodes [37]. The positions of the nodes depend on the splitting between \(d_{yx}\) and \(d_{xy}\) orbital, which was set to 80 meV in the theory, while it is 50 meV in FeSe\(_{0.95}\)S\(_{0.07}\) [Fig. 4(e)]. In this scenario, if a pair of nodes are located very close to a major-axis endpoint of the \(\alpha\) pocket due to a strong nematic order [Fig. 4(e)], the gap would exhibit just one minimum at each endpoint in the data due to the limited momentum resolution, which would be consistent with our findings.

In summary, we have revealed the superconducting gap structure of FeSe\(_{0.95}\)S\(_{0.07}\) under the effect of nematic order and in the absence of magnetic order for the first time. The remarkable anisotropy of the superconducting gap rules out \(s\pm\) pairing purely mediated by orbital fluctuations. The gap amplitude decreases from \(Z\) to \(\Gamma\), till it is undetectable at \(\Gamma\), which is intriguingly different from that of BaFe\(_2\)(As\(_{1-x}\)P\(_{x}\))\(_2\) with a nodal ring around \(Z\). A 2-fold anisotropy of the superconducting gap is observed at the \(\alpha\) hole pocket around \(Z\), which cannot be understood by current theories unless the effects of nematicity are considered. Our results suggest that in order to comprehensively understand this unique family of FeSe\(_{1-x}\)S\(_x\), future theories should include the effects of nematicity and quantum paramagnetism, where multiple spin fluctuation-mediated pairing channels cooperate.

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