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Single-layer FeSe films with an extremely expanded in-plane lattice constant of 3.99 ± 0.02 Å are fabricated by epitaxially growing FeSe/Nb: SrTiO$_3$/KTaO$_3$ heterostructures and studied by in situ angle-resolved photoemission spectroscopy. Two elliptical electron pockets at the Brillouin zone corner are resolved with negligible hybridization between them, indicating that the symmetry of the low-energy electronic structure remains intact as a freestanding single-layer FeSe, although it is on a substrate. The superconducting gap closes at a record high temperature of 70 K for the iron-based superconductors. Intriguingly, the superconducting gap distribution is anisotropic but nodeless around the electron pockets, with minima at the crossings of the two pockets. Our results place strong constraints on current theories.

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After five years of intensive studies on iron-based high-temperature superconductors (FeHTSs), a universal picture of the pairing symmetry has yet to be achieved. The once prevailing $s^\pm$ pairing [1], with the sign reversal between electron and hole Fermi surfaces, was seriously challenged by FeHTSs with only electron Fermi surfaces (called $e$-FeHTSs hereafter), including $A_x$Fe$_{2−x}$Se$_2$ ($A = K$, Cs, Rb, etc.) [2] and single-layer FeSe on SrTiO$_3$ (STO) [3–5]. For these systems, weak coupling theories based on spin fluctuations predict a $d$-wave pairing symmetry [6,7]. However, it is inconsistent with the isotropic superconducting gap observed by angle-resolved photoemission spectroscopy (ARPES) [2,3,8,9], together with evidence for a nodeless superconducting gap from specific heat [10], nuclear magnetic resonance [11], etc. On the other hand, the sign preserving $s$-wave pairing symmetry [12–15] could not account for the spin-resonance mode found in Rb$_2$Fe$_{2−x}$Se$_2$ by inelastic neutron scattering [16], which suggests the sign change of the superconducting order parameter on different Fermi surface sections [17].

To explain the sign-changing isotropic gap in $e$-FeHTSs, several novel pairing scenarios were proposed. For example, it is argued in the bonding-antibonding $s^\pm$ pairing scenario that with strong hybridization between electron pockets, the two reconstructed electron pockets can have different signs [18]. A further study suggested that this pairing likely coexists with the $d$ wave to form an $s + id$-wave pairing symmetry [19]. More recently, the importance of the parity of the 2-Fe unit cell has been emphasized [20], and it has been proposed that there coexist even and odd parity $s$-wave pairing states, which gives a fully gapped state with varied signs in different Fermi surface sections in the absence of hybridization [21,22]. Thus far, these scenarios could not be convincingly tested, since the detailed structure of the two electron pockets could not be resolved in all known $e$-FeHTSs.

Recent ARPES studies have found a gap in single-layer FeSe/STO, which closes at 65 K and suggests a possible record high superconducting transition temperature ($T_c$) of 65 K for FeHTSs [4,5], or at least, it is the pair-formation temperature record, if the superconducting transition there is a Berezinskii-Kosterlitz-Thouless (BKT-)type. In particular, we showed that the high $T_c$ in single-layer FeSe/STO is induced by suppressing the otherwise strong spin density wave (SDW) with electrons transferred from the oxygen-vacancy induced states in the substrate, and the SDW in undoped FeSe is enhanced with an expanded in-plane lattice constant [5]. Consistently, the density functional theory (DFT) calculations found increased superexchange interactions in films under enhanced tensile strain [23]. We suggested that higher $T_c$ might be obtained by doping films with further enlarged lattice [5].

In this Letter, we have fabricated a new kind of $e$-FeHTS, the single-layer FeSe on top of the Nb: SrTiO$_3$ epitaxial thin film grown on a KTaO$_3$ substrate, and expanded the in-plane lattice of FeSe to $3.99 \pm 0.02$ Å. Our ARPES data indicate a gap closing at 70 K. Moreover, the extremely tensile strain increases the ellipticity of the two electron...
Fermi surfaces at the Brillouin zone (BZ) corner, without any detectable hybridization. Intriguingly, the superconducting gap distribution is anisotropic with fourfold symmetry along the individual electron Fermi pocket with minima at the crossings of the two pockets. Our findings provide important information for solving the pairing symmetry puzzle in e-FeHTSs, and also elucidate a new way to manipulate the electronic structure and enhance $T_c$ for FeSe with artificial interface.

The heterostructure in Fig. 1(a) is designed to further enhance the tensile strain on FeSe while preserving a FeSe/Nb:STO interface. KTaO$_3$ (KTO) serves as the substrate, with cubic structure and a lattice constant of 3.989 Å [Fig. 1(b)], 2% larger than that of bulk STO (3.905 Å). To eliminate the photoemission charging effect of KTO, silver paste was attached on the substrate edge, and 35 unit cells (u.c.) of highly conductive 5% Nb doped STO films [24] were grown layer by layer on a KTO substrate with ozone-assisted MBE [25,26]. Afterwards, 5 u.c. of 0.5% Nb doped STO were epitaxially grown, with similar chemical composition as the Nb:STO$_3$ substrate in previous works [3–5]. The Nb:STO$_3$ films were then directly transferred to another MBE chamber, where FeSe thin films were grown and postannealed following the method in Ref. [5]. Details are described in the Supplemental Material [26]. ARPES data were taken in situ under ultrahigh vacuum of 1.5 × 10$^{-11}$ mbar, with a SPECS UVLS discharge lamp (21.2 eV He-I$_z$ light) and a Scienta R4000 electron analyzer. The energy resolution is 6 meV and angular resolution is 0.3°. Data were taken at 25 K if not specified otherwise.

To check the actual strain on FeSe film, an x-ray diffraction reciprocal lattice map was performed on the grown heterostructure around the (103) Bragg reflections. The in-plane reciprocal vector ($Q_{||}$) of the Nb:STO$_3$ film equals that of the KTO substrate [Fig. 1(c)]. Moreover, as shown in Fig. 1(d), based on the high symmetry points of the photoemission intensity maps, a clear expansion of the BZ size with increasing FeSe thickness can be identified. The in-plane lattice constants of FeSe films were calculated by inversing the BZ size and are plotted in Fig. 1(e), demonstrating a relaxation of the in-plane lattice in multi-layer FeSe, which is faster than that in FeSe/Nb:STO$_3$ [5]. Indeed, the lattice constant of single-layer FeSe is 3.99 ± 0.02 Å, which is extremely expanded. The cross-shaped Fermi surface at the BZ corner in films more than 2 ML thick is a hallmark of the SDW [Fig. 1(d)], as shown in our previous studies [5]. Hereafter, we refer to FeSe$^X$ as the extremely tensile strained 1 ML FeSe studied in this Letter, while we refer to FeSe$^M$ as the moderately expanded 1 ML FeSe on a Nb:STO$_3$ substrate.

The detailed electronic structure of FeSe$^X$ is studied. As shown by the photoemission intensity maps [Fig. 2(a)], the Fermi surface of FeSe$^X$ also consists of only electron pockets, similar to $K_{Fe_2-\gamma}Se_2$ and FeSe$^M$. However, instead of the nearly circular and highly degenerate pockets in FeSe$^M$, two elliptical Fermi surfaces perpendicular to each other are observed in Fig. 2(a) and sketched in Fig. 2(b). Based on the Fermi surface volume, the estimated carrier concentration is 0.12e$^-$ per Fe for FeSe$^X$, similar to that of FeSe$^M$. This indicates that strain modifies the Fermi surface shape without much change of the charge transfer from the substrate. DFT calculations were performed on a monolayer FeSe with an in-plane lattice of 3.989 Å, and the chemical potential was shifted to incorporate the extra electrons, resulting in the two elliptical Fermi surfaces that resemble the experiment [Fig. 2(c)].

As shown in Figs. 2(d1) and 2(d2), a parabolic band (assigned as $\omega$ below $E_F$) can be identified around the zone center, with band top at about −72 meV. This is much lower than the calculated one [Fig. 2(c)], probably due to the insufficiently treated correlation effects in our DFT calculations [27]. The $\omega$ band is clearly resolved around 0.21 eV below $E_F$ near $\Gamma$, which is often observed in iron pnictides with $d_{z^2}$ orbital character. Around the zone corner [Figs. 2(e1) and 2(f1)], the two nearly degenerate bands in FeSe$^M$ [3] become the separated $\gamma_1$ and $\gamma_2$ bands in FeSe$^X$. In the simplified 1-Fe BZ, there is only one electronlike band around $M$. However, in the realistic 2-Fe BZ, the band at $M1$ would be folded to $M2$ by the potential of the Se atoms, and vice versa. As shown in Figs. 2(e2) and 2(f2), $\gamma_1$...
FIG. 2 (color online). (a) Photoemission intensity map of FeSeX compared with that of FeSeM, which is reproduced from Ref. [5]. The intensity was integrated over a window of $|E_F - 10$ meV, $E_F + 10$ meV. The measured Fermi surface sheets are shown by the dashed curves. (b) Fourfold symmetrized sketch of the Fermi surface sheets observed in (a) for FeSeX. Cuts #1, #2, #3, and #4 are indicated in the BZ. (c) Calculated band structure and Fermi surface of single-layer FeSe with the in-plane lattice constant of 3.989 Å. An extra 0.12$e^-$ per Fe is included by shifting the chemical potential [23]. (d1) Photoemission intensity along cut #1 through $\Gamma$ as indicated in (b) and (d2) the corresponding energy distribution curves (EDCs). (e1) Photoemission intensity along cut #2, (e2) the corresponding MDCs, and (e3) MDC at $E_F$ fitted by Lorentzian peaks. (f1) Same as (e1) but along cut #3. (g1) MDC at $E_F$ fitted by Lorentzian peaks. (f3) Same as (e1)–(e3) but along cut #3. (g3) Same as (e1)–(e3) but along cut #4. (h) Temperature dependence of the symmetrized EDC at the Fermi crossing of $\gamma_1$ band along cut #2 for FeSeX. The gap is obtained following the standard fitting procedure described in Ref. [28]. The original data, the fitted results, and gap positions are shown in black dots, red curves, and red arrows, respectively. (i) Superconducting gap versus temperature for FeSeX compared with that of FeSeM, which is reproduced from Ref. [5].

($\gamma_2$) is intense along #2 (#3), while its folded band along #3 (#2) is weak in overall intensity but can still be tracked in momentum distribution curves (MDCs) (cf. Supplemental Material [26]). By fitting the MDC at $E_F$ with four Lorentzian peaks [Figs. 2(e3) and 2(f3)], the Fermi wave vector ($k_F$) is resolved, and $2k_F$ is 0.51 Å$^{-1}$ for the major axis and 0.37 Å$^{-1}$ for the minor axis of the elliptical pocket. The deduced $2k_F$ from cut #2 and cut #3 are consistent. Figure 2(g1) shows the photoemission intensity along cut #4 from another FeSeX sample (cf. Supplemental Material [26]) where $\gamma_1$ and $\gamma_2$ pockets intersect. Remarkably, the MDCs [Figs. 2(g2) and 2(g3)] show a single-Lorentzian-peak behavior for both sides, without any hybridization-induced band anticrossing. Normally, this is only expected for a freestanding single-layer FeSe, as illustrated by our DFT calculations, when there is no interlayer hopping and the $S_4$ symmetry is preserved. Upon postannealing under vacuum and Se flux [26], the superconducting gap size and sample quality are tuned. As shown in Fig. 2(h), one could still observe the signature of the gap in the 65 K data and in the corresponding fit [28].

The temperature dependence of the gap can be well fitted by the BCS gap temperature dependence function in Fig. 2(i). These suggest that this film has a possible $T_c$ of 70 K, assuming the gap is not due to Cooper pair preformation in the normal state. The $T_c$ is slightly enhanced in this film compared with FeSeM [Fig. 2(i)], probably due to the enhanced superexchange interactions with increased lattice constant here [5,23]. Nevertheless, compared with the enhancement of $T_c$ from 8 K in bulk FeSe to 65 K in FeSeM with 3.7% expansion of $a$, the 5 K $T_c$ enhancement in FeSeX is rather moderate and much lower than expected for another 2% expansion of $a$. This suggests that besides the magnetic exchange interactions, the substrate effects, such as interfacial electron phonon interactions [29], might need to be considered.

The momentum dependence of the superconducting gap is further investigated around M1. Considering that the band $\gamma_2$ is rather weak around M1 [Fig. 2(a)], and is absent outside the $\gamma_2$ pocket [Fig. 3(a)], the superconducting gap of $\gamma_1$ can be deduced without much interference from $\gamma_2$. Figures 3(b) and 3(c) show the energy distribution curves (EDCs) along the two cuts indicated in Fig. 3(a). The EDCs are symmetrized with respect to $E_F$ to remove the influence of the Fermi-Dirac cutoff. At the $k_F$, the spectra lose half of their intensity and the EDCs bend back. The vertical green and brown dashed lines indicate the coherence peak positions at two $k_F$’s (274° and 224° in the polar coordinates), respectively, and they unambiguously differ from each other. The symmetrized spectra in the
conducting gap is anisotropic in NaFe pnictides. For example, we recently found that the superconducting gap size due to a different postannealing process, an anisotropic but nodeless superconducting gap 

Similar behavior is also observed around superconducting gaps. To quantify the anisotropy, the peaks differ at different momenta, indicating an anisotropy shown in Fig. 3(d). The peak positions of the coherence convolution of these two momentum-dependent pairing components generally produces an anisotropic gap function [22]. In Figs. 4(a) and 4(b), we show that the experimental gap can be well fitted by $\Delta = \Delta_0 + \Delta_1 \cos(2\varphi)$, which could be compatible with the theory if taking $\Delta_o = \Delta_0$ at $\varphi = \pm \pi/4$, $\pm 3\pi/4$ [Fig. 4(c)], and the odd parity pairing causes the pair coupling between the two even parity ones on the two electron pockets, and lifts the nodes with a gap $\Delta_e$. The convolution of these two momentum-dependent pairing states at various $k_F$’s of the $\gamma_1$ pocket are shown in Fig. 3(d). The peak positions of the coherence peaks differ at different momenta, indicating an anisotropy in superconducting gaps. To quantify the anisotropy, the superconducting gap sizes are fitted [28], and they are plotted in a polar coordinate in Fig. 4(a). Beyond the finite error bars, a clear anisotropy of the superconducting gap can be recognized, following fourfold symmetry. The superconducting gap distribution on another sample is shown in Figs. 3(e) and 4(b). Despite the varied superconducting gap size due to a different postannealing process, an anisotropic but nodeless superconducting gap distribution along the electron Fermi surface is robust. Similar behavior is also observed around $M2$ (cf. Supplemental Material [26]).

Although the in-plane anisotropic superconducting gap on the electron Fermi surfaces has not been observed in $\varepsilon$-FeHTSs before, it has been reported in several iron pnictides. For example, we recently found that the superconducting gap is anisotropic in NaFeO$_{0.982}$Co$_{0.0175}$As due to the coexistence of SDW and superconductivity, with its minima at $\varphi = 0$ and $\pi/2$ [30]. In addition, gap minima along $\varphi = 45^\circ$ were reported for an electron pocket of LiFeAs, which is attributed to band hybridization and the mixture of the $\cos k_x + \cos k_y$ term in the gap function [31]. However, none of these could account for the over 50% variation of the gap size in the elliptical Fermi surface of FeSe$^\varepsilon$ as neither SDW nor hybridization is present.

The observed nodeless superconducting gap poses strong constraints on theoretical scenarios, particularly assuming that there is a sign change as indicated by the neutron resonance. Based on the $d$-wave pairing, if the electron pockets are elliptical with negligible hybridization, gap nodes would be induced in the folded BZ, which is not observed here. There are quite a few proposals about a possible $s$-wave state with sign change on the electron pockets [18,19,21,22,32,33]. In Refs. [18,19], this state, called a bonding-antibonding $s^\pm$, was based on a strong hybridization between the two electron pockets, which is inconsistent with the absence of hybridization in our data. In Refs. [32,33], the $s$-wave order parameter has an orbital-dependent sign structure, as sketched in Fig. 4(c). However, such a sign-changing order parameter will unavoidably induce nodes on the electron pockets. To resolve this, Refs. [21,22] suggested that there is another interband (odd parity) $s$-wave pairing in addition to the usual intraband (even parity) one. More specifically, the even parity $s$-wave pairing contributes the gap structure of $\Delta_e \sim \cos(2\varphi)$ around each electron pocket, with nodes at $\varphi = \pm \pi/4$, $\pm 3\pi/4$ [Fig. 4(c)], and the odd parity pairing causes the pair coupling between the two even parity ones on the two electron pockets, and lifts the nodes with a gap $\Delta_e$. The convolution of these two momentum-dependent pairing states can be well fitted by $\Delta = \Delta_0 + \Delta_1 \cos(2\varphi)$, which could be compatible with the theory if taking $\Delta_o = \Delta_0$ at $\varphi = \pm \pi/4$, $\pm 3\pi/4$ and $\Delta_e \approx \Delta_0 + \Delta_1$ at $\varphi = 0, \pm \pi/2, \pi$ [21,22].

To summarize, we have shown that heterostructure provides a novel path for exploring superconductivity in FeHTSs and revealed the novel electronic structure and gap

![Image](https://example.com/image.png)
distribution in extremely tensile strained single-layer FeSe. The lifted degeneracy of the electron pockets with negligible hybridization, together with the anisotropic but nodeless superconducting gap, provide important experimental foundations for solving the pairing symmetry puzzle of \( e^- \text{FeHTSs.} \)

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