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Monolayer FeSe on SrTiO₃

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Abstract

Epitaxial engineering of solid-state heterointerfaces is a leading avenue to realizing enhanced or novel electronic states of matter. As a recent example, bulk FeSe is an unconventional superconductor with a modest transition temperature (T_c) of 9 K. When a single atomic layer of FeSe is grown on SrTiO₃, however, its T_c can skyrocket by an order of magnitude to 65 K or 109 K. Since this discovery in 2012, efforts to reproduce, understand, and extend these findings continue to draw both excitement and scrutiny. In this review, we first present a critical survey of experimental measurements performed using a wide range of techniques. We then turn to the open question of microscopic mechanisms of superconductivity. We examine contrasting indications for both phononic (conventional) and magnetic/orbital (unconventional) means of electron pairing, and speculations about whether they could work cooperatively to boost T_c in a monolayer of FeSe.

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1. INTRODUCTION

Interface engineering lies at the vanguard of current research in condensed matter physics and novel materials. From a fundamental perspective, quantum-size and electron correlation effects are enhanced in reduced dimensionality, often resulting in unexpected phenomena. From a technological perspective, as the pace of electronics miniaturization fast approaches the limit of conventional semiconductors, alternative paradigms, such as atomically-thin materials and interfaces with manifestly quantum behavior, are needed to assume the mantle of next-generation electronics. With improving ability to assemble atomically-sharp interfaces “bottom up” through molecular beam epitaxy (MBE) or mechanical stacking of 2D-layered materials, many possibilities abound.

As the central example of this review, interface engineering holds promise in tuning, boosting, or generating superconducting states of matter – low-temperature quantum phases in which electrons form Cooper pairs and charge transport is lossless. Since its discovery in 1911, superconductivity has continued to fascinate and baffle condensed matter physicists, while the goal of realizing room-temperature superconductivity remains elusive. Within the past decade, various examples of interface superconductivity have been observed. When two insulating oxides, LaAlO_3 and SrTiO_3 , are put together, a superconducting electron gas is formed at the interface, albeit with a low transition temperature (T_c) of 200 mK (1). When a bilayer of insulating La_2CuO_4 and metallic $\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4$ is formed, the aggregate system displays a T_c exceeding 50 K (2). And as the latest example, when a single-unit-cell (1UC) layer of FeSe is deposited on SrTiO_3 (3), its T_c skyrockets up to 65 K (4, 5, 6, 7) or 109 K (8), an order of magnitude above its bulk T_c of 9 K. In this review, we will cover key experimental and theoretical developments related to 1UC FeSe/ SrTiO_3 up to early 2016. We focus on measurements of basic properties and questions of superconducting mechanisms.

1.1. Approaching the 2D limit with FeSe

FeSe possesses the simplest structure among the iron-based superconductors, consisting of superconducting Se-Fe-Se triple layers stacked by van der Waals forces, with no buffer

layers (9). **Figure 1a** shows the structure of one triple layer, which includes Fe atoms arranged in a square lattice and Se atoms staggered above and below the Fe-plane. Due to the staggering, the primitive UC contains two Fe atoms (and two Se atoms). However, since the low-energy bands of FeSe are dominated by Fe 3d orbitals, many theories or spectroscopies reference the 1-Fe UC for convenience.

By virtue of its structural simplicity, FeSe should be the prototypical iron-based superconductor to investigate, except it proved difficult to synthesize in high quality at first. Its superconducting polymorph occupies a narrow region in the Fe-Se alloy phase diagram (10), complicating common melt and self-flux growths. In 2011, Song *et al.* used MBE to grow pristine FeSe films on graphitized SiC (11, 12). Using scanning tunneling microscopy (STM), they resolved clean surfaces with only one atomic defect per 70,000 Se sites. Measurements of tunneling conductance (dI/dV), which is proportional to the local density of states, revealed two signatures of a superconducting state: (1) A V-shaped gap of $\Delta = 2.2$ meV, representing the binding energy of paired electrons, that disappeared above 10 K (**Figure 1b**); (2) vortices in the presence of a perpendicular magnetic field. Although MBE-grown films are not amenable to many bulk and thermodynamic probes, they have other advantages. Both the monolayer limit and interface interactions with different substrates can be readily examined.

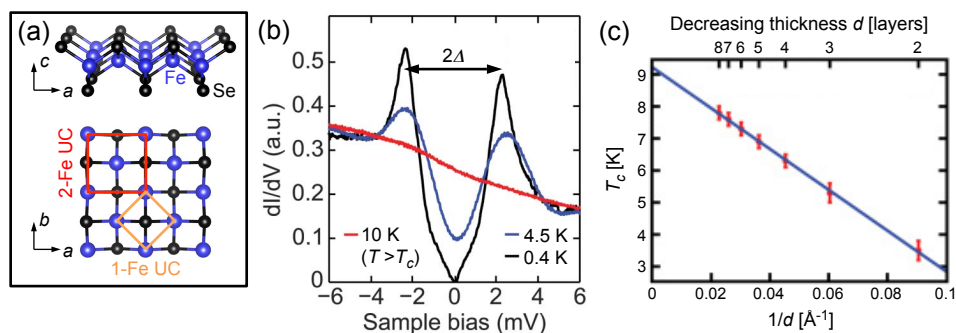


Figure 1

(a) Crystal structure of an FeSe monolayer; side and top views. The orange and red boxes enclose the 1-Fe UC and 2-Fe UC, respectively. (b) STM dI/dV spectra of multilayer FeSe/SiC, exhibiting a V-shaped superconducting gap of $\Delta = 2.2$ meV at $T = 0.4$ K, which disappears above 10 K. Adapted from Ref. (11). (c) Gap-closing temperature, T_c , of multilayer FeSe/SiC as a function of inverse FeSe thickness, $1/d$. Adapted from Ref. (12).

Song *et al.* found that the FeSe films interacted weakly with the graphitized SiC substrate (islands could be displaced by an STM tip), and were thereby close to the free-standing limit (12). Upon decreasing film thickness, T_c , as measured by the gap-closing temperature, dropped from 7.8 K (8UC-thick FeSe) to below 2.2 K (1UC-thick FeSe), the base temperature of their experiment (**Figure 1c**). The drop exhibited a $1 - d_c/d$ dependence, d being the film thickness and d_c being a critical value. This thin-film behavior was explained long ago as resulting from a general, surface boundary condition with the Ginzburg-Landau equation (13). Thus in 2011, it did not appear that the 2D limit of FeSe would be a promising regime to explore, unless new microscopic effects could be introduced.

1.2. Monolayer FeSe gets an oxide boost

It came as a great surprise a year later that monolayer FeSe could undergo an order-of-magnitude T_c enhancement when grown epitaxially on SrTiO₃(001). The lattice mismatch between bulk FeSe ($a = 3.77 \text{ \AA}$ (14)) and SrTiO₃ ($a = 3.905 \text{ \AA}$ (15)) is roughly 3%. STM measurements by Wang *et al.* revealed a topographic period-doubling (**Figure 2a**) and a large U-shaped, double-gap structure (9.0 meV and 20.1 meV) in 1UC FeSe/SrTiO₃ (**Figure 2b**), with closing temperature T_c above their experimental limit of 42.9 K. Intriguingly, this superconductivity boost did not persist or even proximitize low- T_c superconductivity in a second UC of FeSe deposited on the heterostructure. STM dI/dV measurements, whose probing depth is likely limited to the surface FeSe layer, instead showed a semiconducting spectrum on the second FeSe layer (**Figure 2c**). This observation points to an underlying interface effect, one that is atomically localized to the first UC of FeSe on SrTiO₃. Wang *et al.* speculated that electron-phonon coupling could be enhanced at the interface and boost T_c , based on their previous work with Pb/Si(111) and In/Si(111) films (16).

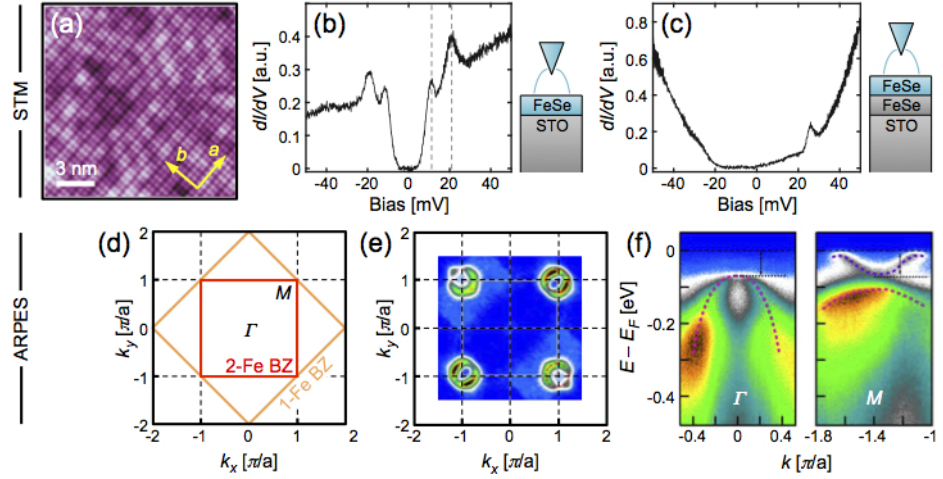


Figure 2

(a)-(c) Initial STM measurements of 1UC FeSe/SrTiO₃, adapted from Ref. (3). (a) Atomically-resolved topography. Each bright spot represents a top-layer Se atom. (b), (c) Contrasting dI/dV spectra of 1UC (superconducting) and 2UC (non-superconducting) FeSe/SrTiO₃. The dashed vertical lines in (b) mark two gap edge peaks at 9 mV and 20.1 mV. The schematics illustrate that the tunneling depth is largely restricted to the surface FeSe layer, so it is not possible to determine from (c) alone whether the presence of the second UC has altered the high- T_c superconductivity in the first UC. (d)-(f) Initial ARPES measurements of 1UC FeSe/SrTiO₃, adapted from Ref. (17). (d) Brillouin zone (BZ) conventions. (e) FS map, revealing electron pockets at the BZ corner M and the overall electron-doped nature of 1UC FeSe/SrTiO₃. (f) High-symmetry cuts across the BZ center Γ and corner M , revealing additional occupied bands.

Due to technical challenges, Wang *et al.* could measure transport only in a Si-capped, 5UC FeSe/SrTiO₃ heterostructure. They measured zero resistance at some temperature lower than 30 K, and extrapolated a resistive onset temperature around 53 K. (As shown by STM spectroscopy in **Figure 2b,c**, the superconducting signal originates from the interface

FeSe layer only.)

Angle-resolved photoemission spectroscopy (ARPES) measurements in the same year provided initial insights into the role of the interface. ARPES can map filled-state band structure in momentum space. Liu *et al.* (17) found that the Fermi surface (FS) of 1UC FeSe/SrTiO₃ comprises nearly-circular electron pockets at the Brillouin zone (BZ) corner M (**Figure 2d,e**). In contrast to bulk FeSe (18, 19, 20, 21), where additional hole FSs exist at the zone center Γ , here the corresponding hole pocket is sunken 65-80 meV below the Fermi energy (E_F) (**Figure 2f**). Assuming doubly-degenerate electron pockets, a Luttinger count yields 0.10 electrons/Fe atom. Thus, relative to its bulk, 1UC FeSe appears to be electron-doped from the substrate. To provide further support for the superconducting nature of 1UC FeSe/SrTiO₃, Liu *et al.* resolved nearly-isotropic gaps on the electron pockets at each M point, of values 13 ± 2 meV and 15 ± 2 meV for two samples. They found the gap-closing temperature to be 55 ± 5 K.

Before proceeding, we reiterate that monolayer FeSe/SrTiO₃ is not monolayer FeSe. A giant T_c enhancement is present only in the former, due to some effect introduced by the SrTiO₃.

2. EXPERIMENTAL CHALLENGES

A foremost challenge related to 1UC FeSe/SrTiO₃ has been the characterization of its growth, atomic structure, and superconducting metrics. As a point of emphasis, bulk probes are not effective for this system. Not only is the cross section of a single UC layer miniscule, but also FeSe exhibits extreme air sensitivity, hampering *ex-situ* measurements. Thus, the basic goal of determining T_c represents a nontrivial endeavor requiring customized and integrated instrumentation in ultra-high-vacuum. Example apparatuses include combined MBE-ARPES-STM systems, double chalcogen-MBE/oxide-MBE chambers, and customized *in-situ*, four-point probes.

In this section, we review various experiments related to film characterization, categorized under three questions: What is T_c ? What are the necessary growth conditions? What is the interface structure? We attempt to reflect the sentiments of the scientific community by conveying both the excitement related to the spectacular findings of *tour-de-force* experiments, and scrutiny related to the challenging nature of these feats and of film quality/homogeneity.

2.1. What is T_c ?

Table 1 presents a comparison of T_c measurements across different probes, heterostructures, and laboratories. Among various *in-situ* ARPES measurements (4, 5, 6), there is consensus in a gap-closing temperature $T_c \sim 65$ K. Some variation exists with the degree of post-growth annealing (4) (see Subsection 2.2 for details). Enhancement of T_c up to 75 K is possible if extra tensile strain is introduced through an additional KTaO₃ substrate (22).

A more robust proof of superconductivity would include (1) a zero-resistance state and (2) the Meissner effect (perfect diamagnetism). Due to air sensitivity, *ex-situ* transport and thermodynamic measurements require film capping, with amorphous Se (28), amorphous Si (3), or epitaxial FeTe (25). In all cases, film characteristics were degraded. Transport measurements of capped heterostructures have found a zero-resistance state below ~ 20 K, and a rough onset temperature possibly up to ~ 50 K. Similarly, magnetization measure-

Table 1 Comparison of T_c measurements across different probes, heterostructures, and laboratories. We distinguish measurements without (*in situ*) and with (*ex situ*) a capping layer.

Technique	Definition	Heterostructure	Value [K]	Ref.
<i>in-situ</i>				
STM	Gap-closing T	1UC FeSe/Nb:SrTiO ₃	>42.9	(3)
STM	Gap-closing T	1UC FeSe/SrTiO ₃	>50.1	(23)
ARPES	Gap-closing T	1UC FeSe/Nb:SrTiO ₃	65±5	(4)
ARPES	Gap-closing T	1UC FeSe/Nb:SrTiO ₃	60±5	(5)
ARPES	Gap-closing T	1UC FeSe/Nb:SrTiO ₃ /KTaO ₃	70	(24)
ARPES	Gap-closing T	1UC FeSe/Nb:BaTiO ₃ /KTaO ₃	75±2	(22)
ARPES	Gap-closing T	1UC FeSe/Nb:SrTiO ₃	58±7	(6)
4-probe	Zero resistance	1UC FeSe/Nb:SrTiO ₃	109	(8)
<i>ex-situ</i>				
Transport	Zero resistance	Si/5UC FeSe/SrTiO ₃	<30	(3)
	Onset T		53	
Transport	Zero resistance	Si/10UC FeTe/1UC FeSe/SrTiO ₃	23.5	(25)
	Onset T		40.2	
Magnetization	Onset T	Si/10UC FeTe/1UC FeSe/SrTiO ₃	21	(25)
Magnetization	Onset T	Si/10UC FeTe/3-4UC FeSe/SrTiO ₃	20–45	(26)
Magnetization	Onset T	10UC FeTe/1UC FeSe/Nb:SrTiO ₃	85	(27)
Magnetization	Onset T	Se/2UC FeSe/2UC Fe _{0.96} Co _{0.04} Se/ 1UC FeSe/Nb:SrTiO ₃	65	(7)

ments of capped samples have suffered from weak signals, broadened onset temperatures, or low superconducting volume fractions.

Given that many potential applications require some degree of atmosphere exposure, it remains crucial to investigate why capping, particularly epitaxial FeTe, has not worked well. FeTe possesses the same crystal structure as FeSe and its layers interact via van der Waals forces, so naively it should not create a severe disturbance of the FeSe layer below. Several hypotheses have been put forward. Ultrafast spectroscopy revealed an acoustic phonon mode in FeTe that may relax phonon-mediated pairing in FeSe (29). Alternatively, cross-sectional TEM revealed that intermixing with the capping layer can occur, whereby Te atoms substitute Se atoms in the FeSe monolayer (30). As a third possibility, Zhao *et al.* proposed that FeTe may hole-dope FeSe, reducing T_c (31).

In **Table 1**, we distinguish heterostructures that have conducting, Nb-doped SrTiO₃ from those that do not (undoped, bulk-insulating SrTiO₃). In general, transport measurements require an insulating SrTiO₃ substrate, but there are speculations that Nb-doped SrTiO₃ produces higher quality films. Sun *et al.* (27) hinted that “high quality FeSe films are easier to be achieved by MBE growth on conductive STO [SrTiO₃] substrates comparing to insulating STO substrates since the conductive STO substrate shows more flat and homogeneous surface for sample growth.”

2.1.1. In-situ, micro-four-point measurements. In late 2014, Ge *et al.* reported an astonishing new record T_c above 100 K in 1UC FeSe/SrTiO₃ (8). Here, we review their experiment in detail. The authors converted a commercial cryogenic STM into an *in-situ*, micro-four-point probe by replacing the single STM tip with a set of four Cu/Au wires, separated by 10-100 μm (**Figure 3a**). The four probes were collectively brought towards the sample at a 20° incline using the STM positioning system, until Ohmic contact with the sample was

established for each probe. **Figure 3c** shows several four-point I - V curves, which transition from a nonlinear (superconducting, zero resistance) to linear (normal state, Ohmic) line shape as the temperature was raised above T_c .

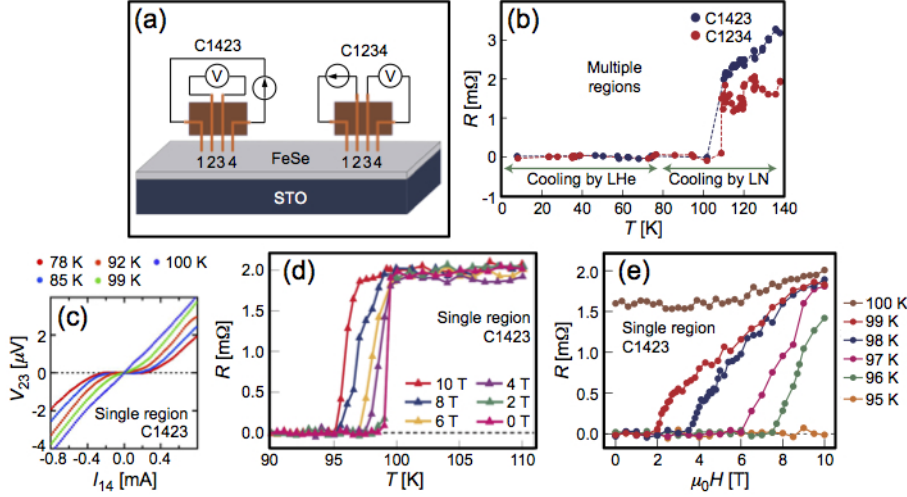


Figure 3

(a) Schematic of *in-situ*, micro-four-point measurements of 1UC FeSe/SrTiO₃. Two possible configurations for applying a current and detecting a voltage drop are shown. (b) Resistance vs. temperature plot, displaying a transition temperature $T_c = 109$ K. The data points are extracted from I - V curves acquired over different regions of the sample. (c) Four-point I - V curves, showing a metal-superconductor transition at a single location of the film. (d) Resistance vs. temperature plot, with data points extracted from I - V curves acquired at a fixed point on the sample with decreasing magnetic field, and increasing temperature at each field (32). (e) Magnetoresistance curves at various temperatures. Adapted from Ref. (8).

Due to sample inhomogeneity or film damage from probes, linear I - V curves were sometimes observed below T_c . As a result, Ge *et al.* compiled resistance vs. temperature (R - T) plots in two manners. First, they acquired four-point I - V measurements from separate locations for each temperature (**Figure 3b**). As long as one I - V curve per temperature showed signs of zero resistance, that temperature was deemed to be below T_c . With this method, Ge *et al.* determined T_c to be 109 K. Alternatively, they were also able to construct R - T plots from measurements at one location, with a sequence of decreasing magnetic fields (**Figure 3d**). With this second method, they demonstrated a similar T_c of 99 K. The magnetoresistance measurements in **Figure 3e** were also acquired at a fixed location.

We enumerate questions that have been raised about this experiment, and the authors' responses:

1. *Question:* Is the result reproducible on multiple samples?
Response: Ten different samples show similar results. Data from four samples are shown in the paper.
2. *Question:* Is it possible that the authors simply lost a current lead contact as they cooled, resulting in a sudden drop of the measured V to zero?
Response: No, the authors measured full I - V curves at each temperature and magnetic field (B), and extracted a T -dependent and B -dependent critical current (e.g.

- see **Figure 3d,e**).
3. *Question:* Is it possible that the actual T of the sample is lower than the recorded T , giving the appearance of higher T_c ?
Answer: No, careful calibration measurements show that the temperature of the sample is never more than 2 K less than the recorded temperature.
 4. *Question:* SrTiO₃ undergoes a structural transition at 105 K. Could this be responsible for the resistive transition observed at 109 K?
Response: The authors performed a control experiment on bare, Nb-doped SrTiO₃, and showed that the structural transition produced a negligible signature in the R - T plot [Figure 3b of Ref. (8)].
 5. *Question:* Don't the measured values of $T_c = 109$ K and $J_c = 1.3 \times 10^7$ A/cm² appear unexpectedly large?
Response: The authors performed a control experiment on optimally-doped Bi₂Sr₂CaCu₂O_{8+ δ} , and found $T_c = 90$ K, $J_c \sim 6000$ A/cm², in line with expectations. Their J_c value is an order of magnitude higher than that of capped 1UC FeSe/SrTiO₃ films (25), but similar to that of YBa₂Cu₃O_{7- x} films (33).
 6. *Question:* Shouldn't there be a Berezinsky-Kosterlitz-Thouless (BKT) effect that broadens the resistive transition for a 2D superconductor? Why is the resistance drop so sharp (**Figure 3b**), such that there are no data points within the transition (34)?
Response: Below T_c , conduction is 2D and restricted to the superconducting FeSe monolayer. Above T_c , conduction is shorted through the Nb-doped SrTiO₃ substrate, which is 3D and has a much lower resistivity than normal-state FeSe. Thus, the BKT transition is masked by shorting through the metallic substrate. It is also possible that there could be a proximity effect downward into SrTiO₃, such that the total system is not exactly 2D. The authors were able to collect data points within this sharp transition (**Figure 3d**).
 7. *Question:* In light of the previous question, why not use an insulating SrTiO₃ substrate?
Response: The authors cited practical challenges (8): "Further limits exist for detecting films grown on an insulating substrate, as the feedback required to control the contact between the film and the tip is extremely difficult."
 8. *Question:* Why doesn't the resistance change when the contact separation is increased tenfold (34)?
Response: When the probe separation distances are uniform, the resistance should scale with probe separation in both an infinite 2D conductor and a half-infinite 3D conductor. However, when the probe distances are unequal, their relationship to the overall resistance is more complicated [see Supplemental Information of Ref. (8)].
 9. *Question:* How could the resistive transition T_c be higher than the gap-closing temperature T_c measured *in-situ* by ARPES?
Response: ARPES averages signal over a beam spot size, but the *in-situ* four-point probe may pick up filamentary superconductivity. Indeed, the authors found non-superconducting regions below T_c , but this could be attributed to both intrinsic sample inhomogeneity or film damage from probes. Alternatively, if the out-of-plane coherence length is short, superconductivity might be stronger at the bottom of the FeSe triple layer than at the top. ARPES and STM measure the top, but transport accesses the lowest-resistivity part, which may be located at the buried interface.
 10. *Question:* Is it possible that the apparent decreasing T_c with increasing B is simply

due to gradual sample damage as B is increased?

Response: No, the authors showed the same result with increasing B and decreasing B at a fixed location.

Despite intense scrutiny, we remain unaware of fatal flaws with the experiment by Ge *et al.* Nevertheless, there are increasing calls for duplication of this result, as well as complementary *in-situ* magnetization measurements of the Meissner effect (34, 35). The latter will require specific instrumentation, but will surely fill in an important piece of the puzzle.

2.2. What are the necessary growth conditions?

An accurate atomic structure is prerequisite to reliable modeling of electronic properties, and yet the former represents another significant experimental challenge for 1UC FeSe/SrTiO₃. Although SrTiO₃ is a workhorse substrate for MBE growth, it is notorious for its numerous nearly-degenerate surface reconstructions that sensitively depend on preparation conditions. With the (001) surface alone, O deficiency can drive the following reconstructions: 2×1 , 2×2 , $c(4\times 2)$, $c(4\times 4)$, 4×4 , $c(6\times 2)$, $\sqrt{5}\times\sqrt{5}$ $R26.6^\circ$, $\sqrt{13}\times\sqrt{13}$ $R33.7^\circ$ (36). Yet some feature of this complex surface interfaced with 1UC FeSe must generate a giant enhancement in T_c . Here, we examine and clarify growth procedures for 1UC FeSe/SrTiO₃. The overall challenge is to identify which steps are necessary and which are supplemental. In the following subsection, we review various measurements of the interface atomic structure.

Figure 4 presents a flowchart with typical growth recipes for 1UC FeSe/SrTiO₃. The recipes can be delineated into a few “primary” steps, which we discuss in turn.

2.2.1. SrTiO₃ treatment (*in situ* and *ex situ*). Commercially available crystals of SrTiO₃ arrive with contaminated surfaces. In their original report, Wang *et al.* introduced a novel strategy to clean Nb-doped SrTiO₃: they annealed the substrates in their MBE chamber at 950 °C for 30 minutes, under a Se flux. (3). This treatment produced atomically-flat terraces amenable to STM imaging (albeit lacking atomic resolution). Subsequently, Bang *et al.* hypothesized that this process created Se substitutions of surface O atoms (38). These Se_O substitutions would then nucleate the growth of the first FeSe monolayer, leaving behind O vacancies that stabilize binding and donate electron carriers.

Later films grown on insulating SrTiO₃ involved more conventional and better documented preparation protocols, involving an *ex-situ* H₂O/acid etch followed by a high-temperature O₂ anneal in a tube furnace (25). The H₂O/acid etch is believed to preferentially remove SrO, which has ionic bonding character, and leave behind a TiO₂-terminated surface (39, 40, 41). It is thus unclear whether the previously-employed Se etch is a necessary procedure for growing epitaxial FeSe on SrTiO₃. Despite the explicit absence of this step here, it is possible that Se_O substitutions are still generated during the deposition of 1UC FeSe.

2.2.2. FeSe deposition. To grow stoichiometric FeSe, two conditions are typically employed (12). First, since Se is significantly more volatile than Fe, the substrate temperature is set between the source temperatures: $T_{\text{Fe}} > T_{\text{substrate}} > T_{\text{Se}}$. At least for growth on “inert,” graphitized SiC, this condition was rationalized as follows: Impinging Fe atoms with temperature $\sim T_{\text{Fe}}$ will be adsorbed with sticking coefficient close to unity, while impinging

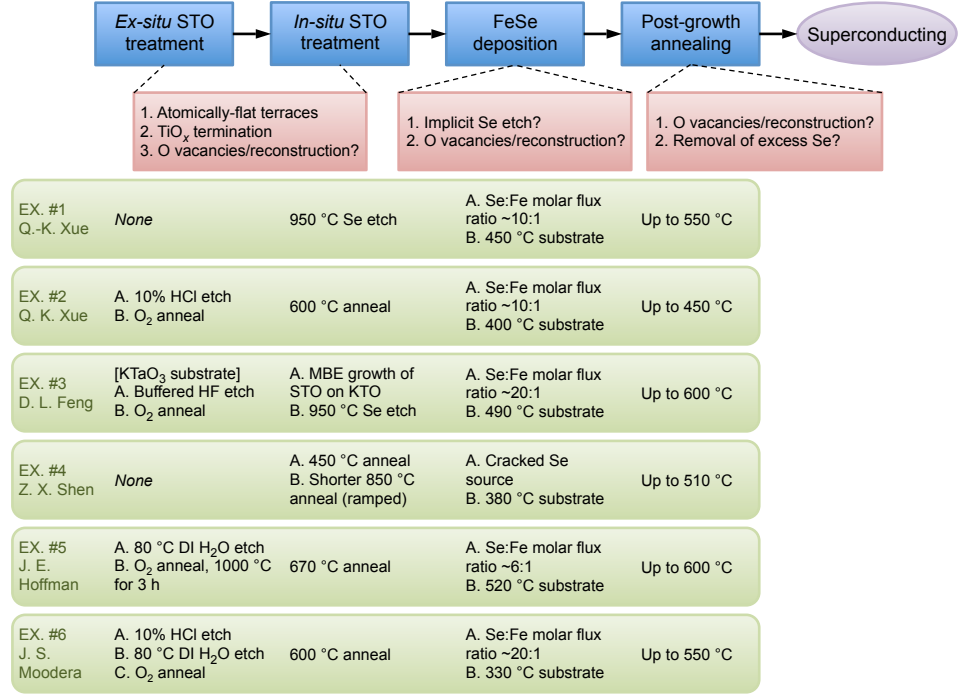


Figure 4

Flowchart of growth procedure. The blue boxes highlight primary steps that lead to superconducting 1UC FeSe/SrTiO₃, while the red boxes describe the possible microscopic picture corresponding to each step. Six example recipes are given (green boxes): #1 [Ref. (3)], #2 [Ref. (25)], #3 [Refs. (24, 5)], #4 [Ref. (6)], #5 [Ref. (37)], and #6 [Ref. (31)].

Se atoms can stick only if they bind to free Fe on the substrate. Second, to compensate for high Se losses and to mitigate excess Fe clustering, typical molar flux ratios $\Phi_{\text{Se}}/\Phi_{\text{Fe}}$ range from 5 to 20. We note that with these two conditions (moderate substrate temperature 400-500 °C, excess Se flux), there may still be a sizeable Se chemical potential at the SrTiO₃ surface driving the kinds of Se reactions proposed by Bang *et al.*, but further investigations by STM or other techniques are needed.

2.2.3. Post-growth annealing. Post growth, the FeSe monolayer on SrTiO₃ becomes superconducting only after an additional vacuum anneal. He *et al.* used ARPES measurements to show that in this process, the FeSe monolayer is progressively doped with electron carriers (4). The electron doping induces a non-rigid band transformation that eventually leaves the FS with only electron pockets and opens up a gap. The source of electron doping remains an open question. He *et al.* suggested that the electron doping could arise from O vacancies in SrTiO₃ created during annealing. Berlijn *et al.* investigated the possibility of Se vacancies, but their calculations revealed Se vacancies to be hole dopants, not electron dopants (42). More recently, cross-sectional TEM imaging by Li *et al.* suggested the presence of interstitial Se atoms trapped at the FeSe/SrTiO₃ interface during growth, which are subsequently released upon annealing. The authors proposed that the removal of these

interstitial Se atoms allows O vacancies in SrTiO₃ to effectively donate electron carriers to the FeSe monolayer (43).

Overall, some elements of “correct” SrTiO₃ pre-treatment and post-growth annealing appear necessary to produce superconducting 1UC FeSe/SrTiO₃, but many aspects of the growth procedure could be clarified through more systematic investigations.

2.3. What is the interface structure?

We begin by comparing and contrasting three tools that have been applied to probe the interface atomic structure.

1. Scanning tunneling microscopy (STM): real-space, atomic-resolution imaging of surface
Pro: An *in-situ* technique commonly integrated with a MBE chamber.
Con: An indirect technique that requires additional modeling to make inferences about the buried interface.
2. Electron diffraction: low-energy (LEED) or reflection high-energy (RHEED): momentum-space information of surface atomic structure
Pro: An *in-situ* technique that can also monitor real-time growth (RHEED).
Con: Phase information is unavailable. The interface signal may sometimes be buried after FeSe deposition (6).
3. Transmission electron microscopy (TEM): real-space, atomic-resolution imaging of exposed cross-section
Pro: Direct atomic-resolution imaging of the interface cross-section.
Con: An *ex-situ* technique that requires capping (commonly FeTe). As evinced by Ref. (30, 43), Te atoms from the cap may unintentionally intermix and substitute at least the top-layer Se atoms of 1UC FeSe. The size mismatch between Se and Te can strain the monolayer film, possibly altering its original binding structure to SrTiO₃. Additionally, the technique averages over each column of atoms in the ~10-100 nm thick section being studied.

2.3.1. 2×1 reconstruction. The first hint of any interface superstructure was the appearance of dark stripes with 2×1 periodicity in STM topographic images (**Figure 5a**) (3, 38). To explain this structure, Bang *et al.* proposed an atomic model where half the O atoms on the surface TiO₂ layer are stripped off, and the bottom-layer Se atoms of the FeSe monolayer are laterally registered with the O vacancy sites (38). The authors argued that such arrangement could increase the binding energy, electron-dope the FeSe monolayer, and cause the FeSe monolayer to relax with a 2×1 superstructure. In addition, since there are two equivalent O sites within a TiO₂ UC, the model could naturally explain the observation of half-UC phase shifts that occur either discontinuously at a trench (44) (**Figure 5a**), or continuously within a few nanometers of a domain boundary (45).

As a word of caution, the 2×1 stripes have not been universally observed. They are absent in AFM topographies (46), which might point to an electronic origin of the stripes, and are also absent in STM topographies of samples prepared in different ways (23, 37).

2.3.2. More reconstructions. Lee *et al.* grew 1UC FeSe on SrTiO₃ with neither *in-situ* Se etching nor *ex-situ* treatment (6). They simply annealed as-bought substrates up to 830 °C in their MBE chamber, until RHEED measurements detected superstructure spots,

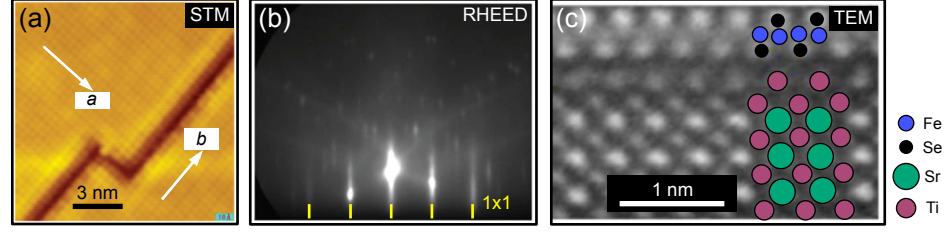


Figure 5

Measurements of interface structure. (a) STM topographic image showing orthogonal domains with dark stripes of 2×1 periodicity. Across the trench, there is a half-UC phase shift. Adapted from Ref. (38). (b) RHEED diffraction patterns of treated SrTiO_3 prior to FeSe deposition, exhibiting reconstruction spots. Adapted from Ref. (6). (c) Cross-sectional TEM image of $\text{FeTe}/1\text{UC FeSe}/\text{SrTiO}_3$, revealing that the SrTiO_3 is terminated with a double- TiO_x layer (atomic model is overlaid). Adapted from Ref. (43).

typically but not necessarily $\sqrt{5} \times \sqrt{5}$ (47) (**Figure 5b**). Subsequent deposition of FeSe and post-growth anneal resulted in superconducting samples with 1×1 diffraction spots.

Peng *et al.* found a qualitatively different behavior in 1UC FeSe/ BaTiO_3 (22). After annealing BaTiO_3 at 950°C under Se flux, their LEED images exhibited 3×3 spots. Curiously, growth of 1UC FeSe produced three distinct domains: one domain commensurate with the BaTiO_3 1×1 UC, with expanded lattice constant $3.99 \text{ \AA}$; two domains rotated by $\pm 18.5^\circ$, commensurate with a BaTiO_3 3×3 supercell, with smaller lattice constant $3.78 \text{ \AA}$. Furthermore, ARPES detected superconducting gaps in all three regions, with closing temperature T_c ranging from 70-75 K.

More recent experiments have detected superconducting gaps in 1UC FeSe on $\text{STO}(110)$ (48, 49), anatase $\text{TiO}_2(001)$ (50), and rutile TiO_2 (51), with different lattice constants and surface reconstructions (prior to growth). Taken together (**Table 2**), the variety may imply that neither lattice constant nor the lateral atomic registry between 1UC FeSe and its underlying substrate are critical factors behind the enhanced superconductivity of this heterostructure.

Table 2 Reconstructions observed in various superconducting $\text{FeSe}/(A)\text{TiO}_x$ heterostructures.

Substrate	Lattice constant [Bulk FeSe: $a_0 = 3.77 \text{ \AA}$]	Reconstruction	Ref.
$\text{SrTiO}_3(001)$	$a_0 = 3.90 \text{ \AA}$	2×1 [STM] $\sqrt{5} \times \sqrt{5}$ [RHEED] $\sqrt{13} \times \sqrt{13}$ [various]	(3, 38, 46, 44, 45) (6, 47) (52)
$\text{SrTiO}_3(110)$	$a_0 = 3.90 \text{ \AA}$ $b_0 = 5.52 \text{ \AA}$	4×1 [STM] 6×1 [STM] 3×1 [LEED]	(48) (48) (49)
$\text{BaTiO}_3(001)$	$a_0 = 3.99 \text{ \AA}$	3×3 [LEED]	(24)
Anatase $\text{TiO}_2(001)$	$a_0 = 3.78 \text{ \AA}$	4×1 [STM]	(50)

2.3.3. Double- TiO_x termination. Perhaps what matters is the vertical structure of the interface. Using cross-sectional TEM, Li *et al.* (43) imaged a double- TiO_x termination at the

interface of FeTe/1UC FeSe/SrTiO₃ (**Figure 5c**). Zou *et al.* (52) also uncovered a double-TiO_x termination using x-ray diffraction, LEED and RHEED. Although such termination had long been proposed as a candidate model for the 2×1 surface reconstruction (53), it had largely been neglected in atomic models of 1UC FeSe/SrTiO₃ until this point. Roughly speaking, the extra TiO_x termination is half as polar as a bulk TiO₂ layer, and helps SrTiO₃ mitigate a divergence of the electrostatic potential towards its bulk (54). Structural and ferroelectric properties are likely modified near this double-TiO_x termination. Zou *et al.* argued that the double-TiO_x termination facilitates epitaxial growth of FeSe through stronger binding, and also improves charge transfer from oxygen vacancies (52).

Li *et al.* also used TEM imaging to extract the structural parameters of their FeTe-capped sample. They found the 1UC FeSe to have a 9.5% reduced chalcogen height with 2.5% in-plane lattice tensile strain (compared to bulk values). Furthermore, within a ~10 nm cross section, the authors imaged a lateral half-UC shift between the bottom Se atoms and topmost Ti atoms. If this feature is characteristic of uncapped 1UC FeSe/SrTiO₃, then it suggests that the heterostructure has local bond disorder due to lattice incommensuration. We note that STM *dI/dV* measurements do reveal spectral and gap inhomogeneity even in pristine regions of FeSe with no in-plane, atomic-scale defects (55). Further systematic investigations and correlation of disorder with growth procedures is needed.

3. ELECTRONIC STRUCTURE AND PAIRING

Having surveyed a range of experiments characterizing the basic properties of 1UC FeSe/SrTiO₃, we turn to the question of electronic structure and pairing. Superconductors are typically categorized into one of two paradigms: conventional or unconventional (**Table 3**). In a conventional superconductor, electrons are bound into Cooper pairs by attractive interactions mediated by phonons. The resulting energy gap has *s*-wave angular symmetry and a uniform sign throughout the BZ. In an unconventional superconductor, many believe that quantum fluctuations from a proximate phase (e.g. magnetism) provide the glue to bind electrons. Since these fluctuations are often repulsive, the resulting gap function harbors sign changes throughout the BZ (to be further discussed in Subsection 3.4). This latter class of superconductors, which includes the cuprates and iron pnictides, has long been associated with higher *T_c* values. However, the tables have turned with the recent discovery of 203 K conventional superconductivity in pressurized H₃S (56).

Table 3 Two paradigms of superconductivity.

	Conventional	Unconventional
Maximum <i>T_c</i>	203 K pressurized H ₃ S (56)	164 K pressurized HgBa ₂ Ca ₂ Cu ₃ O _{8+δ} (57)
Pairing mechanism	Phononic	Electronic (magnetic/orbital)
Gap structure	Sign-preserving	Sign-changing

Within months of the 2008 discovery of iron pnictide superconductors, Mazin *et al.* (58) and Kuroki *et al.* (59) proposed an unconventional mechanism of pairing in these compounds. The basic premise was that first, the electron-phonon coupling constant was too small (60, 58); second, the proximity of the superconductor to an antiferromagnetic metal hinted at the role of spin fluctuations; and third, the multiband FS of these compounds, comprising electron pockets at the zone corner *M* and hole pockets at the zone center *Γ*,

could be crucial. The authors then argued that repulsive spin fluctuations, with wave vector spanning the separated electron and hole pockets, could pair electrons if the gap function reversed sign across the pockets with an overall “ s_{+-} ” symmetry (**Figure 6**). Though not free from controversy (61), this framework prevailed in the early years of iron pnictide superconductors.

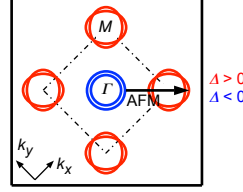


Figure 6

Schematic of unconventional s_{+-} pairing proposed for iron pnictide superconductors (58, 59). The generic FS of these compounds consists of electron pockets at the BZ corner M and hole pockets at the zone center Γ . The dashed line encloses the 2-Fe BZ. The electron and hole pockets are nested by an antiferromagnetic (AFM) wave vector, which can result in pairing if the gap function has one sign on the electron pockets (red, $\Delta > 0$) and the opposite sign on the hole pockets (blue, $\Delta < 0$).

Fast-forwarding to the present, 1UC FeSe/SrTiO₃ poses several theoretical conundrums. First, its FS includes M electron pockets (**Figure 2e**), but not the Γ hole pockets necessary for s_{+-} pairing. Second, it appears to exhibit traits of both conventionality and unconventionality. In this section, we review contrasting indications for both phononic (Subsection 3.1) and electronic (spin/orbital, Subsection 3.2) mechanisms of pairing. We then evaluate ARPES and STM measurements of gap symmetry and structure (Subsection 3.3). Finally, we discuss multiband, multiboson scenarios of pairing that enable phonons and spin/orbital fluctuations to operate constructively to enhance T_c (Subsection 3.4). These latter ideas are far from being a *fait accompli*, but exemplify a potential “best-of-both-worlds” path towards creating higher- T_c superconductors.

3.1. Phononic mechanisms

In their original report, the discoverers of 1UC FeSe/SrTiO₃ proposed some sort of interface-enhanced electron-phonon coupling as the mechanism for high- T_c superconductivity. Here, we discuss subsequent ARPES experiments by Lee, Schmitt, Moore *et al.* that lent support to this notion (6).

3.1.1. Replica bands. What Lee, Schmitt, Moore *et al.* discovered in their ARPES measurements was that each primary electronic band of 1UC FeSe/SrTiO₃ possessed a fainter replica band offset by 100 meV (6). These faint bands were near-duplicates of their primary counterparts, without being offset in momentum or smeared (**Figure 7a,b**). In addition, the replica bands persisted at least to 120 K, well above the gap-opening temperature ($T_c = 58 \pm 7$ K). Such replicas were absent in FeSe films two UC or thicker (**Figure 7c,d**), pointing to an interfacial origin of these features. Similar phenomenology was observed by Peng *et al.* in 1UC FeSe/BaTiO₃ (22).

In their interpretation of the replica bands, Lee, Schmitt, Moore *et al.* first excluded

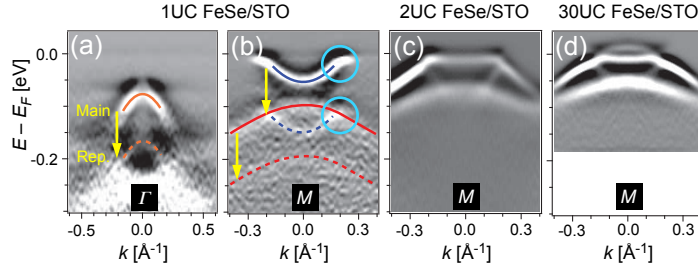


Figure 7

(a), (b) ARPES high-symmetry cuts of 1UC FeSe/SrTiO₃ showing primary electronic bands (solid line overlays) and corresponding “replica” bands (dashed line overlays) – fainter duplicates of the primary bands, shifted down by 100 meV (yellow arrows). These replica features suggest a $\mathbf{q} \sim 0$ coupling to a SrTiO₃ phonon mode. The blue circles highlight the duplication of a back-bending dispersion in the primary band as a superconducting gap opens near the Fermi energy. (c), (d) ARPES high-symmetry cuts of 2UC and 30UC FeSe/SrTiO₃, showing the absence of replica bands. Adapted from Ref. (6).

the possibility of quantum-well states arising from 2D confinement. There is no reason for such states to have identical dispersions. Furthermore, quantum-well states exhibit a well-behaved dependence on layer, in contrast to the abrupt disappearance of replica bands in 2UC FeSe/SrTiO₃. Instead, the authors attributed the replica bands to bosonic shake-off, in analogy to vibrational shake-off observed in photoemission spectroscopy of H₂ molecules. They identified the boson with an optical O phonon band calculated for bulk SrTiO₃ (62). Subsequent calculations of slab SrTiO₃ pointed to a surface phonon mode involving polar vibrations of vertical Ti-O bonds (63). These theoretical comparisons were later corroborated by ARPES measurements that also found replica bands on bare SrTiO₃ (64). However, for an electron-phonon coupling $g(\mathbf{q})$ to produce nearly-identical bands with no momentum smearing, it must be sharply peaked at $\mathbf{q} = 0$. This differs from the usual assumption of a constant $g(\mathbf{q})$ in theories of phonon-mediated superconductivity, and some modeling is needed to understand its origin.

3.1.2. Model of interface electron-phonon coupling. To explain how the electron-phonon coupling $g(\mathbf{q})$ could become sharply peaked at $\mathbf{q} = 0$, Lee, Schmitt, Moore *et al.* presented the following model (6, 65): Assume we have a 2D sheet of FeSe at $z = 0$, and a layer of dipole moments below at the SrTiO₃ surface, $z = -h_0$ (**Figure 8**). The dipole moments come from vertical stretching of surface Ti-O bonds and are represented by $\delta p_z(x, y, -h_0)$. From an electrostatics calculation, these moments induce a potential at the FeSe layer,

$$\delta\Phi(x, y, 0) = \frac{\epsilon_{\parallel} h_0}{\epsilon_{\perp}^{3/2}} \int dx' dy' \frac{\delta p_z(x', y', -h_0)}{[\epsilon_{\parallel} h_0^2 / \epsilon_{\perp} + (x - x')^2 + (y - y')^2]^{3/2}}, \quad (1)$$

where $\epsilon_{\parallel}$, $\epsilon_{\perp}$ are the in-plane and perpendicular dielectric constants in the interface region. Taking the Fourier transform yields

$$\delta\Phi(\mathbf{q}, 0) = \sqrt{\frac{\epsilon_{\parallel}}{\epsilon_{\perp}}} \frac{2\pi}{\sqrt{\epsilon_{\perp}}} \exp \left[-|\mathbf{q}| h_0 \sqrt{\epsilon_{\parallel} / \epsilon_{\perp}} \right] \delta p_z(\mathbf{q}, -h_0). \quad (2)$$

It follows that $g(\mathbf{q}) \propto \delta\Phi(\mathbf{q}, 0) \propto \exp(-|\mathbf{q}|/q_0)$, where $q_0^{-1} = h_0 \sqrt{\epsilon_{\parallel} / \epsilon_{\perp}}$. Intuitively, the $\mathbf{q} \sim 0$ coupling hinges upon (1) the FeSe monolayer being sufficiently removed from the dipole

layer (large h_0), and (2) the interface region screening lateral charge imbalance much more effectively than vertical charge imbalance (large $\epsilon_{\parallel}/\epsilon_{\perp}$).

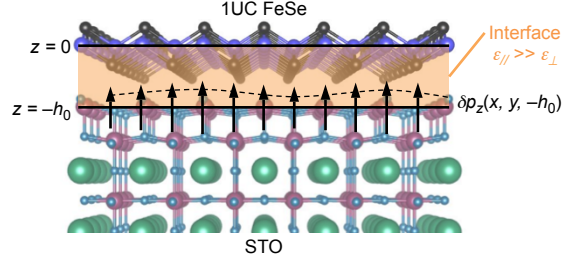


Figure 8

Electrostatic model of interface electron-phonon coupling (6, 65), consisting of a 2D layer of FeSe at $z = 0$ and a layer of vertical dipole moments $\delta p_z(x, y, -h_0)$ at the SrTiO₃ surface, $z = -h_0$. If the interface region has anisotropic dielectric constants, $\epsilon_{\parallel} \gg \epsilon_{\perp}$, then the induced potential $\delta\Phi$ is exponentially peaked at $\mathbf{q} = 0$.

Calculations by Rademaker *et al.* showed that a ratio of $q_0/k_F \sim 0.1$ was needed for replica bands to duplicate primary band features without significant momentum smearing (66). If we take k_F to be $0.20 \text{ \AA}^{-1}$ (17) and h_0 to be $4.9 \text{ \AA}$ (43), the distance between the surface TiO₂ layer and the Fe-plane, then $1/(h_0 k_F) \sim 1$ and we require $\epsilon_{\parallel}/\epsilon_{\perp} \sim 100$ in the interface region. While one should be wary of interpreting the model interface too literally, an argument suggests that it should contain contributions from both SrTiO₃ and FeSe, with the former having $\epsilon_{\parallel}^{\text{STO}} \sim \epsilon_{\perp}^{\text{STO}}$ in its 3D bulk limit, and the latter having $\epsilon_{\parallel}^{\text{FeSe}} \gg \epsilon_{\perp}^{\text{FeSe}}$ due to its 2D nature (65).

Alternative speculations regarding the replica bands include O impurity bands (67), or some form of Raman scattering involving SrTiO₃ phonon modes (68). No model details have been presented for impurity bands, and it is unclear whether sufficient cross section and viable selection rules exist for Raman scattering. Peaks and dips have been detected in STM filled- and empty-state d^2I/dV^2 spectra [Supplemental Material of Ref. (37)], but the authors have not confirmed their identity as replica bands.

3.1.3. FeSe phonon modes. In their initial STM measurements of 1UC FeSe/SrTiO₃, Wang *et al.* reported two gaps in the dI/dV point spectrum, at 9 meV and 20.1 meV respectively (3). This finding appeared to contradict early ARPES measurements of a single isotropic gap on the zone corner electron pockets, with $\Delta = 13 \pm 2$ meV in one film and 15 ± 2 meV in another film (17). Coh *et al.* offered an alternative explanation for the double-gap signature in terms of two FeSe phonon modes, which they argued could enhance T_c when a monolayer of FeSe is locked to a SrTiO₃ substrate (69). Following this report, Tang *et al.* examined d^2I/dV^2 point spectra of 1UC FeSe/SrTiO₃ and K-coated 2-4 UC FeSe/SrTiO₃ (70). They identified positive-energy dips around 11 meV and 21 meV as FeSe phonon modes.

3.2. Electronic mechanisms

A feature of the interface phonon-coupling model is that it does not depend at all on 1UC FeSe, as long as the heterostructure has an interface dielectric constant that is sufficiently

anisotropic. On one hand, such generality could be desirable for reproducing this mechanism in other systems. On the other hand, the model leaves open the possibility of preexisting pairing interactions within FeSe that are subsequently strengthened by SrTiO₃.

Two foil systems suggest that interface phonon coupling plays a secondary role to a primary pairing mechanism within FeSe that is enhanced by electron doping. The first is an FeSe-intercalate, (Li_{1-x}Fe_x)OHFeSe. Fe_{Li} antisite substitutions increase electron transfer from buffer LiOH layers to FeSe (71), resulting in 40 K superconductivity (72). Importantly, ARPES and STM measurements resolved low-energy bands that are nearly identical to those of 1UC FeSe/SrTiO₃ and gaps of similar magnitudes (73, 74, 75, 76); however, no replica bands were visible. The second system involves coating FeSe with K adatoms, which inject electrons into the surface FeSe layer (77, 78, 79, 80, 70, 81, 82). The resulting superconducting phase has a gap-closing temperature up to 48 K, close to the 65 K value of 1UC FeSe/SrTiO₃. The electronic transition induced by progressive K deposition is rather rich and provides clues of unconventional mechanisms of pairing.

3.2.1. Clues from the electron-doping phase diagram. In the paradigm of unconventional superconductors, pairing is likely mediated by quantum fluctuations from nearby electronic phases. Hence, we glean inspiration from the electron-doping phase diagram of FeSe, keeping in mind that it may not be fully representative of 1UC FeSe/SrTiO₃.

The first striking feature in the electron-doping phase diagram of FeSe is that T_c evolves through two domes (82): a low- T_c phase is first suppressed, eventually giving way to a higher- T_c phase (**Figure 9**). In general, domes are hallmarks of unconventional superconductivity, less naturally explained within a purely phononic framework (67). Song *et al.* also found that the higher- T_c phase is insensitive to the disorder of nonmagnetic K adatoms, a point whose implications we revisit in Subsection 3.3.

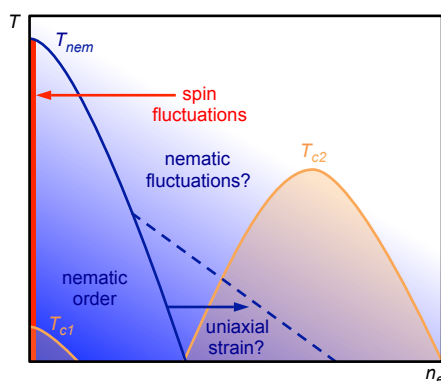


Figure 9

Schematic phase diagram of electron-doped FeSe, consisting of two domes of superconductivity, and the possibility of nematic fluctuations. Adapted from Refs. (77, 83, 79, 82). The existence of spin fluctuations in stoichiometric FeSe was reported by Refs. (84, 85, 86).

A second observation is that nematic order is suppressed preceding the high- T_c phase (77, 78), although a smaller overlapping tail of the nematic phase may persist due to remnant uniaxial strain from underlying bulk FeSe (79). Nematic order is generally defined as broken rotational symmetry that preserves the translational symmetry of the crystal. In

stoichiometric FeSe, nematic order is manifested as a small orthorhombic distortion (87) and a large splitting of the Fe $3d_{xz}$ and $3d_{yz}$ bands (5, 18, 19, 20, 21, 88), without concomitant magnetic order (89). Given the proximity and possible overlap of the nematic phase, it is tempting to ask whether nematic quantum criticality could be at play. Nematic fluctuations would provide attractive $\mathbf{q} \sim 0$ interactions that help bind electrons (90, 91, 92, 93, 94, 95), much like the aforementioned SrTiO₃ phonons.

3.2.2. Nematic fluctuations. Since 1UC FeSe bound to SrTiO₃ is nominally tetragonal, nematic order should be globally suppressed. However, if there truly exists a large underlying nematic susceptibility that produces fluctuations, then nanoscale patches of such fluctuations might be pinned around crystalline imperfections that locally break tetragonal symmetry.

Using STM as a nanoscale probe, Huang *et al.* investigated quasiparticle interference (QPI) patterns generated around anisotropic defects in 1UC FeSe/SrTiO₃ (55) (**Figure 10**). Since QPI anisotropy can arise from random disorder or experimental artifacts, the authors developed a realistic, T -matrix model to specifically detect orbital anisotropy of Fe $3d_{xz}$ and $3d_{yz}$ bands. By sampling multiple spatial regions of a film, they excluded xz/yz orbital ordering with domain size larger than $\delta r^2 = 20 \text{ nm} \times 20 \text{ nm}$, xz/yz Fermi wave vector difference larger than $\delta k = 0.014 \pi$, and energy splitting larger than $\delta E = 3.5 \text{ meV}$. The lack of detectable ordering pinned around defects disfavors scenarios of a proximate nematic quantum critical point in 1UC FeSe/SrTiO₃, in contrast to K-coated FeSe (**Figure 9**).

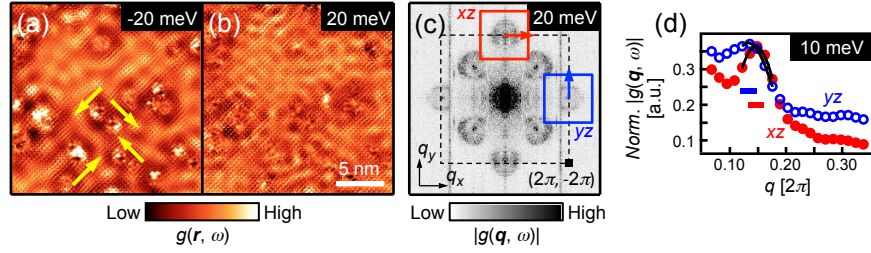


Figure 10

Bounds on nanoscale nematicity in 1UC FeSe/SrTiO₃. (a), (b) STM conductance maps $g(\mathbf{r}, \omega)$ over a region of 1UC FeSe/SrTiO₃ containing several atomic-scale defects, revealing dispersive quasiparticle interference (QPI) patterns. The prevalent defects are anisotropic and appear in four possible orientations (yellow arrows). (c) Fourier transform amplitude $|g(\mathbf{q}, \omega)|$ of (b). The red and blue boxes enclose ring intensities that arise from scattering between Fermi electron pocket states of Fe $3d_{xz}$ and $3d_{yz}$ orbital characters, respectively. (d) Normalized line cuts across the arrows in (c), used to compare xz/yz scattering wave vectors. The horizontal bars mark the peak locations determined from Gaussian fits (solid lines), with inherent resolution $\delta q = 0.028 \pi$. No signature of orbital nematicity was detected. Adapted from Ref. (55).

3.2.3. Spin fluctuations. Given the importance of spin fluctuations in many iron pnictide superconductors, their role in pairing should also be considered in 1UC FeSe/SrTiO₃ (96). Several inelastic neutron scattering measurements found that in stoichiometric FeSe, there are stripe spin fluctuations that are enhanced below the orthorhombic transition temperature (84, 85, 86) (**Figure 9**). However, magnetic order is absent, owing to some sort of frustration (97, 98, 99) or quadrupolar order (100). The nature of spin excitations in

1UC FeSe/SrTiO₃ remains an important open question, especially since both doping and the Se height may tune exchange interactions. Some experimental ingenuity is required, as *ex-situ* neutron scattering measurements are likely not feasible on 1UC films. One possible approach is the use of STM to map the magnetic-field dependence of impurity signatures, in comparison with theoretical modeling (101).

3.3. Gap symmetry and structure

We shift gears and consider pairing from the viewpoint of gap symmetry and structure. In general, such questions have proven more challenging to address in the iron-based superconductors than in the cuprates. Unlike the cuprates, with a single Cu *d* band and universal $d_{x^2-y^2}$ gap symmetry, the multiband FS of iron-based superconductors can allow a variety of gap structures across their member compounds. Even within the same compound, such as KFe₂As₂, different pairing symmetries can be tuned by pressure (102). To add to the challenge, many candidate gap structures share the same angular symmetry (103), and thus cannot be differentiated by the corner junction experiments that proved instrumental in revealing the *d*-wave gap of YBa₂Cu₃O_{7-x} (104). ARPES can resolve gap magnitudes on each specific band, but not their signs. STM QPI measurements carry phase-sensitive information, but can be challenging to interpret or normalize (105).

With these complications in mind, there is less likely to be a clear, “smoking-gun” experiment revealing the gap symmetry of 1UC FeSe/SrTiO₃. A more likely scenario is that through multiple experimental measurements, consensus will begin to converge upon a candidate gap function.

3.3.1. The candidates. Given the Fermi surface of 1UC FeSe/SrTiO₃, with only electron pockets, the primary gap symmetry candidates are “plain” *s*, “nodeless” *d*, “bonding-antibonding” *s*, and “incipient” *s*₊₋ (**Figure 11**). Nodal candidates are inconsistent with the fully-gapped structures detected by STM and ARPES (**Figure 2b**).

“Plain” *s* gap symmetry (**Figure 11a,b**) will be discussed in Subsection 3.3.3. “Nodeless” *d* (**Figure 11c,d**), which appears most similar to the gap in cuprates, is strictly defined in a 1-Fe, “pseudocrystal momentum” BZ ($\tilde{\mathbf{k}}$) that only exists when FeSe has exact glide-plane symmetry. When the gap structure is folded into the proper 2-Fe BZ, it is no longer *d*-wave with respect to regular crystal momentum ($\mathbf{k}$). In addition, nodes are technically created when opposite-sign gaps meet at the pocket crossings (106). However, based on microscopic details, the nodal quasiparticle weight could be weak and elude spectroscopic detection (107, 108).

If the folded pockets in the 2-Fe BZ hybridize and detach from each other, then nodes will certainly be avoided, leading to a “bonding-antibonding” *s* scenario (**Figure 11e**). Here, the inner and outer pockets host gaps of opposite sign.

“Incipient” *s*₊₋ posits that an opposite-sign gap develops on a sunken zone center hole pocket (**Figure 11f,g**). In the weak-coupling limit, such a gap can still be sizeable (109), the reasons for which we discuss in Subsection 3.4.

3.3.2. ARPES measurements. Early ARPES investigations of 1UC FeSe/SrTiO₃ reported isotropic gaps ($\Delta = 13\text{--}15$ meV) on nearly-circular electron pockets (17, 4, 5, 6). To resolve finer structure, Peng *et al.* grew 1UC FeSe on SrTiO₃/KTaO₃, whose expanded lattice constant increased pocket ellipticity (24). Alternatively, Zhang *et al.* changed photon po-

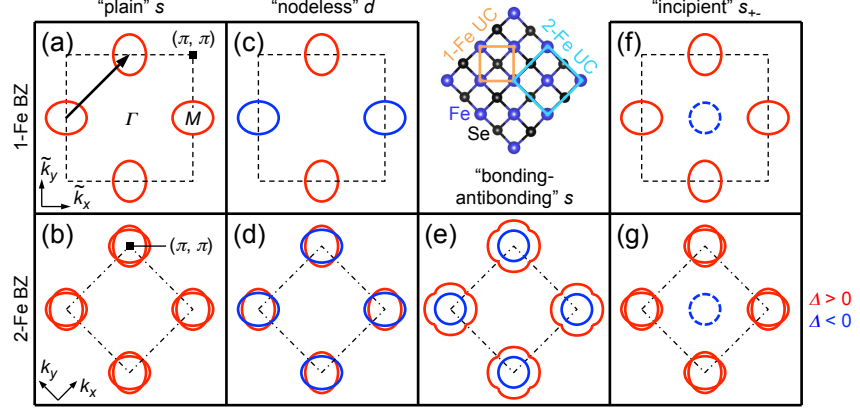


Figure 11

Gap symmetry candidates for 1UC FeSe/SrTiO₃. The top row depicts these structures in a 1-Fe Brillouin zone (BZ) ($\vec{k}$), and the bottom row depicts their folded counterparts in the 2-Fe BZ ($\vec{k}$). The arrow in (a) marks the folding wave vector, and the schematic illustrates the 1-Fe and 2-Fe unit cells (UCs). Note that the “bonding-antibonding” s structure in (e) cannot be unfolded. The dashed pockets for “incipient” s_{+-} in (f), (g), represent bands that lie completely below (or above) the Fermi energy.

larizations to selectively probe bands of different orbital characters (110). In both cases, the authors observed two pockets at each corner (main and folded), with no signs of hybridization (**Figure 12a-c**). Momentum distribution cuts across the intersection of the main and folded pockets revealed a single band, with no detectable splitting. Furthermore, gap measurements on equivalent segments of the main and folded pockets showed identical structure. Such lack of sizeable hybridization remains to be understood, given that both spin-orbit coupling or the SrTiO₃ substrate can break glide-plane symmetry. More importantly, it also disfavors scenarios of “bonding-antibonding” s -wave pairing. The authors in both reports also resolved gap anisotropy, with minima directed along the Fe-Se axes. These measurements will provide useful feedback for theoretical gap function calculations.

3.3.3. STM measurements. Fan *et al.* employed a multi-pronged STM approach, involving phase-sensitive QPI and defect imaging, to build support for “plain” s -wave superconductivity in 1UC FeSe/SrTiO₃ (45). In particular, the authors found that magnetic adatoms (Cr, Mn) induced in-gap bound states, while non-magnetic adatoms did not (Zn, Ag, K) (**Figure 12d-g**). This observation is consistent with an underlying gap structure without sign changes, but not a fool-proof guarantee of such. Anderson’s theorem states that a superconductor with a sign-preserving gap should be robust against the disorder of nonmagnetic impurities. Taken in its equivalent, contrapositive form, the observation of in-gap states induced by nonmagnetic impurities would thereby signal a sign-changing gap. However, the converse statement (“robustness against nonmagnetic impurities” $\Rightarrow$ “sign-preserving gap”) is not logically identical to the original theorem, so it lacks a “smoking-gun” nature (103, 111). In the case of 1UC FeSe/SrTiO₃, with the “nodeless” d and “bonding-antibonding” s gap structures, the opposite-sign gaps reside on normal-state Fermi pockets with different orbital characters. Given that the impurities in the Fan *et al.* experiment

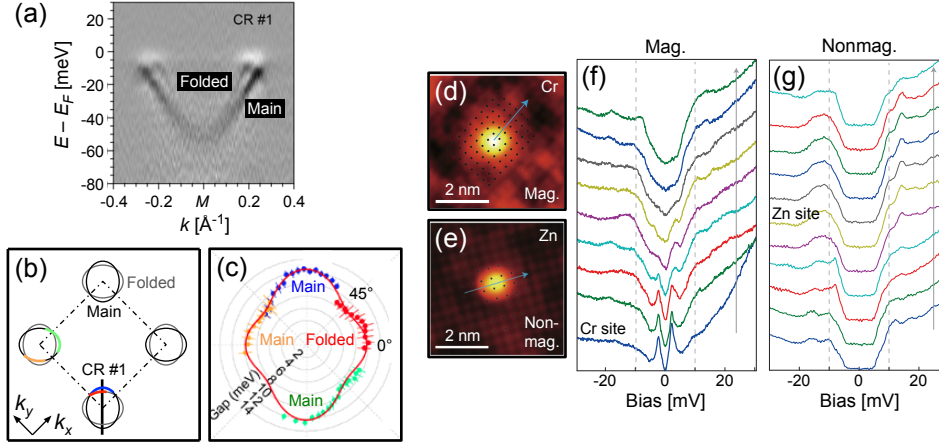


Figure 12

(a)-(c) ARPES measurements of gap anisotropy. The nearly-identical gap structures on equivalent segments of the main and folded pockets (red and orange cuts) disfavors scenarios of “bonding-antibonding” s -wave pairing. Adapted from Ref. (110). (d)-(g) STM dI/dV line cuts across magnetic (Cr) and non-magnetic (Zn) adatoms. In-gap states are produced in the former, while no changes are visible in the latter. These observations favor “plain” s -wave symmetry. Adapted from Ref. (45).

outside the Fe-plane, they may have had insufficient interorbital scattering strength to produce a pair-breaking effect. This complication is alleviated in the case of s_{+-} pairing in the iron pnictides. Since both the electron and hole pockets hosting opposite-sign gaps share the same orbital characters, interband scattering mixing the signs is easier.

Despite these caveats, the preponderance of current experiments favor same-sign gaps on all Fermi pockets of 1UC FeSe/SrTiO₃ above the other possibilities.

3.4. Multiband, multiboson scenarios of pairing

In this final subsection, we examine pairing scenarios in which multiple bosons work cooperatively across multiple bands to boost T_c . More specifically, we consider various ways in which attractive interactions (e.g., mediated by phonons) and repulsive interactions (e.g., mediated by spin fluctuations) can fit under the same roof in 1UC FeSe/SrTiO₃ (112, 6, 94, 109).

The basic picture can be explained from the $T = 0$ gap equation of a one-band superconductor in the weak-coupling limit:

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{k}'} \frac{V_{\mathbf{k},\mathbf{k}'} \Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}}. \quad (3)$$

Here, $V_{\mathbf{k},\mathbf{k}'}$ is an effective potential that scatters a Cooper pair from $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ to $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$, $E_{\mathbf{k}'} = \sqrt{\xi_{\mathbf{k}'}^2 + |\Delta_{\mathbf{k}'}|^2} > 0$ is the Bogoliubov quasiparticle energy, $\xi_{\mathbf{k}'}$ is the normal-state quasiparticle energy, and $\Delta_{\mathbf{k}}$ is the gap function. Since any such $\Delta_{\mathbf{k}}$ must obey Eq. 3 self-consistently, its form is determined by $V_{\mathbf{k},\mathbf{k}'}$ as follows:

1. Attractive interactions ($V_{\mathbf{k},\mathbf{k}'} < 0$) increase the gap amplitude if they connect segments of the FS hosting same-sign gaps ($\Delta_{\mathbf{k}} > 0$ and $\Delta_{\mathbf{k}'} > 0$, or $\Delta_{\mathbf{k}} < 0$ and

$$\Delta_{\mathbf{k}'} < 0).$$

2. Repulsive interactions ($V_{\mathbf{k},\mathbf{k}'} > 0$) increase the gap amplitude if they connect segments of the FS hosting opposite-sign gaps ($\Delta_{\mathbf{k}} > 0$ and $\Delta_{\mathbf{k}'} < 0$, or $\Delta_{\mathbf{k}} < 0$ and $\Delta_{\mathbf{k}'} > 0$).

Attractive and repulsive interactions can therefore simultaneously increase the gap amplitude, if the interactions connect *different* segments of the FS, with appropriate signs in the gap function. In the limit of forward scattering ($\mathbf{k} = \mathbf{k}'$), attractive interactions have the form $V_{\mathbf{k},\mathbf{k}'} \propto -\delta_{\mathbf{k},\mathbf{k}'}$, and from Eq. 3, increase the gap amplitude irrespective of the gap sign or functional form.

Figure 13 illustrates a pairing framework for 1UC FeSe/SrTiO₃ involving multiple bosons. We postulate the existence of a “primary” interband interaction peaked around $\tilde{\mathbf{q}} = (\pi, \pi)$, connecting the disparate electron pockets and dictating the overall gap symmetry (**Figure 13a,b**). This interaction could be a repulsive antiferromagnetic spin fluctuation, stabilizing *d*-wave pairing, or an attractive antiferroorbital fluctuation, stabilizing *s*-wave pairing. Then in addition, there may be “enhancer” intraband interactions that are necessarily attractive and peaked around $\tilde{\mathbf{q}} = (0, 0)$ (**Figure 13c,d**). These interactions universally boost pairing irrespective of the underlying gap symmetry, and may come from SrTiO₃ phonons (6), and/or nematic fluctuations.

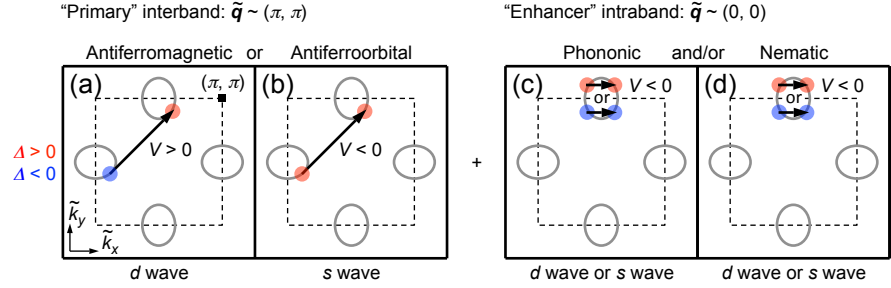


Figure 13

Multiband, multiboson scenarios of pairing in 1UC FeSe/SrTiO₃. For simplicity, we work in a 1-Fe, pseudocrystal momentum ($\tilde{\mathbf{k}}$) BZ. (a), (b) *Step 1* - the gap (Δ) symmetry is determined by a “primary” interband interaction, peaked around $\tilde{\mathbf{q}} = (\pi, \pi)$, which may be attractive ($V < 0$) or repulsive ($V > 0$). (c), (d) *Step 2* - T_c is further boosted by “enhancer” intraband interactions that are attractive. Due to their forward-scattering nature [i.e., peaked around $\tilde{\mathbf{q}} = (0, 0)$], they can raise T_c for any gap symmetry.

Although this pairing framework is appealing due to its inclusive nature, we emphasize that other than the SrTiO₃ phonon mode, there have been no experimental indications of the other interactions shown in **Figure 13**. Some suggest that DFT calculations of 1UC FeSe/SrTiO₃ with checkerboard antiferromagnetism [$\tilde{\mathbf{q}} = (\pi, \pi)$] best resemble experimental data (113, 114, 69), thus motivating the possible existence of related spin fluctuations. Others take the orbitally-ordered state of bulk FeSe as a hint of possible ferroorbital [nematic, $\tilde{\mathbf{q}} = (0, 0)$] or antiferroorbital [$\tilde{\mathbf{q}} = (\pi, \pi)$] fluctuations (93, 94).

3.4.1. Pairing involving incipient bands. Alternatively, we recall that inelastic neutron scattering measurements have detected stripe spin fluctuations [$\tilde{\mathbf{q}} = (\pi, 0)$] in bulk FeSe (84, 85, 86), similar to many iron pnictide compounds. At first glance, it is unclear whether such interactions, if they persist in 1UC FeSe/SrTiO₃, would be useful for pairing.

The usual hole pocket at the BZ center, located $\Delta\tilde{\mathbf{k}} = (\pi, 0)$ away from the Fermi electron pockets, is sunken 65–80 meV below the Fermi energy (**Figure 2**). However, ARPES measurements have demonstrated that in LiFeAs, a superconducting gap can develop on a sunken hole pocket 10 meV below the Fermi energy (115). Motivated by this observation, Chen *et al.* proposed a “bootstrap” mechanism of pairing involving incipient bands in 1UC FeSe/SrTiO₃ (109).

The basic picture proposed by Chen *et al.* is illustrated in **Figure 14a**. In the weak-coupling limit, interactions such as $\tilde{\mathbf{q}} = (\pi, 0)$ spin fluctuations between a Fermi sheet and an incipient band cannot open up a superconducting gap by themselves. However, if there are preexisting interactions, such as phonons, that stabilize a small gap within the Fermi sheet, then spin fluctuations from incipient bands can come into play and enhance pairing. In 1UC FeSe/SrTiO₃, this mechanism results in “incipient” s_{+-} symmetry, where the Fermi electron pockets host same-sign gaps and the sunken hole pocket at the zone center hosts an opposite-sign gap. From the author’s calculations, incipient bands can boost T_c by an order of magnitude, although numbers are sensitive to estimates of interaction strengths and cutoff.

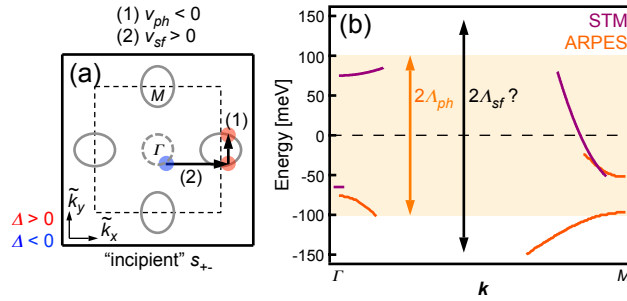


Figure 14

“Bootstrap” mechanism of pairing (109). (a) *Step 1* - An attractive intraband interaction, such as $\tilde{\mathbf{q}} \sim (0, 0)$ coupling to SrTiO₃ phonons, opens up a same-sign gap within the Fermi pockets at M . *Step 2* - A repulsive interband interaction, possibly $\tilde{\mathbf{q}} \sim (\pi, 0)$ spin fluctuations, “bootstraps” to the M pocket gaps and opens up an additional opposite-sign gap on the sunken hole pocket at Γ . Together, the gap function has overall s_{+-} symmetry. (b) Band structure diagram informed by STM (37) and ARPES (6) measurements. The energy scales of phonons and spin fluctuations (interactions v_{ph} , v_{sf} and cutoffs Λ_{ph} , Λ_{sf}), along with the low-lying bands, determine the extent to which “bootstrapping” can enhance T_c .

An appealing feature of this model in the context of 1UC FeSe/SrTiO₃ is that the Fermi electron pockets and sunken hole pocket barely or do not overlap in energy (depending on the degree of electron doping). Such a superconducting state would likely be immune to nonmagnetic impurities (116), as elastic scattering would not mix opposite-sign quasiparticles. Indeed, QPI measurements have confirmed that there is no electron-hole pocket scattering near the gap energy (37, 45). Thus, the defect experiments by Fan *et al.* could also be consistent with “incipient” s_{+-} gap symmetry.

Recently, Huang *et al.* uncovered a Γ electron pocket 80 meV above E_F (**Figure 14b**), using empty-state STM measurements (37). This pocket may be similar to one discovered in K-coated bulk FeSe_{0.55}Te_{0.45} (117) and FeSe (78), or a shallow Z -electron Fermi pocket in 3D (Tl, Rb)_yFe_{2-x}Se₂ (118). Given that this pocket lies within the SrTiO₃ phonon

energy (100 meV), it may be interesting to explore whether it has any positive contribution to T_c in 1UC FeSe/SrTiO₃ (119).

4. SUMMARY AND OUTLOOK

In this review, we have surveyed key experimental and theoretical developments related to 1UC FeSe/SrTiO₃ from its time of discovery, 2012, to early 2016. The major themes we have presented and developed can be captured in the following five statements:

1. Monolayer FeSe on SrTiO₃ exemplifies a dramatic interface effect, in which a unit-cell layer of free-standing FeSe is non-superconducting down to 2.2 K, but subsequently exhibits T_c ranging from 65 K to 109 K when coupled to SrTiO₃.
2. Experiments probing an air-sensitive, monolayer film are demanding in nature, but this challenge motivates the development and use of improved *in-situ* instrumentation, such as four-probe STM, which in turn may lead to discoveries of new systems.
3. Capping of 1UC FeSe/SrTiO₃ has not yet been optimized. Not only is it crucial for protecting films from atmospheric exposure, it simultaneously provides a second interface that could yet be engineered to enhance electronic properties.
4. Experiments have uncovered clues of both conventional and unconventional mechanisms of pairing in 1UC FeSe/SrTiO₃. While the ARPES replica bands are best explained by cross-interface coupling to SrTiO₃ phonon modes, more experiments verifying their nature and influence on T_c are desirable (120). And although accumulated experience with iron-based superconductors might suggest the importance of spin (and orbital) fluctuations, direct measurements of magnetic excitations in 1UC FeSe/SrTiO₃ are still needed.
5. Various pairing scenarios have been proposed in which multiple bosons, such as phonons and spin fluctuations, can work cooperatively in a multiband environment to enhance T_c in 1UC FeSe/SrTiO₃. Although these theories still require experimental confirmation, they represent an appealing “best-of-both-worlds” approach to finding and creating superconductors with even higher T_c . Combined with the layered 2D architecture of 1UC FeSe/SrTiO₃ in which these cooperative effects may be realized and engineered, many possibilities abound down the road.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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