Structure of monolayer FeSe on $SrTiO_3$ deciphered

Picoscale structural insight into superconductivity of monolayer FeSe/$SrTiO_3$

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Recommended with a Commentary by Atsushi Fujimori, National Tsinghua University

In 2012, an order of magnitude enhancement of T_c (up to $\sim$ 40-80 K) in monolayer FeSe grown on a $SrTiO_3$ (STO) substrate [1] invoked tremendous interest. Possible mechanisms of the T_c enhancement such as coupling to high-energy phonons of STO have been proposed. In particular, forward scattering of electrons by the STO phonons are considered to boost the T_c [2,3]. Another remarkable characteristic of the FeSe/STO is heavy electron doping. The hole Fermi surfaces at the Brillouin-zone (BZ) center disappear and the electron pockets at the BZ corner expand, invalidating the widely accepted nesting mechanism of superconductivity for Fe pnictides. (Note that bulk FeSe has small hole pockets at the BZ center and small electron pockets centered at the BZ corner, and shows a low T_c of $\sim$8 K.) The large electron pocket at the BZ corner and the relatively high T_c of 30-50 K have also been reported for other FeSe-based superconductors such as $K_xFe_{2-y}S_2$, alkali-deposited multilayer FeSe, and $Li_{1-x}Fe_xFeSeOH$ (see a commentary in Ref. [4]).

The discovery and most of subsequent studies on monolayer FeSe/STO have been made using surface-sensitive techniques such as STM and ARPES since the system is not accessible for many bulk experimental techniques. Lateral spatial periodicities such as a 2×1 superstructure [5] and stripe-type charge modulation (a smectic state with the wave length of $\sim$1.9 nm) near defects [6] have been observed by STM. In order to supplement the limited experimental information, structural optimization utilizing density-functional theory (DFT) predicted a large number of oxygen vacancies, leading to the 2×1 superstructure observed by STM, and strong bonding of the bottom Se atoms of the FeSe layer to the Ti-hollow sites of STO [5]. However, the stacking of atomic layers, their chemical compositions, and the position of each atom in each layer had remained unknown until recently.

In 2016, a transmission-electron-microscope (TEM) study revealed that the topmost layer of the STO substrate is indeed TiO_2 double layers rather than the TiO_2 layer of simple bulk termination [7]. The top layer of the double TiO_2 layers may, however, be highly oxygen-deficient, considering the DFT study mentioned above [5]. In the recommended article, Peng et al. determined the atomic positions and chemical compositions of several atomic layers at

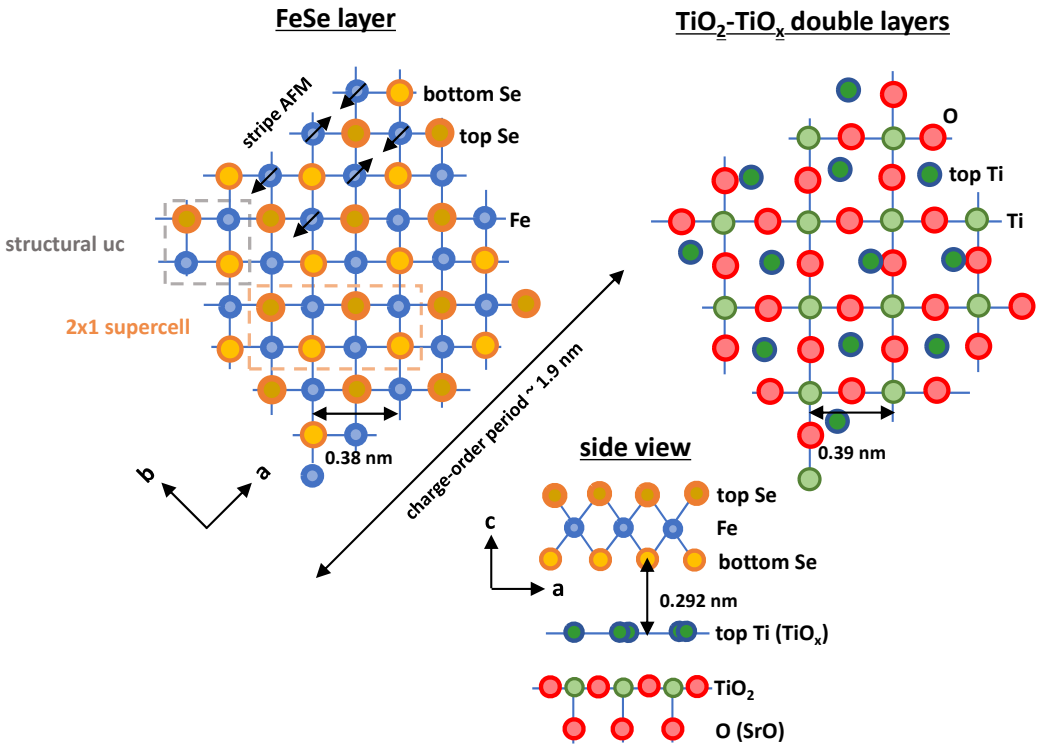

Figure 1: Structures of the monolayer FeSe/$SrTiO_3$(001) as revealed by Peng et al. in the recommended article. a and b denote the orthorhombic axes of the FeSe layer. b is slightly shorter than a in the nematic and (bulk) stripe-type antiferromagnetic (AFM) phases. In the topmost TiO_x layer of the STO substrate, the number of oxygen atoms (not shown) is small and Ti atoms are heavily displaced from the ideal positions.

the FeSe/STO interface by x-ray diffraction (XRD) on in-situ prepared samples. XRD from a surface or interface yields Bragg rods instead of Bragg spots, so-called crystal-truncation rods (CTR), whose intensity profile can be used to determine the atomic positions perpendicular to the interface/surface as well in the lateral directions and their site occupancies. (The CTR analysis has been successfully applied, e.g., to the celebrated $LaAlO_3/SrTiO_3$ interface [8].) Salient features of the CTR analysis were:

1. The topmost layer of the TiO_2 double layers is highly oxygen deficient: TiO_x. This provides the FeSe layer with the high concentration of electrons.

2. The registry of the FeSe lattice relative to the STO substrate is such that the bottom Se atoms are located above hollow sites between two Ti atoms of the TiO_x layer, as shown in Fig. 1.

3. The monolayer FeSe is thus coherently strained by the substrate. The strain is tensile and reduces the Se-Fe-Se bond angle, making it closer to the optimal value of 109.5° (for the ideal $FeSe_4$ tetrahedron).

4. The distance between the bottom Se and the TiO_x layer is as small as 0.292 nm (Fig. 1). This results in strong bonding between the FeSe layer and the substrate and hence strong coupling of electrons in FeSe to STO phonons.

Among the above findings, 2-4 likely favor the enhancement of the T_c. As for 1, the dramatic changes in the electronic structure caused by the heavy electron doping lead to the large shift of the spin-fluctuation spectrum towards higher energies as probed by resonant inelastic x-ray scattering (RIXS) [9], which will enhance the T_c within the spin-fluctuation-mediated pairing scenario.

All the above effects of 1-4 should be the strongest for monolayer FeSe and would fade away as the number of FeSe layers increases. If the doped electron concentration decreases away from the interface, the bulk-like nematic order will revive and compete with the superconductivity, thereby reducing the T_c. This was proved by a recent STM study, which showed that a stripy charge-ordered phase (a smectic phase emerging from the nematic state) with a long wavelength of $\sim$1.9 nm appeared and the superconductivity disappears for FeSe-film thicknesses above two monolayer [10]. Also, K deposition on the smectic FeSe suppressed the charge order and superconductivity of T_c $\sim$50 K recovered.

Considering the strong coupling between magnetism and crystal structures known for bulk Fe compounds and related materials [11], it is likely that the characteristic hardening of spin fluctuatiuons observed by RIXS [9], which can lead to the T_c enhancement, is caused not only by the increased electron doping as discussed above but also by the characteristic structure of the monolayer FeSe/STO.

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