Dichotomy of the Electronic Nematicity in FeSe Thin Films

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The nematic state is often considered to be critical for understanding the superconducting mechanism of iron-based superconductors, but the intrinsic effect of nematicity on the electronic structure remains controversial. Here, we fabricate multilayer FeSe films on SrTiO$_3$(001) substrates using molecular beam epitaxy and study the nematic properties by combining angle-resolved photoemission spectroscopy, $^{77}$Se nuclear magnetic resonance (NMR), and scanning tunneling microscopy experiments. The dichotomy of nematicity in FeSe thin films depending on the thickness is substantiated. When the film thickness is less than 35 monolayers (MLs) where sizeable tensile strain exists, a single-domain structure is revealed by scanning tunneling microscopy and NMR measurements. In 15-ML film, there is no band splitting of the outer hole band and a circular hole pocket is formed at $\Gamma$, the $d_{x^2}/d_{y^2}$ splitting around $\Gamma$ further shows little change upon cooling, together suggesting the absence of nematic order. When the tensile strain is negligible further away from FeSe/SrTiO$_3$ interface ($\geq$35 MLs), the double-peak splitting in $^{77}$Se NMR spectra shows the presence of twinned orthorhombic domains, indicating the occurrence of electronic nematicity in the bulk region. Our observations not only shed light on the recent controversy of nematicity, but also offer fresh insights into the relationship between nematicity and superconductivity in FeSe thin films.

Electronic nematicity, which breaks rotational symmetry but preserves translational symmetry of lattice [1], has been widely observed in cuprates [2,5] and iron-based superconductors [6,12]. In iron-based superconductors, nematicity is usually accompanied by a tetragonal-to-orthorhombic structural transition [13]. Besides, the stripe-ordered magnetism sets in at or just below the nematic transition in iron pnictides [14,15], further implying a strong coupling between lattice, spin, and orbital degrees of freedom [10,16,17], rendering the origin of nematicity controversial [18,21]. FeSe is an attractive system to study this issue, as it exhibits nematicity below $T_{\text{nem}} \sim 90$ K without magnetic order at any temperature [22,27]. FeSe also provides a versatile platform for studying the interplay of nematicity and superconductivity since its superconductivity is highly tunable [23,36].

The relationship between nematicity and superconductivity is under hot debate in FeSe. Their competition is proposed in an electron irradiation experiment, where the disorder enhances $T_c$, while lowers $T_{\text{nem}}$ of FeSe [37], as hydrostatic pressure [38] and uniaxial strain do [39,40]. Upon the increased sulfur doping in FeSe, the sizeable enhancement of $T_c$ is accompanied by an enlarged orthorhombic distortion below $T_c$, indicating a cooperative effect of superconductivity and nematicity [41]. On the other hand, thermal-expansion measurements find a lack of coupling between superconductivity and nematicity in FeSe [42].

Thus the origin of nematicity in FeSe and its effect on the electronic structure remain highly interesting. In FeSe crystals, the $d_{x^2}$ and $d_{y^2}$ bands at Brillouin zone (BZ) corner are reported to either have a $\sim 50$ meV splitting [25,26,43,45] or be degenerate [46,47], questioning whether the energy bands at BZ corner are appropriate for understanding the nematicity in FeSe. Instead of $\sim 50$ meV nematic energy scale [45], the value is subsequently suggested to be smaller ($\sim 10-15$ meV) which agrees with the $T_{\text{nem}}$ scale [46,48]. In multilayer FeSe films, although the SrTiO$_3$-induced tensile strain is present [34], the twinning effect is observed by scanning tunneling microscopy (STM) measurements [49,50]. The interpretation of electronic structure remains an open question. A sign-change momentum-dependent nematic order parameter is proposed in 35-monolayer (ML) FeSe film [51]. Bilayer FeSe film is suggested to host a nematic order arising from the Fermi surface (FS) distortion at BZ corner induced by the $d$-wave Pomeranchuk instability [52].

In order to clarify the intricate effect of nematicity on the electronic structure and gain insights into its relation to superconductivity in FeSe, we present here combined angle-resolved photoemission spectroscopy (ARPES), $^{77}$Se nuclear magnetic resonance (NMR), and STM studies on multilayer FeSe films grown by molecular beam epitaxy. The single-domain structure near FeSe/SrTiO$_3$ interface ($<35$ MLs) under noticeable tensile strain is validated by STM and NMR measurements. In 15-ML film, the formation of the single circular hole pocket and the $T$-independent $d_{x^2}/d_{y^2}$ splitting around $\Gamma$ indicate the absence of nematicity. The NMR data further reveal the existence of twinned orthorhombic domains further away from FeSe/SrTiO$_3$ interface ($\geq$35 MLs), suggesting the emergence of nematicity in the bulk region with negligible tensile strain.

Multilayer FeSe films were fabricated on either Nb:SiTiO$_3$(001) (for ARPES and STM) or SrTiO$_3$(001) (for NMR) substrates [53]. The surface and structural characterization of 15-ML FeSe film are presented in Fig. 1. Figure 1(a) shows a typical reflection high-energy electron diffraction (RHEED) pattern of SrTiO$_3$(001) substrate. After the deposition of 15-ML FeSe film, the sharp diffraction spots
of SrTiO$_3$ [Fig. 1(a)] are replaced by uniform RHEED streaks of FeSe film in Fig. 1(b). A typical STM topographic image of 15-ML film at ~4.5 K is displayed in Fig. 1(c), where the surface consists of a single crystallographic domain. This single-domain feature is observed in a number of scan areas over the sample surface, unlike the presence of multiple domains and twin boundaries previously reported in multilayer FeSe films \cite{49,50} and FeSe crystals \cite{57}. The atomic-resolution STM image in Fig. 1(d) reveals a square-like lattice of the topmost Se atoms (see also the Fourier transform in the inset). As in previous studies \cite{49,50,57,59}, the Fe (dumbbell-like) and Se (cross-like) vacancies are observed. Recently, a unidirectional charge ordering has been found to be pinned in the vicinity of Fe vacancies and proposed to be intimately associated with nematicity in FeSe thin films \cite{49}.

However, there is no signature of such stripe patterns near the dumbbell-like impurities in our film [Fig. 1(d)].

To further clarify the domain structure of our films, we conduct NMR measurements on 210-ML film. Figure 2(a) shows the frequency-swept NMR spectra of the $^{77}$Se nuclei for an in-plane magnetic field of 13.977 T \cite{53}. At $T = 40$ K, a prominent $^{77}$Se line (~113.85 MHz) is revealed for $H \parallel [100]$. The much weaker signal at ~114.06 MHz is attributed to Se-etched SrTiO$_3$ substrate [see detailed discussion in Sec. 2 of Supplemental Material (SM)]. Upon cooling, the spectra of FeSe film shift to lower frequencies with a decrease of the NMR linewidth. While it is difficult to observe a signal below 30 K and above 40 K due to the longer spin-lattice relaxation time and smaller nuclear spin polarization at lower and higher temperatures, respectively (see more discussion in Sec. 3 of SM).

By a closer look, we notice that the main line has a shoulder structure at higher frequency, thus several components are contained in the spectra of FeSe film. By a quantitative fit of the spectra [for example, 40 K in Fig. 2(b)], each $^{77}$Se line consists of three Lorentzian peaks at frequencies $f_1$, $f_2$, and $f_3$, in contrast to the double-peak splitting below $T_{\text{nem}}$ in FeSe crystals \cite{24,60,61}, which is an evidence for the twinned orthorhombic domains. We extract the frequency splitting of FeSe crystals at 40 K under different fields \cite{24,60,61} and plot the values together with $|f_1 - f_2|$ and $|f_2 - f_3|$ of FeSe film at 40 K in the inset of Fig. 2(b). One obtains that $|f_1 - f_2|$ of FeSe film (red star) follows the linear field dependence of frequency splitting of FeSe crystals, while $|f_2 - f_3|$ (black triangle) noticeably deviates from it. This implies that the $f_1 - f_2$ splitting here may arise from the twinned domains like in FeSe crystals below $T_{\text{nem}}$, and the $f_3$ could be involved in a single-domain structure. The volume fraction of single-domain region is estimated to be ~17% by counting the peak intensities.

Then, we show the temperature dependence of $^{77}$Se Knight shift of FeSe film and an FeSe$_{0.95}$S$_{0.05}$ crystal \cite{62} in Fig. 2(c). The Knight shift is determined from $K = (f_{\text{res}} - \gamma B)/\gamma B$, where $f_{\text{res}}$ is the peak frequency of NMR spectrum, $\gamma = 8.13$ MHz/T is the nuclear gyromagnetic ratio for $^{77}$Se, and $B$ is...
the external field. Although the Knight shifts in FeSe film decrease faster than that in FeSe crystal upon cooling, calling for future investigations, their Knight shift splittings between $f_1$ and $f_2$ lines at low temperatures, $\Delta K = K_2 - K_1 \approx |f_1 - f_2|$, are comparable and exhibit similar temperature evolution [inset of Fig. 2(c)] as in a previous study of FeSe crystals 24. Upon warming, $\Delta K$ first increases until $\sim 50$ K, then it decreases to zero towards $T_{\text{nem}}$. This fact further indicates that the $f_1$-$f_2$ splitting in FeSe film is most likely the consequence of an in-plane $C_4$ lattice symmetry breaking as in the nematic state of FeSe crystals. We suggest that the SrTiO$_3$-induced tensile strain plays an essential role in the dichotomy of the domain structure in FeSe thin films. The strain effect is found to be sizeable until the FeSe film thickness reaches $\sim 35$ MLs 24, which is $\sim 16.7\%$ of 210-ML film. This ratio is comparable with the volume fraction of single-domain region estimated above. Therefore, the single-domain structure near FeSe/SrTiO$_3$ interface ($\sim 35$ MLs) with isotropic tensile strain is characterized by the $f_2$ line, which is in contrast to the single NMR line in detwinned FeSe crystals 63 (see detailed discussion in Sec. 4 of SM), the twinned domains of bulk FeSe further away from the interface ($\geq 35$ MLs) under negligible tensile strain lead to the $f_1$-$f_2$ splitting.

Having established the single-domain character of thin films near FeSe/SrTiO$_3$ interface, we study the electronic structure of 15-ML film by ARPES measurements. The FS mapping at $E_F$ [Fig. 3(a)] and band dispersions along the $\Gamma$-$M$ direction [Fig. 3(b)] are analogous to earlier results of multilayer FeSe films 34$-$51. Due to the complicated band structure around $\tilde{M}$ in FeSe, the orbital assignment of multiple 3d bands and the energy scale of $d_{xz}/d_{yz}$ anisotropy at $\tilde{M}$ are controversial 25$-$26, 44$-$48, 63, 65. Here we focus on the relatively simple band structure around $\tilde{M}$. The ellipse-like hole pocket in Fig. 3(a) contrasts strongly with that in detwinned FeSe crystals below $T_{\text{nem}}$ 45, 47, 60, 66, 67 because of their completely different polarization dependence (see Fig. S2 and Sec. 5 of SM for detailed discussion). The present 15-ML film and detwinned FeSe crystals share the similarity of single-domain structure, however, there is no preferred orientation for the films under SrTiO$_3$-induced tensile strain, distinct from the uniaxial strain mechanically added to the crystals 45, 47, 60, 67.

The FS of twinned FeSe crystals below $T_{\text{nem}}$ consists of two crossed elliptical pockets at $\tilde{M}$. This FS anisotropy has been discussed as a sign of the twinned domains associated with nematicity, where the dispersions of $d_{xz}/d_{yz}$ bands are different for distinct domains 26, 46, 48, 68, 69. To understand the complete topology of the hole pocket in current case, we measure the band structure along $\Gamma$-$M$ and $\Gamma$-$X$ directions in $k_z = 0$ [Figs. 3(c)-(e)] and $\pi$ [Figs. 3(f)-(h)] planes. As evidenced by the well-defined single set of $k_F$ peaks in momentum distribution curves (MDCs) along the $\Gamma$-$M$ directions [blue curves in Figs. 3(e) and 3(h)], no band splitting is observed on the outer hole band when crossing $E_F$, in marked contrast to that in twinned FeSe crystals 26, 48, 68. The hole pocket is further found to be circular in shape by comparing the $k_{\nu}$'s along $\Gamma$-$M$ and $\Gamma$-$X$ directions. In light of this, the ellipse-like FS contours in Figs. 3(a) and S2 are actually some segments of the circular pocket. In a previous study of FeSe$_{1-x}$S$_x$ crystals 68, as the reduction of nematicity by the increasing sulfur doping 70, the degree of FS anisotropy at $\tilde{M}$ is lowered with reduced splitting of the outer hole band. It is expected that the outer hole pocket would evolve into an isotropic circular FS when the nematicity is quenched in FeSe$_{1-x}$S$_x$. Therefore, we suggest that electronic nematicity is absent in 15-ML film, consistent with the single-domain structure near FeSe/SrTiO$_3$ interface determined above. In Figs. 3(i) and 3(j), we sketch the low-temperature FS topology around $\tilde{M}$ of single-domain FeSe without nematicity. (j) Same as (i) of twinned FeSe with nematicity.

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The anisotropy between $d_{xz}$ and $d_{yz}$ has been considered as a hallmark of nematicity within the framework of ferro-orbital ordering scenario 20, 21. Regarding the temperature evolution of $d_{xz}/d_{yz}$ splitting at $\tilde{M}$ in FeSe, it has been proposed based on previous results that spin-orbit coupling (SOC) defines the splitting above $T_{\text{nem}}$ and $d_{xz}/d_{yz}$ orbital polarization contributes an extra splitting ($\sim$10-20 meV) below $T_{\text{nem}}$ 46, 51, 67, 69. As shown in Figs. 4 and S3, we record the band structure around $\tilde{Z}$ at different temperatures. Upon warming, the inner hole band exhibits little change with its band top $\sim$13 meV below $E_F$, as illustrated by the curvature intensity plots and energy distribution curves (EDCs) in Figs.
FIG. 4: (a) EDC curvature intensity plots \((\hbar \nu = 23 \text{ eV}, \text{ LH polarization}, k_{\parallel} = \pi)\) taken on 15-ML FeSe film along the \(Z-A\) direction at 30 and 150 K. (b) Respective EDCs of raw data \((-0.40 < k_{\parallel} < 0.40 \text{ Å}^{-1})\). Diamond markers indicate the dispersions of inner hole band. (c) Extracted band dispersions around \(Z\) at 30 and 150 K from EDCs and MDCs together. Solid curves are the parabolic fittings, which are also superimposed on (a). (d) Temperature dependent MDCs taken at –40 meV. Triangle and diamond markers indicate the outer and inner hole bands around \(Z\), respectively.

4(a), 4(b), and S3. The outer hole band is also less temperature sensitive as evidenced by the nearly constant momentum values from the MDCs in Fig. 4(d), which are taken at –40 meV to avoid the influence of thermal population effect. We compare the band dispersions at 30 and 150 K in Fig. 4(c). By a parabolic fit to raw data, we estimate the \(d_{xz}/d_{yz}\) splitting as \(\sim 22 \text{ meV}\) for both temperatures, which is comparable with the SOC-induced gap of \(\sim 20 \text{ meV}\) determined in FeSe \([48, 65]\). The \(T\)-independent splitting dominated by SOC effect, further implying the absence of nematicity in 15-ML film, is distinct from the \(T\)-dependent one previously reported in 35-ML film \([51]\) with the thickness almost reaching the bulk region \([34]\).

Tensile strain has been previously suggested to account for the enhancement of spin density waves in FeSe thin films with decreasing thickness \([34]\). In the present case, the absence of nematicity near FeSe/SrTiO\(_3\) interface further indicates the essential and complicated effect of tensile strain on modifying the ordered phases, where the general electronic correlation and orbital and spin fluctuations all change due to the changes in bond angle and bond length compared to FeSe crystals. Owing to the presence of \(f_{1}-f_{2}\) splitting in NMR spectra, the emergence of nematicity is expected in FeSe films thicker than 35 MLs with twinned domains and negligible tensile strain further away from FeSe/SrTiO\(_3\) interface. Consistently, in an earlier ARPES work, the splitting of the outer hole band at \(\Gamma\) is clearly observed in 50-ML FeSe film, while it is not revealed in films thinner than 35 MLs \([34]\).

Tensile strain has also been previously reported to strongly suppress superconductivity in multilayer FeSe films \([71]\). So far, superconductivity is not detected by STM or ARPES for 2-ML and thicker (\(<30\) MLs at least) FeSe films on SrTiO\(_3\) substrates \([49, 72]\). Extensive studies have been performed to uncover the relationship between nematicity and superconductivity in FeSe crystals, but the findings are multifarious as described above, leaving it still rather mysterious. Based on our current results, in multilayer FeSe films, nematicity and superconductivity disappear simultaneously when there is non-negligible tensile strain (\(<35\) MLs), and nematicity could appear after tensile strain is switched off in the bulk region (\(\geq 35\) MLs). No evidence shows that nematicity directly hinders the emergence of superconductivity in FeSe thin films. A recent STM study of 30-ML FeSe film suggests that the suppression of superconductivity stems from the competition with a stripe-type charge ordering associated with nematicity \([49]\). The existence of antiferromagnetic order has further been suggested to prohibit the recovery of superconductivity in multilayer FeSe films \([23]\). Thus whether superconductivity could recover is still a profound mystery that calls for future studies. On the other side, theoretical calculations have suggested that tensile strain could enhance the next-nearest antiferromagnetic interaction in FeSe thin films \([74]\). The impurity-pinned charge ordering related to nematicity \([49]\) has recently been proposed as an antiferromagnetic order \([73, 75]\). Moreover, a spin-density-wave phase has been observed to exist in proximity to both nematic and superconducting states in FeSe \([75]\), indicating that the magnetism could be strongly coupled to nematicity and superconductivity respectively. Therefore, the potential relevance between nematicity and superconductivity in FeSe thin films is most likely bridged through the magnetism, where the antiferromagnetic order stabilized by SrTiO\(_3\)-induced tensile strain (\(<35\) MLs) and nematicity-related impurity pinning (\(\geq 35\) MLs) could suppress superconductivity.

In summary, we have substantiated the dichotomy of nematicity in multilayer FeSe films. We find a single-domain structure near FeSe/SrTiO\(_3\) interface (\(<35\) MLs) under noticeable tensile strain, as demonstrated by STM and NMR measurements. In 15-ML film, we observe no band splitting of the outer hole band and a circular hole pocket around \(\bar{\Gamma}\), further implying the absence of nematicity in 15-ML film, distinct from the \(T\)-dependent one previously reported in 35-ML film \([51]\) with the thickness almost reaching the bulk region \([34]\).

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