Evolution of electronic structure and electron-phonon coupling in ultrathin tetragonal CoSe films

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(Received 29 June 2018; published 20 November 2018)

Two-dimensional materials have attracted considerable research attention recently due to their extraordinary physical and chemical properties. In this paper, we systematically investigate the electronic structure of ultrathin tetragonal CoSe films with different thicknesses that are isostructural to two-dimensional high-temperature superconductor FeSe using high-resolution angle-resolved photoemission spectroscopy, scanning tunneling microscopy, and ab initio calculation. Interestingly, the nonsymmorphic symmetry of the CoSe monolayer protects both exotic saddle band degeneracy and Dirac points, realizing two-dimensional Dirac fermions. Our temperature and film-thickness-dependent measurements reveal momentum-dependent electron-phonon coupling in CoSe films, which is enhanced with reduced film thickness. Moreover, the electronic states in the CoSe monolayer strongly couple to high-frequency phonons in the SrTiO3 substrate, similar to the situation in the FeSe monolayer. Our results not only present a platform to investigate the electronic properties in close vicinity of the high-temperature superconductor FeSe monolayer, but also shed light on the understanding of the coupling between two-dimensional materials and substrates beneath.

DOI: 10.1103/PhysRevMaterials.2.114005

I. INTRODUCTION

Two-dimensional (2D) materials represent a large variety of ultrathin films or heterostructures that surprisingly survive the thermodynamic fluctuation at finite temperatures. By being thinned to their physical limit, 2D materials exhibit diverse and fascinating properties, such as quantum Hall effect and Dirac fermions in graphene [1,2], valley transport in atomically thin transition-metal dichalcogenides [3–7], and quantum spin/anomalous Hall effect in topological quantum materials [8–14]. In addition, the substrate that supports the 2D materials can significantly impact their electronic behaviors, which provides a feasible opportunity to engineer the physical properties of quantum materials.

One of the intriguing examples of substrate-induced phenomena is the interfacial superconductivity [15–18]. Especially, the discovery of high-temperature superconductivity (HTSC) in monolayer FeSe interfaced with SrTiO3 (STO) has stimulated significant research interest [18,19]. It not only sets the record for superconducting transition temperature in the whole family of iron-based superconductors (Fe-SCs) and interfacial superconductors [15–18], but also exhibits extraordinary properties, such as extremely large critical currents and magnetic fields [20,21]. It is commonly accepted that the STO substrate, especially its charge transfer to a FeSe mono-

layer and high-frequency phonons, plays a significant role in the HTSC of the FeSe monolayer [19,22–27]. However, the underlying mechanism for the enhanced superconductivity is still under debate [19,22–32]. In order to further comprehend the role of the substrate in the novel properties of FeSe, it is of preferable interest to investigate the electronic behaviors in close vicinity of a FeSe-STO interface.

On the other hand, inspired by the HTSC in cuprates and Fe-SCs, it is proposed that cobalt and nickel may be other central elements to realize HTSC [33]. Although several Co- and Ni-based superconductors have been known for decades, their superconducting transition temperatures are relatively low [34–38], even if they crystallize into the same ThCr2Si2-type structure as Fe-SCs [34–37]. Since FeSe in an anti-PbO structure shows dramatically enhanced superconductivity at a FeSe-STO interface, a natural question arises whether there exists unconventional superconductivity in anti-PbO-type Co- or Ni-based materials interfaced with STO. Therefore, anti-PbO-type CoSe provides a preferable isostructural system to investigate the physics in close vicinity of FeSe. However, bulk CoSe naturally crystallizes into a hexagonal structure, and tetragonal CoSe is not stable in its bulk form [39]. Although it is possible to synthesize tetragonal CoSe by extracting K atoms from tetragonal KCo2Se2, such a topochemical deintercalating method requires the sample to be soaked in the solution, and obtained crystals are actually metastable [40,41]. Fortunately, state-of-the-art molecular-beam epitaxy system is capable to synthesize artificial films layer by layer, thus providing a feasible method to stabilize an anti-PbO-type

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CoSe film that is a structural counterpart of the FeSe-STO interface.

In this paper, we systematically investigate the electronic structure of ultrathin CoSe films grown on the STO (001) surface using high-resolution angle-resolved photoemission spectroscopy (ARPES), scanning tunneling microscopy (STM), and ab initio calculation. In contrast to the FeSe monolayer that harbors only electron pockets around the M point on the Fermi surface (FS) [22–24,26], we observe multiple Fermi pockets in the CoSe monolayer. The nonsymmorphic symmetry of CoSe protects a nodal line along the XM direction, which is gapped into Dirac points and exotic degeneracy at saddle points by spin-orbital coupling (SOC), realizing 2D Dirac fermions. In addition, we observe momentum-dependent electron-phonon coupling (EPC) in CoSe films, which is enhanced with reduced film thickness. We also observe strong coupling between CoSe electrons and STO Fuchs-Kliewer (F-K) phonon mode as manifested by continuumlike spectral weight in ARPES spectra [42]. Our experiment not only presents a feasible method to engineer the band structure and electron properties of ultrathin CoSe films, but also provides important insights into the interplay between the film and the substrate, which will further shed light on the understanding of the novel physical properties of other 2D materials.

II. METHODS

Ultrathin CoSe films were grown by coevaporating high-purity Co and Se on 0.5 wt % Nb-doped STO (001) substrates that were kept at 360 °C. The films were grown along the tetragonal c axis with a growth rate of 0.12 monolayer per minute. STM measurements were conducted in a constant current mode at 4.8 K. The samples were transferred using a high vacuum suitcase for ARPES measurements in the laboratory-based system in Tsinghua University, China. The base pressure of our ARPES system was below 7 × 10−11 mbars. Data were recorded using a Scienta DA30 analyzer and a Scienta UVU5k helium lamp. The total convolved energy and angle resolutions were 15 meV and 0.2°, respectively.

Electronic structures were calculated based on the unit cell shown in the Supplemental Material [43] using the density-functional theory method which is implemented in the Vienna ab initio simulation package [44]. The core electrons were represented by the projected augmented-wave method [45]. The exchange correlation was considered in the generalized gradient approximation [46], and SOC was included self-consistently. The cutoff energy for the plane-wave basis was 350 eV. Experimental lattice parameters were used in the construction of a slab model with one-, two-, and five-unit-cell thicknesses. The distance between the slab and its periodic images is at least 12 Å to avoid the interaction between them. Relaxations were performed without symmetry constraints until the Feynman-Hellman force on each atom was smaller than 0.01 eV Å. The reciprocal space integrations were calculated by summing in a 14 × 14 × 1 Monkhorst-Pack mesh. The convergence of the mesh has also been checked in our calculations.

III. RESULTS

A. Electronic structure of the CoSe monolayer

Figure 1(a) schematically shows the crystal structure of a bilayer CoSe film with two Se-Co-Se sandwich layers parallel stacking on the STO (001) surface. The STM topographic map in Fig. 1(b) suggests the high quality of our monolayer CoSe film. With atomic resolution, the tetragonal structure of the monolayer and bilayer CoSe films is evidenced in Figs. 1(c) and 1(d). We observe 2 × 1 stripes in monolayer CoSe, which are also observed in the FeSe monolayer and are argued to play a role in its HTSC [18,47]. The in-plane lattice constant of the CoSe film is about 3.74 Å, about 3% smaller than KCo2Se2 [48,49] as obtained from the self-correlation analysis of the moiré pattern induced by the lattice mismatch between the CoSe and the SrTiO3 (001) surfaces. The height of the CoSe monolayer is about 5.6 Å as obtained from the height profile across the step between the monolayer and the substrate.
FIG. 2. Band structure of monolayer CoSe along high-symmetric directions. (a) Three-dimensional illustration of the band structure of monolayer CoSe film. (b) FS map obtained by integrating ARPES intensity over an energy window of 15 meV around $E_F$. Data were symmetrized along the $\Gamma X$ and $\Gamma Y$ directions. (c) Constant energy contour at 250 meV below the Fermi energy. (d) Calculated FS of the monolayer CoSe film. (e)–(g) Band dispersions along (e) $\Gamma X$, (f) $M M'$, and (g) $M X M$ directions. The dashed curves in panel (f) are the calculated band structure after renormalization. (h) and (i) Calculated band dispersions along high-symmetric directions in the paramagnetic state without (h) and with (i) SOC. The orange curve in panel (h) indicates the nodal line along $XM$ near $E_F$. (j) Zoom-in plot of the calculation with SOC near the $A$, $B$, $C$, and $D$ regions in panel (i). (k) Three-dimensional illustration of the exotic band degeneracy at a saddle point near $X$. (l) Illustration of the distribution of band degeneracies in the Brillouin zone. Data were collected using 21.2-eV photons from a He-discharge lamp at 5 K.

In Fig. 2, we investigate the electronic structure of the CoSe monolayer using high-resolution ARPES. Figure 2(a) shows the evolution of the band structure along the $k_x-k_y$ plane with binding energy. Different from the FeSe monolayer [22–26], the FS of the CoSe monolayer consists of multiple Fermi pockets together with a $X$-shaped spectral weight distribution near $M$ [Fig. 2(b)]. The evolution of the constant energy contour with binding energy [Figs. 2(b) and 2(c)] suggests the electron and hole nature of the pockets near the $M$ and $X$ points. Our ab initio calculation well captures the structure of experimental FS as shown in Fig. 2(d), suggesting a weak charge transfer from a STO substrate to a CoSe film. Evaluation with Bader analysis [50] gives a charge transfer of only 0.026 electrons from STO to each Co atom, which is much less than the value of 0.12 electrons at the FeSe-STO interface [22,23].

The band dispersions along the high-symmetry directions are shown in Figs. 2(e)–2(g), which agree with our ab initio calculation in the paramagnetic state of the CoSe monolayer in Fig. 2(b). We observe two electron bands ($\alpha$ and $\beta$) around $\Gamma$. The $\beta$ band crosses the Fermi level in the $\Gamma M$ direction but not in the $\Gamma X$ direction, forming the hole pocket around $X$ [marked as $h$ in Figs. 2(b) and 2(d)]. Due to band hybridization, the $\beta$ band turns around and disperses to high binding energies after touching the Fermi level, in parallel with the electron band $\delta$ around $M$ that forms the electron pocket [marked as $e$ in Figs. 2(b) and 2(d)] near $M$. We renormalize the calculated band structure by a factor of 1.73,
superimpose it on top of our data in Fig. 2(f), and obtain an overall agreement between experiment and calculation. We do not observe any indication of band splitting due to the formation of ferromagnetic states down to 5 K, suggesting a common paramagnetism of CoSe and FeSe monolayers at low temperatures. The metallic nature in the CoSe film is consistent with the recent transport measurement in polymorph bulk CoSe [41]. On the other hand, the ferromagnetic ordering below 10 K in bulk CoSe is absent in CoSe films, which may be due to the variation of both the in-plane Co-Co distance and the out-of-plane interlayer coupling in CoSe films [40,41]. We note that the band dispersion and the constant energy contour near 250 meV below the Fermi energy (\(E_F\)) mimic the band structure of FeSe [Figs. 2(c)–2(h)], suggesting a much higher electron density in CoSe due to the additional 3d valence electron in the Co atom.

Interestingly, the band dispersion along XM is doubly degenerate, forming a 2D nodal line [orange curve in Fig. 2(b)] and connected electron and hole pockets on the FS [Figs. 2(d) and 2(h)]. The CoSe film encapsulates two screw axes \(C_{2x}\) and \(C_{2y}\), preserving nonsymmorphic symmetries that protect the band degeneracy along XM. This 2D nodal line can be gapped by SOC as shown in Figs. 2(i) and 2(j), suggesting a much higher electron density in CoSe due to the additional 3d valence electron in the Co atom.

Figure 3 investigates the evolution of the CoSe electronic structure with film thickness. From the FS, we resolve an additional Fermi pocket around the \(\Gamma_1\) point (indicated by the black arrows near \(\Gamma_1\)) in the bilayer and five-layer films, compared to the blurred spectral weight distribution near \(\Gamma_1\) in the monolayer [Figs. 3(a)–3(c)]. From the band dispersions in bilayer CoSe in Fig. 3(e), we reveal clear band splitting of the \(\beta_1\) band near \(\Gamma_1\) into \(\beta_1^1\) and \(\beta_1^2\) bands due to interlayer interaction [43]. After splitting, the \(\beta_1^1\) band crosses \(E_F\) in both \(\Gamma M\) and \(\Gamma X\) directions, whereas the \(\beta_2\) band remains below \(E_F\) along \(\Gamma M\). They form the additional electron pocket around \(\Gamma_1\) and the hole pocket around \(X\), respectively [Fig. 3(b)]. The electron pocket around the \(M\) point also splits at specific momenta, which is better visualized in the second BZ of the FS in Fig. 3(b) [indicated by the red arrow in Fig. 3(b)]. Both the band splitting and the FS structure in the bilayer film are in good consistence with our calculation in Figs. 3(d) and 3(f).

B. Evolution of the electronic structure of CoSe films with thickness

Figure 3 investigates the evolution of the CoSe electronic structure with film thickness. From the FS, we resolve an additional Fermi pocket around the \(\Gamma\) point (indicated by the black arrows near \(\Gamma\)) in the bilayer and five-layer films, compared to the blurred spectral weight distribution near \(\Gamma\) in the monolayer [Figs. 3(a)–3(c)]. From the band dispersions in bilayer CoSe in Fig. 3(e), we reveal clear band splitting of the \(\beta\) band near \(\Gamma\) into \(\beta_1\) and \(\beta_2\) bands due to interlayer interaction [43]. After splitting, the \(\beta_1\) band crosses \(E_F\) in both \(\Gamma M\) and \(\Gamma X\) directions, whereas the \(\beta_2\) band remains below \(E_F\) along \(\Gamma M\). They form the additional electron pocket around \(\Gamma\) and the hole pocket around \(X\), respectively [Fig. 3(b)]. The electron pocket around the \(M\) point also splits at specific momenta, which is better visualized in the second BZ of the FS in Fig. 3(b) [indicated by the red arrow in Fig. 3(b)]. Both the band splitting and the FS structure in the bilayer film are in good consistence with our calculation in Figs. 3(d) and 3(f).
is noticeable that the Fermi level of bilayer CoSe only slightly shifts compared to the monolayer, further confirming the weak charge transfer from the STO substrate to CoSe.

C. Momentum-dependent electron-phonon coupling in CoSe films

In order to investigate the crucial EPC in CoSe films, we have conducted a systematic temperature-dependent self-energy analysis as shown in Fig. 3(g). The imaginary part of the electron self-energy can be obtained by the product of the width of the momentum distribution curve and Fermi velocity. Near $E_F$, it is approximately linearly proportional to the temperature with the slope related to the EPC strength $\lambda$ [52–54]. The linear dependence of the imaginary part of the electron self-energy at different momenta is plotted in Fig. 3(g). By linear fitting of the curves in Fig. 3(g), we obtain $\lambda$ and plot it in Fig. 3(h) as a function of the film thickness. We observe a momentum dependence of $\lambda$, which is greatly enhanced with reduced film thickness. Notably, $\lambda$ is as high as 0.58 along the ΓX direction, similar to the value in the FeSe-STO interface [26,55,56]. This observation alludes common enhancement of EPC in STO-interfaced 2D materials, which provides a promising method to engineer the EPC in other 2D superconductors.

We note strong spectral weight distribution connected to the bottom of the $\beta$ band near the $\Gamma$ point, which is quickly suppressed with increased film thickness [Figs. 4(a)–4(c)], suggesting its intimate relationship with the substrate. The spectral weight forms a weak sideband near 175 meV in the CoSe monolayer, which is about 95 meV from the band bottom near $\Gamma$ in bilayer and five-layer films [Figs. 4(b) and 4(c)] as can be better visualized in the energy distribution curves (EDCs) [Fig. 4(d)] and the second derivative of the spectra [Figs. 4(e)–4(g)]. Such a continuumlike feature is usually attributed to strong electron-bosonic coupling. It is robust in a large temperature range as shown in the temperature evolution of the EDCs near $\Gamma$ [Fig. 4(h)]. We argue that it is due to the strong coupling between the CoSe film and the STO $F$-$K$ phonon mode, similar to the situations in the FeSe monolayer and bare SrTiO$_3$ [57]. We reveal another feature near 55 meV below $E_F$, which is about 42 meV below the bottom of the $\alpha$ band near $\Gamma$. It is possibly due to the coupling with other STO phonon modes or plasmons [58].

IV. DISCUSSION

CoSe and FeSe monolayers harbor similar crystal structures, magnetic properties, orbital natures of electrons near $E_F$, and EPC parameters [26,55,56]. The absence of the superconductivity in CoSe films alludes to the minor roles of these parameters in the HTSC of the monolayer FeSe film. On the other hand, a drastic difference indeed exists between CoSe and FeSe films. First of all, the much higher electron
density in the CoSe film induces a complex FS structure, in contrast to the simple distribution of electron pockets on the FS of the FeSe monolayer. Second, the electronic correlation also shows a great difference between FeSe and CoSe films (renormalization factor of about 3 in FeSe [23–25] vs 1.73 in CoSe), which may be crucial for the HTSC in the FeSe film. Third, at the FeSe-STO interface, the charge transfer from the STO substrate to the FeSe monolayer is as large as 0.12 e− per unit cell, which is considered to be crucial in the HTSC of the FeSe monolayer [22–25]. It induces a shift of the Fermi level and a change in the FS structure in the monolayer FeSe compared to the bilayer FeSe. In contrast, there is only a slight shift of the Fermi level between the monolayer and the bilayer CoSe, suggesting a much weaker charge transfer from the STO substrate to the CoSe film, which is supported by the agreement between the measured and the calculated FS of monolayer CoSe [Figs. 2(b) and 2(d)] and the Bader analysis.

Moreover, the global band structure of the FeSe monolayer is replicable by the STO phonons [26], whereas only a small portion of the band near Γ is scattered in the CoSe monolayer, suggesting a difference in the coupling of FeSe and CoSe monolayers to the STO substrate. There have been debates regarding the origin of the observed replica bands, such as the strong EPC vs electron energy loss during the photoemission process [26,27,29]. The absence of the replica bands in our experiment suggests that the coupling between the FeSe and the STO substrates indeed plays a significant role in the observation of replica bands. Further experimental and theoretical comparisons between the EPCs in FeSe and CoSe monolayers will deepen our understanding of HTSC in the FeSe monolayer.

V. CONCLUSIONS

To summarize, we have systematically investigated the electronic structure of the CoSe-STO interface that is isostuctural to the HTSC FeSe-STO interface by performing ARPES measurements. Due to its nonsymmorphic symmetry, the CoSe monolayer harbors both a peculiar band degeneracy at the saddle point and the Dirac points, realizing 2D Dirac fermions. We observe momentum-dependent electron-phonon coupling that is enhanced with reduced film thickness. Compared to the FeSe-STO interface, the CoSe-STO interface shows clear differences, including much higher carrier density, much weaker electronic correlation, much weaker charge transferring from the STO substrate, and different coupling strength or mechanisms between the films and the substrate. Our results will deepen our understanding of HTSC in the FeSe-STO interface and shed light on a general understanding of the coupling between the 2D materials and the substrate beneath.

ACKNOWLEDGMENTS

This paper was supported by the National Natural Science Foundation of China (Grants No. 11774190 and No. 11674229), the National Key R&D program of China (Grants No. 2017YFA0304600 and No. 2017YFA0305400), the EPSRC (UK) Platform Grant (Grant No. EP/M020517/1).

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