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# **Atomic and Electronic Structures of Single-Layer FeSe on SrTiO<sub>3</sub>(001):**

## **The Role of Oxygen Deficiency**

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## Abstract

Using first-principles calculation, we propose an interface structure for single triple-layer FeSe on SrTiO<sub>3</sub>(001) surface, a high- $T_c$  superconductor found recently. The key component of this structure is the oxygen deficiency on the top layer of the SrTiO<sub>3</sub> substrate, as a result of Se-etching used in preparing the high- $T_c$  samples. The O vacancies strongly bind the FeSe triple-layer to the substrate giving rise to a (2×1) reconstruction, as observed by STM. The enhanced binding correlates to the significant increase of  $T_c$  observed in experiment. The O vacancies also serve as the source of electron doping, which modifies the Fermi surface of the first FeSe layer by filling the hole pocket near the center of surface Brillouin zone, as suggested from ARPES measurement.

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High transition temperature ( $T_c$ ) superconductors were mainly cuprate-based materials [1]. The recent discovery of iron-based superconductors [2-9] has significantly enriched the family of high- $T_c$  superconductors. Probably of greater importance is that the new iron-based superconductors could serve as a critical test bed for the theories that have been proposed to understand the mechanism of high- $T_c$  superconductivity. Currently, pnictides hold the highest  $T_c$  achieved in iron-based superconductors [8, 9].  $T_c$  above liquid nitrogen temperature (77 K), however, has not been realized yet. A recent report of  $T_c$  around 77 K from scanning tunneling microscopy (STM) measurement [10] on an iron chalcogenide, namely FeSe, is particularly interesting and calls for a thorough understanding.

The findings in Ref. [10] are important from at least two aspects. First, the high  $T_c$  was observed on one-unit-cell-thick (1UC) FeSe deposited on SrTiO<sub>3</sub>(001) surface. So, this system represents the simplest building blocks of most high- $T_c$  superconductors, which are usually layered materials [1]. Understanding the mechanism in such a simple system could provide important insights to the understanding of more complex high- $T_c$  superconductors. Second, bulk FeSe has a  $T_c$  of about 8 K only [7]. The drastic increase in  $T_c$  after deposition on the SrTiO<sub>3</sub> substrate indicates a critical role of the strong coupling between the 1UC FeSe and the substrate. In contrast, the deposited FeSe layers thicker than 1UC do not exhibit high  $T_c$  [10]. It is worthwhile to note that such strong coupling could exist in most layered superconductors and be an important component of the mechanism for high- $T_c$  superconductivity.

A thorough understanding on this system requires the knowledge of the atomic structures of the 1UC FeSe layer and its interface with the SrTiO<sub>3</sub> substrate. STM and angle-resolved photoemission spectroscopy (ARPES) have provided some important information on the atomic

and electronic structures of this system. From STM measurement, the surface is  $(2\times 1)$  reconstructed [10]. Figure 1 shows an STM image of 1UC FeSe on SrTiO<sub>3</sub>(001). Two domains with a trench-like boundary can be seen in this image, where one domain exhibits dimers along the [100] direction and the other along the [010] direction. From ARPES measurement, the Fermi surface of the 1UC FeSe on SrTiO<sub>3</sub> substrate does not exhibit a hole pocket at the center of the surface Brillouin zone, which exists in bulk FeSe however [11]. In addition to the features above, it has been noted that Se-etching before the deposition of FeSe layer is an important step in preparing the high- $T_c$  samples [10].

In this paper, by using first-principles calculation we reveal the role of oxygen deficiency at SrTiO<sub>3</sub> surface in determining the atomic and electronic structures of the FeSe layer. We propose an interface structure that reproduces the above-mentioned features from STM and ARPES experiments. The key component of this structure is O vacancies on the top layer of SrTiO<sub>3</sub> substrate, which are in accord with the Se-etching used to prepare the high- $T_c$  samples. The O vacancies are ordered along the [100] direction and strongly anchor the FeSe layer to the substrate, giving rise to a  $(2\times 1)$  reconstruction. The O vacancies serve as the electron donors, which fill the hole pocket of the Fermi surface of the FeSe layer near the center of surface Brillouin zone in agreement with the ARPES measurement.

Our calculations are based on density functional theory (DFT) with the Perdew-Burke-Ernzerhof exchange-correlation functional [12], as implemented in the VASP code [13]. Projector augmented wave potentials [14] are used to represent ion cores. Plane waves with an energy cutoff of 400 eV are used as basis set. The SrTiO<sub>3</sub> substrate is modeled by a 10-atomic-layer slab, which is separated from its periodic images by 12-Å vacuum regions. The surface

Brillouin zone is sampled by  $k$ -point meshes that are equivalent to the  $4\times 4$  Monkhorst-Pack mesh [15] for a  $(1\times 1)$  cell. Atoms in the lower four layers of  $\text{SrTiO}_3$  substrate are fixed at the bulk geometry, while all other atoms are fully relaxed until the residual forces are less than  $0.03 \text{ eV/\AA}$ .

$\text{FeSe}$  is a layered material, where a 1UC-thick  $\text{FeSe}$  contains a triple-layer of  $\text{FeSe}$  and the binding between the triple-layers is from the van der Waals (vdW) interaction. We first studied the deposition of a triple-layer of  $\text{FeSe}$  on a pristine  $\text{SrTiO}_3(001)$  surface. The  $\text{SrTiO}_3$  surface was terminated by a  $\text{TiO}_2$  layer, as suggested from the experiment [10]. Such a model with  $(1\times 1)$  periodicity has been employed in recent studies on this system [16-19]. Fig. 2(a) shows the optimized structure. The thickness of the  $\text{FeSe}$  layer as measured from the top Ti layer to the top Se layer is  $5.65 \text{ \AA}$ , which is similar to the lattice constant of bulk  $\text{FeSe}$  ( $c=5.48 \text{ \AA}$ ) indicating a weak vdW binding. The calculated binding energy is only about  $0.05 \text{ eV}$  per  $\text{FeSe}$  unit cell. In order to confirm that we did not miss other possible strong binding configurations, we performed molecular dynamics simulations. The starting structure was very different from the structure in Fig. 2(a), but was purposely chosen so that Se-Ti distances are in the typical range of chemical bonds (about  $2.6 \text{ \AA}$ ). The simulation was done at  $850 \text{ K}$ , which is the temperature for deposition of the  $\text{FeSe}$  layer in experiment [10]. After only  $2 \text{ ps}$  simulation, we found that the structure already changed back to that in Fig. 2(a).

The results above led us to conclude that  $\text{FeSe}$  triple-layer does not bind to pristine  $\text{SrTiO}_3$  surface strongly, which is intriguing because the formation of the  $(2\times 1)$  reconstruction observed in STM experiments suggests that the first  $\text{FeSe}$  layer grows epitaxially. The stress built in the epi-layer needs to be compensated by a strong binding between the  $\text{FeSe}$  layer and

the substrate. This prompts us to study strong anchoring sites on the SrTiO<sub>3</sub> surface that can bind the FeSe layer more strongly. An important clue from the ARPES measurement is that the FeSe layer is electron doped [11, 17]. Thus, an immediate candidate would be the O vacancies on the SrTiO<sub>3</sub> surface as the O vacancies are usually efficient electron donors in metal oxides, e.g., in TiO<sub>2</sub> [20].

Given the Se-etching used in preparing the high- $T_c$  samples, it is possible that the surface O atoms are replaced by Se atoms. The SrTiO<sub>3</sub>(001) surface has two exposed O atoms per unit cell on the top layer. We consider substitution of one or both of the two O atoms by Se. The thermodynamic stability of these substituted surfaces are compared with the pristine surface according to the calculated formation energy per unit cell

$$E_{\text{form}} = E(n\text{Se}_O \text{ on SrTiO}_3) - E(\text{SrTiO}_3) + n\mu_{\text{Se}} - n\mu_{\text{O}},$$

where  $E(n\text{Se}_O \text{ on SrTiO}_3)$  and  $E(\text{SrTiO}_3)$  are the total energies of SrTiO<sub>3</sub>(001) surface with  $n$  Se substituting for O (denoted as Se<sub>O</sub>) and the pristine surface, respectively, and  $\mu_{\text{Se}}$  ( $\mu_{\text{O}}$ ) is the chemical potential of Se (O). By definition, the formation energy of the pristine surface is zero. A negative formation means that the substituted surface is more stable. Here, we consider a Se-rich condition, i.e.,  $\mu_{\text{Se}} = E(\text{Se}_2)/2$ , where  $E(\text{Se}_2)$  is the total energy of a Se<sub>2</sub> molecule. Fig. 3(b) shows the formation energy  $E_{\text{form}}$  as a function of  $\mu_{\text{O}}$ . It can be seen that in the region  $-3.6 \text{ eV} < \mu_{\text{O}} < -2.4 \text{ eV}$ , the half-substituted surface containing one Se<sub>O</sub> per unit cell, as shown in the inset of Fig. 3, becomes more stable than the pristine surface. The surface could even become fully substituted if the growth condition becomes more O-poor (i.e.,  $\mu_{\text{O}} < -3.6 \text{ eV}$ ). Given the experimental temperature for Se-etching of 950 °C and typical ultra-high vacuum pressure of 10<sup>-10</sup>

<sup>12</sup> bar, we estimate that  $\mu_{\text{O}}$  is about -3.0 eV [21,22], at which the half-substituted surface is the most stable.

In the subsequent growth of FeSe layer, the Se-substituted surfaces are the actual substrate. Thus, the Se atoms already existing on the surface can participate in the growth of the first triple-layer of FeSe. Because the position of the Se substituting for O coincides with that of the Se in the first triple-layer FeSe, no significant atomic redistribution is necessary. This effectively creates O vacancies at the interface. An interesting finding from our calculations is that after the deposition of a triple-layer FeSe on the half-substituted surface, a (2×1) reconstruction becomes more stable, even though in the case without the FeSe layer the unreconstructed (1×1) surface is more stable. The optimized structure of the (2×1) reconstructed surface is shown in Fig. 2(b), which can be viewed as having alternately missing rows of O atoms (called missing-row structure hereafter). In this structure, there are two different spacings between Se-atom rows on the top layer, which are 4.08 and 3.81 Å, respectively. Another noticeable feature is the significant relaxation in the top layer of Ti atoms, which also form a dimer-like structure. The two Ti-Se-Ti bond angles are 74.8° and 101.5°, respectively, and two Ti-Se bond lengths are 2.97 and 2.71 Å, respectively. Compared with the case of deposition on pristine surface, the FeSe layer sinks down to the substrate with a thickness of 4.49 Å.

With the interface reconstruction, the binding energy between the FeSe layer and the substrate significantly increases to 0.75 eV per FeSe (1×1) cell according to our calculation. This strong binding is important in determining the growth mode of the FeSe film. To allow stable epitaxial growth of the FeSe layer, the binding energy should be able to compensate the stress built in the epi-layer. Otherwise, an incommensurate ad-layer will be favored. Our calculation



shows that a change in the lattice constant of FeSe by 4.6%, which is the mismatch between the lattice constants of FeSe and SrTiO<sub>3</sub>, results in a total-energy change by 0.28 eV per FeSe (1×1) cell, which is smaller than the binding energy between the FeSe layer and the substrate in our structure. This explains why the first FeSe layer favors epitaxial growth in experiment.

Next, we study the effect of the O vacancy on the Fermi surface of the FeSe triple-layer. In Fig. 4(a), we show the band structure for a free-standing FeSe triple-layer, where the hole pocket is clearly seen from  $\Gamma$  to about 1/6 of  $\Gamma$ -Y. Bulk FeSe band structure is similar to that in Fig. 4(a). After deposition on the SrTiO<sub>3</sub> surface containing O vacancies, our band structure calculation shows that the hole pocket is dipped under the Fermi surface of the combined system, as shown in Fig. 4(b), where for clarity we have projected each electronic state in the band structure onto individual atoms and used grayscale to represent the contribution from the FeSe layer (the darker, the more contribution from the FeSe layer). Recent ARPES measurement [11] shows that the hole pocket at  $\Gamma$  point, which has been proposed to play a role in Cooper-pairing mechanism for bulk FeSe within a spin-fluctuation mediated framework [23], disappears after deposited on the SrTiO<sub>3</sub> surface. So, our structure is consistent with the ARPES experiment. The electrons filling the FeSe hole pocket at  $\Gamma$  point are contributed by the O vacancies. Figure 4(d) shows the charge transfer between the SrTiO<sub>3</sub> substrate and the FeSe layer, as characterized by the charge density difference ( $\Delta\rho$ ) obtained by subtracting the valence charge densities of the isolated FeSe layer and SrTiO<sub>3</sub> substrate from that of the combined system. From Fig. 4(d), clear charge transfer from the SrTiO<sub>3</sub> substrate to FeSe layer can be seen, which fills the hole pocket of the FeSe layer and provides strong Coulomb binding between the FeSe layer and the substrate.

Experimentally, the high  $T_c$  was only observed on the first FeSe layer, but not on the thicker films [10]. To address this observation, we studied the case with a second layer FeSe deposited on the first layer. In this case, the binding energy between the first and second layers is found to be 0.03 eV per FeSe ( $1\times 1$ ) cell, indicating a pure vdW interaction. This is significantly lower than that between the first layer and the substrate (0.75 eV). Our results thus indicate a clear correlation between the change in  $T_c$  and the strength of interface coupling. Interestingly, the hole pocket that is absent on the first layer, reappears at the  $\Gamma$  point on the second layer, as shown in Fig. 4(c) in blue color.

As a final note, we also considered other known structures of SrTiO<sub>3</sub>(001) surface. Even though a number of reconstructions have been observed on the SrTiO<sub>3</sub>(001) surface [24-26], we focused on the so-called double-layer-TiO<sub>2</sub> ( $2\times 1$ ) surfaces [27,28] because other more complex surfaces are not compatible with the ( $2\times 1$ ) reconstruction under study here. It has been found that, on the double-layer-TiO<sub>2</sub> ( $2\times 1$ ) surface, the role of O vacancy is the same as that in the missing-row structure described above.

In summary, the atomic and electronic structures of single triple-layer FeSe deposited on SrTiO<sub>3</sub>(001) surface have been studied using first-principles calculations. We unveil the critical role of O vacancies at the interface in providing a strong binding and donating electrons to the FeSe layer, which provides important insights to the enhancement of the superconducting transition temperature. An interface structure has been proposed to address the features observed in STM and ARPES experiments. By providing a credible interface structure, our study paves the way for further understanding the mechanism of superconductivity in this important system.

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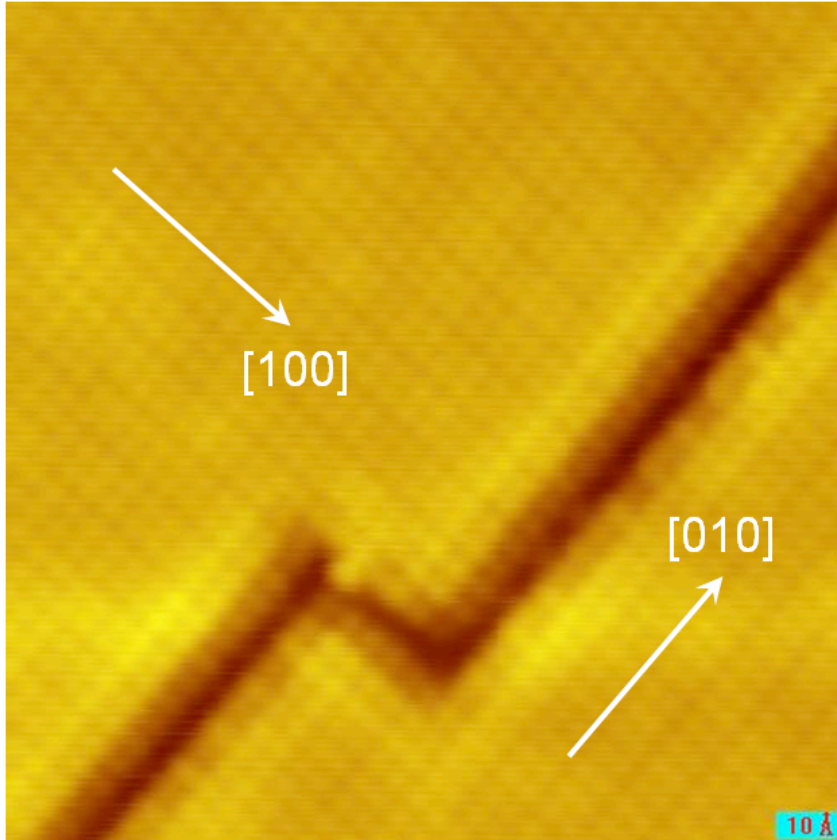


FIG. 1. (Color online) STM image of 1UC FeSe on SrTiO<sub>3</sub>(001) surface. Two domains are shown, which are separated by a trench-like structure. One domain exhibits (2×1) reconstruction along the [100] direction, while the other one along the [010] direction. The scanning area is 12.8×12.8 nm<sup>2</sup>. The bias voltage and tunneling current for obtaining this image were 0.6 V and 46.5 pA, respectively.

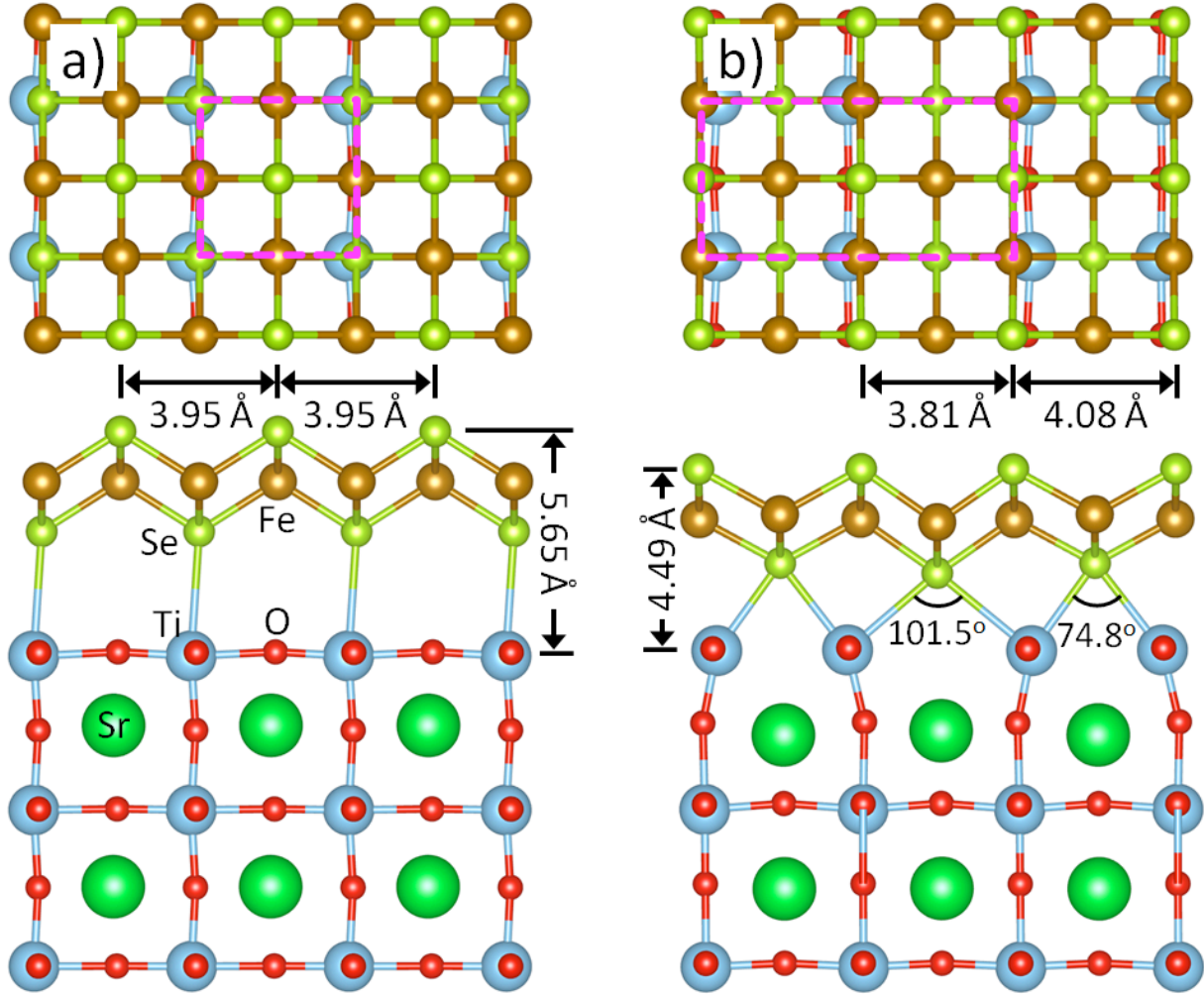


FIG. 2. (Color online) Structural models of 1UC FeSe (a) on pristine SrTiO<sub>3</sub>(001) surface, which is terminated by a TiO<sub>2</sub> layer and (b) on O-deficient surface, which is characterized by alternately missing O-atom rows. The top panels show top views, while the bottom panels show side views. The surface unit cells are shown in the top views. Several characterizing structural parameters are shown.

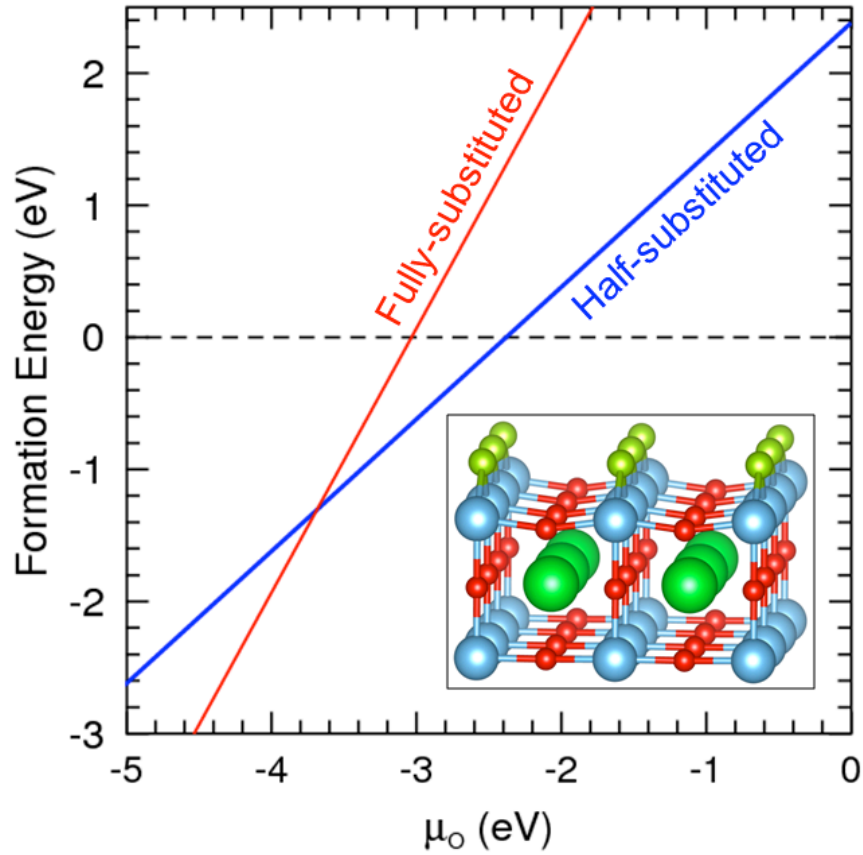


FIG. 3. (Color online) Formation energy of Se-substitution of O atoms in the top layer of  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3(001)$  surface as a function of O chemical potential,  $\mu_{\text{O}}$ . By definition, the formation energy of the pristine surface without Se-substitution is zero, as marked by the dashed line. The inset shows the structure of the half-substituted surface.



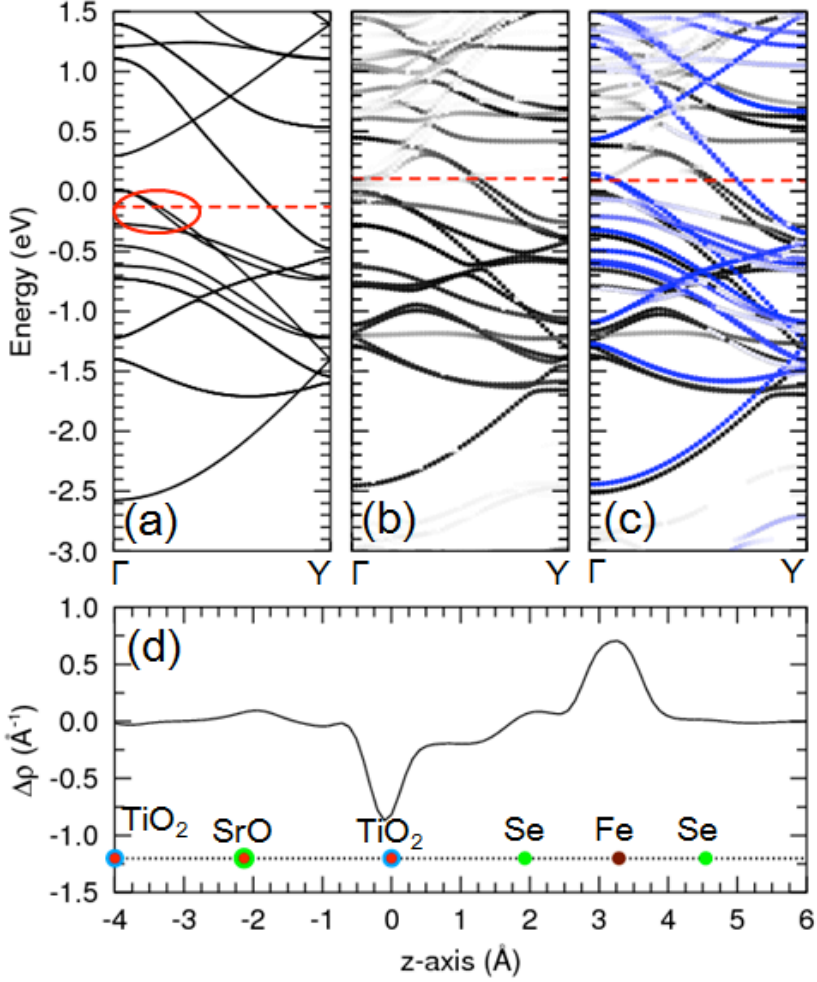


FIG. 4. (Color online) Band structure of (a) a free-standing triple-layer FeSe, (b) one triple-layer, and (c) two triple-layers of FeSe deposited on the SrTiO<sub>3</sub>(001) surface containing O vacancies. The hole pocket in the free-standing case is marked by a red circle in (a). Each state in (b) and (c) is projected on to the first (in black) or the second (in blue) FeSe layers. The larger the projection is, the darker the dot is used for that state. Panel (d) shows the charge density difference obtained by subtracting the valence charge densities of the isolated FeSe layer and SrTiO<sub>3</sub> substrate from that of the combined system. A charge transfer from the top TiO<sub>2</sub> layer to the FeSe layer can be clearly seen.