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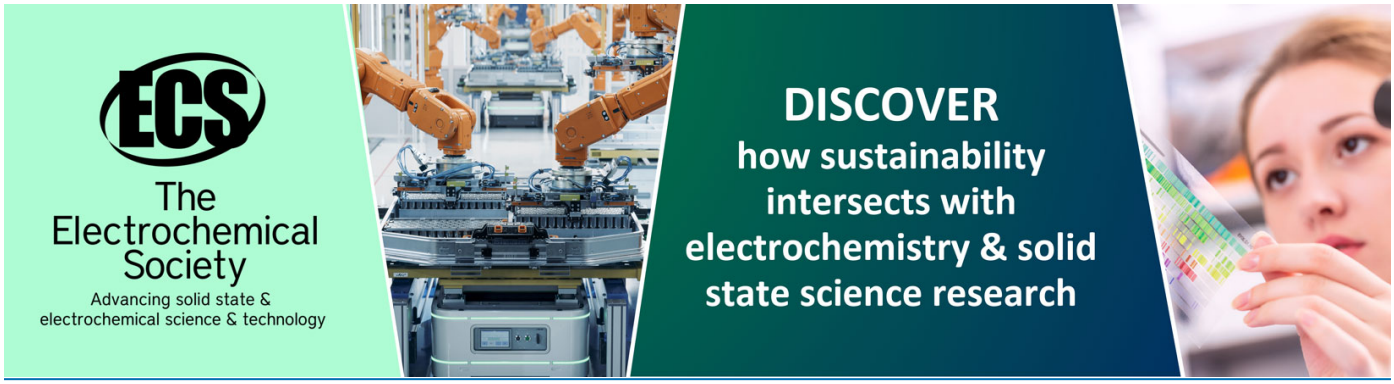

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ARPES study of cesium-coated FeSe thin films on $SrTiO_3$

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Abstract. We have performed *in-situ* angle-resolved photoemission spectroscopy measurements of cesium(Cs)-deposited FeSe thin films on $SrTiO_3$. We found that Cs deposition enables heavily electron doping into the FeSe layer. In properly doped films, we also revealed the occurrence of superconductivity accompanied by the suppression of electronic nematicity. The present result demonstrates that Cs deposition is an effective way to realize and enhance superconductivity in FeSe.

1. Introduction

Recent discovery of possible high-temperature (T_c) superconductivity in one-monolayer (1-ML) FeSe film on $SrTiO_3$ [1] has brought great excitements. The reported T_c value by *ex-situ* transport measurements reaches around 40 K [1-4], which is much higher than T_c (8 K) of bulk FeSe [5]. Angle-resolved photoemission spectroscopy (ARPES) [6, 7] and two-coil mutual inductance measurements [8] reported a higher T_c value of 65 K, which exceeds the highest T_c (56 K) [9] for bulk iron-based superconductors discovered so far. Possible further enhancement of T_c up to 109 K has been suggested by *in-situ* transport study [10]. These observations generated fierce debates on the origin of the T_c enhancement in 1-ML FeSe film.

Besides the origin of high-T_c superconductivity in 1-ML film, another mystery is that multilayer (2-ML or thicker) FeSe films have been reported to be non-superconducting [1]. Previous ARPES measurements revealed a striking difference in the electron carrier density between 1-ML and multilayer films [7]; namely, 1-ML film is heavily electron-doped due to the electron transfer from the substrate, whereas multilayer films are almost non-doped because the electron transfer between FeSe layers is very small. This finding provides a question as to whether high-T_c superconductivity emerges in multilayer films if one can dope sufficient electrons. However, the difficulty in controlling the carrier density has hindered the elucidation of this essential question.

A novel approach to control the electron doping of FeSe thin films has been recently proposed by some of the present authors. They demonstrated that *in-situ* deposition of potassium (K) atoms onto the film markedly expands the accessible doping range [11]. Using this technique, non-superconducting multilayer films have been converted into superconductors with T_c values as high as 48 K [11, 12], establishing the importance of electron doping to realize high-T_c superconductivity. Subsequent study utilized Na atoms to control the carrier density but obtained low T_c of 20 K with the

reduced superconducting pairing [13]. Significantly different T_c values obtained by K and Na deposition call for the further investigation on the suitable electron donor to achieve high-T_c superconductivity.

In this paper, we report our high-resolution ARPES study on Cs-deposited multilayer FeSe films. We have succeeded in achieving heavily electron doping and realizing superconductivity. We present the obtained electronic phase diagram and compare it with the previous results for the K- and Na-deposited samples.

2. Experiment

20-ML FeSe films were fabricated on TiO_2-terminated Nb(0.05wt%)-doped $SrTiO_3$ substrates (SHINKOSHA) by molecular-beam-epitaxy (MBE) technique, as described in detail in our previous work [11]. Cs atoms were deposited at room temperature using a Cs dispenser (SAES Getters). *In-situ* ARPES measurements were performed in an ultrahigh vacuum better than 8×10^{-11} Torr using a Scienta-Omicron SES2002 electron analyzer with a He discharge lamp ($h\nu$ = 21.218 eV) at Tohoku University. The energy and angular resolutions were set to 4-30 meV and 0.2°, respectively. The Fermi level (E_F) of the film was referenced to that of a gold film evaporated onto the sample holder.

3. Results and discussion

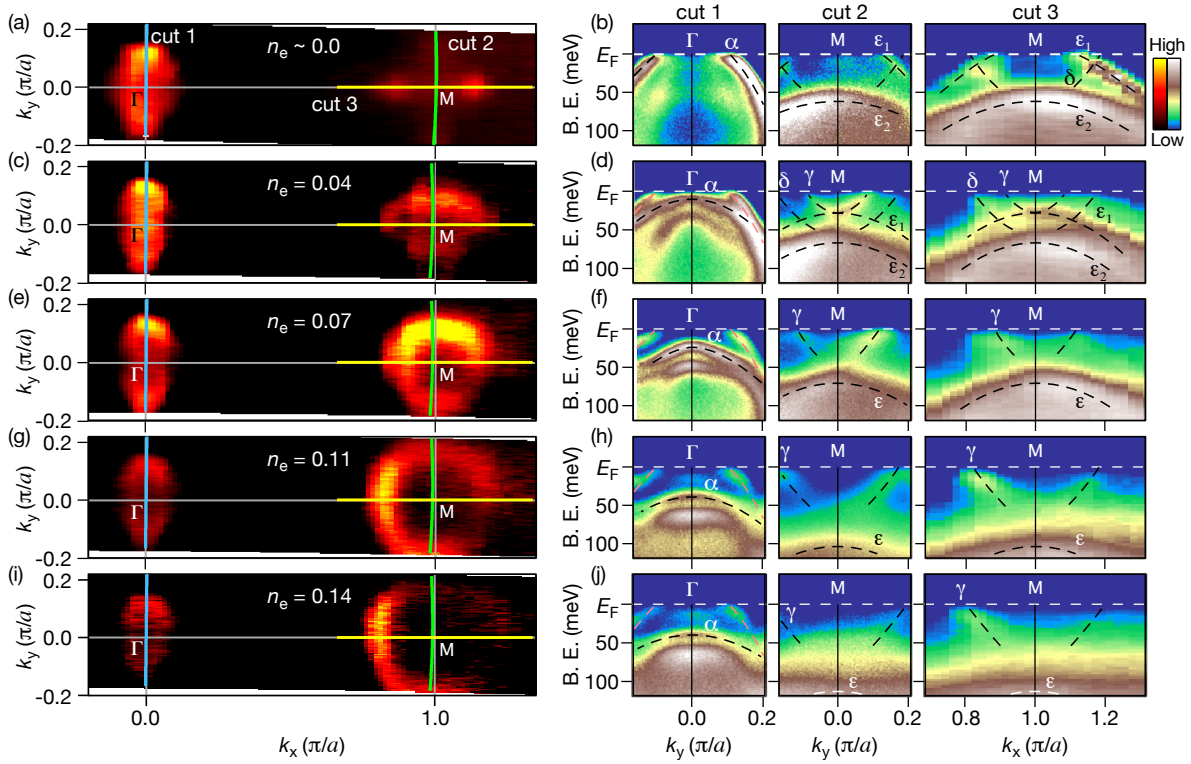

Figure 1. (a) ARPES intensity mapping at T = 30 K for the pristine 20-ML film plotted as a function of a two-dimensional wave vector. The intensity is obtained by integrating the spectral intensity within ±5 meV of E_F. (b) ARPES intensity plot near E_F as a function of binding energy and wave vector measured along the cuts 1-3 shown in (a). (c) and (d) Same as (a) and (b), but for Cs-deposited 20-ML film with n_e = 0.04 electrons/Fe. (e)-(j) Same as (c) and (d) but for n_e = 0.07 ((e) and (f)), 0.11 ((g) and (h)), and 0.14 ((i) and (j)).

Figures 1(a) and 1(b) show the Fermi surface and the band dispersion, respectively, for pristine 20-ML FeSe film measured at T = 30 K. We found signatures of the nematicity around the M point such as the two hole-like band dispersions originating from the lifting of d_{xz}/d_{yz} orbital degeneracy [see ε_1 and ε_2

bands in the right panel of Fig. 1(b)] [14, 15] and Dirac-cone-derived small electron-like Fermi surfaces [Fig. 1(a)] [16]. We also observed a hole-like pocket (α) around the Γ point, consistent with a semimetallic character of the pristine film. After deposition of Cs atoms onto the FeSe surface, we found sinking of the α band below E_F and the appearance of a larger electron-like Fermi surface (γ) centered at the M point [Fig. 1(c)], accompanied by a decrease of the energy separation between the ε_1 and ε_2 bands (ΔE_{nem}) [compare the right panels of Figs. 1(b) and 1(d)]. These observations indicate a successful electron doping by Cs deposition and the resultant suppression of the nematicity. It is noted that we still see the band structure of non-doped FeSe, e.g. a hole-like band crossing E_F around the Γ point indicated by gray dashed curves in the left panel of Fig. 1(d). This band structure would originate from interior FeSe layers which are kept non-doped even after Cs deposition, as discussed in the Na-deposited case [13]; namely, doped electrons would be confined in the topmost FeSe layer. Further Cs deposition results in a systematic downward shift of the α band as well as an expansion of the γ Fermi surface [Figs. 1(e)-1(j)]. The electron carrier concentrations (n_e) estimated from the Fermi-surface volume in Figs. 1(c), 1(e), 1(g), and 1(i) are 0.04, 0.07, 0.11, and 0.14 electrons/Fe, respectively. The largest n_e of 0.14 achieved by Cs deposition exceeds the accessible limit in 1-ML FeSe (~ 0.12) [6], demonstrating that Cs deposition is useful to control the electron doping over a wide range.

Next we performed high-resolution measurements at the Fermi wave vector (k_F) of the pristine and Cs-deposited films at low temperature (T = 13 K) to investigate the doping-induced evolution of superconductivity. As seen in Fig. 2(a), the leading-edge midpoint, which is located around E_F in the pristine (n_e ~ 0) and lightly doped (0.04) films, is clearly shifted toward higher binding energy for the doping range between 0.06 and 0.11, indicative of a superconducting-gap opening in properly doped films. The gap opening is confirmed by the observation of two-peaked structure in the symmetrized spectra in Fig. 2(b), where the influence of the Fermi-Dirac distribution function is eliminated. It is also noted that the superconducting gap is suppressed by heavily electron doping (n_e = 0.14).

Figure 3 shows the magnitude of the superconducting gap (Δ_{SC}) and the strength of the nematicity (ΔE_{nem}) plotted as a function of n_e. It is clearly seen that superconductivity is realized when the nematicity is suppressed by an electron doping through Cs deposition, pointing to the anti-correlation between superconductivity and nematicity. With increasing electron doping, the superconducting

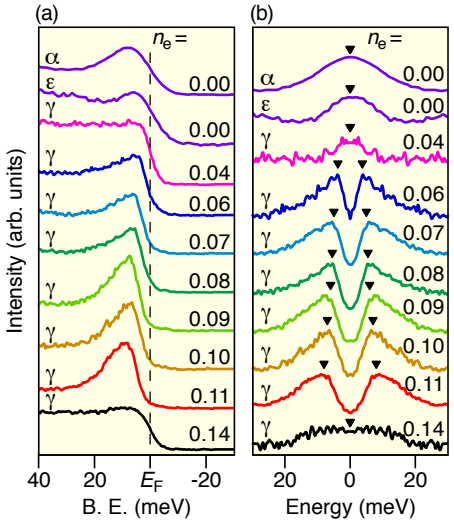

Figure 2. (a) Representative ARPES spectra measured at the k_F point of the α and ε_1 bands at T = 30 K for pristine 20-ML film (upper two spectra) and those of the γ band at T = 13 K for Cs-deposited films

with different doping levels (lower eight spectra). (b) Symmetrized spectra of (a). Triangles are a guide for the eyes to trace the peak position.

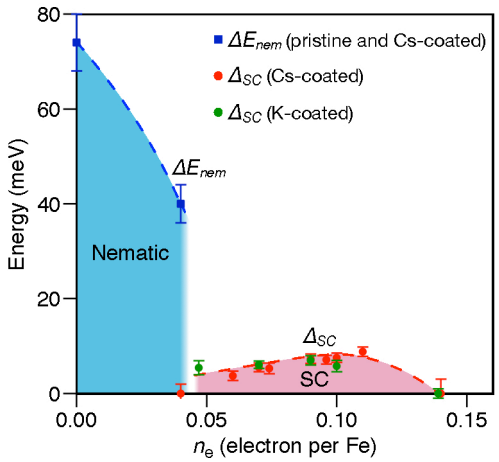

Figure 3. Electronic phase diagram for Cs- and K-deposited 20-ML FeSe films. Red and blue circles represent experimentally determined superconducting-gap size (Δ_{SC}) for Cs- and K-deposited 20-ML films, respectively. Each data has been extracted from the ARPES spectra shown in Figs. 2(b) and S1(b). Energy difference between the ε_1 and ε_2 bands at the M point (ΔE_{nem}) at T = 30 K, extracted from the data in Fig. 1, is plotted in blue square.

pairing is gradually enhanced until reaching the optimal doping ($n_e \sim 0.11$) and then suppressed in the overdoped regime, forming a dome-shaped superconducting phase which is a characteristic of high-T_c superconductors.

Now we discuss the implication of the present results in relation with the alkali-metal dependence. As described above, electron doping to a thick film or bulk crystal has been achieved by deposition of K or Na atoms [11-13]. However, the reported Δ_{SC} value is significantly different between the K- and Na-deposited cases (the maximum Δ_{SC} is ~10 meV [12] and ~4 meV [13], respectively), suggesting that the search for a suitable electron donor is of crucial importance to realize high-T_c superconductivity. In the present study, we have succeeded in achieving heavy electron doping by Cs deposition and realizing the superconductivity with the maximum Δ_{SC} up to 10 meV. The observed Δ_{SC} is much larger than that for the Na-deposited sample and is quantitatively similar to that for the K-deposited sample (compare red and green circles in Fig. 3) [17]. This result demonstrates that Cs is one of the suitable electron donors to realize and enhance superconductivity in FeSe. We think that the alkali-metal dependence of the maximum Δ_{SC} value may be related to a difference in the chemical stability of the surface. While the Cs- and K-deposited surfaces were found to be stable in an ultrahigh vacuum for at least 24 h, the lifetime of Na-deposited surface has been reported to be very short [13]. This suggests the occurrence of a chemical reaction at the Na-deposited surface, which may result in the smaller Δ_{SC} value in Na-deposited FeSe.

4. Summary

We reported high-resolution ARPES results on Cs-deposited 20-ML FeSe films grown on $SrTiO_3$ substrate. We found that Cs deposition enables the systematic investigation on the evolution of superconductivity and nematicity as a function of electron carrier density. By using this technique, we determined the electronic phase diagram. The observed characteristics in the phase diagram, such as the anti-correlation between nematicity and superconductivity and the dome-shaped nature of the superconducting region, would provide key insights into the origin of high-T_c superconductivity.

Acknowledgements

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References

[1] Wang Q-Y *et al*. 2012 *Chin. Phys. Lett*. **29** 037402
[2] Zhang W-H *et al*. 2014 *Chin. Phys. Lett*. **31** 017401
[3] Zhang A W *et al*. 2014 *Phys. Rev. B* **89** 060506(R)
[4] Sun A Y *et al*. 2014 *Sci. Rep*. **4** 6040
[5] Hsu F-C *et al*. 2008 *Proc. Natl. Acad. Sci*. **105** 14262-14164
[6] He S *et al*. 2013 *Nat. Mater*. **12** 605-610
[7] Tan S *et al*. 2013 *Nat. Mater*. **12** 634-640
[8] Zhang Z *et al*. 2015 *Sci. Bull*. **60** 1301-1304
[9] Wang C *et al*. 2008 *Europhys. Lett*. **83** 67006
[10] Ge J-F *et al*. 2015 *Nat. Mater*. **14** 285-289
[11] Miyata Y *et al*. 2015 *Nat. Mater*. **14** 775-779
[12] Wen C H *et al*. 2016 *Nat. Commun*. **7** 10840
[13] Seo J J *et al*. 2016 *Nat. Commun*. **7** 11116
[14] Nakayama K *et al*. 2014 *Phys. Rev. Lett*. **113** 237001
[15] Shimojima T *et al*. 2014 *Phys. Rev. B* **90** 121111(R)
[16] Tan S Y *et al*. 2016 *Phys. Rev. B* **93** 104513
[17] While a superconducting gap was not clearly observed in our previous study on 20-ML film [11], recent data with higher resolution show a clear gap opening as shown in Supplementary Information (Figure S1).
[18] Fan Q *el at*. 2015 *Nat. Phys*. **11** 946-952