

From monolayer back to bulk FeSe-based high-temperature superconductors

1. X. H. Niu, R. Peng, H. C. Xu, Y. J. Yan, J. Jiang, D. F. Xu, T. L. Yu, Q. Song, Z. C. Huang, Y. X. Wang, B. P. Xie, X. F. Lu, N. Z. Wang, X. H. Chen, Z. Sun, and D. L. Feng, Surface electronic structure and isotropic superconducting gap in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, Phys. Rev. B **92**, 060504 (2015).
2. L. Zhao, A. Liang, D. Yuan, Y. Hu, D. Liu, J. Huang, S. He, B. Shen, Y. Xu, X. Liu, L. Yu, G. Liu, H. Zhou, Y. Huang, X. Dong, F. Zhou, K. Liu, Z. Lu, Z. Zhao, C. Chen, Z. Xu and X. J. Zhou, Common electronic origin of superconductivity in $(\text{Li,Fe})\text{OHFeSe}$ bulk superconductor and single-layer FeSe/SrTiO₃ films, Nat. Commun. **7**, 10608 (2016).

Recommended with a Commentary by Atsushi Fujimori, University of Tokyo

Recently, a dramatic increase of the critical temperature T_c has been reported in some exotic forms of FeSe from the bulk value of $T_c \sim 8$ K to $T_c \sim 30$ K in alkali-doped Fe-deficient $\text{A}_x\text{Fe}_{2-z}\text{Se}_2$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) [1] and $T_c \sim 65$ K up to ~ 100 K in one-monolayer (1 ML) FeSe grown on SrTiO₃ substrates [2,3], invoking hot discussions on possible pairing mechanisms in the Fe-based superconductors. Because $\text{A}_x\text{Fe}_{2-z}\text{Se}_2$ consists of a mesoscopic mixture of the insulating $\text{K}_2\text{Fe}_4\text{Se}_5$ and superconducting phases, the importance of misfit strain and interfaces were highly suspected [4]. For 1 ML FeSe/STO, on the other hand, lattice mismatch with the STO substrate was minimal, but the effect of the FeSe/STO interfaces, in particular, enhanced electron-phonon coupling was suggested to enhance the T_c [5].

It should also be noted that intercalation enhanced the T_c of FeSe dramatically: $T_c = 45$ K for $\text{Li}_x(\text{C}_2\text{H}_8\text{N}_2)_y\text{Fe}_{2-z}\text{Se}_2$ [6] and $T_c = 43$ K for $\text{Li}_x(\text{NH}_2)_y(\text{NH}_3)_{1-y}\text{Fe}_2\text{Se}_2$ [7]. The latter reports suggest that the large distance between the Fe layers (8-11 Å in the intercalated compounds compared to 5.5 Å in pristine FeSe) leads to the enhanced T_c . The superconducting phase of $\text{A}_x\text{Fe}_{2-z}\text{Se}_2$, too, which has an intermediate Fe-layer distance of ~ 7 Å and an intermediate $T_c \sim 30$ K, follows this trend. (The Fe-layer distance is “infinite” in 1 ML FeSe/STO, where the T_c is the highest.)

Remarkable findings by ARPES experiments common to $\text{A}_x\text{Fe}_{2-z}\text{Se}_2$ [8] and 1 ML FeSe/STO [2,5] were:

- (i) There were only electron pockets centered at the corners of the two-dimensional Brillouin zone and the hole pockets centered at the Γ point were missing, resulting in a relatively high electron carrier concentration of $n \sim 0.1$ per Fe or more;
- (ii) The superconducting gap opens uniformly on the electron pockets.

These observations challenged the general belief that the coexistence of the electron and hole pockets and nesting between them play an essential role in Cooper pairing. For the observed Fermi surface topology without hole pockets, s/\pm pairing cannot occur and only plain s -wave pairing is possible. More recently, it was found that one can dope the systems with high concentration of electrons by K evaporation on FeSe multilayers [9] and even on bulk FeSe [10], and can induce superconductivity up to $T_c \sim 30$ K. They obtained a “ T_c dome” with the maximum T_c at $n \sim 0.1$ and vanishing T_c at $n \sim 0.15$.

Very recently, a new FeSe system “intercalated” with $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ layers has been synthesized as a bulk compound $\text{Li}_{0.8}\text{Fe}_{0.2}\text{FeSeOH}$ (referred to as FeSe1111 hereafter, having the crystal structure shown in Fig. 1) [11]. In the two recommended articles, Niu et al. and Zhao et al. performed ARPES experiments on its single crystals, and observed results similar to those on $\text{A}_x\text{Fe}_{2-z}\text{Se}_2$ and 1 ML FeSe/STO, that is, only the electron pockets at zone corner have been observed and a quite uniform superconducting gap opens. However, unlike 1 ML FeSe/STO, no strong phonon replica was

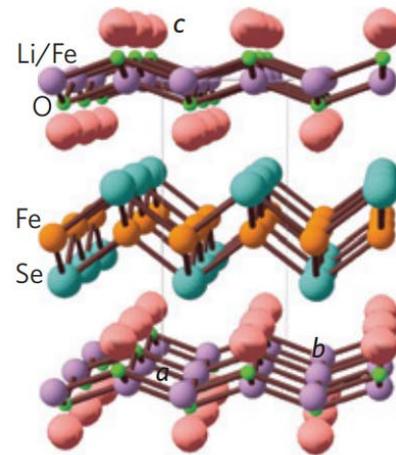


Fig.1 Crystal structure of $\text{Li}_{0.8}\text{Fe}_{0.2}\text{FeSeOH}$ [11].

observed, indicating that electron-phonon interaction is not as strong as in 1 ML FeSe/STO. As discussed by Zhao et al., the ARPES results may give answers to the remaining question about the origin of the T_c enhancement in the FeSe-based superconductors, namely, the question about the role of the FeSe/STO interface or the interface between the superconducting and insulating domains in $A_x\text{Fe}_{2-x}\text{Se}_2$ including the enhancement of electron-phonon interaction. The effect of the interfaces between different phases can be excluded since the bulk compound is a single phase, but the “intercalated” $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ layer and its immediate contact with the FeSe layer might play some roles analogous to the STO substrate in contact with the FeSe monolayer.

An obvious role of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ layers is to provide the FeSe layers with electron carriers, just like the n-type STO substrate provides the monolayer FeSe with the electron carriers. The number of carriers in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ is predicted to be $n \sim 0.2$ if the Fe^{2+} valence state is assumed. Zhao et al. have obtained a smaller value of $n \sim 0.1$ from the Fermi pocket area, but Niu et al. have corrected this value for the electronic reconstruction effect at the polar surface and deduced $n \sim 0.2$. This value is consistent with a detailed chemical analysis of FeSe1111 [12]. Whether the T_c maximum occurs at $n \sim 0.1$ or 0.2 makes much difference, but can be understood if we remember the single versus double T_c domes seen in $\text{RFeAsO}_{1-x}\text{H}_x$ ($\text{R}=\text{La, Ce, Sm}$, referred to FeAs1111 hereafter) [13]. In the case of $\text{R} = \text{La}$, the first and second T_c maxima occur at $n (= x) \sim 0.1$ and ~ 0.4 , respectively, but merge into a single dome with the T_c maximum at $n \sim 0.2$ under pressure or for $\text{R} = \text{Ce}$ and Sm .

Another role of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ layers is to increase the Fe-layer distance, as pointed out by Zhao et al. In fact, the positive correlation between the Fe-layer distance and the T_c is not restricted to the FeSe-based superconductors but also is extended to the FeAs-based superconductors: The Fe-layer distance is 8.5-8.7 Å in FeAs1111 with $T_c = 40$ -50 K, and 6.5 Å in the 122-type FeAs compounds with $T_c \sim 30$ K. (The T_c 's of Fe-site-substituted compounds may not follow the same trend because of the strong disorder effect.) If the origin of the correlation between the Fe-layer distance and T_c is known on a microscopic level, it will greatly contribute to the elucidation of the pairing mechanism. The larger the Fe-layer distance is, the stronger the two-dimensionality of energy bands and Fermi surfaces becomes. Also, the large electric polarizability of the thick intercalated/charge reservoir layer would favor excitonic mechanisms of superconductivity, which so far have been based on the large polarizability of the large As^{3-} ion [14].

In conclusion, the discovery of the heavily electron-doped FeSe1111 compound and its ARPES studies by Niu et al. and Zhao et al. allow us to view the 1 ML FeSe/STO and the bulk FeSe-based superconductors on a common ground. Furthermore, they also bridge our understanding of the FeSe-based superconductors and the FeAs-based superconductors, if combined with the recent results on the heavily electron-doped FeAs1111 superconductors, and will contribute to a unified phenomenological (and eventually microscopic) understanding of the Fe-based superconducting materials.

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