The 45 K Onset Superconductivity and the Suppression of the Nematic Order in FeSe by Electrolyte Gating *

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The electronic doping effect on both the superconductivity and the nematic order in the FeSe nanoflake are investigated by using the electric-double-layer transistor configuration. The superconductivity can be effectively controlled by electronic doping, and the onset superconducting transition temperature T_c reaches as high as 45 K at a gate voltage of $V_g = 4$ V. Meanwhile, the nematic phase is gradually suppressed with the increase of electronic doping (or V_g). The results provide an effective method with variable charge doping for investigation of the rich physics in the FeSe superconductor.

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Among the Fe-based superconductors, the 11-type FeSe compound with a relative lower superconducting transition temperature T_c of 8 K[1] has attracted extensive attention in recent years due to the fact that it contains rich unusual physical behavior. For example, its T_c can be adjusted up to 36.7 K under a high pressure,[2–5] or 40 K by intercalating alkali metals or molecules into its spacer layers.[6–14] Even more, the monolayer FeSe film grown on the $SrTiO_3$ substrate shows incredibly a T_c as high as 100 K.[15] While the high-T_c obtained in the monolayer FeSe film may have an origin of interface effect,[16–18] the electronic structure found in the intercalated system almost shares a common feature. It is found that the intercalated FeSe only exists in electron pockets at the Fermi surface (FS),[8,19–21] which is in contrast to that in the FeSe single crystal, where both electron and hole pockets are observed.[22–24] This indicates that even without intercalating, the electronic doping might be efficient to largely improve the superconductivity in FeSe if the hole pocket can be 'killed', as revealed by the theoretical calculation.[25] Indeed, a high-T_c of 48 K was achieved recently through purely electronic doping.[26,27]

In addition, FeSe crystal undergoes a structural transition from the tetragonal to the orthorhombic phase with very weak lattice distortion at a temperature of T_S ∼90 K,[1,28] at which the temperature-dependent resistance presents a kink. The driving force for this structural transition is considered to be the electronic nematic order rather than the lattice degree of freedom or magnetic fluctuation.[22,24,29–32] As a result, the resistive kink can be regarded as a probe to detect the electronic nematic order. Recently, it is found that in S-substituted FeSe, the increase of T_c is coincidently accompanied by the suppression of structural transition, suggesting that they may be closely related.[33] For the superconductivity in bulk FeSe occurring at the orthorhombic phase, it is natural to ask whether the electronic nematic order can also be tuned by electronic doping. If it is true, what will be the relationship between the nematic order and the superconductivity?

In this Letter, we present the electronic doping effect in the FeSe nanoflake by using the electric-double-layer transistor (EDLT) configuration. The positive voltage allows a large accumulation of electrons within the channel. We show that when a positive voltage V_g is applied, the onset superconductivity can be systemically tuned to 45 K at $V_g = 4$ V, accompanied by the gradual vanishing of the resistive kink at T_S due to the suppression of the nematic order. These results suggest that both the superconductivity and nematicity can be effectively controlled by electronic doping, and thus demonstrate a method to simultaneously study the physics of superconductivity and nematicity in FeSe.

Single crystal FeSe is synthesized by the KCl-$AlCl_3$ flux method.[30] The as-grown crystals are resealed in an evacuated quartz tube and further annealed at 400℃ for four days. The crystals have a plate-like shape with typical dimensions of $3 \times 3 \times 0.4\,mm^3$. The crystalline quality is examined by x-ray diffractometer (XRD). Figure 1(a) shows the XRD pattern of a crys-

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tal determined at room temperature, all the diffraction peaks nicely fit the $(00l)$ tetragonal phase, indicating the single crystalline character of the sample. The temperature (T) dependence of the electrical resistance R at zero field of the crystal is measured by using the standard four-probe configuration, as shown in Fig. 1(b). The crystal shows the metallic behavior, i.e., $dR/dT > 0$, in the normal state except a kink observed at a temperature $T_S = 90\,\mathrm{K}$, which is consistent with the previous reports.[1] The onset of the superconducting transition occurs at $T_c = 9.8\,\mathrm{K}$, with a narrow transition width ΔT of about 0.8 K (inset of Fig. 1(b)), indicating that the FeSe crystal has a high quality.[29,34]

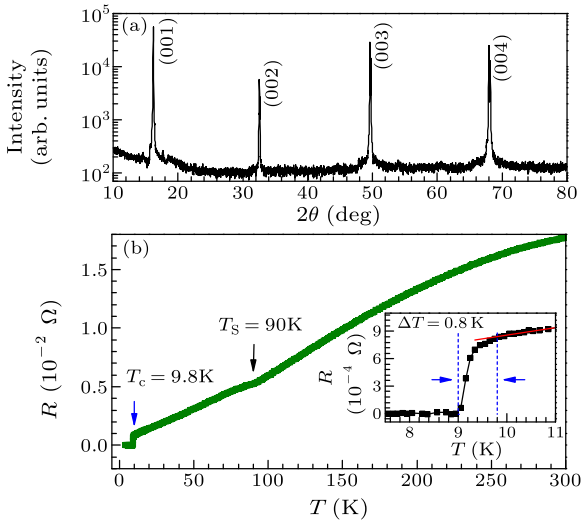

Fig. 1. (a) XRD pattern of the FeSe single crystal, only $(00l)$ peaks related to the tetragonal phase can be observed. (b) Temperature-dependent resistance at zero field of the FeSe single crystal. The inset is an enlarged view of the superconducting transition.

FeSe possesses a PbO-type binary element structure at room temperature with stacks of Fe_2Se_2 layers by van der Waals force (see Fig. 2(a)). It can be easily exfoliated into a nanoflake by commercial scotch tape. Flakes with thickness of about 50 nm are transferred to a silicon substrate covered with 300-nm-thick silicon dioxide on top of the surface. Conventional six terminal electrical contacts with a large gate electrode are made by using electron-beam lithography (EBL) followed by deposition of Ti/Au (5 nm/80 nm). The distance between the flake and the gate electrode is about 100 μm. The electrolyte used in this work is N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis (trifluoromethyl-sulfonyl) imide (DEME-TFSI), its freezing point is about 200 K, below which the DEME-TFSI becomes a glass-like solid where the ionic mobility falls to zero.[35] Before the drop of the electrolyte, we have patterned a 200-nm-thick hard-baked poly-methyl methacrylate (PMMA) photoresist as a separator to ensure that the electrolyte can only contact the gate electrode and channel. A schematic diagram of the device, i.e., the EDLT, is presented in Fig. 2(b). When a positive gate voltage V_g is applied at temperatures above 200 K, the EDLT allows a large number of electrons to accumulate in the channel, i.e., the FeSe flake. The temperature-dependent resistance of a flake at $V_g = 0\,\mathrm{V}$ is shown in Fig. 2(c), where the inset shows an optical image of the flake with patterned electrodes. With the decrease of temperature, R decreases almost linearly until it reaches a temperature $T_S = 78\,\mathrm{K}$, then presents an anomalous upturn. Here T_S in the flake is 12 K lower than that in the bulk. Further decreasing the temperature, a distinct drop of R occurs at 2.4 K due to the superconducting transition. Here T_c (2.4 K) of the FeSe flake is decreased significantly compared with the bulk (Fig. 1(b)), which is reasonably caused by the enhanced disorder in the flake during the process of device fabrication. It should be mentioned that T_c varies in different flakes, e.g., we have observed a $T_c = 6.36\,\mathrm{K}$ in another flake, as shown in the inset of Fig. 3(a) (square point).

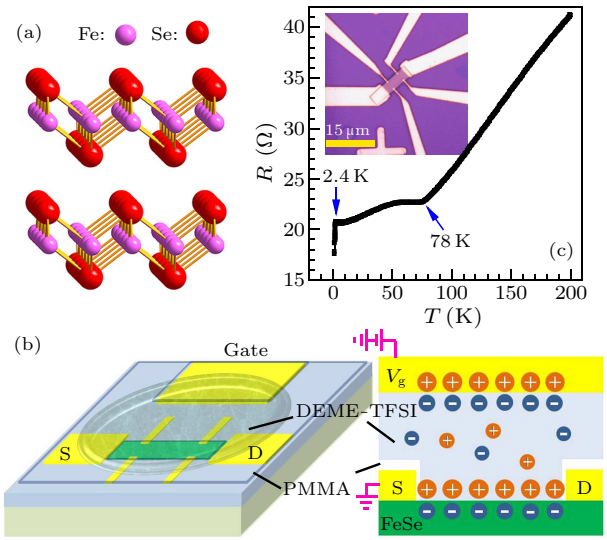

Fig. 2. (a) Schematic crystal structure of FeSe. (b) Left: diagram of our EDLT with a drop of ionic liquid electrolyte (DEME-TFSI) only contacting the FeSe channel and the gate electrode. The other Au electrodes and the Si/SiO_2 substrate are separated from the ionic liquid electrolyte by a layer of hard-baked photoresist (PMMA). Right: the cross section of the EDLT illustrating the charge accumulation under positive gate voltage V_g at the interface between the ionic liquid electrolyte and the FeSe channel. (c) Temperature-dependent resistance of the FeSe flake in the channel of the EDLT with a thickness of about 50 nm under $V_g = 0\,\mathrm{V}$. Inset: optical image of the FeSe flake on the Si/SiO_2 substrate with patterned electrodes.

The temperature-dependent R of the flake under different V_g is measured by a physical properties measurement system. During the measurement, V_g is set at 220 K (slightly above the freezing point) and keeps at this temperature for more than 30 min to make the EDLT reach equilibrium. The leakage current through the gate is less than 5 nA. Before switching to another V_g, the sample is warmed up to 220 K. After gating, the R–T curves of the flake present two distinct prop-

erties compared with the initial one ($V_g = 0$) as shown in Fig. 3(a).

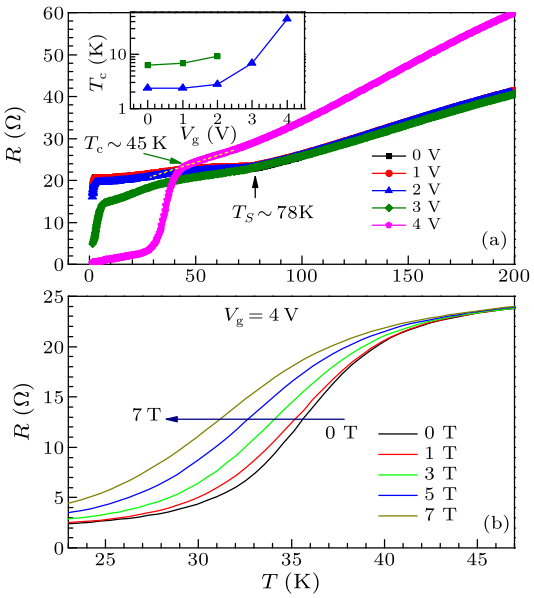

Fig. 3. (a) Temperature-dependent resistance of the FeSe-based EDLT under various V_g at zero field. The inset shows the onset temperature T_c as a function of V_g, where the square points are measured from another FeSe-based EDLT device. (b) Temperature-dependent resistance of the flake at $V_g = 4$ V under a set of perpendicular magnetic field.

First, the R–T curve shows a large resistance drop at 45 K under $V_g = 4$ V although a zero resistance is still not achieved at 2 K. To confirm that this drop is a superconducting transition, we have measured the T-dependence of R under various magnetic fields aligned perpendicular to the surface of the flake at $V_g = 4$ V, as shown in Fig. 3(b). The critical temperature of the resistance drop is indeed shifted gradually to low temperatures with the increase of magnetic fields, as expected for a superconductor. The value of T_c as a function of V_g is summarized in the inset of Fig. 3(a), where T_c of another flake with an initial $T_c = 6.36$ K ($V_g = 0$ V) is also presented (square point). The value of T_c increases slowly with V_g, and then rapidly to 45 K at $V_g = 4$ V, demonstrating that the superconductivity in FeSe can indeed be largely improved by electronic doping without intercalation. The second interesting feature is that, in the normal state, for $V_g < 3$ V, the electronic doping can only affect the magnitude of the resistance below $T_S = 78$ K, while T_S itself is insensitive to the gating voltage. For $V_g = 4$ V, the resistance in the whole temperature range has been tuned by gating, and the resistance at 200 K is about 1.4 times larger than that under other V_g. For clarity, the R–T curves obtained under different V_g are replotted in Fig. 4, where some curves are shifted vertically as indicated by arrows. It is seen that the upturn of R gradually vanishes as the increase of V_g, or in other words, the resistive anomaly has been suppressed effectively by electronic doping, indicating that this anomaly of R is very likely driven by the nematicity rather than the lattice degree of freedom only. It is well known that in the electrolyte gating process, the electrochemical reaction, which may affect the properties of the sample, is another factor that should be taken into account.[18] We believe that below 3 V, the electrochemical reaction could be ignored, for the resistance above 78 K is almost identical. If not, the occurrence of the electrochemical reaction should influence the resistance in the whole temperature range. Under $V_g = 4$ V, we cannot exclude the possibility of electrochemical reaction due to the change of resistance, while the possibility should be small because the leakage current under this voltage is still less than 5 nA. Therefore, the observation of the increase of superconductivity and the suppression of nematicity should be mainly induced by the effect of electrostatics.

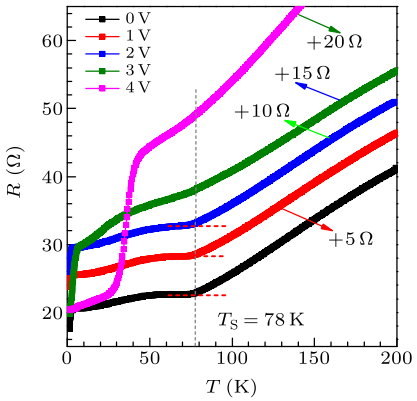

Fig. 4. The R–T curves obtained under different V_g of the FeSe-EDLT, which have been shown in Fig. 3(a). Some curves are shifted vertically to clarify as indicated by arrows.

To understand these gating-induced peculiar behaviors, we first focus our attention on the data below $V_g = 3$ V, and attribute the gating-induced variations of R to the multi-band nature of FeSe. It has been found that in FeSe, at high temperatures ($>T_S$), the dominant carriers are hole-type, while the electron-type carriers become significant at low temperatures.[36] Therefore, with the increase of V_g (≤ 3 V), the resistance decreases below T_S due to the increase of the electron-type carriers, while the doping concentration of electrons is still smaller compared with the hole concentration at high temperatures, and thus the resistance remains unchanged above T_S. While for $V_g = 4$ V, the population of electrons is increased rapidly, the hole bands might be suppressed so that the electron bands may dominate the conduction in the entire temperature range. The fact that the higher T_c of 45 K at $V_g = 4$ V is always accompanied by the disappearance of the electronic nematic phase below T_S suggests that the nematic order below T_S may play an important role in the formation of superconducting order, but it still needs further study.

In summary, we have investigated the

temperature-dependent resistance of the FeSe flake under various electronic doping levels by controlling the gate voltage V_g in an electric-double-layer transistor. It has been found that with the increase of V_g, T_c can be increased systematically and reach as high as 45 K at $V_g = 4$ V, which is about 5 times larger than that of the bulk. At the same time, the structural transition-induced resistive kink at T_S vanishes gradually, possibly due to the suppression of nematicity in FeSe. Control of the electronic doping allows control of the superconductivity and possibly the nematicity, which provides a new route for experimental observation of the possible hidden criticality in this two-band superconductor.[37] Also, it is of crucial importance for practical applications and a better understanding of the superconductivity in FeSe.

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