Journal of Superconductivity and Novel Magnetism (2020) 33:159–163
https://doi.org/10.1007/s10948-019-05300-8

ORIGINAL PAPER

In situ Magnetic Measurements of Ionic-Liquid-Gated Superconducting Films

Mingyang Qin[1,2] · Ruozhou Zhang[1,2] · Zefeng Lin[1,2] · Zhongpei Feng[1,2] · Xinjian Wei[1,2] · Sylvain Blanco Alvarez[3] · Chao Dong[4] · Alejandro V. Silhanek[3] · Beiyi Zhu[1] · Jie Yuan[1] · Qing Qin[2,4] · Kui Jin[1,2,5]

Abstract

By means of the ionic-liquid-gating technique (ILG), we have successfully tuned the critical transition temperatures (T_c) of superconducting FeSe and $La_{1.9}Ce_{0.1}CuO_4$ (LCCO) films, whose thicknesses largely exceed the working depth of electrostatic fields. The magnetic responses of gated samples were measured in situ using the homemade two-coil mutual inductance devices. Through the analysis of the imaginary part of the induced pick-up coil voltage, we conclude that the gating process influences the entire film thickness rather than just a few layers near the surface. This bulk effect suggests that the electrochemical effect rather than electrostatic effect plays a primary role in our experiments. These findings will shed new light on the mechanisms of ILG in tuning superconducting films.

Keywords Superconducting films · Ionic liquid gating · Two-coil mutual inductance technique · In situ magnetic measurements

1 Introduction

The ionic-liquid-gating technique is a powerful tool to manipulate material properties due to its prominent ability to modulate carrier concentration [1]. In particular, ILG could be employed to induce or modify the superconducting properties via electrostatic or electrochemical processes [2–9]. Whereas the electrostatic effect is a short-range effect typically restricted to the Thomas-Fermi screening length of a few angstroms [10], the electrochemical process caused by ion injection or removal does not remain confined to the layers near the film surface. Unfortunately, it is difficult to distinguish the two mechanisms only by resistivity measurement because the higher T_c channel will electrically short the lower T_c layers [11]. In contrast to that, the magnetic screening response delivers the information of the whole sample, which allows one to determine the volume fractions of superconducting phases with different T_c's [12]. As such, the ac magnetic measurement technique represents an appealing approach to discern the intrinsic processes of ILG. In this work, we used the ionic liquid to gate two prototypes of high T_c superconductors with thicknesses larger than 150 nm, while simultaneously inspecting in situ the magnetic response of the samples. We found out that the modulation of superconductivity takes place almost throughout the entire thickness of the film, implying that the electrochemical process plays a dominant role in the gating process.

2 Experimental Methods

The high-quality superconducting films were prepared by the pulsed laser deposition technique with a KrF excimer laser ($\lambda = 248$nm) (see more details in ref. [13, 14]). The 150-nm-thick FeSe film and 200-nm-thick LCCO film were grown on LiF and $SrTiO_3$ substrates, respectively. The (001)-oriented substrates are $5 \times 5 \times 0.5$ mm^3 in size.

✉ Kui Jin
kuijin@iphy.ac.cn

[1] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

[2] School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

[3] Experimental Physics of Nanostructured Materials, Q-MAT, CESAM, Université de Liège, B-4000 Sart Tilman, Liège, Belgium

[4] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

[5] Songshan Lake Materials Laboratory, Dongguan 523808, Guangdong, China

In the ILG experiment, the sample and Pt electrode were immersed in the ionic liquid, N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulphonyl)imide (DEME-TFSI) (see Figs. 1a and 3a). By applying a gating voltage V_G between the film and a gate electrode, we can induce ion accumulation near the film surface. As a consequence, the carrier concentration in the film is significantly changed, resulting in a shift of T_c. The gating temperatures for FeSe and LCCO are 245 K and 250 K, respectively.

The in situ magnetic measurements were achieved by our homemade two-coil mutual inductance (MI) devices, composed of a drive coil and a pick-up coil as described in ref. [15–18]. Both coils were sealed in a sapphire block with epoxy and aligned axially with the center of the sample. The devices were mounted on the 3 K platform of a Montana Instruments cryocooler. An ac current was applied to the drive coil using a Stanford Research SR830 lock-in amplifier. The drive current had a frequency of 30 kHz and an amplitude of 0.05 mA. The same lock-in amplifier with a reference phase of 0 was used to measure the induced pick-up coil voltage $V = V_x + iV_y$, where V_x and V_y represent the real and imaginary components, respectively. When the film becomes superconducting, the induced voltage V will change due to the diamagnetic response from the sample [19].

3 Experimental Results

In order to validate the accuracy of our device, we measured the four-terminal resistance simultaneously with the magnetic response of the pristine FeSe film using a *reflection*-type MI device (see schematic illustration in Fig. 1a). As shown in Fig. 1b, the zero-resistance critical temperature (T_{c0}) of the film is ~ 9 K and the width of superconducting transition is less than 1 K. The

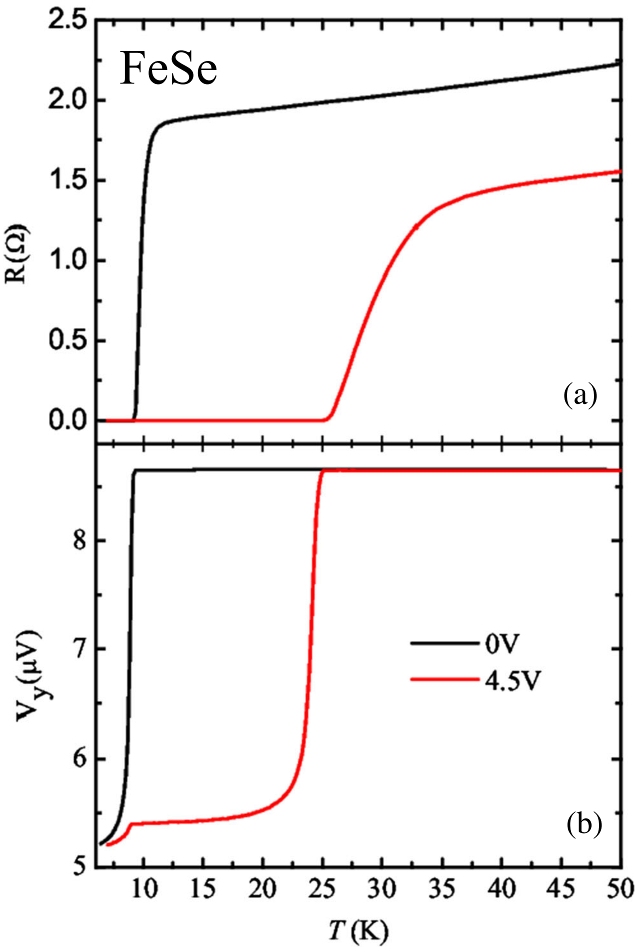

Fig. 2 **a** The resistance versus temperature for the FeSe film gated using DEME-TFSI containing lithium cations. At $V_G = 4.5$ V, the normal-state resistance of the film decreases and T_{c0} increases up to 25 K. **b** The V_y as a function of temperature. For $V_G = 4.5$ V, it displays two transitions at 9 K and 25 K, corresponding to the unaffected and gate-affected fractions of the sample, respectively

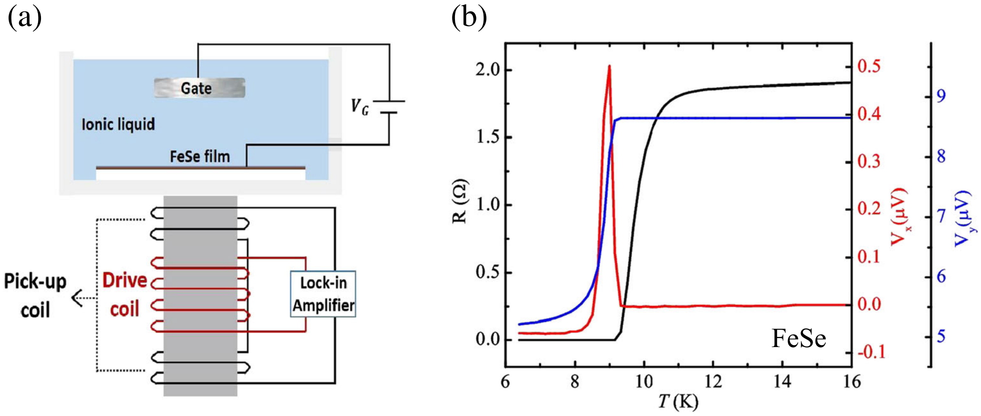

Fig. 1 **a** Schematic of the *reflection*-type MI device. Here, the drive and pick-up coils are placed on the same side of the FeSe sample. The pick-up coil consists of two oppositely wound sections. **b** Temperature dependence of the resistance and the pick-up coil voltage for the pristine FeSe film. The black curve is the temperature-dependent resistance measured using the standard four-terminal method. The red and blue curves are the real and imaginary components of the pick-up coil voltage, respectively

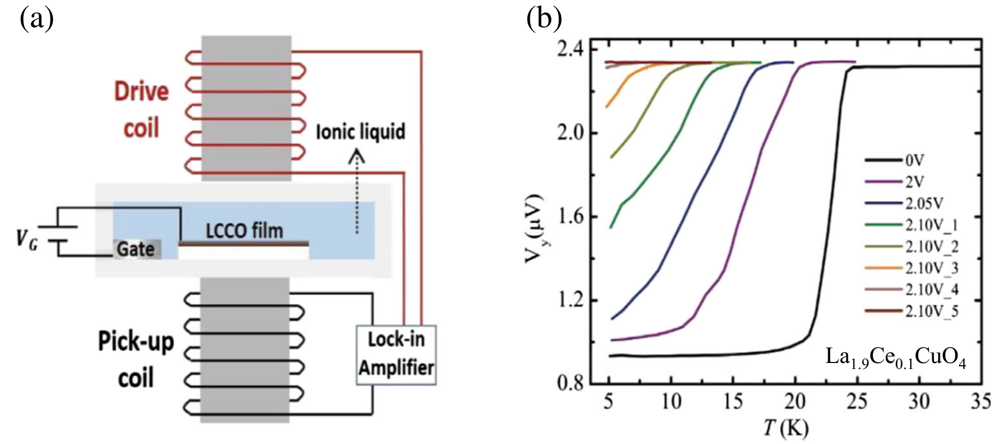

Fig. 3 **a** Schematic of the *transmission*-type MI device. Here, the drive and pick-up coils are placed on opposite sides of the LCCO sample. **b** Temperature dependence of V_y for an optimally doped LCCO film under different V_Gs. T_{c0} decreases as the gate voltage increases from 0 to 2.1 V. To exhibit that the electrochemical process is associated with duration time as well, the sample was gated at $V_G = 2.1$ V for five times (2.10V_1, 2.10V_2, 2.10V_3, 2.10V_4, and 2.10V_5)

strong diamagnetic screening, reflected as a sudden drop of V_y in the pick-up coil, emerges exactly at T_{c0} (see blue line). Correspondingly, V_x has a clear peak whose full width at half maximum is less than 0.5 K, indicating good film quality [20].

Figure 2 shows the temperature dependence of the resistance and the magnetic screening response of a gated FeSe film. Before applying the gating voltage, the T_{c0} of the FeSe film is ~ 9 K. Upon applying a $V_G = 4.5$ V, we observed a large shift in T_{c0} as evidenced from both $R(T)$ and $V_y(T)$ curves. Conceptually, the imaginary component V_y is mainly determined by the penetration depth or the superfluid density of the sample [21–23]. That is, the magnitude of V_y will reflect the volume fractions of different superconducting phases [24]. We note that there exists an inconspicuous transition in $V_y(T)$ around 9 K (see red line in Fig. 2b), which is ~ 6% of $\Delta V_y = V_y(T > T_c) - V_y(T_{\min})$. This implies that only a small fraction of the film remains unaffected by gating. Namely, most of the 150-nm-thick FeSe film underwent a transition into the higher T_c phase. Considering the fact that the film thickness is much larger than the Thomas-Fermi screening length, we can safely conclude that the electrochemical gating is the dominant mechanism ruling the overall response of the sample.

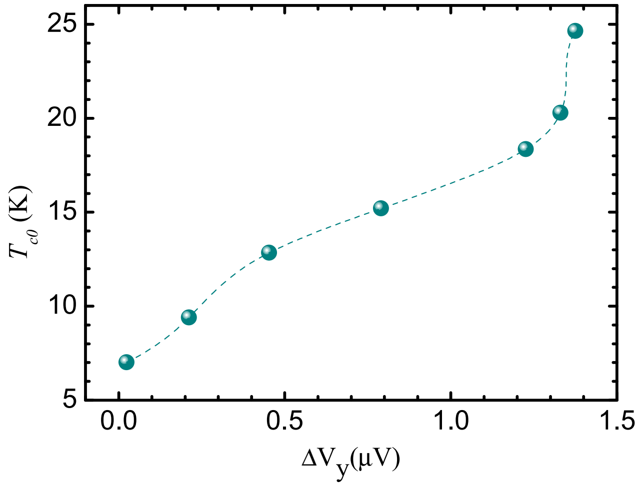

Fig. 4 T_{c0} as a function of $\Delta V_y = V_y(T > T_c) - V_y(T_{min})$ for a gated LCCO film, where ΔV_y has a positive correlation with the superfluid density. The dashed line is a guide for the eye

In order to further confirm that the electrochemical effect is commonly seen in the ILG experiments, the in situ magnetic measurements were also performed on the 200-nm-thick LCCO film using a *transmission*-type MI device (see schematic illustration in Fig. 3a). In principle, the electron density in the LCCO film will increase under a positive V_G, driving the optimally doped sample to the overdoped region and giving rise to a decrease of T_c. We indeed observe that the transition temperature shown on the $V_y(T)$ curve gradually moves to the lower temperature as the V_G changes from 0 to 2.1 V (see Fig. 3b). More importantly, no 24 K transition originating from the pristine film survived in the gated sample, indicating that the 200-nm-thick LCCO film has been fully tuned under the electrochemical process.

In addition, we extracted T_{c0} and $\Delta V_y = V_y(T > T_c) - V_y(T_{min})$ for each curve in Fig. 3b. As shown in Fig. 4, the larger the ΔV_y, the higher the T_{c0}. This implies that T_{c0} is positively correlated with the superfluid density, reminiscent of previous observations in copper oxide compounds [23, 25, 26]. Actually, we could expect to get the absolute value of the penetration depth and thereby the superfluid density by employing a *transmission*-type MI device [27–29]. Primary calibrations have been done on NbN films, which will be reported elsewhere.

4 Conclusions

We measured in situ the magnetic response of the ionic-liquid-gated FeSe and LCCO films using two types of the two-coil mutual inductance devices. By analyzing the imaginary component of the induced pick-up coil voltage, we conclude that our thick films have been almost fully tuned by ILG. This indicates that the gating process in our experiments should mainly be electrochemical rather than purely electrostatic. In fact, we provide a simple method to unveil the intrinsic process of ionic-liquid gating. Besides, such kind of device is promising in establishing a reliable database of penetration depth for superconductors and high-efficiency research on superconductivity [30].

Acknowledgments The authors would like to thank Ge He, Xingyu Jiang, and Liping Zhang for useful discussions about the manuscript.

Funding information This work was supported by the CAS Interdisciplinary Innovation Team, the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB25000000), the National Key Basic Research Program of China (Grant Nos. 2015CB921000, 2016YFA0300301, 2017YFA0303003, 2017YFA0302902 and 2018YFB0704102), the National Natural Science Foundation of China (Grant Nos. 11674374, 11834016 and 11804378), and the Key Research Program of Frontier Sciences, CAS (Grant Nos. QYZDJ-SSW-SLH001, QYZDB-SSW-SLH008, and QYZDY-SSW-SLH001).

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