Supplemental Material

$(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ superconductor: Ion-exchange synthesis of large single crystal and highly two-dimensional electron properties

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1. Experimental Methods

Crystal growth of $K_{0.8}Fe_{1.6}Se_2$ insulator precursor. High purity metallic K (Alfa Aesar, 99.95%) and powders of Fe (Sinopharm Chemical, 99.99%) and Se (Alfa Aesar, 99.999%) were used as the raw materials. First, the powders of Fe and Se in the molar ratio of 1.6:2 were ground and mixed, and then pressed into separate columnar shapes in a glove box filled with high purity argon gas. They were subsequently sealed in an evacuated quartz tube and heated at 630 °C for 16 hours. The obtained product was well ground again and mixed with a stoichiometric amount of K, before loaded into an alumina crucible. These manipulations were also performed in the glove box. The alumina crucible containing the materials was sealed in an evacuated thick-wall quartz tube. In order to avoid a too violent reaction due to the presence of metallic K, the quartz tube was first slowly heated to 70 °C at a rate of 30 °C/h and, after dwelled for 0.5 hour, continued to be heated to 90 °C at a much slower rate of 5 °C/h, dwelled again for 0.5 hour. It was then heated to a soaking temperature of 1050 °C. After soaked at 1050 °C for 24 hours, the melt was slowly cooled to 700 °C at a rate of 50 °C/h, followed with a natural cooling to the room temperature. Shiny nominal $K_{0.8}Fe_{1.6}Se_2$ crystal pieces, measuring up to 15 mm in size and orientating along its (001) crystal plane, were obtained through easy cleavages of the as-grown ingots. The chemical composition of the as-prepared crystals was very close to the nominal one, with K:Fe:Se = 0.76:1.64:2, based on ICP-AES analysis and no impurity phases were detected by powder XRD. These $K_{0.8}Fe_{1.6}Se_2$ crystal pieces were carefully stored in the glove box due to their air sensitivity until used as a kind of matrix for the novel hydrothermal ionic exchange reaction described below.

Hydrothermal ion-exchange synthesis of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ superconductor single crystal. The hydrothermal ionic exchange reactions were performed in stainless steel autoclaves of 25 ml capacity with Teflon liners. For each batch, 0.012 mol selenourea (Alfa Aesar, 99.97% purity), 0.00375 mol Fe powder (Alfa Aesar, 99.998% purity), 4 g $LiOHH_2O$ (Alfa Aesar, 99.996% purity) and one piece of nominal $K_{1.8}Fe_{0.6}Se_2$ matrix crystal were mixed with 5 ml de-ionized water and loaded into the autoclave. The autoclave was tightly sealed and heated at 120 °C for 96 hours. The eventually ion-exchange synthesized big single crystal was washed by de-ionized water for several times.

XRD phase identification and composition analysis. XRD measurements on powder samples and crystal pieces of both $K_{0.8}Fe_{1.6}Se_2$ and $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ were carried out at room temperature on a Rigaku Ultima IV (3KW) diffractometer using Cu K_α radiation, with a 2θ range of 5 ° ~ 80 ° and 2θ scanning steps of 0.02° (for the powder samples) or 0.01° (for the crystal pieces). The chemical composition of the matrix crystal (KFS245) was analyzed by ICP-AES, and that of hydrothermally ion-exchange synthesized crystal (FeSe11111) by both EDX and ICP-AES.

Magnetic and charge transport measurements. All magnetic measurements were conducted on a Quantum Design MPMS-XL1 system with a remnant field lower than 4 m Oe, except a high temperature (T > 300 K) measurement on a Quantum Design PPMS-9 system. Both the in-plane and out-of-plane electric resistivity and Hall resistivity data were collected with a Quantum Design PPMS-9 on crystal samples.

2. Supplemental Figures and Table.

The powder XRD patterns for $K_{0.8}Fe_{1.6}Se_2$ and $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ crystals are shown in Fig. S1.

Figure S2 shows the normalized in-plane electric resistivity of $K_{0.8}Fe_{1.6}Se_2$ precursor crystal.

Figure S3 shows the in-plane and out of plane electric resistivity of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ single crystal.

Figure S4 shows that the normal state Hall resistivity of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ single crystal is proportional to the applied magnetic field.

Figure S5 demonstrates perfectly linear field dependences of magnetization for $Li_{0.84}Fe_{0.16}OHFe_{0.98}Se$ single crystal at various temperatures under applied fields of and above 0.1 Tesla.

Table S1 lists the crystallographic data of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ resulting from the structural refinement based on single crystal XRD data collected at 180 K.

Figure S1

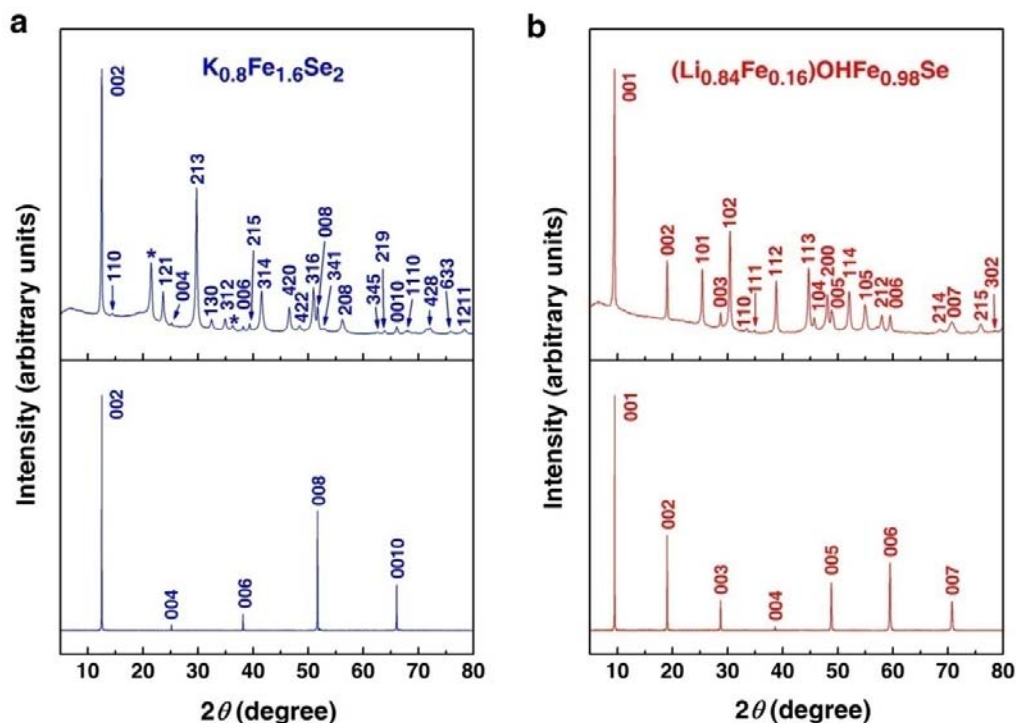**Figure S1**. The upper panels of **(a)** and **(b)** are the room-temperature powder XRD patterns for $K_{0.8}Fe_{1.6}Se_2$ and $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ crystals, respectively. No impurity phases are detected. The two peaks marked by a star in (a) are from a plastic film for sealing the very air sensitive powder sample. The corresponding XRD patterns on crystal pieces shown in Fig. 1b and c of the main part are also presented here in the lower panels for a direct comparison of the (00l) reflections. All the detected diffraction peaks for $K_{0.8}Fe_{1.6}Se_2$ sample can be well indexed on a known tetragonal unit cell [1] with refined a = 8.7248 (6) Å and c = 14.1339 (12) Å, while those for $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ sample on another known tetragonal unit cell [2-4] with refined a = 3.7827 (4) Å and c = 9.3184 (7) Å. The indexed hkl's for $K_{0.8}Fe_{1.6}Se_2$ agree with a body-centered lattice, with $h + k + l = 2n$ (n = integer), and those for $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ a primitive lattice, without integral systematic extinctions.
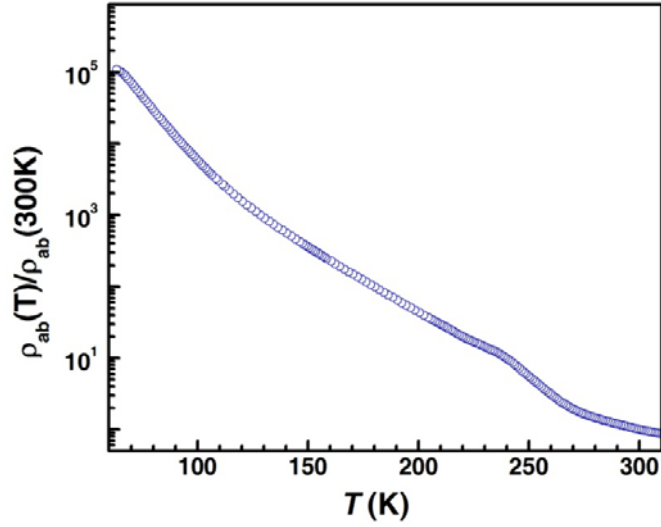
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Figure S2. The normalized in-plane electric resistivity of $K_{0.8}Fe_{1.6}Se_2$ precursor crystal as a function of temperature shows a typical insulating behavior.
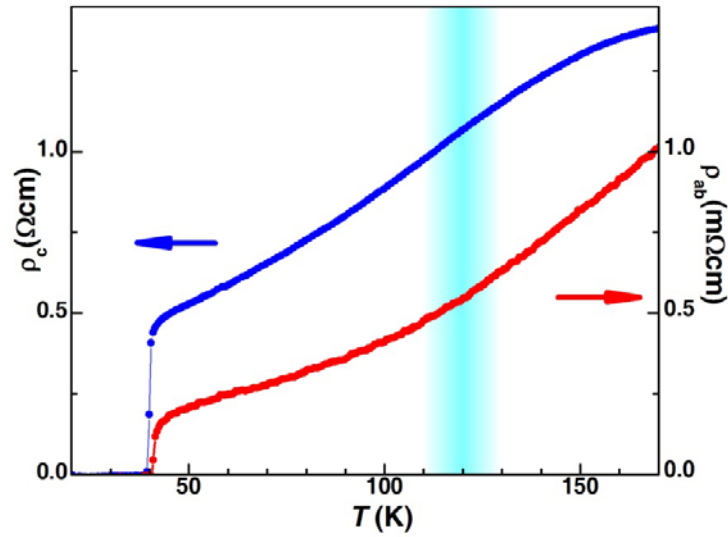

Figure S3. The in-plane (ρ_{ab}, red circles) and out of plane (ρ_c, blue circles) electric resistivity data of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ superconducting single crystal as functions of temperature, showing the significant slope change in ρ_{ab} around $T^*=120$ K compared to ρ_c.
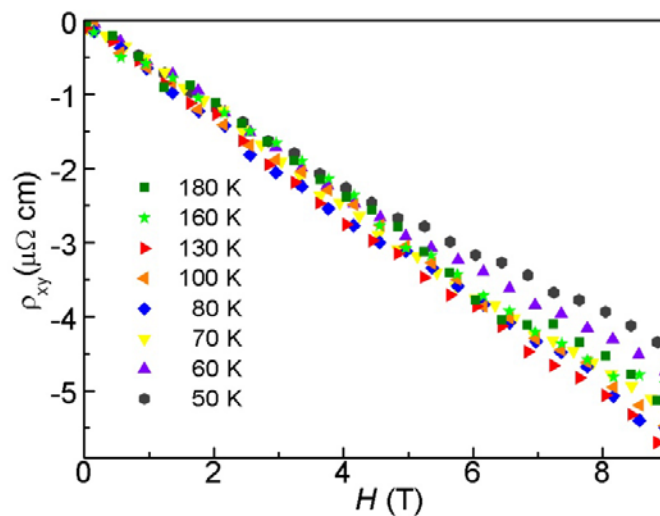
Figure S4. The meaured normal state Hall resistivity ρ_{xy} of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$ single crystal is proportional to the applied magnetic field along c-axis sweeping at fixed temperatures.

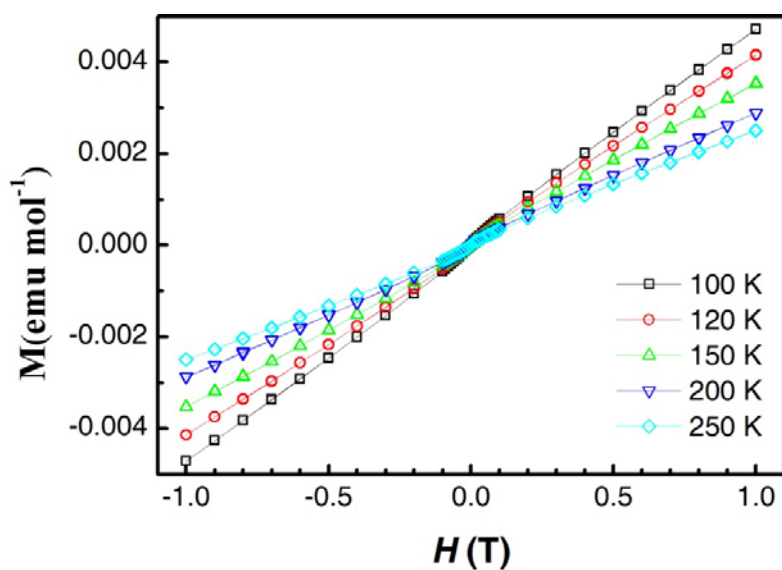**Figure S5**. Isothermal magnetizations of $Li_{0.84}Fe_{0.16}OHFe_{0.98}Se$ single crystal under applied fields between -1 to 1 Tesla at various temperatures. Although a slight s-shape appears below 0.1 tesla, no M-H loop is detectable. Under fields of and above 0.1 Tesla, the M vs. H curves display perfect linear behaviours.

Table S1. Crystallographic data of $(Li_{0.84}Fe_{0.16})OHFe_{0.98}Se$

Estimated chemical formula	$Fe_{2.28}H_2Li_{1.68}O_2Se_2$
Formula weight, *Z*	330.93, 1
Temperature (K), Wavelength (Å)	180.01(10), 0.7107
Crystal system, Space group	Tetragonal, *P4/nmm*
a (Å), c (Å), V (Å^3), ρ_{calcd} (g/cm^3)	3.7705(3), 9.215(2), 131.01(3), 4.194
Crystal size (μm), μ (mm^{-1}), θ range (^{o})	79×42×42, 20.034, 4.41 ~ 29.09
Meas., Uniq. Reflns., *Rint*	323, 109, 0.0260
R_1, *wR2*, GOF	0.0317/0.0339, 0.0810/0.0824, 1.047

Atomic positions and isotropic/anisotropic displacement parameters

Atom	W*yck.*	x	y	z	occup.	U_{iso}(Å^2)	U_{11}(Å^2)	U_{22}(Å^2)	U_{33}(Å^2)
Se	2*c*	0.25	0.25	0.66013(7)	1	0.0070(2)	0.0033(2)	0.0033(2)	0.0142(4)
Fe1	2*b*	0.75	0.25	0.5	0.980(3)	0.0057(3)	0.0010(3)	0.0010(3)	0.0151(5)
H	2*c*	0.25	0.25	0.1667(17)	1 (fixed)	0.021			
O	2*c*	0.25	0.25	0.0752(5)	1 (fixed)	0.0143(14)	0.0121(18)	0.0121(18)	0.019(3)
Li	2*a*	0.75	0.25	0	0.838(4)	0.0227(15)	0.0055(14)	0.0055(14)	0.057(4)
Fe2	2*a*	0.75	0.25	0	0.162(4)	0.0227(15)	0.0055(14)	0.0055(14)	0.057(4)

Selected bond lengths (Å) and angles (^{o})

Fe1-Se	2.3941(4) ×4	**Se-Fe1-Se**	103.90(3) ×2	112.328(14) ×4
Li/Fe2-O	2.0087(17) ×4	**O-Li/Fe2-O**	139.6(3) ×2	96.84(9) ×4

Single crystal XRD data were collected on an Agilent Supernova diffractometer with micro-focus Mo Kα radiation at 180 K. The data collection and reduction were done by CrysAlis program. Due to the strong absorption of X-ray and plate morphology, the big crystal was cut into small ones to avoid the difficulty for the absorption correction. The absorption correction was done by the gaussian method with $R_{int} = 0.026$.

References

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