Robust superconductivity and transport properties in (Li$_{1-x}$Fe$_x$)OHOFeSe single crystals

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The recently discovered (Li$_{1-x}$Fe$_x$)OHOFeSe superconductor with $T_c$ about 40K provides a good platform for investigating the magnetization and electrical transport properties of FeSe-based superconductors. By using a hydrothermal ion-exchange method, we have successfully grown crystals of (Li$_{1-x}$Fe$_x$)OHOFeSe. X-ray diffraction on the sample shows the single crystalline PbO-type structure with the c-axis preferential orientation. Magnetic susceptibility and resistive measurements show an onset superconducting transition at around $T_c$=38.3K. Using the magnetization hysteresis loops and Bean critical state model, a large critical current $J_c$ is observed in low temperature region. The critical current density is suppressed exponentially with increasing magnetic field. Temperature dependences of resistivity under various currents and fields are measured, revealing a robust superconducting current density and bulk superconductivity.

Since the discovery of high temperature superconductivity in LaFeAsO$_{1−y}$F$_y$ [1], at least eight different structures of iron-based superconductors have been found in succession [2-4]. Therein, FeAs-based as well as FeSe-based superconductors are two most common and important families. For the electric neutrality of FeSe-layers, by the normal high temperature sintering method, no spacer layer can be easily intercalated in between FeSe-layers, whose structure is similar to FeAs-layers. As far as we know, FeSe-based superconductors cover the phases of Fe$_{1+y}$Se, monolayer FeSe film on SrTiO$_3$ substrate, $A_x$Fe$_{2−y}$Se$_2$, $A_x$(NH$_3$)$_y$Fe$_{2−y}$Se$_2$ ($A$ is alkali or alkali-earth metal), Li$_x$X$_y$Fe$_{2−y}$Se$_2$ ($X$ is an organic molecule) and so on [2]. Among them, Fe$_{1+y}$Se single crystal has a low superconducting transition temperature of only about 8K at ambient pressure [6]. Although monolayer FeSe film with $T_c$ about 65K [7] indicates a possibility of high $T_c$ superconductivity in FeSe-based superconductors, it is made on oxide substrates like SrTiO$_3$ by MBE and is extremely sensitive to air [7,8]. The FeSe monolayer thin film without covering with FeTe layers will be damaged after being taken out of the vacuum chamber. So it is very hard to measure the magnetization and electrical transport properties in situ. For the $A_x$Fe$_{2−y}$Se$_2$ system with superconducting $T_c$ about 32K, single crystals can be grown by the high temperature sintering method [8,9]. However, the superconducting phase is always inter-grow with the insulating phase $A_{0.8}$Fe$_{1.6}$Se$_2$ (or called as the 245 phase) which has a $\sqrt{5} \times \sqrt{5}$ ordered structure of Fe-vacancies [10]. In the phase of $A_x$Fe$_{2−y}$Se$_2$, through the scanning electron microscopy (SEM) analysis, it was shown the the superconducting phase takes over only about 20% volume of the total phase. Thus, this phase separation clearly obstacles the investigation of intrinsic superconducting properties of the FeSe-based superconducting phase. Meanwhile, the $A_x$(NH$_3$)$_y$Fe$_{2−y}$Se$_2$ and Li$_x$X$_y$Fe$_{2−y}$Se$_2$ phases are very sensitive to air. Up to now, no single crystals of them are available for measurements.

The newly found superconductor (Li$_{1-x}$Fe$_x$)OHOFeSe can be conveniently synthesized by the hydrothermal method [12]. Comparing with other FeSe-based superconductors, the superconducting transition temperature $T_c$ of about 40K of (Li$_{1-x}$Fe$_x$)OHOFeSe is much higher than that in Fe$_{1+y}$Se and comparable to the monolayer FeSe thin film system [7]. It was shown that the (Li$_{1-x}$Fe$_x$)OHOFeSe phase has very little Fe-vacancies in the FeSe-layers with a measured ration about Fe:Se=0.98:1 [13]. Therefore, this system has some advantages over the $A_x$Fe$_{2−y}$Se$_2$ which has a great quantity of Fe-vacancy and accompanies with the phase separation. Moreover, by a hydrothermal ion-exchange method, one can obtain crystals of (Li$_{1-x}$Fe$_x$)OHOFeSe with large sizes and good quality [12]. And the single crystals can keep stable in the air for a period of time. Therefore, it is a good platform to study the intrinsic properties of FeSe-based superconductors, from which a further comprehension to the mechanism of iron-based superconductors can be acquired. In the (Li$_{1-x}$Fe$_x$)OHOFeSe systems, several measurements have already been employed, such as scanning tunneling microscopy (STM), angle resolved photoemission spectroscopy (ARPES), ionic field gating effect, etc. [13,14]. Our previous STM work [14], based on the high quality crystals, has clearly indicated the presence of double anisotropic gaps in (Li$_{1-x}$Fe$_x$)OHOFeSe, which mimics that in the monolayer FeSe thin film. Previously Dong et al. have done some electrical transport measurements on the single crystals [14]. Here, we show some further measurements on magnetic and electrical properties of (Li$_{1-x}$Fe$_x$)OHOFeSe, in order to know
how robust the superconductivity is, and whether it is bulk superconductive or it is phase separated, like in $A_2Fe_{2−y}Se_2$. The $(Li_{1−x}Fe_x)OHFeSe$ crystals investigated in this work are synthesized using a hydrothermal ion-exchange method, as reported previously[14]. Firstly, $K_{0.8}Fe_2Se_2$ crystals were grown using the self-flux method. Next, LiOH (J&K, 99% purity) liquid was dissolved in deionized water in a teflon-linked stainless-steel autoclave (volume 50mL). Then, iron powder (Aladdin Industrial, 99.99% purity), selenourea (J&K, 99.9% purity), and several pieces of $K_{0.8}Fe_2Se_2$ crystals were added to the solution. After that, the autoclave was sealed and heated up to 120 °C followed by staying for 40 to 50 hours. Finally, the $(Li_{1−x}Fe_x)OHFeSe$ crystals with a metallic-grey colored surface can be obtained by leaching. The X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advanced diffractometer with the Cu-Kα radiation. DC magnetization measurements were carried out with a Quantum Design instrument Physical Property Measurement System (PPMS). In measuring the resistivity, the current was switched from positive to negative alternatively in order to remove the contacting thermal power.

Fig. 1 shows the X-ray diffraction (XRD) spectra for the $(Li_{1−x}Fe_x)OHFeSe$ single crystal. The sample turns out to be very layered feature and can be easily cleaved. Only (00l) reflections can be seen in the XRD pattern, indicating highly orientation along the c-axis. The $l$ containing both odd and even numbers, which indicates the structural changing from $I4/mmm$ of $K_{0.8}Fe_2Se_2$ to $P4/nmm$ of $(Li_{1−x}Fe_x)OHFeSe$. The c-axis lattice constant is about 9.27 Å which is close to the reported results in $(Li_{1−x}Fe_x)OHFeSe$[12]. The inset shows the schematic structure of $(Li_{1−x}Fe_x)OHFeSe$ which has a typical layered structure of iron-based superconductors.

In Fig. 2 we present the temperature dependence of resistivity from 10K to 300K at zero field with a measuring current of 20μA. The resistivity decreases monotonically from room temperature to the lower temperature, which shows a highly metallic conductivity. The solid line shows the fit in the low temperature range by the formula $ρ(T)=ρ(0)+AT^n$ with $ρ(0)=5.65mΩ*cm$, $A=0.00016mΩ*cm/K^2$, $n=2.32$. The residual resistivity ratio, defined as $RRR=ρ(300K)/ρ(0K)≈7.9$, which is comparable to the previous reported value[14]. In the normal state, the temperature dependent resistivity here exhibits a positive curvature and the ratio $dρ/dT$ becomes smaller at high temperature. This is similar to $Fe_{1+y}Se$ single crystals[8], but quite different from some $A_2Fe_{2−y}Se_2$ single crystals[15], where a positive curvature at low temperature and a negative curvature at high temperature are generally observed. In the low temperature region, an abrupt resistivity drop can be clearly seen. Using the criterion of 90% of the normal state resistivity $ρ_n$, the onset superconducting transition temperature $T_{c,onset}$ is determined, which gives a value of about 38.3K. The inset presents the temperature dependence of magnetic susceptibility under an applied field of 200e measured in the zero-field-cooled (ZFC) and field-cooled (FC) modes. The sample for the magnetization measurements is one taken from the same batch of that for the resistive measurements. Similar to the resistivity curves, a sharp superconducting transition can be clearly seen at about 38K in the magnetic measurements. The transition temperature is higher than that in $A_xFe_{2−y}Se_2(A=K, Rb, Cs, Tl)$[18–21] and $Fe_{1+y}Se$ at ambient pressure[3]. Furthermore, the magnetic susceptibility measured in...
BaFe$_{2-x}$Co$_x$As$_2$. This value is at least one order of magnitude larger than that of K$_x$Fe$_{2-y}$Se$_2$ [18], which reveals the good quality and bulk pinning of our samples. The monotonically decreasing of $M$ with increasing field reveals the absence of fish-tail effect below 7T. For a further analysis, we calculate the critical current density using the Bean critical state model [22]. In this model, the superconducting critical current density $J_s$ is expressed by

$$ J_s = 20 \frac{\Delta M}{a(1 - a/3b)} $$

where $a(cm)$ and $b(cm)$ ($a \leq b$) are the in-plane sample sizes. The calculated results are illustrated in Fig. 3(b) in a semi-logarithmic scale. Obviously, the critical current density $J_s$ of (Li$_{1-x}$Fe$_x$)OHFeSe is weakly dependent with the magnetic field at temperatures below 9K. The critical current density $J_s$ is as large as 2.47 $\times$ 10$^5$ A/cm$^2$ at 2K in the low field limit. The magnitude is comparable to that in the optimally doped BaFe$_{2-x}$Co$_x$As$_2$, and much larger than 10$^4$ A/cm$^2$ in the Fe$_{1+y}$Se and K$_x$Fe$_{2-y}$Se$_2$ [22] crystals. At higher temperatures over 9K, $J_s$ decreases rapidly with increasing temperature and finally becomes vanishingly small after 25K. In addition, the $J_s$ in the high temperatures region is depressed exponentially with the increasing field. And it is interesting that this type of MHL shape looks very similar to those in many superconductors, but is very different from K$_x$Fe$_{2-y}$Se$_2$ [25] in which phase separations are expected.

In order to check the homogeneity of superconductivity in (Li$_{1-x}$Fe$_x$)OHFeSe crystals, we measured the temperature dependence of resistivity at various currents from 10K to 50K, and the data are presented in Fig. 4. The current $I$ is always applied in the ab-plane. It is found...
that when a larger measuring current is used, the normal state resistivity $\rho_n$ becomes slightly increased. The enhancement of the normal state resistivity may be induced by the local heating effect when the measuring current is high. It is interesting to note that the value of $T_c$ drops down slowly when the measuring current $I$ is increased from 0.001mA to 5mA (corresponding to the current density of about 0.0136 to 68A/cm$^2$). The current dependence of the superconducting transition temperature $T_c$ is shown in the inset of Fig. 4. Here, $T_{c_{\text{onset}}}$ is determined with the criterion of 90% $\rho_n$ and $T_{c}^0$ with 1% $\rho_n$. This weak suppression of $T_c$ by the measuring current density may suggest that the sample should not have the phase separation like that in K$_x$Fe$_2$−ySe$_2$. If phase separation would exist in the system, the superconducting transition and the related transition temperature should be strongly influenced by the measuring current density. This seems not the case here. This conclusion is also consistent with the large MHL width and $J_c$ value observed in the (Li$_{1-x}$Fe$_x$)OHFeSe crystal.

In Fig. 5 we show the temperature dependence of resistivity for the (Li$_{1-x}$Fe$_x$)OHFeSe crystal at zero field and various magnetic fields with the field directions parallel to c-axis, while the current is always applied in the ab-plane. As the applied field is increased, the superconducting transition temperature is suppressed gradually, and the normal state resistivity $\rho_n$ reveals a negative magnetoresistivity. This abnormal negative magnetoresistivity has not been found in the previous report[14], and might be caused by some magnetic impurities arising from the partial substitution of Li by Fe in the Li layers. A negative magnetoresistance is expected in a system with magnetic scattering centers. In addition, the magnetic field induces a clear broadening of the superconducting transition. This broadened transition is induced by the vortex motion since the (Li$_{1-x}$Fe$_x$)OHFeSe system has a large spatial distance between the FeSe layers and thus the anisotropy is quite high. However, the upper critical field $H_{c2}$ defined by 90% $\rho_n$ remains robust, suggesting a strong pairing strength since $H_{c2}$ is proportional to $\Delta^2_n$ with $\Delta_n$ the superconducting gap. Through our measurements of the magnetization and the resistive transitions under different magnetic fields and current, and the thoughtful analysis, we can conclude that the superconductivity is robust, uniform without the phase separation as that occurring in K$_x$Fe$_{2−y}$Se$_2$.

In summary, we successfully synthesized the (Li$_{1-x}$Fe$_x$)OHFeSe crystals with large size and good quality by the hydrothermal ion-exchange method. The magnetic hysteresis loops at various temperatures are measured which exhibit a symmetric shape, indicating a vortex bulk pinning property and thus bulk superconductivity. By using the Bean critical state model, we calculated the superconducting current density $J_c$ which amounts to $2.47 \times 10^5$ A/cm$^2$ at 2K and zero magnetic field. This value of $J_c$ of (Li$_{1-x}$Fe$_x$)OHFeSe is very large compared with that in K$_x$Fe$_{2−y}$Se$_2$. The latter was proved to have phase separation. In addition, we measured the temperature dependence of resistivity with different transport currents in (Li$_{1-x}$Fe$_x$)OHFeSe. It is found that the superconducting transition temperature drops down slightly when the measuring current density is increased from 0.0136 to 68A/cm$^2$, suggesting again the absence of phase separation. Finally the resistive transition has been measured under different magnetic fields. A clear broadening of the transition is observed, which indicates a strong vortex motion due to the high anisotropy of the system.

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