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Effect of varying iron content on the transport properties of the potassium-intercalated iron selenide $K_xFe_{2-y}Se_2$

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We report the successful growth of high-quality single crystals of potassium-intercalated iron selenide $K_xFe_{2-y}Se_2$ by the Bridgman method. The effect of iron vacancies on transport properties was investigated by electrical resistivity measurement. With varying iron content, the system passes from a semiconducting or insulating state to a superconducting state. Compared with superconductivity, the anomalous "hump" effect in the normal-state resistivity is much more sensitive to the iron deficiency. The electrical resistivity exhibits a perfect metallic behavior ($R_{300\,\mathrm{K}}/R_{35\,\mathrm{K}} \approx 42$) for the sample with little iron vacancies. Our results suggest that the anomalous hump effect in the normal-state resistivity may be due to the ordering process of the cation vacancies in this nonstoichiometric compound rather than to a magnetic or structure transition. A trace of superconductivity extending up to near 44 K was also detected in some crystals of $K_xFe_{2-y}Se_2$, which has the highest T_c of the reported iron selenides.

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The discovery of superconductivity in iron-based pnictides has attracted a great deal of research interest.[1] The PbO-type α-$FeSe_x$, which has an extremely simple structure with only $FeSe_4$ tetrahedral layers stacked along the c axis (the same as the $FeAs_4$ tetrahedral layers found in pnictides), was discovered subsequently superconducting at 8 K in samples prepared with Se deficiencies.[2] The superconductivity of $FeSe_x$ can be further enhanced up to 14 K by partially replacing Se with Te.[3] High-pressure studies at 4.5 GPa have dramatically yielded the superconductivity at 37 K.[4] Very recently, by intercalating potassium between the FeSe layers, i.e., $K_xFe_2Se_2$, superconductivity has been observed up to 30 K,[5] which is the same as those in optimal doped pnictides AFe_2As_2, where A is Ca, Sr, Ba, or Eu.[1] In iron pnictides, many open questions are waiting to be solved, especially the relationship between superconductivity, structural change, and magnetic order. Hence, systematic investigations on the superconductivity in $K_xFe_2Se_2$ can provide us some hints on the difference or common features between pnictide and selenide systems, and further shed light on the mechanism of superconductivity in Fe-based superconductors.

In this Brief Report, we report the successful growth of high quality single crystals of $K_xFe_{2-y}Se_2$ with different Fe-deficiencies using a Bridgman method and a systematic study on the effect of Fe-deficiency on transport properties. We find that the system displays unique properties, such as electrical resistivity ranging from superconducting to semiconducting or insulating, which can be tuned by adjusting the growth conditions. Compared with superconductivity, the anomalous "hump" effect in the normal-state resistivity in superconducting samples is much more sensitive to the iron deficiency. We speculate that the anomalous hump effect in the normal-state resistivity may be due to the ordering process of the cation vacancies in this nonstoichiometric compound rather than a magnetic or structure transition. Furthermore, a trace of superconductivity extending up to near 44 K was detected in some batches of $K_xFe_{2-y}Se_2$, which has the highest T_c of the reported iron selenides. The appropriate nominal compositions and growth conditions are important key parameters in modulating transport properties in $K_xFe_{2-y}Se_2$.

All the samples were prepared by the Bridgman method. $Fe_{1+z}Se$ was first synthesized as a precursor by reacting Fe powder with Se powder at 750 °C for 20 h. K pieces and $Fe_{1+z}Se$ powder were put into an alumina crucible with nominal compositions $K_xFe_{2+z}Se_2$ ($0.6 \leqslant x \leqslant 1.0$; $0 \leqslant z \leqslant 0.3$). The alumina crucible was then sealed into a tantalum tube with argon gas under a pressure of 1.5 atmosphere; then, the sealed tantalum tube was vacuum sealed into a quartz tube. In some cases, the alumina crucible was directly sealed into a thick walled quartz tube with Ar under a pressure of 0.4 atmosphere. The sample was put in a box or tube furnace and slowly heated to 1050 °C and held there for 2 h; then, it was cooled to 750°C from over 60 to 200 h to grow the single crystals. The obtained crystals with sizes up to $8 \times 8 \times 5$ mm have the form of platelets with shiny surfaces. These crystals were characterized by x-ray diffraction (XRD). The elemental compositions of the obtained crystals were checked by inductively coupled plasma (ICP) analysis. The resistivity was measured by a standard four-probe method. The DC magnetic susceptibility was measured with a magnetic field of 10 Oe. These measurements were performed down to 2 K in a physical property measurement system (PPMS) of quantum design with the vibrating sample magenetometer (VSM) option provided.

Figure 1 shows the x-ray-diffraction pattern of $K_{0.84}Fe_{1.59}Se_2$ with the 00ℓ ($\ell = 2n$) reflections, which is consistent with previous reports. The lattice constant $c = 14.15$ Å was calculated from the higher-order peaks, comparable to the result from powder diffraction.[5] A picture of the grown crystal $K_{0.84}Fe_{1.59}Se_2$ is presented in the inset of Fig. 1.

First, we investigated the relation between K concentration and the behavior of the resistivity. Figure 2(a) shows clearly that with the increase in K doping, the system evolves from a semiconductor-like (superconducting) to a typical structure (the same as was described in a previous report) with a broad peak around 140 K; then, it becomes a semiconductor-like or insulator-like system without superconducting observed

TABLE I. Nominal composition in the starting materials, the chemical composition for the grown crystals determined by ICP elemental analysis, the superconducting transition temperature T_c^{zero}, and the hump temperature T_{hump} in resistivity.

Nominal composition	Chemical composition (ICP)	T_c^{zero} (K)	T_{hump} (K)
$K_{0.6}Fe_2Se_2$	$K_{0.77}Fe_{1.60}Se_2$	25.9	
$K_{0.8}Fe_2Se_2$	$K_{0.84}Fe_{1.59}Se_2$	30.2	143
$K_{0.8}Fe_{2.1}Se_2$	$K_{0.83}Fe_{1.60}Se_2$	30.7	174
$K_{0.8}Fe_{2.2}Se_2$	$K_{0.85}Fe_{1.62}Se_2$	31.2	225
$K_{0.8}Fe_{2.3}Se_2$	$K_{0.82}Fe_{1.63}Se_2$	31.5	
$K_{1.0}Fe_2Se_2$	$K_{0.99}Fe_{1.48}Se_2$		

inside. Based on the composition analysis by ICP (see Table I) for the crystals grown from different starting compositions, we can see that as the content of K was increased from 0.8 to 1.0, the iron content in the obtained single crystals systemically decreased from 1.6 to 1.5 and the superconductivity finally disappeared. This indicates that a high deficiency of Fe has a major detrimental effect on transport properties.

Second, we systematically changed the concentrations of Fe ions with K fixed to study the transport behavior. Figure 2(b) shows the temperature dependence of resistivity for $K_xFe_{2-y}Se_2$ crystals between 2 and 300 K. It is obvious that the behavior of the electrical transport has changed with the increase of Fe concentrations (corresponding to the decrease of Fe deficiency.) When the Fe deficiency is large, the resistivity curve possesses an obvious metal-insulator (MI) transition at around 140 K. At high temperatures, the sample shows semiconductor-like behaviors, while below the transition temperature, it presents a metallic behavior.[5] With increasing Fe concentration, the hump diminishes gradually, its position shifts to high temperature, and finally it vanishes in the sample with chemical composition $K_{0.82}Fe_{1.63}Se_2$. Here, the electrical resistivity exhibits a perfectly metallic behavior. However, the superconducting critical temperature T_c increases slightly (less than 0.8 K) with decreasing Fe deficiency. We note that there is not any anomaly in the temperature dependence of the magnetic susceptibility, and there is also no structural phase transition occurring over the temperature range from 60 to 300 K.[6] The semiconductor-like-metal-like transition may be attributed to the ordering process of the cation vacancies in the nonstoichiometric compound of $K_xFe_{2-y}Se_2$, and it significantly influences the electrical resistivity. The similar issues concerning order-disorder phenomena have been discussed in the transition metal carbides and the high-T_c compounds, where the ordering of the vacancies play an important role in controlling the normal-state resistivity and superconductivity.[7,8] Interestingly, the temperature dependence of electrical resistivity under high pressure has been investigated by Guo *et al.*,[6] where the hump was successively suppressed by applying pressure, and the superconductivity was destroyed simultaneously, in contrast to the results of our study. There is no obvious correlation between the superconducting critical temperature and the broad hump.

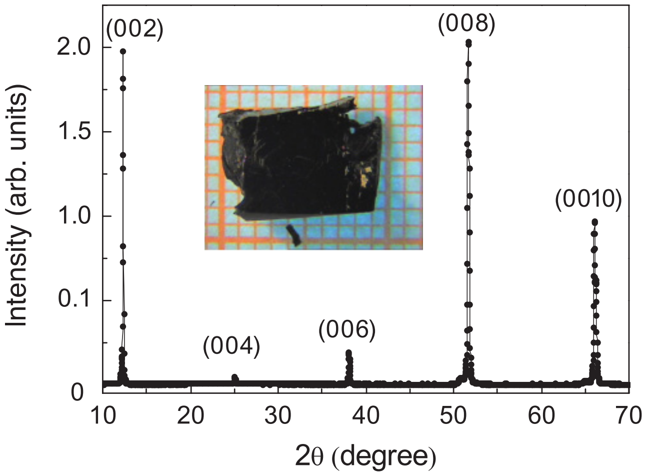

FIG. 1. (Color online) The x-ray-diffraction pattern of a $K_{0.84}Fe_{1.59}Se_2$ crystal with mainly (00ℓ) reflections indicates that the crystal is cleaved along the *ab* plane. Inset shows the typical photography of the grown $K_{0.84}Fe_{1.59}Se_2$ crystal.

Figure 3(a) presents the magnetic susceptibility as a function of the temperature from 3 to 35 K for the sample with chemical composition $K_{0.82}Fe_{1.63}Se_2$ under the magnetic field of 10 Oe. The zero-field cooling (ZFC) and field cooling (FC) susceptibility both show sharp transitions at around 32 K. From the ZFC, it can be estimated that the superconducting volume fraction at 10 K is about 100%, which demonstrates the bulk superconductivity in the samples. The inset of Fig. 3(a) shows the typical resistivity curve of $K_{0.82}Fe_{1.63}Se_2$, which clearly shows the metallic behavior with a high residual resistivity ratio ($R_{300\text{ K}}/R_{35\text{ K}} \approx 42$).

Figures 3(b) and 3(c) show the behavior of resistivity of $K_{0.82}Fe_{1.63}Se_2$ in an external magnetic field up to 12 T. In Fig. 3(b), the applied field is within the *ab* plane ($H\|ab$) while in Fig. 3(c), the applied field is parallel to the *c* axis ($H\|c$). We see the superconducting transition is suppressed in both conditions, but the effect of the magnetic field is much larger when the field is applied along the *c* axis of the single crystals instead of within the *ab* plane. The corresponding upper critical field H_{c2} as a function of temperature obtained from a determination of the midpoint of the resistive transition is plotted in Fig. 3(d). The curves are steep with slopes $-dH_{c2}/dT|_{T_c} = 7.20$ T/K for $H\|ab$ and $-dH_{c2}/dT|_{T_c} = 2.17$ T/K for $H\|c$. According to the Werthamer-Helfand-Hohenberg (WHH) formula,[9] $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$ and taking 32 K as T_c, the upper critical fields are estimated to be $H_{c2}^{\text{ab}} = 159$ T and $H_{c2}^{c} = 48$ T. The ratio of $H_{c2}^{\text{ab}}/H_{c2}^{c}$ is about 3.3, which is consistent with previous reports.[10]

One issue we want to point out is that a trace of superconductivity with T_c up to 44 K has been observed in several batches of samples with nominal

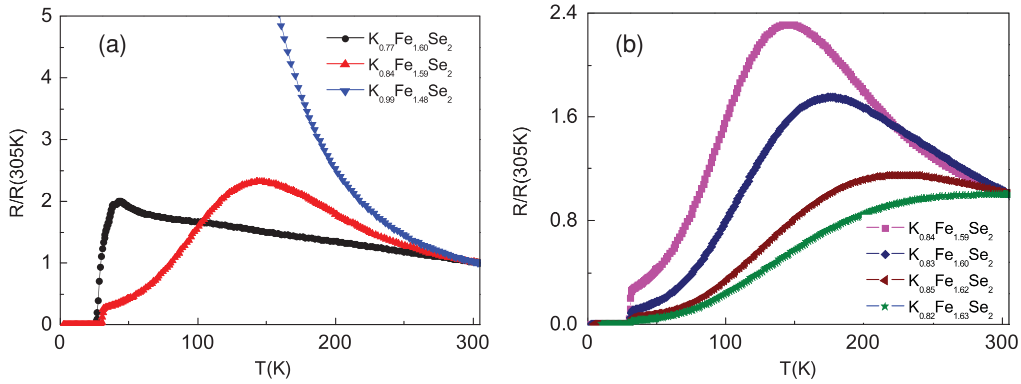

FIG. 2. (Color online) Temperature dependent resistivity of grown $K_xFe_{2-y}Se_2$ crystals. Different electronic transport properties demonstrated by the resistivity curves have been observed.

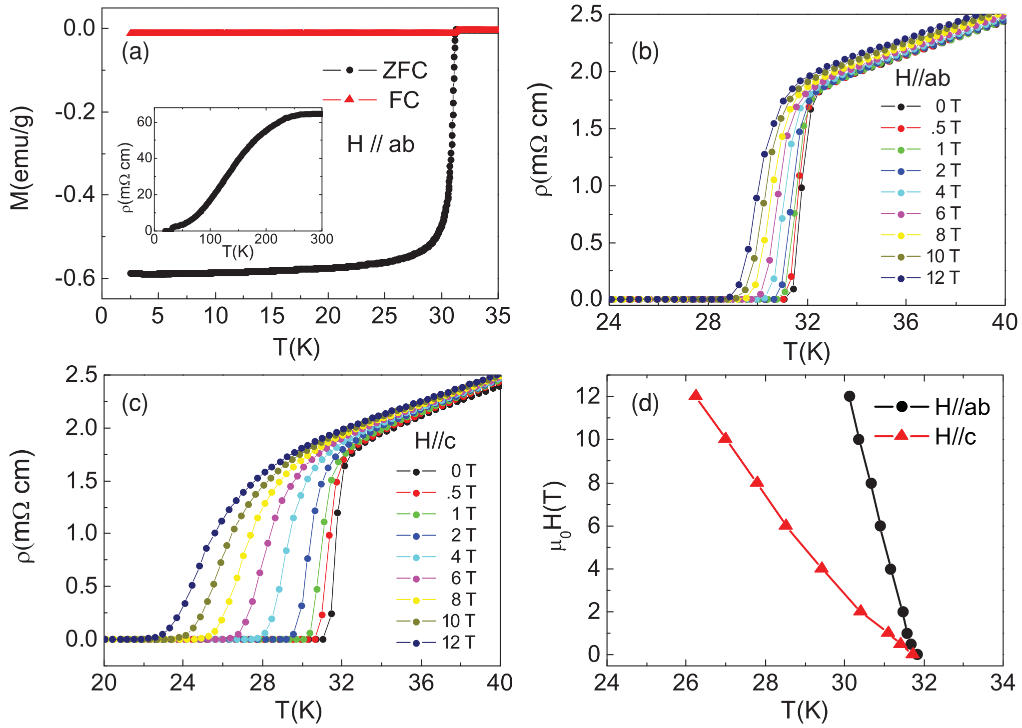

FIG. 3. (Color online) (a) DC magnetic susceptibility of the $K_{0.82}Fe_{1.63}Se_2$ crystal. Inset shows the temperature dependence of resistivity between 300 and 20 K. The temperature dependence of resistivity for the $K_{0.82}Fe_{1.63}Se_2$ crystal with the applied field (b) parallel and (c) perpendicular to the *ab* plane. (d) Temperature dependence of $H_{c2}(T)$ for the $K_{0.82}Fe_{1.63}Se_2$ crystal.

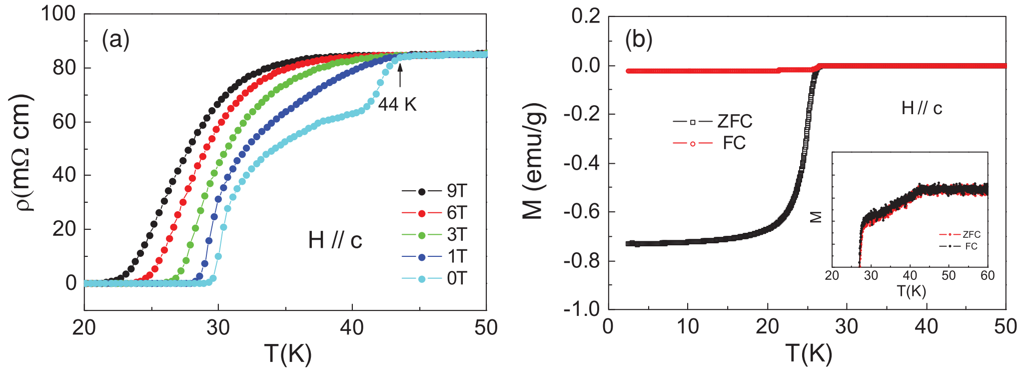

FIG. 4. (Color online) (a) Temperature dependence of the resistivity under different magnetic fields for a selected crystal grown from the starting composition $K_{0.8}Fe_2Se_2$. (b) Magnetic susceptibility of the the same samples. Inset is the enlarged part from (b), which clearly indicates the transition around 44 K.

composition $K_{0.8}Fe_2Se_2$. Figure 4(a) shows the temperature dependence of the electrical resistivity in the low-temperature region. It is clear that there exist two transition steps on the resistivity curve measured under zero field, one at about 38 K and another at about 44 K. To verify whether the transition at 44 K is due to superconductivity, we measured the field dependence of resistivity and observed the resistivity curves change at around 44 K, and the kink shifts to low temperature with increasing magnetic fields. The fact that the transition at 44 K was suppressed slowly by applying the magnetic fields indicates the superconductivity is intrinsic. Magnetic susceptibility has also been measured on the same samples, and it is clearly shown in the Fig. 4(b) that once the temperature is lower than around 44 K, the magnetization begins to decrease and the rate of decrease greatly increases once the temperature is lower than 28 K, which corresponds to the transition temperature of zero resistivity. Hence, it raises one question: Where does the superconductivity come from, the $K_xFe_{2-y}Se_2$ (122) phase with super-high quality or another phase? A detailed characterization of the superconducting phase is in progress.

In conclusion, we have successfully grown series of single crystals $K_xFe_{2-y}Se_2$ with different Fe vacancies. A trace of superconductivity extending up to near 44 K was also observed in some $K_xFe_{2-y}Se_2$ crystals, which has the highest T_c of the reported iron selenides. The anomalous semiconductor-like-metal-like transition is observed only in the sample with the high level of Fe vacancies. We speculate that the anomaly is associated with the ordering of the framework vacancies, which significantly influences the electrical resistivity. The more-ordered phase showing a large reduction in residual resistivity is due to the reduction of electron-vacancy scattering. A more detailed study is needed in order to better understand the correlation of superconductivity with the anomalous metal-insulator transition.

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