Superconductivity at 32 K in single crystal Rb$_{0.78}$Fe$_2$Se$_{1.78}$

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(Dated: December 30, 2010)

We successfully grew the high-quality single crystal of Rb$_{0.78}$Fe$_2$Se$_{1.78}$, which shows sharp superconducting transition in magnetic susceptibility and electrical resistivity. Resistivity measurements show the onset superconducting transition ($T_c$) at 32.1 K and zero resistivity at 30 K. From the low-temperature iso-magnetic-field magnetoresistance, large upper critical field $H_{c2}(0)$ has been estimated as high as 180 T for in-plane field and 59 T for out-of-plane field. The anisotropy $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ is around 3.0, right lying between those observed in K$_x$Fe$_2$Se$_2$ and Cs$_x$Fe$_2$Se$_2$.

PACS numbers: 74.70.Xa, 75.30.Gw, 72.15.-v

The newly discovered iron-based superconductors have attracted worldwide attention in past three years$^{1-5}$ because of their high superconducting transition temperature ($T_c$ as high as 55 K) and the fact that superconductivity emerges proximity to magnetically ordered state$^{6}$ The fact that superconductivity in iron-pnictide compounds is closely related to magnetic correlations inspires researchers tending to connect them with the high-$T_c$ cuprates, in which superconductivity is realized by suppressing the antiferromagnetic Mott-insulating state, and attempting to understand the superconducting mechanism in the same theoretical scenario for the both families. Up to now, a variety of Fe-based superconductors, such as ZrCuSiAs-type LnFeAsO ($Ln$-1111, $Ln$ is rare earth elements)$^{6,7}$, ThCr$_2$Si$_2$-type $Ae$Fe$_2$As$_2$ ($Ae$-122, $Ae$ is alkali earth elements)$^{8}$, Fe$_2$As-type $AF$eAs ($A$-111, $A$ is Li or Na)$^{8,10}$ and anti-PhO-type Fe(Se,Te) (11)12, have been discovered. Antiferromagnetic spin density wave instability usually exists in the parent compound of superconducting Ln-1111 and Ae-122, and even coexists with the superconductivity in slightly doping levels of Ln-1111, Ae-122 and A-111. While for 11 phase, the magnetism is quite complicated and its relationship to superconductivity remains more unrecognized.

All of the above mentioned Fe-based superconductors have a common structural feature with the edge-sharing FeAs$_4$ (FeSe$_4$) tetrahedra forming FeAs (FeSe) layers. The superconductivity in these compounds is thought to be intimately associated with the height of anion from Fe layer$^{11}$. FeAs-based compounds usually possess cations or building block between the FeAs layers, while Fe(Se,Te) family has an extremely simple structure with only FeSe layers stacking along c-axis without other cations between them.$^{12}$ High pressure has been used to change the height of anion from Fe layer in Fe(Se,Te). Especially, $T_c$ can reach 37 K (onset) under 4.5 GPa from 8 K in FeSe$^{13}$ with a pressure dependent ratio of $T_c$ as large as $dT_c/dP \sim 9.1$ K/GPa, which is the highest pressure effect among all the Fe-based superconductors.$^{13}$ Tl has been attempted to intercalate into between the FeSe layers to change the local structure of FeSe family. However, an antiferromagnetic ordering forms at the temperature as high as 450 K$^{14}$ and no superconductivity is observed in TlFe$_2$Se$_2$. Very recently, the alkali atoms K and Cs are successfully intercalated into between the FeSe layers, and superconductivity has been enhanced from $T_c = 8$ K of pure FeSe to 30 K and 27 K (onset) without any external pressure.$^{15-18}$ It indicates that $T_c$ in FeSe family can really be enhanced by intercalating cations into between the FeSe layers. In this communication, we successfully grew the single crystals of a new superconductor Rb$_2$Fe$_2$Se$_2$ by using self-flux method. The crystals showed the onset $T_c$ of 32.1 K and zero resistivity at about 30 K. Nearly 100% superconducting volume fraction was observed through the zero-field-cooling (ZFC) magnetic susceptibility measurements. Upper critical field $H_{c2}(0)$ was estimated from iso-magnetic-field magnetoresistance as high as 180 T with field applied in ab-plane and 59 T with field applied along c-axial.

Single crystals Rb$_2$Fe$_2$Se$_2$ were grown by self-flux method. Starting material FeSe was obtained by reacting Fe powder with Se powder with Fe: Se = 1: 1 at 700°C for 4 hours. Rb pieces and FeSe powder were put into a small quartz tube with nominal composition of Rb$_{0.8}$Fe$_2$Se$_2$. Due to the high activity of Rb metal, the single wall quartz tube will be corrupted and broken during the growth procedure. Therefore, double wall quartz tube is used here. The small quartz tube was sealed under high vacuum, and then was put in a bigger quartz tube following by evacuating and being sealed. The mixture was heated to 980°C in 10 hours and kept for 4 hours, and then melt at 1080°C for 2 hours, and later slowly cooled down to 780°C with 6°C/hour. After that, the temperature was cooled down to room temperature by shutting down the furnace. The obtained single crystals show the flat shiny surface with dark black color. The crystals are easy to cleave and thin crystals with
thickness less than 100 µm can be easily obtained.

The single crystals were characterized by X-ray diffraction (XRD), Energy dispersive X-ray (EDX) spectroscopy, magnetic susceptibility, and electrical transport measurements. Powder XRD and single crystal XRD were performed on TTRAX3 theta/theta rotating anode X-ray Diffractometer (Japan) with Cu Kα radiation and a fixed graphite monochromator. Magnetic susceptibility measurements were carried out using the Quantum Design MPMS-SQUID. The measurement of resistivity and magnetoresistance were done on the Quantum Design PPMS-9.

Figure 1 shows the X-ray single crystal diffraction (Fig. 1a) and powder XRD (Fig. 1b) after grounding the single crystals into powder. Only (00l) reflections were recognized in Fig. 1a, indicating that the crystals of Rb₂Fe₂Se₂ were perfectly grown along c-axis. From the powder XRD patterns in Fig. 1b, the lattice constants were calculated based on the symmetry I4/mmm with lattice parameters \( a = 3.925 \) Å and \( c = 14.5655 \) Å. Lattice constants of \( a \) and \( c \) lie between those of K₂Fe₂Se₂ and Cs₂Fe₂Se₂, respectively. It is consistent with the expectation based on variation of the radius of the K, Rb, Cs ions (K 1.51Å, Rb 1.63Å, Cs 1.78Å). The actual compositions of the crystals were determined by EDX using an average of different 4 points. It is found that the composition is homogeneous in the crystals. The actual composition is Rb: Fe: Se = 0.78: 2: 1.78, indicating the existence of deficiencies at K sites and Se sites. Such deficiency is similar to our previous report for K₂Fe₂Se₂ with the magnetic field of 5 T applied parallel and perpendicular to the c-axis from 10 K to 400 K.

Figure 2 shows magnetic susceptibility as a function of temperature below 35 K for single crystal Rb₀.₇₈Fe₂Se₁.₇₈ under a magnetic field of 10 Oe. The zero-field-cooling (ZFC) and field cooling (FC) susceptibilities show that the superconducting shield begins to emerge at about 30.6 K and then show a sharp transition. The ZFC magnetic susceptibility becomes saturation below 10 K, indicating high quality of single crystal. The superconducting volume fraction estimated from the ZFC magnetization at 4 K is 100%. All of these demonstrate a bulk superconductivity nature in Rb₀.₇₈Fe₂Se₁.₇₈ single crystals.

Figure 3 shows the magnetic susceptibility at 5 T for single crystal Rb₀.₇₈Fe₂Se₁.₇₈ with the magnetic field along and perpendicular to c-axis.

[FIG. 1: (Color online) X-ray diffraction patterns for Rb₂Fe₂Se₂. (a): The single crystal X-ray diffraction pattern; (b): X-ray diffraction pattern of the powdered Rb₂Fe₂Se₂.]

[FIG. 2: (Color online) Temperature dependence of the Zero-field cooling and field cooling susceptibility taken at 10 Oe with the magnetic field parallel to the ab-plane for the single crystal Rb₀.₇₈Fe₂Se₁.₇₈.]

[FIG. 3: (Color online) The magnetic susceptibility at 5 T for single crystal Rb₀.₇₈Fe₂Se₁.₇₈ with the magnetic field along and perpendicular to c-axis.]

[13]but is sharply in contrast to other reports of both K and Fe deficiencies in K₂Fe₂Se₂ and Cs₂Fe₂Se₂. [14]
K. At low temperature, superconducting trace can still be found because of a drop of susceptibility. When magnetic field was applied along c-axis, the magnetic susceptibility gradually decreases with decreasing the temperature. The susceptibility shows a minimum at about 120 K with the magnetic field applied within ab-plane. Above 120 K, the susceptibility monotonically increases with increasing temperature; while gradually increases with decreasing temperature down to about 40 K just above superconducting transition temperature. Although the in-plane $\chi(T)$ shows a minimum 120 K above $T_c$, the magnitude of the susceptibility only changes by less than 2.5 % in the temperature range from 40 K to 400 K. Such behavior of susceptibility in Rb$_{0.78}$Fe$_2$Se$_{1.78}$ is exactly the same as that observed in Cs$_{0.86}$Fe$_{1.66}$Se$_2$. Therefore, such peculiar behavior of susceptibility is common feature. The continuous decrease of susceptibility with decreasing the temperature suggests a strong antiferromagnetic spin fluctuation. Such spin fluctuation could be related to the superconductivity.

Figure 4 shows the in-plane resistivity as the function of temperature for the Rb$_{0.78}$Fe$_2$Se$_{1.78}$. The Rb$_{0.78}$Fe$_2$Se$_{1.78}$ shows the semiconductor-like behavior at the high temperature, and displays a maximum resistivity at about 150 K, and shows a metallic behavior below 150 K and a superconducting transition at about 32 K. Similar resistivity has been observed in K$_x$Fe$_2$Se$_2$ and K$_2$Fe$_2$Se$_2$. It seems that the resistivity behavior observed here is common feature. The temperature corresponding to the maximum resistivity in Rb$_{0.78}$Fe$_2$Se$_{1.78}$ is higher than that for K$_2$Fe$_2$Se$_2$ reported by Guo et al. (around 100 K) and by Ying et al. (around 120 K), while less than that reported by Mizuguchi et al. (ca. 200 K). The maximum resistivity in Rb$_{0.78}$Fe$_2$Se$_{1.78}$ crystal here (~37 $\Omega$ cm) is much larger than that of K$_2$Fe$_2$Se$_2$ in previous report (~3 $\Omega$ cm). The temperature of the maximum resistivity strongly depends on the sample. The different temperature of the maximum resistivity could arise from the vacancies at Fe or Se sites. The residual resistance ratio between 150 K and 33 K is as large as 9. With further decreasing the temperature, superconductivity emerges at about 32.1 K and resistivity reaches zero at around 30 K. These values are very close to those observed in K$_2$Fe$_2$Se$_2$. The resistivity of Rb$_{0.78}$Fe$_2$Se$_{1.78}$ crystal are 6 $\Omega$ cm at room temperature, which is much larger than those of FeSe single crystals and the other iron-pnictide superconductors. This may arise from the large disorder induced by deficiencies of Fe or Se. Occurrence of superconductivity in a system with so high resistivity demands further theoretical and experimental investigation.

Resistivity as a function of temperature under the magnetic field applied in ab-plane and along the c-axis is shown in Fig. 5a and 5b. The transition temperature of
superconductivity is suppressed gradually and the transition is broadened with increasing the magnetic field. Obvious difference for the effect of field along different direction on the superconductivity can observed. In order to study this difference clearly, we defined the $T_c$ as the temperature where the resistivity was 90% drop right above the superconducting transition. The anisotropic $H_c2(T)$ are shown in Fig. 5c for the two field directions, respectively. Within the weak-coupling BCS theory, the temperature where the resistivity was 90% drop right above the superconducting transition is larger than 1.70 K, respectively. Within the weak-coupling BCS theory, the transition is broadened with increasing the magnetic field applied in $ab$-plane and along the $c$-axis, respectively. These values are less than that in $K_xFe_2Se_2$ and CsFe$_2$Se$_2$, respectively, larger than that in CsFe$_2$Se$_2$ and Rb$_x$Fe$_2$As$_2$, respectively. A maximum resistivity as shown in Fig. 4 is widely observed in K$_x$Fe$_2$As$_2$ and Rb$_x$Fe$_2$As$_2$. Another common feature is that peculiar behavior of normal state susceptibility as shown in Fig.3 is widely observed in Cs$_x$Fe$_2$As$_2$ and Rb$_x$Fe$_2$As$_2$. It is found based on the observation in Fig. 3 and 4 that the maximum resistivity nearly coincides with the minimum susceptibility with magnetic field applied within $ab$-plane. It suggests that there exists a correlation between the maximum susceptibility and the minimum in-plane susceptibility. It should be addressed that the deficiency of Fe and Se is related to the ionic radius of alkali metals K, Rb and Cs. The actual compositions of superconducting crystals are K$_{0.86}$Fe$_2$Se$_1.82$, Rb$_{0.78}$Fe$_2$Se$_1.78$ and Cs$_{0.66}$Fe$_{1.66}$Se$_2$. It indicates that the vacancy in conducting FeSe layers changes from Se site to Fe site with increasing the ionic radius of alkali metals from K to Cs. It is found that normal state resistivity and susceptibility strongly depend on the vacancy in conducting FeSe layers. Further study on the origin of the deficiency of Fe and Se should be required to understand the normal state behavior, even the superconductivity of $A_x$Fe$_2$Se$_2$ materials.

In conclusion, we successfully grew a new superconductor Rb$_{0.78}$Fe$_2$Se$_1.78$ single crystals. $T_c$ is 32.1 K determined by resistivity measurement and zero resistivity is reached at 30 K. The ZFC dc magnetic susceptibility indicates that the crystal is fully diamagnetic. The large $H_c2(0)$ is observed, being similar to that in other the iron-pnictide superconductors. The anisotropy $H_c2(0)/H_c2(0)$ is 3.0, right lying between those of K$_x$Fe$_2$Se$_2$ and Cs$_x$Fe$_2$Se$_2$. A common peculiar susceptibility at the normal state is observed in Rb$_{0.78}$Fe$_2$Se$_1.78$.

ACKNOWLEDGEMENT This work is supported by the Natural Science Foundation of China and by the Ministry of Science and Technology of China, and by Chinese Academy of Sciences.

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