Anisotropy in transport and magnetic properties of K$_{0.64}$Fe$_{1.44}$Se$_{2.00}$

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We report a study of anisotropy in transport and magnetic properties of K$_{0.64}$Fe$_{1.44}$Se$_{2.00}$ single crystals. The anisotropy in resistivity is up to one order of magnitude between 1.8 K and 300 K. Magnetic susceptibility exhibits weak temperature dependence in the normal state with decrease in temperature with no significant anomalies. The lower critical fields $H_{c1}$ of K$_{0.64}$Fe$_{1.44}$Se$_{2.00}$ are only about 3 Oe and the anisotropy of $H_{c2}/H_{c1}$ is about 1. The critical currents for $H\parallel ab$ and $H\parallel c$ are about 100 A/cm$^2$, smaller than in iron pnictides and in FeTe$_{1-x}$Se$_x$ and nearly isotropic.

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I. INTRODUCTION

Superconductivity discovery in LaFeAsO$_{1-x}$F$_x$ has triggered intense research activity that resulted in critical temperatures up to 56 K in pnictide materials. Soon after, several types of iron-based superconductors have been discovered, such as AFe$_2$As$_2$ (A = alkaline or alkaline-earth metals, 122-type), LiFeAs (111-type), (Sr$_x$MgO$_{6-y}$)(Fe$_{2+y}$P$_{2-y}$) (M = Sc, Ti or V, 42222-type), FeSe$_2$, and α-PbO type FeSe (11-type) et al. The 11-type materials FeSe, FeTe$_{1-x}$Se$_x$, and FeTe$_{1-x}$S$_x$ provide an example of iron based superconductivity in a rather simple crystal structure without the charge reservoir layer. Yet, these simple binary structures share a square-planar lattice of Fe with tetrahedral coordination and similar Fermi surface topology with other iron-based superconductors. Furthermore, 11-type superconductors contain some distinctive structural and physical features, such as interstitial iron Fe$_{1+y}$Te and the significant pressure effect. Under external pressure, the $T_c$ can be increased from 8 K to 37 K and the $dT_c/dP$ can reach 9.1 K/GPa, the highest increase in all iron-based superconductors. This behavior may be understood from the observation related to the anion height between Fe and As (or Se, Te) layers. There is an optimal distance around 1.38 Å with a maximum transition temperature $T_c \approx 55$ K. The anion height in FeSe decreases gradually with the pressure increase towards the optimal value thereby increasing $T_c$. Quite importantly, high upper critical fields and currents were demonstrated in iron based superconductors.

Another method for tuning of the anion height is the intercalation of alkaline metals decreases Se height and changes the average space group from P4/nmm of FeSe to I4/mmm of AFeSe-122 type. The Fe-Se interlayer distances are only about 3 Oe and the anisotropy of $H_{c2}/H_{c1}$ is about 1. The critical currents for $H\parallel ab$ and $H\parallel c$ are about 10-100 A/cm$^2$, smaller than in iron pnictides and in FeTe$_{1-x}$Se$_x$ and nearly isotropic.

II. EXPERIMENT

Single crystals of K$_x$Fe$_2$Se$_2$ were grown by self-flux method with nominal composition K$_{0.64}$Fe$_{1.44}$Se$_{2.00}$. Pre-reacted FeSe and K pieces (purity 99.999%, Alfa Aesar) were put into the alumina crucible, and sealed into the quartz tube with partial pressure of argon. The quartz tube was heated to 1030 °C, kept at this temperature for 3 hours, and then slowly cooled to 730 °C with 6 °C/hour. Plate-like crystals up to 5×5×1 mm$^3$ can be grown. X-ray diffraction (XRD) spectra were taken with Cu K$_o$ radiation ($\lambda = 1.5418$ Å) using a Rigaku Miniflex X-ray machine. The lattice parameters were obtained by fitting the XRD spectra using the Rietica software. The elemental analysis was performed using an energy-dispersive x-ray spectroscopy (EDX) in an JEOL JSM-6500 scanning electron microscope. Electrical resistivity $\rho(T)$ measurements were performed in Quantum Design PPMS-9. The in-plane resistivity $\rho_{ab}(T)$ was measured using a four-probe configuration on rectangularly shaped and polished single crystals with current flowing in the ab-plane of tetragonal structure. The c-axis resistivity...
\[ \rho(T) \] was measured by attaching current and voltage wires on the opposite sides of the plate-like sample. Since the sample surface is easily oxidized, sample manipulation in air was limited to 10 minutes. Sample dimensions were measured with an optical microscope Nikon SMZ-800 with 10 um resolution. Electrical transport and heat capacity measurements were carried out in PPMS-9 from 1.8 to 300 K. Magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System (MPMS) up to 5 T.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the X-ray diffraction (XRD) results of the ground crystal. It confirms phase purity with no extrinsic peaks. The powder pattern can be indexed in the \( 4/mmm \) space group with fitted lattice parameters \( a = 0.39109(2) \) nm, \( c = 1.4075(3) \) nm (Fig. 1(a)). The powder pattern can be indexed in the \( 4/mmm \) space group with fitted lattice parameters \( a = 0.39109(2) \) nm, \( c = 1.4075(3) \) nm (Fig. 1(a)).

The average stoichiometry was determined from EDX by examination of multiple points on the crystals. The measured compositions are \( K_{0.64(4)}Fe_{1.44(4)}Se_{2.00(0)} \) (noted as K\(_{x}\)Fe\(_{2−y}\)Se\(_2\)), indicating substantial with of formation and the existence of K and Fe vacancies. We also measured the composition mapping using EDX. The results exhibit that the spatial distribution of K, Fe, and Se are homogenous.

The main panel of Fig. 2(a) shows the temperature dependence of resistivity in zero field from 1.9 K to 300 K for current along ab plane and c axis. At higher temperatures, both \( \rho_{ab}(T) \) and \( \rho_{c}(T) \) of K\(_{x}\)Fe\(_{2−y}\)Se\(_2\) with and without \( H=90 \) kOe along c axis. Inset: enlarged resistivity curve near \( T_{c} \). (b) Temperature dependence of ac magnetic susceptibility of K\(_{x}\)Fe\(_{2−y}\)Se\(_2\) in \( H_{ac}=1 \) Oe. Inset: temperature dependence of dc magnetic susceptibility with ZFC and FC.
both of $\rho_{ab}(T)$ and $\rho_c(T)$ undergo a very sharp superconducting transition at $T_{c,\text{onset}} = 33$ K, shown in the inset of Fig. 2(a). At 90 kOe, the resistivity transition width is broader and the onset of superconductivity shifts to 28 K. However, the $\rho_{\text{max}}$ curve has no obvious shift in magnetic field up to 90 kOe for current transport along both crystallographic axes.

Fig. 2(b) shows the temperature dependence of the ac susceptibility of K$_x$Fe$_2$-$y$Se$_2$ single crystal with $H\parallel ab$. A clear superconducting transition appears at $T = 31$ K. This is consistent with the resistivity results. The superconducting volume fraction is about 75% at 1.8 K, indicating the bulk superconductivity in the sample. The broad transitions in $\chi'$ and $\chi''$ point to microscopic inhomogeneity. Inset in Fig. 2(b) shows the dc magnetic susceptibility for $H\parallel ab$ with zero-field cooling (ZFC) and field cooling (FC). Diamagnetism can be clearly observed in both measurement and the $T_{c,\text{onset}}$ is almost the same as that determined from the ac susceptibility. On the other hand, the magnetization measured with FC is very small, which is a common behavior in two-dimensional superconductors, such as (Pyridine)$_{1/2}$TaS$_2$ and Ni$_x$TaS$_2$. The small magnetization values for FC is likely due to the complicated magnetic flux pinning effects in the layered compounds. The small magnetization values for FC is likely due to the complicated magnetic flux pinning effects in the layered compounds.

Temperature dependence of magnetic susceptibility in the normal state is shown in Fig. 3(a) for $H\parallel ab$ and $H\parallel c$ with $H = 1$ kOe. A sudden drop at about 30 K corresponds to the superconducting transition. For $H\parallel c$, $\chi_c$ weakly decreases with temperature below 300 K and exhibits a weak upturn below 120 K. When the magnetic field is in the ab plane, $\chi_{ab}$ exhibits similar behavior but the minimum of susceptibility is located at about 175 K. The magnetic susceptibility enhancement with increase in temperature above 200 K is neither Pauli nor Curie-Weiss. It suggests the presence of magnetic interactions. This has not only been observed in other AFeSe$_{122}$ compounds but also in BaFe$_2$As$_2$ due to two dimensional short range AFM spin fluctuations. The AFM interaction is possibly related to the Fe deficiency and is an intrinsic properties of AFe$_2$Ch$_2$ ($Ch = S, Se$).

The initial dc magnetization versus field $m(H)$ at $T = 1.8$ K for both directions is shown in Fig. 3(b). The shape of the $m(H)$ curves points that K$_x$Fe$_2$-$y$Se$_2$ is a typical type-II superconductor. The peak in $m(H)$ is about 2 kOe for $H\parallel c$, consistent with the previous report. However, it should be noted that $H_{c1}$ is often much smaller than the peak value in $m(H)$ curve. In K$_x$Fe$_2$-$y$Se$_2$, the $m(H)$ curve deviates from linearity at much lower field. The enlarged parts are shown in Fig. 3(c) and (d). The $H_{c1}$ is usually determined by the field where the $m(H)$ deviates from linear relation. However, small $H_{c1}$ introduces the significant error, so it is hard to evaluate the $H_{c1}(0)$ using $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2]$. The approximate $H_{c1,ab}(T = 1.8$ K) and $H_{c1,c}(T = 1.8$ K) are 3.0(5) Oe.

Fig. 4(a) and (b) show the magnetization loops for $H\parallel c$ and $H\parallel ab$ with field up to 50 kOe. The paramagnetic background exists for both directions, and is more obvious for $H\parallel ab$. This paramagnetic background originates from the non-superconducting fraction. The shapes of $M(H)$ and $M(T)$ (Fig. 3) are typical of type-II superconductors with some electromagnetic granularity. The critical current is determined from the Bean model. For a rectangular-shaped crystal with dimension $c < a < b$, when $H\parallel c$, the in-plane critical current density $J_{c}^{ab}(H)$ is given by

$$J_{c}^{ab}(H) = \frac{20\Delta M(H)}{a(1 - a/3b)}$$

where $a$ and $b$ ($a < b$) are the in-plane sample size in
cm, $\Delta M(H)$ is the difference between the magnetization values for increasing and decreasing field at a particular applied field value, measured in emu/cm$^3$, and $J_{c}^{ab}(H)$ is the critical current in A/cm$^2$. It should be noted that the paramagnetic background has no effect on the calculation of $\Delta M(H)$. The situation is more complex when $H_{ab}$. There are two different current densities: one is the vortex motion across the planes, $J_{c}^{c}(H)$, and another is parallel to the planes, $J_{c}^{ab}(H)$. Usually $J_{c}^{ab}(H) \neq J_{c}^{c}(H)$ if assuming $a, b \gg c/3 \cdot J_{c}^{c}(H)/J_{c}^{ab}(H)$ we can obtain $J_{c}^{c}(H) \approx 20\Delta M(H)/c$. Magnetic field dependence of $J_{c}^{c}(H)$ and $J_{c}^{ab}(H)$ is shown in Fig. 4(c) and (d). It can be seen that the critical current decreases with applied field and the ratio of $J_{c}^{c}(H)/J_{c}^{ab}(H)$ is approximately 1. The critical current densities for both directions are $10^{-1} - 10^{-3}$ A/cm$^2$, which is much smaller than those of BaFe$_{2-x}$Co$_{x}$As$_{2}$ in the same temperature range.  

IV. CONCLUSION

In summary, we have presented anisotropic transport and magnetic properties of K$_{0.64(4)}$Fe$_{1.44(4)}$Se$_{2.00(0)}$ single crystals with $T_{c,\text{onset}} = 33$ K and free of iron impurities. The resistivity anisotropy is much smaller than in other AFeSe-122 compounds. Magnetization decreases in the normal state with decreasing temperature from 300 K, which suggest that the presence of AFM interactions. The lower critical fields $H_{c2}$ are only about 3 Oe at 1.8 K and the anisotropy of $H_{c1,c}/H_{c1,ab}$ is about 1. The critical current values are isotropic and is about $10^{-1} - 10^{-3}$ A/cm$^2$ for both directions below 50 kOe.

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