Single-crystal growth and extremely high $H_{c2}$ of 12442-type Fe-based superconductor KCa$_2$Fe$_4$As$_4$F$_2$

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Millimeter sized single crystals of KCa$_2$Fe$_4$As$_4$F$_2$ were grown using a self-flux method. The chemical compositions and crystal structure were characterized carefully. Superconductivity with the critical transition temperature $T_c = 33.5$ K was confirmed by both the resistivity and magnetic susceptibility measurements. Moreover, the upper critical field $H_{c2}$ was studied by the resistivity measurements under different magnetic fields. A rather steep increase for the in-plane $H_{c2}$ with cooling, $dH_{c2}^{ab}/dT|_{T_c} = -50.9$ T/K, was observed, indicating an extremely high upper critical field. Possible origins for this behavior were discussed. The findings in our work is a great promotion both for understanding the physical properties and applications of 12442-type Fe-based superconductors.

I. INTRODUCTION

The Fe-based superconductors (FeSCs) share at least one common feature with the cuprate superconductors: the crystal structure consists of insulating layers serving as the carrier reservoir and conducting layers which are the key section for the superconductivity. Meanwhile, the subtle difference is also noticed by the material scientists. For the cuprates, superconductivity can be observed in systems with monolayers [2][3], bilayers [4], trilayers [5], and infinite layers [6] between two neighboring insulating layers. More importantly, typically the bilayered and trilayered materials have a clear higher critical transition temperature $T_c$ than monolayered ones [3]. For the FeSCs, however, only monolayered (e.g. 1111 system and 213 system) [4][5] and infinite-layered systems (e.g. 11 system and 122 system) [3][6] were discovered for a rather long time. Recently, by the intergrowth of 1111- and 122-type FeSCs, a series of bilayered compounds AB$_2$Fe$_4$As$_4$C$_2$ (A = K, Rb, Cs; B = Ca, Nd, Sm, Gd, Tb, Dy, Ho; C = F, O) were reported with $T_c = 28$–$37$ K [10][11]. This 12442 system blaze a new trail to explore materials with higher $T_c$ and possible new physical manifestations of FeSCs. For example, the breaking of the $S_4$ symmetry in the crystal lattice leads to a more complicated band structure with ten Fermi surfaces [12].

The high-quality single crystals are essential to investigating the intrinsic properties of this system. Up to now, most of the work on this system were carried out based on the polycrystalline samples [13][19], although the CsCa$_2$Fe$_4$As$_4$F$_2$ single crystals have been grown and the gap structure was studied by heat transport and lower critical field measurements [20][21]. The KCa$_2$Fe$_4$As$_4$F$_2$ compound with a stronger interlayer coupling within a FeAs-K/Cs-FeAs block possesses a higher $T_c$ and more luxuriant properties can be expected. In this paper, with the successful growth of high-quality single crystals of KCa$_2$Fe$_4$As$_4$F$_2$, we really observed the unusual steep increase of the upper critical field with cooling, suggesting a very robust superconductivity against the external magnetic field near $T_c$. Understanding the mechanism of such an extraordinary behavior is a severe challenge and will promote the progress of this field. Moreover, the present finding may have potential values in the applications under high fields.

II. EXPERIMENTAL

Single crystals of KCa$_2$Fe$_4$As$_4$F$_2$ were grown using KAs as the self flux. The raw materials are K chunk (purity 99%), Ca granules (purity 99.5%), Fe powders (purity 99+%), As powders (purity 99.999%) and CaF$_2$ powders (purity 99.95%). KAs was synthesized with stoichiometric ratio of K and As in the alumina crucible, which was loaded into a stainless steel pipe container [22] and heated at 650 °C for 10 hours. Precursors CaAs and Fe$_3$As$_2$ were synthesized via solid-state reactions in evacuated quartz tubes by heating the mixed reagents at 700 °C and 750 °C for 12 hours, respectively. These precursors and CaF$_2$ were mixed in an appropriate ratio with excess 15 times KAs as the flux. We found that the crystals of 122 system KFe$_2$As$_2$ was very easy to be produced if the stoichiometric ratio was used. Thus we added additional amounts of 100% CaAs and 50% CaF$_2$ to restrain the formation of KFe$_2$As$_2$. The mixtures were put into an alumina crucible, subsequently sealed in a stainless
FIG. 1: (color online) (a)-(b) The surface pictures of the single crystal taken with the optical microscope and SEM, respectively. (c) The EDS microanalysis spectrum taken on the surface of the sample.

Table 1: Compositions of the KCa$_2$Fe$_4$As$_4$F$_2$ single crystal characterized by EDS measurements.

| Element | Weight (wt.%) | Atomic (at.%) | Error(3σ) |
|---------|--------------|---------------|-----------|
| K       | 5.48         | 7.34          | 0.56      |
| Ca      | 12.97        | 16.96         | 1.17      |
| Fe      | 33.13        | 31.09         | 2.61      |
| As      | 43.20        | 30.22         | 3.71      |
| F       | 5.22         | 14.40         | 2.16      |

The microstructure was examined by scanning electron microscopy (SEM, Zeiss Supra55). The composition of the single crystals was checked and determined by energy dispersive x-ray spectroscopy (EDS) measurements on an Bruker device with the model Quantax200. The crystal structure and lattice constants of the materials were examined by a DX-2700 type powder x-ray diffractometer using Cu K$_{\alpha}$ radiation. The electrical resistivity was measured on the physical property measurement system (Quantum Design, PPMS). The magnetic susceptibility measurement was carried out on the magnetic property measurement system (Quantum Design, MPMS 3) with the magnetic field oriented parallel to the ab-plane of the samples.

III. RESULTS AND DISCUSSION

The morphology of the single crystals was examined by the optical microscope and the scanning electron microscopy, which are shown in Figs. 1(a) and (b) respectively. The surface observed from the optical microscope is shining. The SEM picture shows the clean and flat surface. The typical crystal size was found to be as large as 1 mm $\times$ 0.8 mm $\times$ 0.06 mm. The composition of the crystals was examined by the EDS analysis and the typical spectrum is shown in the Fig. 1(c). The result of the composition analysis is shown in table 1. The ratio of K : Ca : Fe : As : F is 0.94 : 2.18 : 4 : 3.89 : 1.85, which is close to the the expected 1 : 2 : 4 : 4 : 2.

The structure of the crystals was checked by the x-ray diffraction (XRD) measurement, where the x-ray was incident on the ab-plane of the crystal. The diffraction patterns are shown in Fig. 2. All the diffraction peaks can be indexed to the 12442 compound with a tetragonal structure. Only sharp peaks along (00 2l) orientation can be observed, suggesting a high c-axis orientation. The full width at half maximum (FWHM) of the diffraction peaks is only about 0.10$^\circ$ after deducting the K$_{\alpha}$ contribution, indicating a rather fine crystalline quality. The c-axis lattice constant was obtained to be 30.991 Å by analyzing the diffraction data, which is consistent with the previous report on the polycrystalline samples [10].

Temperature dependence of resistivity in the temperature range from 0 to 300 K for is shown in Fig. 3(a). The $\rho$ - $T$ curve shows a clear negative curvature in a wide temperature region before entering the superconducting states, which is similar with that observed in...
CsCa$_2$Fe$_4$As$_4$F$_2$ \cite{29} and seems to be a common feature for the hole-doped FeSCs \cite{23,24}. The onset of the superconducting transition appears at about 33.5 K, whereas the zero resistivity is reached at about 32.5 K. The dc magnetic susceptibility for the same sample was measured under a magnetic field of 1 Oe in zero-field-cooling and field-cooling processes, which is presented in Fig. 3(b) with temperature between 0 and 40 K. In order to minimize the effect of the demagnetization, the magnetic field was applied parallel to the ab-plane of the crystal. The absolute value of magnetic susceptibility $\chi$ is about 101\%, indicated a high superconducting volume fraction of our samples. An enlarged $\rho - T$ curve is also shown in figure Fig. 3(b) in order to have a comparison with susceptibility curve expediently. Both the $\rho - T$ and $\chi - T$ curves display a rather sharp superconducting transition, indicating the high quality of our samples. The onset transition temperature revealed by the $\chi - T$ curve is roughly corresponding to the zero resistivity temperature, which is rather reasonable and common for the compound superconductors.

In order to study the upper critical field $H_{c2}$ and irreversible field $H_{irr}$, we perform the measurements of temperature dependent electronic resistivity with the magnetic field along two different orientations. As shown in Figs. 4(a) and (b), the SC transition point shifts to lower temperature with the increase of the magnetic field for both the orientations: $H \parallel c$ and $H \parallel ab$. In all the measurements, the current was applied with the ab plane and always perpendicular to the magnetic field. It is worthy to note that the SC transition for the orientation of $H \parallel c$ shifts much quicker than that of $H \parallel ab$ by comparing the two sets of data. Remarkably, the superconductivity is very robust against the in-plane field: a magnetic field as high as 9 T reduces the superconducting transition merely about 0.2 K and 1 K if we check the onset point and zero-resistivity point respectively. Quantitatively, we use the criteria 90\%$\rho_n$ and 10\%$\rho_n$ to determine the values of $H_{c2}$ and $H_{irr}$ respectively. The temperature dependence of $H_{c2}$ and $H_{irr}$ is shown in the inset of Fig. 4(b) for both the two orientations. The vortex-liquid regions between $H_{c2}$ and $H_{irr}$ for the orientation $H \parallel c$ is much larger than that with $H \parallel ab$, in accordance with the two-dimensional feature of this material where the pancake-like and Josephson-like vortices will form in the two cases respectively \cite{25}.

The most important issue is about the upper critical field $H_{c2}$. We deduced the slope of the tangent of the $H_{c2} - T$ curves (as shown in the inset of Fig. 4(b)) near $T_c$, $d\mu_0H_{c2}/dT|_{T_c}$. We obtained an unexpectedly high value for the $H \parallel ab$ case, $d\mu_0H_{c2}^{ab}/dT|_{T_c} = -50.9$ T/K. For $H \parallel c$, the slope is $-6.4$ T/K which is also large, although so not conspicuous as the in-plane case. These two values give an estimation for the anisotropy of about 8 near $T_c$. To have a concise impression, we have summarized the results of different FeSC systems in Table I. Similar criteria (90\% or 95\%$\rho_n$) were adopted in these reports \cite{20,26,28}, which facilitates the comparison with our results. One can see that, for the in-plane $H_{c2}^{ab}$, a slope around -10 T/K is a typical value for various systems of FeSCs including the 1111 system, 122 system, 1144 system, etc. In the 1242 system CsCa$_2$Fe$_4$As$_4$F$_2$, an abnormally steep slope of about -18.2 T/K has been reported previously, which revealed preliminarily the peculiarity of this bilayered FeSC system. Now with our result, a slope of -50.9 T/K in the KCa$_2$Fe$_4$As$_4$F$_2$ system further highlights this tendency. Applying the Werthamer-Helfand-Hohenberg (WHH) relation $29$

\[
\mu_0H_{c2}(0) = -0.693d\mu_0H_{c2}(T)/dT|_{T_c}T_c
\]

we get a vary high value, about 1180 T, for the in-plane upper critical field at zero temperature $\mu_0H_{c2}^{ab}(0)$. Obviously this value is very impressive, although the WHH relation may over-estimated the $\mu_0H_{c2}^{ab}(0)$ in such a multi-band material.

It is difficult to see through the hidden physical mechanism for such an observation at the present stage. Nevertheless, comparing the two 1242 cousins, CsCa$_2$Fe$_4$As$_4$F$_2$ and KCa$_2$Fe$_4$As$_4$F$_2$, can still sup-

\[\text{FIG. 3: (a) Temperature dependence of resistivity measured in a wide temperature range 0 - 300 K under zero magnetic field. (b) The magnetic susceptibility measured in zero-field-cooled (ZFC) and field cooled (FC) models and the resistivity data in the low temperature range near the superconducting transition.}\]
The inset of (b) shows the upper critical fields $H_{c2}$ and irreversible field $H_{irr}$, as a function of temperature for two different orientations.

TABLE II: Slope of the upper critical fields with temperature for different systems of FeSCs.

| Materials          | $d\mu_0 H_{c2}^a /dT|_{Tc}$ | $d\mu_0 H_{c2}^b /dT|_{Tc}$ | Ref. |
|--------------------|-----------------------------|-----------------------------|------|
| NdFeAsO$_{0.82}$F$_{0.18}$ | $-9$                      | $-2.09$                      | $[20]$ |
| Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ | $-9.35$                  | $-5.49$                      | $[27]$ |
| CaKFe$_4$As$_4$   | $-10.9$                    | $-4.4$                       | $[25]$ |
| CsCa$_2$Fe$_4$As$_4$F$_2$ | $-18.2$                  | $-2.9$                       | $[20]$ |
| KCa$_2$Fe$_4$As$_4$F$_2$ | $-50.9$                  | $-6.4$                       | This work |

For the abnormally steep slope of $d\mu_0 H_{c2}^b /dT|_{Tc}$, of course, this needs the verifications of further investigations in the future. Another clue stems from the comparison with other FeSC systems. As can be seen in Table II, the out-of-plane slope $d\mu_0 H_{c2}^b /dT|_{Tc}$ of 122 system Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ is also rather high and only slightly lower than that of KCa$_2$Fe$_4$As$_4$F$_2$. It seems that it is the small anisotropy that restrains the further great enhancement of the in-plane slope in 122 system. According to this idea, the present 12442 system reserves the high out-of-plane value of the hole-doped 122 system, and meanwhile achieves a high anisotropy due to the intergrowth with the 1111 component. This may explain phenomenologically the possible origin of our observations. Besides, but not less important, the present system also have a good potential for the applications in high field because of the rather high in-plane irreversible field $H_{irr}^a$. 

IV. CONCLUSIONS

In this work, millimeter sized single crystals of KCa$_2$Fe$_4$As$_4$F$_2$, a bilayered FeSC resembling the famous Bi-2212 system, were successfully grown by a self-flux method. The chemical compositions, crystal structure, resistivity, and magnetization susceptibility were investigated systematically. The $T_c$ of the single crystals was confirmed to be about 33.5 K by both the resistivity and magnetic susceptibility. The most important, it is found that the slope of the $H_{c2}^a - T$ curve adjoining $T_c$ is very large, indicating an extremely high upper critical field in this system. Our findings demonstrate that the KCa$_2$Fe$_4$As$_4$F$_2$ material has significant values in the superconducting fundamental research and applications.

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