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Effect of annealing temperature on the properties of $K_{0.8}Fe_{2+x}Se_2$

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Abstract

$K_{0.8}Fe_{2+x}Se_2$ single crystals ($x = -0.3, 0, 0.3$) have been successfully grown by one-step method. The as-grown crystals all don’t show superconductivity; however, the superconductivity appears after annealing. The data of $R-T$ and $M-T$ indicate that the Fe-content and annealing-temperature have visibly effect on the superconducting properties of $K_{0.8}Fe_{2+x}Se_2$ single crystals. The crystal of $K_{0.8}Fe_{2.3}Se_2$, annealed at 400 °C for 1 hour, demonstrates the best superconducting properties. Furthermore, the pinning potential of $K_{0.8}Fe_{2.3}Se_2$ is visibly lower than that of BaK-122, indicating different pinning mechanism caused by large size non-superconducting phase in $K_{0.8}Fe_{2.3}Se_2$.

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Keywords: $K_{0.8}Fe_{2+x}Se_2$; annealing-temperature; Fe content; pinning potential

1. Introduction

The iron-based superconductors have attracted great research interest due to their high transition temperature and possibly unconventional pairing mechanism. The simple binary 11-type iron chalogenide has no charge reservoir layer and the superconductivity can be induced by doping FeTe with S [1] and Se [2]. Furthermore, 11-type superconductors contain some distinctive structural and physical features, such as without static magnetic order and its transition temperature can be increased up to 37 K by applying pressure [3], the highest increase in all iron-based superconductors.

Very recently, a new system $A_xFe_{2-y}Se_2$ made of FeSe superconducting layers intercalated by spacer layers $A = K$ [4-5], Cs [6-7], Rb [8] etc, with $T_c$ above 30 K, has been achieved. Recent studies on these materials reveal some novel phenomena: abnormal minimum of magnetization near zero fields, two-step magnetic penetration on the magnetization hysteresis loops (MHL) curve, and very small width of the MHL compared with Ba-122 single crystals at the same condition. All these results illustrate that there is obvious superconducting phase separation in these $K_xFe_{2-y}Se_2$ superconductors [9]. In 2011, Li et al successfully grew high-quality $K_xFe_{2-y}Se_2$ film by molecular beam epitaxy technology and they observed that a $K_xFe_{2-y}Se_2$ sample contained two distinct phases: an insulating phase with well-defined $\sqrt{5} \times \sqrt{5}$ order of Fe vacancies, and a superconducting $KFeSe_2$ phase containing no Fe vacancies [10]. All these phenomena indicate that the superconductivity of $K_xFe_{2-y}Se_2$ has close relationship to the intensity of Fe vacancy. In this work, we give a systematic research on the influence of annealing temperature and Fe content to the superconductivity of $K_xFe_{2-y}Se_2$. The results indicate the superconducting properties become better with increasing Fe content and annealing temperature. The present results may provide useful information to further study the superconductivity of $K_xFe_{2-y}Se_2$.

2. Experimental details

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Single crystals of K$_{0.8}$Fe$_{2+x}$Se$_2$ ($x = -0.3$, 0, 0.3) were synthesized through a simple one-step method. Stoichiometric amount of K pieces, Se and Fe powder, were ball milled in Ar atmosphere. To avoid the reaction between K vapor and quartz glass, we have employed stainless steel tube to substitute quartz ampoule. Then an alumina crucible containing the starting materials was put into the steel tube. The sealing process of the steel tube has been reported in reference [11]. To avoid oxidization during the sintering process, the steel tubes were sealed in quartz ampoules. All the samples were placed in a muffle furnace and heated up to a high temperature (1030 – 1080 °C) to melt completely. Then the samples were cooled down to temperature below 750 °C. Finally, the furnace was powered off. Unfortunately, the as-grown crystals, obtained in this process, can’t show any superconductivity. To reemerge the superconductivity, we annealed the samples at 300 °C, 400 °C, 500 °C for 1 hour and fast quenching to room temperature. The phase identification was characterized using X-ray diffraction (XRD) with Cu-K$_\alpha$ radiation from 10 to 70°. The diffraction peaks could be well indexed on the basis of tetragonal ThCr$_2$Si$_2$-type structure with the space group I4/mmm. The superconducting properties were studied by magnetization and standard four-probe resistivity measurements using a physical property measurement system (Quantum Design).

3. Results and discussion

The crystal structure for all the as-grown and post-annealed K$_{0.8}$Fe$_{2+x}$Se$_2$ is determined by X-ray diffraction. The results are very similar, and so only the result of K$_{0.8}$Fe$_{1.7}$Se$_2$ is given, as shown in Fig. 1. It clearly demonstrates that the crystals have a tetragonal basic structure with the space group of I4/mmm. It is noted that another series of small reflect peaks are also found in all the specimens, which may come from the modulation structure along the c-axis due to the existence of Fe vacancy [4]. In addition, EDX technology was also employed to determine the composition of the crystals. It is surprising to find that there is no visible difference in atomic ratio for all the crystals, which is approximately satisfied with K$_{0.72}$Fe$_{1.50}$Se$_2$ according to the EDX data.

In Fig. 2, we display the dependence of resistivity on the annealing-temperature and Fe-content. It should be pointed out that all the samples don’t show superconductivity before annealing, and the typical result is shown in Fig. 2(a).
It can be seen that the annealing-temperature has visibly influence on the superconductivity for all the samples, as shown in Figs. 2 (b-d). For example, the samples, with Fe-content \( \sim 1.7 \), annealed at 300°C don’t show superconductivity from 300 K to 10 K, and the resistivity has a sharp decrease at the temperature point about 31 K. The drop of the resistivity may come from the weak superconductivity. The other researches have revealed that the temperature of order-disorder phase transition is about 307°C (580K) [12], and the ordered Fe-vacancy phase is non-superconductivity. The annealing-temperature of 300 °C just locator below the critical temperature point of order to disorder phase transition. Thus, such an annealing-temperature is not enough to excite the ordered state to transfer to disordered state. The superconductivity becomes much clearer with the increasing annealing temperature, and the sample displays superconductivity when the annealing-temperature gets up to about 500°C, as shown in Fig. 2(b). For the other Fe-content, temperature-dependence of resistivity shows a similar behaviour. Furthermore, the Fe-content seems to have obvious effect on superconducting properties. The higher of Fe-content, the lower annealing-temperature is needed to get superconductivity. For example, the samples with \( x = 0.3 \) can get superconductivity after annealing at 300 °C. The temperature-dependence of resistivity also reveals hump-like anomaly phenomena. In present experiments, we find the position of the hump-like anomaly shifts to high temperature with increasing the annealing-temperature in the samples with the least Fe-content (\( x = -0.3 \)). The hump-like anomaly should be a metal-semiconductor transition, because R-T curves exhibits a metallic and semiconducting behaviours below and up of the ‘hump’ temperature. The semiconductor-metal like transition and its behaviours under different Fe-content and annealing-temperature may have close relationship with the ordering-disordering process of the cation vacancies, which will significantly influence the resistivity.

Fig. 3 M-T relationships for \( K_{0.8}Fe_{2+x}Se_2 \) single crystals. (a) annealed at 500 °C for 1 hour with \( x = -0.3, 0 \) and 0.3, (b) annealed at 300, 400 and 500 °C for 1 hour with \( x = 0.3 \), respectively.

Fig. 3 elucidates the typical magnetization curves. It clearly illustrate that the superconducting volume fraction increases with increasing the Fe-content and annealing-temperature, and the samples after annealing at 400 °C have the highest superconducting volume fraction. as shown in Figs. 3(a) and (b). The results of magnetization are consistent with that obtained from R-T data. It is well known now that there are two competing phases in \( K_{1-x}Fe_2Se_2 \) single crystal [12]: One is a magnetic phase with ThCr_2Si_2 structure, and another is non-magnetic phase having an in-plane compressed lattice constant. The present results suggest that the reasonable Fe-content and annealing-temperature can effectively restrain non-superconducting phase and improve the superconductivity properties of \( K_{1-x}Fe_2Se_2 \) superconductor.

The temperature dependence of the resistance at various applied magnetic field for a \( K_{0.8}Fe_2Se_2 \) crystal annealed at 400°C is shown in Figs. 4 (a) and (b). It can be seen that the superconducting transition width for \( H // c \) increases with the increasing applied fields from 0 to 9 T, indicating obvious flux motion. The superconducting transition becomes more precipitous for field applied to \( ab \) plane, revealing much stronger flux pinning ability in \( ab \) plane than that in \( c \)-axis. The \( H_{c2}(0) \) is estimated by using the Werthamer-Helfand-Hohenberg (WHH) formula:

\[
H_{c2}(0) = -0.693T_c \cdot \frac{dH_{c2}}{dT}, \text{ with } \frac{dH_{c2}}{dT} \text{ at } T = T_c.
\]

Using the criterion of the \( H_{c2} \), which is taken from the resistive transition by 90% \( R_n \), where \( R_n \) denotes the normal state resistance. The roughly estimated \( H_{c2}(0) \) is about 46 T and 114 T for the samples in applied field parallel to \( c \)-axis and \( ab \) plane, respectively. If we take \( R = 10\% R_n \) as the criterion of the irreversibility field, then the relationship between irreversibility field and temperature is also displayed, as shown in inset of Figs. 4 (a) and (b).

According to the thermally activated model of flux flow, the temperature dependence of the resistivity can be described by the equation \( R(T, B) = R_0 \exp \left( -U_0 / K_B T \right) \), where \( R_0 \) is a parameter, \( K_B \) is the Boltzmann constant, and \( U_0 \) is the vortex pinning potential. The pinning potential can be obtained from the slope of the linear part of the
plot, log $R(T, B)$ versus $1/T$, in a temperature interval below $T_c$. The data of log($R$) vs. $1/T$ is plotted in Figs. 4 (c) and (d). The linearity of log($R$) vs. $1/T$ in the low temperature region indicates the thermally activated behavior of the vortex. The slope of the curve is the pinning potential $U_0$. The estimated values of pinning potential is 2300 K and 1800 K for $H // ab$ and $H // c$, respectively, at the low field of 1 T. The values are similar to the values of NdFeAsO$_{0.7}$F$_{0.3}$ single crystal and much lower than the reported values of $U_0 / k_B = 6000$-$9000$ K for Ba$_{0.78}$K$_{0.32}$Fe$_2$As$_2$ single crystals [13-14].

4. Conclusion

The influence of Fe-content and annealing-temperature on the superconducting properties of K$_{0.8}$Fe$_{2+x}$Se$_2$ single crystals has been investigated. XRD results indicate that the Fe-content and annealing-temperature have no visibly effect on the crystal structure. However, the superconducting volume fraction increases with increasing the annealing-temperature and Fe-content according to the R-T and M-T data. The present experiments clearly show that the reasonable annealing-temperature and Fe doping level may be an effective method to improve the superconducting properties of K$_{0.8}$Fe$_{2+x}$Se$_2$ single crystals. However, the pinning potential of K$_{0.8}$Fe$_{2.3}$Se$_2$ single crystal is obvious lower than that of BaK-122, indicating a different pinning mechanism induced by large size non-superconducting phase in K$_{0.8}$Fe$_{2.3}$Se$_2$.

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