Strong Pauli paramagnetic effect in the upper critical field of KCa$_2$Fe$_4$As$_4$F$_2$

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Recently, 12442 system of Fe-based superconductors has attracted considerable attention owing to its unique double-FeAs-layer structure. A steep increase in the in-plane upper critical field with cooling has been observed near the superconducting transition temperature, $T_c$, in KCa$_2$Fe$_4$As$_4$F$_2$ single crystals. Herein, we report a high-field investigation on upper critical field of this material over a wide temperature range, and both out-of-plane ($H_{c2\perp}$) and in-plane ($H_{c2\parallel}$) directions have been measured. A sublinear temperature-dependent behavior is observed for the out-of-plane $H_{c2\perp}$, whereas strong convex curvature with cooling is observed for the in-plane $H_{c2\parallel}$. Such behaviors could not be described by the conventional Werthamer–Helfand–Hohenberg (WHH) model. The data analysis based on the WHH model by considering the spin aspects reveals a large Maki parameter $\alpha = 9$, indicating that the in-plane upper critical field is affected by a very strong Pauli paramagnetic effect.

Keywords: 12442, upper critical field, Pauli paramagnetic effect

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1 Introduction

Unconventional superconductivity is closely related to the electronic and crystal structures of the materials. Adjustment of the crystal structure often leads to abundant physical manifestations. From this viewpoint, the 12442 system, which is the only system with two FeAs layers between neighboring insulating layers in Fe-based superconductors (FeSCs), has gained considerable attention in the field of superconducting (SC) materials. Depending on the detailed compositions, materials in this system are superconducting with $T_c = 28–37$ K. The recent advances in the field of high-quality single crystal growth have greatly promoted studies on the intrinsic physical properties of this system. For example, a large anisotropy of the upper critical field $\Gamma = H_{c2\parallel}/H_{c2\perp}$ and very steep increase of the in-plane $H_{c2\parallel}$ with cooling are observed in the temperature region near $T_c$ in CsCa$_2$Fe$_4$As$_4$F$_2$ and KCa$_2$Fe$_4$As$_4$F$_2$ single crystals. These findings may be significant both for the fundamental physics and potential applications. Currently, however, the behavior at lower temperatures and higher magnetic fields is still unknown.

Generally, for type-II superconductors, the upper critical field can be affected by the interactions between the external magnetic field and orbital motion of the SC electrons, by the effect of the field on the electron spin magnetic moments (Pauli paramagnetic effect), and by the spin-orbit scattering. In the case of FeSCs, the Pauli paramagnetic effect is significant, severely limiting the in-plane $H_{c2\parallel}$ when approaching zero temperature. Therefore, almost all the FeSCs exhibit isotropic characteristics in low temperature. Hence, the behavior of the upper critical field of 12442 system has gained great research interest. The pulsed magnetic field can provide a vital platform for studying this subject. In this study, we conducted an in-depth examination of the upper critical field of KCa$_2$Fe$_4$As$_4$F$_2$ single crystals using a pulsed magnetic field of up to 50 T. Strongly convex curvature with cooling was observed in the $H_{c2\parallel}^b - T$ curve; this convexity interrupts the sharp upward trend of $H_{c2\parallel}$ near $T_c$. The Werthamer–Helfand–Hohenberg model considering the spin aspects fitted the experimental data, and a significantly strong Pauli paramagnetic effect was revealed.

2 Materials and methods

The KCa$_2$Fe$_4$As$_4$F$_2$ single crystals were grown using the KAs self-flux method. CaF$_2$ powder and homemade CaAs, KAs, and Fe$_2$As were mixed together in a stoichiometric ratio and placed in an alumina crucible; then, they were sealed in a stainless steel pipe. Fifteen times excess KAs was added as the flux. Moreover, appropriate amounts of CaAs and CaF$_2$ were added to suppress the formation of 122 phase KFe$_2$As$_2$. The materials were heated at 980 °C for 20 h and cooled down to...
900 °C at a rate of 1.6–4 °C/h, followed by rapid cooling to room temperature. The detailed characterizations of the samples has been reported in our previous work.18

Electronic resistivity was measured with a DC magnetic field of up to 9 T on a physical property measurement system (PPMS, Quantum Design). The experiments were also conducted under the pulsed magnetic fields of up to 50 T. The magnetic fields were applied along the c-axis (H∥c) and H∥ab, respectively. The interval for the field is 1 T/step.

3 Results and discussion

In our previous work, we reported that χ − T data measured with H∥ab represents a superconducting volume fraction very close to 100%. Herein, we show the temperature dependence of magnetic susceptibility data χ − T with H∥c, see Fig. 1(a). The data reveals a very sharp SC transition at Tc = 33.2 K, indicating that our sample is of high quality and good homogeneity. The in-plane resistivity as a function of temperature was measured under different fields up to 9 T. In Figs. 1(b) and (c), we show the ρ − T data with H∥c and H∥ab, respectively. The SC transition displays a width of approximately 1 K under zero field, which is broadened by the external magnetic field. Such a broadening has been reported in 1111 system of FeSCs and cuprates, which is a consequence of the formation of a vortex-liquid state.21–24 Note that the scale of the x-coordinates for these two graphs are different, representing a clear anisotropy in the suppression of the SC transition by the magnetic field. Because of the limitation of the magnetic field, we only obtained information in a very narrow temperature region near Tc. Hence, we conducted transport measurements under the pulsed magnetic fields of up to 50 T.

Normalized resistivity as a function of pulsed magnetic field is shown in Figs. 2(a) and (b). With the decrease of temperature, the SC state can survive under a higher
field. In the case of $H||c$ (see Fig. 2(a)), the SC transition becomes broadening in the low temperature region, indicating a wide area of the vortex-liquid state. This is consistent with the observations shown in Fig. 1(b). As shown in Fig. 2(b), such a broadening behavior is not observed in the case of $H||ab$. This difference in behavior is a consequence of the different types of vortices in the different field orientations in a quasi-two-dimensional layered material. It is believed that the presence of SC fluctuation near the onset of the SC transition and vortex-liquid state near zero-resistivity will affect the determination of upper critical field in the dirty limit, according to the WHH theory, the upper critical field can be obtained from the function

$$\ln \frac{1}{t} = \sum_{\nu=-\infty}^{\infty} \frac{1}{|2\nu+1|^\alpha} - \sum_{\nu=-\infty}^{\infty} \frac{1}{|2\nu+1|^\alpha} + \frac{\hbar^2}{t} \left| 2\nu + 1 + (\hbar + \lambda \rho) / t \right|^{-1},$$

where $t = T/T_c$, $\hbar = 4H_c2/\pi^2H^2T_c$, and $\alpha$ and $\lambda \rho$ are parameters reflecting the strength of the spin paramagnetic effect and spin-orbit interaction, respectively. The parameter $\alpha$ was proposed by Maki, known as Maki parameter. For the orientation of $H||ab$, the conventional scenario without spin-paramagnetic effect and spin-orbit interaction ($\alpha = 0, \lambda \rho = 0$) could not describe the experimental data (see the red dashed line in Fig. 3); the conventional scenario gives an estimation exceeding thrice the experimental value at 25 K. By adjusting the values of $\alpha$ and $\lambda \rho$, the data can be roughly represented by the theoretical model with the parameters $\alpha = 9$ and $\lambda \rho = 0.3$, as shown by blue dashed line in Fig. 3. Note that the value of $\alpha$ obtained herein is very large, and the previous maximum value of $\alpha = 6.5$ is found in the 11111 system. This indicates a very strong spin-paramagnetic effect in the present system. Meanwhile, the spin-orbit interaction with a strength $\lambda \rho = 0.3$ is essential to describe the experimental data. To give a vivid impression for the necessity of such a large $\alpha$, we also show the theoretical curve with $\alpha = 5$ and $\lambda \rho = 0.3$, as shown by yellow dashed line in Fig. 3, which fails to reflect the strongly convex curvature at approximately 25 K.

In the case of out-of-plane case ($H||c$), as shown by pink dotted line in Fig. 3, the conventional WHH model again fails to describe the experimental data. This means that the introduction of $\alpha$ and $\lambda \rho$ can not improve the situation because typically the spin-paramagnetic effect further suppresses the value of the upper critical field. We note that this sublinear feature of the $H_c2 - T$ is common in the family of FeSCs and is widely believed to be a consequence of the multiband effect. The feature of multiband effect is more pronounced for the orientation with $H||c$ than that with $H||ab$. The ratio $\eta = D_h / D_e$, where $D_h$ and $D_e$ are the diffusivities of the hole and electronic bands respectively, is the key factor controlling the $H_c2 - T$ behavior of the multiband superconductors in the dirty limit. Typically, the in-plane value $D_h^{ab}$ is much smaller than $D_e^{ab}$ because of the large effective mass of the hole-type carriers. When the field is applied along the $c$ axis, only the in-plane diffusivity is involved. Hence, we obtain a quite small value of $\eta$, leading to the pronounced feature of the multiband effect. For $H||ab$, on the contrary, the out-of-plane values of $D_h^c$ and $D_e^c$ should be considered when

![Pulsed DC](image-url)
calculating $\eta$, and hence, $\eta$ is enhanced. This may explain the observed indistinctive multiband feature in the case of $H_{ab}$. Such a tendency was noticed and discussed by Hunte et al. when studying the LaFeAsO$_{0.89}$F$_{0.11}$ system\textsuperscript{39}.

Finally, we performed a quantitative comparison of the studied system with other systems of FeSCs\textsuperscript{23, 28-30, 49-52}. In Fig. 4(a), the anisotropic parameter $\Gamma = H_{ab}^H/H_{ab}^c$ is plotted as a function of the reduced temperature $t = T/T_c$. The spin Maki parameter $\alpha$ as a function of the slope $H' = -d\mu_b H_{ab}^H/dT|_{T_c}$. Red dashed line denotes the Maki relation in the weak-coupling limit. The references for the data are denoted in the figure.

According the Maki formula\textsuperscript{30}, $\alpha$ can be expressed as

$$\alpha = \frac{\sqrt{2}H_{ab}^{orb}(0)}{H_P(0)},$$

where $H_{ab}^{orb}(0) = 0.693 \times H' \times T_c$ is the upper critical field in the absence of the spin term, and $H_P(0)$ is the Pauli limited field. In the weakly coupled BCS scenario, we have $H_P^{BCS}(0) = 1.84 \times T_c$. Therefore, a very simple relation $\alpha = 0.53H'$ can be obtained if $H'$ is expressed in units of $T/K$. This relation, which is represented by the red dashed line in Fig. 4(b), reveals the close relation between $\alpha$ and slope of $H_{ab}^H$ vs $T$ at $T_c$. The experimental data roughly follows the tendency of the Maki formula. The departure of the data from the red dashed line is a consequence of the enhancement of $H_P(0)$ over $H_P^{BCS}(0)$ due to the strong coupling effect. The present 12442 system also exhibits this tendency to a greater extent than that in the other FeSC systems.

The value of $\alpha$ can be determined using the physical quantities in the normal state\textsuperscript{32}.

$$\alpha \propto \gamma_n \rho_n,$$

where $\gamma_n$ and $\rho_n$ are the normal state electronic specific heat (SH) coefficient and normal state dc resistivity, respectively. This may provide clues for exploring the origin of the large $\alpha$ in KCa$_2$Fe$_4$As$_4$F$_2$. The SH measurements revealed a rather high SH jump $\Delta C/T|_{T_c} = 32.5 - 37.5$ mJ/mol-Fe K$^2$ in KCa$_2$Fe$_4$As$_4$F$_2$\textsuperscript{37, 49, 43}; this value is the second-largest after the value for the K-doped 122 system Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ ($\approx 49$ mJ/mol-Fe K$^2$)\textsuperscript{44} in the family of FeSCs. This suggests a large magnitude of $\gamma_n$ in KCa$_2$Fe$_4$As$_4$F$_2$, assuming a proportional relationship between $\gamma_n$ and $\Delta C/T|_{T_c}$. From the viewpoint of the normal state dc resistivity, $\rho_n$ of KCa$_2$Fe$_4$As$_4$F$_2$ is thrice (5 times) that of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ at 300 K (40$K$)\textsuperscript{18, 44}. In other FeSCs systems, e.g., the 1111 system, the value of $\rho_n$ is large, whereas $\gamma_n$ is small\textsuperscript{45, 46}. Considering the above two factors synthetically and comprehensively, we find that the large value of $\alpha$ in KCa$_2$Fe$_4$As$_4$F$_2$ can be attributed qualitatively to the fact that both $\gamma_n$ and $\rho_n$ are relatively larger.

4 Conclusions

In summary, the high magnetic field dependence of the resistivity for the KCa$_2$Fe$_4$As$_4$F$_2$ single crystals was measured. The extremely steep increase of in-plane $H_{ab}^H$ with cooling near $T_c$ changes to a bending behavior, resulting in a rapid decrease in the anisotropy $\Gamma$ with cooling. The evolution feature of the $H_{ab}^H - T$ curve can only be described by the WHH model with a large Maki parameter $\alpha = 9$, indicating a strong Pauli paramagnetic effect in the present system. The relatively large $\gamma_n$ and $\rho_n$ may explain the observed large value of $\alpha$.

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