Low temperature specific heat of the 12442-type KCa$_2$Fe$_4$As$_4$F$_2$ single crystals

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Form the structural point of view, most of the Fe-based superconductors (FeSCs) belong to the monolayered, e.g. 1111 and 21311 systems, and infinite-layered systems, e.g. 11 and 122 systems. The only exception is the 12442 system which has double FeAs layers between neighboring insulating layers. This new system has the general chemical formula AB$_2$Fe$_4$As$_4$C$_2$ (A = K, Rb, Cs; B = Ca, Nd, Sm, Gd, Tb, Dy, Ho; C = F, O) and attracted wide research interests in the recent years. The first-principal calculations revealed a rather complicated band structure with ten Fermi surfaces around the Fermi level. The superconducting (SC) transition temperature could be tunable by cobalt substitution. Single crystals were also obtained by the using the self-flux method and an abnormally high slope of the upper critical field vs $T_c$ was reported. The SC gap structure has been investigated by the muon spin relaxation ($\mu$SR) measurements, heat transport measurements, lower critical field measurements, and optical spectroscopy measurements. However, the conclusions are rather controversial. The lower critical field study revealed a clear multi-gap feature with a large anisotropy. The nodal gap structure was indicated by the $\mu$SR measurements. Whereas the heat transport and optical spectroscopy measurements have supported a nodeless scenario. Consequently, more experiments by other techniques are urgently required to clarify this argument.

Specific heat is a bulk tool to detect the quasiparticle density of states (DOS) at the Fermi level, which can provide information about the gap structure. The variation of the electronic SH in the SC states vs temperature and field is rather different for different gap structures, which can be used as a reliable criterion to probe the information of superconducting gap. Although SH data have been exhibited in the previous studies, an in-depth investigation is still lacking up to now. In this Letter, we present an in-depth low temperature SH study of the 12442-type KCa$_2$Fe$_4$As$_4$F$_2$ single crystal. A clear SH jump with the height of 130 mJ/mol K$^2$ was observed. The field induced electronic SH coefficient showed a very quick increase with field in the low-field region, revealing the very large anisotropy of the gap structure. Moreover, the feature of the SH anomaly around $T_c$ under field diverges from the BCS picture and indicates an evolution tendency towards the Bose-Einstein condensation (BEC).

The KCa$_2$Fe$_4$As$_4$F$_2$ single crystals were grown by the self-flux method. The sample for the SH measurement had a mass of 2.3 mg. The detailed growth conditions and sample characterizations has been reported in our previous work. The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, MPMS 3). The specific heat were measured on the physical property measurement system (Quantum Design, PPMS). We employed the thermal relaxation technique to perform the
specific heat measurements. The external field was applied along the \(c\) axis of the single crystal during the SH measurements. The first-principles calculations were performed using the all-electron full potential linear augmented plane wave plus local orbitals (FP-LAPW+lo) method \[25\] as implemented in the WIEN2K code \[26\]. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) as proposed by Pedrew, Burke, and Ernzerhof \[27\]. Throughout the calculations, we fixed the crystal structure to the experimental values \[5\].

The superconducting transition of the single crystal was checked by the dc magnetization measurements. As shown in Fig. 1(a), the clear and sharp SC transition at about 32.5 K can be seen from the \(\chi - T\) curve, indicating a high quality of the selected sample. The magnetic field was applied parallel to the \(ab\)-plane of the crystal to minimize the effect of the demagnetization. The absolute value of magnetic susceptibility \(\chi\) is very close to 100\%, indicated a high superconducting volume fraction of our sample. In Fig. 1(b) we show the raw data of SH coefficient \(\gamma = C/T\) vs \(T\) at 0 T and 9 T. Here one mole means Avogadro number of the formula units (f.u.), \(\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2\). A clear and sharp SH anomaly due to the SC transition can be seen near \(T_c\) from the raw data of 0 T. While for the data under 9 T, this anomaly becomes obscure. Within a limited temperature range above \(T_c\), \(C/T\) reveals a linear temperature dependence as shown.

FIG. 1: (color online) (a) Temperature dependence of dc magnetization for the \(\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2\) single crystal. The applied magnetic field is 1 Oe. (b) Temperature dependence of specific heat plotted as \(C/T\) vs \(T\) under two fields 0 T and 9 T.

FIG. 2: (color online) (a) The SH data after subtracting the linear background from the normal states. (b) SH jump height as a function of superconducting transition temperature \(T_c\). The result of 12442 system (red star) is from the present work. The data of other systems were collected from the references \[21, 28–34\]. (c) Calculated electron DOS of \(\text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2\) plotted on a per Fe atom basis with both spins.
by the red dashed line in Fig. 1(b), which can be used as an estimation for the SH contribution of the normal states including the phonon term and the normal electronic term in this local temperature region around $T_c$.

Thus we have subtracted this linear straight line from the raw data and the results is shown in Fig. 2(a). The SH anomaly $\Delta C/T|_{T_c}$ at zero field was determined to be about 130 mJ/mol K$^2$, as indicated by the blue arrowed line. We must note that there are 4 Fe atoms in one formula unit of KCa$_2$Fe$_2$As$_4$F$_2$, which is twice that of 122 system, e.g. Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. So the SH anomaly needs to be reduced by half when comparing with the 122 system, which amounts to 65 mJ/mol K$^2$ for the 2-Fe-atoms case. We found that this magnitude commendably conforms to the plot based on the Bud’ko, Ni and Canfield (BNC) law, $\Delta C \propto T_c^3$ (see Fig. 2(b)). Assuming a weak-coupling BCS picture where the ratio $\Delta C/\gamma_n T|_{T_c} = 1.43$, we can estimated the normal state electronic SH coefficient $\gamma_n \approx 91$ mJ/mol K$^2$. In order to have a comparison with the theoretical prediction, we carried out the first-principals calculations and displayed the results of electron DOS in Fig. 2(c). The electronic SH data is related to the value of DOS at the Fermi level, which is $N(E_F) = 4.75$ eV$^{-1}$/Fe with both spins included. This value is quite consistent with the previous report on this material and remarkably larger than that obtained in the 1111 ($\sim 2.62$ eV$^{-1}$/Fe) and 122 ($\sim 2.3$ eV$^{-1}$/Fe) systems. Without regard to any coupling with the electrons, the bare specific-heat coefficient $\gamma_{bare}$ can be calculated using the formula $\gamma_{bare} = \pi^2 k_B^2 N(E_F)/3 = 11.2$ mJ/mol K$^2$ (per mol Fe) = 44.8 mJ/mol K$^2$ (per mol f.u.), where $k_B$ is the Boltzmann constant. This bare value is about one half of the experimental result, indicating a rather strong coupling of the electrons in the real material.

We next focus our attention on the SH data in the low temperature range to study the low-energy excitations. Here we plot the raw data of SH as $C/T$ vs $T^2$ in Fig. 3(a). In low temperature range below 3.5 K, which is about 1/10 of $T_c$, all the curves under different fields show a linear behavior and no Schottky anomaly can be observed, which facilitates the following analysis of our data. By extrapolating this linear tendency to zero temperature (as shown by the dashed lines in Fig. 3(a)), we can obtain the field dependence of the electronic SH coefficient $\gamma(H)$ because the phonon contribution vanishes as the temperature is reduced to 0 K. A rather large residual term $\gamma_0 \equiv \gamma(0) = 19.5$ mJ/mol K$^2$ was revealed. Typically this term was attributed to the non-superconducting fraction of the sample and/or the residual quasiparticle DOS in the SC materials with d-wave or $S^\pm$ gap symmetry. Since a SC volume fraction approximate to 100% was confirmed by the magnetization measurement, the former possible origin should be ruled out and $\gamma_0$ may come from the residual quasiparticle DOS due to the unconventional gap symmetry of the present system. The field-induced term $\Delta \gamma = \gamma(H) - \gamma_0$ can reflect the information of the SC gap, which is shown in Fig. 3(b). It is difficult to describe the field dependence of $\Delta \gamma$ using a simple formula due to the multi-band effect in the present system. Nevertheless, qualitatively $\Delta \gamma$ increases more quickly in the system with a small minimum for the gap size and thus a highly anisotropic gap structure, as has been observed in cuprates and MgB$_2$. This is because considerable quasiparticle DOS can be induced by the magnetic field around the Fermi surface with the gap minimum. Thus the very quick increase of $\Delta \gamma$ with field below 3 T in our data indicates a rather large anisotropy for the SC gap(s), being consistent with the studies on CsCa$_2$Fe$_4$As$_4$F$_3$ by lower critical field measurements. This behavior is in sharp contrast with the hole-doped 122 system Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, where a slow and roughly linear increase of $\Delta \gamma$ was observed. Considering the multi-band feature of this system, such a large anisotropy...
may occur on an individual Fermi surface (FS) sheet or originate from the great difference between different FS sheets. At this stage, we could not distinguish these two situations. In addition, the possibility for the presence of gap nodes could not be ruled out based on our data.

We noticed that the quick increase of $\Delta \gamma$ is accompanied by the severe suppression of the SH jump around $T_c$ under magnetic fields. In order to have a vivid impression, we plot the SH data around $T_c$ of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [21] and KCa$_2$Fe$_4$As$_4$F$_2$ (12442, this work). The scales of both coordinate axes are normalized.

![Graph](image)

FIG. 4: (color online) SH data at the transition for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (122, Ref. [21]) and KCa$_2$Fe$_4$As$_4$F$_2$ (12442, this work). The scales of both coordinate axes are normalized.

almost unchanged onset point of the SH anomaly under 9 T as compared with the zero field data (see the black arrowed line in Fig. 4(b)). It is important because within the BCS picture this onset point should shift monotonously to lower temperature, just as that observed in conventional superconductors [20, 39]. Such an abnormal behavior has been reported in cuprates and attracted great attentions in the 1990s [10, 42]. With the effort from both the experimental and theoretical sides, this was interpreted by a crossover from BCS-like superconductivity for weak coupling to BEC-like superconductivity for strong coupling [42]. The variable that control such a crossover was identified as $k_F\xi$ [43], where $k_F$ is the Fermi electron wave number and $\xi$ the coherence length. The unexpected high values of $d\mu_0H_c^2/dT|_{T_c}$ and $d\mu_0H_c^{ab}/dT|_{T_c}$ may result in a rather small coherence length $\xi$, which leads to the reduction of parameter $k_F\xi$. We speculated that this is the internal reason for the departure from the BCS limit and tending to the BEC limit of our system. A more precise estimation and analysis are needed in the future to further confirm our speculation.

In summary, we studied the low-temperature specific heat of the 12442-type KCa$_2$Fe$_4$As$_4$F$_2$ single crystal. We found a clear SH jump with the height of 130 mJ/mol K, which is consistent with the scaling based on the BNC law. The electronic SH coefficient $\Delta \gamma$ shows a very quick increase with field in the low-field region below 3 T, indicating a rather small minimum and large anisotropy of the SC gap(s). This conclusion is further supported by the severe suppression of the SH jump by the magnetic field. Moreover, the onset point of the SH jump is not affected by the field, which is inconsistent with the BCS picture and locates the present system on the crossover from the BCS to BEC limit.

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