Single crystal growth and effects of Ni doping on the novel 12442-type iron-based superconductor RbCa2Fe4As4F2

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Abstract

The recently discovered 12442-type iron-based superconductors (IBSs), ACa2Fe4As4F2 (A = K, Rb, Cs), are intrinsically self-hole doped stoichiometric compounds that exhibit superconductivity with \( T_c = 30–33.5 \) K. In this paper, single crystals of Ni doped RbCa2(Fe1−xNi)xAs4F2 with 0 \( \leq x \leq 0.1 \) have been successfully grown for the first time using a RbAs flux method and characterized by energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), electrical resistivity, magnetic susceptibility, and Hall effect measurements. EDS and XRD measurements suggest that the Ni dopants are successfully doped into the crystal lattice. Based on the electrical resistivity and magnetization data, we construct the \( T_c - x \) phase diagram. Furthermore, it is found that Ni dopants not only introduce extra electrons that modify the topology of Fermi surface, but also act as impurity scattering centers that contribute to the pair breaking effect, i.e., the superconducting transition temperature \( T_c \) is suppressed with a rate of \( \Delta T_c/Ni=1\% = -2.7 \) K. Intriguingly, such suppression of \( T_c \) and those in other similar hole doped IBSs, such as Ba0.6K0.4Fe2As2, Ba0.5K0.5Fe2As2, and EuRbFe4As4 with multiple nodeless gaps, can be well scaled together. Combining with relevant experimental data reported so far, we speculate that the pairing symmetry in 12442 system is very likely to be nodeless \( s^\pm -wave \).

1. Introduction

Since the discovery of high-\( T_c \) superconductivity in 1111-type LaFeAs(O, F) [1], many different families of iron-based superconductors (IBSs) have been discovered, such as 11, 111, 122, 112, 1038/1048, and 11111, etc [2]. For most of these materials, superconductivity generally emerges after the suppression of antiferromagnetic (AFM) order in the parent compound by carrier doping or application of external pressure [2]. Recently, by the intergrowth of 1111-type CaFeAsF and 122-type AFe2As2 (A = K, Rb, Cs), several novel 12442-type ACa2Fe4As4F2 (A = K, Rb, Cs) compounds, which consist of alternate stacking of the conducting Fe2As2 layers and insulating Ca2F2 layers, were successfully synthesized [3, 4]. A typical crystal structure of RbCa2Fe4As4F2 is depicted in figure 2(a) for reference. Contrary to other IBSs, 12442 compounds are the only IBSs with double FeAs layers between neighboring insulating layers, mimicking the case of double CuO2 layers in cuprates. ACa2Fe4As4F2 (A = K, Rb, Cs) compounds are superconducting in their stoichiometric state with \( T_c = 30–33.5 \) K without extra carrier doping. The formal charge of Fe is given as +2.25, indicating that 12442-type compounds are intrinsically self-hole doped (0.25 holes/Fe2+) IBSs, similar to the analogous 1144-type IBSs and optimally K doped 122-type Ba1−xKxFe2As2.
\( (x = 0.4–0.5) \) [5, 6]. The upper critical field shows large anisotropy near \( T_c \), and strong Pauli paramagnetic effect at low temperatures is demonstrated by the pulsed field measurements [7]. The first-principal calculations reveal a rather complicated electronic structure, consisting of six hole-like pockets at the center of Brillouin zone \( \Gamma \) point and four electron-like pockets at the zone corner M point [8, 9].

Very recently, the bilayer splitting effect contributed by the interlayer coupling is clearly identified by angle-resolved photoemission spectroscopy (ARPES) measurement [10]. Moreover, the coexistence of such multiple Fermi surfaces provides a novel platform to identify the sign change and pairing symmetry of IBSs and shed light on the mechanism underlying high-\( T_c \) superconductivity.

The pairing symmetry is very much crucial for understanding the superconducting mechanism. It has been demonstrated that the pairing symmetry in cuprates is nodal \( d \)-wave type [11], while its form in IBSs has not been settled. Theoretically, from the viewpoint of the multiband Fermi surfaces, within the full gap scenario, the interband sign reversal \((s\pm)\) and sign preserving \((s\mp)\) wave superconducting states, which are respectively mediated by the AFM spin fluctuation and Fe 3d orbital fluctuation, are generally accepted in IBSs [12–16]. In addition, nodal \( d \)-wave and accidental nodal \( s \)-wave gaps are also expected in some special compounds with gap nodes, such as in the heavily hole doped \((Ba_{1-x}K_x)Fe_2As_2\) and FeP-based superconductors [17–21]. Consequently, in order to identify the pairing symmetry, it is necessary to demonstrate the anisotropy of the gap structure. To date, the gap structure of 12442 system has been detected by various experiments [10, 22–27], but is still controversial whether there exists gap nodes or not. The muon spin relaxation (\( \mu \)SR) experiments suggest it has a nodal gap [22, 23], whereas ARPES, thermal conductivity, and optical spectroscopy measurements reveal a nodeless gap [10, 25, 26]. Impurity substitution is an alternative and effective way to further address this issue, because the pair breaking effect induced by impurities strongly depends on the pairing symmetry as well as the gap structure. Previously, many transition metals, such as Co, Ni, Mn, Cu, Zn, Cr, Ru, Ir, etc, have been regarded as substitutions to study the impurity induced pair breaking effect in IBSs [28–35]. Therefore, detailed studies on the impurity effect are expected to give an important hint for understanding the mechanism of superconductivity in 12442 system. Initial experiment on Co doped \( KCa_2Fe_4As_4F_2 \) polycrystalline samples has argued that Co dopants provide extra electrons and also act as an impurity scattering centers that result in the suppression of \( T_c \) [9]. In order to better understand the intrinsic impurity effect and pairing symmetry in 12442 system, further studies performed on single crystals by using more substitutions are clearly desired. Also, the obtained single crystals can allow us to study the doping effect on superconducting anisotropy. To date, except for \( RbCa_2Fe_4As_4F_2 \), single crystals of \( ACa_2Fe_4As_4F_2 \) with \( A = K, Cs \) have been grown by using KAs and CsAs flux [27, 36], while doped single crystals in 12442 system are still lacking.

In this paper, we synthesize a series of Ni doped \( RbCa_2(Fe_{1-x}Ni_x)\),\( _2\)\,\( _4\)\,\( _2\)\,\( _4\)\,\( _4\)\,\( _2\) (0 \( \leqslant x \leqslant 0.1 \)) single crystals for the first time using a RbAs flux and study the doping effects on this system. We find that the topology of Fermi surface is gradually changed with increasing \( x \). Moreover, Ni dopants also introduce impurity scattering centers that suppress the superconducting transition temperature \( T_c \) with a rate of \( \Delta T_c/Ni-1\% = -2.7 \) K. Of particular interest is such suppression of \( T_c \) and those in \( Ba_{0.6}K_{0.4}Fe_2As_2 \), \( Ba_{0.5}K_{0.5}Fe_2As_2 \), and \( EuRbFe_2As_4 \), which have multiple nodeless superconducting gaps and almost the same hole doping levels (\( 0.25 \) holes/\( Fe^\text{2+} \)) with 12442 system, can be well scaled together, indicative of the possible existence of nodeless \( s\pm \)-wave gaps in 12442 system. Finally, owing to the successful growth of high-quality single crystals, doping evolution of the upper critical field and its anisotropy are also obtained and discussed in detail.

2. Experiment

Single crystals of \( RbCa_2(Fe_{1-x}Ni_x)\),\( _2\)\,\( _4\)\,\( _2\)\,\( _4\)\,\( _2\) were grown by the self-flux using RbAs, similar to the procedure used for the \( KCa_2Fe_4As_4F_2 \) crystal growth as reported elsewhere [36]. A mixture with a molar ration of \( RbAs:CaAs:Fe_2As:Ni_2As:CaF_2 = 16:2.2:2:2:1.5, \) totally about 2 g in mass, was grounded and loaded into an alumina crucible. Additional amounts of 100\% \( CaAs \) and 50\% \( CaF_2 \) were added to reduce the possibility of \( RbFe_2As_2 \) phase formation. All the weighing and mixing procedures were carried out in an argon-filled glove box with the water and oxygen content below 0.1 ppm. The mixtures were then subsequently sealed in a stainless steel pipe [37]. The pipe was placed into a furnace preheated to 1000 °C, held at for 20 h, and slowly cooled down to 900 °C with a rate of 2.5 °C h\(^{-1}\), then extracted from the furnace and quenched to room temperature by quenching in water. Plate-like single crystals with typical dimension of 1.5 \( \times \) 1 \( \times \) 0.05 mm\(^3\) were easily separated from RbAs flux by rinsing them with deionized water. The optical image of a typical \( RbCa_2(Fe_{1-x}Ni_x)\),\( _2\)\,\( _4\)\,\( _2\) single crystal with \( x_{\text{nominal}} = 0.1 \) on millimeter scale paper is shown in the bottom inset of figure 1.
The real concentration of Ni dopants as a function of the nominal one. The top and bottom insets show the EDS spectrum and optical image of a typical RbCa2(Fe1−xNi)xAs4F2 single crystal with x_{nominal} = 0.1, respectively. The dashed line is a straight line with x_{real} = 0.67x_{nominal}.

3. Results and discussion

3.1. Chemical and structural characterization

Firstly, in order to check whether or not the Ni atoms are really doped into the crystal lattice and determine the real Ni concentration, we performed EDS measurement on RbCa2(Fe1−xNi)xAs4F2 single crystals. For each crystal, 5–10 different spots were selected and the average was used to determine the real Ni concentration. The top inset of figure 1 shows a typical EDS spectrum with x_{nominal} = 0.1, it is clear that all elements including Rb, Ca, Fe, Ni, As, and F are detected. The results of EDS analyses are summarized in the main panel of figure 1. As can be seen, the real concentration has a nearly linear relationship with the nominal one, i.e., x_{real} = 0.67x_{nominal}. It is found that the maximum Ni doping achieved is at x_{real} = 0.1, and no crystals can be synthesized successfully once the nominal Ni concentration is more than 15%. Hereafter, we will refer to the single crystals by their real Ni concentration x.

Figure 2(b) plots the XRD patterns of RbCa2(Fe1−xNi)xAs4F2 single crystals used in this study. Only (002l) (l is an integer) diffraction peaks are observed with a relatively small full width at half-maximum (FWHM), indicating good c-axis orientation and high crystalline quality of our samples. As expected, all (002l) diffraction peaks shift systematically to higher 2θ with increasing Ni concentration due to the smaller ionic radius of Ni2+ than Fe2+. Such shift can be seen more clearly from figure 2(c), in which the enlarged view of representative (0026) peaks are presented, providing further evidence that Ni atom was successfully doped into the crystal lattice. By refining the (002l) diffraction patterns, the c-axis lattice parameters are estimated and plotted as a function of the Ni concentration x in figure 2(d). For the pristine sample (x = 0), the c-axis lattice parameter is 31.651 Å, consistent with the previous report on polycrystalline samples [4]. With increasing x, the c-axis lattice parameter monotonically decreases. At x = 0.1, the c-axis lattice parameter is reduced by ~1%.

3.2. Electrical resistivity, magnetic susceptibility and T_c–x phase diagram

Figure 3(a) presents the temperature dependence of in-plane resistivity $\rho(T)$ of RbCa2(Fe1−xNi)xAs4F2 single crystals at different doping levels. It is found that the resistivity at T = 300 K, $\rho(300 \text{ K})$, monotonically increases with Ni doping, different from the case of KCa2(Fe1−xCo)xAs4F2 polycrystalline samples in which $\rho(300 \text{ K})$ shows a nonmonotonic trend with doping [9]. By decreasing temperature, $\rho(T)$
Figure 2. (a) Crystal structure of 12442-type RbCa$_2$Fe$_4$As$_4$F$_2$. (b) XRD patterns of RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4$F$_2$ single crystals used in this study. (c) Peaks of the (0026) reflections of RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4$F$_2$ single crystals. (d) The c-axis lattice parameters plotted as a function of the doping concentration $x$. The curve of RbCa$_2$Fe$_4$As$_4$F$_2$ shows a convex behavior, and a gradual change in the slope of $\rho(T)$ curve appears at the characteristic temperature $T^\rho$, where a coherence-incoherence crossover is generally proposed to be occurred in the heavily hole doped IBSSs [38]. With increasing $x$, such crossover becomes less pronounced. An enlarged view of the resistivity curves at low temperatures is shown in figure 3(b), clearly, the superconducting crystals exhibit sharp transitions, indicating the high-quality of our samples. The superconducting transition temperature, $T_c$, is defined when the resistivity drops to 50% of the normal state value $\rho_n$. The value of $T_c$ decreases nearly linearly, upon Ni doping, from 31.3 K for $x = 0$, to 25 K for $x = 0.03$, 20.6 K for $x = 0.05$, 14.7 K for $x = 0.07$, and 7.5 K for $x = 0.09$. The superconductivity is almost killed when the doping level reaches $x \approx 0.1$. Similar consistent results were also obtained through the $T$-dependent magnetic susceptibility measurements as shown in figure 3(c).

To gain more information about the normal state properties, we analyze the resistivity data in the range of $T_c < T < 70$ K according to the power law function, $\rho = \rho_0 + AT^n$, where $\rho_0$ is the residual resistivity and $A$ is a constant. The fitting parameters are given in figures 4(a) and (b), which shows similar tendency with that in Co doped KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4$F$_2$ [9]. For both Ni and Co doping series, the magnitudes of exponent $n$ show a nonmonotonic dependence on doping, which reside in the range of 0.75–1.15 below certain doping level and then increase up to $\sim 1.6$ with further increasing $x$, indicating that the ground state evolves from a non-Fermi liquid to more like Fermi liquid behavior by chemical doping. $\rho_0$ linearly increases with increasing of the doping concentration $x$. An interesting feature is that the residual resistivity $\rho_0$ takes a negative value for the pristine sample, which has also been observed in CsCa$_2$Fe$_4$As$_4$F$_2$ single crystals and other IBSSs [27, 39]. This fact is suggestive that the $\rho(T)$ curves should develop significant positive curvature at lower temperatures. It also suggests that the pristine samples of 12442 system have quite high residual resistivity ratio, RRR, in $T \rightarrow 0$ limit. Since the $\rho_0$ of pristine sample is negative, herein, we adopt $\rho(T_c)$, defined as the normal state resistivity near the superconducting transition, to calculate the RRR = $\rho(300 \text{ K})/\rho(T_c)$. The values of RRR are systematically reduced with increasing $x$, as shown in figure 4(c). Hence, together with the increased $\rho_0$, it clearly suggests that the strength of impurity scattering induced by the substituted Ni/Co atoms becomes strongly enhanced. Moreover, we also plot the $T_c$ as a
Figure 3. (a) Temperature dependence of in-plane resistivity $\rho(T)$ of RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4$F$_2$ single crystals. (b) An enlarged view of $\rho(T)$ near the superconducting transition. (c) Temperature dependence of magnetic susceptibility of RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4$F$_2$ single crystals with $H = 5$ Oe. (d) $T_c$-$x$ phase diagram, superconducting transition temperatures $T_c$ are determined from the resistivity and magnetic susceptibility measurements, respectively.

function of $\Delta$RRR/RRR($x = 0$) in figure 4(d), here $\Delta$RRR is the difference of the residual resistivity ratio between the pristine and doped single crystals, i.e., $\Delta$RRR = RRR($x = 0$) − RRR($x$). It can be clearly seen that the suppression of $T_c$ is intimately related to the enhanced impurity scattering, a detailed discussion of this point is given in later section 3.4.

3.3. Doping induced the change of Fermi surface topology
To proceed, we measured the field dependence of Hall resistivity $\rho_{xy}$ for RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4$F$_2$ single crystals. In all cases, $\rho_{xy}$ exhibits a linear field dependence up to 9 T, data for several selected samples with $x = 0$, 0.07, and 0.1 are shown in figures 5(a)–(c), respectively. Figure 6(a) depicts the temperature dependence of Hall coefficients $R_H$, calculated from $R_H = \rho_{xy}/H$. Upon Ni doping, the magnitude of $R_H$ at fixed temperatures monotonically decreases and gradually changes sign from positive to negative, indicative of the effective electron doping from Ni dopants. As a representative, the doping dependence of $R_H$ at $T = 50$ K is given in figure 6(b). Furthermore, one can see that the behaviors of $R_H$ show different temperature dependences at various doping levels. For $x \leq 0.05$, $R_H$ shows a nonmonotonic temperature dependence at low temperatures, consistent with previous study on KCa$_2$Fe$_4$As$_4$F$_2$ polycrystalline samples [3]. While, it becomes more monotonic like at higher doping levels. For $x = 0.07$, $R_H$ becomes almost temperature independent at high temperatures and keeps a constant value close to zero. By decreasing temperature, a sign reversal from positive to negative occurs around 80 K, indicating that the dominant carriers changed from holes to electrons. Upon further doping, $R_H$ monotonically decreases with lowering temperature and remains negative over the whole temperature range. Note that, the Hall signal of $x = 0.09$ in the high temperature region is too weak to be distinguishable, revealing that $R_H$ is also close to zero in this sample.

The first-principal calculations and ARPES measurement have demonstrated the presence of multiple electron- and hole-like Fermi surfaces in 12442-type compounds [8, 10]. Herein, we propose to use a two-band model to explain above observations. For a system with multiband electronic structure involving
Figure 4. (a) and (b) show the exponent $n$ and residual resistivity $\rho_0$ obtained by fitting the power law $\rho = \rho_0 + A T^n$. For comparison, the corresponding parameters of Co doped KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4F_2$ taken from [9] are also plotted. (c) Doping dependence of the residual resistivity ratio, $\text{RRR} = \rho(300 \text{ K})/\rho(T_c)$, where $\rho(T_c)$ is the normal state resistivity near the superconducting transition. (d) $T_c$ as a function of $\Delta \text{RRR}/\text{RRR(x=0)}$.

two types of charge carriers, the field dependence of $\rho_{xy}(H)$ can be expressed as

$$\rho_{xy}(H) = 1 \frac{\left(\mu_e^2 n_h - \mu_h^2 n_e\right) + (\mu_e \mu_h)^2 H^2 (n_h - n_e)}{\mu_e n_e + \mu_h n_h} + (\mu_h \mu_e)^2 H^2 (n_h - n_e)^2,$$

where $n_{e,h}$ and $\mu_{e,h}$ are carrier density and mobility of electrons and holes, respectively [9, 40]. Considering that the linear field dependence of $\rho_{xy}(H)$ in the RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4F_2$ samples, the nonlinearity term, $(n_h - n_e)H^2$, can be negligible, indicating that the number of electron ($n_e$) and hole ($n_h$) carriers are nearly same in RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4F_2$, consistent with the Co doped KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4F_2$ that has been proposed to be in the proximity of a compensated semimetal [9]. In this case, the Hall coefficient based on equation (1) can be simplified as

$$R_H \approx \frac{1}{e} \frac{\left(\mu_e^2 n_h - \mu_h^2 n_e\right)}{\mu_e n_e + \mu_h n_h} \approx \frac{1}{n_e} \frac{\mu_h - \mu_e}{\mu_h + \mu_e}.$$

Therefore, the strong temperature dependence of $R_H$ and its sign reversal observed above can be mainly attributed to the different temperature dependencies of $\mu_e$ and $\mu_h$. That is, $\mu_h > \mu_e$ for $R_H > 0$, $\mu_h \approx \mu_e$ for $R_H \approx 0$, and $\mu_h < \mu_e$ for $R_H < 0$. On the other hand, the doping evolution of $R_H$ should be reconciled with the calculations of electronic structures. In KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4F_2$, electronic structure calculations have identified that Co doping deeply affects the topology of Fermi surface [31]. In light of the Co doping effects on KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4F_2$, a two-band schematic of the Ni doping evolution of the Fermi pockets and band structure is depicted in figure 6(c). For the underdoped samples, the magnitudes of the electron and hole pockets are unbalanced, the hole pockets at the Brillouin zone center $\Gamma$ point are much larger than the electron ones at the corner $M$ point, the hole pockets dominate the electronic transport with $R_H > 0$. As doping content increases, part of the electrons fill the large hole pockets and part of them distribute to the electron pockets, resulted in the radii of each pocket are balanced with $R_H \approx 0$ at certain levels. Upon further doping, the electron pockets become larger than the hole ones and then dominate the electronic transport, corresponding to the case of $R_H < 0$. 
3.4. Impurity effect and possible nodeless $s^{±}$-wave state

When the radii of each pocket are balanced by Co/Ni doping in 12442 system, one would expect that the spin density wave (SDW) transition might be occurring due to the good nesting conditions. Nevertheless, no anomalies associated with the SDW transition are observed, different from that in 1144-type CaKFe$_4$As$_4$ where the AFM order is enhanced by Co/Ni doping [41]. Meanwhile, one would also expect the increase of $T_c$ after the suppression of the SDW order in IBSs. However, instead of increasing $T_c$ through electron introduction, we find that Co/Ni dopants continuously suppress $T_c$. These facts together with the results of Hall effect indicate that the substitution of Fe with Co/Ni not only introduces electrons into the FeAs layer, but also introduces disorders that suppress the possible SDW transition and simultaneously contribute to the pair breaking effect in 12442 system [31]. Moreover, upon Co/Ni doping, it is expected that the carrier density will be increased and result in a decrease of the resistivity. Unexpectedly, our results reveal that both residual resistivity $\rho_0$ and $\rho(300\,K)$ increase with the increase of Ni dopants, meanwhile, the values of RRR are obviously decreased accompanied with the suppression of $T_c$, as clearly seen in figures 4(b)–(d). Therefore, although one may argue that electrons introduction possibly leads to small changes of $T_c$, we believe that the $T_c$ suppression in our case is mainly induced by the impurity scattering.

In order to gain more insights into the pair breaking effect ($T_c$ suppression), which will give important information on the gap structure as well as the pairing symmetry, we plot the normalized $T_c$ versus doping content for RbCa$_2$(Fe$_{1-x}$Ni$_x$)$_4$As$_4F_2$ and KCa$_2$(Fe$_{1-x}$Co$_x$)$_4$As$_4$F$_2$ in figure 7 [9]. For comparison, similar data of the analogous 1144-type EuRb(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ [42], 122-type Ba$_{0.6}$K$_{0.4}$(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ [33], Ba$_{0.5}$K$_{0.5}$(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ [34], and K(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [30] are also plotted and discussed. All of these samples with $x = 0$ are hole doped and the absence of AFM order, similar to the situation in 12442 system. Through the calculation of the slopes, the average change of $T_c$ values per doping percent in 12442 system are obtained to be $\Delta T_c/Ni\cdot1\% = -2.7$ K and $\Delta T_c/Co \cdot 1\% = -1$ K. According to the Abrikosov–Gorkov formula [43], if the impurities act as strong pair breakers, the suppression of $T_c$ due to pair breaking is essentially related to the impurity scattering rate $k_B\tau_{imp} \propto \rho_0$, where $\tau_{imp}$ is the quasiparticle
lifetime of the impurity and $\rho_0$ is the residual resistivity. As seen from figure 4(b), Ni doping results in a higher rising rate of $\rho_0$ than that of Co doping, and therefore leads to the much stronger $T_c$ suppression. The suppression of $T_c$ in both Ni and Co doped ACa$_2$Fe$_4$As$_4$F$_2$ (A = K, Rb) is distinctly different from that in Co doped nodal superconductor KFe$_2$As$_2$, where the superconductivity can be killed completely with only 4% doping of Co impurities [30]. Such effective suppression of $T_c$ by Co doping was also observed in nodal superconductors LiFeP and LaFePO, and consequently Wang et al have argued that the rapid suppression of $T_c$ from impurity may be an intrinsic property of stoichiometric IBSs with nodal gap [30]. While, of particular interest is that the suppression of $T_c$ induced by Ni doping in RbCa$_2$Fe$_4$As$_4$F$_2$ mimics those in optimally K doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (0.2 holes/Fe$^{2+}$) [33], Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ (0.25 holes/Fe$^{2+}$) [34], and the analogous self-hole doped EuRbFe$_4$As$_4$ (0.25 holes/Fe$^{2+}$) [42]. For these typical compounds, the formal hole doping level is close or equal to the stoichiometric RbCa$_2$Fe$_4$As$_4$F$_2$ and the multiple nodeless gaps have been identified by various experimental studies [16, 44–46]. Indeed, in 12442 system, the multiple nodeless superconducting gaps have been supported by thermal conductivity [26], optical spectroscopy [25], and very recently ARPES measurements [10]. The nodal superconducting gap evidenced by previous $\mu$SR measurements in 12442-type polycrystalline samples may be influenced by the minor impurity phase of KFe$_2$As$_2$ or CsFe$_2$As$_2$ that is known to be a nodal superconductor [20, 26, 30, 47].

The pairing symmetry in IBSs with full gap structure has two possibilities, i.e., the sign reversal ($s^\pm$) and sign preserving ($s^{++}$) states. It is known that the $T_c$ suppression rates in the $s^\pm$- and $s^{++}$ states exhibit different responses to the doped nonmagnetic impurity [28]. For the IBSs with the $s^\pm$ wave state, $T_c$ should be sensitive to the impurities, regardless of magnetic or nonmagnetic impurities. In contrast, the $s^{++}$ wave state is robust against the nonmagnetic impurities. In IBSs, Co/Ni has been regarded as a nonmagnetic or very weak magnetic impurity [33, 48], in contrast with the case of Mn [31]. On the other hand, the multiple nodeless gaps in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $x \leq 0.55$ are consistent with the $s^\pm$-wave pairing [16, 45, 49]. Recently, the inelastic neutron scattering and optical conductivity measurements also present the strong evidence in favor of the nodeless $s^\pm$-wave superconducting state in EuRbFe$_4$As$_4$ [46, 50]. Note that, although the suppression rate of $T_c$ may be not as strong as expected by the scenario of $s^\pm$ pairing in IBSs, presumably resulted from the effect of multiple pairing channels as previously proposed [33]. Thus, combining these results mentioned above, we can speculate that the pairing symmetry in 12442 system is very likely to be nodeless $s^\pm$-wave, similar to that in the analogous self-hole doped 1144-type IBSs [50–53].

Figure 6. (a) Temperature dependence of Hall coefficients $R_H$ at various doping levels. (b) The doping concentration dependence of Hall coefficients $R_H$ at a typical temperature $T = 50$ K. The black dotted lines are guide to the eye. (c) A two-band schematic of the Ni doping evolution of the Fermi pockets and band structures.
3.5. Doping evolution of the upper critical field, anisotropy, and the crossover from 2D to 3D superconductivity

Finally, we investigate the doping evolution of the upper critical field and its anisotropy. Figure 8 shows the $T$–dependent in-plane resistivity $\rho(T)$ of the pristine and doped samples under the magnetic fields for $H||ab$ (top panels) and $H||c$ (bottom panels). For all samples, with increasing fields up to 9 T, the onset superconducting transition temperature remains almost no change for $H||ab$, and only shifts slightly to lower temperatures for $H||c$. However, the transition width becomes broader at higher fields, which is more pronounced for $H||c$, showing a tail structure at low temperatures. Such behavior has also been observed in 1111-[54], 112-[55], 11111-type IBSs [56, 57], and cuprates [58, 59], which is a consequence of the formation of a wide vortex-liquid phase for $H||c$.

In order to minimize the effects of superconducting fluctuation near 90\%\(\rho_n\) and vortex motion in the vortex-liquid region near 10\%\(\rho_n\) on the determination of upper critical field $\mu_0H_{c2}$, we also use the 50\%\(\rho_n\) criteria as adopted early, to define the $\mu_0H_{c2}$ values, plotted as a function of temperature for both field orientations in figure 9(a). As seen, all curves of $\mu_0H_{c2}(T)$ remain almost linear near $T_c$, which is given as $\mu_0H_{c2}^{ab}(0) = -0.693$ $T_c(d\mu_0H_{c2}/dT)_{T=T_c}$ in the dirty limit and $\mu_0H_{c2}^{ab}(0) = -0.73$ $T_c(d\mu_0H_{c2}/dT)_{T=T_c}$.
in the clean limit. The optical spectroscopy measurement has provided evidence for a band-selective coexistence of clean- and dirty-limit superconductivity in 12442 system [25]. Herein, we adopt the case of the pristine sample to its maximum 8.1 at 0 K should be distinctly different from \( \mu_0 H_{c2}^{orb}(0) \) due to the effect of Pauli paramagnetic effect. Knowing the slope of \( \mu_0 H_{c2} \), allows us to further estimate the superconducting coherence length and the anisotropy of \( \mu_0 H_{c2} \). The values of coherence lengths \( \xi \) near \( T_c \) can be calculated in both field orientations using the Ginzburg–Landau (GL) formula \( \xi_{ab} = \sqrt{\Phi_0/(2\pi T_c)|d\mu_0 H_{c2,ab}|dT|_{T=T_c}} \) and \( \xi_c = \Phi_0/(2\pi T_c|d\mu_0 H_{c2,c}|dT|_{T=T_c}) \), where \( \Phi_0 \) is the flux quantum (2.07 \times 10^{-15} \text{ Wb}) [61]. The corresponding GL coherence lengths \( \xi_{ab} \) and \( \xi_c \) at various doping levels are shown in figure 9(c). For \( x < 0.07 \), the value of \( \xi_{ab} \) is smaller than the FeAs interbilayer distance \( d_{\text{inter}} = 8.612(4) \AA \) [4] and exceeds \( d_{\text{inter}} \) at \( x = 0.09 \), indicating that the nature of superconductivity changes from quasi 2D (\( \xi_c > d_{\text{inter}} \)) to 3D (\( \xi_c < d_{\text{inter}} \)).

In figure 9(d), we plot the doping evolution of the anisotropy of \( \mu_0 H_{c2} \) near \( T_c \), \( \gamma_H = H_{c2,ab}/H_{c2,c} = (d\mu_0 H_{c2,ab}/dT)_{T=T_c}/(d\mu_0 H_{c2,c}/dT)_{T=T_c} = \xi_{ab}/\xi_c \). As seen, \( \gamma_H \) increases from 6.7 at the pristine sample to its maximum 8.1 at \( x = 0.03 \), and then abruptly decreases to 3.7 at \( x = 0.09 \). Interestingly, the minimum value of exponent \( n \) derived from the electrical resistivity is also appeared at \( x = 0.03 \) (see figure 4(a)), which suggests that the anisotropy \( \gamma_H \) may be correlated to the electrical properties of the normal state. It has been argued that the values of \( \gamma_H \) can provide important information about the anisotropy of the electrical resistivity, \( \gamma_R = \rho_a/\rho_c \). In the temperature range close to \( T_c \), zero-field, the anisotropy of \( \mu_0 H_{c2} \) for \( s \)-wave superconductors in the both clean and dirty limits can be roughly written as \( \gamma_H \sim v_a/v_c \), where \( v_a \) and \( v_c \) are Fermi velocities for \( a \) and \( c \) directions, respectively [62]. Assuming that the

Figure 9. (a) Temperature dependence of upper critical field \( \mu_0 H_{c2} \) for RbCa\(_2\)(Fe\(_{1-x}\)Ni\(_x\))\(_x\)As\(_2\) single crystals for both \( H || ab \) and \( H || c \) directions. Doping evolution of the slope of the \( \mu_0 H_{c2} \) near \( T_c \), \( d\mu_0 H_{c2}/dT \) (b, upper panel) and \( \mu_0 H_{c2}^{orb}(0) \) (b, low panel), of the Ginzburg–Landau coherence length \( \xi \) (c), and of the anisotropy of \( \mu_0 H_{c2} \) close to \( T_c, \gamma_H \) (d).
mean-free path is isotropic, \( \gamma_\mu = \mu / \rho_d = \sigma_d / \sigma_c \sim N_d / N_c D, \) where \( N \) is density of states and \( D \) is diffusivity, which are both proportional to \( v \) [39]. Hence \( \gamma_\mu = (v_d / v_c)^2 \), and \( \gamma_\mu^2 \sim \gamma_\rho. \) This approximation was verified semi-quantitatively in IBSSs [39, 63, 64]. Additional contribution to the doping evolution of the anisotropy of the \( \gamma_{1\parallel} \) can come from the change of the superconducting gap structure [65]. Recently, ARPES measurement suggests that KC\(_2\)Fe\(_4\)As\(_4\)F\(_2\) has multiple nodeless gaps that show an obvious Fermi surface dependence, i.e., the size of which varies among different Fermi surface sheets [10]. Indeed, our results suggest that the topology of the Fermi surface in RbCa\(_2\)Fe\(_4\)As\(_4\)F\(_2\) changes obviously upon Ni doping, in analogy to the case of Co doped KC\(_2\)Fe\(_4\)As\(_4\)F\(_2\) as revealed by the band structure calculations [9]. Lastly, note that the recent high field studies have revealed that, similar to many other systems [54, 55], the \( \mu_0 H_{c2} \) for \( H \parallel ab \) in KC\(_2\)Fe\(_4\)As\(_4\)F\(_2\) exhibits a convex curvature at low temperatures due to the strong Pauli paramagnetic effect, whereas two-band effect might be responsible for the sublinear temperature dependence for \( H \parallel c \) [7]. Such combined effect results in a decreasing \( \gamma_{1\parallel} \) toward 1 upon cooling temperature [7]. Although the specific physical mechanism of the nonmonotonic doping dependence of \( \gamma_{1\parallel} \), in particular, the peculiarity at \( x = 0.03 \), is currently unknown, we believe that the change of the Fermi surface topology together with the multiband physics as mentioned above should be responsible for it. Further ARPES and high field studies on over a wide doping range in the future are of interest and expected to clarify the details about the doping evolution of the topology of Fermi surface, superconducting gap structure, and Pauli paramagnetic effect in 12442 system.

4. Conclusion

In conclusion, by using RbAs flux, a series of Ni doped 12442-type RbCa\(_2\)(Fe\(_{1-x}\)Ni\(_x\))\(_4\)As\(_4\)F\(_2\) (0 \( \leq x \leq 0.1 \)) single crystals have been grown and characterized by structural, magnetic, and electrical transport measurements. \( T_c – x \) phase diagram, based on the electrical resistivity and magnetization measurements, were constructed. The Fermi surface topology is gradually modified with Ni doping as revealed by the doping evolution of Hall coefficient \( R_H \) and previous band structure calculation. Moreover, Ni dopants also act as impurity scattering centers that induce the pair breaking, and superconducting transition temperature \( T_c \) is suppressed with a rate of \( \Delta T_c / \Delta x \approx -2.7 \) K. Such suppression of \( T_c \) mimics those in Ni doped 122-type Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\), Ba\(_{0.5}\)K\(_{0.5}\)Fe\(_2\)As\(_2\), and the analogous 1144-type EuRb\(_4\)Fe\(_4\)As\(_4\) with multiple nodeless superconducting gaps. By comparing with the experimental data in relevant IBSSs, we speculate that the pairing symmetry in 12442 system is very likely to be nodeless \( s\pm \)-wave. Finally, doping evolution of the upper critical field and its anisotropy are also obtained and discussed in detail. More experiments, such as ARPES, inelastic neutron scattering, and scanning tunneling spectroscopy measurements, are desired to identify the sign change and evolution of the gap structures with doping in the future, which will be helpful to shed light on the superconducting mechanism in this system.

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