Anomalous electron doping independent two-dimensional superconductivity

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Abstract

Transition metal (Co and Ni) co-doping effects are investigated on an underdoped Ca0.94La0.06Fe2As2 compound. It is discovered that electron doping from substituting Fe with transition metal (TM = Co, Ni) can trigger high- \( T_c \) superconductivity around 35 K, which emerges abruptly before the total suppression of the innate spin-density-wave/anti-ferromagnetism (SDW/AFM) state. Remarkably, the critical temperature for the high- \( T_c \) superconductivity remains constant against a wide range of TM doping levels. And the net electron doping density dependence of the superconducting \( T_c \) based on the rigid band model can be nicely scaled into a single curve for Co and Ni substitutions, in stark contrast to the case of Ba(Fe1−\( x \)TM\( x \))2As2. This carrier density independent superconductivity and the unusual scaling behavior are presumably resulted from the interface superconductivity based on the similarity with the interface superconductivity in a La2−\( x \)Sr\( x \)CuO4-La2CuO4 bilayer. Evidence of the two-dimensional character of the superfluid by angle-resolved magneto-resistance measurements can further strengthen the interface nature of the high- \( T_c \) superconductivity.

1. Introduction

Since the discovery of high- \( T_c \) (>40 K) superconductivity in 122-type iron-based Ca\( _{1-x} \)REFe2As2 (RE = rare earth elements) compounds, the debate on their high- \( T_c \) origin has continued [1–12]. Due to the filamentary nature of high- \( T_c \) superconductivity, a natural hypothesis is inhomogeneous chemical RE doping [2]. While in Ca\( _{1-x} \)Pr\( _x \)Fe2As2, scanning tunneling microscopy (STM) study has demonstrated rather homogeneous Pr doping at very short length scales [5]. By contrast, in another STM study, the authors have identified cloverlike defects associated with Pr dopants [7]. And these cloverlike defects have been suggested as the original sites from which the high- \( T_c \) superconductivity emerges, namely, defect-induced superconductivity [7]. This idea is supported by a recent annealing study which reveals some clear evidence of a strong correlation between the low superconducting volume fraction and the defect density [9, 10]. And a threshold of defect density has been proposed to explain the absence of high- \( T_c \) superconductivity in the underdoped region in Ca\( _{1-x} \)REFe2As2 [10]. These research studies strongly indicate that the RE-dopant-associated defect (abbreviated as ‘RE-dopant-defect’) and its density play very important roles in dominating the occurrence of high- \( T_c \) superconductivity.

However, the proposal of defect-density-dominated superconductivity may be problematic because the application of high pressure has also proved to be an alternative way to stir high- \( T_c \) superconductivity in underdoped Ca\( _{1-x} \)La\( _x \)Fe2As2 [8]. Note that, the application of high pressure could not heavily tune the RE-dopant-defect density. Why then can high- \( T_c \) superconductivity also be triggered by the application of pressure?
Presumably, some other unknown factors rather than the defect density must exist in controlling the occurrence of high-$T_c$ superconductivity. To make this clear, the role of RE element doping must be considered.

It is known that the substitution of RE for Ca can increase both the RE-dopant-defect density and the electron doping density in the system. To distinguish the double-role of RE substitution, Deng et al carried out a detailed annealing experiment which was believed not to alter the electronic structure or doping, and concluded the existence of a strong correlation between the RE-dopant-defect density and the occurrence of high-$T_c$ superconductivity [10]. It is still of great interest to separately investigate the role of electron doping in the occurrence of high-$T_c$ superconductivity. To achieve this goal, we have therefore designed a transition metal (TM = Co, Ni) co-doping study on an underdoped Ca$_{1-x}$La$_x$Fe$_2$As$_2$ $(x = 0.06)$ crystal which primarily does not exhibit high-$T_c$ superconductivity. Since the TM substitutions take place on the Fe sites, the RE-dopant-defect density can be approximately kept unchanged while the electron doping density can be continuously tuned in a wide range via a gradual change in the TM doping levels. As a benefit, the separate role of electron doping in the occurrence of high-$T_c$ can be individually investigated. Additionally, for the easy control of the TM co-doping level, the electron overdoped region of Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ which is difficult to achieve by RE elemental doping or the application of high pressure can also be realized.

In this paper, we discover that both Co and Ni substitutions can trigger a high-$T_c$ superconductivity around 35 K in an underdoped Ca$_{1-x}$La$_x$Fe$_2$As$_2$ $(x = 0.06)$. And the high-$T_c$ is found to be independent of electron doping in a wide range. On the basis of the rigid band model, the relations between the net electron doping density and the superconducting $T_c$ for the Co and Ni substitutions can be surprisingly scaled into a single curve, revealing a close correlation between the electron doping and the occurrence of high-$T_c$ superconductivity. Besides, the superconducting fluid is found to be two-dimensional in nature. These anomalous phenomena jointly suggest that high-$T_c$ superconductivity possibly originates from the RE-dopant-defect-associated interface effect, in which the electron doping level rather than the defect density is a dominating factor in controlling the occurrence of high-$T_c$ superconductivity.

2. Experiment

Single crystals of Ca$_{0.94}$La$_{0.06}$(Fe$_{1-x}$TM$_x$)$_2$As$_2$ were grown using the FeAs self-flux method as reported before [3, 6]. Special attention was paid during the weighing of the starting materials to achieve precise control of the La and TM doping levels. After a vacuum heating process, shiny crystals with flat surface can be easily cleaved. Elemental analyses of these crystals were carried out by energy-dispersive x-ray spectroscopy (EDS) on a field emission scanning electron microscopy (SEM). To accurately determine the doping levels, crystal’s compositions were determined by averaging the multi-point EDS measurements on the surface of each crystal. As expected, the La doping level keeps approximately invariable as the TM doping level $x$ increases gradually, and the actual TM doping levels are very close to the nominal values (see figures 1(a) and (b)). In the following, the actual TM and La doping levels will be used in both the figure descriptions and the related calculations. Furthermore, the quality of the crystalline was checked by single crystal x-ray diffraction (XRD) measurements (see figures 1(c) and (d)). No phase separation was witnessed. All (002)$_f$ peaks move gradually toward higher angles with increasing the TM doping levels for the smaller ionic radii of Co and Ni than Fe, indicating the successful realization of continuous TM co-doping. The electrical transport data were collected by the standard four-probe method. In the Hall measurements, to cancel the electrode asymmetric factor, Hall resistivity $\rho_{xy}$ is calculated via the formula $\rho_{xy} = [\rho_{xy}(\mu_0 H > 0) - \rho_{xy}(\mu_0 H < 0)]/2$.

3. Results and discussion

3.1. Doping independent superconductivity

Figure 2 shows the temperature dependencies of resistivity ($\rho(T)$) for Ca$_{0.94}$La$_{0.06}$(Fe$_{1-x}$TM$_x$)$_2$As$_2$ crystals with different doping level ($x$) values. Without TM doping, a resistivity upturn which is associated with a SDW/AFM transition at temperature $T_{r} \sim 150$ K and a resistivity drop for a low-$T_c$ superconducting transition around 10 K can be witnessed. This low-$T_c$ may originate from the filamentary superconductivity like in the case of BaFe$_2$As$_2$ and SrFe$_2$As$_2$ [13, 14] and will not be discussed in this paper. As $x$ increases, the SDW/AFM transition temperature $T_r$ is gradually suppressed, similar to the case with many Fe-based superconductors [15, 16]. When $x$ reaches a certain doping level, a high temperature resistivity drop emerges suddenly around 35 K for both the Co and Ni substitutions. As seen in the inset in figure 2(a), magnetization data were also collected and a consistent transition to weak diamagnetism is observed, indicating the occurrence of superconductivity. Based on previous studies [9, 10], this weak diamagnetism may be resulted from possible interface superconductivity. As is known, for bulk superconductivities with layered structures, many screening current loops from different
layers can be formed easily; thus, a strong diamagnetic signal can be measured. While for interface superconductivity, because of the very limited superconducting layers (usually one layer), the superconducting diamagnetism is intrinsically weak. This rule of weak diamagnetism for interface superconductivity has been demonstrated in many interface systems, like in the monolayer FeSe \cite{17} and the La$_2$$_{−x}$Sr$_x$CuO$_4$-La$_2$CuO$_4$ bilayer \cite{18}. Therefore, the observed weak diamagnetism for the present crystals may be related to the previously argued origin of interface superconductivity which is also supported by other evidence that will be shown later in this work. Here, according to the simultaneous observation of the transition to weak diamagnetism as well as the previous knowledge of this system, we ascribe the above resistivity drop to a high-$T_c$ superconducting transition. Intriguingly, this high-$T_c$ superconductivity does not evolve from any low-$T_c$ phase in the samples with low TM doping levels but emerges abruptly. This sudden appearance of high-$T_c$ superconductivity has rarely been seen in high temperature superconducting systems, which is in stark contrast to the dome-shaped doping phase diagrams \cite{19, 20}. As $x$ increases further, the onset critical temperature ($T_c$) for the high-$T_c$ superconducting transition is surprisingly found to keep almost invariable with doping to a very large range. This phenomenon is observed in both the cases of Co and Ni doping. This strange behavior can be seen more clearly in the enlarged views of the superconducting transitions shown in figures 2(c) and (d). The vertical dash lines in figures 2(c) and (d) are guides for the coincident onset $T_c$ for different doping levels. Thus, this feature of doping independent $T_c$ is very apparent. With further TM doping, the superconducting transition starts to shift gradually to lower temperatures.

In figure 3(a), an electron doping relevant phase diagram is presented. The nominal net doping electron density $n_e$ is adopted here. In calculation of $n_e$, both the contributions from the substitution of La for Ca and the substitution of TM for Fe have been taken into account based on the rigid band model. That is, every substitution of La for Ca, Co for Fe, and Ni for Fe will correspondingly introduce 1 e, 1 e, and 2 e into the system. Under the same consideration, Co and Ni doping phase diagrams of 122-type BaFe$_2$As$_2$ are also summarized in the same figure as a typical example for comparison. Here, two anomalous phenomena can be easily noted. First, the high-$T_c$ superconductivity is almost independent on electron doping for a large range after its first

![Figure 1. Elemental and crystalline structural analyses.](image-url)
curves near the superconducting $K$ takes place when $n_e$ reaches around 0.1 (e/Fe) and remains essentially constant for $0.1 \leq n_e \leq 0.21$ (e/Fe). This special $T_c(n_e)$-constant region spans a wide doping interval which almost covers the superconducting dome in TM-doped BaFe$_2$As$_2$ or CaFe$_2$As$_2$ [15, 16, 18, 19, 21]. In fact, $T_c(n_e)$-constant behavior can also be noted in the TM-free Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ crystals (see figure 3(d) and [12, 22]) as well as in pressure experiments on the underdoped Ca$_{1-x}$La$_x$Fe$_2$As$_2$ samples [8] if the onset $T_c$ is adopted. Especially, the critical $n_e$ for the first observation of high-$T_c$ ($n_e \sim 0.1$) is very similar to each other for the TM co-doping and the bare La doping. All these cases share a very similar phase diagram (see figures 3(b)–(d)). That is, there is an apparent $T_c(n_e)$-constant region just after the first appearance of high-$T_c$ superconductivity. And the $T_c(n_e)$-constant region is followed by a nearly linear suppression of the superconducting transition. For the present TM-doped Ca$_{0.94}$La$_{0.06}$Fe$_2$As$_2$, the linear $T_c(x)$ suppression rate for Co-doping is $-116.7$ K/Fe, which is about half of that for Ni doping ($-223.8$ K/Fe). Linear suppression of superconductivity against TM co-doping has also been observed in other Fe-based superconducting systems [23].

The second anomalous phenomenon is the scaling behavior of the superconductivity phase diagrams for the Co and Ni substitutions. On the basis of the rigid band model, the $T_c(n_e)$ curves for Co and Ni doping are found to almost fall into one curve by considering the contributions of electron doping from both the La and TM substitutions. Both the $n_e$ range for the constant high-$T_c$ and the $T_c$ linear suppression region are nicely identical to each other for Co and Ni substitutions. This behavior is in sharp contrast to those in TM-doped BaFe$_2$As$_2$ or CaFe$_2$As$_2$ especially on the following two points [19, 24, 25]. On the one hand, since the actual number of electrons that participate in the formation of the Fermi surface (FS) is found to decrease from Co to Ni for a fixed nominal extra electron, the $T_c(n_e)$ domes show a significant mismatch for Co and Ni doping (see the phase diagrams of Ba(Fe$_{1-x}$TM)$_2$As$_2$ (TM = Co and Ni) in figure 3(a)). On the other hand, influenced by the different impurity potentials of the substituted atoms, the electronic structure is possibly changed and thus results in different $T_c$ maxima for Ba(Fe$_{1-x}$TM)$_2$As$_2$ with different TM species. Both points reveal that the electronic phase diagrams in many Fe-based systems depend strongly on the doping element species. While in the present case of RE- and TM-co-doped CaFe$_2$As$_2$, the effective electron doping density dependent electronic phase
diagrams for different doping element species can surprisingly be normalized together based on the rigid band model. To sum up, we believe that the consistent \(T_c(n_e)\) constant regions, the equal maximum \(T_c\) values, and the scaling behavior of superconductivity phase diagrams for Co and Ni doping are anomalous and unique properties only belonging to the present system. And the high-\(T_c\) superconductivity origin in \(\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2\) must be different from the bulk superconductivity in other Fe-based materials. However, at all events, the above observations of the strange electron doping behavior clearly indicate that there exist some unknown strong correlations between the occurrence of high-\(T_c\) superconductivity and the electron doping density.

To understand this strange doping behavior, especially the unexpected carrier doping independent \(T_c\), a starting point would be to exclude possible experimental artifacts and pitfalls, like crystalline phase separation, doping inhomogeneity, and charge carrier cancellation (depletion) effect. First, we should make clear whether co-growth of \(\text{Ca}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2\) and \(\text{Ca(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2\) has taken place during the crystal growth procedure, since one could argue that under the phase separation, the constant \(T_c(n_e)\) phenomenon could be ascribed to an invariable La doping level in \(\text{Ca}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2\), and the gradual suppression of the SDW/AFM transitions could be associated with the bulk doping in \(\text{Ca(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2\). However, we can remove this phase separation speculation from both the XRD patterns and the \(\rho T\) curves. On the one hand, the XRD patterns for different TM doping levels have demonstrated no crystalline phase separation. On the other hand, from the \(\rho T\) curves one can note that the resistivity upturn standing for the SDW/AFM transition should persist up to a doping level at \(x = 0.056\) for bare Co-doping and at \(x = 0.053\) for bare Ni doping in \(\text{Ca(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2\) as inferred from [19, 25]. While, as shown in figure 2, the SDW/AFM transitions disappear \((x < 0.050\) for Co, \(x < 0.031\) for Ni\) much faster than those in bare TM-doped \(\text{Ca(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2\), which means the electron doping contributed by the substitution of La for Ca cannot be separated with the substitution of TM for Fe in the present \(\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2\) crystals. That is, phase separation should be impossible.

The second issue to address is whether there exists a macroscopic elemental enriching effect or serious non-uniform chemical doping. To address this issue, we emphasize the elemental analysis. In figures 1(a)–(b), the standard deviation is shown as the error bar of the actual doping level for every crystal. As can be seen, all error bars are extremely small, i.e., only small deviations occur among the measurements on different points. We
define the TM doping level change strength for the $T_c (n_d)$-constant region as $\delta = (x_{\text{end}} - x_{\text{onset}}) / x_{\text{onset}}$, where $x_{\text{onset}}$ ($x_{\text{end}}$) is the onset (end) TM doping level in the $T_c (n_d)$-constant region. Then $\delta$ for the Co and Ni substitutions can be calculated to be 245% and 210%, respectively. We note that any elemental distribution fluctuation, which can be represented by the standard deviations (usually $<0.2\%$), is far below the $\delta$ values. Therefore, consistent with the previous STM microscopic elemental study, element doping for the present material system is macroscopically homogeneous, but local RE dopant defects exist at microscopic scale. The small microscopic elemental distribution fluctuation can’t take charge of the macroscopic $T_c (n_d)$-constant behavior.

The third issue that needs to be resolved is the possible charge carrier cancellation (depletion) effect. From the view of crystal growth, TM doping may induce additional crystalline defects, such as As aggregations. If undesired crystalline defects coincidentally grow with $x$ increasing, and also these crystalline defects could just compensate the electron doping from TM doping, there is a possibility that the net density of mobile charge carriers (electrons) stays constant with varying TM doping. As a result, we can observe the $T_c (n_d)$-constant behavior. To rule out this possibility, we have performed systematic Hall measurements on Ca$_{0.94}$La$_{0.06}$ (Fe$_{1-x}$ Ni$_x$)$_2$As$_2$. As can be seen in figure 4, Hall coefficient $R_{H}(T)$ curves for Ca$_{0.94}$La$_{0.06}$ (Fe$_{1-x}$ Ni$_x$)$_2$As$_2$ shift smoothly with $x$ increasing, indicating a gradual evolution of the electronic band structure versus doping. For the underdoped crystals ($x = 0.010$, 0.019), the SDW/AFM transition is clearly evidenced by a sudden decrease in $R_{H}$ with lowering $T$, which agrees well with other Fe-based systems [21]. This drastic change in $R_{H}(T)$ for different $x$ values can apparently rule out the possibility of a constant net mobile charge carrier (electron) density. We should point out that this gradual change in mobile charge carrier density against doping is just a normal characteristic of the bulk in the case of macroscopic uniform doping. The normal state transport behavior should have no direct connection to high-$T_c$ superconductivity if the superconductivity is aroused by the proposed microscopic RE–dopant-defect [7, 10]. For defect-induced superconductivity, the correlation between the local mobile carrier density and the superconducting $T_c$ is an open question.

Note that a similar unexpected charge carrier doping independent $T_c$ has been reported in a La$_{2-x}$Sr$_x$CuO$_4$-La$_2$CuO$_4$ bilayer system in which the superconductivity is believed to have resulted from the interface effect [18]. It has been confirmed from a large set of about 800 samples with a wide Sr doping range from 0.15 < $x$ < 0.47 that the critical superconducting transition temperature remains essentially constant. This constant $T_c (x)$ behavior poses a big challenge to ordinary Fermi liquids because a constant chemical potential against charge carrier doping has to be supposed in the possible explanations. Constant chemical potential against charge carrier doping is hard to understand in ordinary bulks and could only be associated with unknown interfacial effect. The similar $T_c (n_d)$-constant behavior reminds us to suppose whether there is any interfacial effect for the occurrence of high-$T_c$ in these iron-based single crystals. To examine this, we have tried to check the 2D superconductivity which is an intrinsic property bound up with interface superconductivity. As will be shown later, the superfluid of these crystals has indeed been demonstrated to be 2D in nature.

### 3.2. 2D nature of high-$T_c$ superconductivity

In the case of La$_{2-x}$Sr$_x$CuO$_4$-La$_2$CuO$_4$ bilayer, the superfluid is believed to be confined to a single CuO$_2$ plane located near the interface between La$_{2-x}$Sr$_x$CuO$_4$ and La$_2$CuO$_4$ layers because of the 2D superfluid nature [18]. To corroborate the 2D superfluid, an angle-resolved magneto-resistance measurement has been adopted. We
have therefore performed the same experiments on our superconducting crystal. As shown in figure 5, we first keep the magnitude of $H$ at 1.5 T and gradually increase the angle $\theta$ between $H$ and the $ab$-plane (see figure 5(a)). With increasing $\theta$, the $H$ component along the $c$-axis is gradually enhanced and the superconductivity is continuously suppressed. Apparently, there is a big difference in the magnetic-resistance effect between the $c$-axis and $ab$-plane, indicating a large anisotropy. Then we intentionally keep the $c$-axis component of $H$ fixed and gradually increase the $H$ component in the $ab$-plane (see figure 5(b)). As we can see, the measured resistance curves are overlapped for different $\theta$ values. That is, the superconducting transition under magnetic field is extremely sensitive to the $H$ component perpendicular to the crystal’s surface, in sharp contrast to the $H$ component in the $ab$-plane. This large anisotropy, the same as that in La$_{2−x}$Sr$_x$CuO$_4$-La$_2$CuO$_4$ bilayer, is characteristic of 2D superconductivity.

We further double-check the nature of the 2D superconductivity with the Tinkham model of an angle-dependent critical field for extremely thin films. As is known, for sufficiently thin superconducting films with thickness $d$ satisfying $d \ll \xi_c$ ($\xi_c$ is the $c$-axis coherence length), Tinkham’s formula for angular dependence of the upper critical field $H_{c2}$ is satisfied. Tinkham’s formula is expressed as [28]

$$\left| \frac{H_{c2}(\theta) \sin \theta}{H_{c2}^c} \right| + \left( \frac{H_{c2}(\theta) \cos \theta}{H_{c2}^c} \right)^2 = 1.$$  

(2D)

Here, $\theta$ is angle between the magnetic field orientation and the crystal surface, and $H_{c2}^c$ ($H_{c2}^\parallel$) is the upper critical field with the field perpendicular (parallel) to the crystal’s surface. For 3D bulk superconductors, the angle dependence of $H_{c2}$ can be interpreted by the Ginzburg–Landau (GL) anisotropic mass model with formula

$$H_{c2}(\theta) = H_{c2}^\parallel \sqrt{\cos^2 \theta + \left(\frac{H_{c2}^\parallel}{H_{c2}^\perp}\right)^2 \sin^2 \theta}.$$  

(3D)

The GL model has been frequently applied in iron-based superconductors [29]. The most remarkable difference between the two models is the slope $|dH_{c2}/d\theta|$ value when $\theta \to 0^\circ$. Under Tinkham’s model, $|dH_{c2}/d\theta|$ near $\theta \to 0^\circ$ is a finite value while it approaches zero in the GL model. To check the 2D superfluid, we measured the resistance curve as a function of magnetic field for different field orientations at three selected temperatures below $T_c$, and extracted the angle-dependent $H_{c2}$ using different $H_{c2}$ criteria (see figures 6(a) and (b)). For field orientation close to the crystal’s surface, the measurement angle interval has been set as small as 1°. Indeed, a cusplike behavior for $\theta$ near $0^\circ$ is observed in the $H_{c2}(\theta)$ curves (see figure 6(b)). As expected, the 2D Tinkham model is much better than the 3D GL model in reproducing the $H_{c2}(\theta)$ curve. The $|dH_{c2}/d\theta|$ value near $0^\circ$ slightly falls below the Tinkham interpolation curve which is common to the Nb/Cu samples in the 2D region [30]. Deviation from the 3D GL model has also been observed in a Bi$_{2−x}$Sr$_x$Ca$_{12}$O$_{19+c}$ superconductor with a strong anisotropy (see figure 6(c)) [26]. In Bi$_{2−x}$Sr$_x$Ca$_{12}$O$_{19+c}$, the separation between the two superconducting layers is as large as 12 Å, which is far beyond the coherence length $\xi_c$ (≈1.6 Å). While in other copper-based high temperature superconductors, the shorter separation between the $[\text{CuO}_2\text{La}_2]$ planes seems insufficiently large to arouse 2D superconductivity. In iron-based superconductor FeS (layer distance $\sim$5.034 Å, $\xi_c \approx 343$ Å), even though the anisotropy is large, the angle dependence of the upper critical field strictly follows the 3D GL model (see figure 6(d)) [27]. Therefore, we can see that a large distance between superconducting layers and a short $c$-axis coherence length $\xi_c$ are the crucial factors for the occurrence of 2D superconductivity.
Based on the 2D superfluid observed in the present studied samples, we can infer the distance between superconducting layers is very large in comparison to its c-axis coherence length $\xi_c$ (around 3–16 Å [6]). And the coupling between two adjacent superconducting layers is very weak. The superconducting layers could not be very thick. Accordingly, high-$T_c$ superconductivity is 2D in nature, which is a further strong support for the existence of the interface effect.

3.3. Discussion of the origin of high-$T_c$ superconductivity

It is suggested that the cloverlike defects associated with Pr dopants are responsible for the high-$T_c$ superconductivity in $\text{Ca}_{1-x}\text{Pr}_x\text{Fe}_2\text{As}_2$ [7]. One can easily notice that for the underdoped $\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2$ without high-$T_c$ superconductivity, the RE-dopant-associated defects already existed. The absence of high-$T_c$ superconductivity in the underdoped $\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2$ cannot be ascribed to the low RE-dopant-defect density as previously proposed [10] because of the observations of high-$T_c$ superconductivity both in the pressurized underdoped $\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2$ [8] and in the present $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}, \text{TM})_2\text{As}_2$ with a low and nearly constant RE-dopant-defect density. Through our above TM co-doping experiments, we can definitively infer that a tuning factor in controlling the occurrence of high-$T_c$ superconductivity is the charge carrier (electron) doping. When the sufficient electron doping from chemical doping or application of high pressure is satisfied, high-$T_c$ superconductivity appears. That is, an enough electron concentration is essential for the abrupt occurrence of high-$T_c$ superconductivity. Besides, the interface effect is a non-negligible factor. The notably higher $T_c$ values in comparison with the iso-structural compounds [31], the anomalous electron doping independent superconductivity, and the evidences of 2D superconductivity are all strong indications of the existence of an interface effect in the occurrence of high-$T_c$ superconductivity in $\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2$. 

![Figure 6](image_url)

**Figure 6.** Angle dependence of the upper critical field. $\theta$ is angle between the magnetic field orientation and the crystal surface. (a) The angle $\theta$ dependence of the upper critical field $H_{c2}$ in comparison with $H_{c2}$ for temperatures at 15, 20, and 25 K for a $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}, \text{Ni})_2\text{As}_2$ ($x = 0.052$) sample. For $T = 15$ K and 20 K (25 K), a criteria $\rho_\parallel = 0.5\rho_\perp$ ($\rho_\parallel = 0.9\rho_\perp$) is used to extract the $H_{c2}($/$\theta$) values, where $\rho_\parallel$ is the normal state resistivity. Different $H_{c2}$ criteria result in $H_{c2}($/$\theta$) curves with the same shape. (b) is an enlarged view for $\theta$ near 0°. (c) and (d) is extracted from [26, 27]. Copyrighted by the American Physical Society. In all figures, the red solid line and the blue dashed line represent the fitting curves based on Tinkham (2D) and GL (3D) formulas for angular-dependent $H_{c2}$. 


In a La$_{2-x}$Sr$_x$CuO$_4$-La$_x$CuO$_4$ bilayer system, the interface is the boundary between the La$_{2-x}$Sr$_x$CuO$_4$ layer and the La$_x$CuO$_4$ layer. Charge transfer may occur from the La$_{2-x}$Sr$_x$CuO$_4$ layer (superconducting $T_c$ depends on doping level) to the La$_x$CuO$_4$ layer (non-superconducting), which will cause the existence of a strange local inhomogeneous electronic state near the interface. The local inhomogeneous electronic state should be closely related to the observation of interface superconductivity at the ‘hot’ CuO$_2$ layers near the interface. While in Ca$_{1-x}$RE$_x$Fe$_2$As$_2$, the interface superconductivity should also be confined within the FeAs layers. However, not all FeAs layers can host high-$T_c$ superconductivity. The high-$T_c$ superfluid only flows on those ‘hot’ FeAs layers near the RE-dopant-associated defects. Analogous to the interface in an La$_{2-x}$Sr$_x$CuO$_4$-La$_x$CuO$_4$ bilayer system, those RE-dopant-associated defects cause a local inhomogeneous electronic state and are presumably acted as the ‘interface’ for the occurrence of high-$T_c$ interface superconductivity. According to the above observation of 2D superfluid, one can naturally infer that the RE-dopant-defect where high-$T_c$ superconductivity develops should posses 2D structures and spread along the $ab$-plane of the crystals. And also, the coupling between the superconducting layers along the $c$-axis should be very weak.

For conventional BCS (Bardeen–Cooper–Schrieffer) type superconductors [32], superconductivity is mediated by electron–phonon coupling, and the superconducting $T_c$ is determined by the electron–phonon coupling constant and the density of state or mediated by the charge carrier density. For the CuO$_2$- and FeAs-based high temperature superconducting families, the fundamental assumption of weak electron–electron interaction for the BCS theory becomes invalid. The electron correlation in these materials becomes non-negligible. The origin of the strong electron correlation is aroused by magnetic fluctuation. Therefore, superconductivity is believed to be controlled by magnetic interactions and also the charge carrier density [33]. For the above mentioned interfacial high-$T_c$ superconducting systems, we believe that the superconductivity is still confined to the FeAs or CuO$_2$ layer. The only difference comes from the additional interface effect which usually lead to an enhancement of superconductivity [17, 34, 35]. Indeed, theoretical calculation has considered the situation of competing order parameters (charge density wave or spin-density wave and ‘hidden’ superconductivity) for an interface system, and the result is the appearance of local superconductivity with an enhanced $T_c$ at the interface [36]. Another interesting prediction from this calculation is that the local superconductivity occurs at ‘quantized’ temperatures and doping levels, which is somewhat similar to our observed $T_c(n_e)$-constant behavior.

In summary, on the basis of the peculiar doping independent superconductivity as observed in a La$_{2-x}$Sr$_x$CuO$_4$-La$_x$CuO$_4$ bilayer and the 2D superfluid, our present data strongly support the conjecture that the unusual enhancement of superconductivity in (Ca, RE)Fe$_2$As$_2$ in comparison with its counterparts may be closely related to an unknown interfacial effect. The origin of this interfacial effect has presumably arisen from the RE-dopant-associated defects as previously proposed in [7, 10]. This depicts a picture of a RE-dopant-defect-associated interface effect induced high-$T_c$ superconductivity in Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ single crystals. It is theoretically predicted that quantized superconducting temperatures and doping levels could occur in interface superconducting systems [36]. Whether there is a connection between this quantized behavior and the observed $T_c(n_e)$ constant phenomenon merits further investigation.

4. Conclusion

We have investigated the effect of the substitution of the TM element on high-$T_c$ superconductivity in a (Ca, La)Fe$_2$As$_2$ compound. The onset high $T_c$ has been found to remain almost invariable for a rather wide doping interval (0.1 $\leq n_e \leq$ 0.21). Additionally, a scaling behavior of doping dependent superconducting phase diagrams for Co and Ni co-doping is observed, indicating strong correlations between electron doping and the occurrence of high-$T_c$ superconductivity. Based on the observed $T_c(n_e)$-constant behavior, a possible origin based on interface superconductivity is proposed. The verified 2D nature of high-$T_c$ superconductivity further supports the existence of interface superconductivity. These data provide strong supports for the interface-effect-induced high-$T_c$ superconductivity in iron pnictides and can provide an opportunity to explore a new perspective in understanding interface superconductivity.

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