Reemergence of superconductivity by 4\textit{d} transition-metal Pd doping in over-doped 112-type iron pnictide superconductors Ca$_{0.755}$La$_{0.245}$FeAs$_2$

Xiangzhuo Xing$^{1, 2}$, Zhanfeng Li$^1$, Ivan Veshchunov$^1$, Xiaolei Yi$^1$, Yan Meng$^1$, Meng Li$^1$, Bencheng Lin$^1$, Tsuyoshi Tamegai$^1, 3$ and Zhixiang Shi$^{1, 3}$

1 School of Physics and Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 211189, People’s Republic of China
2 Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan
3 Authors to whom any correspondence should be addressed.

E-mail: xzxing@seu.edu.cn and zxshi@seu.edu.cn

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Abstract

In 112-type iron-based superconductors (IBSs), rare earth (e.g. La) doping enhanced antiferromagnetic (AFM) order and 3\textit{d} transition-metal (e.g. Co, Ni) doping induced reemergence of superconductivity (SC) in the over-doped regime (non-SC) are of particular interest, providing a significant opportunity to further understand the relationship between SC and AFM order in IBSs. Recently, 4\textit{d} transition-metal Pd-doped 112-type Ca$_{1-y}$La$_y$Fe$_{1-x}$Pd$_x$As$_2$ ($x > 0.2$, $0 \leq y \leq 0.3$) compounds, which crystallized in new orthorhombic and tetragonal structures, have been identified (Inorg. Chem. 56 3030 (2017)). However, none of them exhibit SC, probably due to the oversubstitution of Pd for Fe. Here, to reveal the impact of slight Pd doping on the over-doped Ca$_{1-y}$La$_y$FeAs$_2$, we compare to 3\textit{d} Co/Ni doping series, single crystals of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ with $0 \leq x \leq 0.08$ are successfully grown using the self-flux method. We find that, upon only a small amount of Pd doping ($x = 0.013$), bulk SC with a maximum $T_c$ of 28.5 K is reemerged, in contrast to the case with high Pd doping level. Moreover, based on the electrical resistivity and magnetization data, we construct the temperature-composition ($T$–$x$) phase diagram, the shape of which, particularly for the region where the AFM and SC phases coexist microscopically, is almost identical to that of Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$, but is distinctly different from that of Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, presumably due to the presence of complex doping mechanism in 112-type IBSs. Finally, for one selected single crystal with $x = 0.013$, superconducting properties including critical current density, vortex pinning mechanism, and vortex diagram are systematically studied by magnetization, magneto-optical imaging, and magnetoresistivity measurements. Our work provided more insight into the phase diagrams and superconducting properties of 112-type IBSs, allowing better understanding of its superconducting mechanism and developing the potential applications.

1. Introduction

In most iron-based superconductors (IBSs), superconductivity (SC) generally emerges after the suppression of the antiferromagnetic (AFM) transition in the parent compound by chemical doping or physical pressure [1–3]. The fundamental interest in IBSs therefore lies in understanding the symbiosis of SC and AFM orders. Among several possible models of pairing mechanism, a pairing model with the gap structure of e.g. Co, Ni doping series, single crystals of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ with $0 \leq x \leq 0.08$ are successfully grown using the self-flux method. We find that, upon only a small amount of Pd doping ($x = 0.013$), bulk SC with a maximum $T_c$ of 28.5 K is reemerged, in contrast to the case with high Pd doping level. Moreover, based on the electrical resistivity and magnetization data, we construct the temperature-composition ($T$–$x$) phase diagram, the shape of which, particularly for the region where the AFM and SC phases coexist microscopically, is almost identical to that of Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$, but is distinctly different from that of Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, presumably due to the presence of complex doping mechanism in 112-type IBSs. Finally, for one selected single crystal with $x = 0.013$, superconducting properties including critical current density, vortex pinning mechanism, and vortex diagram are systematically studied by magnetization, magneto-optical imaging, and magnetoresistivity measurements. Our work provided more insight into the phase diagrams and superconducting properties of 112-type IBSs, allowing better understanding of its superconducting mechanism and developing the potential applications.

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no sizable low-energy spin fluctuations and long-range magnetic order are observed above/below $T_c$, respectively [8–10]. Accordingly, instead of spin fluctuations, an alternative scenario where fluctuations stemming from orbital degree of freedom play a primary role has proposed and aroused great interest [8, 9, 11, 12]. In 1111-type system, $\text{LaFeAsO}_{1-x}\text{Fe}_x$, a second SC dome at high doping levels centered at $x \sim 0.5$ is reemerged, whereas no magnetism or even magnetic fluctuations is found in this regime [13, 14]. Furthermore, in $H$-doped LaFeAsO$_{1-y}$, another SC dome is also detected, but the AFM order emerges after SC disappears for $x$ beyond 0.5 [3, 15, 16]. Hence, all these discoveries have raised questions regarding the spin fluctuations scenario envisaged in most IBSs. Despite tremendous efforts in the past years, elucidating the exact superconducting pairing mechanism still remains a great challenge.

112-type $\text{Ca}_{1-x}\text{RE},\text{FeAs}_2$ (RE = rare earth element), which crystallized in a low-symmetry monoclinic structure with unique As zigzag bond metallic layers, is a new family of IBSs [17]. Theoretically, the ground state of undoped $\text{CaFeAs}_2$ is suggested to be collinear AFM as observed in many IBSs [18]. Although $\text{CaFeAs}_2$, has not yet been synthesized experimentally, RE doping on the Ca site is found to be effective to stabilize the 112-phase and to induce SC [19, 20]. Herein, taking La doped $\text{Ca}_{1-x}\text{La},\text{FeAs}_2$ case as a representative, SC with $T_c$ of 35 K is achieved at $y = 0.15$, with further doping, $T_c$ is gradually suppressed and finally disappeared when La doping concentration $y$ is around 0.24 [21]. Simultaneously, the results of nuclear magnetic resonance (NMR) measurements, strikingly different from other IBSs, have revealed that the AFM order in $\text{Ca}_{1-x}\text{La},\text{FeAs}_2$ is robust against and even enhanced by La doping, i.e. Néel temperature $T_N$ is unexpectedly increased from 62 K ($y = 0.15$) to 70 K ($y = 0.24$) [22]. To date, the mechanism of the increase of $T_N$ by doping is still an open question. Later on a similar AFM transition was also detected in the electron over-doped $\text{Ca}_{1-x}\text{La},\text{FeAs}_2$ with $y = 0.27$ (non-SC), which was regarded as a ‘parent’ compound of 112-type IBSs [23]. Intriguingly, if one further introduces electrons through Co co-doping for $\text{Fe}$ in $\text{Ca}_{0.755}\text{La}_{0.245}\text{FeAs}_2$, AFM transition is found to be gradually suppressed and a seemingly second superconducting phase with a maximum $T_c$ around 25 K is unexpectedly reemerged [24]. Similar phenomenon was also found in recent Ni-doped $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_1\text{.}_x\text{Ni}_x\text{As}_2$ [25]. A summarized phase diagram in the combination of both La and Co dopants has been depicted in our previous reports [26, 27]. Although both La and Co/Ni dopants are believed to introduce electrons, the doping responses of the AFM and SC are quite opposite, depending on the doping site. Such unique phase diagram along with the reemergence of SC in the over-doped regime is not yet fully understood and rarely seen in other IBSs, making the 112-type superconductors an ideal new platform to test existing theories, and further study the interplay between the AFM and SC in IBSs.

As just mentioned, SC has been achieved in the La over-doped regime (non-SC) by substituting Fe with Co/Ni dopants. In IBSs, it has been found that, except for the 3d transition-metal (TM) doping, SC can also be induced when the AFM transition is suppressed by substitution of Fe with 4d or 5d TM such as Ru, Rh, Ir, Pd, and Pt [28–32]. Specifically, electron doping with Co and Rh or Ni and Pd, which pairwise are located in the same group of the periodic table, the respective phase diagrams are essentially identical as observed in Ba-122, Sr-122, and Na-111 systems [30, 31, 33]. Given this result, it is interesting to know whether such an analogous situation exists in other systems with different crystal structure such as 112-type compounds, especially in the La over-doped non-SC regime. Also, comparison of the $T_x$ phase diagrams of 4d and 3d TM doping is helpful for better understanding the unconventional SC. Recently, two unprecedented 4d TM Pd-doped 112-type $\text{Ca}_{1-x}\text{La},\text{Fe}_{1-x}\text{Pd},\text{As}_2$ compounds crystallized in orthorhombic and tetragonal structures were reported by Tamura et al., which have new various arsenic network structures that are different from monoclinic structure [34]. A schematic phase diagram of $\text{Ca}_{1-x}\text{La},\text{Fe}_{1-x}\text{Pd},\text{As}_2$ as a function of La content ($y$) and Pd content ($x$) is illustrated in figure 1. As can be seen, both orthorhombic and tetragonal phases show non-SC, probably as a result of the oversubstitution of Pd for Fe [34]. Accordingly, it is instructive to investigate how SC and AFM order of $\text{Ca}_{1-x}\text{La},\text{FeAs}_2$ can be tuned by a slight substitution of Fe with Pd, particularly for the La over-doped non-SC samples (i.e. the blue shadow regime in figure 1), which will provide insight into the reemergence of SC compared with the results of 3d Co/Ni doping series. On the other hand, bearing a different monoclinic structure with unique metallic blocking layers compared with other IBSs, investigation of upper critical field and its anisotropy, critical current density, and pinning mechanism is an interesting topic, which is also helpful for practical applications of 112-type IBSs. Our previous reports have demonstrated that the critical current density in 112-type single crystals can be significantly enhanced exceeding $10^6$ A cm$^{-2}$ through 3d Co doping, isovalent Sb doping, and proton irradiation that introduce more pinning centers [35, 36]. As critical current density, pinning mechanism, and vortex dynamic are intimately related to the dopants in superconductors, it is of interest to study what happens in the 4d Pd doping series. The above-mentioned curiosities both from superconducting mechanism and application point of view constitute the motivations of our present study.

In this paper, we select the La over-doped $\text{Ca}_{0.735}\text{La}_{0.265}\text{FeAs}_2$ (non-SC), the location of which is labelled by the red star in figure 1, as a candidate to study the impact of slight 4d Pd substitution in 112-type IBSs. Results show that SC reemerges upon slight Pd substitution on the Fe site, similar to the case of 3d Co/Ni doping series, albeit electron heavily doped. Furthermore, $T_x$ phase diagram shows similarities to that of 3d Ni doped $\text{Ca}_{0.72}\text{La}_{0.28}\text{Fe}_1\text{.}_x\text{Ni}_x\text{As}_2$, 


but distinctly differs from that seen in 3d Co doped Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, indicative of complex doping mechanism in 112-type IBSs. Lastly, for one selected single crystal with $x = 0.013$, superconducting properties including critical current density, vortex pinning mechanism, and vortex phase diagram are systematically studied by magnetization, magneto-optical (MO) imaging, and magneto-resistivity measurements.

2. Experiment

Single crystals of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ ($0 \leq x \leq 0.09$, in nominal composition) were grown by the self-flux method. The precursors CaAs, LaAs, FeAs, and PdAs were firstly synthesized by solid state reaction as described elsewhere [25]. Then, stoichiometric mixtures of CaAs, LaAs, FeAs, and PdAs were grounded and mixed in a molar ratio of 0.7:0.3:($1 - x'$):$x'$, loaded into an aluminum crucible, and sealed in an evacuated quartz tube. 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 mixture was heated at 800 °C for 10 h, then heated up to 1150 °C and held for 15 h to ensure the homogenization, followed by slowly cooling down to 900 °C at a rate of 2.5 °C h$^{-1}$. Finally, the temperature was cooled down to room temperature by switching off the furnace. Sizable plate-like single crystals were easily separated after exposing the mixture in the air for several hours. It is noticed that no crystals can be synthesized once the nominal Pd content $x'$ is more than 0.09, similar to the case of Co doped 112-type compounds [24].

Single crystal x-ray diffraction (XRD) measurements were performed at room temperature using a commercial Rigaku diffractometer with Cu Kα radiation. In order to determine the actual percentage ($x$) of the dopant as opposed to the nominal doping level ($x'$), elemental analysis of single crystals was performed by a scanning electron microscope equipped with an energy dispersive x-ray spectroscopy (EDS) probe. The electrical resistivity and Hall effect measurements were performed using the Quantum Design Physical Property Measurement System (PPMS-9 T). Magnetic measurements were performed via the VSM option of PPMS. For MO imaging, an iron-garnet indicator film was placed in direct contact with the sample surface and the whole assembly was attached to the cold finger of a He-flow cryostat (Microstat-HR, Oxford Instruments). MO images were acquired by using a cooled-CCD camera with 12-bit resolution (ORCA-ER, Hamamatsu).

3. Results and discussion

3.1. Chemical and structural characterization

Considering that both La and Pd concentrations can vary as it does for Co doped Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, EDS measurements were performed on at least 3 pieces for each doping level and 5–8 spots on each selected crystal to...
determine the actual element concentration. Figure 2(a) presents a typical EDS spectrum for the single crystal with \( x = 0.05 \), it is clear that all elements including Ca, La, Fe, Pd, and As are detected, and their contents can be roughly estimated from the spectrum weight. The actual La and Pd contents as a function of nominal Pd content \( x' \) are depicted in figure 2(b), where the error bars represent the compositional spread of measured La and Pd concentrations, and are taken as twice the standard deviation of the collected values. As one can see, the actual Pd concentration has a linear relationship with the nominal one, i.e. \( x = 0.9x' \). Also, the actual La concentration \( y \) for each doping level has a random variation as 0.245, 0.246, 0.237, 0.243, 0.242, 0.238, 0.252, 0.251, and 0.255 for \( x = 0, 0.007, 0.013, 0.016, 0.022, 0.04, 0.05, 0.058, 0.072, \) and 0.08, respectively, which are slightly lower than that of Co doped Ca0.74La0.26Fe1−xCoxAs2 single crystals [24]. Since La concentration shows some variation, we therefore label it as 0.245 (average value of all doping levels) in the chemical formula for simplicity, and refer to the single crystals by the actual Pd stoichiometry composition \( x \) throughout this paper.

Figure 2(c) shows the typical XRD patterns of several selected Ca0.755La0.245Fe1−xPdxAs2 crystals, in which only (00l) narrow diffraction peaks are detected. By refining the (00l) diffraction patterns, the interlayer distances of the FeAs layers are obtained. The evolution of the interlayer FeAs distance with \( x \) is shown in figure 2(d). As expected, this distance decreases monotonically from 10.382 Å to 10.361 Å with increasing \( x \). Such tendency is similar to what is found for 3d Co/Ni doping series [24, 25], and 4d Pd substitutions in Ba-122 and Sr-122 systems [28, 30], providing the further evidence that Pd is incorporated into the lattice.

### 3.2. Doping dependent magnetic susceptibility

Figure 3 presents the \( T \)-dependent magnetic susceptibility data taken in a field of 10 Oe for the superconducting crystals. As one can see, clear diamagnetism signal appears below \( T_c \sim 13 \) K for the crystal with \( x = 0.007 \), but the superconducting transition is relatively broad and magnetic shielding fraction is estimated to be ~60%. Interestingly, \( T_c \) can be greatly improved to 28.5 K with a sharp transition, and the shielding fraction reaches 100% for the \( x = 0.013 \) sample. Such significant enhancement of SC induced by only a small amount of Pd doping is similar to what is observed in the Ni-doped Ca0.72La0.28Fe1−xNixAs2 [25]. Then, \( T_c \) is gradually decreased with further Pd doping, and finally disappears for \( x = 0.072 \) (not shown). The superconducting
transition temperature $T_c$ in the magnetic measurement is consistent with or slightly higher than the zero resistivity temperature in the electrical measurement, which will be shown below.

3.3. Doping dependent electronic transport properties

Figures 4(a) and (b) present the temperature dependence of the in-plane resistivity normalized to their respective 300 K values for the crystals used in this study. All resistivity data exhibit a metallic behavior over the entire temperature range. Upon cooling temperature, SC reemerges at $x = 0.007$ with a broad superconducting transition, and with substitution of as little as 1.3% Pd in place of Fe, $T_c$ dramatically reaches the highest value with $T_c^{\text{max}} = 33.3$ K ($T_c^{\text{zero}} = 28$ K), in agreement with the magnetic measurement and similar to the Ni doping series [25]. Then further increasing $x$ results in an eventual suppression of SC, and at $x = 0.08$, SC is totally suppressed.

For the Pd-free sample, an anomaly associated with the magnetic transition from paramagnetic (PM) to AFM order at $T_N \sim 63$ K is observed, consistent with the previous report [26]. Upon Pd doping, the resistivity anomaly shifts to lower temperatures, which can be clearly seen in the derivative of normalized resistivity shown in figure 5(a). Extending to higher substitution levels ($x > 0.013$), no detectable feature of resistivity measurement can be employed to infer $T_N$. It should be noted that only a single peak is visible in figure 5(a), in contrast to the Co doped Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, in which another small kink corresponding to the structural transition at a slightly higher temperature appears prior to $T_N$ [23], probably because of the different crystal growth conditions. In order to get more insight into the doping effect on the electronic transport properties, we analyze the $\rho/\rho_{300K}$ data according to the empirical formula that combines $T$-linear and $T^2$ components, i.e. $\rho/\rho_{300K} = \rho_0 + AT + BT^2$, which is initially proposed and subsequently used in studies of the resistivity of cuprates, heavy-fermion compound, organic superconductors, and IBVs [37–41]. In this model, the $BT^2$ term describes the Fermi liquid behavior, and the $AT$ term reflects electronic correlations and scattering, e.g. the electron-boson interaction and/or the critical fluctuations, and $\rho_0$ is the normalized residual resistivity. Meanwhile, we can also get the residual resistivity ratio $\text{RRR} = \rho(300 \text{K})/\rho(0 \text{K}) = 1/\rho_0$, which is intimately related to the strength of impurity scattering. For all of the doping concentrations, such a fitting agrees very well within a wide temperature range from 20 K above the $T_N$ or $T_c$ to 300 K. The doping dependence of fitting parameters are given in figures 5(b) and (c), along with the results of 3$d$ Ni-doped Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$ for the comparison [25]. As can be seen, $A$ and $B$ show opposite behaviors for both Pd and Ni doping series, suggesting that the transport behaviors become more like Fermi liquid with the increasing more electrons in this system. Moreover, the magnitudes of RRR reduce with increasing $x$, this is reasonable since higher electron doping level means stronger scattering from the impurity effect and larger $\rho_0$.

To proceed, we measured the Hall resistivity $\rho_{xy}$ of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ single crystals with different Pd contents. For all of the measured crystals, $\rho_{xy}$ exhibits a linear field dependence up to 9 T, data for a representative crystal with $x = 0.04$ is shown in the inset of figure 5(d). The $T$-dependent Hall coefficients $R_{H}(T)$ calculated from $R_H = \rho_{xy}/H$ are depicted in the main panel of figure 5(d), which remains negative in the whole temperature region, indicating that electrons dominate the charge transport in Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ crystals. For the sample with $x = 0$, a kink associated to the AFM transition is observed at low temperatures [26].
consistent with the resistivity result. For the samples with $x \leq 0.04$, $R_H$ shows a strong temperature dependence, indicative of the multiband effect which is a common feature in IBSs. With further Pd doping, such temperature dependence becomes weak and almost vanishes for the higher Pd doping crystals, which resembles that of Pt doped 10-3-8 system \[42\]. In addition, the absolute values of $R_H$ are reduced monotonically with increasing $x$, except for the Pd-free sample, which has a smaller value than the others at low temperatures. This phenomenon was also observed in our previous high pressure study \[27\] and Co doping series \[24\], which can be explained by introducing more electrons into the system through Pd doping considering a single-band model, i.e. $|R_H| \sim 1/|n_e|$. The smaller $|R_H|$ value of Pd-free crystal at low temperatures is also understandable, which could be ascribed to the AFM transition induced Fermi-surface reconstruction or AFM spin fluctuations that result in the change of carrier density and mobility \[23, 26\]. Also, Pd doping naturally leads to the change of relevant electronic structure, hence, future angle-resolved photoemission spectroscopy measurements and band structure calculations may help to further understand the remarkable doping and temperature dependencies of the $R_H$ in Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$.

3.4. $T$–$x$ phase diagram
Combing the magnetization and the electrical resistivity data, we traced the evolution of AFM order and SC phase transitions of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ single crystals as a function of Pd content. The $T$–$x$ phase diagram is constructed in figure 6, where $T_N$ denotes the AFM transition, $T^{\text{onset}}_c$ is determined as the intercept of the extrapolation of the normal-state data and the mid-transition data, and $T^{\text{zero}}_c$ is obtained from zero resistivity, which is close to $T^{\text{ML}}_c$ determined from the magnetic susceptibility. As seen, accompanied by the suppression of AFM, SC occurs rapidly and shows an asymmetric SC dome, exhibiting a maximum $T_c$ at $x = 0.013$. Note that, as mentioned above, due to no feature related to the AFM transition is visible from the $T$-dependent resistivity for $x > 0.013$, an extrapolation of $T_N$ from lower doping level (as shown by dashed line) is employed, inspired by

![Figure 4](image-url)

(a) Temperature dependence of the normalized in-plane resistivity, $\rho/\rho_{300K}$, of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ single crystals for different doping $x$. The data for each doping are offset vertically by 0.8 for clarity except for $x = 0$. (b) An enlarged view of the normalized resistivity curves at low temperatures.
the recent neutron scattering study on Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$ in which the AFM transition has been proven to be robust even for certain doping levels that no distinct feature in resistivity can be detected [25]. Nonetheless, it is apparent that the AFM and SC phases coexist microscopically in a finite doping range, similar to that observed in Co/Ni doping series [24, 25].
To better evaluate this phase diagram, it is instructive to compare it with 3d Ni/Co doping series. For the 3d Ni doped Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$, the phase diagram shows obvious similarities as that of 4d Pd doped Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ in the present study except that the SC dome is extended slightly beyond that seen in the Pd-doped system, i.e. with a larger range of concentrations ($x \sim 0.1$) exhibiting SC [25]. Such a similarity between phase diagrams for 3d Ni and 4d Pd dopants is reminiscent of other IBSSs, e.g. Ba-122 and Sr-122 systems [30, 33]. However, the shape of phase diagram in Pd and Ni doped compounds differs from that of Co doping series in 112-type IBSSs. That is, in the SC region, the dome maximum of both Pd and Ni doping series systems might be resulted from the various La doping concentration and different crystal growth conditions. For compound are intimately affected by the growth conditions. Therefore, more work is required to properly compare high-quality specimens grown under similar conditions before grander conclusions can be made.

Finally, upon TM (e.g. Co, Ni, and Pd) doping in 112-type IBSSs, the suppression of AFM transition and the reemergence of SC in the over-doped non-SC regime are indeed unexpected, as the AFM transition is significantly enhanced, and the SC is suppressed by RE doping [21, 22]. These observations clearly demonstrate that different doping mechanisms exist between doping the conducting layer (FeAs) and block layer (CaAs) in 112-type IBSSs, indicating that the effects of RE and TM dopants are more complicate than those cases simply introducing electrons to suppress the AFM and induce SC in most IBSSs. Different approaches are warranted to specify the origin of this contrasting doping dependence of AFM order and SC in CaAs and FeAs layers in the future.

3.5. Critical current density, pinning mechanism, and vortex diagram of Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ single crystal with $x = 0.013$

It is well known that investigation of the critical current density $J_c$, vortex pining mechanism, upper critical field $H_{c2}$, and vortex dynamic are important for practical applications, as well as for the superconducting pairing mechanism in high-$T_c$ superconductors. Our previous reports have demonstrated that $J_c$ can be significantly enhanced exceeding $10^6$ A cm$^{-2}$ by 3d Co doping or proton irradiation in 112-type IBSSs [35, 36]. Moreover, 3d Co doping in 112-type IBSSs also caused interesting effects in the vortex dynamics, such as thermally activated flux flow, vortex-glass to vortex-liquid transition, and the emergence of second-peak effect [44, 45]. Hence, in order to gain insight into $J_c$ and vortex pinning mechanism of this novel 4d Pd-doped crystals, we measured the magnetization hysteresis loops (MHLs) of a representative single crystal with $x = 0.013$ that shows the maximum $T_c$ at different temperatures, as shown in figure 7(a). The almost perfect symmetry of the MHLs with respect to the $x$-axis indicates the dominance of the bulk pinning. Meanwhile, second-peak effect is also observed, similar to the effects of Co doping in this system [24, 45]. We calculated the field dependence of $J_c$ from the MHLs based on the Bean model $J_c = 20\Delta M/[a(1 - a/3b)]$, where $\Delta M = M_{down} - M_{up}$, $M_{up}$ and $M_{down}$ (emu cm$^{-3}$) are the magnetization when sweeping fields up and down, respectively, $a$ (cm) and $b$ [cm] are sample widths ($a < b$) [46]. The derived $J_c$ as a function of magnetic field is shown in figure 7(b), which exhibits a weak field dependence at low temperatures ($T < 10$ K), indicative of the strong vortex pinning effect. $J_c$ reaches up to $5.5 \times 10^6$ A cm$^{-2}$ at 3 K (self-field), comparable to that of Ca$_{0.75}$La$_{0.25}$Fe$_{0.925}$Co$_{0.075}$As$_2$ [24], suggestive of the bulk SC and potential for applications of 112-type IBSSs. Next, to understand vortex pinning of Ca$_{0.755}$La$_{0.245}$Fe$_{0.985}$Pd$_{0.015}$As$_2$ single crystal, we investigated the field dependence of pinning force density. According to the Dew-Huges model [47], if one pinning mechanism is dominant in a certain temperature range, the normalized vortex pinning force density $f_p = F_p/F_{p,max}$ at different temperatures can be scaled with $H^*$, where $F_p$ is the pinning force density and $F_{p,max}$ is the maximum pinning force density, $H = H/H_{irr}$ is the ratio between external field $H$ and irreversibility field $H_{irr}$. Note the uncertainty of determining the accurate value of $H_{irr}$ in high-$T_c$ superconductors, the $f_p$ data were rescaled by the reduced field $H = H/H_{max}$ ($H_{max}$ is the magnetic field corresponding to $F_{p,max}$) instead of $H^*$ $= H/H_{irr}$ as widely adopted in cuprates and IBSSs [48-50], and then the scaling of $f_p$ data can be given by the following equations:

$$f_p = 3h^2\left(1 - \frac{2h}{3}\right)$$ for $\Delta \kappa$ pinning, \hspace{1cm} (1)
The field dependence of $f_p$ derived from the Bean model. (c) Normalized vortex pinning force density $f_p = F_p / F_{p,max}$ as a function of reduced field $h = H / H_{max}$ at different temperatures. Dotted lines respectively represent the fitting curves of equations (1)–(3) for different vortex pinning mechanisms.

\[ f_p = \frac{9}{4} (1 - h/3)^2 \]  
\[ f_p = \frac{25}{16} (1 - h/5)^2 \]  

The $f_p$ as a function of $h = H / H_{max}$ at different temperatures are shown in figure 7(c) together with the theoretical curves of equations (1)–(3). One can see that the experimentally derived value resides in between curves of equations (1) and (2) in a wide field range. The fact that the normalized $f_p$ resides between the predictions for the normal point pinning and $\Delta \kappa$ pinning indicates both pinning mechanisms may coexist. In $\text{Ca}_{0.755}\text{La}_{0.245}\text{Fe}_{0.987}\text{Pd}_{0.013}\text{As}_2$ single crystal, the $f_p$ data is much closer to the theoretical curve of equation (2).

Figure 7. (a) The MHLs of $\text{Ca}_{0.755}\text{La}_{0.245}\text{Fe}_{0.987}\text{Pd}_{0.013}\text{As}_2$ single crystal at different temperatures for $H \perp ab$ plane. (b) The field dependence of $J_c$ derived from the Bean model. (c) Normalized vortex pinning force density $f_p = F_p / F_{p,max}$ as a function of reduced field $h = H / H_{max}$ at different temperatures. Dotted lines respectively represent the fitting curves of equations (1)–(3) for different vortex pinning mechanisms.
along the red dashed line shown in Figure 8(a) will generate the spatial origin, is more dominant, similar to what is found in many other IBSs [24, 45, 51]. Meanwhile, the Pd dopants will generate the spatial fluctuations of the transition temperature \( T_c \) and hence also contribute to the \( \Delta \kappa \) pinning. Moreover, it should be noted that, a deviation, which has been observed in \( \text{YBa}_2\text{Cu}_3\text{O}_7-\text{FeTe}_{0.6}\text{Se}_{0.4}, \text{Ca}_{10} \) single crystals and some IBSs due to the effect of flux creep [48–50], also starts to take place at high fields \( (H > H_{\text{max}}) \), implying that the flux creep may appear and become dominant in high field regime at evaluated temperatures in \( \text{Ca}_{0.755}\text{La}_{0.245}\text{Fe}_{0.987}\text{Pd}_{0.013}\text{As}_2 \) single crystal.

The above estimate of \( J_c \) is based on the Bean model with the assumption that the homogeneous current is flowing within the sample. To examine this assumption, we performed MO imaging of a \( \text{Ca}_{0.755}\text{La}_{0.245}\text{Fe}_{0.987}\text{Pd}_{0.013}\text{As}_2 \) single crystal (an optical micrograph can be seen in figure 8(d)) to check its homogeneity and the value of \( J_c \) at several temperatures. The remnant state is prepared by applying 1600 Oe perpendicular to the \( ab \)-plane for 0.2 s and removing it after zero-field cooling. Figures 8(a)–(c) show the MO images of \( \text{Ca}_{0.755}\text{La}_{0.245}\text{Fe}_{0.987}\text{Pd}_{0.013}\text{As}_2 \) single crystal in the remnant state at 5, 10, and 15 K, respectively. At lower temperatures, the field fully penetrates the sample, and the MO image manifests a typical roof-top pattern, similar to that observed in \( \text{Ba(Fe}_{1-x}\text{Co}_x)_{2}\text{As}_2, \text{FeTe}_{0.6}\text{Se}_{0.4}, \text{Ca}_{10}(\text{Pt}_{4.4}\text{As}_9)(\text{Fe}_{2.8}\text{Pt}_{4.8}\text{As}_2)_3 \) and \( \text{CaKFe}_4\text{As}_4 \) single crystals [52–55], indicating the homogeneous current flow throughout the sample. Figure 8(d) shows profiles of the magnetic induction at different temperatures along the red dashed line shown in figure 8(a). \( J_c \) for a thin superconductor is roughly estimated by \( J_c \sim \Delta B/t \), where \( \Delta B \) is the trapped field and \( t \) is the thickness of the sample. At 5 K, with \( \Delta B = 310 \text{ G} \) and \( t = 11 \mu \text{m} \), \( J_c \) is estimated as \( \sim 2.8 \times 10^5 \text{ A cm}^{-2} \), which is in good agreement with the value derived from Bean model.

After checking \( J_c \) and pinning mechanism, now let us turn to the upper critical field and vortex dynamic. Resistivity profiles \( \rho(H) \) in magnetic fields up to 9 T for \( H//ab \) and \( H\perp ab \) are shown in figure 9(a) and (b). With increasing field, the superconducting transition gradually shifts to lower temperatures accompanied by an increase in the transition width, especially for \( H\perp ab \) plane, which indicates the presence of the strong thermal fluctuations of vortices. However, the broadening is almost negligible for \( H//ab \). By taking the criterions of 50% \( \rho_n \) and 19% \( \rho_m \), we determine the upper critical field \( H_{c2} \) and irreversibility field \( H_{c1m} \), as shown in figure 9(c). The slopes of \( H_{c2} \), \( \mathrm{d}H_{c2}/\mathrm{d}T = -4.5 \text{ and } -1.6 \text{ T K}^{-1} \), for \( H//ab \) and \( H\perp ab \), respectively. According to the Werthamer-Helfand-Hohenberg formula [56] \( H_{c2}(0) = -0.693T_c\mathrm{d}H_{c2}/\mathrm{d}T\big|_{T=T_c} \) and taking \( T_c = 31.85 \text{ K} \), the values of orbital-limited upper critical fields are roughly estimated as \( H_{c2}(0) = 99.3 \) and 35.3 T for \( H//ab \) and \( H\perp ab \), respectively. Inset of figure 9(c) shows the temperature dependence of anisotropy \( \Gamma = |H_{c2}^{||ab}|/|H_{c2}^{||ab}| \).
and $\Gamma = \Sigma$.

In conclusion, a series of slightly Pd-doped Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ single crystals were successfully grown using self-flux method, and the $T$–$x$ phase diagram was determined based on the magnetization and electrical resistivity data. Bulk SC with a maximum $T_c$ of 28.5 K is reemerged by only a small amount of Pd doping with $x = 0.013$, and as a representative, its superconducting properties including critical current density, pinning mechanism, and vortex diagram were investigated by magnetization, MO imaging, and magneto-resistivity measurements. The $T$–$x$ phase diagram shows similarities to that of 3$d$ Ni-doped Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$, but differs from that of 3$d$ Co-doped Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, suggesting complex

values of $\Gamma$ close to $T_c$ are around 5, comparable to that of Co doped Ca$_{1-x}$La$_x$FeAs$_2$ [24, 35], and lower than that of 10-3-8 and 10-4-8-type IBSs which has similar FeAs interlayer distance but insulating space layers [54, 57], indicating a stronger FeAs interlayer coupling in 112-type IBSs arising from the metallic spacer layers. Moreover, as an accumulation of knowledge, the temperature dependence of the irreversibility fields $H_{irr}$ are also well fitted by the expressions $H_{irr}^{ab} = H_{irr}^{ab}(0)(1 - T/T_c)^{1.24}$ and $H_{irr}^{ab} = H_{irr}^{ab}(0)(1 - T/T_c)^{1.32}$, as shown in figure 9(c). Such a $(1 - T/T_c)^{\alpha}$-type temperature dependence of $H_{irr}$ can be explained by using a thermally activated flux creep model [38]. The power exponent for Ca$_{0.755}$La$_{0.245}$Fe$_{0.985}$Pd$_{0.015}$As$_2$ is close to that of Ba(Fe$_{0.85}$Co$_{0.15}$)$_2$As$_2$ and YBa$_2$Cu$_3$O$_{7-x}$ [59, 60]. In figure 9(d), we present the vortex phase diagram of the Ca$_{0.755}$La$_{0.245}$Fe$_{0.985}$Pd$_{0.015}$As$_2$ single crystal, in which the second-peak $H_{sp}$ obtained from the magnetization measurement and $H_{irr}$ together with $H_{c2}$ are shown. Similar to the case of cuprate superconductors, 122-type Ba(Fe$_{1-y}$Co$_y$)$_2$As$_2$, and 10-4-8-type Ca$_{10}$(Pt$_{0.4}$As$_{0.8}$)(Fe$_{2.3}$Pt$_{0.7}$As$_2$)$_3$ IBSs [54, 59], four different regimes are clearly distinguishable: (1) Normal state, the region above $H_{c2}$; (2) Vortex-liquid phase, which governs the region between the $H_{irr}$ line and the $H_{c2}$ line. (3) Plastic creep region, which holds between $H_{sp}$ and $H_{irr}$, in this region, the plastic deformation becomes dominant and governs the vortex dynamics. (4) Collective pinning and creep, the region below the $H_{sp}$ line, where the vortex behavior can be described by the elastic motion of vortices.

4. Summary

In conclusion, a series of slightly Pd-doped Ca$_{0.755}$La$_{0.245}$Fe$_{1-x}$Pd$_x$As$_2$ ($0 \leq x \leq 0.08$) single crystals were successfully grown using self-flux method, and the $T$–$x$ phase diagram was determined based on the magnetization and electrical resistivity data. Bulk SC with a maximum $T_c$ of 28.5 K is reemerged by only a small amount of Pd doping with $x = 0.013$, and as a representative, its superconducting properties including critical current density, pinning mechanism, and vortex diagram were investigated by magnetization, MO imaging, and magneto-resistivity measurements. The $T$–$x$ phase diagram shows similarities to that of 3$d$ Ni-doped Ca$_{0.76}$La$_{0.24}$Fe$_{1-x}$Ni$_x$As$_2$, but differs from that of 3$d$ Co-doped Ca$_{0.74}$La$_{0.26}$Fe$_{1-x}$Co$_x$As$_2$, suggesting complex

![Figure 9. T-dependent resistivity of Ca$_{0.755}$La$_{0.245}$Fe$_{0.987}$Pd$_{0.013}$As$_2$ single crystal under different magnetic fields for (a) $H//ab$ and (b) $H.L.ab$. (c) T-dependent upper critical field $H_{c2}$ and irreversible field $H_{irr}$ for $H//ab$ and $H.L.ab$ obtained with the 50% and 1% criteria from the resistivity data in (a) and (b). The solid lines are fits to $H_{irr)^{ab}} = H_{irr}^{ab}(0)(1 - T/T_c)^{1.24}$ and $H_{irr)^{ab}} = H_{irr}^{ab}(0)(1 - T/T_c)^{1.32}$. The inset shows the anisotropic parameter $\Gamma(T) = H_{irr)^{ab}}/H_{irr^{ab}}$ near $T_c$. (b) Vortex phase diagram as determined by combination of magneto-transport and magnetization measurements for $H.L.ab$ in the mixed state. $H_{c2}$ is taken from $M(H)$ curves.](image-url)
doping mechanism in 112-type IBSs beyond the cases of most IBSs. Certainly, this warrants further investigation, for instance via careful inspections of the phase diagrams arisen by other TM dopants, and the role of crystalline quality and disorder on the SC.

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ORCID iDs

Xiangzhuo Xing © https://orcid.org/0000-0002-2147-8949
Zhixiang Shi © https://orcid.org/0000-0003-3881-5152

References

[1] Johnston D C 2010 Adv. Phys. 59 803–1061
[2] Stewart G R 2011 Rev. Mod. Phys. 83 1589–652
[3] Hosono H and Kuroki K 2015 Physica C 514 399–422
[4] Mamin H J, Singh D J, Johannes M D and Du M H 2008 Phys. Rev. Lett. 101 057003
[5] Hirschfeld P J, Korshunov M M and Mamin H J 2011 Rep. Prog. Phys. 74 124508
[6] Christianson AD et al 2008 Nature 456 930–2
[7] Hanaguri T, Nitta A, Kuroki K and Takagi H 2010 Science 328 474
[8] Back S H, Efremov D V, Ok J M, Kim J S, van den Brink J and Buchner B 2015 Nat. Mater. 14 210–4
[9] Bohmer AE, Ari A, Hardy F, Hattori T, Iye T, Wolf T, Lohneysen H V, Ishida K and Meingast C 2015 Phys. Rev. Lett. 114 027001
[10] Imai T, Ahilan K, McQueen T M and Cava R J 2009 Phys. Rev. Lett. 102 177001
[11] Sato Y et al 2018 Proc. Natl Acad. Sci. USA 115 1227–31
[12] Onari S, Yamakawa Y and Kontani H 2016 Phys. Rev. Lett. 116 227001
[13] Yang J, Zhou R, Wei L-L, Yang H-X, Li J-Q, Zhao Z-X and Zheng G-Q 2015 Chin. Phys. Lett. 32 107401
[14] Limura S, Matsuishi S, Sato H, Hanna T, Muraba Y, Kim S W, Kim J E, Takata M and Hosono H 2012 Nat. Commun. 3 943
[15] Fujiwara N, Tsutsui S, Limura S, Matsuishi S, Hosono H, Yamakawa Y and Kontani H 2013 Phys. Rev. Lett. 111 097002
[16] Hiroishi M et al 2014 Nat. Phys. 10 300
[17] Kitagawa S et al 2013 J. Phys. Soc. Japan 82 123702
[18] Wu X, Le C, Liang Y, Qin S, Fan H and Hu J 2014 Phys. Rev. B 89 205102
[19] Sala A et al 2014 Appl. Phys. Express 7 073102
[20] Xing Z, Xu C, Zhou W, Xu X, Chen B, Zhao H, Xu M and Shi Z 2017 J. Alloys Compd. 721 261–7
[21] Kudo K, Mizukami T, Kitahama Y, Matsuishi S, Iba K, Fujimura K, Nishimoto H, Hiraoka Y and Nohara M 2014 J. Phys. Soc. Japan 83 025001
[22] Kawasaki S, Mabuchi T, Maeda S, Adachi T, Mizukami T, Kudo K, Nohara M and Zheng G 2015 Phys. Rev. B 92 180508 (R)
[23] Jiang S et al 2016 Phys. Rev. B 93 054522
[24] Jiang S et al 2016 Phys. Rev. B 93 174513
[25] Xie T et al 2017 Supercond. Sci. Technol. 30 095002
[26] Xing Z et al 2018 J. Phys.: Condens. Matter. 30 023501
[27] Zhou W et al 2017 Phys. Rev. B 96 144503
[28] Han F et al 2009 Phys. Rev. B 80 024506
[29] Zhu X, Han F, Mu G, Cheng P, Tang J, Ju J, Tanigaki K and Wen H-H 2010 Phys. Rev. B 81 104525
[30] Ni N, Thaler A, Kracher A, Yan J Q, Bud’ko S L and Canfield P C 2009 Phys. Rev. B 80 024511
[31] Steckel F et al 2015 Phys. Rev. B 91 184516
[32] Kirshenbaum K, Saha S R, Drye T and Paglione J 2010 Phys. Rev. B 82 144518
[33] Saha S R, Butch N P, Kirshenbaum K and Paglione J 2009 Phys. Rev. B 79 224519
[34] Tamura S, Kitagawa Y, Sugiyama Y, Sugawara K and Sawa H 2017 Inorg. Chem. 56 3030–5
[35] Xing Z, Zhou W, Zhao H, Yin J, Pan Y, Nohara M and Shi Z 2016 Supercond. Sci. Technol. 29 055006
[36] Park A et al 2016 Supercond. Sci. Technol. 29 055006
[37] Analysis J G, Kuo H-H, McDonald R D, Mark-Wartenbe, Rourke P M C, Hussey N E and Fisher J R 2014 Nat. Phys. 10 194
[38] Doiron-Leyraud N, Auban-Senzier P, René de Cotret S, Bourbonnais C, Jérôme D, Bechgaard K and Taillefer L 2009 Phys. Rev. B 80 214531
[39] Wang H et al 2019 Phys. Rev. B 99 024504
[40] Cooper R A et al 2009 Science 323 603
[41] Mackenzie A P, Julian S R, Sinclair D C and Lin C T 1996 Phys. Rev. B 53 5848
[42] Xiong Z J, Luo X G, Ying J J, Wang X F, Yan Y J, Wang A F, Cheng P, Ye G J and Chen X H 2012 Phys. Rev. B 85 224527
[43] Kitagawa S et al 2017 J. Phys. Soc. Japan 86 115705
[44] Xing Z et al 2018 Sci. China-Phys. Mech. Astron. 61 127406
[45] Zhou W, Xing X, Wu W, Zhao H and Shi Z 2016 Sci. Rep. 6 22278
[46] Bean C P 1964 Rev. Mod. Phys. 36 31–9
[47] Dew-Hughes D 1974 Phil. Mag. 30 293–305
[48] Li M, Chen L, You W, Ge J and Zhang J 2014 Appl. Phys. Lett. 105 192602
[49] Higuchi T, Yoo S I and Murakami M 1999 Phys. Rev. B 59 1514
[50] Klein L, Yacoby E R, Yeshurun Y, Erb A, Müller-Vogt G, Breit V and Wühl H 1994 Phys. Rev. B 49 4403 (R)
[51] Yang H, Luo H, Wang Z and Wen H-H 2008 Appl. Phys. Lett. 93 142506
[52] Nakajima Y, Taen T and Tamegai T 2009 J. Phys. Soc. Japan 78 023702
[53] Sun Y, Taen T, Tsuchiya Y, Ding Q, Pyon S, Shi Z and Tamegai T 2013 Appl. Phys. Express 6 043101
[54] Ding Q-P, Tsuchiya Y, Mohan S, Taen T, Nakajima Y and Tamegai T 2012 Phys. Rev. B 85 104512
[55] Pyon S et al 2019 Phys. Rev. B 99 104506
[56] Werthamer N R, Helfand E and Hohenberg P C 1966 Phys. Rev. 147 295–302
[57] Yuan F F et al 2015 Appl. Phys. Lett. 107 012602
[58] Blatter G, Feigel’man M V, Geshkenbein V B, Larkin A I and Vinokur V M 1994 Rev. Mod. Phys. 66 1125
[59] Shen B, Cheng P, Wang Z, Fang L, Ren C, Shan Land Wen H-H 2010 Phys. Rev. B 81 014503
[60] Yeshurun Y and Malozemoff A P 1988 Phys. Rev. Lett. 60 2202