Physical properties of superconducting \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.92}\text{Pt}_{0.08})_2\text{As}_2)_5 \) crystal and comprehensive cognition on the transition temperature for \( \text{Ca}_{10}-3(4)-8 \)

Dapeng Wu \(^*\), Yingying Zhai \(^1\), Zhen Chen \(^1\), Henan Zhu \(^1\), Yanru Huang \(^1\), Zhaoyuan Song \(^1\), Xin Liu \(^1\), Hao Sheng \(^1\), Songyang Liu \(^1\), Miaochoao Chen \(^1\), Mingyang Wang \(^1\) and Qing Li \(^1\)

\(^1\) College of Science, Liaoning Petrochemical University, Fushun, Liaoning 113001, People’s Republic of China
\(^2\) College of Computer Science and Engineering, Northeastern University, Shenyang, Liaoning 110004, People’s Republic of China
\(^3\) School of Civil Engineering, Liaoning Petrochemical University, Fushun, Liaoning 113001, People’s Republic of China

E-mail: wudapeng@lnpu.edu.cn

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Abstract

Superconducting single crystal of \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.92}\text{Pt}_{0.08})_2\text{As}_2)_5 \) has been prepared using flux method, and the physical properties of which are carefully examined. Resistivity anisotropy between \( ab \) plane and \( c \)-axis is observed, \( T^0.5 \) term originated from the interlayer Josephson coupling is essential to be added to the formula used to describe the out-of-plane resistivity. The density of state (DOS) value at Fermi level derived from the fitting of specific heat data is consistent with the calculation results. Both direct and indirect platinum doping effect have influences on the superconducting transition temperature \( (T_c) \) of \( \text{Ca}_{10}-3(4)-8 \) system, the \( T_c \) of our sample falls well into the trend strip formed by the data reported previously.

1. Introduction

The discovery of superconductivity in \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)\text{Fe}_2\text{As}_2)_3 \) (\( \text{Ca}_{10}-3-8 \)) and \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)\text{Fe}_2\text{As}_2)_5 \) (\( \text{Ca}_{10}-4-8 \)) has generated great interest in the condensed matter community \([1-6]\). Since the year of 2011, a number of reports appeared and showed that this compound has a wide range of transition temperatures \( (T_c) \) \([1-3,7-12]\). As in other traditional Fe-based superconductors, \( \text{Ca}_{10}(\text{Pt}_n\text{As}_8)\text{Fe}_2\text{As}_2)_5 \) \((n = 3, 4)\) forms layered structure building of FeAs superconducting layers separated by the intermediary layers of \( \text{Ca}-\text{Pt}_n\text{As}_8-\text{Ca} \), and such arrangement is shown in figures \( 1(a) \) and \( (b) \). Pt atoms in the \( \text{Pt}_n\text{As}_8 \) spacer layer could be divided into two categories: the substitutional ones that can stay in the plane, others are interstitial, and the interstitial Pt atoms crowd out the As atoms from their original positions in the lattice, which also helps to form the As-As dimers \([2]\).

Most iron based parent superconductor compounds only exhibit superconductivity upon doping. The reported doping of \( \text{Ca}_{10}(\text{Pt}_n\text{As}_8)\text{Fe}_2\text{As}_2)_5 \) is mainly concentrated in Ca and Fe sites. Nevertheless, changing the replacement rate of Pt for Fe in \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)\text{(Fe}_{1-x}\text{Pt}_x\text{As}_2))_2\text{As}_2)_5 \) could result in a large range of \( T_c \) values, for example, \( T_c \approx 5.9 \text{ K for } x = 0.07 \text{ and } T_c \approx 10 \text{ K for } x = 0.13 \text{ under } n = 3 \) \([2]\), that means that Pt, as the fundamental component of Pt\(_n\text{As}_8 \) spacer layer, also plays a key role in the substitution within FeAs superconducting layer. On the other hand, even for the same \( x \), there has a large difference in \( T_c \) between \( \text{Ca}_{10}-3-8 \) and \( \text{Ca}_{10}-4-8 \), and the relationship between \( T_c \) and spacers is complicated, as the spacers change not only interlayer coupling strength, but also act as charge reservoirs, thereby influencing the electronic properties. Empirically, \( T_c \) correlates with the interlayer distance \( (d) \) in a cusp-shaped curve in both cuprates \([13, 14]\) and Fe-based superconductors \([15]\). However, the \( \text{Ca}_{10}(\text{Pt}_n\text{As}_8)\text{Fe}_2\text{As}_2)_5 \) seems to violate this empirical rule, where \( T_{c,max} \approx 10 \text{ K for } n = 3 \) with \( d \approx 10.5-10.7 \text{ Å} \) and \( T_{c,max} \approx 38 \text{ K for } n = 4 \) with \( d \approx 11.2 \text{ Å} \) \([1, 2]\). Given similar \( d \) values for both \( n = 3 \) and \( n = 4 \), the large difference in \( T_c \) ought to be attributed to the interlayer spacer: \( \text{Ca}_{10}\text{Pt}_n\text{As}_8 \).
Both first-principles calculations and angle resolved photoemission spectroscopy (ARPES) experiments [3, 16–18] suggest that Pt₈As₈ and FeAs layers are weakly coupled. Through studying the relationship between the structure, constituents and physical properties, the origin of superconductivity for Fe based superconductors may be elucidated. In this contribution, our goal is to synthesize Ca₁₀(Pt₄As₈)(Fe₁₋ₓPtₓ)₂As₂ with appropriate Pt doping rate by controlling the preparation conditions, such as initial element composition, maximum heating temperature and the cooling rate, then measure the physical properties of the samples, through a comparison with the earlier reported data, discuss the reasons for large Tc difference in the Ca₁₀(Pt₄As₈)(Fe₂As₂)₅ system and seek to an universal interpretation on the transition temperatures in such family.

2. Sample synthesis and characterization approaches

Synthesis for Ca₁₀(Pt₄As₈)(Fe₁₋ₓPtₓ)₂As₂ employs a conventional flux method by the process described elsewhere [2, 7]. Single crystals preparation starts from mixing of high purity Ca shot (99.999%, Alfa Aesar, Haverhill, MA, USA), Fe powder (99.95%, Alfa Aesar, Haverhill, MA, USA), Pt powder (99.95%, Alfa Aesar, Haverhill, MA, USA), and As powder (99.999%, Alfa Aesar, Haverhill, MA, USA) with a stoichiometric amounts ratio of 13:11:6:23. The mixture was put in a crucible and then sealed in a quartz tube under 1/4 atmospheric pressure of Argon. The whole assembly was heated to 700 °C for 5 h within a box furnace and maintained at this...
temperature for 4 h. It was further heated up to 1080 °C for the next 5 h, and, after being held for 60 h at this maximum heating temperature, it starts to cool. The assembly was firstly cooled to 900 °C at a rate of 3 °C per hour, and, in the next 50 h, it was further cooled to 600 °C. Finally, by turning power off, the furnace was cooled down to the room temperature, and, then, the shiny plate-like single crystals were obtained in the crucible. The cooling process is important to the preparation because it is not only the key factor on the formation of a stable phase, but also has an influence on the diffusion intensity of Pt in the FeAs layer when temperature decreasing, which makes the $x$ changeable. A photo showing the as prepared sample, owning a typical size of $5 \times 4 \times 1$ mm$^3$, is shown in figure 1(c).

Crystal structure and phase purity were checked by a Rigaku-D/max x-ray diffractometer (XRD), employing Cu-Kα ($\lambda = 1.5406 \text{ Å}$) radiation. The surface morphology of the samples was observed by a FEI Quanta 450 scanning electron microscope (SEM) with Oxford EDS detector. The chemical constituent for the sample and Pt self-doping ratio $x$ were determined by Energy Dispersive x-ray Spectroscopy (EDX). Electrical properties and specific heat were measured in a Physical Property Measurement System (PPMS). The standard four-probe method was used for both ab plane and c-axis resistivity measurements. Magnetic susceptibility measurement of the sample was accomplished in a Magnetic Property Measurement System (MPMS).

3. Results and discussion

Figure 1(d) shows the XRD pattern for the as-grown Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{1-x}$Pt$_x$)$_2$As$_2$)$_3$ crystal along its c axis. It is noted only (00l) peaks appear and their positions match very well with those previously reported in [7, 10], and the FWHM of the (002) peak is 0.1051°, indicative of a high crystallinity of the sample. The crystal 0.020 $\times$ 0.075 $\times$ 0.125 mm$^3$ in size was stuck on a glass fiber and used for the single crystal x-ray diffraction. The cell parameters of the sample are $a = 8.7165(40)$ Å, $b = 8.7274(37)$ Å, $c = 10.7113(56)$ Å, and angles are
\[ \alpha = 94.704^\circ, \beta = 104.992^\circ, \gamma = 90.136^\circ \] at the room temperature, indicative of the sample crystallizing in triclinic space group P\( \bar{1} \). These parameters are fairly close to those obtained in \([1, 10]\).

The SEM images of the Ca\(_{10}\)(Pt\(_4\)As\(_8\))(Fe\(_{1-x}\)Pt\(_x\)As\(_2\))\(_5\) single crystal are shown in figure 2(a). As can be seen that the crystal does not only own a surface with large flat and homogeneous area, but also exhibit the layered nature. The chemical constituents were determined by the EDX measurements. We selected five scattered spots on each sample, then calculated the average value of these scan results. The measured composition is Ca\(_{10}\)Pt\(_{4.8}\)Fe\(_{9.2}\)As\(_{18}\), implying a formula of Ca\(_{10}\)(Pt\(_4\)As\(_8\))(Fe\(_{0.92}\)Pt\(_{0.08}\)As\(_2\))\(_5\) for the sample, if platinum self-doping effect is considered. Compared with the work of \(x = 0.14\) \([10]\), besides that the content of Pt in the original mixture was reduced, the cooling time is also shortened, which is not advantageous to the interlayer diffusion of Pt, and this may be other reason for the decrease of the Pt doping level \(x\) in the FeAs layer.

Both ab plane \(\rho_{ab}\) and c-axis \(\rho_c\) electrical resistivities of Ca\(_{10}\)(Pt\(_4\)As\(_8\))(Fe\(_{0.92}\)Pt\(_{0.08}\)As\(_2\))\(_5\) are shown in figure 3. The overall features of \(\rho_{ab}\) are consistent with the previous reports \([1, 2, 7]\). The \(\rho_{ab}\) values decrease monotonously from 0.375 mΩ⋅cm at 300K to 0.15 mΩ⋅cm before superconducting transition in its normal state, exhibiting a metallic character \(\sigma > 0\), then the residual resistivity ratio (RRR) \(\rho_{ab}(300K)/\rho_{ab}(T_{c\text{--onset}})\) is 2.5. At \(T_{c\text{--onset}} = 31.6K\), \(\rho_{ab}\) starts to fall steeply and touch to zero at 28.7 K, implying the transition width in temperature is \(\Delta T_c = 2.9K\). Relatively small RRR and large \(T_{c\text{--onset}}\) indicate that there are platinum ions taking the place of iron in the FeAs layers \([1 -- 3, 7 -- 9]\), and the narrow transition process indicates high quality and spatial composition uniformity of grown crystal. By contrast, the behavior of \(\rho_c\) is different with that of \(\rho_{ab}\), it rises very slowly with descending \(T\) at high temperatures between 200 and 300 K and starts to increase with decreasing \(T\) rapidly under 150K, manifesting a semiconductor-like behavior \(\rho_c > 0\). Then, it forms a peak at 35 K before dropping to zero resistivity. In the Ca10-4-8 system, this kind of transport anisotropy between ab plane and c axis is regarded as intrinsic.
Owing to the layered structure, the ab plane resistivity for Ca10(Pt4As8)((Fe0.9xPt0.08)2As2)3 could be described by a shunt resistor connection model. Figure 4(a) displays such a schematic.

The value of net resistance (R) follows the formula below:

$$\frac{1}{R} = n \left( \frac{1}{R_{FeAs}} + \frac{1}{R_{PtAs}} + \frac{2}{R_{Ca}} \right)$$

where $n$, $R_{FeAs}$, $R_{PtAs}$ and $R_{Ca}$ are the number of FeAs-Ca-Pt4As8-Ca layers, the resistance of the Ca layer, Pt4As8 layer and FeAs layer, respectively. In a parallel configuration, the current always seeks to the path with the minimum resistance to flow, and deviates from any obstruction. Here, Ca layer could be treated as insulating and the value of $R_{Ca}$ tends to infinity, while the FeAs and Pt4As8 layers contribute the most of electronic states to the Fermi level, and they carry the majority of the electric current. Thus, only the first two items in formula (1) need to be considered, and the representation of $\rho_{ab}$. It is also larger than that of LaO1−$x$F,FeAs [22], the most anisotropic system among traditional Fe based superconductors. The value is also larger than that of the work $\gamma$ at $T_c \sim 34$ K with $x = 0.14$ [10]. It appears that for Ca10−4−8, the smaller Pt doping level x, the lower $T_c$ and a much more anisotropic system acquires.

![Figure 5. Anisotropic parameter $\gamma = \sqrt{\rho_{ab}/\rho_{ab}}$ in the normal state versus temperature.](image-url)
The temperature dependence of ab plane and c-axis resistivities under different applied magnetic fields ($H$) are shown in figure 6, through which it could give an estimation about the resistivity anisotropy ($\Delta R$) of Ca$_{10}$Pt$_4$As$_8$($\text{Fe}_{0.92}\text{Pt}_{0.08}$)$_2$As$_2$$_5$ in the superconducting state.
| Standard in Determining $H_{c2}$ | $\frac{dH_{c2}}{dT}$ (T/K) | $\frac{dH_{c2}}{dT}$ (T/K) | $H_{c2}^0$ (Tesla) | $H_{c2}^0$ (Tesla) | $\xi_{ab}(0)$ (Å) | $\xi_c(0)$ (Å) |
|-----------------------------|------------------|------------------|-----------------|-----------------|-----------------|-----------------|
| $0.9 \rho_n$ | $-6.1 \pm 0.1$ | $-2.2 \pm 0.1$ | $139 \pm 9$ | $47 \pm 2$ | $26.5 \pm 0.4$ | $8.9 \pm 0.7$ |
| $0.5 \rho_n$ | $-4.2 \pm 0.1$ | $-1.2 \pm 0.1$ | $91 \pm 2$ | $25 \pm 2$ | $36.4 \pm 1.4$ | $9.7 \pm 0.4$ |
| $0.1 \rho_n$ | $-3.9 \pm 0.1$ | $-0.8 \pm 0.1$ | $85 \pm 2$ | $23 \pm 2$ | $38.0 \pm 1.6$ | $10.2 \pm 0.5$ |

WHH: Werthamer–Helfand–Hohenberg

Table 1. The coherence length and upper critical field determined by WHH approach for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.92}$Pt$_{0.08}$)$_2$As$_2$)$_3$.

Figure 9. Magnetic susceptibility of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.92}$Pt$_{0.08}$)$_2$As$_2$)$_3$ versus temperature under (a) 20 Oe and (b) 0.1 Tesla.

It can be seen that, in the condition of current flowing within ab plane (I//ab) and the applied magnetic field along the c axis (H//c) of the sample, $T_{c,\text{onset}}$ is invariant with the rising $H$, while the transition temperature of zero resistivity ($T_{c,\text{zero}}$) decreases monotonously. Thus, the transition width in temperature $\Delta T_c$ increases with the increasing field. Under $H = 14$ T, $T_{c,\text{zero}}$ falls to 14K and $\Delta T_c = 17.6$ K if $T_{c,\text{onset}}$ is taken as 31.6 K. Because of the existence of strong thermal vortices fluctuations in the system, the phenomenon of $\Delta T_c$ widening with rising applied field is only observed in the copper based superconducting materials previously [23]. By contrast, in the case of current flowing along c-axis and applied field parallel to the ab plane of the sample, both $T_{c,\text{zero}}$ and $T_{c,\text{onset}}$ shift to lower temperatures synchronously, as shown in figure 6(b). Therefore, $\Delta T_c$ seems unchanged with the increasing applied field, and $\Delta T_c$ under such condition is also far smaller than that in the case of I//ab and H//c shown in figure 6(a).

The variation of the upper critical field $H_{c2}(T)$ with temperature for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.92}$Pt$_{0.08}$)$_2$As$_2$)$_3$ is shown in figure 7. The values of $H_{c2}(T)$ are determined as the field at the 90%, 50% and 10% of the normal resistivity $\rho_n$ before superconducting resistive drop, which is indicated by dot lines in figure 6.

The $H_{c2}$ anisotropic parameter $\Gamma_{H} = \frac{H_{c2}^0}{H_{c}^0}$ could be acquired from $H_{c2}(T)$ curves in figure 7, and the temperature dependence of $\Gamma_{H}$ is presented in figure 8. $\Gamma_{H}$ reaches 8.9 near $T_c$ under the 0.9$\rho_n$ criterion, which is the most approximate to the $\gamma$ value derived from the normal state resistivity analysis.

The $H_{c2}$ at 0 K can be evaluated using the Werthamer–Helfand–Hohenberg (WHH) law [24]:

$$H_{c2}(0) = -0.69 T_c \times \left| \frac{dH_{c2}}{dT} \right|_{T_c}$$

and the coherence lengths for the sample could be calculated via

$$\begin{cases} 
\xi_{ab}(0) = \sqrt[4]{\varphi_0} \\
\xi_c(0) = \frac{\varphi_0}{2 \pi \xi_{ab}^2 H_{c2}^0(0)}
\end{cases}$$

Where $\varphi_0 = 2.07 \times 10^{-15}$ Wb. Table 1 lists the obtained parameters. The large difference between $H_{c2}^0(0)$ and $H_{c2}^0$ indicates that, even in the superconducting state, there exists a large anisotropy between ab plane and c direction in the Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.92}$Pt$_{0.08}$)$_2$As$_2$)$_3$ system. What’s more, all $\xi_c(0)$ obtained from different standards are smaller than the c cell parameter (10.7113 Å), confirming the reasonability of adding the term of $S^2/T^{0.5}$ when fitting the $\rho_n$, which gives a description of the impact of the interlayer Josephson tunneling effect on the c-axis resistivity.
Temperature dependence of specific heat $C_p(T)$ between 2 and 4 K for $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$, inset: $C_p(T)/T$ versus $T^2$ the solid line shows the fitting using $C_p(T)/T = \gamma + \beta T^2$. 

Figure 10. (a) $C_p(T)/T$ versus $T$, where $C_p(T)$ is the specific heat of $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ and $T$ is the temperature. (b) Temperature dependence of specific heat $C_p(T)$ for $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$, inset: $C_p(T)/T$ versus $T^2$, the solid line shows the fitting using $C_p(T)/T = \gamma + \beta T^2$. 

Table 2. The density of states (DOS) and Debye temperature of $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ under applied magnetic field 0 T and 5T. 

| $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ | $\gamma$ (mJ mol$^{-1}$ K$^{-2}$) | $\beta$ (mJ mol$^{-1}$ K$^{-4}$) | $\Theta_D$ (K) |
|---|---|---|---|
| H = 0 T | 73.30(3) | 10.45(6) | 31.2(1) |
| H = 5 T | 105.46(4) | 10.64(5) | 44.7(9) |

The superconducting magnetic susceptibility of $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ is shown in figure 9(a). Under a low applied field of 200Oe, the zero field cooling (ZFC) curve starts to exhibit a diamagnetic signal at 31.2K, which is in agreement with our resistivity analysis given in figure 3. Below 15K, the full diamagnetism appears, indicative of bulk superconductivity in the sample.

Normal state susceptibility $\chi$ measured at relatively high magnetic field 0.1Tesla is observed in figure 9(b). An anomaly could be found at around 75K for both ZFC and FC measurements. Above 75K, the susceptibility does not only decrease with decreasing temperature, but exhibits a quasi-linear $T$ dependence in a wide temperature range, the black solid line is the fitting for $\chi$ in figure 9(b). This kind of unusual paramagnetic state is also existed in other Fe based superconductors or compounds, such as the 1111, 122 and 11 family [25–29], and the theoretical investigations have shown that it may originate from the strong (π, π) short-range antiferromagnetic (AFM) spin fluctuation in the system [30, 31]. Below 75 K, $\chi$ starts to increase as temperature decreases, and this upturn could also be found in previous reports on Ca10–(3–4)–8 system [2, 32]. Considering its order of magnitude ($\sim 10^{-3}$) as well as the fact that $\chi$ manifests no saturation at low temperature region, this upturn acts more like the ‘Curie tail’ phenomenon rather than an influence from the ferromagnetic impurities inside the sample.

Figure 10(a) presents the temperature dependent $C_p(T)/T$ data, where $C_p(T)$ is the specific heat of $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ and $T$ is the temperature. As it can be seen, an apparent slope change happens at 31.2 K, confirming the bulk superconducting transition of our sample, which is fully consistent with the observation in the resistivity and susceptibility measurements.

Figure 10(b) shows the tail of the $C_p(T)$ curve in the temperature range between 2 and 4 K under the magnetic fields $H = 0$ and 5 T for $\text{Ca}(\text{Pt}_4\text{As}_8)(\text{Fe}_{0.92}\text{Pt}_{0.08}\text{As}_2)_5$ with $H \perp ab$, the inset displays its corresponding $C_p(T)/T$ versus $T^2$ plots. Below 4 K, assuming no magnetic excitation exists, $C_p(T)/T$ should follow the relation of $C_p(T)/T = \gamma + \beta T^2$, where $\gamma$ is the electronic specific heat coefficient and $\beta$ reflects the contribution from phonon to $C_p(T)$. Fitting results listed in table 2 show that the magnetic field has nearly no impact on the values of $\beta$, but affects $\gamma$ significantly. This is because that $H$ could kill Cooper pairs in the superconducting state and release more free electrons to the system, and then increases $\gamma$ and enhances the electrons specific heat consequently.

The density of states (DOS) at the Fermi level for both spin directions $N(E_F)$ could be estimated by $\gamma$ using the following relation [33],

$$\gamma = \frac{\pi^2}{2} k_B^2 N(E_F)(1 + \lambda_{sp})$$  \hspace{1cm} (4)
\[ k_B = 1.38 \times 10^{-23} \text{J/K} \]

is the Boltzmann constant and \( \lambda_{ep} \) is the electron-phonon coupling constant. In the first approximation, \( \lambda_{ep} = 0 \) can be adopted, which gives \( N(E_F) = 31.2 \) and 44.7 states/\((\text{eV}\cdot\text{f.u.}) \) at \( H = 0 \) T and 5 T, individually. These results are also listed in table 2. The value of \( N(E_F) \) at \( H = 0 \) T is close to but a little larger than that of the reported in [16] ~28.54 states/(\text{eV}\cdot\text{f.u.}) and our calculation result ~29.87 states/(\text{eV}\cdot\text{f.u.}) shown below. The fact that \( \lambda_{ep} \) could be set to zero illustrates unlike the traditional superconductors which mainly depend on the help of strong interactions between electrons and phonons to form Cooper pairs, for example \( \lambda_{ep} = 1.67 \) for Hg and \( \lambda_{ep} = 1.8^{35} \) for Nb3Sn [34], the electron-phonon coupling is relatively weak in the Fe based superconductors. From the value of \( \beta \), the Debye temperature \( \Theta_D \) of the crystal can be evaluated using the expression [33],

\[ \Theta_D = \left( \frac{12\pi^4 RN}{5\beta} \right)^{1/3} \]  

where \( R = 8.31 \text{J/K} \cdot \text{mol} \) is the universal gas constant, \( N \) is the number of atoms per formula unit. The values for \( \beta \) yield \( \Theta_D = 198.38(7) \) K and 197.19(9) K under \( H = 0 \) T and 5 T, separately, which are listed in table 2 together.

The value of DOS derived from the specific heat data is consistent with our calculation results mapped out in figure 11.

As can be seen from figure 11, after transferring all its conductive electrons to the Pt4As8 and FeAs layers, the Ca sheet nearly gives no contribution to the DOS around Fermi level (\( E_F \)), which should be regarded as insulate as we treated in the resistivity analysis. For Ca10-3-8 and Ca10-4-8, the Fe-3d PDOS are similar, the Fermi levels all locate at the hillside of their Fe-3d peaks, confirming that iron contributes the majority of electronic states near Fermi level in both compounds, and conduction for the two compounds is expected to be anisotropic. With regard to Pt4As8 layer, the Pt-5d PDOS forms a quasi-gap around the Fermi level, indicating the contribution of
Pt₄As₈ layer to DOS at $E_F$ to be relatively small. However, things are not exactly the same for those two compounds, the Fermi level almost crosses the gap in the Ca₁₀-₃-₈ phase, but is pushed up slightly above this gap for Ca₁₀-₄-₈. This does not only make the Pt₄As₈ layer to be semi-metalic, but also lead to the band filling for Ca₁₀-₄-₈ around the gap in Pt states mainly fills the Fe states, which is equivalent to an indirect electron doping from Pt₄As₈ layer to the FeAs layer.

To comprehend the transport properties in Ca₁₀-₃-₈ and Ca₁₀-₄-₈ systems, it is necessary to understand: 1, the electronic properties of both the Ptₙ₋₄As₈ and Feₓ₋₄Pt₄As₈ layers, 2, the relationship between $T_c$ and variables $n$, $x$ and $\delta$. In figure 12(a), we plot $T_c$ versus total Pt concentration ($n = \delta + 10x$) of Ca₁₀(Ptn₋₄As₈)(Feₓ₋₄-Pt₄)₂As₂₃ available in the literature [1–3, 7–12].

As can be seen in figure 12(a), the points are clearly divided into two sets, those for Ca₁₀-₃-₈ with relatively smaller $T_c$ flock together at the left lower corner, while the points with higher $T_c$ on the top half of the graph all belong to Ca₁₀-₄-₈, which increase with increasing $x$. In other words, even with the same platinum contents, the superconducting transition temperature for Ca₁₀-₄-₈ is far larger than that for Ca₁₀-₃-₈. We know that the FeAs layer serves as the superconducting layer in the Fe based superconductors, and, then, any excessive change or deterioration of which will greatly reduce the transition temperature. Compared with Ca₁₀-₄-₈ containing the same amount of platinum, Ca₁₀-₃-₈ have one less Pt atom in its PtAs layer and it means that much more Pt atoms will enter FeAs layer, some of them replace the Fe atoms and others may be the interstitial acting as the scattering centers, which add lattice disorder and lead to the free carriers localization within the system [35].

Similar cases also occur in other directly Fe substituted compounds, for example, a maximum $T_c$ of 16.5 K is achieved at $x \approx 0.29$ for isovalent doped Ba(Fe₁₋₄Ruₓ)₂As₂ [36], even for the electron-doped Ba(Fe₁₋₄RE₂)₂As₂ (RE = Co, Rh) [37, 38] with maximum $T_c$ values are around 24 K. However, the same electron-doped SmFeAsO₁₋ₓFₓ, which leaves the FeAs layer untouched, has $T_c$ as high as 55 K [39], more than double the former. Thus, it can be concluded that under the precondition of same total Pt concentration, the accumulation of redundant Pt⁺⁺ in FeAs layer is the main reason that limits $T_c$ of Ca₁₀-₃-₈.

To understand the influences of doping level for Ca₁₀(Ptn₋₄As₈)(Feₓ₋₄-Pt₄)₂As₂₃ on the transition temperature in detail, the relationship of $T_c$ versus $x$ available in previous reports is plotted in figure 12(b).

In ReFe₂As₅ (Re = Ba, Sr) system, despite the isovalent, a certain amount of non-magnetic Pt⁺⁺ ions replacing the Fe²⁺ would disturb the AFM order in the FeAs layer, and it suppresses the spin density wave (SDW) transformation and induces superconductivity. In such condition, the typical features are, first, $T_c$ is rarely beyond the limits of 25K, and the reason has been stated above. Second, in a certain doping range, $T_c$ increases with increasing $x$ and eventually reaches saturation. Third, only when the doping level reach a certain value, for example $x > 0.02$, superconductivity emerges [40–42]. It is found that the relation of $T_c$ with $x$ of Ca₁₀-₃-₈, as shown in figure 12(b), meets these three points accurately, indicating that Ca₁₀-₃-₈ and Re(Fe₂₋₄Pt₄)₂As₂ (Re = Ba, Sr) type compounds may share the very similar even the same superconducting mechanism, and the $n = 3$ compound with $x = 0$ could be regarded as the parent of this family of superconductors.

With regard to Ca₁₀-₄-₈, things turn wholly different. Compared with Ca₁₀-₃-₈, an extra Pt atom on the Pt₄As₈ layer makes Ca₁₀-₄-₈ exceed the Zintl-Klemm concept (ZKC), leading to a configuration of (Ca²⁺Fe⁺⁺As⁺⁺)₃Pt₂⁺⁺[(As₂⁺⁺)₄−]¹⁻ + 2e⁻. The two unbound electrons push the Fermi surface of Ca₁₀-₄-₈ higher than its Pt-5d energy gap, this realizes the indirect electron-doping to the FeAs layer, which greatly increases $T_c$ values for Ca₁₀-₄-₈. That is the reason why even if $x \sim 0$, Ca₁₀-₄-₈ could gain such a higher $T_c$ as 30 K, which is also same as the case that La replaces the Ca in Ca₁₀-₃-₈ and raises its $T_c$ to up to ~30K [4, 8, 11, 32]. Generally, in the Ca₁₀-₄-₈ system, Pt element has both direct and indirect doping of FeAs layer, the indirect doping enhances $T_c$ conspicuously, and the direct makes $T_c$ increase with increasing $x$ almost linearly in a certain doping range. Under the combined effects, the reported $T_s$ form and distribute into a quasi-linear strip in the upper part of figure 12(b).

4. Conclusions

To summarize, Pt doping level $x$ in the FeAs layer can be adjusted, within a certain degree for Ca₁₀-₄-₈, by controlling the initial element portion and the cooling rate during the heating stage in the synthesis process. XRD, EDX, resistivity, magnetoresistance, magnetic susceptibility and specific heat were measured on the high quality Ca₁₀(Ptn₋₄As₈)(Feₓ₋₄Pt₆₋₄Reₓ)₂As₂₃ single crystal. The anisotropic property between ab plane and c-axis resistivity is observed, a $T^ '-'$ ($\gamma \sim 0.8$) type of temperature dependence for the normal state ab plane resistivity should be the consequence of disorder, and $S$/$T^{0.5}$ term originating from Josephson coupling is needed to add to the formula that describes the c-axis resistivity, which is intrinsic to Ca₁₀-₄-₈. The $H_{c2}$ and $\xi$ parameters were obtained through the magnetoresistance in the superconducting state, and $H_{c2}$ was relatively large for our sample. The DOS at Fermi level was estimated by specific heat and it was comparable to the calculated results.
Both direct and indirect Pt doping effects on FeAs layer push transition temperature of Ca10−4.8 over 30 K, and $T_c$ of sample with $x = 0.08$ falls well into the trend strip formed by the collective data reported previously.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

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**ORCID iDs**

Dapeng Wu @ https://orcid.org/0000-0003-1946-7308

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