Single Crystal Growth and Physical Property Investigations of Ca-FeAs-Based Superconductors

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SINGLE CRYSTAL GROWTH AND PHYSICAL PROPERTY INVESTIGATIONS OF Ca-FeAs-BASED SUPERCONDUCTORS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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by

Jiayun Pan
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Abstract

The discovery of Fe-based superconductors marked the beginning of a new era in unconventional superconductors. To date, the underlying superconducting mechanism has not yet been fully understood. Among Fe-based superconductors, the relatively new members are Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3, 4$) and CaFeAs$_2$. They are unique because they contain special adjacent layers, i.e., metallic Pt$_4$As$_8$ in Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$, semiconducting Pt$_3$As$_8$ in Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$, and As chains in CaFeAs$_2$. The focus of this research is to understand the electrical and magnetic properties of Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3, 4$) and CaFeAs$_2$ in both the normal and superconducting state. Single crystals Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ and Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ with different dopings have been grown by the self-flux method. Using the same growth method, polycrystals CaFeAs$_2$ and Ca$_{0.85}$La$_{0.15}$FeAs$_2$ have been obtained. The experimental investigation of electrical resistivity, Hall effect, magnetoresistivity, magnetization, vortex imaging of Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3, 4$) single crystals has been proceeded. The electrical resistivity, magnetoresistivity and magnetization of CaFeAs$_2$ have also been measured. We observed anisotropy in the superconducting and normal state of Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3, 4$) which is larger than many Fe-based superconductors. The results we obtained for Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ with different doping not only reveal the doping effect on the in-plane and out-of-plane transport properties, but also indicate superconducting transition temperature $T_c$ increases with increasing interlayer distance $d$. Among different doping, La is the most efficient in enhancing $T_c$ and its normal state shows a total metallic behavior. Instead of having quadratic dependence to applied magnetic field like normal conductors, magnetoresistivity of Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3, 4$) is linear to $H$ at fixed temperatures. It is rare in materials without strong disorder or Dirac-cone like electronic structure around the Fermi surface. Although its cause remains uncertain, we discussed the possibility that it may be related to the quantum interference effect. Through growth of
CaFeAs$_2$, we found La doping on the Ca site helps form stable crystal phase. Surprisingly, although CaFeAs$_2$ has Dirac-cone like electronic structure around the Fermi surface which should lead to the linear $H$ dependence of MR according to the quantum model developed by Abrikosov, magnetoresistivity of Ca$_{0.85}$La$_{0.15}$FeAs$_2$ shows a quadratic dependence on $H$. 
Chapter 1. Introduction

1.1 Background of Superconductivity

Electrical conductivity is an intrinsic property of an electronic material, which measures its ability of conducting electric current. For example, metals, such as copper or iron, consist of a set of atoms whose outer shell electrons dissociate freely from their atomic nucleus and travel through the lattice with small interruption. Thus they can conduct electric current with small electrical resistivity, for example, $\rho (\text{Fe})_{293 \text{K}} = 9.71 \times 10^{-8} \Omega \text{m}$, $\rho (\text{Cu})_{293 \text{K}} = 1.68 \times 10^{-8} \Omega \text{m}$ [1]. Insulators such as rubber or glass, consist of atoms each holding electrons so tightly around themselves that almost no free electrons can flow freely. So their electrical resistivities are much larger than metals, for example, $\rho (\text{rubber})_{293 \text{K}} = (1-100) \times 10^{13} \Omega \text{m}$, $\rho (\text{glass})_{293 \text{K}} = (1-1000) \times 10^{10} \Omega \text{m}$ [1]. Superconductors, different from metals or insulators, are materials that will conduct electric current without resistivity below a critical temperature ($T_c$). In 1911, superconductivity was first observed by Dr. Heike Kamerlign Onnes when he cooled mercury to 4 K and witnessed the sudden disappearance of its resistivity [2]. The properties of superconductors give them great opportunities in technological applications, for example, superconductor-based quantum computer. For decades, researchers are dedicated to search for new superconductors and understand their mechanism. Not only does the maximum of $T_c$ keep increasing, but also the theories to explain their properties are constantly under review. For this reason, this thesis focuses on searching new superconductors and investigating their properties.

1.2 Conventional Superconductors

Categorized by the superconducting mechanism, superconductors are classified as conventional superconductors and unconventional superconductors. Conventional superconductors are those can be explained by the BCS theory. Developed by J. Bardeen, L. N.
Cooper and J. R. Schrieffer (BCS) in 1957 [3], BCS theory describes the formation of Cooper pairs each consisting of two electrons traveling through the system together. Itinerant electrons suppose to have repulsive interactions between each other. The BCS theory proposed that there is an attractive interaction between electrons that comes from electron-phonon interaction strong enough to overcome the Coulomb repulsion. Figure 1 provides a schematic plot of the electron-phonon interaction mechanism. As illustrated in Figure 1, as a free electron labeled as #1 in a material passes through the lattice formed by positively charged ions, it attracts the nearby ions causing a distortion of the lattice, moving ions slightly towards itself. As a result, the positive charge density of the lattice in this area increases shown as the red cloud in Figure 1. Since ions have much larger mass than electrons, the lattice keeps being distorted for a while after electron #1 passes through, attracting another free electron #2 when electron #2 passes by [4]. It leads to

Figure 1. A schematic plot of the formation of Cooper pairs mediated by electron-phonon interaction. A moving electron #1 attracts the nearby atoms resulting in a distortion of lattice structure and forming a positively charged area shown as the red cloud. The latter attracts another nearby electron #2. These two electrons are then bounded together and called a Cooper pair.
an effective attractive interaction which at long distance overcomes two electrons’ repulsive interaction in time and cause them to pair up. The pairing mechanism of conventional superconductors is experimentally proven to be caused by electron-phonon interaction [5]. Superconductivity described by the BCS theory yields an s-wave symmetry order parameter [6]. In this case, Cooper pairs are formed by electrons with opposite spins with total spin $S$ is 0 [6].

Cooper also proved that the Cooper pairs are not formed individually, but a vast number below the critical temperature ($T_c$). The electron states rearrange to form a superconducting state that is completely different from the normal state [7]. In the limit of weak electron-phonon coupling ($\frac{\hbar \omega_c}{k_B T_c} \gg 1$, $\omega_c$ is the cyclotron frequency), BCS theory predicts $T_c$.

$$T_c = 1.14 \frac{\omega_p}{k_B} e^{-\frac{1}{N(E_F)V_{eff}}}$$

in which $\omega_p$ is the Debye frequency, $k_B$=1.38×10^-23 J/K is the Boltzmann constant, $E_F$ is the Fermi energy, $N(E_F)$ is the density of states at the Fermi level and $V_{eff}$ is the effective attractive potential between electrons. According to Eq. 1, the higher Debye frequency, larger density of states at the Fermi surface and stronger electron-phonon interaction lead to higher $T_c$. P.W. Anderson and Cohen et al. estimated the maximum $T_c \sim 10$ K by discussing the maximum value the Debye frequency can reach for all values of the electron-phonon coupling constant [8]. McMillan derived the maximum $T_c$ with characteristic parameters including the electron-coupling constant, density of states at Fermi surface, etc and gave $T_c^{\text{max}} \sim 40$ K [9]. At $T < T_c$, electrons form Cooper pairs condensing into the same ground state; as a result, their states overlap with each other. At $T > T_c$, the thermal energy of the lattice is too strong for Cooper pairs to survive. Because energy to break a Cooper pair is finite, an energy gap ($\Delta$) appears between the superconducting
ground state and the exciting state. This energy gap is high at low temperatures, and when $T$ close to $T_c$, $\Delta$ is a function of temperature given by Eq. 2.

$$\frac{\Delta(T)}{\Delta(0)} \approx 1.74 \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}}, \quad T \approx T_c$$

where $\Delta(0) = 1.764k_BT_c$ is the superconducting gap at 0 K. Thus, $\Delta(T)$ decreases with increasing $T$ and eventually vanishes at $T_c$.

Other than the zero-resistivity property at $T < T_c$, superconductors exhibit Meissner effect when they are placed into a magnetic field $H$ less than a critical field $H_c$. Meissner effect describes that internal current is induced inside a superconductor which ultimately cancel the interior field at $T < T_c$ and $H < H_c$. When $H > H_c$, Meissner effect breaks down, and superconductivity is destroyed. $H_c$ can also be given by the BCS theory as Eq. 3.

$$H_c(T) \approx H_0[1 - \left(\frac{T}{T_c}\right)^2]$$

where $H_0$ is the critical temperature at $T = 0$ K. According to Eq. 3, $H_c$ decreases quadratically with the decreasing temperature. Depending on how superconductivity breaks down, superconductors can be categorized into two classes: type-I superconductors and type-II superconductors.

As seen in Figure 2a, the $H$-$T$ diagram of a type-I superconductor is divided into the following two regions. Below the $H_c(T)$ curve, a type-I superconductor is in the Meissner state where the interior net magnetic field $B = 0 = H - 4\pi M$ in which $H$ is the induced magnetic field strength and $M$ is magnetization. Above the $H_c(T)$, Meissner effect breaks down, and superconductivity is destroyed. The H-T diagram of a type-II superconductor is shown in Figure 2b. There are two critical fields of a type-II superconductor: the lower critical field $H_{c1}$ and the
Figure 2. (a) The $H$-$T$ diagram of a type-I superconductor; (b) the $H$-$T$ diagram of type-II superconductors, $H_{c1}$ is the lower critical field and $H_{c2}$ is the upper critical field.

The upper critical field $H_{c2}$. Compared with a type-I superconductor, a type-II superconductor exhibits an additional state called the mixed state between $H_{c1}(T)$ and $H_{c2}(T)$. In the mixed state, the normal and superconducting regions coexist within the material. The magnetic flux can penetrate through the normal region forming vortices. A vortex is surrounded by a circulating supercurrent, as illustrated in Figure 3. Furthermore, the mixed state is split into two sub-regions. Below the

![Diagram of supercurrent and normal core](image)

Figure 3. A schematic of the surface of a type-II superconductor in the mixed state.
dashed line illustrated in Figure 2b, the vortices are pinned in space and they form highly regular arrays. Above the dashed line, the vortices are unpinned so that they become mobile and randomly distributed. As applied field increases, vortices become tightly packed and eventually take over the entire superconductor so that superconductivity breaks down above $H_{c2}(T)$. The magnetic flux within a vortex is quantized. It turns out each vortex contains just one flux quanta $\phi_0 = \frac{hc}{2e} = 2.07 \times 10^{-15}$ T m$^2$ [10].

As shown in Figure 4a, when a type-I superconductor is placed in a magnetic field $H < H_c$, the field is allowed to enter a short distance at the surface of the superconductor and its strength decreases exponentially. The parameter to characterize such distance is called the penetration depth $\lambda$. Another important parameter is the coherence length ($\xi$) which is the characteristic variable of the propagation of Cooper pair density ($n_c$). The coherence length $\xi$ of a type-I superconductor is larger than its penetration depth $\lambda$. Figure 4b illustrates the evolution of the magnetic

![Figure 4](image.png)

Figure 4. Schematic diagrams of the evolution of the magnetic field strength $H$ and the Cooper pair density ($n_c$) at the interface of the normal region and superconducting region: (a) type-I superconductor in which the coherence length $\xi$ is larger than the penetration depth $\lambda$; (b) type-II superconductor in which the coherence length $\xi$ is smaller than the penetration depth $\lambda$. 
field strength and the Cooper pair density at the interface of each normal core and its surrounding superconducting area when a type-II superconductor is in the mixed state. The coherence length $\xi$ of a type-II superconductor is smaller than its penetration depth $\lambda$.

According to the Ginzburg-Landau theory of superconductivity, $\lambda$ and $\xi$ is given by Eq. 4 and Eq. 5 [4].

\[
\lambda = \sqrt{\frac{m^*}{4\mu_0 q^2 \psi_0^2}} \quad (4)
\]

\[
\xi = \sqrt{\frac{\hbar^2}{2m^*|\alpha|}} \quad (5)
\]

where $m^*$ is the mass of a Cooper pair, $\psi_0$ is the equilibrium value of the order parameter $\psi$ in the absence of electromagnetic fields. At $T$ near $T_c$, $\lambda$ and $\xi$ are given by Eq. 6 and Eq. 7 [4].

\[
\lambda(T) = \frac{\lambda_0}{\left[2 \left(1 - \frac{T}{T_c}\right)^2\right]^{1/4}}, \quad T \sim T_c
\]

\[
\xi(T) = 0.74 \frac{\xi_0}{\left(1 - \frac{T}{T_c}\right)^{1/2}}, \quad T \sim T_c
\]

where $\lambda_0$ and $\xi_0$ are lengths at $T = 0$ K. Hence, when $T$ increases and approaches $T_c$, $\lambda$ and $\xi$ keep increasing and eventually diverge at $T = T_c$.

The ratio of $\lambda$ and $\xi$ is the Ginzburg-Landau parameter $\kappa$. Its value can identify the type of a superconductor as Eq. 8 [4].
\[ \kappa = \frac{\lambda}{\xi} \begin{cases} < \frac{1}{\sqrt{2}}, & \text{type - I superconductor} \\ > \frac{1}{\sqrt{2}}, & \text{type - II superconductor} \end{cases} \] (8)

By evaluating the boundary condition of the Ginzburg-Landau free energy of a type-II superconductor, the lower critical field \( H_{c1} \) and the upper critical field \( H_{c2} \) are given as Eq. 9 and Eq. 10 [4]. According to Eq. 9 and Eq. 10, superconductors with large penetration depth \( \lambda \) have large lower critical field \( H_{c1} \), while the upper critical field increases with decreasing coherence length \( \xi \).

\[ H_{c1} = \frac{\phi_0}{4\pi \lambda^2} \ln \kappa \] (9)

\[ H_{c2} = \frac{\phi_0}{4\pi \xi^2} \] (10)

Conventional superconductors can be either type-I or type-II superconductors. Figure 5 shows the timeline for discoveries of some superconductors with different \( T_c \) values. In more than half century (1911-1980), experimentalists found that the highest \( T_c \) achieved was \( \sim 23.3 \) K in superconductors with the cubic A15 structure such as Nb₃Ge [11]. In this period of time, the discovery of new superconductors higher-\( T_c \) was guided by the maximum \( T_c \sim 40 \) K predicted by the BCS theory [8][9]. In this sense, the discovery of \( MgB_2 \) was remarkable for its high \( T_c \sim 39 \) K [12]. \( MgB_2 \) has a few properties that resembles unconventional superconductors, one of which is that it crystallizes in a hexagonal layered structure [12]. Moreover, some of its experimental results including the quadratic \( T \)-dependence of the penetration depth [13]as well as the sign change of the Hall coefficient near \( T_c \) also support the argument [14]. But according to experimental results, the bonding force between Cooper pairs in \( MgB_2 \) is phonon mediated [15][16]. Thus, it is still believed to be a conventional superconductor.
Figure 5. The discovery of various conventional superconductors over years.

Cooper pairs in conventional superconductors are sensitive to impurities [6]. Nonmagnetic impurities reduce $T_c$ weakly, while the magnetic impurities tend to have a destructive effect on superconductivity because they align the spins of the neighboring electrons and break up Cooper pairs [6]. Experiments indicate even a small concentration of magnetic impurities can completely destroy superconductivity in conventional superconductors [6] [17].

1.3 Unconventional Superconductors

The unconventional superconductors consist of heavy-fermion superconductors, organic superconductors, cuprates, Fe-based superconductors, etc. The attractive interaction between two electrons of a Cooper pair may have sources from not only the electron-phonon coupling but also other interactions, for example, spin fluctuations [18]. Different from s-wave pairing in conventional superconductors, Cooper pairs in a lot of unconventional superconductors such as cuprates are believed to have non s-wave symmetry [19]. The upper bound of $T_c$ obtained for conventional superconductors is no longer accurate for unconventional superconductors. In fact,
some of the unconventional superconductors have much higher $T_c$ than the maximum $T_c$ in the conventional superconductors, for example $T_c = 85$ K for Bi$_2$Sr$_2$CaCu$_2$O$_8$ [20]. This suggests that there is an attractive interaction stronger than electron-phonon coupling to bound electrons that can overcome the lattice vibration at such high temperature. Antiferromagnetism is suggested to be one possible source through which electrons exchange quanta due to the fluctuations of the local antiferromagnetic order [21] [22]. Yet, nature of the pairing mechanism is actively debated. Is superconductivity associated with antiferromagnetism, charge-density waves, spin-density waves, nematic correlations, or a combination of effects? Besides, will impurities enhance or suppress superconductivity? How do crystal structures relate to physical properties? There are so many unanswered questions in unconventional superconductors that call for intensive theoretical and experimental research.

Atom iron is usually considered to suppress superconductivity for its strong local magnetic moment, so it aligns nearby spins and may destroy the formation of Cooper pairs. Out of unconventional superconductors, Fe-based superconductors are unusual for containing Fe, yet still exhibit superconductivity in relatively high $T_c$. The discovery of Fe-based superconductors triggers researchers’ interest when LaO$_{1-x}$F$_x$FeAs was found to superconduct at 26 K [23]. It marked a new era in the history of unconventional superconductors. Since then, massive amounts of theoretical and experimental papers have been published, but there are still a lot of questions waiting to be answered. We choose to study the physical properties of Fe-based superconductors hoping to shine light on the origin of superconductivity.

1.3.1 Cuprates

The discovery of unconventional superconductors has a significant breakthrough when J. G. Bednorz and K. A. Muller reported La$_{5-x}$Ba$_x$Cu$_5$O$_{5(3-y)}$ (LBCO) exhibits superconductivity at...
\[ T_c \approx 30 \text{ K with } x = 0.75 \text{ and } y > 0 \]\cite{24}. It provoked extensive research activities on unconventional superconductors. Because of the common CuO\(_2\) in their compositions, they are also referred as Cuprates. Cuprates share many similarities with Fe-based superconductors. Between 1986-2008, a lot of cuprate superconductors have been identified. The blue dots in Figure 6 are some important cuprates discovered over years.

Most cuprates exhibit \( T_c \) higher than the boiling temperature of liquid nitrogen \( T = 77 \text{ K} \), for example, \( Y_{1.2}\text{Ba}_{0.8}\text{CuO}_4 \) (YBCO) superconducts below 93 K\cite{25}, \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x \) (Bi-2223)\cite{26} and \( \text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) (Tl-2223)\cite{27} have similar \( T_c \sim 120 \text{ K} \), the record value of \( T_c \) of \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) (Hg-1223) is 130 K at ambient pressure\cite{28}. Hence, they are referred as members of high-\( T_c \) superconductors. Figure 7 shows the crystal structures of \( \text{La}_{2.3}\text{Sr}_x\text{CuO}_4 \) (LSCO), \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) (YBCO), \( \text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) (Tl-2223), \( \text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10} \) (Hg-1234) and \( \text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{10} \) (Hg-1245). All of them have layered crystal structures consisting of blocks of

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**Figure 6.** The discoveries of unconventional superconductors over years: the blue dots are cuprates, and the red triangles are Fe-based superconductors.

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Figure 7 shows the crystal structures of \( \text{La}_{2.3}\text{Sr}_x\text{CuO}_4 \) (LSCO), \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) (YBCO), \( \text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) (Tl-2223), \( \text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10} \) (Hg-1234) and \( \text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{10} \) (Hg-1245). All of them have layered crystal structures consisting of blocks of
CuO$_2$ layers separated by spacer layers containing metallic atoms such as Ba, La, Y, etc. Here, $n$ is the number of CuO$_2$ planes in one unit cell. The ab plane is parallel to the CuO$_2$ plane, and the direction perpendicular to the ab plane is along the c-axis.

Figure 7. Crystal structures of La$_{2-x}$Sr$_x$CuO$_4$, YBa$_2$Cu$_3$O$_7$, Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$, HgBa$_2$Ca$_2$Cu$_4$O$_{10}$, HgBa$_2$Ca$_4$Cu$_5$O$_{12}$, in which $n$ is the count of CuO$_2$ layers in each unit cell.

Superconductivity occurs only in CuO$_2$ planes and the spacer layers provide charge carriers to the CuO$_2$ planes [29]. Previous reports have noted that $T_c$ of optimally doped cuprates with the same $n$ is higher when the charge of the atoms in the spacer layers is smaller [30]. For example, the electron count of atom Y in YBa$_2$Cu$_3$O$_{7-\delta}$ is $+3$, and the compound exhibits superconductivity at 93 K [31]. While the electron count of Ca which has the same position in the crystal structure of HgBa$_2$CaCu$_2$O$_{6-\delta}$ as Y in YBa$_2$Cu$_3$O$_{7-\delta}$ is $+2$ and $T_c$ of the compound is 128 K [32]. Figure 8
shows $T_c$ as a function of the bonding length between the metal ion ($M_c$) in the spacer layer and the oxygen ion in the CuO$_2$ layer [33]. Data of a collection of cuprates with $M_c = Y$ or Ca implies $T_c$ decreases with the increasing bonding length between $M_c$ ion and oxygen ion [33]. It is further demonstrated that $T_c$ is sensitive to the size of the spacer layer (A) and the distance ($d_{CuO_2-A}$) from A to the adjacent CuO$_2$ layer [33] [34] [35] [36]. For example, $T_c$ of La$_{1.9}$Sr$_{0.1}$CuO$_4$ changes from 25 K to 49 K by active epitaxial compression decreasing the lattice parameter $a$ by 0.02 Å and increasing $c$ by 0.1 Å [37].

![Image of Figure 8](image-url)

**Figure 8.** The relationship between $T_c$ and the bonding length between the metal ion ($M_c = Y$ or Ca) in the spacer layer and the oxygen ion in the CuO$_2$ layer [33].

Figure 9 plots $T_c$ of various cuprates vs the count ($n$) of CuO$_2$ planes per unit cell. There is an overall trend that $T_c$ first increases with $n$ and reaches to maximum at $n = 3$, then tends to decrease. Based on the assumption that the strength of the interlayer coupling between CuO$_2$ layers is the same, Ginzburg-Landau theory predicts $T_c$ of cuprates would increase monotonically with increasing $n$ [38] [39]. Chakaravarty et al. also explained the increasing trend by showing the close spacing of the $n$ layers stabilize the 3D fluctuations using the theory of quantum tunneling [40].
Researches propose the explanation of the decreasing trend of $T_c$ with increasing $n$ by showing CuO$_2$ planes in cuprates are categorized into two types: the interior CuO$_2$ planes whose adjacent planes are also CuO$_2$ planes and the exterior CuO$_2$ planes whose adjacent planes are spacer layers. When $n$ increases from 3 to 4, the hole concentrations in the interior CuO$_2$ planes become different from the exterior CuO$_2$ planes which eventually induces the decreasing trend of $T_c$ [41]. Hence, superconductivity of unconventional superconductors is influenced by their crystal structure.

The illustrated phase diagrams of cuprates with electron and hole doping are plotted in Figure 10 [6]. Shown in Figure 10a, the parent compounds of cuprates are Mott insulators. The parent compounds of cuprates and underdoped cuprates with elements contributing extra electrons show antiferromagnetic ordering. Upon electron doping, electrons in cuprates form pairs resulting in a partial energy gap around the Fermi surface above the phase transition temperature ($T_N$), and cuprates change from antiferromagnetic ordering to pseudogap state above $T_N$. Increasing electron doping level $n$ suppresses $T_N$. Cuprates turn into the normal metal state above $T^*$ exhibiting
properties similar to normal metals [42] [43]. Superconductivity emerges upon doping below $T_c$, and its region forms a dome-like shape. There is a small area where antiferromagnetism coexists with superconductivity [44]. At overdoped region, cuprates behave similar to normal metals. When cuprates have hole doping shown in Figure 10b, $T_N$ decreases much faster with increasing doping level $p$ than the case in the electron doping. Cuprates turn into strange metal state above $T^*$ where the resistivity is linear to the temperature. Superconductivity is presented at around $0.05 < p < 0.27$ and its dome-like shaped region has no coexisting area with antiferromagnetism [42].

![Phase diagram of cuprates](image)

Figure 10. Phase diagram of cuprates: (a) the universal phase diagram of cuprates with electron doping; (b) the universal phase diagram of cuprates with hole doping [6].

The quasi-2D crystal structure of cuprates implies the normal state property is highly anisotropic quantitatively and qualitatively. The penetration depth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is 120 nm in the ab plane which is much smaller than 800 nm along the c axis [45]. And its normal-state resistivity also exhibits a large anisotropy ($\frac{\rho_c}{\rho_{ab}} \sim 10^4 - 10^5$) [46]. Such a large anisotropy implies
that electrons can barely move along the c-axis. Figure 11 shows an example of the anisotropy by plotting the temperature dependence of the in-plane resistivity $\rho_{ab}$ and c-axis resistivity $\rho_c$ of underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with doping level $x$ from 0.01 to 0.1. As shown in Figure 11a, for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x \geq 0.08$, the normal state $\rho_{ab}$ shows a metallic behavior and has a linear relationship to $T$ over a large temperature region. Moreover, it is discussed by Anderson [47] and he believed the behavior of resistivity implies the electron-phonon scattering is dominated by the inelastic scattering whose rate has a linear $T$ dependence. As shown in Figure 11b, the magnitude of the normal state c-axis resistivity $\rho_c$ of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is much larger than $\rho_{ab}$ and its nonmetallic behavior implies a large anisotropy. The normal state $\rho_c$ can be fitted by equation $\rho_c = A/T + BT$ where $A$ and $B$ are constants [47]. It is believed to be a characteristic behavior of non-Fermi liquid [47].

Figure 12 plots the temperature dependence of $\rho_{ab}$ and $\rho_c$ of optimal doped and overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [48] [49]. The normal state $\rho_{ab}$ for the overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.3$) can be described using function $\rho_{ab} = A T^{1.5}$ where $A$ is a fitting coefficient [48] [49]. On the other hand, the normal state $\rho_c$ changes from being nonmetallic for underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ to totally metallic in the overdoped region. The similar $T^{1.5}$ dependence was found in the normal state $\rho_c$ for the overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.25$) [49]. It suggests the overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is gradually changing into normal metal as it approaches the superconducting phase boundary. The resistivity anisotropy calculated as $\rho_c/\rho_{ab}$ is plotted in the inset of Figure 12b. It is demonstrated that $\rho_c/\rho_{ab}$ decreases with the increasing doping level, and it changes from being temperature dependent at $x \leq 0.2$ to almost constant (~100) at $x = 0.3$. It implies $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ behaves like a three-dimensional metal when it is overdoped.
Figure 11. The temperature dependence of the in-plane resistivity $\rho_{ab}$ (a) and the c-axis resistivity $\rho_c$ of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x$ from 0.01 to 0.1 [50].

Figure 12. The temperature dependence of the in-plane resistivity $\rho_{ab}$ (a) [48] and the c-axis resistivity $\rho_c$ of optimal doped and overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [49]. The inset in (b) is the temperature dependence of the resistivity anisotropy $\rho_c/\rho_{ab}$ [49].
1.3.2 Fe-based Superconductors

There are two sub-families in Fe-based superconductors: FeAs-based and FeSe-based superconductors. We chose to study FeAs-based superconductors because of interesting structure and physical properties. Superconductors in this group have several similarities with cuprates. Both cuprates and FeAs-based superconductors are layered materials with 3d transition metal ions in the building blocks. Both have d electrons playing a major role in superconductivity. The physical properties of these two types of superconductors change upon doping. FeAs-based superconductors also have crucial differences from cuprates. Unlike copper, Fe has strong local magnetic moment, so it was considered to be destructive to superconductivity. Hence, the properties of FeAs-based superconductors are expected to be distinct. Cooper pairs in cuprates are believed to have d-wave symmetry, while the pairing symmetry in FeAs-based superconductors differs from material to material [51]. The mechanism determining the gap symmetry is yet to be clarified. Different from the parent compounds that cuprates are insulating, the parent compounds of FeAs-based superconductors are discovered to be poor conductors. Furthermore, the dominating $d_{xy}$ orbitals near the Fermi level in cuprates reduce the multiband electronic structure to an effective one-band structure. While the $t_{2g}$ Fe d-orbitals hybridize with As orbitals which demand a multiband electronic structure [51].

Experimental results show that the physical properties of FeAs-based superconductors are influenced by their crystal structures [52] [53] [54]. It is reflected by the fact that superconductivity in some FeAs-based superconductors can be induced by either the application of pressure [52] [53] or substituting As with P which has a smaller ionic size [54]. FeAs-based superconductors have layered crystal structure consisting of superconducting FeAs layers separated by various types of spacer layers. The plane parallel to the FeAs planes is the ab plane, and the direction perpendicular...
to the ab plane is along c axis. Different types of spacer layers lead to a variety of FeAs-based superconductors with different $T_c$ values. The crystal structures of a few FeAs-based superconductors are plotted in Figure 13. The spacer layers can be classified into the following four groups.

1. Alkali ions (A) or alkali earth ions (Ae) (AFeAs or AeFe$_2$As$_2$), for example, LiFeAs [55] and BaFe$_2$As$_2$ [59]. The crystal structure of LiFeAs is plotted in Figure 13a. The substitution of the A or Ae site by other alkali metals or the Fe site by Fe’s neighbor elements can result in electron or hole doping. The crystal structure of another member CaFeAs$_2$ is plotted in Figure 13d [58]. The spacer layers of CaFeAs$_2$ consists of Ca, FeAs and As chain layers which makes this compound a candidate for topological superconductors. It will be further discussed in Chapter 5.

2. Rare-earth (Re) oxides or alkaline (A) earth fluorides (ReFeAsO, AFeAsF), for example, SmFeAsO [56]. Its crystal structure is plotted in Figure 13b. Dopants such as F on the oxygen site provide extra electrons or holes to the superconducting FeAs layers.

![Figure 13. The crystal structure of FeAs-based superconductors: (a) LiFeAs [55], (b) SmFeAsO [56], (c) Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ [57], (d) CaFeAs$_2$ [58].](image)
(3) Complex metal oxides, for example, Sr$_3$Sc$_2$O$_5$Fe$_2$As$_2$ [60]. This type of FeAs-based superconductor has a large $c$ parameter. The $c$ parameter of Sr$_3$Sc$_2$O$_5$Fe$_2$As$_2$ is reported to be 26.876 Å [60].

(4) Combinations of alkali ions and platinum group arsenide, for example, Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3$ or 4) [57] [61]. The crystal structure of the $n = 4$ compound is plotted in Figure 13c. Compared with the first two groups, the spacer layers of the $n = 4$ compound arranges as Ca-Pt$_4$As$_8$-Ca resulting in a relatively large $c$ parameter (~10.6 Å).

Figure 14 shows the possible underlying relationship between $T_c$ and the interlayer distance $d_{Fe-Fe}$ in FeAs-based superconductors [62]. According to the experimental results, $T_c$ tends to increase with increasing $d_{Fe-Fe}$ below 9 Å which suggests superconductivity prefers two-dimensionality. However, $T_c$ shows a decreasing trend when $d_{Fe-Fe}$ is above 15 Å. The relationship

![Figure 14](image)

Figure 14. $T_c$ as a function of the interlayer distance $d_{Fe-Fe}$ [62].

between $T_c$ and $d_{Fe-Fe}$ is unclear when $d_{Fe-Fe}$ is between 9 and 15 Å. It requires more experiments on materials whose $d_{Fe-Fe}$ is in the region 9 Å < $d_{Fe-Fe}$ < 15 Å. We chose to study
Ca_{10}Pt_nAs_{8}(Fe_{2}As_{2})_5 (n = 3 or 4) whose interlayer distance is about 10.4 Å [61] and CaFeAs$_2$ in which $d_{Fe-Fe}$ is about 10.311 Å [63].

Because the crystal structures of FeAs-based superconductors have a quasi-2D nature, these superconductors are expected to exhibit large anisotropy. Figure 15 shows the anisotropy parameters $\gamma$ obtained through the upper critical field measurements and Density Functional Theory (DFT) calculations for various FeAs-based superconductors [64]. Among the experimental results, LiFeAs which has a smaller interlayer distance and lower $T_c$ than SrFe$_2$As$_2$ also exhibit a smaller anisotropy [55] [65]. Superconductor SmFeAsO$_{0.75}$F$_{0.25}$ has a higher $T_c$ than LaFeAsO$_{0.9}$F$_{0.1}$, yet it has a smaller anisotropy than LaFeAsO$_{0.9}$F$_{0.1}$ [66] [67]. What is the relationship between $T_c$, $\gamma$ and $d_{Fe-Fe}$? Both $n = 3$ and $n = 4$ phases of Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ ($n = 3$ or 4) are reported to have larger interlayer distances than it of LaFeAsO$_{0.9}$F$_{0.1}$ [57] [61] [68]. Will the anisotropy of both phases be larger than LaFeAsO$_{0.9}$F$_{0.1}$?

Figure 15. Anisotropy parameters $\gamma$ obtained from upper critical field measurements vs $\gamma$ obtained from density functional theory (DFT) calculation for various FeAs-based superconductors [64].
The anisotropy of the normal state in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$) resistivity is sample dependent. For BaFe$_{2-x}$Co$_x$As$_2$ ($d_{Fe-Fe} = 6.49$ Å), both the in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$) resistivities exhibit metallic behavior with small resistivity anisotropy in the normal state [69]. Much larger disparity between $\rho_{ab}$ and $\rho_c$ is seen in systems with larger $d$ values such as (Sr$_4$V$_2$O$_6$)(Fe$_2$As$_2$) ($d_{Fe-Fe} = 15.809$ Å [70]), where normal-state $\rho_{ab}$ remains metallic but $\rho_c$ is non-metallic [71]. To answer the question how interlayer distance change anisotropy requires more study on the interlayer transport.

The doping effect on the FeAs-based superconductors is constantly being studied. Different from cuprates, FeAs-based superconductors allow doping not only on the spacer layers but also on the Fe site. Figure 16 shows the phase diagram of BaFe$_2$As$_2$ with Co doping on the Fe site (a) [72] and K doping on the Ba site (b) [73]. The former case introduces electron doping into the compound while the later is hole doping. The underdoped BaFe$_{2-x}$Co$_x$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ show antiferromagnetism ascribed to the spin-density-wave ordering of itinerant electrons [74]. As seen in Figure 16, upon electron or hole doping, BaFe$_2$As$_2$ exhibits both a structural transition at $T_s$ (from orthorhombic below $T_s$ to tetragonal above $T_s$) and a magnetic phase transition at $T_N$ (from antiferromagnetism below $T_N$ to paramagnetism above $T_N$). For materials with low doping levels, the structural and magnetic transition happens at the same temperature, i.e., $T_s=T_N$. Both $T_s$ and $T_N$ decrease with increasing doping level. $T_s$ is usually a little higher than $T_N$. By tuning doping to a moderate level, superconductivity emerges, and $T_c$ has a dome-like shape. The maximum $T_c$ is about 23 K and 38 K obtained by Ba(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. For both doping types, there is an area where superconductivity coexists with antiferromagnetism. Hence, the physical properties of FeAs-based superconductor are largely influenced by dopant and
doping level. It is not clear yet if there is a universal phase diagram for FeAs-based superconductors.

Figure 16. The phase diagram of doped BaFe₂As₂: (a) Ba(Fe₁₋ₓCoₓ)₂As₂ [72], (b) Ba₁₋ₓKₓFe₂As₂ [73].

Among numerous types of FeAs-based superconductors, I chose my research focus as Ca-FeAs-based superconductors: Ca₁₀PtₙAs₈(Fe₂As₂)₅ (n = 3 or 4) and CaFeAs₂ for several reasons. The adjacent FeAs layers are separated by the thick spacer layers consisting of Ca layers and PtₙAs₈ layers, resulting in a large $d_{Fe-Fe} \sim 10.4$ Å [61] [75], falling into the gap of $9 \, \text{Å} < d_{Fe-Fe} < 15$ Å. It makes Ca₁₀PtₙAs₈(Fe₂As₂)₅ an excellent candidate to study the relationship between $T_c$ and $d_{Fe-Fe}$ that Ref. [62] could not specify. The arrangement of atoms in PtₙAs₈ layers cause Ca₁₀PtₙAs₈(Fe₂As₂)₅ to form different crystal structures: Ca₁₀Pt₃As₈(Fe₂As₂)₅ forms a triclinic crystal structure and Ca₁₀Pt₄As₈(Fe₂As₂)₅ is reported to crystallize in three possible space groups including $P4/n$ (tetragonal) [61] [75], $P2_1/n$ (monoclinic) [76] and $P\overline{1}$ (triclinic) [57] [75]. The crystal structure and interlayer distance are expected to influence the anisotropy of Ca₁₀PtₙAs₈(Fe₂As₂)₅. Hence, they are good candidates to study the relationship between
superconductivity and anisotropy. Another interesting aspect of \( \text{Ca}_{10}\text{Pt}_n\text{As}_8(\text{Fe}_2\text{As}_2)_3 \) is that the \( n = 3 \) and \( n = 4 \) compounds display significant different features in physical properties [77]. Studying their physical properties will help understand the role of the spacer layers. Further, we extend our research to the newly discovered Fe-based superconductor \( \text{CaFeAs}_2 \) [58] [78]. Its spacer layers consist of Ca layer and an As chain layer which may cause intriguing properties of topological superconductors [58]. Electronic band structure study of \( \text{CaFeAs}_2 \) showed a linearly dispersing band cross each other around the Fermi surface [79]. The interlayer distance is 10.311 Å which also falls in the region that \( 9 \text{ Å} < d_{\text{Fe-Fe}} < 15 \text{ Å} \) [58].
Chapter 2. Experimental Techniques

2.1 Synthesis of Single Crystals

In order to study the physical properties of Ca-FeAs-based superconductors, single crystals are essential for determining the intrinsic properties, minimizing the influence of grain boundaries and impurities, and particularly determining anisotropy of properties. We grow single crystals via the self-flux method. The flux method requires less sophisticated equipment than the floating zone method and can grow single crystals in a short period of time. It allows the growth at temperatures lower than the melting point of the solute phase. The temperature reduction helps grow uniform crystals \[80\] \[81\]. Moreover, the crystal grows without explosion to steep temperature gradients so that crystals can grow free of mechanical or thermal strains \[81\]. The self-flux method uses elements in the crystal composition to be the flux, so the impurities that the flux may cause are eliminated. An example of sample assembly is shown in Figure 17.

![Figure 17. The sample assembly for single crystal growth using the flux method.](image)

The weight of each element required is determined by the chemical nominal composition. After weighing each element powder, they are mixed evenly and put in an alumina crucible. The
crucible is then sealed in a quartz tube under vacuum to be completely isolated from air. The whole sample assembly is heated in a box furnace from the room temperature following temperature profiles. Figure 18 shows an example of temperature profiles. The highest temperature is held for a long period of time so that each element can dissolve sufficiently and mix evenly. The slow cooling process allows the mixture to form single crystals in a stable phase naturally.

![Temperature Profile](image)

Figure 18. The temperature profile to grow Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ single crystals.

### 2.2 Structure Characterization of Single Crystals

#### 2.2.1 Powder X-ray Diffraction

Because atoms in single crystals are in a periodic arrangement, the symmetry of the single crystals can be identified by X-ray diffraction (XRD) measurement using a Panalytical Empyrean X-ray diffractometer equipped with a Cu k$_\alpha$ radiation source ($\lambda = 1.5406$ Å). Figure 19 plots the XRD measurement setup.

![X-ray Diffraction Setup](image)

Figure 19. X-ray diffraction measurement setup.
The incident X-ray beam is focused on the sample surface at an angle $\theta$ which is the angle between the sample surface and incident beam. The detector collects the diffraction beam which is diffracted only from planes parallel to the sample surface is collected. A sketch of the process is shown in Figure 20.

![Figure 20](image)

Figure 20. The schematic diagram of the X-ray diffraction; (b) A close-up sketch inside the dashed circle in (a): the incident X-ray beams get reflected by the atoms of the sample resulting in the diffracted X-ray beams.

The distance between such adjacent planes is $d$. According to the Bragg’s law, $d$ and $\theta$ have the relationship as Eq. 11.

$$n\lambda = 2d \sin \theta$$

(11)

With the rotation of the incident beam $\theta$, the collected diffraction beam forms a spectrum consisting of peaks from different lattice planes. Using Eq. 11 to identify the lattice constants, $a$, $b$, $c$ and the angles between them $\alpha$, $\beta$, $\gamma$, the crystal symmetry can then be distinguished.

### 2.2.2 Energy Dispersive X-ray Diffraction

The actual composition of a single crystal is identified with Energy Dispersive X-ray Spectroscopy (EDX) equipped by FEI Quanta 200 Scanning electron microscope (SEM). The measurement proceeds by placing a crystal sample in a vacuum environment. A beam of X-ray is focused onto the crystal where an atom contains unexcited electrons in discrete energy levels.
bound to the nucleus. The incident beam excites an inner shell electron ejecting it to the higher energy shell, and a higher energy shell electron fills into the hole where the former electron was. The energy difference between the higher energy shell and lower energy shell releases as a photoelectron whose number and energy can be measured by an energy-dispersive spectrometer. Because each element has a unique atomic structure, it allows the measurement of the elemental composition of the specimen. The limitation of the EDX analysis is that the elements must be heavier than Beryllium, and depending on the roughness of the sample surface, the accuracy of the measurement can vary from 1% to 5%.

The EDX measurement is done at several spots on the sample surface and constructs the resulting spectrum by measuring the energy of the X-rays and count the number of the photoelectrons for specific energy. An example is given in Figure 21 for a Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ single crystal.

![Figure 21](image)

Figure 21. (a) An example of SEM image measured on the surface of Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$; (b) Spectrum of EDX measurement on a single spot.

Each peak location identifies the element from which the detected beam is ejected, while the count is used to calculate its elemental ratio (a) in the chemical composition using Eq. 12.
\[ a = At\% \times \frac{s}{100} \]  

(12)

where \(At\%\) is the atomic ratio, \(s\) is the sum of the atomic numbers of all elements from the nominal composition.

2.3 Physical Property Characterization techniques

The physical properties of single crystals are measured using Physical Property Measurement System (PPMS) (Quantum Design), Magnetic Property Measurement System (MPMS) (Quantum Design) and Magnetic Force Microscopy (MFM) (Attocube).

2.3.1 Resistivity, Magnetoresistivity and Hall Coefficient Measurement Techniques

Electrical resistivity, magnetoresistivity, and Hall coefficient measurements are conducted in PPMS using the four-probe method. The electrical resistivity is a fundamental quantity to classify insulators, metals, semiconductors and identifies the superconductivity. The electrical resistivity along the ab plane (\(\rho_{ab}\)) and along c axis (\(\rho_{c}\)) of a single crystal is measured as a function of temperature. Both \(\rho_{ab}\) and \(\rho_{c}\) are measured between 2 K and 300 K. The advantage of the four-probe method is that the electrical resistivity is measured avoiding the influence by the resistivity of lead wires and contacts.

Figure 22a plots the circuit diagram of the four-probe method. It uses platinum wire for connection and silver epoxy for contact. The method dedicates two connections to enable the current flow and the other two to the voltage measurement in the way that the voltage loop does not have current flow, so contact resistance causes no voltage drop. Figure 22b and Figure 22d show the configuration for \(\rho_{ab}\) and \(\rho_{c}\), respectively. The current (I) is applied via the current leads I+ and I-. In order to make the current passes through the cross-section uniformly, it is crucial to
cover the cross section in Figure 22b and the ring-shaped contacts in Figure 22d with an even layer of epoxy. The potential difference (U) is then measured between the voltage leads V+ and V-. The voltage leads are attached to the crystal via point-like contacts on the surface of the sample. The way to mount the sample on a puck with its four leads connecting to the current and voltage electrodes is shown in Figure 22c.

Figure 22. (a) A sketch of the four-probe method; (b) The four-probe connection for the in-plane resistivity measurement: the connection wires (brown) is mounted to the sample using silver epoxy (blue); (c) A sketch of the method that a sample is mounted on the puck; (d) The four-probe connection for the c-axis resistivity measurement.

Soldering each platinum wire to a corresponding solder pad on the base of the puck makes the sample electrically connected to the measurement system. The resistivity is calculated through the Ohm’s law (Eq. 13).
\[ \rho = \frac{U}{I} \times \frac{w \times t}{l} \]  

(13)

where parameters \( w, t, \) and \( l \) are the width, thickness, and the voltage leads separation, respectively. The quasi-2D crystal structure of our studied materials implies electrical resistivity anisotropy which we expect to observe in \( \rho_{ab} \) and \( \rho_c \). The normal-state anisotropy can be calculated via Eq. 14. The superconducting-state anisotropy is evaluated by Eq. 15.

\[
\gamma_{\rho} = \frac{\rho_c}{\sqrt{\rho_{ab}}} 
\]

(14)

\[
\gamma_{H} = \frac{H_{c2}(H \parallel ab)}{H_{c2}(H \parallel c)} = \frac{H_{c2}^{ab}}{H_{c2}^{c}}
\]

(15)

where \( H_{c2}(H \parallel ab) \) and \( H_{c2}(H \parallel c) \) is extracted by \( \rho_{ab} \) measurements with an applied magnetic field \( H \) along \( H/ab \) and \( H//c \).

Magnetoresistance (MR) is a quantity reflecting the change of the electrical resistivity in an external applied magnetic field. The in-plane magnetoresistivity (MR\(_{ab}\)) of the single crystal is measured with the same four-probe sample configuration shown in Figure 22b. We measure the electrical resistance \( R(H) \) of a sample with a varying applied magnetic field along the c axis. Then \( MR_{ab} \) can be calculated using Eq. 16.

\[
MR_{ab} = \frac{R(H) - R(0)}{R(0)} \times 100\%
\]

(16)

where \( R(H) \), \( R(0) \) are electrical resistances with and without \( H \) applied, respectively.

The Hall effect of a conductor is induced by the Lorentz force that carriers experienced when a magnetic field is applied perpendicular to the field. As a result of the force, carriers accumulate at the edge of the conductor and a voltage difference emerges across the conductor,
transverse to the current. As shown in Figure 23, we measure the Hall resistivity in PPMS using the four-probe method.

![Figure 23](image.png)

**Figure 23.** A sketch of the four-probe method used in a Hall resistivity measurement.

The current is applied along the ab plane passing through the entire cross section. With the magnetic field along the c-axis, the voltage difference is measured between V+ and V- electrodes. In order to eliminate the uncertainty induced by the misalignment of V+ and V-, the Hall resistivity ($\rho_H$) is measured with both positive and negative magnetic field. Then it can be calculated in Eq. 17.

$$\rho_H = \frac{R(+H) - R(-H)}{2} \times t \quad (17)$$

where $t$ is the thickness of the sample, $R(+H)$ and $R(-H)$ are electrical resistances with positive and negative $H$. A plot of $\rho_H$ versus $H$ will yield a straight line with slope to be the Hall coefficient ($R_H$). The Drude model predicts the Hall coefficient is a function of the carrier concentration (Eq. 18).

$$R_H = \frac{1}{nq} \quad (18)$$

where $n$ is the charge carrier concentration in the sample and $q$ is the charge of the carriers. So the sign of $R_H$ predicts the sign of the charge carriers: it is negative for electrons and positive for holes.
2.3.2 Magnetic Property Measurement Techniques

The DC magnetization of a single crystal is measured with MPMS. MPMS consists of four major parts: a superconducting magnet to generate magnetic field, a superconducting detection coil which couples inductively to the sample, a superconducting quantum interference device (SQUID) connected to the detection coil and a superconducting magnetic shield surrounding the SQUID [82]. The system does not detect magnetic field from the sample directly. Instead, it measures the voltage change resulting from the magnetic moment of a sample [83]. As shown in Figure 24, a sample is mounted in a straw-like tube and can move through the superconducting detection coils. As the sample moves along the direction parallel to the applied magnetic field, the magnetic moment of the sample induces electric current in the detection coils, producing change in the persistent current in the detection circuit. Because the detection coil and the SQUID input coil form a closed superconducting loop through the connecting wires, any current change in the detection coil produces corresponding variation in the SQUID output voltage. Hence, the magnetic moment ($\mu$) of the sample can be proportionally converted to the output voltage that the system measures. The magnetic field ($H$) that MPMS can apply is from -7 Tesla to +7 Tesla. The magnetization of a sample can be calculated by Eq. 19.

$$M = \frac{\mu}{m}$$  \hspace{1cm} (19)

where $m$ is the mass of the sample. Moreover, the susceptibility ($\chi$) of the sample is calculated by Eq. 20.

$$\chi = \frac{M}{H}$$  \hspace{1cm} (20)

The magnetization of a superconductor measured under zero-field-cooling (ZFC) process and field-cooling (FC) process is different. ZFC measurement starts applying magnetic field when
the sample is below its critical temperature, and FC measurement switches on magnetic field when the sample is in its normal state. In this way, the sample screens the applied magnetic field itself in ZFC process, while it screens the change of the applied magnetic field in FC process. We measure the magnetization of our samples in both ZFC process and FC process.

![Diagram](image)

Figure 24. A scheme of the MPMS working principle.

### 2.3.3 Vortex Imaging Technique

Magnetic force microscopy (MFM) is a technique for imaging, characterizing and analyzing the magnetic structure on a sample surface. MFM images the spatial variation of magnetic field within the sample surface, through local magnetic interaction between a sharp tip and a sample. Forces such as magnetostatic force whose range is longer than the atomic force require non-contact mode using a tip coated with a thin layer of magnetic material. Hence, we use the non-contact mode to image the vortices on the surface of superconductors. In our MFM setup, PPP-MFMR (Point Probe Plus Magnetic Force Microscopy Reflex Coating) (*NANOSENSORS*) probes are used the tip of which is coated thinly with Co offering magnetic resolution better than 50 nm.
The noncontact mode MFM measures the derivative of the vertical component of the force \( \ddot{F} \) between the tip and the sample. Figure 25 plots the simplified setup for noncontact mode measurements. \( \ddot{F} \) acting on a flexible cantilever causes it bend towards or away from the sample surface according to Hooke’s Law \( F_z = -k \Delta z \), where \( k \) is the force constant. The motion of the cantilever follows the equation describing a damped harmonic oscillation (Eq. 21).

\[
m \frac{d^2 z}{d t^2} + \Gamma \frac{dz}{dt} + k (z - z_0) = F_{ex}(t) + F_z(z)
\]  

(21)

where \( m \) is the mass of the cantilever, \( \Gamma \) is the damping coefficient, \( z \) is the distance between the tip and the sample surface, \( z_0 \) is the equilibrium position of the cantilever, \( F_{ex} \) is the external driving force, \( F_z \) is the component of the force between the tip and the sample surface in the direction of \( \dot{z} \). Assuming \( F_z \) is small and \( \frac{dF_z}{dz} \ll k \), we get the relationship between the force gradient along the \( z \) direction and the change of the frequency as Eq. 22.

\[
\frac{\partial F_z}{\partial z} = \frac{2k}{f_0} (f' - f_0)
\]  

(22)

where \( f_0 \) is the natural resonant frequency of the cantilever.

Figure 25. A sketch of noncontact mode MFM sample and cantilever setup.
We image superconducting vortices via the constant height mode. The tip scans across the sample at a certain elevation. During the scan, the cantilever is excited at its resonant frequency and constant amplitude. The phase-shift between the excitation source and the cantilever is measured which is proportional to the force gradient shown in Eq. 23.

\[
\Delta \theta = \frac{Q}{k} \frac{\partial F}{\partial z}
\]

(23)

in which the quality factor \( Q \) is a cantilever related parameter. We can obtain \( Q \) value from the resonance frequency curve: \( Q = \frac{f_0}{\Delta f} \) where \( \Delta f \) is the full width at half maximum. Hence, by measuring the phase shift, the derivative of magnetic interaction force \( \frac{\partial F}{\partial z} \) can be calculated and eventually be used to analyze the magnetic domain properties of the measured sample.

There are several models proposed to describe the magnetic interaction between the tip and the magnetic field from the sample [84] [85] [86]. Based on the theoretical analysis [87] [88], Ref. [84] calculate \( \frac{\partial F}{\partial z} \) using the Meissner repulsion that a single magnetic dipole experiences. When the distance \( (z) \) between the tip and the sample surface is larger enough \( (z >> \lambda_{ab}) \), \( F \) is equivalent to the force due to the interaction between the original magnetic tip and its image by mirroring the original tip at a plane \( \lambda_{ab} \) beneath the surface of the sample [84] [87]. The actual magnetic tip we use is a truncated cone illustrated in Figure 26 rather than a perfectly sharp cone. As shown in Figure 26, the tip is characterized by parameters including the cone half-angle \( (\theta) \), the length of the cone edge \( (h) \) and the effective magnetic height of the tip \( (H) \). The derived equation of \( \frac{\partial F}{\partial z} \) is a function of \( \theta, h \) and \( H \). And when \( H \rightarrow \infty \), \( \frac{\partial F}{\partial z} \) can be written as Eq. 24.

\[
\frac{\partial F}{\partial z} = \frac{\mu_0 m^2}{2k} \left( \frac{1}{z+\lambda_{ab}} + \frac{h}{(z+\lambda_{ab})^2} + \frac{h^2}{2(z+\lambda_{ab})^3} \right)
\]

(24)
where $f_0$ is the resonance frequency of the magnetic tip, $\mu_0$ is the permeability of the vacuum.

Figure 26. An illustration of the model for the magnetic tip: $\theta$ is the cone half angle, $h$ is the length of the cone truncation and $H$ is the effective magnetic height of the tip.

The separation between nearby vortices and the size of a single vortex all depend on the penetration depth $\lambda$. So we can evaluate $\lambda$ by imaging the superconducting vortices at different temperatures and magnetic fields.
Chapter 3. \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5 \)

3.1 Motivation

The \( \text{Ca-Fe-Pt-As} \) system was first reported to exhibit superconductivity up to 38 K in 2011 [68]. Soon after, two other groups have reported similar results with \( T_c \sim 35 \text{ K} \) [57] [75] As discussed in Chapter 1.3.2, the crystal structure of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) plotted in Figure 27a has layered structure consisting of superconducting \( \text{FeAs} \) layers separated by the spacer layers arranged as \( \text{Ca-Pt}_4\text{As}_8-\text{Ca} \). This superconductor has been reported to crystallize in possible space groups including \( P4/n \) (tetragonal) [61] [75], \( P2_1/n \) (monoclinic) [76] and \( P\overline{1} \) (triclinic) [57] [75]. The structure of \( \text{Pt}_4\text{As}_8 \) spacer layer plotted in Figure 27b is similar to a square lattice of \( \text{As} \) atoms. 1/5 of the \( \text{As} \) atoms are replaced by substitutional \( \text{Pt} \) atoms labeled \( \text{Pt1} \) [61]. \( \text{Pt} \) atoms

![Figure 27](image)

Figure 27. (a) Crystal structures of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \); (b) a schematic illustration of the formation of the \( \text{Pt}_4\text{As}_8 \) layer; (c) the \( \text{Pt}_4\text{As}_8 \) cutoff layer.
labeled as Pt2 are interstitial which lead to displacements of As atoms from their ideal positions and forming As dimers [61]. Because of the constraint from the As-As dimers and the FeAs sublattices, Pt1 atoms can sit in plane and Pt2 atoms can only sit at one side of the plane. Each Pt2 atom is blocked from only one side of the plane by Ca ions so that it can sit on the site either above the plane or below the plane. The resulting Pt4As8 cutoff layer is plotted in Figure 27c.

\[ \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \]

allows doping on the Ca site or on the Fe site. Figure 28 plots \( T_c \) of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) as a function of the level (\( y \)) of Pt doping on the Fe site [77]. The maximum \( T_c \) is obtained by the superconductor without doping. Further Pt doping results in the decrease of \( T_c \). As discussed in Chapter 1.3.2, most FeAs-based superconductors need doping to induce the superconductivity, so the emergence of superconductivity in undoped of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) is rare. By studying its structure and physical properties, origin of superconductivity may be elucidated. The interlayer distance of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) reported to be \( \sim 10.4 \) Å [75] [61], larger than many other FeAs-based superconductors, its properties are expected to be anisotropic.

Figure 28. \( T_c \) of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) against Pt substitution ratio on the Fe site (\( y \)) [77].
The low-lying electronic structure is studied via angle resolved photoemission spectroscopy (ARPES) [89]. The sketch of the Fermi surface of $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ is shown in Figure 29. Overall, there are a hole pocket and an electron pocket around the zone center, several electron pockets around the zone corner among which two are suggested to be contributed by FeAs layer and several are contributed by Pt$_4$As$_8$ layers [89]. Thus, the Pt$_4$As$_8$ layer is suggested to be metallic [89]. Furthermore, the $d_{xz}$ and $d_{yz}$ bands are not degenerate at the Brillouin zone center ($\Gamma$ point) and there is only hole-like Fermi surface at the $\Gamma$ point originated from $d_{xy}$ orbitals [89]. It may be caused by the interaction between the Pt$_4$As$_8$ and FeAs layers [89]. Hence, in order to understand how the interaction between Pt$_4$As$_8$ and FeAs layers influences the physical properties, we planned to study the properties of $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ along its c axis.

![Figure 29](image_url)

Figure 29. A sketch of the Fermi surface of $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{1-y}\text{Pt}_y)_2\text{As}_2)_5$ [89]. The Brillouin zone in blue is for the FeAs layer and the one in red is for the Pt$_4$As$_8$ layer.

3.2 Crystal Growth

We use the flux method described in Chapter 2.1 to grow high-quality single crystals. The sample growth was conducted by heating a mixture of 99.999% pure Ca shot (Alfa Aesar), 99.95% Pt powder (Alfa Aesar), 99.95% Fe powder (Alfa Aesar) and 99.999% As powder (Alfa Aesar). The powder mixture was in the ratio Ca: Pt: Fe: As = 9.5: 2.5: 10: 18. The temperature profile to is shown in Figure 18. The whole sample assembly is heated in a box furnace from the room
temperature. First, it is heated to 700 °C in 5 hours and held for 5 hours, then in another 5 hours, heated up to 1100 °C where it is held for 50 hours. The system cools down to 1050 °C in 40 hours, and slowly further cools down to 500 °C in the next 100 hours, then cools down to the room temperature quickly to get the samples out. The cooling process is crucial because the sample powder mixture melt when it heats up and forms in a stable phase when it cools down. Shiny plate like single crystals are obtained with a typical size of $5 \times 5 \times 0.2$ mm$^3$. A photo of prototypical $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ single crystals is shown in Figure 30.

![Figure 30. A prototypical $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ single crystals.](image)

### 3.3 Structure Characterization

The crystal structure is determined by single-crystal X-ray refinement. The crystal used for this experiment was selected from the same batch as used for physical properties measurements and mounted on a glass fiber with epoxy. The size of this crystal was approximately $0.025 \times 0.075 \times 0.125$ mm$^3$. At room temperature, the lattice parameters are $a = 8.7640(11)$ Å, $b = 8.7550(13)$ Å, and $c = 10.69001(7)$ Å, and angles are $\alpha = 94.672(8)^\circ$, $\beta = 104.398(9)^\circ$, and $\gamma = 90.038(10)^\circ$. The lattice parameters are consistent with the reported data: $a = b = 8.733$ Å, $c = 10.481$ Å [61] and $a = b = 8.716$ Å, $c = 10.462$ Å [75]. Figure 31 shows the XRD diffraction spectrum for $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ single crystal along the c axis. Compared to other published data, the single
Crystal X-ray diffraction result confirms that the sample crystallizes in a triclinic structure with space group symmetry \( P_1 \). The powder XRD diffraction spectrum shown in Figure 32 is obtained by XRD measurements on the powder grounded from single crystals of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \). The result exhibits the peaks from diffractions not only \([00l]\) planes but also \([hkl]\) planes with nonzero \( h, k, l \). The peak locations confirm the lattice parameters we obtained from the single crystal refinement.

![Intensity vs. 2theta](image1)

Figure 31. XRD spectrum of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) measured on single crystals along the \( c \) axis at room temperature.

![Intensity vs. 2theta](image2)

Figure 32. XRD spectrum of powder \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) at room temperature.
The chemical composition is identified by the EDX measurement described in Chapter 2.2.2. The samples were selected from the same batch as the XRD measurements. A SEM image measured on the surface of the single crystal is shown in Figure 33 inset. Every peak in Figure 33 identifies an orbital of a designated atom. For each sample, we chose 5 locations scattered on the surface for EDX measurement. An average of these scans was calculated, and the results of different samples were consistent with each other implying we obtained homogenous growth throughout the batch. The average deviation is 5% for Ca, 8% for Pt, and 1% for Fe. The actual composition of the single crystals is $\text{Ca}_{10}\text{Pt}_{4.5}\text{Fe}_{9.5}\text{As}_{18}$. The Electron Energy Loss Spectroscopy (EELS) image is shown in Figure 34. It indicates that Fe is partially substituted by Pt. Thus, $\text{Ca}_{10}\text{Pt}_{4.5}\text{Fe}_{9.5}\text{As}_{18}$ actually corresponds to $\text{Ca}_{10}\text{Pt}_{4}\text{As}_{8}((\text{Fe}_{0.95}\text{Pt}_{0.05})_{2}\text{As}_{2})_{5}$.

![Figure 33](image.png)

Figure 33. EDX measurement spectrum of $\text{Ca}_{10}\text{Pt}_{4.5}\text{Fe}_{9.5}\text{As}_{18}$; the inset figure is a surface SEM image of the measured sample.
3.4 Physical Properties

3.4.1 Electrical Resistivity, anisotropy and discussion

The temperature dependence of the in-plane resistivity ($\rho_{ab}$) and out-of-plane resistivity ($\rho_{c}$) of $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$ is shown in Figure 35a-b. Both $\rho_{ab}$ and $\rho_{c}$ are measured between 2 K and 300 K. The magnitude of $\rho_{ab}$ and its overall feature are similar as the previous reports [61] [44]. The normal-state $\rho_{ab}$ decreases with decreasing $T$ ($\frac{d\rho_{ab}}{dT} > 0$) showing a metallic behavior. It drops sharply below ~34 K, reaching zero-resistivity state at 32.2 K. Thus, $T_{c0}$ is 32.2 K for $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$. The reported $T_c$ corresponding to polycrystals with $y = 0.05$ shown in Figure 28 from Ref. [77] is abt 25 K, so $T_c$ of our sample is much higher than the reported one. Yet, compared with previous reports on single crystals, our sample exhibits almost same $T_c$ with $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.82}\text{Pt}_{0.18})_2\text{As}_2)_5$ [57] and larger $T_c$ than $\text{Ca}_{10}\text{Pt}_{3.75}\text{As}_8((\text{Fe}_{0.97}\text{Pt}_{0.03})_2\text{As}_2)_5$ [61] and $\text{Ca}_{10}\text{Pt}_{3.51}\text{As}_8((\text{Fe}_{0.98}\text{Pt}_{0.02})_2\text{As}_2)_5$ [90]. It implies $T_c$ of $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ is influenced by not only Pt doping level on the Fe site but also the Pt concentration in the $\text{Pt}_{4-\delta}\text{As}_8$ layers. The out-of-plane resistivity $\rho_{c}$ also drops at $T_c$, but not as

Figure 34. Electron Energy Loss Spectroscopy (EELS) measurement of $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$; red arrows point to the contrast at the Fe layer in the Pt mapping image.
sharp as that of $\rho_{ab}$. While this should be attributed to the imperfection of the crystal sample along the c direction, our data clearly indicates three-dimensional (3D) superconductivity in this system. More strikingly, $\rho_c$ in the normal state increases with decreasing $T$, i.e., $\frac{d\rho_c}{dT} < 0$, showing a nonmetallic behavior. The property anisotropy between $\rho_{ab}$ and $\rho_c$ is not noted in previous reports [57] [61] [90].

![Figure 35](image.png)

The temperature dependence of the in-plane resistivity $\rho_{ab}$ (a) and out-of-plane resistivity $\rho_c$ (b).

Due to the layered crystal structure of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$, we may understand the in-plane resistivity as a net resistivity of parallel connected resistors. A schematic of such system is plotted in Figure 36a. Here we do not consider the resistance from Ca layer because FeAs layer and Pt$_4$As$_8$ layers are main contributors of the electronic structure around the Fermi surface [89]. The net resistance ($R$) is $R = 1/[n \left( \frac{1}{R_{FeAs}} + \frac{1}{R_{Pt4As8}} \right)]$, in which $n$ is the number of Pt$_4$As$_8$-FeAs layers, $R_{FeAs}$ and $R_{Pt4As8}$ are the resistance of the FeAs layer and Pt$_4$As$_8$ layer correspondingly. If Pt$_4$As$_8$ layer is semiconducting or insulating, it should have a much larger resistance than the FeAs layer. Then, the net resistance $R$ should be dominated by the resistance of the Pt$_4$As$_8$ layer and exhibit nonmetallic behavior. Yet, according to our result, the normal state
\( \rho_{ab} \) shows metallic behavior indicating the spacer layer \( \text{Pt}_4\text{As}_8 \) is metallic which agrees with the previous report \[89\].

![Diagram of resistors](image)

Figure 36. (a) A schematic plot of resistors made of FeAs layers and \( \text{Pt}_4\text{As}_8 \) layers connected in parallel; (b) a schematic plot of resistors made of FeAs layers and \( \text{Pt}_4\text{As}_8 \) layers connected in series.

As discussed in Ch. 1.3.1, the normal state \( \rho_{ab} \) of some cuprates shows metallic behavior and may have linear dependence on temperature due to the inelastic scattering dominated electron-phonon interaction. And in some cuprates, \( \rho_{ab} \) has \( T^{1.5} \) dependence implying the Fermi-liquid behavior. Yet, the temperature dependence of the normal state \( \rho_{ab} \) of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5 \) is not linear, quadratic temperature dependent or \( T^{1.5} \) dependent as observed in cuprates or other FeAs-based compounds \[91\]. The normal state \( \rho_{ab} \) from 50 K to 300 K can be well fitted by

\[
\rho_{ab} = A + B\sqrt{T}
\]

with \( A = 0.079 \pm 0.009 \) m\( \Omega \) cm and \( B = 0.267 \pm 0.002 \) m\( \Omega \) cm / \( \sqrt{K} \). The red solid line in Figure 35a is the fit to the experimental data of the normal state \( \rho_{ab} \). The reported \( \rho_{ab} \) for \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) has the similar square-root temperature dependence regardless \( T_c \) \[57\] \[61\] \[90\]. Thus, it may be an intrinsic property to \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \). The square-root temperature dependence of electrical resistivity is normally expected at low temperatures in disordered metals.
and degenerate semiconductors because of interference with scattering by impurities [92] [93]. As discussed in Ch. 3.1, the studies about the Fermi surface of Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ imply that Pt$_{4-\delta}$As$_8$ layer contributes several electron pockets. Thus, there may be competition between Pt$_{4-\delta}$As$_8$ layer and another negatively charged FeAs layer for electrons leading to Pt deficiency in the Pt$_{4-\delta}$As$_8$ layer and partial substitution of Fe by Pt in the Fe$_{1-x}$Pt$_x$As layer [75] [77] [94] [95] [96]. As a result, charge carriers in both the Pt$_{4-\delta}$As$_8$ and Fe$_{1-x}$Pt$_x$As layers could experience the effect of disorder which may be the reason why the in-plane electrical resistivity has the square-root temperature dependence. As shown in Figure 35, $\rho_c$ is much larger than $\rho_{ab}$. It can be understood with a schematic plot of the net resistance ($R$) is $R = n \left( R_{FeAs} + R_{Pt4As8} \right)$ along the out-of-plane direction. Different from the normal state $\rho_c$ of some cuprates discussed in Ch. 1.3.1 which can be described using the equation $\rho_c = A/T + BT$ exhibiting the non-Fermi liquid behavior, the nonmetallic normal state $\rho_c$ of Ca$_{10}$Pt$_4$As$_8$(Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$$_5$ can be fit using the equation $\rho_c = A' + B' \sqrt{T} + C'T^{-1}$. The solid line in Figure 35b shows the fit of $\rho_c$ from 90 K to 300 K. The fitting parameters are calculated: $A' = 2.6 \pm 0.5$ mΩ cm, $B' = 0.31 \pm 0.03$ mΩ cm K$^{-1/2}$, and $C' = 668 \pm 29$ mΩ cm K. The square-root temperature dependent component in $\rho_c$ is due to the in-plane scattering, which may be intrinsic as Anderson proposed for high-$T_c$ cuprates [47] or extrinsic due to possible stacking fault [61]. The $T^{-1}$ term can be attributed to interlayer incoherent scattering, similar to the properties of high-$T_c$ cuprates [47], (Sr$_4$V$_2$O$_6$)Fe$_2$As$_2$ [97] and NaFe$_{1-x}$Co$_x$As [98]. It implies the spacer layer Ca$_{10}$Pt$_4$As$_8$ is not superconducting in nature so that Josephson junctions are formed along the c axis of Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ by stacking of FeAs superconducting layer, Ca$_{10}$Pt$_4$As$_8$ insulating layer and FeAs superconducting layer. It is also observed in (Sr$_4$V$_2$O$_6$)Fe$_2$As$_2$ [97]. The resistivity anisotropy $\gamma$ is calculated by Eq. 12 and it increases from ~4.2 at 300 K to ~7.8 at around $T_c$ as displayed in Figure 37. It is larger than $\gamma$ of YBa$_2$Cu$_3$O$_{0.65}$ [99].
and smaller than $\gamma$ of La$_{1.83}$Sr$_{0.17}$CuO$_4$ [49]. The interlayer distance of YBa$_2$Cu$_3$O$_{0.65}$ and La$_{1.83}$Sr$_{0.17}$CuO$_4$ is about 10 Å [4] and 6.6 Å [100] respectively, so the interlayer distance of our sample is similar to YBa$_2$Cu$_3$O$_{0.65}$ and much larger than La$_{1.83}$Sr$_{0.17}$CuO$_4$. Thus, $\gamma$ is not increasing monotonically with the interlayer distance. Compared with other Fe-based superconductors in Figure 15, $\gamma$ of Ca$_{10}$Pt$_4$As$_8$(Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$ is larger than the largest $\gamma$ obtained by LaFeAsO$_{0.9}$F$_{0.1}$. Considering LaFeAsO$_{0.9}$F$_{0.1}$ has a smaller interlayer distance than Ca$_{10}$Pt$_4$As$_8$(Fe$_{2}$As$_2$)$_5$ [62], our result confirms that $\gamma$ is not increasing monotonically with the interlayer distance.

Figure 37. The temperature dependence of the normal state anisotropy $\gamma = \sqrt{\rho_c/\rho_{ab}}$.

3.4.2 Upper Critical Field, Anisotropy and Discussion

The resistivity anisotropy ($\gamma$) in the superconducting state of Ca$_{10}$Pt$_4$As$_8$(Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$ is evaluated through resistivity measurement with an applied magnetic field $H$. Figure 38a-b temperature dependence of $\rho_{ab}$ under the application of $H$ along the c axis and ab plane. In both cases, $H$ pushes the superconducting transition to lower temperatures and broaden the transition, indicating that magnetic field gradually suppresses superconductivity. Shown in Figure 39a-b, the upper critical field $H_{c2}(T)$ is extracted by identifying $T_c(H)$ at which $\rho_{ab}$ drops to 90% $\rho_n$, 50% $\rho_n$
Figure 38. The temperature dependence of $\rho_{ab}$ with an applied magnetic field $H \parallel c$ (a) and $H \parallel ab$ (b) in the superconducting state.

Figure 39. The temperature dependence of the upper critical field $H_{c2}$ with $H \parallel c$ (a) and $H \parallel ab$ (b).

and 10% $\rho_n$. $\rho_n$ is the normal resistivity as indicated as dash lines in Figure 39a-b. $H_{c2}$ increases almost linearly with decreasing temperature. $\gamma = \frac{H_{c2}^{ab}}{H_{c2}^c}$ is presented in Figure 41. $\gamma$ taken at 50 % resistivity drop is $\sim 6$ near $T_{c0}$ which is very close to the normal-state $\gamma$ we obtained previously in
resistivity measurements. Compared to 122 type, for example $\gamma \sim 2$ for BaFe$_2$As$_2$ [101] [102] [103] [104], our result is much larger, while it is similar to 1111 type where $\gamma \sim 5 - 10$ for SmFeAsO [105].

![Figure 40](image)

The temperature dependence of the resistivity anisotropy $\gamma = \frac{H_{c2}(H//ab)}{H_{c2}(H//c)}$.

We estimated $H_{c2}$ at 0 K using the Werthamer-Helfand-Hohenberg (WHH) approximation

$$H_{c2}(0) = -0.69 \frac{dH_{c2}}{dT} |_{T_c} \times T_c.$$ And the corresponding coherence length are calculated via $\xi_{ab}(0) = \frac{\Phi_0}{\sqrt{2\pi H_{c2}^\xi(0)}}$ and $\xi_{c}(0) = \frac{\Phi_0}{2\pi \xi_{ab} H_{c2}^{ab}(0)}$. The obtained results are listed in Table 1. Although the WHH approximation may not valid as demonstrated by Din et. al., and all derived values depend on how $H_{c2}(T)$ is extracted, the large difference of $H_{c2}^{ab}$ and $H_{c2}^\xi$ implies Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ exhibits a large anisotropy in its superconducting state. Furthermore, compared with other Fe-based superconductors, our $\xi_{ab}$ and $\xi_{c}$ calculated at 0.5$\rho_\pi$ are larger than these of NdFeAsO$_{0.7}$F$_{0.3}$, Ba(Fe$_{0.5}$Co$_{0.1}$)$_2$As$_2$ and FeSe$_{0.5}$Te$_{0.5}$ [106]. For a superconductor with a small mean free path $l$ and
intrinsic coherence length $\xi_0$, its coherence length $\xi = (\xi_0 l)^{1/2}$. Thus, a superconductor with larger $\xi$ implies it has a larger mean free path.

Table 1. The upper critical field and coherence length of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$.

<table>
<thead>
<tr>
<th>Criteria in Determining $H_{c2}$</th>
<th>$\frac{dH_{c2}^C}{dr}$ $T_c$ (T/K)</th>
<th>$\frac{dH_{ab}^{ab}}{dr}$ $T_c$ (T/K)</th>
<th>$H_{c2}^C(0)$ (Tesla)</th>
<th>$H_{ab}^{ab} (0)$ (Tesla)</th>
<th>$\xi_{ab}(0)$ (Å)</th>
<th>$\xi_c(0)$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.9 \rho_n$</td>
<td>$-6.4 \pm 0.2$</td>
<td>$134 \pm 5$</td>
<td>$-13.9 \pm 0.1$</td>
<td>$309 \pm 5$</td>
<td>$15.7 \pm 0.2$</td>
<td>$6.8 \pm 0.3$</td>
</tr>
<tr>
<td>$0.5 \rho_n$</td>
<td>$-0.87 \pm 0.1$</td>
<td>$19.3 \pm 2$</td>
<td>$-4.4 \pm 0.1$</td>
<td>$98 \pm 2$</td>
<td>$41 \pm 1$</td>
<td>$8.1 \pm 0.3$</td>
</tr>
<tr>
<td>$0.1 \rho_n$</td>
<td>$-0.72 \pm 0.1$</td>
<td>$16 \pm 1$</td>
<td>$-3.7 \pm 0.1$</td>
<td>$82 \pm 3$</td>
<td>$45 \pm 2$</td>
<td>$8.8 \pm 0.5$</td>
</tr>
</tbody>
</table>

### 3.4.3 Magnetoresistivity and Discussion

The anomalous in-plane electrical transport is further studied in transverse magnetoresistivity ($MR_{ab}$). Figure 41a shows the field dependence of $MR_{ab}$ with $H \perp I$ at various temperatures above $T_c$. Between 40 K and 300 K, $MR_{ab}$ shows an overall positive feature. Plotted as a function of temperature at a fixed magnetic field, $MR_{ab}$ shown in Figure 41b decreases with

![Figure 41](image-url)
the increasing temperature. The temperature-dependent sources that contribute to the resistivity such as spin-wave scattering become more effective with the increasing temperature [107] [108], causing the decrease of the slope $\frac{dMR_{ab}}{dH}$. Thus Remarkably, $MR_{ab}$ exhibits a linear $H$-dependence between 0 and 14 T at each fixed temperature. It is different from the expectation.

According to the band theory of solids with a single carrier type, $MR$ changes quadratically with $H$ at low fields and saturates at high fields. For solids with two types of charge carriers, $MR$ and $H$ has a relationship as $MR = \frac{aH^2}{b + cH^2}$ where $a$, $b$, $c$ are positive constants. In both cases, $MR$ is not expected to be linear to the applied field. During 1928-1929, Kapitza found a list of metals in which magnetoresistance shows linear dependence on the applied large magnetic field [109] [110]. In 1958, Lifshits and Peschansky [111] proposed a classical model describing that when the Larmor radius of a moving electron in metals in a magnetic field is smaller than its mean free path, the metal has an energy spectrum of electrons with open Fermi surfaces and the magnetoresistance is linear to the applied field. This model fitted well with Kapitza’s findings in polycrystalline samples of metals except Bismuth [111]. Over the years, linear $H$-dependent MR has been observed in systems other than metals, for example semi-metals [109] [112], multi-layer graphene [113] [114], topological insulators [115] [116] [117] and some FeAs-based superconductors [118] [119] [120]. Some theoretical approaches haven been made to interpret these linear behaviors. Another classical approach explains the linear MR property in materials with sufficient strong disorder, i.e. disordered metals or semiconductors [121] [122] [123]. Parish and Littlewood proposed this classical model describing a disordered semiconductor by a $N \times M$ resistor network. A schematic diagram of the resistor network is shown in Figure 42b. Each node of this network is a resistor unit plotted in Figure 42a. The model considers the resistor unit as a homogenous disk
with four current terminals and four voltage differences between the terminals. Thus, the resistor network in Figure 42b has 2N-1 current terminals. When N→∞, the resistivity of this model can describe the resistivity of a strongly inhomogeneous system. In this case, the numerical analysis shows magnetoresistivity is linear to the applied magnetic field H at low H as well as high H (cμH >> 1 in which μ is the carrier mobility and c is the volume fraction, c<<1). Furthermore, this model also shows the magnitude of MR decreases with the decreasing average carrier mobility which may be caused by the increasing temperature.

In our case, the square-root temperature dependence of ρ_{ab} implies the normal state transport property of Ca_{10}Pt_{4}As_{8}((Fe_{0.95}Pt_{0.05})_{2}As_{2})_{5} may be influenced by disorder. So this classical model may explain the linear MR property we observed in our Ca_{10}Pt_{4}As_{8}((Fe_{0.95}Pt_{0.05})_{2}As_{2})_{5} if the disorder in this system is strong enough. The model fits in the scenario in several aspects. Firstly, MR is linear to H at fields as low as 0 Tesla. Secondly, MR is nonsaturating at fields as high as 14 Tesla. Thirdly, the magnitude of MR decreases with the increasing temperature at a given magnetic field. However, the STM result on our

Figure 42. A schematic diagram of an N×M resistor network: (a) a four-terminal resistor unit is a homogenous conducting disk with currents i entering the terminals and voltage differences v between the terminals; (b) the N×M resistor network of which each node is a four-terminal resistor unit [122].
$\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$ exhibits good $\text{Pt}_4\text{As}_8$ layers and $\text{FeAs}$ layers [124], so disorder in our system should not be strong enough to dominate the transport property. Hence, this classical model is not sufficient to explain the linear MR property in our $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$.

Classical models fail to explain the linear MR behavior found in bismuth, so Abrikosov constructed a quantum model originally to explain this behavior [109]. The quantum $MR$ becomes noticeable when the extreme quantum limit is reached, meaning the cyclotron frequency ($\omega_c = \frac{eH}{m^*c}$) is so large that $\hbar\omega_c > E_F$ [125] [126] [127]. Electrons can concentrate into the lowest quantum state of the transverse motion with magnetic field applied. Further conditions that need to be satisfied are $n_e \ll \left(\frac{eH}{\hbar c}\right)^2$ and $T \ll \frac{e\hbar}{m^*c}$ [128]. The first condition describes the electron density $n_e$ is small so that only the lowest Landau band participate in the transport property, and the second condition requires the temperature is lower than the band splitting. In these circumstances, transverse components of magnetoresistance are derived to have the linear dependence on the magnetic field [125] [126] [127]. Furthermore, magnetoresistance is positive, non-saturating and the linear dependence holds at low fields. Experiments found that the extreme quantum limit can be realized in semimetals [109] [112] and semiconductors, for example, InSb [115]. Their Fermi surface have tiny pockets with a small effective mass. Such a situation is common in layered metals, for example, graphite, $\text{BaFe}_2\text{As}_2$. In these materials, the electron band and the hole band overlap in a point forming a Dirac-cone like energy dispersion around the Fermi surface leading to a large carrier mobility due to the zero effective mass and the long relaxation time of carriers [129]. Previous reports about $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ show no small pocket around the Fermi surface [95] [96], so it is unlikely to form the Dirac-cone. Thus, the linear $MR$ we observed in $\text{Ca}_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{0.95}\text{Pt}_{0.05})_2\text{As}_2)_5$ does not fit into this quantum model.
Quantum interference effect is widely used to describe the magnetic field influence on the electrical conductivity in disordered metals [130] [131]. Such phenomena has also been observed in certain ferromagnets [108] [132], for example, Fe thin films [108], FeCoSi [132]. Due to the short elastic mean free path of conduction electrons, their propagation is diffusive. Quantum interference exists when oppositely directed electron partial scattered waves traverse the same closed path [131]. When a system with quantum interference is placed in a magnetic field, a spin gap ($\Delta$) is induced and its magnitude is $g\mu_BH$ in which $g$ is the g factor and $\mu_B$ is the Bohr magneton [108]. In ferromagnets, the applied magnetic field adds an extra term to the existing gap $\Delta(0)$ between subbands of spin-up and spin-down s electrons: $\Delta(H) = \Delta(0) + \gamma g\mu_BH$ where $\gamma = 1$ if the moments of s electrons and d electrons are parallel and $\gamma = -1$ if they are antiparallel [108]. In the conditions that $g\mu_BH<<\Delta(0)$ and $kT<<\Delta(H)$, magnetoresistance is proved to be linear to the applied magnetic field and the linear dependence is independent of temperature [108]. Furthermore, magnetoresistance is positive for systems with $\gamma = 1$ and is negative if $\gamma = -1$ [108]. For our Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$, quantum interference effect may fit in the scenario because we observed linear H dependence of MR at a large magnetic field range, but it fails to explain MR decreases with the increasing temperature at a fixed magnetic field shown in Figure 41b.

3.4.4 Hall Coefficient and Discussion

For a normal metal with Fermi liquid behavior, the Hall coefficient is independent of temperature. While the situation is more complex if the material has multiband or non-Fermi liquid behavior, for example cuprates or heavy fermions. Their Hall coefficient exhibits strong temperature and doping dependencies. Figure 43 shows the temperature dependence of Hall coefficient ($R_H$) of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ in the normal state. The transverse $R_H$ remains negative at all temperatures above $T_c$, indicating the charge carrier is dominated by electrons. The
The temperature dependence of the Hall resistivity $R_H$ (left) and the carrier concentration (right) of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$.

The magnitude of $R_H$ increases with decreasing temperature which suggests a multiband or non-Fermi liquid behavior. Even though the doping in the FeAs layers is considered to be isovalent (i.e., Pt$^{2+}$ replaces Fe$^{2+}$) [61] [77], it may still influence the property of $R_H$, as observed in other isovalent-doped cases [133] [134]. In fact, our result is similar with previous reports [57] [61]. However, our $R_H(T)$ exhibits stronger temperature dependence than that reported in Ref. [57] and is similar to the result obtained in Ca$_{10}$(Pt$_3$As$_8$)((Fe$_{1-x}$Pt$_x$)$_2$As$_2$)$_5$ [61]. It suggests that carrier concentration cannot be solely determined by the Pt concentration in the material. If a single band model is adopted, the corresponding carrier concentration ($n$) calculated with $R_H$ via Eq. 16. The temperature dependence of $n$ is shown as the red dash line in Figure 43. Generally, $n$ decreases monotonically with decreasing $T$. The calculated $n$ is about $2 \times 10^{22}$ cm$^{-3}$ at 300 K which is about 4 times of that reported in Ref. [61]. It is comparable to other FeAs-based superconductors, for
example, $n$ of SrFe$_2$As$_2$ is about $1.52 \times 10^{22}$ cm$^{-3}$ at 300 K [135]. The large carrier concentration indicates that the normal state of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ behaves as a good metal.

3.4.5 Magnetization and Discussion

The magnetic property of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ is measured using methods described in Chapter 2.3.2. The superconducting susceptibility ($\chi$) of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ measured at 20 Oe is shown in Figure 44a as $4\pi\chi$. It exhibits bulk superconductivity as evidenced by a complete diamagnetic shielding signal with a transition temperature at $T_c = 32$ K. It is consistent with the transport property measurement analyzed in Chapter 3.4.1. The temperature dependence of the normal-state $\chi$ measured at 1000 Oe is shown in Figure 44b. For our measurements during both the field cooling (shown in blue color) and zero field cooling (shown in red color), we observed an anomaly at about 160 K. Above 160 K, the normal-state $\chi$ shows a weak linear T dependence as indicated by the solid fitting line in Figure 44b.

Figure 44. The temperature dependence of the superconducting-state susceptibility of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$: (a) $H = 20$ Oe, (b) $H=1000$ Oe.
The normal-state $\chi$ above 160 K increases with the decreasing temperature. To understand it, we start from the spin-density-wave (SDW) of iron based superconductors. An order parameter $\bar{n}$ is used to describe the SDW order. Applying the mean-field theory, $\bar{n}$ is independent of time and space. Above $T_{SDW}$, $\bar{n}$ is about 0 and global antiferromagnetism is absent. At $T_{SDW}$, $\bar{n}$ becomes nonzero and the directional long-range order develops which induces the SDW transition. Thus from the mean-field picture, we may expect to observe the normal metallic behavior with no antiferromagnetic behavior above $T_{SDW}$ in our sample. Hence, paramagnetic $\chi$ is expected in high temperature [136]. According to the Curie-Weiss law, $\chi$ increases with the decreasing temperature above the Curie temperature ($T_C$) due to the short-range exchange interaction between spins and exhibits a singularity at $T_C$ because of the ferromagnetic ordering under $T_C$. The normal-state $\chi$ behavior above 160 K and at 160 K in our samples fits in the scenario, yet leaving the linear behavior of normal-state $\chi$ unsolved. The linear $T$ dependence of $\chi$ is observed in the normal state of some FeAs-based superconductors, for example BaFe$_{1.8}$Co$_{0.2}$As$_2$ [137]. It has been shown theoretically that the linear $T$ dependence of $\chi$ is caused by the strong short range antiferromagnetic fluctuations [136]. Thus the observed normal-state $\chi$ behavior implies that it may be a result of both short-range paramagnetic fluctuation and antiferromagnetic fluctuation. Yet different from other FeAs-based superconductors whose $\chi$ drops quickly below the magnetic transition temperature [138], our result shows $\chi$ increases rapidly below the anomaly at 160 K. This phenomenon is similar to some cuprates, for example, La$_{2-x}$Sr$_x$CuO$_4$ [139].
Chapter 4. \( (Ca_{1-x}RE_x)_{10}Pt_3As_8((Fe_{1-y}Pt_y)As_2)_5 \) with RE= La/Gd

4.1 Motivation

\( Ca_{10}Pt_3As_8(Fe_2As_2)_5 \) is a sister compound of \( Ca_{10}Pt_4As_8(Fe_2As_2)_5 \). These two superconductors share similarities, yet have very different physical properties. The crystal structure of \( Ca_{10}Pt_3As_8(Fe_2As_2)_5 \) is plotted in Figure 45a. The spacer layers in \( Ca_{10}Pt_3As_8(Fe_2As_2)_5 \) consist of Ca layers and \( Pt_3As_8 \) layers. A plot of the \( Pt_3As_8 \) cutoff layer is shown in Figure 45b. Both sides of the Pt site in the middle are blocked by Ca atoms, so no Pt atoms can sit on this site.

Contrast to the phenomenon in \( Ca_{10}Pt_4As_8(Fe_2As_2)_5 \) whose \( T_c \) is maximum when there is no Pt doping on the Fe site, \( Ca_{10}Pt_3As_8(Fe_2As_2)_5 \) only displays superconductivity upon doping \([141][142][76]\). It has been reported that \( T_c \) of \( Ca_{10}Pt_3As_8(Fe_2As_2)_5 \) can be enhanced to 13.6 K by Pt doping on the Fe site \([141]\). While doping on the Ca site is more efficient in enhancing \( T_c \). The optimal \( T_c \) of \( Ca_{10-x}La_xPt_3As_8(Fe_2As_2)_5 \) is 35 K \([77][142]\). A list of elements has been used as dopants on the Ca site including Y, La-Nd, Sm-Lu by Sturzer et. al. \([76]\). The authors stated that
superconductivity arises in all studied compounds and depends only on the doping level instead of the type of doping. Among them, the highest $T_c$ is reached at 15% doping [76]. Hence, how superconductivity of $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ is influenced by doping is unclear. Furthermore, the anisotropy of $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ is studied by measuring the upper critical fields. The anisotropy parameter is reported to be 10 around $T_c$ [141] [143]. It makes $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ one of the most anisotropic FeAs-based superconductors. So we were intended to study the interlayer transport property of $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ with different doping to answer the question that how crystal structure influences anisotropy.

Several previous papers have reported the phase diagrams of different dopings for $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ as shown in Figure 46 [141] [142] [144]. Figure 46a-b is the phase diagrams of $\text{Ca}_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ with Pt doping on the Fe site, and $y$ is the doping level. $T_{\text{min}}$ in Figure 46a is defined as the temperature at which the normal-state electrical resistivity is minimum [144]. Below $T_{\text{min}}$, the parent compound and its underdoped compound behave as heavily doped semiconductors with no sign of magnetic ordering [141]. $T_{\text{min}}$ decreases with increasing doping level. Superconductivity region starts at $y \sim 0.02$ and it has a non-perfect dome-like shape. The overdoped region is incomplete for the reason that the properties of this region are affected by $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$. The maximum $T_c = 13.6$ K is achieved at the region $0.050 < y < 0.065$ [141]. Cho et. al. got a different result by analyzing the transport properties and the polarized-light images of the single crystals [141]. They find there is a structural transition at $T_s$, below $T_s$ the parent compound and the underdoped compounds show antiferromagnetic ordering [144]. Shown in Figure 46b, superconductivity emerges at $y = 0.028$ and reaches to the maximum 10.5 K at $y = 0.097$ [144]. Furthermore, they claim there is a clear separation between antiferromagnetism and superconductivity with the observation of the non-coexistence of zero resistivity and domain in
the polarized-light image [144]. Figure 46c plots the phase diagram for the $n = 3$ compound with La doping on the Ca site. $T_1$ is the magnetic phase transition at which the parent and underdoped compounds changes from paramagnetic ordering (higher temperature) to antiferromagnetic ordering (lower temperature) [142]. With the increasing doping level, the magnetic phase transition is suppressed. $T_c^R$ and $T_c^M$ are critical temperatures obtained from resistivity measurement and magnetization measurement, respectively. They are consistent with each other. Superconductivity occurs with a maximum $T_c \sim 26$ K at doping level $x = 0.145$ Figure 46c. It is unclear if there is a region where antiferromagnetism coexists with superconductivity. Thus, how doping influences the physical properties of the $n = 3$ compound remains to be unsettled.

Figure 46. The phase diagram of (Ca$_{1-x}$La$_x$)$_{10}$Pt$_3$As$_8$(Fe$_{1-y}$Pt$_y$)$_2$As$_2$: (a) The phase diagram of Pt doped $n = 3$ compound on the Fe site with the doping level $y$ [144] [141]; (c) The phase diagram of La doped $n = 3$ compound on the Ca site with the doping level $x$ [142].

More questions haven’t been answered including whether the doping on the Ca site change only $T_c$ or it also influences interlayer transport properties such as $\rho_c$. How does doping influence the anisotropy in the superconducting state and normal state? In order to answer these questions, we planned to study Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2)_5$ with Pt doping on the Fe site as well as La/Gd doping on the Ca site.
4.2 Crystal Growth

We prepare the samples in the single crystal form using the flux method described in Ch. 2.1. Single crystals were grown by heating a mixture of 99.999% pure Ca shot (Alfa Aesar), 99.95% Pt powder (Alfa Aesar), 99.95% Fe powder (Alfa Aesar) and 99.999% As powder (Alfa Aesar). For growing Ca$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$ single crystals, powder mixture with the ratio Ca: Pt: Fe: As = 9.5: 2.5: 10: 18 is used. This nominal ratio is found to grow Ca$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$, and the stoichiometric ratio with 10: 3: 10: 18 leads to the Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ phase. For growing (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ single crystals with RE = La, Gd, the mixture is RE: Ca: Pt: Fe: As = 1.0: 8.5: 2.5: 10: 18. The temperature profile is the same as the one used in growing Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ plotted in Figure 18. Each powder mixture is placed in an alumina crucible and double sealed in quartz tubes under vacuum. The whole assembly is then heated in a box furnace to 700 °C in 5 hours and held for 5 hours, further heated up to 1100 °C in another 5 hours and held at 1100 °C for 50 hours. It is then slowly cooled down to 1050 °C in 40 hours, and further cooled down to 500 °C in 100 hours. The sample is finally cooled down to room temperature by taking out of the furnace. We obtain plate-like crystals for

Figure 47. A prototypical Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ single crystal.

up to 1100 °C in another 5 hours and held at 1100 °C for 50 hours. It is then slowly cooled down to 1050 °C in 40 hours, and further cooled down to 500 °C in 100 hours. The sample is finally cooled down to room temperature by taking out of the furnace. We obtain plate-like crystals for
all studied materials among which a photo of Ca$_{10}$Pt$_3$As$_8$(Fe$_1$-$y$Pt$_y$)$_2$As$_2$ single crystal is shown in Figure 47.

4.3 Structure Characterization

XRD measurements are done on the doped Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ using the method described in Chapter 2.2. Figure 48 shows the XRD diffraction patterns for the doped Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ single crystals along the c axis. As indicated in Figure 48, all peaks can be indexed as [00$l$] ($l=2$-8) in the triclinic structure with space group symmetry P$_1$, which describes the Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ phase [140]. Each peak is sharp with the peak width ~ 0.1°, an indication of high-quality single crystals. With different doping concentration, these peaks shift, as demonstrated in Figure 49a for the [006] peak. It indicates that the lattice parameter $c$ (equivalent to the interlayer distance $d$) varies with doping concentration. The calculated $d$ is

![XRD diffraction peaks along c-axis of the doped Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$.](image)

Figure 48. The XRD diffraction peaks along c-axis of the doped Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$. 63
shown in figure Figure 49b, which apparently increases with increasing doping level. Furthermore, the chemical compositions of the single crystals are measured using EDX measurements described in Ch. 2.2.2. The EDX measurement results are summarized in Table 2. The overall results confirm the uniformity in a batch.

Figure 49. (a) The [006] peak of the doped Ca₁₀Pt₃As₈(Fe₂As₂)₅; (b) Calculated interlayer distance \( d \) of the doped compounds.

Table 2. EDX measurements results for the \( n = 3 \) compounds with various dopings.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Actual Doping</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La/Gd: Ca: Pt: Fe: As} )</td>
<td>( (\text{Ca}_{1-x}\text{RE}<em>x)</em>{10}\text{Pt}_3\text{As}<em>8((\text{Fe}</em>{1-y}\text{Pt}_y)_2\text{As}_2)_5 )</td>
</tr>
<tr>
<td>0: 9.5: 2.5: 10: 18</td>
<td>( x = 0, y = 0.022 \pm 0.003 )</td>
</tr>
<tr>
<td>0: 9.5: 2.5: 10: 18</td>
<td>( x = 0, y = 0.078 \pm 0.002 )</td>
</tr>
<tr>
<td>1: 8.5: 2.5: 10: 18</td>
<td>( x ) (La) = 0.126 ( \pm 0.003 ), ( y \approx 0 )</td>
</tr>
<tr>
<td>1: 8.5: 2.5: 10: 18</td>
<td>( x ) (Gd) = 0.071 ( \pm 0.001 ), ( y \approx 0 )</td>
</tr>
</tbody>
</table>

4.4 Physical Properties

4.4.1 Electrical Resistivity, Anisotropy and Discussion

Both the electrical resistivity and Hall effect are measured using methods described in Ch. 2.3.1. Figure 50a-b show the temperature dependence of in-plane \( \rho_{ab} \) and out-of-plane resistivity.
(ρ_c) between 2 K and 300 K. While the magnitudes of ρ_ab and ρ_c decrease with increasing doping concentration, data is normalized with room-temperature resistivity to avoid possible error introduced by geometric dimensions. Overall, ρ_ab and ρ_c have similar temperature profile for each doping. For y_{Pt} = 2.2% in the FeAs plane (x = 0), ρ_ab initially decreases with decreasing T then shows an upturn \( \frac{d\rho_{ab}}{dT} < 0 \) below \( T_x \sim 240 \) K. It quickly drops below \sim 16 K, reaching zero-resistivity state at 9.4 K. While it shows very similar temperature dependence, ρ_c does not reach the zero-resistivity state at 3.0 K (see Figure 50b). This indicates that there is poorer electrical conduction along the c axis than the ab plane. Nevertheless, magnetic susceptibility χ exhibits diamagnetism below 8.5 K, as shown in Figure 61a. Thus, we believe that the resistivity drop is due to the superconducting transition with \( T_c (y_{Pt} = 2.2\%) = 9.0 \pm 0.5 \) K. Upon the increase of Pt concentration to \( y_{Pt} = 7.8\% \) in the FeAs plane, ρ_ab has lower magnitude (not shown) and Figure 50. Electrical resistivities of \((Ca_{1-x}RE_x)_{10}Pt_3As_8((Fe_{1-y}Pt_y)_2As_2)_5\): (a) temperature dependence of in-plane resistivity \( \rho_{ab} \) plotted as \( \rho_{ab} / \rho_{ab}(300 \text{ K}) \) versus \( T \), where \( T_x \) is the crossover temperature for \( \rho_{ab} \) at which its behavior changes from metallic at high temperatures to non-metallic at low temperatures; (b) temperature dependence of out-of-plane resistivity \( \rho_c \) plotted as \( \rho_{c} / \rho_{c}(300 \text{ K}) \) versus \( T \).
smaller upturn range with $T_x \sim 183$ K. It reaches the zero-resistivity state at $T_c$ ($y_{Pt} = 7.8\%$) = 25.8±0.2 K (see Figure 2a), below which $\chi < 0$ as well (see Fig. 36c). For compounds that have partial substitution of Ca by Gd and La, the normal-state $\rho_{ab}$ is almost metallic with much smaller magnitude compared to the previous cases, and the superconducting transitions are much sharper with $T_c (x_{Gd} = 7.1\%) = 24 \pm 1$ K, and $T_c (x_{La} = 12.6\%) = 34.5 \pm 0.5$ K. Different of the normal state $\rho_{ab}$ of $x_{Gd} = 7.1\%$ sample which shows nonmetallic behavior below $T_x = 114$ K, $\rho_{ab}$ of $x_{La} = 12.6\%$ shows metallic behavior in its entire measured normal state and can be well described by the equation $\rho_{ab} = (0.449\pm0.002)+(0.00175\pm0.00001) T$. The linear T dependence of $\rho_{ab}$ is observed in some cuprates, for example LSCO as mentioned in Ch. 1.3.1 and it is suggested to be due to the inelastic scattering dominated electron-phonon interaction whose rate has a linear $T$ dependence. Our observation suggests that the enhancement of $T_c$ tends to suppress $T_x$. Combining the result we obtained from $\rho_{ab}(Ca_{10}Pt_4As_8(Fe_2As_2)_5)$, we plot $T_c$ as a function of the interlayer distance $d$ shown in Figure 51. There is a clear trend that compound with higher $d$ tends to exhibit higher $T_c$.

![Figure 51. Superconducting transition temperature $T_c$ versus the interlayer distance $d$.](image-url)
Unlike the in-plane resistivity $\rho_{ab}$ of Ca$_{10}$Pt$_4$As$_8$((Fe$_{0.95}$Pt$_{0.05}$)$_2$As$_2$)$_5$ which shows the metallic behavior at the normal state, the normal state $\rho_{ab}$ of (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$ shows a transition from being metallic at high temperatures to non-metallic at low temperatures. We may explain it as a similar system of parallel connected resistances we used in Chapter 3.4.1. A schematic plot of such system is shown in Figure 52a. The net resistance (R) is 

$$R = \frac{1}{n \left( \frac{1}{R_{FeAs}} + \frac{1}{R_{Pt3As8}} \right)}$$

in which $n$ is the number of unit cells in one sample, $R_{FeAs}$ and $R_{Pt3As8}$ are resistance of the FeAs layer and Pt$_3$As$_8$ layer. According to Ref. [61], the spacer layer Pt$_3$As$_8$ is semiconducting, then its resistivity should be much larger than FeAs layer. Thus, the net resistance R is dominated by the resistance from Pt$_3$As$_8$ and show an overall nonmetallic behavior in the normal state. According to our measurement results, such situation happens at $T < T_x$ for the normal state (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$. The normal state $\rho_{ab}$ of the sample with $x_{La} = 12.6$ % shows an overall metallic behavior. It implies 12.6 % La doping on the Ca site reduces the resistance of the spacer layer and Ca$_{1-x}$La$_x$ may contributes to the in-plane transport properties. Shown in Figure 50b, (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$ exhibits much poorer conduction along the out-of-plane direction in the normal state than the in-plane direction. Figure 52b gives a schematic plot of the out-of-plane resistors which consist of the series connecting FeAs layers and Pt$_3$As$_8$ layers. As a result, the net resistance along the out-of-plane is $R = n(R_{FeAs} + R_{Pt3As8})$. It implies the spacer layer Pt$_3$As$_8$ is semiconducting. Thus although FeAs layers maintains their metallic property, Pt$_3$As$_8$ layers between FeAs layers obstruct electron transportation along the out-of-plane direction making the net resistance showing the semiconducting behavior.
Figure 52. (a) A schematic plot of the parallel connecting FeAs layers and Pt$_3$As$_8$ layers; (b) a schematic plot of the series connecting FeAs layers and Pt$_3$As$_8$ layers.

Figure 53 shows the normal-state anisotropy calculated by $\gamma = \sqrt{\frac{\rho_c}{\rho_{ab}}}$ above 40 K. The layered nature of the system manifests itself in large anisotropy. Overall, $\gamma$ increases with the decreasing temperature for each measured compound. For $y_{Pt} = 2.2\%$ in the FeAs plane, $\gamma$ changes from 8.5 at 300 K to 9.5 at 40 K. It is larger than $\gamma$ of the sample with $y_{Pt} = 7.8\%$ which changes from 3.4 at 300 K to 5.0 at 40 K. It suggests that the sample with higher Pt doping tends to show lower anisotropy. Samples with La or Gd doping on the Ca site also have smaller $\gamma$ than sample with $y_{Pt} = 2.2\%$. Unlike the Pt doped sample whose $\gamma$ changes a lot with the changing temperature, $\gamma$ of the sample with $x_{La} = 12.6\%$ only increases slightly with the decreasing temperature. $\gamma$ is 6.3 at 300 K and changes to 6.5 at 40 K. And $\gamma$ of the sample with $x_{Gd} = 7.1\%$ changes from 4.6 at 300 K to 5.4 at 40 K. As discussed in Ch. 1.3, anisotropy is suggested to change with crystal structure in Fe-based superconductors. Among our results, the sample with the lowest $T_c$ and smallest interlayer distance (Ca$_{10}$Pt$_3$As$_8$((Fe$_{0.978}$Pt$_{0.022}$)$_2$As$_2$)$_s$) has the highest anisotropy. Thus, superconductivity does not prefer materials with high anisotropy. Compared
with other Fe-based superconductors shown in Figure 15, the experimental \( \gamma \) of LaFeAsO\(_{0.9}\)F\(_{0.1}\) is about 4 which is comparable to \( \gamma \) of the sample with \( x_{Gd} = 7.1\% \) and smaller than our other \((\text{Ca}_{1-x}\text{RE}_x)_{10}\text{Pt}_3\text{As}_8((\text{Fe}_{1-y}\text{Pt}_y)_2\text{As}_2)_5\).

![Graph](image)

**Figure 53.** The temperature dependence of the normal-state anisotropy \( \gamma \) above 40 K.

### 4.4.2 Upper Critical Field, Anisotropy and Discussion

The anisotropy (\( \gamma \)) in the superconducting state of \((\text{Ca}_{0.874}\text{La}_{0.126})_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5\) is evaluated through \( \rho_{ab} \) measurement under the application of magnetic field \( H \) along \( H//c \) and \( H//ab \). Figure 54a-b show temperature dependence of \( \rho_{ab} \) at \( T < 40 \text{ K} \). At both \( H//c \) and \( H//ab \), the superconducting transition is pushed to lower temperatures by the application of \( H \), indicating \( H \) suppressing superconductivity. The upper critical field \( H_{c2}(T) \) for \( \rho = 0.9\rho_n, 0.5\rho_n, 0.1\rho_n \) is identified as what we did for \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \). The extracted \( H_{c2} \) is then plotted as \( H_{c2} \) vs \( T \) in Figure 55a-b for \( H//c \) and \( H//ab \). In each case, \( H_{c2} \) increases monotonically with decreasing temperature. We calculated \( H_{c2}(0) \) using WHH approximation, as well as \( \xi_{ab}(0) \) and \( \xi_c(0) \) using
the same method as we did for Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$. The estimated values are presented in Table 3. Similar to Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$, (Ca$_{0.874}$La$_{0.126}$)$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ exhibits large anisotropy in either criteria. The ratio $\gamma = \frac{H_{c2}^{ab}}{H_{c2}^{c}}$ is plotted in Figure 56. The normal-state anisotropy we obtained from $\gamma = \sqrt{\rho_c/\rho_{ab}}$ around $T_c$ is almost identical for $\gamma$ from the upper critical field taken at 90 % resistivity drop. Compared to 122 type, for example $\gamma \sim 2$ for BaFe$_2$As$_2$ [101] [102] [103] [104], $\gamma = 7$ around $T_c$ is larger, while it is similar to 1111 type where $\gamma \sim 5 - 10$ for SmFeAsO [105].

Figure 54. The temperature dependence of $\rho_{ab}$ for (Ca$_{0.874}$La$_{0.126}$)$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ with an applied magnetic field $H \parallel c$ (a) and $H \parallel ab$ (b) in the superconducting state.

Figure 55. The upper critical field $H_{c2}$ with $H \parallel c$ (a) and $H \parallel ab$ (b).
4.4.3 Hall Coefficient and Discussion

To understand the doping effect on the electrical transport, we have measured the Hall effect of the four compounds. Figure 57a shows the temperature dependence of normal-state Hall coefficient ($R_{H}$) for $(Ca_{1-x}Re_{x})_{10}Pt_{3}As_{8}(Fe_{2}Pt_{2}As_{2})_{5}$ obtained by measuring the Hall resistivity under both positive and negative field. $R_{H}$ is negative between 40 K and 300 K for all four compounds, suggesting that charge carriers are electron dominant despite the doping site and the doping level. This is consistent with the negative thermopower measured previously in Pt-doped
compounds [145]. For each compound, \( R_H \) becomes more negative with decreasing temperature, as reported in Ref. [140]. While there is almost no difference at \( T > 150 \) K, they start to diverse below \( \sim 150 \) K with faster dropping in lower doping. Due to its multiband nature with both the electron and hole bands at the Fermi level [96], interpretation of \( R_H \) is not straight forward.

![Figure 57](image1)

Figure 57. (a) Temperature dependence of the Hall coefficient \( (R_H) \) in the normal state; (b) Temperature dependence of Hall mobility \( (\mu) \) of the studied samples at \( H = 1 \) T.

![Figure 58](image2)

Figure 58. \( 1/R_H \) as a function of \( T_c \) at \( T = 50 \) K.
Since the mobility \(\mu = -\frac{R_H}{\rho_{ab}}\) is insensitive to the doping site and the doping level as shown in Figure 57b, it is suggestive that the difference seen below 150 K reflects the change of carrier concentration. In order to compare \(R_H\) among the studied compounds, we plot \(1/ R_H\) vs \(T_c\) at \(T = 50\text{ K}\) in Figure 58. Note that larger \(1/ R_H\) gives rise to higher \(T_c\), suggesting all doping increases the enhanced electron concentration. While it is obvious for the partial substitution of Ca\(^{2+}\) by La\(^{3+}\) or Gd\(^{3+}\), less apparent is the replacement of Fe by Pt, which was considered to be isovalent [68].

The above information helps to understand the normal-state electrical transport behavior. As predicted theoretically [146] and observed experimentally [141] [143], the undoped Ca\(_{10}\)Pt\(_3\)As\(_8\)(Fe\(_2\)As\(_2\))\(_5\) is non-metallic due to the semiconducting Ca\(_{10}\)Pt\(_3\)As\(_8\) spacer [75] [147]. Upon doping of Pt in the Fe site, the better electrical conduction of the Fe\(_2\)As\(_2\) plane reduces both \(\rho_{ab}\) and \(\rho_c\) but remaining non-metallic character due to the insulating Ca\(_{10}\)Pt\(_3\)As\(_8\). If Ca is partially replaced by La\(^{3+}\)/Gd\(^{3+}\), additional electron carriers result in conductive Ca\(_{10-x}\)RE\(_x\)Pt\(_3\)As\(_8\), leading to metallic \(\rho_{ab}\) and \(\rho_c\) in the normal state.

### 4.4.4 Magnetoresistivity and Discussion

Figure 59 shows the field dependence of normal-state transverse magnetoresistivity \(\text{(MR}_{ab}\text{)}\) of \((\text{Ca}_{1-x}\text{RE}_x)_{10}\text{Pt}_4\text{As}_8((\text{Fe}_{1-y}\text{Pt}_y)_{2}\text{As}_2)\)\(_5\), H from 0 Tesla to 14 Tesla. With as little as 2.2 % Pt replacing Fe, the normal state \(\text{MR}_{ab}\) has a linear relationship to \(H\) as seen in Figure 59a. And negative \(\text{MR}_{ab}\) is shown with higher temperature indicating a strong spin-orbit interaction. It shows an explicit difference from the normal situation where the resistance of a conductor with an applied magnetic field changes quadratically with the field when there is a single carrier type. More Pt replacing Fe \((y_{\text{Pt}} = 7.8\% )\) results in a decrease of the magnitude of \(\text{MR}_{ab}\), while the property of
linear $MR_{ab}$ holds in Figure 59b. Shown in Figure 59c-d, Gd doping in the Ca-site leads to positive linear $MR_{ab}$ in the normal state, while La doping results in a much smaller magnitude of $MR$, but it doesn’t eliminate the linearity of $MR_{ab}$. Figure 60 plots $MR_{ab}$ as a function of temperature at 14 T for each measured sample. While $MR_{ab}$ of $(Ca_{0.929}Gd_{0.071})_{10}Pt_3As_8(Fe_2As_2)_5$ decreases with the increasing temperature similar to $Ca_{10}Pt_4As_8((Fe_{0.95}Pt_{0.05})_2As_2)_5$ shown in Ch. 3.4.3, $MR_{ab}$ of other three measured samples shows a small upturn at $T_1 = 110$ K for $Ca_{10}Pt_3As_8((Fe_{0.978}Pt_{0.022})_2As_2)_5$, 200 K for $Ca_{10}Pt_3As_8((Fe_{0.922}Pt_{0.078})_2As_2)_5$ and 130 K for $(Ca_{0.874}La_{0.126})_{10}Pt_3As_8(Fe_2As_2)_5$.

Figure 59. The field dependence of the transverse magnetoresistivity ($MR_{ab}$) of $(Ca_{1-x}RE_x)_{10}Pt_3As_8((Fe_{1-y}Pt_y)_2As_2)_5$: (a) $y_{Pt} = 2.2\%$; (b) $y_{Pt} = 7.8\%$; (c) $x_{Gd} = 7.1\%$; (d) $x_{La} = 12.6\%$. 

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Figure 60. The temperature dependence of MR\textsubscript{ab} at a fixed magnetic field.

In Chapter 3.4.3, the possible causes of linear MR have been discussed. Here we discuss if the classical or quantum causes can be applied in (Ca\textsubscript{1-x}RE\textsubscript{x})\textsubscript{10}Pt\textsubscript{3}As\textsubscript{8}(Fe\textsubscript{1-y}Pt\textsubscript{y})\textsubscript{2}As\textsubscript{2}\textsubscript{5}. The classical model fits in the scenario when the system has a strong disorder. In our results, the linear MR\textsubscript{ab} behavior shows up in compounds with doping or without doping, and when the system is doped, the linear MR\textsubscript{ab} behavior is independent of the doping elements or doping level. So it may also not be able to fit in the existing classical model [122] [123] [121]. On the other hand, the quantum model describes the system when there is a Dirac cone forming around the Fermi surface. According to the already published electronic structure and ARPES (Angle-Resolved Photo Emission Spectroscopy) image of Ca\textsubscript{10}Pt\textsubscript{3}As\textsubscript{8}(Fe\textsubscript{2}As\textsubscript{2})\textsubscript{5} [96], there is no trace of Dirac cone energy dispersion around its Fermi surface, so our results are unlikely to fit in the quantum model [126] [127] [125]. Thus, the linear MR\textsubscript{ab} in our studied compound is quite unique and cannot be explained.
by the existing theories. Despite the doping method, the normal state transversal $MR_{ab}$ is much larger than the longitudinal $MR_c$ ($\sim 0.05 \%$) suggesting all the studied compounds have a large resistivity anisotropy in the normal state. Another possible cause for the linear $MR_{ab}$ behavior is the quantum interference effect. It may fit in the scenario of $(Ca_{1-x}RE_x)_{10}Pt_3As_8((Fe_{1-y}Pt_y)_{2}As_2)_{5}$ for its ability to explain the linear behavior over large magnetic field range in systems with disorder [108] [131]. Furthermore, systems in which the moments of s electrons and d electrons are antiparallel exhibit negative $MR$ [108]. In our observation, $MR_{ab}$ of $Ca_{10}Pt_3As_8((Fe_{0.978}Pt_{0.022})_{2}As_2)_{5}$ and $(Ca_{0.874}La_{0.126})_{10}Pt_3As_8(Fe_{2}As_2)_{5}$ is negative above their upturn temperature $T_1$. Because $T_1$ is very close to the crossover temperature $T_2$ observed in the magnetization measurements which we will discuss in the next section, the negative $MR_{ab}$ may be related to the antiferromagnetic fluctuation.

### 4.4.5 Magnetization and Discussion

From both electrical resistivity and magnetic susceptibility, it is noticeably that both $T_c$ value and normal-state metallicity increase with increasing doping concentration regardless the doping site. However, the normal-state magnetic susceptibility seems to be strongly doping dependent as shown in Figure 61b. The normal state $\chi_{ab}$ of $Ca_{10}Pt_3As_8((Fe_{0.78}Pt_{0.22})_{2}As_2)_{5}$ shown as red dots in Figure 61b has similar features with other FeAs-based superconductors [70] [136], for example, LaFeAsO$_{1-x}$F$_x$ [139] and CaFe$_2$As$_2$ [139] [148]. Its $\chi_{ab}$ has linear dependence on temperature above $T_2 = 131$ K. This behavior is not Pauli paramagnetic like and Ref. [138] suggests it is due to the short-range antiferromagnetic fluctuations. $T_2$ is likely due to the magnetic/structural transition [149]. There is no such transition observed in the sample with larger Pt doping level $y_{Pt}=7.8\%$, similar to LaFeAsO$_{0.94}$F$_{0.06}$ which is nearly optimal doping [139]. The linear $T$ dependence of $\chi_{ab}$ is also observed in the sample with $x_{La} = 12.6\%$ shown as blue dots in Figure 61b. While the
positive $d\chi/dT$ still exists in the case of $x_{La} = 12.6\%$, there is an upturn below $\sim 150$ K. Such upturn is much more obvious in the Gd-doped case. By doing Curie-Weiss fitting $\chi = \frac{C}{T+\theta}$ on the Gd-doped case, the Curie constant $C$ is calculated as $(4.60 \pm 0.05) \text{ cm} \cdot \text{K/mol}$ and the Weiss constant $\theta$ is $(6.0 \pm 0.5) \text{ K}$. The positive Weiss constant implies the contribution of short-range antiferromagnetic interaction to the magnetic susceptibility. As discussed in Ch. 4.1, there is a debate on whether the parent compound and underdoped compounds of Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ are antiferromagnetic or not [140] [141] [143]. Our results support the existence of antiferromagnetism in the doped Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$.

![Figure 61](image)

The temperature dependence of the susceptibility $\chi$ measured at $H = 0.002$ T (a) and $\ln \chi$ at $H = 0.1$ T (b). The red, orange, black and blue dots are obtained by measuring (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$ with $y_{Pt} = 2.2\%$, $y_{Pt} = 7.8\%$, $x_{Gd} = 7.1\%$ and $x_{La} = 12.6\%$, respectively.

### 4.4.6 Magnetic Force Microscopy Images and Discussion

For a type-II superconductor, another important parameter is the penetration depth ($\lambda$) which describes the decay length of magnetic flux quanta in the mixed state. We investigate the mixed state property of Ca$_{10}$Pt$_3$As$_8$((Fe$_{0.922}$Pt$_{0.078}$)$_2$As$_2$)$_5$ and (Ca$_{0.874}$La$_{0.126}$)$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$.
using magnetic force microscopy (MFM) (Attocube). In our MFM setup, NANOSENSORS PPP-MFMR (Point Probe Plus Magnetic Force Microscopy Reflex Coating) probes are used the tip of which is coated thinly with Co offering magnetic resolution $\geq 50$ nm. The tip is subjected to the Meissner response of the superconducting sample as well as the magnetic field from the vortices if they are presented. We studied the phase modulated MFM in which the phase ($\phi$) of the oscillation of the tip is shifted by the $z$-component of magnetic forces ($F_z$) while the frequency ($f$) is kept as constant: $\Delta \phi \approx \frac{Q}{k} \frac{\partial F_z}{\partial z}$ where $Q$ is vibrating system quality factor and $k$ is the force constant. During the measurement, the tip is scanned at a fixed height $z$ above the sample surface. As discussed in Ch. 2.3.3, parameters regarding the sharpness of the tip on the cantilever are used to model the force between the tip and the sample surface [84] [85] [86]. Thus we scanned the SEM images of several tips to calculate the parameters. Figure 62 shows the scanning electron microscopy (SEM) image of an MFM tip measured using Quanta 3D DualBeam Field Emission Gun (FEG) Focused Ion Beam (FIB) - SEM (FEI). The tip has a polygon based pyramid shape and is characterized by a few geometric parameters: the cone half-angle ($\theta = 15.43^\circ$), the length of the cone edge ($h = 285$ nm) and the effective magnetic height of the tip ($H = 11$ $\mu$m).

![SEM image of MFM tip](image)

Figure 62. The SEM image of the entire tip of a cantilever, $h$ is the length of the cone edge and $\theta$ is the cone half-angle.
Figure 63 shows MFM image of vortices of Ca$_{10}$Pt$_3$As$_8$((Fe$_{0.922}$Pt$_{0.078}$)$_2$As$_2$)$_5$ under 4.2 K and 100 Oe. The two hole-like vortices have almost the same size and their radius is about 50 nm. We obtained clearer vortex image of (Ca$_{0.874}$La$_{0.126}$)$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ at various temperatures and magnetic fields shown in Figure 65. The MFM image strength is influenced by the quality factor ($Q$). Figure 64a-b exhibit the resonance frequency curves measured at $T = 4.2$ K and 10 K, respectively. The resonance frequency $f_0$ are then extracted: $f_0(4.2$ K) = 88.108 kHz and $f_0(10$ K) = 88.098 K. $Q$ of the scans are calculated using the equation $Q = f_0/\Delta f$ in which $\Delta f$ is the width at half of the maximum resonance frequency: $Q(4.2$ K) = 8010 and $Q(10$ K) = 2670. Figure 65a-d show MFM images of vortices under different temperatures and applied fields. At $T = 4.2$ K, vortices are clearly seen, and are ordered (Figure 65a-d) with a tendency to melt under high field (Figure 65c). Upon warming to 10 K, the vortex lattice remains under 50 Oe (figure 5d). Figure 65e-f are the line profiles of vortex under $H = 50$ Oe and $T = 4.2$ K. For a fair comparison, each line profile is corrected by the quality factor under the corresponding scan temperature.

![MFM image of vortices](image)

Figure 63. The vortices image of Ca$_{10}$Pt$_3$As$_8$((Fe$_{0.922}$Pt$_{0.078}$)$_2$As$_2$)$_5$ at 4 K under an applied field $H = 100$ Oe.
Figure 64. The resonance frequency curve under $T = 4.2$ K (a) and $T = 10$ K (b).

Figure 65. MFM images of vortices of $(Ca_{0.874}La_{0.126})_{10}Pt_3As_8(Fe_2As_2)_5$ under different temperatures and magnetic fields: (a) $T = 4.2$ K, $H = 50$ Oe, (b) $T = 4.2$ K, $H = 100$ Oe, (c) $T = 4.2$ K, $H = 150$ Oe, (d) $T = 10$ K, $H = 50$ Oe; (e) the averaged line profiles along a single vortex cut-through under $H = 50$ Oe and different temperatures; (f) the averaged line profiles along a single vortex cut-through under $T = 4.2$ K and different magnetic fields.

The magnetic field distribution of a single vortex from its core can be described by $B(x) = B(0) \exp[x/\lambda]$. Then the gradient of the phase shift $\Delta \theta$ should be a function of the gradient of
B. By examining \( \ln\left(\frac{\partial \Delta \theta}{\partial x}\right) = \alpha \ln(\lambda/x) + C \) in which \( \alpha \) and \( C \) are functions of \( B(0) \) and \( x \), the derivative of \( \Delta \theta \) at \( x = \lambda \) shows a sudden change. Using this method, the penetration depths are extracted: \( \lambda(4\text{K}, 50\text{ Oe}) = (0.243 \pm 0.008) \mu\text{m} \), \( \lambda(10\text{K}, 50\text{ Oe}) = (0.17 \pm 0.01) \mu\text{m} \), \( \lambda(4\text{K}, 100\text{ Oe}) = (0.177 \pm 0.008) \mu\text{m} \), \( \lambda(4\text{K}, 150\text{ Oe}) = (0.17 \pm 0.02) \mu\text{m} \). Because the range of the magnetic field is too small compared to the residual magnetic field of PPMS, the estimated \( \lambda \) of 50 Oe, 100 Oe and 150 Oe are similar to each other.
Chapter 5. CaFeAs$_2$ and Ca$_{0.85}$La$_{0.15}$FeAs$_2$

5.1 Motivation

The newly discovered Fe-based superconductor CaFeAs$_2$ shed light on the topic of topological superconductor [58] [150] [151]. CaFeAs$_2$ has similar spacer layers as Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ as shown in Figure 66a. The crystal structure of this new plate-like crystal unit cell consists of Fe$_2$As$_2$ layer, Ca layer and a As chain layer. With La doping on the Ca site, Ca$_{1-x}$La$_x$FeAs$_2$ has been reported to crystallize in a monoclinic structure with the space group P2$_1$ [150]. The interlayer distance is 10.311 Å which is also similar to Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ [58]. Yet, its upper critical field exhibits a smaller anisotropy ($\gamma = 2 - 4.2$) than Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ [63]. Pr doped CaFeAs$_2$ exhibits superconductivity at $T_c \sim 20$K [58], and $T_c$ of P/Sb doped Ca$_{1-x}$La$_x$FeAs$_2$ can be up to 43 K at certain doping level [152]. The intriguing aspect about CaFeAs$_2$ is that the p$_x$ and p$_y$ orbitals of the As atoms form an anisotropic Dirac Cone near the Fermi surface [78] [79] which is a common feature in topological insulators (Figure 66b). It makes CaFeAs$_2$ a good candidate to study the topological superconductor. The ARPES study on this compound suggests its electronic structure is largely influenced by the interaction between the superconducting layer and the spacer layers [153]. So, we chose to extend our research in studying CaFeAs$_2$ in comparison to Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ for its similar crystal structure, yet smaller anisotropy. In this way, we hope to answer the question that if high $T_c$ prefers high anisotropy and how doping changes $T_c$ as well as the physical properties. We also want to explore if CaFeAs$_2$ exhibits any physical properties of topological superconductors, for example the linear magnetoresistivity.
Figure 66. (a) The crystal structure of Ca\textsubscript{0.73}Pr\textsubscript{0.27}FeAs\textsubscript{2} [58]; (b) The orbital characters of bands near Fermi surface [78].

5.2 Crystal Growth

We were intended to grow single crystals of CaFeAs\textsubscript{2} by the flux method described in Ch. 2.1 with pure elements Ca, As and a precursor FeAs. The usage of the precursor was experimentally proved to help grow a more stable phase of CaFeAs\textsubscript{2}. We conducted the precursor growth by mixing the high-quality Fe powder (99.95 % Alfa Aesar) and As powder (99.999 % Alfa Aesar) in a 1:1 ratio, and followed the temperature profile illustrated in Figure 67. The resulting precursor is then grounded finely for the purpose of even distribution in growing CaFeAs\textsubscript{2}. The Calcium shot (99.999 % Alfa Aesar), FeAs and As powder is then mixed in a 1:1:1 ratio. The temperature profile shown in Figure 68 is also different from the growth of our previous studied two materials. The annealing process after the cool-down allows atoms migrate in the crystal lattice leading to a more equilibrium growth. The method was adopted from the single crystal growth of (Ca,Pr)Fe\textsubscript{2}As\textsubscript{2} [154]. Besides the parent compound, the La doped CaFeAs\textsubscript{2} is grown using the same temperature profile. The nominal doping levels for La on the Ca site 10% are and 15%. It was reported that the 12.7% doping on the Ca site helps to form stable crystal
structure of (Ca,Pr)Fe$_2$As$_2$ [155]. In multiple trials of growing CaFeAs$_2$, we found that crystals of undoped CaFeAs$_2$ as well as Ca$_{0.9}$La$_{0.1}$FeAs$_2$ are more difficult to form stable phases than Ca$_{0.85}$La$_{0.15}$FeAs$_2$. Polycrystals of CaFeAs$_2$ and Ca$_{0.85}$La$_{0.15}$FeAs$_2$ are obtained. Because of the instability of the CaFeAs$_2$ polycrystals, we were only able to investigate the physical properties of Ca$_{0.85}$La$_{0.15}$FeAs$_2$.

![Temperature profile to grow FeAs precursor](image1)

**Figure 67.** The temperature profile to grow FeAs precursor.

![Temperature profile to grow CaFeAs$_2$](image2)

**Figure 68.** The temperature profile to grow CaFeAs$_2$. 
5.3 Structure Characterization

The powder XRD measurements are done using the method described in Ch. 2.2.1. Compared to the reported data from previous paper [58] [156], most of the peaks from the XRD spectrum of both CaFeAs$_2$ and Ca$_{0.9}$La$_{0.1}$FeAs$_2$ presented in Figure 69 match the reported spectrum which suggests that the samples we obtained have the same triclinic symmetry as the reported ones.

![Powder XRD spectrum of CaFeAs$_2$ and Ca$_{0.85}$La$_{0.15}$FeAs$_2$.](image)

Figure 69. Powder XRD spectrum of CaFeAs$_2$ and Ca$_{0.85}$La$_{0.15}$FeAs$_2$.

5.4 Physical Properties

5.4.1 Electrical Resistivity and Discussion

The resistivity ($\rho$) of Ca$_{0.85}$La$_{0.15}$FeAs$_2$ is measured from 2 K to 300 K and plotted as $\rho/\rho(300 \text{ K})$ shown in Figure 70. The normalized $\rho$ starts to drop at 130 K and drop sharply below 70 K. Although the normalized $\rho$ is nonzero at 2 K, its small value implies that the superconducting sample has non-superconducting impurities which influences the overall resistivity feature. The transition is broad which may be due to the inhomogeneous La concentration of the
superconducting phases in the polycrystalline sample. Between 250 K and 130 K, the normal state \( \rho \) shows an overall metallic behavior which is consistent with the in-plane resistivity from the reported data [150]. The overall shape of \( \rho \) is very similar to the reported data of \( \text{Ca}_{0.9}\text{La}_{0.1}\text{FeAs}_2 \) [58] [157].

![Graph](image)

Figure 70. Temperature dependence of the resistivity \( \rho \) plotted as \( \rho/\rho(300 \text{ K}) \) versus T.

### 5.4.2 Magnetoresistivity and Discussion

Figure 71a shows the field dependence of the normal-state transverse \( MR \) of \( \text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2 \). At each fixed field, \( MR \) decreases with the increasing temperature. Different from \( \text{Ca}_{10}\text{Pt}_{n}\text{As}_8(\text{Fe}_2\text{As}_2)_5 \), \( MR \) of \( \text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2 \) shows a quadratic dependence on \( H \) at low \( H \) which fits in the situation of normal metals with single carrier type. Figure 71b plots \( MR \) as a function of \( H^2 \). According to Ref. [125] [126] [127], materials with Dirac cone shape electronic structure around the Fermi surface will have MR linear to the applied magnetic field. But in our data, although the Dirac cone shows up in \( \text{CaFeAs}_2 \) [78] [79], \( MR \) of low temperatures shows an overall \( H^2 \) dependence rather than the linear dependence. \( MR \) of iron is reported to first decrease
with increasing field at small $H$ and increases with increasing $H$ at high $H$ [158], so one possibility causing the feature we observed in $\text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2$ may come from the Fe impurities.

Figure 71. (a) Field dependence of the magnetoresistivity ($MR$) of $\text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2$ above 40 K; (b) $MR$ as a function of $H^2$.

5.4.3 Magnetization and Discussion

Figure 72 shows the temperature dependence of the superconducting-state and the normal state $\chi$ of $\text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2$. The measurement is done on pieces selected from the same growth batch and arrange at the direction that $H//ab$ plane. The zero-field-cooling (ZFC) superconducting-state $\chi$ starts to drop at 19.8 K and drop sharply below 9.2 K as seen in Figure 72a confirming the polycrystals we obtained are superconducting. The normal-state $\chi$ shown in Figure 72b first increases with decreasing $T$ and changes to decreases with decreasing $T$ below $\sim190$ K. The crossover temperature is almost the same as the temperature where resistivity starts to drop with temperature shown in Figure 70. Considering the nature of polycrystalline sample, it may be due to the inhomogeneous La distribution or Fe impurities.
Figure 72. Temperature dependence of the superconducting-state susceptibility ($\chi$) at $H = 0.002\ T$ (a) and the normal-state Susceptibility at $H = 0.1\ T$.
Chapter 6. Summary

In this work, we have explored the synthesis and physical properties of Ca-FeAs-based superconductors including Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$, (Ca$_{1-x}$RE$_x$)$_{10}$Pt$_3$As$_8$((Fe$_{1-y}$Pt$_y$)$_2$As$_2$)$_5$ using RE = La or Gd and Ca$_{1-x}$La$_x$FeAs$_2$. We have obtained high-quality single crystals of Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$, Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ as well as its doped samples and polycrystals of Ca$_{1-x}$La$_x$FeAs$_2$. By studying their resistivity, upper critical field, Hall effect, magnetoresistivity, magnetization and vortex image, we investigated the following questions: how the extra Pt in the Pt$_n$As$_8$ layer changes the superconductivity and normal state in the Ca$_{10}$Pt$_n$As$_8$(Fe$_2$As$_2$)$_5$ system; how the crystal structure influences $T_c$; how doping affects the anisotropy in the Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$.

We observed metallic in-plane resistivity but non-metallic out-of-plane resistivity for Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$. The property anisotropy is unusual and its normal state resistivity exhibits a large anisotropy (~7.5) near $T_c$ making it one of the most anisotropic FeAs-based superconductors. The normal state in plane resistivity has the square root temperature dependence which may be intrinsic to Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$. The interlayer incoherent scattering contributes to the out of plane transport property. Large coherence length and upper critical field are observed.

Moreover, our observation in Ca$_{10}$Pt$_3$As$_8$(Fe$_2$As$_2$)$_5$ suggests chemical doping is an effective way to induce superconductivity. Although doping rare-earth elements in the Ca site result in higher $T_c$ than the Pt doping in the Fe site, it is found that $T_c$ is more or less linearly depending on $1/R_H$ and the interlayer distance d. This suggests that the low dimensionality and high carrier concentration favor superconductivity. On the other hand, the normal-state electrical resistivities ($\rho_{ab}$ and $\rho_c$) change from non-metallic character to metallic behavior upon the increase of $T_c$, indicating the coherent electrical transport between the ab plane and the c axis. This is further...
reflected in the small temperature dependence of the resistivity anisotropy, even though it is ~7 near $T_c$. Nevertheless, the high $H_{c2}$ and short $\xi$ estimated from superconducting $(\text{Ca}_{0.874}\text{La}_{0.126})_{10}\text{Pt}_3\text{As}_8(\text{Fe}_2\text{As}_2)_5$ are similar to that found in other Fe-based superconductors.

Linear $H$ dependent magnetoresistivity has been observed in both $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ and $(\text{Ca}_{1-x}\text{RE}_x)_{10}\text{Pt}_3\text{As}_8((\text{Fe}_{1-y}\text{Pt}_y)_2\text{As}_2)_5$ which may be related to the quantum interference effect. While their susceptibility suggests the existing antiferromagnetic fluctuation.

Our investigation on $\text{CaFeAs}_2$ implied that $\text{CaFeAs}_2$ and $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ are difficult to obtain the stable single crystals. Yet between these two, La doped compound is more stable than the undoped compound. $\text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2$ shows superconducting property in transport and magnetic property measurements. Although the band structure study suggests the Dirac-cone shape energy dispersion around the Fermi surface which should cause the linear $H$ dependence of magnetoresistivity, $MR$ of $\text{Ca}_{0.85}\text{La}_{0.15}\text{FeAs}_2$ shows quadratic dependence on $H$. 
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Vita

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