Electrical and Thermal Transport Properties of Layered Superconducting \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.86}\text{Pt}_{0.14})_2\text{As}_2)_5 \) Single Crystal

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Abstract: We have synthesized single crystals of iron-based superconducting \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.86}\text{Pt}_{0.14})_2\text{As}_2)_5 \) and performed extensive measurements on their transport properties. A remarkable difference in the behavior and a large anisotropy between in-plane and out-of-plane resistivity was observed. Disorder could explain the in-plane square-root temperature dependence resistivity, and interlayer incoherent scattering may contribute to the out-of-plane transport property. Along the ab plane, the estimated value of the coherence length is 15.5 Å. From measurements of the upper critical magnetic field \( H_{c2} \) (\( T \geq 20 \) K), we estimate \( H_{c2}(0) = 313 \) T. Thermal conductivity for \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.86}\text{Pt}_{0.14})_2\text{As}_2)_5 \) is relatively small, which can be accounted for by the disorder in the crystal and the low-charge carrier density as verified by the Hall effect.

Keywords: electronic anisotropy; coherence length; upper critical field; Hall effect; thermal conductivity

1. Introduction

The \( \text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) (\( n = 3 \) or 4) system was first reported to exhibit superconductivity with a wide range of transition temperatures in 2011 [1–3]. After that, many studies have appeared in the past seven years [4–8]. \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) has a layered structure consisting of superconducting FeAs layers separated by the spacer layers arranged as Ca–Pt\(_4\)As\(_8\)–Ca, which is shown in Figure 1a. This superconductor has been reported to crystallize in possible space groups including \( P4/n \) (tetragonal) [2,3], \( P2_1/n \) (monoclinic) [7], and \( \tilde{P}T \) (triclinic) [1,3]. The structure of the Pt\(_4\)As\(_8\) spacer layer is similar to a square lattice of As atoms, one fifth of the As atoms are replaced by substitutional Pt\(_1\) atoms [2], and the same amount of Pt\(_2\) atoms are interstitial, which leads to the displacement of As atoms from their ideal positions to form As dimers [2]. Because of the constraint from the As–As dimers and the FeAs sublattices, substitutional Pt\(_1\) atoms can sit in plane while the interstitial Pt\(_2\) atoms sit on the site either above or below the plane against Ca ions.

Most FeAs-based superconductors need doping to induce the superconductivity; \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) allows doping on the Ca site or on the Fe site. In particular, Pt doping on the Fe site could bring faults and disorder into the crystal and also adjust the \( T_c \) [2,5]. By studying its structure and physical properties, the origin of superconductivity may be elucidated. The interlayer distance of \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) is reported to be \( \sim 10.5 \) Å [2,3], which is larger than many other FeAs-based superconductors, and thus its properties are expected to be anisotropic.
The electronic structure for Ca\textsubscript{10}(Pt\textsubscript{4}As\textsubscript{8})(Fe\textsubscript{2}As\textsubscript{2})\textsubscript{5} has been studied via angle resolved photoemission spectroscopy (ARPES) \cite{9}. Generally, there is a hole pocket and an electron pocket around the zone center. There are several electron pockets around the zone corner, among which two are suggested to be contributed by the FeAs layer, and several are contributed by Pt\textsubscript{4}As\textsubscript{8} layers. Thus, the Pt\textsubscript{4}As\textsubscript{8} layer is suggested to be metallic. Furthermore, the d\textsubscript{xy} and d\textsubscript{yz} bands are not degenerate at the Brillouin zone center (Γ point) and there is only hole-like Fermi surface at the Γ point originated from d\textsubscript{xy} orbitals, it may be caused by the interaction between the Pt\textsubscript{4}As\textsubscript{8} and FeAs layers \cite{9}.

In this paper, we studied the electrical properties of Ca\textsubscript{10}(Pt\textsubscript{4}As\textsubscript{8})(Fe\textsubscript{2}As\textsubscript{2})\textsubscript{5} along its c-axis in order to understand how the interaction between Pt\textsubscript{4}As\textsubscript{8} and FeAs layers influences the physical properties and anisotropy in this system. In addition, thermal conductivity has not yet been reported as another approach in measuring transport properties, and thus we also provide more extensive measurements and discussion on this approach.

2. Material Preparation and Characterization Methods

The preparation process is similar to descriptions provided elsewhere \cite{2,4}. To grow single crystals of Ca\textsubscript{10}(Pt\textsubscript{4}As\textsubscript{8})(Fe\textsubscript{2}−\textsubscript{x}Pt\textsubscript{x}As\textsubscript{2})\textsubscript{5}, stoichiometric amounts of high purity Ca shot (99.999%, Alfa Aesar, Haverhill, MA, USA), Fe powder (99.95%, Alfa Aesar, Haverhill, MA, USA), Pt powder (99.95%, Alfa Aesar, Haverhill, MA, USA), and As powder (99.999%, Alfa Aesar, Haverhill, MA, USA) were mixed in the ratio of 17:14:9:31. The mixture was placed in an Al\textsubscript{2}O\textsubscript{3} crucible (Gongtao Ceramics, Shanghai, China) and sealed in a quartz tube (Gongtao Ceramics, Shanghai, China) under vacuum. The whole ampule was heated to 700 °C in a box furnace (Henan Sante, Luoyang, China) at a rate of 140 °C/h and kept at this temperature for 5 h. It was further heated to 1100 °C at a rate of 80 °C/h where it was held for 50 h and then cooled to 1050 °C at a rate of 1.25 °C/h. It was further cooled to 500 °C in the next 100 h and finally cooled down to room temperature naturally by switching the power off. The cooling process is crucial because the mixture melts when it heats up and forms in a stable phase when it cools down. Shiny plate-like single crystals were obtained with a typical size of 3 mm × 3 mm × 0.8 mm, and a photo of the as prepared sample is shown in Figure 1b.

Crystal structure and phase purity were checked by both single-crystal and powder X-ray diffraction, which were carried out on a Rigaku-D/max X-ray diffractometer (XRD) (Rigaku, Tokyo, Japan) using Cu-Kα radiation (λ = 1.54056 Å). Powder X-ray diffraction employed the powder grounded from the as-grown single crystals. The crystal used for this experiment was selected from the same batch as that used for composition and physical properties measurements. The chemical composition of the sample was identified by Energy Dispersive X-Ray Spectroscopy (EDX) (Hitachi, Tokyo, Japan). Electrical resistivity, magnetoresistance, Hall effect, thermal conductivity, and Seebeck coefficient measurements were performed in a Quantum Design PPMS System. Both ab plane and c-axis resistivities were measured using the standard four-probe technique.

3. Results and Discussion

Figure 1c shows the X-ray diffraction spectrum for the as-grown thin, plate-like single crystal along the c-axis. Note that only (00l) peaks are observed and the pattern matches very well with that previously reported in \cite{4}. A powder XRD spectrum is shown in Figure 1d. The result exhibits the peaks from diffractions not only (00l) planes but also (hk0) planes with nonzero h, k, l. X-ray structure determination confirms that the lattice parameters and angles for the sample are a = 8.7548(12) Å, b = 8.7642(10) Å, c = 10.69005(8) Å, and α = 94.674(9)°, β = 104.396(8)°, γ = 90.037(10)°, respectively, indicating our sample crystallizes in a triclinic structure with space group symmetry $P\overline{1}$ at room temperature. No other impurities such as FeAs and PtAs\textsubscript{2} were observed in any X-ray spectrum.
Figure 1. (a) Crystal structure of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8\text{(Fe}_2\text{As}_2)_5 \); (b) as prepared \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5 \) single crystals; (c) XRD spectrum with index peaks of \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5 \) measured on single crystals along the c-axis at room temperature; (d) XRD spectrum of powder \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5 \) at room temperature.

The chemical composition was identified by the EDX measurement. A scanning electron microscope (SEM) image measured on the surface of the single crystal is shown in the Figure 2 inset. For each sample, five locations scattered on the surface were chosen for EDX measurement. An average of these scans was calculated. The results of the different samples are consistent with each other, implying homogenous growth was acquired throughout the batch. The average deviation is 3% for Ca, 5% for Pt, and 1% for Fe. The measured composition of the single crystals is \( \text{Ca}_{10}\text{Pt}_{5.4}\text{Fe}_{8.6}\text{As}_{18} \), corresponding to a formula of \( \text{Ca}_{10}\text{Pt}_4\text{As}_8\text{(Fe}_{0.86}\text{Pt}_{0.14}\text{As}_2)_5 \) if considering the Pt substitution effect.
The residual resistivity ratio (RRR) can be written as:

$$\rho_{\text{ab}}$$

shown by the measured sample. The residual resistivity ratio (RRR) is 2.4. Relatively large $T_c$ onset, and small RRR reflects the presence of Pt doping on the Fe site in FeAs layers as suggested in [1–3]. However, the out-of-plane resistivity $\rho_c$ behaves strikingly different with $\rho_{\text{ab}}$; it exhibits nearly independent $T$ at higher temperatures and starts to increase with decreasing $T$ ($\frac{d\rho_c}{dT} < 0$) below 200K, showing a nonmetallic behavior. It then goes through a sharp peak around 38 K before dropping to zero. The anisotropic property between $\rho_{\text{ab}}$ and $\rho_c$ has not been noted in previous reports [1,2,4]. We acknowledge that this $\rho_c$–$T$ profile is reproducible and it should be an intrinsic property of Ca$_{10}$Pt$_x$As$_8$(Fe$_2$–$_x$Pt$_x$As$_2$)$_5$.

Figure 3 displays the temperature dependence of the in-plane ($\rho_{\text{ab}}$) and out-of-plane resistivity ($\rho_c$) of Ca$_{10}$Pt$_x$As$_8$)Fe$_{0.86}$Pt$_{0.14}$As$_2$_5 single crystals between 2 K and 300 K. The magnitude of $\rho_{\text{ab}}$ and its overall features are similar to the previous reports [2]. The normal-state $\rho_{\text{ab}}$ decreases with decreasing $T$ ($\frac{d\rho_c}{dT} > 0$), showing a metallic behavior. It drops sharply at $T_c$ onset = ~34 K, reaching zero-resistivity state at 31.2 K. The transition width in temperature is less than 3 K, indicating that our sample has high quality and spatial homogeneity. The residual resistivity ratio (RRR) $(300K)/\rho(T_c\text{onset})$ is 2.4. Relatively large $T_c$ onset and small RRR reflects the presence of Pt doping on the Fe site in FeAs layers as suggested in [1–3]. However, the out-of-plane resistivity $\rho_c$ behaves strikingly different with $\rho_{\text{ab}}$; it exhibits nearly independent $T$ at higher temperatures and starts to increase with decreasing $T$ ($\frac{d\rho_c}{dT} < 0$) below 200K, showing a nonmetallic behavior. It then goes through a sharp peak around 38 K before dropping to zero. The anisotropic property between $\rho_{\text{ab}}$ and $\rho_c$ has not been noted in previous reports [1,2,4]. We acknowledge that this $\rho_c$–$T$ profile is reproducible and it should be an intrinsic property of Ca$_{10}$Pt$_x$As$_8$)Fe$_{2}$–$_x$Pt$_x$As$_2$)$_5$.

Due to the layered crystal structure of Ca$_{10}$Pt$_x$As$_8$)Fe$_{0.86}$Pt$_{0.14}$As$_2$_5, the in-plane resistivity may be understood as a net resistivity of parallel connected resistors. A schematic of such a system is shown in Figure 4a. Here, we do not consider the resistance from the Ca layer because the FeAs
and Pt$_4$As$_8$ layers are the main contributors of the electronic structure around the Fermi surface [9]. The net resistance ($R$) can be written as:

$$ R = 1/n \left( \frac{1}{R_{\text{FeAs}}} + \frac{1}{R_{\text{Pt}_4\text{As}_8}} \right) $$

in which $n$ is the number of Pt$_4$As$_8$–FeAs layers, and $R_{\text{FeAs}}$ and $R_{\text{Pt}_4\text{As}_8}$ are the resistance of the FeAs layer and Pt$_4$As$_8$ layer, respectively. If the 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 may have linear dependence on temperature due to the inelastic scattering originating from electron-phonon interactions.

Figure 4. (a) A schematic plot of resistors made of FeAs layers and Pt$_4$As$_8$ layers connected in parallel; (b) a schematic plot of resistors made of FeAs layers and Pt$_4$As$_8$ layers connected in series.

The normal state $\rho_{ab}$ of some traditional FeAs-based superconductors shows metallic behavior and may have linear dependence on temperature due to the inelastic scattering originating from electron-phonon interactions. 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 Ca$_{10}$(Pt$_4$As$_8$)(Fe$_{0.86}$P$_{0.14}$)$_2$As$_2$S$_5$ is neither linear, quadratic temperature dependent, nor $T^{1.5}$ dependent, as observed in cuprates or other FeAs-based compounds [10]. The normal state $\rho_{ab}$ from 50 K to 300 K can be well fitted by $\rho_{ab} = A + B \sqrt{T}$ with $A = 0.079 \pm 0.008$ m$\Omega$ cm and $B = 0.031 \pm 0.003$ m$\Omega$ cm $K^{-1/2}$. The red solid line in Figure 3a is the fit to the experimental data of the normal state $\rho_{ab}$. All reported $\rho_{ab}$ for Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ has the similar square-root temperature dependence regardless of $T_c$ [1,2,4], and thus, it may be an intrinsic property to Ca$_{10}$Pt$_4$As$_8$(Fe$_2$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 [11,12]. The studies on the Fermi surface of Ca$_{10}$Pt$_4$As$_8$(Fe$_2$As$_2$)$_5$ imply that the Pt$_4$As$_8$ layer contributes several electron pockets. Thus, there may be competition between the Pt$_4$As$_8$ layer and the negatively-charged FeAs layer for electrons, leading to possible Pt deficiency in the Pt$_4$As$_8$ layer and partial substitution of Fe by Pt in the Fe$_{1-x}$Pt$_x$As layer [3,5,13,14]. As a result, charge carriers in both the Pt$_4$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 3b, $\rho_{c}$ is much larger than $\rho_{ab}$ in the normal state. It can be understood with a schematic plot of the net resistance $R = n (R_{\text{FeAs}} + R_{\text{Pt}_4\text{As}_8})$ along the out-of-plane direction.
shown in Figure 4b. Different from the normal state $\rho_c$ of some cuprates which can be described using the equation $\rho_c = A/T + B \times T$ exhibiting the non-Fermi liquid behavior, the nonmetallic normal state $\rho_c$ of $\text{Ca}_{10}Pt_4\text{As}_8((\text{Fe}_{0.86}\text{Pt}_{0.14})_2\text{As}_2)_5$ can be appropriately fitted using the equation $\rho_c = A' + B'\sqrt{T} + C'T^{-1}$. The solid line in Figure 3b shows the fit of $\rho_c$ from 90 K to 300 K. The fitting parameters are calculated as follows: $A' = 2.642 \pm 0.009 \text{ m}\Omega \text{ cm}$, $B' = 0.308 \pm 0.006 \text{ m}\Omega \text{ cm K}^{-1/2}$, and $C' = 667.7 \pm 15 \text{ m}\Omega \text{ cm K}$.

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 [15] or extrinsic due to a possible stacking fault [2]. The $T^{-1}$ term can be attributed to interlayer incoherent scattering, similar to the properties of high-$T_c$ cuprates [15] and $(\text{Sr}_4\text{V}_2\text{O}_6)\text{Fe}_2\text{As}_2$ [16]. It implies the spacer layer $\text{Ca}_{10}\text{Pt}_4\text{As}_8$ is not superconducting in nature, so Josephson junctions are formed along the c-axis of $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ by stacking of the FeAs superconducting layer, the $\text{Ca}_{10}\text{Pt}_4\text{As}_8$ semiconducting layer, and the FeAs superconducting layer.

The resistivity anisotropy $\gamma$ is calculated by $\gamma = \sqrt{\rho_c/\rho_{ab}}$ and it increases from ~4.1 at 300 K to ~7.9 around $T_c$ as displayed in Figure 5. The $\gamma$ of $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$ is larger than that of $\text{LaFeAsO}_{1.9}\text{F}_{0.1}$ [17]. Relatively large anisotropy and a conspicuous difference in the behavior of $\rho_c$ and $\rho_{ab}$ suggests a strong 2D nature of electronic structures in $\text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5$, which is rarely encountered in traditional Fe-based superconductors.

![Figure 5](image-url)

Figure 5. The temperature dependence of normal state anisotropy $\gamma = \sqrt{\rho_c/\rho_{ab}}$.

The resistivity anisotropy ($\gamma$) in the superconducting state of $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)((\text{Fe}_{0.86}\text{Pt}_{0.14})_2\text{As}_2)_5$ was evaluated through resistivity measurements with an applied magnetic field $H$. Figure 6 shows the temperature dependence of $\rho_{ab}$ and $\rho_c$ under $H$ along both the c-axis and the ab plane.

In the case of $I//ab$ and $H//c$-axis, it can be seen that the zero resistivity transition temperature ($T_{c0}$) decreases with the rising applied magnetic field accompanied by an increase in the transition width. The $T_{c0}$ is 18 K and the transition width $\Delta T_c$ is 16 K for $H = 14$ T, considering $T_{c\text{, onset}}$ is 34 K. This type of superconducting transition broadening with increasing magnetic field ($H$) is rarely seen in Fe-based superconductors but very common in cuprates due to the presence of strong thermal vortices fluctuations [18].

Interestingly, the superconducting transition width $\Delta T_c$ does not change with an applied field when $I//c$ and $H//ab$ plane (Figure 6b) and $H$ pushes both $T_{c\text{, onset}}$ and $T_{c0}$ to the lower temperature by the same amount. This shift is also much smaller than that of $\Delta T_c$ for cases $I//ab$ and $H//c$. 
Figure 6. (a) The temperature dependence of ρ_{ab} with applied magnetic field \( H = 0, 1, 3, 5, 8, 10, \) and 14 T along the c direction in the superconducting state; (b) the temperature dependence of ρ_{c} with applied magnetic field \( H = 0, 1, 3, 5, 8, 10, \) and 14 T along the ab plane in the superconducting state.

As shown in Figure 7, the \( H_{c2} (T) \) of Ca_{10}(Pt_{4}As_{8})((Fe_{0.86}Pt_{0.14})_{2}As_{2})_{5} \) was extracted by identifying the \( T_c(H) \) at which resistivity drops to 90% \( \rho_n \), 50% \( \rho_n \) and 10% \( \rho_n \). \( \rho_n \) is the normal resistivity before superconducting transition, as indicated by dashed lines in Figure 6.

Figure 7. Temperature dependence of the upper critical field \( H_{c2}(T) \) with (a) \( H//c \) and (b) \( H//ab \).

The temperature dependence of the \( H_{c2} \) anisotropy parameter \( \Gamma_H = \frac{H_{c2}^{ab}}{H_{c2}^{c}} \) obtained from Figure 7 is presented in Figure 8. \( \Gamma_H \) taken at 90% resistivity drop reaches 8 near \( T_c \), which is very close to the
normal-state $\gamma$ we obtained previously in the resistivity measurements. $\Gamma_H$ varies from 4 to 6 using a 50% criteria as compared to 122 type. For example, with $\Gamma_H = \sim 2$ for BaFe$_2$As$_2$ [19,20], the $H_{c2}$ anisotropy of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ is much larger.

It also can be noted from Figure 7b that $H_{c2}^{ab}(T)$ increases almost linearly with decreasing temperature, while $H_{c2}^c(T)$ exhibits an upward shape with a steep increase at low temperatures. This phenomena quite possibly originates from the multi-band effect such as in the NdFeAsO$_{0.7}$F$_{0.3}$ and MgB$_2$ systems [21,22]. Thus, the positive curvature of $H_{c2}^c(T)$ reflects a multi-band nature in electrical structure for Ca$_{10}$(Pt$_4$As$_8$)(Fe$_2$As$_2$)$_5$.

![Figure 8](image)

**Figure 8.** The temperature dependence of the $H_{c2}$ anisotropy parameter $\Gamma_H = \frac{H_{c2}^c}{H_{c2}^a}$. Upper critical field $H_{c2}$ is an important parameter for all superconductors especially in their practical applications. We estimated $H_{c2}$ at 0 K using the Werthamer–Helfand–Hohenberg (WHH) approximation [23]:

$$H_{c2}(0) = -0.69T_c \times \left| \frac{dH_{c2}}{dT} \right|_{T_c}$$  \hspace{1cm} (2)

The corresponding coherence lengths are calculated via the Ginzburg Landau (GL) formula:

$$\left\{ \begin{array}{l}
\xi_{ab}(0) = \frac{\varphi_0}{\sqrt{2\pi\xi_{c2}(0)}} \\
\xi_c(0) = \frac{\varphi_0}{2\pi\xi_{ab}H_{c2}^c(0)}
\end{array} \right.$$  \hspace{1cm} (3)

where $\varphi_0 = 2.07 \times 10^{-15}$ Wb. The obtained results are listed in Table 1. Although all derived values depend on how $H_{c2}(T)$ is extracted, the large difference of $H_{c2}^a$ and $H_{c2}^c$ implies Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ exhibits a large anisotropy in its superconducting state. Furthermore, the values of $\xi_c(0)$ derived from different criteria are all less than 10.69005(8) Å, i.e., the length of c-axis of the unit cell, suggesting that Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ meets the dimensional requirement of fabricating the intrinsic Josephson junctions (iJJs).
Table 1. The upper critical field and coherence length of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$.

| Criteria in Determining $H_{c2}$ | $\frac{dT_c}{dT}$ $T_c$(T/K) | $H_{c2}(0)$(Tesla) (WHH Approach) | $\frac{dH_{c2}}{dT}$ $T_c$(T/K) | $H_{c2}^{ab}(0)$(Tesla) (WHH Approach) | $\xi_{ab}(0)$ (Å) | $\xi_c(0)$ (Å) |
|----------------------------------|-----------------------------|----------------------------------|----------------------|----------------------------------|----------------|----------------|
| $0.9 \rho_n$                     | $-6.5 \pm 0.2$              | 138 $\pm$ 5                      | $-14.1 \pm 0.1$      | 313 $\pm$ 6                     | 15.5 $\pm$ 0.2 | 6.8 $\pm$ 0.3 |
| $0.5 \rho_n$                     | $-0.89 \pm 0.1$             | 19.7 $\pm$ 2                     | $-4.4 \pm 0.1$       | 99 $\pm$ 2                      | 40.9 $\pm$ 0.5 | 8.1 $\pm$ 0.3 |
| $0.1 \rho_n$                     | $-0.74 \pm 0.1$             | 16.4 $\pm$ 1                     | $-3.8 \pm 0.1$       | 84 $\pm$ 3                      | 44.8 $\pm$ 0.4 | 8.7 $\pm$ 0.5 |

WHH: Werthamer–Helfand–Hohenberg.
For a normal metal with Fermi liquid behavior, the Hall coefficient ($R_{H}$) is independent of temperature. The situation is more complex if the material has multi-band or non-Fermi liquid behavior such as, for example, cuprates or heavy fermions. Their Hall coefficient exhibits strong temperature and doping dependencies. The $H_f(T)$ curves show the multi-band nature of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$, so the Hall effect was measured by applying a magnetic field $H \perp ab$, and the data is presented in Figure 9.

Figure 9. Hall coefficients $R_H(T)$ (blue dots) and carrier concentration (red circles) between 40 K and 300 K for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$. The solid lines are guides for the eye.

The transverse $R_H$ remains negative at all temperatures above $T_c$, indicating that the charge carrier is dominated by electrons. The magnitude of $R_H$ increases with decreasing temperature, suggesting a multi-band and non-Fermi liquid behavior. Even though the doping in the FeAs layers is considered to be isovalent (i.e., Pt$^{2+}$ replaces Fe$^{2+}$) [2,5], it may still influence $R_H$. Our $R_H(T)$ is similar with previous reports [1,2], but it exhibits stronger temperature dependence, which suggests that the carrier concentration cannot be solely determined by the Pt concentration in this material.

If a single band model is adopted, the corresponding carrier concentration ($n$) could be calculated with $R_H$ via $n = -1/eR_H$. The temperature dependence of $n$ is shown as the red line in Figure 9. Generally, $n$ decreases monotonically with decreasing $T$. The calculated $n$ is about $2.5 \times 10^{22}$ cm$^{-3}$ at 300 K. 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 [24]. The carrier concentration indicates that the normal state of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ behaves as a good metal. Before superconducting transition, the carrier concentration drops to $0.5 \times 10^{22}$ cm$^{-3}$; however, it is still an order of magnitude larger than that of Ca103-8 (~$10^{21}$ between 2 K and 300 K) [2]. This is because the one extra Pt atom in the Pt$_4$As$_8$ intermediary layer exceeds the Zintl valence satisfaction requirement and introduces redundant electrons into the system, leading to enhanced metallicity and a relatively higher $T_c$.

A different method of probing conduction mechanism is provided by thermal conductivity. We measured the temperature dependence of thermal conductivity and the Seebeck coefficient for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ from 2 K to 350 K, and the results are shown in Figure 10a.

The Seebeck coefficient ($S$) is negative at the measured temperature range above $T_c$, with a value of $-25.5604$ μV/K at 300 K and a minimum value of $-29.1345$ μV/K near 154 K resulting from a phonon-drag contribution. This confirms that the electron-type charge carrier dominates in Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$, which is consistent with the Hall effect measurement. Then, $S$ starts to increase with decreasing temperature and reaches zero steeply at the superconducting transition.
temperature. In addition, the Seebeck curve shows no anomalous enhancements associated with the crystal structure or spin density wave (SDW) transitions widely observed in undoped compounds such as SmFeAsO and BaFe$_2$As$_2$ [25,26], suggesting that there were no corresponding transitions in our sample at the temperatures measured.

![Figure 10. (a) Temperature dependence of thermal conductivity and the Seebeck coefficient for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$; (b) electronic contribution to thermal conductivity above transition temperature $T_c$ evaluated by the Wiedemann–Franz law.](image)

With regard to the thermal conductivity ($\kappa$), it drops monotonously above $T_c$ when temperature is lower than $T_c$, $\kappa$ and decreases sharply with the opening of the superconducting gap. Before the drastic drop, $\kappa$ first displays an abrupt increase with a bump feature upon entering the superconducting (SC) state, and a similar behavior is commonly observed in the cuprate superconductors, e.g., YBa$_2$Cu$_3$O$_7$ [27] and Bi$_2$Sr$_2$CaCu$_2$O$_8$ [28]. The enhancement of $\kappa$ below $T_c$ reflects the increase of the phonon mean free path by the condensation of charge carriers. Phonons then cease to dissipate their momentum in collisions with such a condensate.

The electronic contribution to thermal conductivity ($\kappa_e$) above $T_c$ could be evaluated by the Wiedemann–Franz law $\kappa_e = \sigma LT$, where $\sigma$ is the electrical conductivity of a metal and $T$ is the temperature, $L$ known as the Lorenz number, which is equal to:

$$L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ W} \Omega \text{K}^{-2}$$

in which $e$ is elementary charge and $k_B$ is the Boltzmann constant. The calculated results are presented in Figure 10b. $\kappa_e$ is smaller by about 5 orders of magnitude than $\kappa$ as shown in Figure 10a. Thus, heat in Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ is mainly carried by phonons, and the electron contribution can be negligible. This is wholly different from the copper oxide superconductors. Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ is a relatively low-charge carrier density system.

It is worth noting that the $\kappa$ value for Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ is smaller than that for LaFeAsO$_{0.89}$F$_{0.11}$ [29]. We know that the main scattering mechanisms for phonons in crystal are carriers and structural defects, and intrinsic phonon–phonon scattering only exists in clean materials. While in the Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ system, both the off-centered Pt atoms in the Pt$_4$As$_8$ plane and the substitutional Pt atoms in the FeAs plane introduce disorder into the crystal, which causes phonons to be strongly scattered and the crystal lattice vibration to localize, resulting in the rather smaller thermal conductivity of Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$.

4. Conclusions

In conclusion, X-ray diffraction, resistivity, Hall effect, Seebeck coefficient, and thermal conductivity measurements were performed on high quality Ca$_{10}$(Pt$_4$As$_8$)((Fe$_{0.86}$Pt$_{0.14}$)$_2$As$_2$)$_5$ single crystals. We observed metallic in-plane resistivity but non-metallic out-of-plane resistivity for
Ca_{10}Pt_4As_8(Fe_2As_2)_5. The anisotropic property is unusual, and its normal state resistivity exhibits a large anisotropy (~8) near $T_c$, making it one of the most anisotropic FeAs-based superconductors. The normal state in-plane resistivity has a square-root temperature dependence which is intrinsic to Ca_{10}Pt_4As_8(Fe_2As_2)_5. The interlayer incoherent scattering contributes to the out-of-plane transport property. A large coherence length along the ab plane and upper critical field were observed. Disorder and low-charge carrier density in the crystal may account for the relatively small thermal conductivity. The layered structure and the relatively higher transition temperature with the large electrical transport anisotropy of Ca_{10}Pt_4As_8(Fe_2As_2)_5 implies it may be a new good candidate for and have potential application in the fabrication of high frequency microelectronic devices such as next generation intrinsic Josephson junctions (IJJs).

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