

**EXPLORATION OF POSSIBLE ENHANCEMENT OF
SUPERCONDUCTIVITY BY INTERFACE, DOPING,
AND PRESSURE EFFECTS**

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the Faculty of the Department of Physics
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
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Dedication

To my parents and my wife

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Abstract

The superconductivity in CaFe_2As_2 , both at ambient and elevated pressures, remains an open question. Both interface-associated superconductivity and spontaneous phase separation (producing a new phase at low temperature) have been proposed. Thus far, superconductivity has been only observed below 12 K and within a narrow pressure range. As the evidence for filamentary superconductivity, a slight resistivity drop below 10 K has only been detected in a few extraordinary CaFe_2As_2 samples. In this dissertation we show that superconductivity with a noticeable Meissner effect and a T_c up to 25 K can be induced at ambient pressure. These occur only when the two coexisting phases, *i.e.*, the tetragonal-to-orthorhombic phase P1 and the tetragonal-to-collapsed tetragonal phase P2, are mesoscopically organized in a layer-stacking manner. The X-ray diffraction profile-analysis reveals a possible formation of dense interfaces, which is correlated with the superconductivity. The magnetic data further suggest that the spin-density-wave excitation in the P1 phase is largely suppressed along the interfaces. The microstress along the interfaces, therefore, may play a crucial role in the interface-associated superconductivity.

The ambient-pressure superconducting CaFe_2As_2 sample we obtained unexpectedly demonstrates two superconducting transitions under high pressure from 0 to 17 kbar, and they have distinctive responses to external pressure. The higher transition with $T_c \sim 25$ K at ambient pressure can be further enhanced to 30 K under a pressure of 17 kbar. The pressure study further supports that the enhanced T_c is associated with the interfaces between phase P1 and P2. The work presented in this dissertation provides the most direct evidence for interface-enhanced T_c in undoped CaFe_2As_2 to date. To further explore other possible T_c enhancement in CaFe_2As_2 , doping studies

with Sm and Eu were also conducted. Superconductivity has been observed in the samples with Sm doping at ambient pressure and in the samples with Eu doping under high pressures. Related work are also presented as we attempted to search for enhancement of superconductivity in another layered compound β -PdBi₂.

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Chapter 1

Introduction

In this chapter, the basic properties of superconductors are presented first, followed by a brief review of the historic discoveries in superconductivity research. Sections 1.3–1.5 are more relevant to the main content of the dissertation. In section 1.3, we introduce CaFe_2As_2 , a parent compound in the iron-based superconductors and discuss some recent work as well as the unsettled issues about superconductivity in this compound. In section 1.4, we discuss the interface-enhanced superconductivity, which can possibly account for our observation of an enhanced $T_c \sim 25$ K ($T_c < 12$ K as previously reported) in the CaFe_2As_2 with heterostructures. These constitute the motivations that inspired us to study this compound and further our investigations in several related materials thereafter. An overview of the dissertation will be given at the end of section 1.5.

1.1 Review of the fundamental properties of superconductors

From the birth of superconductivity in 1911 to the extensive investigation of this area to date, many great discoveries and new physics have emerged from unexpected phenomena. In July 1908, Kamerlingh Onnes first successfully liquefied helium, which made it possible to reach a temperature below 4.25 K. In 1911, he found that the electrical resistance of mercury was “practically zero” below 4.2 K, announcing the first observation of superconductivity [1].

Immediately Kamerlingh Onnes also observed that the electrical resistance of other metals, such as lead and tin, disappeared below their critical temperatures T_c . The vanishing of electrical resistivity, as a transition from a state with finite resistivity above the critical temperature to a state with zero resistivity, is the first fundamental property of superconductors (Fig. 1.1a). In addition to the zero resistance, a persistent current has been observed in superconducting rings. For a superconducting current loop, the current $\mathbf{I}$ remains unchanged and so does the induced magnetic field $\mathbf{H}$. Experiments have demonstrated that the current can persist for years without degradation. Experimental evidence also suggested that the value of the induced magnetic field at a particular position will depreciate its magnitude in a lifetime of 105 years. Theoretically, the lifetime of a persistent current can be infinitely long [2].

Although a superconductor can conduct electricity perfectly, a perfect conductor

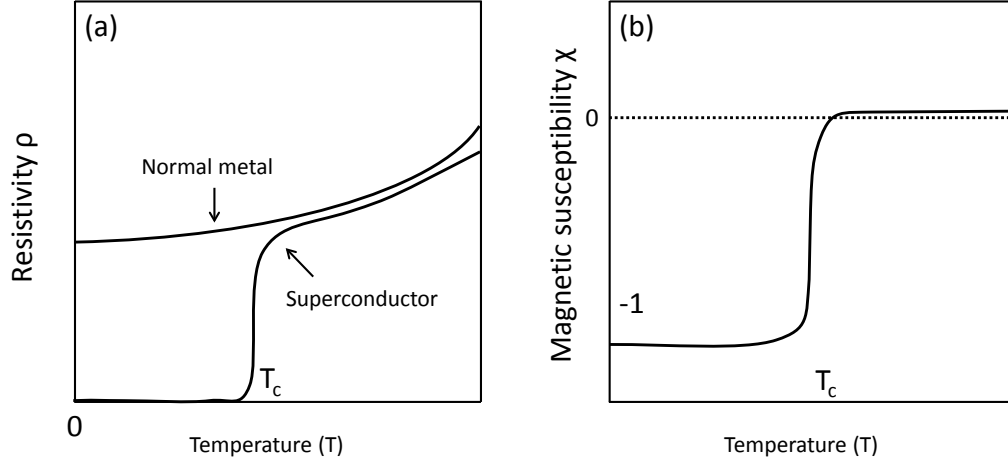


Figure 1.1: (a) Temperature dependence of resistivity for a normal metal compared to a superconductor; (b) temperature dependence of magnetic susceptibility for a superconductor.

is different from a superconductor due to the second fundamental property of superconductors – the Meissner effect, which was discovered by W. Meissner and R. Ochsenfeld in 1933 [3]. Suppose we have a superconductor and a perfect conductor reaching zero resistance below the T_c . If they are both cooled below their T_c s and a magnetic field is then applied (zero-field cool), the magnetic flux will be excluded from entering them. This is well explained by Lenz' law where a current is induced to screen the applied field in order to maintain a zero field inside the perfect conductor. However, if a magnetic field is applied above the T_c and then they are both cooled below the T_c (field cool), the magnetic field can still be expelled from a superconductor. While this holds for a superconductor, the flux would be trapped for a perfect conductor according to Lenz' law. The Meissner effect indicates that the total expulsion of magnetic flux will occur in a superconductor regardless of whether it is zero-field cooled or field cooled. Therefore superconductivity is a thermodynamic

state, which was first shown by the specific-heat experiment carried out by Kok and Keesom [4].

As the magnetic field lines are expelled from inside a superconductor, the magnetic field inside

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} = 0,$$

where $\mathbf{M}$ is the induced magnetization in the superconductor. The diamagnetic susceptibility χ is equal to $-1/4\pi$, which means perfect diamagnetism. According to the Meissner effect, superconductors in the superconducting state exhibit perfect diamagnetism at low fields. The transition temperature of a superconductor can be extracted from the $\chi(T)$ curve (Fig. 1.1b).

The reversible Meissner effect, regardless of field and cooling sequence, implies the existence of a critical field H_c which can destroy superconductivity. When $T > T_c$, the energy density of the sample in the normal state

$$F_n = f_n - \frac{1}{2}\mathbf{H} \cdot \mathbf{M} = f_n \quad (\mathbf{M} = 0),$$

where f_n is the free energy of the conducting sphere in the presence of $\mathbf{H}$. Suppose $T < T_c$, the free energy of a sample in the superconducting state

$$F_s = f_s - \frac{1}{2}\mathbf{H} \cdot \mathbf{M} = f_s + \frac{H^2}{8\pi}.$$

If we have $f_n > f_s + \frac{H^2}{8\pi}$, then the superconducting state is stable; otherwise the normal state is stable. There exist a critical field H_c satisfying

$$f_n = f_s + \frac{H^2}{8\pi},$$

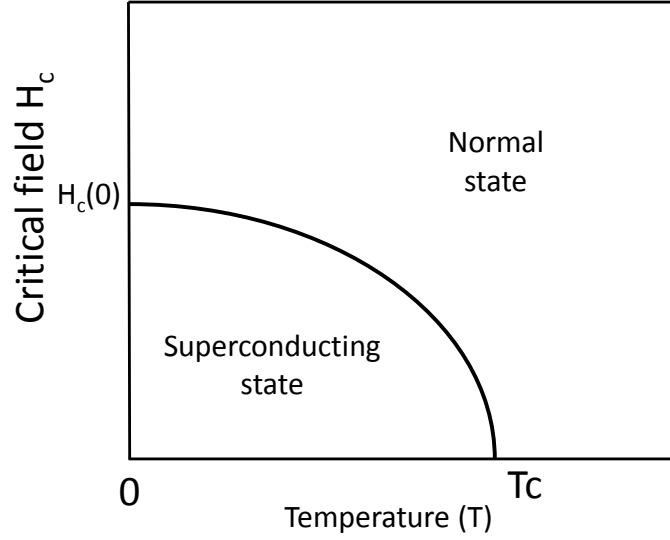


Figure 1.2: Temperature dependence of the critical field.

where $\frac{H^2}{8\pi} = f_n - f_s$ is the superconducting condensation energy. The sample remains in the superconducting state when $H < H_c$; it goes to the normal state when $H > H_c$. Experimental results show that H_c depends on the temperature following

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

with $T \leq T_c$ (Fig. 1.2).

The existence of a critical field implies there will be a critical current I_c for a superconducting wire, since the current generates a magnetic field (see Fig. 1.3). The superconductivity will be destroyed when $I > I_c$. The I_c can be derived from the Amperes law.

$$\oint \mathbf{B} dl = \mu_0 \mathbf{I}$$

At the surface of the wire, the magnetic field is

$$\mathbf{B} = \frac{\mu_0 \mathbf{I}}{2\pi r}$$

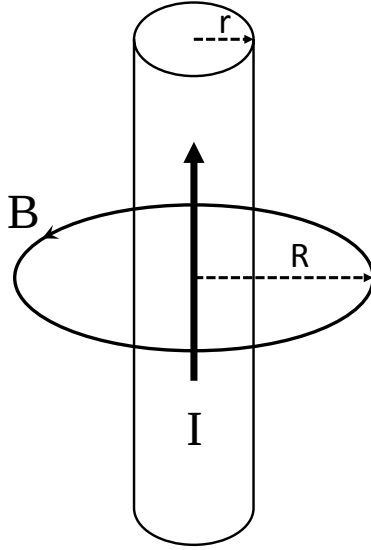


Figure 1.3: Schematic drawing of a magnetic field induced by the current in a superconducting wire.

Then the critical current of a superconducting wire can be calculated with a known critical field $\mathbf{B}$ ($= H_c$).

In addition to the two fundamental properties mentioned above, superconductors also demonstrate other macroscopic quantum phenomena such as fluxoid quantization and the Josephson effects. Based on the different responses to magnetic fields (Fig. 1.4), superconductors can be classified into two types. Type I superconductors exhibit perfect diamagnetism until the critical field is reached. On the other hand, type II superconductors differ in that there exist two different critical fields H_{c1} and H_{c2} . The sample behaves the same as type I superconductor below H_{c1} . In the region between H_{c1} and H_{c2} , however, the magnetic field can partially penetrate the sample. Thus there exist non-superconducting regions which are distributed as filaments filled with magnetic field through the sample. Such a state is called the vortex state,

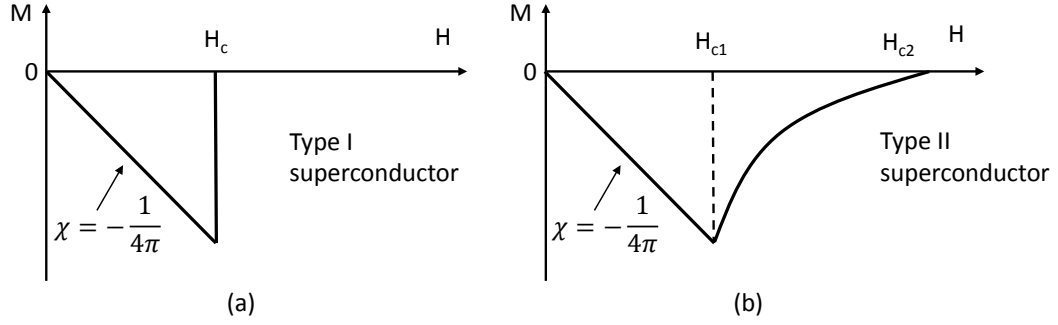


Figure 1.4: Magnetization as a function of magnetic field of type I (a) and type II (b) superconductor.

as vortices of the shield current form around the non-superconducting regions.

1.2 High-temperature superconductors – beyond the BCS theory

In the area of superconductivity research, the experimental observation of new phenomena always seems to precede the foundation of new theoretical frameworks. An important early development in the theory of superconductivity is the two-fluid model raised by C. J. Gorter and H. B. Casimir in 1934 (more than two decades after the discovery of superconductivity in mercury) [5]. The model divides the electrons into two components: the superconducting electrons and the normal electrons. The ratio of the former to the latter grows steadily from 0 at T_c to 1 at $T = 0$ K, where all the electrons are condensed to a superfluid. In the following year, the London equations, a phenomenological theory, were proposed by the brothers F. and H. London to interpret the two fundamental electrodynamic properties in superconductivity [6]. The

London theory was extended by Ginzburg and Landau in 1950 as they introduced a complex condensate wavefunction to describe the local density of the superconducting electrons [7].

A significant step in better understanding which forces turn the condensate into a superfluid came after the experimental discovery of the isotope effect in 1950. The isotope effect gave evidence that superconductivity arises from the interaction of electrons with phonons [8]. Finally, the complete microscopic theory of superconductivity was finally established in 1957 by Bardeen, Cooper and Schrieffer [9]. The BCS theory introduced the concept of Cooper pairs, formed by two electrons pairing through the electron-phonon interaction, and the formation of an energy gap that is isotropic in the momentum space. With the formation of Cooper-pair Bosons, the condensation of electrons occurs near the Fermi surface. Thus the superconducting current can be explained as a superfluid of Cooper pairs, which can move without resistance. The BCS theory can be used to successfully explain the perfect conductivity, perfect diamagnetism, and the energy gap in the excitation spectrum of superconductors.

The BCS theory worked well for virtually all superconductors, low- T_c elements as well as alloys, up to that time. However, with the discovery of high-temperature superconductors (HTS) – the cuprate superconductors, the BCS theory seemed unable to describe the high transition temperature, low dimensionality, and the unusual physical properties in high-temperature superconductors. While the presence of Cooper pairs was confirmed, the pairing symmetry and the mechanism of high-temperature superconductors were considered to be unconventional.

The first cuprate high-temperature superconductor, Ba-doped La_2CuO_4 , with T_c of 35 K, was discovered by Muller and Bednorz in 1986 [10]. Soon after in 1987 Chu and his colleagues discovered the first cuprate family that displays a T_c in the 90s K [11]. The first compound among them, YBCO (Y123), as the first high-temperature superconductor with $T_c \sim 93$ K (above the boiling temperature of nitrogen), still remains the most desirable material for HTS application to date. The cuprates still hold the current T_c record of 134 K in HBCCO (Hg1223) at ambient pressure [12] and 164 K in the same compound under pressure [13] (*A $T_c \sim 203$ K shown in H_2S under an extremely high pressure of 150 GPa has been recently reported [14]). The parent compounds of the high- T_c cuprates, without chemical doping, are mostly poor conductors and considered as Mott insulators. At low temperature, they enter into an antiferromagnetic (AFM) state, which can be suppressed with chemical doping. Consequently, a superconducting dome in the phase diagram is established with adequate doping. These comprise the generic phase diagram of the cuprate superconductors [15]. While the proximity of antiferromagnetism suggests that the superconducting electron pairing might be mediated by spin fluctuations, possible mechanisms are still the subject of considerable debates and continued research.

As evidenced by the cuprate superconductors, the discovery of new materials, particularly a new class of superconductors, invariably leads to the development of new physics. While other materials, *e.g.*, MgB_2 , fulleride superconductors, some organic superconductors, and even heavy fermion superconductors are considered as high-temperature superconductivity, another breakthrough article was published

in 2008, when Hosono and co-workers reported 26 K superconductivity in fluorine-doped LaFeAsO [16]. This marked that the iron-based superconductors, a new class of materials, joined the family of HTS. In the ensuing several years, a large number of compounds have been found and categorized into five different structural types (For example, the 1111-family RFeAs(O,F), where R = rare earth, with the ZrCuSiAs structure (P4/nmm)) [17]. They all share a common layered structure based on a planar layer of Fe atoms with tetrahedrally coordinated pnictogens or chalcogens. It is widely believed the interaction that leads to high- T_c superconductivity originates within the iron layers and is similar to the copper-oxygen blocks in the cuprate superconductors. Thus efforts have been made to increase the structure complexity in Fe-based superconductors, as it is known that the T_c of the cuprates rises with the complexity of layer structure through the addition of CuO_2 building blocks per unit cell. Such an approach to increase the T_c based on this analogy, however, to date has been ineffective. In addition, unlike the cuprates, the Fe pnictides and chalcogenides demonstrate the ability to directly accept dopants within the active pairing layer.

Furthermore, the generic phase diagram of the Fe-based superconductors looks similar to that of the cuprate superconductors, with the complex interplay between magnetism and superconductivity. Remember that the cuprates' parent compounds are Mott insulators; In contrast, the parent compounds of Fe-based superconductors are antiferromagnetic metals with sufficient conduction carriers. It is suggested that the antiferromagnetic order in these materials is a spin density wave (SDW) arising from itinerant electrons, where either chemical doping or external pressure can suppress the SDW and induce superconductivity.

Among the five structural types, AFe_2As_2 (so-called 122 compounds), where $\text{A}=\text{Sr}$, Ba , Ca and Eu , with the well-known ThCr_2Si_2 structure (see Fig. 1.5) has drawn great interest. In this 122-family, superconductivity with T_c approaching 40 K was first found in $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ and $(\text{Sr}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ [18, 19]. It is worth mentioning that the AFe_2As_2 ($\text{A} = \text{K}$, Rb , Cs) compounds were all found to be superconducting without additional doping, though their onset T_c s are much lower, ranging from 2.6 K for CsFe_2As_2 to 3.8 K for KFe_2As_2 [19]. The phase diagram of the 122 compounds roughly looks similar to that of the 1111-type Fe-pnictides (see Fig. 1.6). A remarkable difference, however, arises that it is unclear whether the AFM and superconducting phases can coexist or not [20]. In the 1111-family, the regions showing AFM and superconductivity are separated or are just barely overlapping, whereas the 122-type materials exhibit an AFM region which is overlapping with a high T_c value. The optimal T_c is reached at the temperature point corresponding to the extrapolation of the SDW curve to zero temperature. Namely, a superconducting dome appears around the quantum critical point of SDW [21].

1.3 CaFe_2As_2 – the underlying origin for superconductivity at ambient pressure and under pressure?

CaFe_2As_2 , one of the parent compounds in the 122 family, manifests superconductivity and other interesting physical properties through chemical substitution as well

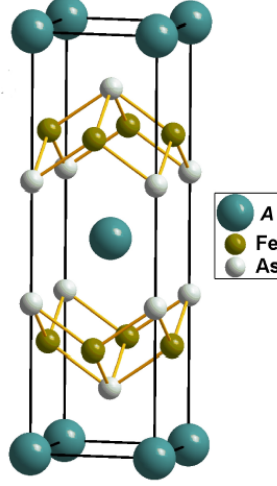


Figure 1.5: Crystal structure of AFe_2As_2 , where A =Sr, Ba, Ca and Eu

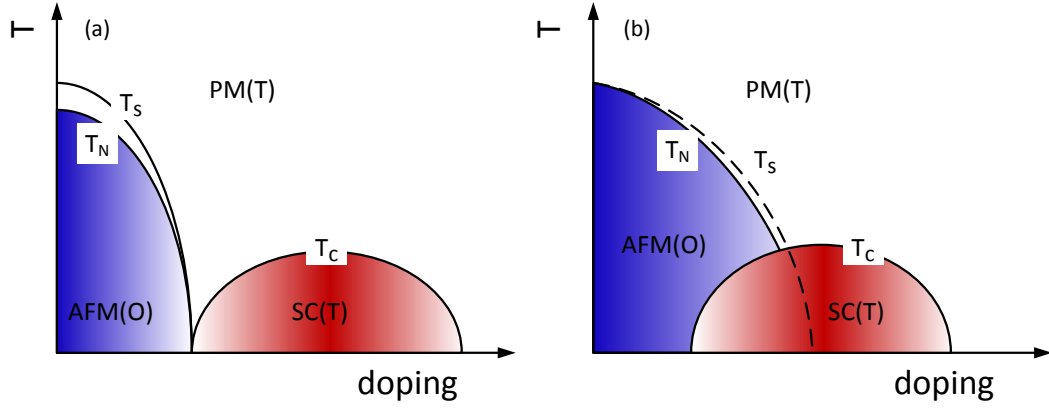


Figure 1.6: Schematic phase diagram of 1111 and 122 Fe pnictides. PM: paramagnetism; AFM: antiferromagnetism; SC: superconductivity. T: tetragonal structure; O: orthorhombic structure. T_N : spin-density-wave transition; T_S : structural transition from tetragonal to orthorhombic structure; T_c : superconducting transition temperature.

as application of external pressure. The CaFe_2As_2 single crystal at ambient pressure exhibits a structural transition from tetragonal (T) to orthorhombic (O) at ~ 170 K. The structural transition is accompanied with a spin-density-wave (SDW) excitation, with the magnetic property switching from paramagnetic (PM) to an antiferromagnetic (AFM) state at low temperature [22, 23]. CaFe_2As_2 is supposed to be non-superconducting without doping to suppress its SDW excitation. However, partial superconductivity with a transition temperature $T_c \leq 12$ K is reproducibly induced by a moderate non-hydrostatic pressure within a narrow regime, *i.e.*, between ~ 0.4 GPa and ~ 0.9 GPa [24, 25]. Initially, the applied pressure suppresses the SDW, which is fully suppressed under ~ 0.4 GPa. Superconductivity appears until a collapsed tetragonal (cT) phase at low temperature starts to develop from ~ 0.9 GPa. The cT phase seems to be detrimental to superconductivity, as no superconductivity is observed after the full establishment of the cT phase. On the other hand, CaFe_2As_2 is quite sensitive to pressure homogeneity and superconductivity is absent under hydrostatic pressure generated by He-gas as the pressure medium [26]. The hydrostatic pressure suppresses the SDW transition in such a different way that the transition occurs at a lower temperature without reducing its amplitude. Before the SDW transition is fully suppressed, the cT phase transition is abruptly established at ~ 0.35 GPa. Those responses to pressures are significantly different from its sister compounds SrFe_2As_2 and BaFe_2As_2 , whose superconductivity is robust under pressure with much higher T_c of 35 K at 5.5 GPa and 37 K at 3.3 GPa, respectively [27, 28, 29, 30]. Meanwhile, the presence of a cT phase in CaFe_2As_2 also triggered wide interests as well as debates, followed by extensive investigations on

the nature of cT phase and its relation to superconductivity [31, 32].

Why is partial superconductivity induced by non-hydrostatic pressure? Two types of interpretations have been offered. One puts the emphasis on the coexistence of different phases, *e.g.*, the collapsed tetragonal phase and the orthorhombic phase, where superconductivity is induced through the spin-charge dynamics in domain walls [24, 25]; the other points to a new low temperature T' phases, which is stabilized by pressure and correlates with the superconducting volume [33]. As the proposed T' phase exhibits some intriguing features such as the broad diffraction lines located exactly between the cT and O phases, another question naturally arises: could the two interpretations share a common root?

With the above questions in mind, we found that the situation at ambient pressure became even more peculiar. A resistivity drop below 10 K has been observed in some CaFe_2As_2 crystals, which is interpreted as an evidence for filamentary superconductivity [34]; however, it should be noted that no diamagnetic shift or Meissner effect has been detected in these samples. Interfaces between adjacent AFM twin domains have been suggested to be responsible for the superconductivity, *i.e.*, spontaneous nanoscale inhomogenization under thermodynamic equilibrium [35]. In our view, one key fact may have been overlooked as superconductivity was only observed only in a few extraordinary CaFe_2As_2 crystals. A thermodynamically equilibrated state, however, should be universal for a given lattice structure even if there exist spontaneous phase separations (and/or lattice distortion). Therefore the sample-dependent phenomena would imply metastable states which vary with time. If this is the case, then superconductivity is expected to be eventually suppressed if the

non-superconducting phase is the equilibrium state.

Though the issue was complicated by the observation of trace superconductivity at ambient pressure, the latter actually provided insight into the former one. The answer to previous question depends strongly on the underlying physics that differentiate in such two cases. If the key factor is the properly arranged interfaces (or domain boundaries), there could be a good chance to achieve similar or even stronger ambient-pressure superconductivity since it is known that numerous CaFe_2As_2 phases can be mutually converted through post-growth thermal treatments [36, 37]. To be more specific, considering the annealing-pressure analogy (see Fig. 1.7) proposed by Ran *et.al.* [36], we would be able to induce superconductivity at the border of the cT phase and O phase, where the interfaces presumably exist, through properly designed thermal treatments. On the other hand, the chance will be trivial if the superconductivity is limited within a particular crystalline phase existing only under certain pressure. This would provide a promising way to examine the two models proposed and thereby motivated our initial investigation on CaFe_2As_2 .

1.4 Possible interface-enhanced superconductivity

Among the many theoretical mechanisms proposed for higher T_c , the interfacial mechanism in various forms has been the one most explored theoretically and experimentally since 1964 when Little and Ginzburg [38] first proposed it. However, an analytic study was not completed until 1973 when Allender, Bray, and Bardeen

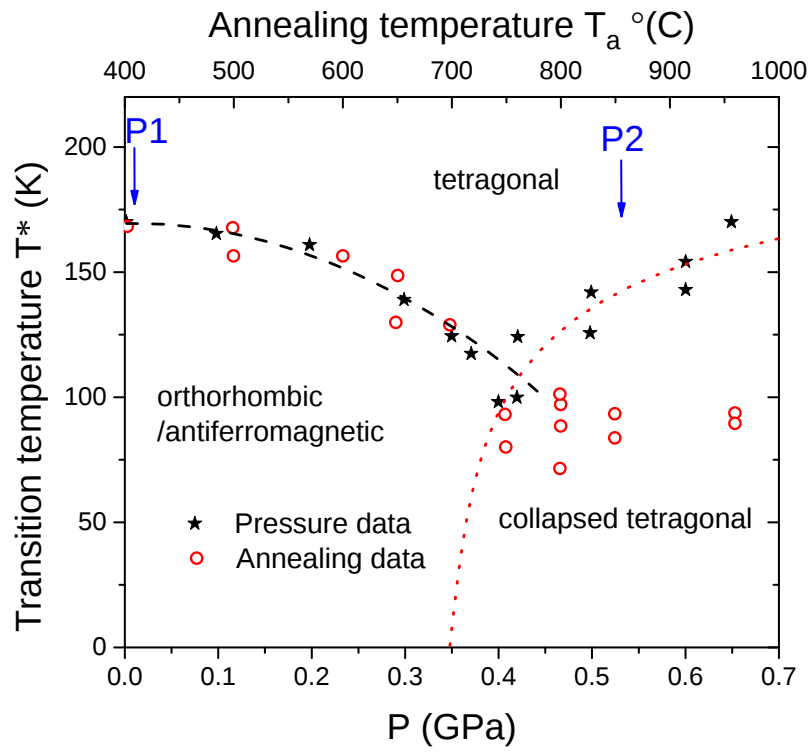


Figure 1.7: Transition temperature vs. annealing temperature phase diagram. (adapted from [36])

(ABB) considered a physical model that consists of an interface between a thin metal-layer and a semiconductor [39]. Their realistic estimations showed that a substantial T_c -enhancement is possible via the exchange of excitons with a higher characteristic energy should the stringent requirements on the interfaces and materials be met, although questions have also been raised. As was pointed out by ABB, the realization of interfacial mechanism might not only lead to a substantial T_c -enhancement, but would also be a notable achievement by itself. Numerous experiments inspired by the general concept of interface-induced T_c -enhancement have subsequently been carried out on samples with heterostructures that consist of insulating, semiconducting, metallic, and superconducting bilayers, trilayers, or superlattices [40]. In the cuprate family, for example, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4/\text{La}_2\text{CuO}_4$ (LSCO/LCO) System has been studied by Ivan Bozovics group at Brookhaven National Laboratory. They designed heterostructures composed of bilayer, trilayer, or superlattices, in which each layer is undoped (insulating) or overdoped (metallic and non-superconducting). In such a system, they found the T_c was strongly correlated with the layer sequence [41].

In the Fe-based family, two systems have manifested superconducting properties that might be associated with the interface effect. One is the non-bulk superconductivity with $T_c > 40$ K in the RE (rare earth) doped CaFe_2As_2 , where RE = La, Ce, Pr and Nd [42, 43, 44]. The other refers to the superconductivity above 100 K in the single-layer FeSe thin films on SrTiO_3 [45, 46]. In the RE doped system, the Pr-doped single-crystalline CaFe_2As_2 with an onset T_c up to ~ 49 K is higher than any T_c s previously known for compounds at ambient or under high pressure

that contain one or more of the constituent elements Pr, Ca, Fe, and As. The extensive investigations on the RE-doped system carried out by our group exclude possible trivial artifacts and reveal that the enhanced T_c is associated with naturally occurring interfaces. In addition, another fact capturing our attention is the ambient-pressure superconductivity universally observed in other undoped 122 compounds, SrFe_2As_2 and BaFe_2As_2 [47, 48]. These observations together inspired us to search for ambient-pressure superconductivity in undoped CaFe_2As_2 and to explore possible interface-enhanced superconductivity as the heterostructure composed of O and cT layers (phases) could naturally be created through the annealing process discussed above.

In this dissertation, a systematic annealing procedure was developed to reproducibly induce (or suppress) the ambient-pressure superconductivity in CaFe_2As_2 . A much higher $T_c \sim 25$ K with noticeable diamagnetic shielding and Meissner effect was observed. Superconductivity was observed to only appear within a well-defined annealing-time window, when the tetragonal-to-orthorhombic phase (T-to-O, see P1 in Fig. 1.7) and the tetragonal-to-collapsed tetragonal (T-to-cT, see P2 in Fig. 1.7) phase coexist. Both the X-ray diffraction (XRD) profile-analysis and the magnetization analysis are used to probe the mesostructure of the annealed samples. An “intergrowth model” with randomly stacked layers of two phases is adopted to successfully simulate and explain the XRD spectra. Therefore, dense interfaces may form epitaxially between the two types of layers. Based on the model, the deduced interface density correlates with the superconducting volume fraction. On the other hand, the analysis of magnetization data suggests that the SDW excitation near the

boundaries of P1 block is suppressed, likely due to the lattice mismatch between the two phases. Thus the interface superconductivity may naturally be understood here.

In order to comprehensively understand the superconductivity in CaFe_2As_2 , a phase-conversion diagram is constructed and compared with the phase diagrams of CaFe_2As_2 under hydrostatic pressure and non-hydrostatic pressure [26, 25, 49]. The comparison reveals that the regime where both SDW transition and cT transition are suppressed is essential for the occurrence of superconductivity. In addition, the previous pressure studies were all carried out on CaFe_2As_2 in the P1 phase. We also performed quasi-hydrostatic pressure studies on samples in the mixed phase and in the P2 phase that we obtained through the annealing procedure. For the sample in the mixed phase, it unexpectedly exhibits two distinguishable superconducting transitions, which demonstrate distinct responses to the external pressure. As a result, the higher transition is further enhanced up to 30 K under a pressure of 17 kbar. On the contrary, no trace of superconductivity has been detected through applying pressure to the sample in the P2 phase. The comparison of the pressure studies on the three CaFe_2As_2 with distinct phase compositions further supports our interpretation based on the interface mechanism.

1.5 Overview of the dissertation

In short, both the enhanced T_c in the mixed phase and the extended pressure range where CaFe_2As_2 remains superconducting suggest that superconductivity is associated with the nature of the interface. Back to the two interpretations of the superconductivity under pressure discussed above, our results seem to support the first interpretation, but also imply the T' phase might be identical to the intergrowth phase we observed. Such an interpretation from our perspective may reconcile the two seemingly contradictory interpretations proposed before. The details will be discussed in chapter 3, which is the core of this dissertation.

Unlike the parent compound, the high T_c in the RE-doped CaFe_2As_2 can be induced regardless of whether the cT phase emerges or not. Due to the interesting observations in the parent compound, we decided to extend our investigation and attempted to search for similar phenomena in other two RE-doped compounds, *i.e.* $(\text{Sm}, \text{Ca})\text{Fe}_2\text{As}_2$ and $(\text{Eu}, \text{Ca})\text{Fe}_2\text{As}_2$. In the rare-earth elements, Sm and Eu are both located after Nd. Since the ionic radius of Sm^{3+} (109.9 pm) is much smaller than Ca^{2+} (114 pm), substantial Sm substitution would shrink the lattice. The first principles calculation of rare-earth-doped CaFe_2As_2 including Sm, which is fixed to 25%, suggests that such amount of Sm doping can induce a collapsed tetragonal phase at ambient pressure [50]. If so, we can examine whether the high T_c as well as the naturally-occurring interfaces can be induced in $(\text{Sm}, \text{Ca})\text{Fe}_2\text{As}_2$. If so, the results may further reveal the relation of superconductivity with the cT phase. Eu, on the other hand, carries a 2+ valence, resulting in a much larger ionic radius

of 131 pm. Eu doping is isovalent so that no charge disorder will be introduced into the system. Meanwhile, effective Eu substitution would largely expand the lattice and eradicate the cT phase, even when it is moderately pressurized. Thus we can reexamine whether the O and cT phase boundary is a prerequisite for the emergence of superconductivity through systematic doping and pressure studies. As Eu^{2+} carries a large spin moment of $\sim 7 \mu_B$, it demonstrates an antiferromagnetic order at ~ 20 K. Such a system may also offer us a ground to study the interplay between magnetism and superconductivity. The interplay could be twofold. One is the superconductivity with the SDW transition at high temperature that is associated with the Fe moment; the other is with the AFM order below 20 K that originates from Eu^{2+} . The studies of these doped CaFe_2As_2 compounds are combined to be chapter 4.

In chapter 5, we briefly introduce our study on another superconductor— $\beta\text{-PdBi}_2$. From materials' point of view, $\beta\text{-PdBi}_2$ is an intermetallic compound, which is unrelated to the Fe-based superconductors. However, an unexpected spin excitation, possibly a SDW transition, was induced in this compound by Na intercalation, which causes a suppression of T_c [51]. The behavior of the spin excitation is then compared to some observations in the Fe-based family. In addition, several recent reports have identified $\beta\text{-PdBi}_2$ as a topological superconductor [52], which makes this compound even more interesting. Therefore, we put this work as an individual chapter at the end.

Chapter 2

Methods

2.1 Sample preparation

The materials investigated in this dissertation were synthesized by flux-growth and melt-growth techniques. The growth involves many equipment or considerations as follows: 1. materials (reactants, flux, vapor pressure *etc.*); 2. crucibles (alumina, magnesia *etc.*), tubes (glass or silica); 3. arc-melt and glass-sealing stations; 4. furnace (box furnace, tube furnace *etc.*).

2.1.1 Syntheses of CaFe_2As_2 and related compounds

CaFe_2As_2 is a major parent compound in the AFe_2As_2 (122) family with the well-known ThCr_2Si_2 structure, where $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ and Eu . CaFe_2As_2 single crystals, similar to BaFe_2As_2 and SrFe_2As_2 , can be synthesized through both Sn-flux and

FeAs-flux (self-flux) growth methods. The former one, however, introduces about $1 \sim 2\%$ Sn ($T_c = 3.722$ K) contaminant, which is incorporated into Fe sites and causes a slight decrease in the spin-density-wave (SDW) transition. Meanwhile, the crystals grown by the Sn-flux method are relatively small. Therefore, the FeAs self-flux method is preferred in order to prevent the Sn-contamination and to effectively grow larger crystals.

Single crystals of CaFe_2As_2 , with size $\sim 5 \text{ mm} \times 5 \text{ mm}$, were successfully grown from a self-flux technique. The FeAs precursor was first synthesized from stoichiometric amounts of Fe pieces (Sigma Aldrich, 99.999+%) and As chunks (Alfa Aesar, 99.9999 %) inside a silica tube, which was slowly heated to 800°C for 30 hours. Though As has a high vapor pressure, which requires additional precautions, the binary compound FeAs is relatively stable. Then Ca-pieces (Alfa Aesar, 99.9999 %) were mixed with FeAs powder at the mole ratio of Ca: FeAs = 1: 4 and loaded in an alumina crucible, which was sealed inside a silica tube under reduced argon atmosphere ($\sim 1/3$ atmosphere). The silica tube was subsequently sealed in a larger and thicker silica tube under vacuum; the purpose of the double sealing procedure was to prevent the reactants from being exposed to air if the inner tube fails. The assembly was first heated to 1180°C over 8 hours in a furnace, held at 1180°C for an additional 24 hours, and then cooled to 980°C at a rate of 2°C/h . At last the assembly was “furnace cooled” to room temperature by simply turning off the power of the furnace. The grown single crystals with shiny surface were easily cleaved from the melt. The preparation procedures were carried out in a glovebox under purified argon atmosphere with total O_2 and H_2O levels < 0.1 ppm.

Similarly, (Sm,Ca)Fe₂As₂ and (Eu,Ca)Fe₂As₂ discussed in Chapter 4 were grown through similar routes.

2.1.2 Postgrowth thermal treatments on CaFe₂As₂

A systematic study of annealing and quenching on FeAs-grown CaFe₂As₂ was first carried out by Ran *et.al.* [36] and consequently a phase diagram of structural transition vs. annealing temperature was developed. In our investigation, we attempted to tune the annealing time as the key parameter, while fixing the annealing temperature.

Our postgrowth thermal treatment was carried out on CaFe₂As₂ by sealing the crystal in an evacuated quartz tube, annealing it in a pre-heated furnace at 350 °C for a certain time (varies from 3.5 to 6 hours) and then quenching the quartz tube in ice water. After each annealing and quenching process, the corresponding measurements and characterizations were performed on the sample. Then the sample was carefully cleaned for the next annealing process. The detailed procedures will be discussed in Chapter 3.

2.1.3 Syntheses of β -PdBi₂, PdBi_{2-x}Pb_x and Na_xPdBi₂

The Pd-Bi binary compounds exist in different phases (see Fig. 2.1). The β -PdBi₂ (the high temperature phase) single crystals were synthesized through a melt-growth method. Stoichiometric amounts of Pd and Bi grains were sealed in an evacuated quartz tube, which was heated up to 700 °C, kept for 10 hours, and then slowly

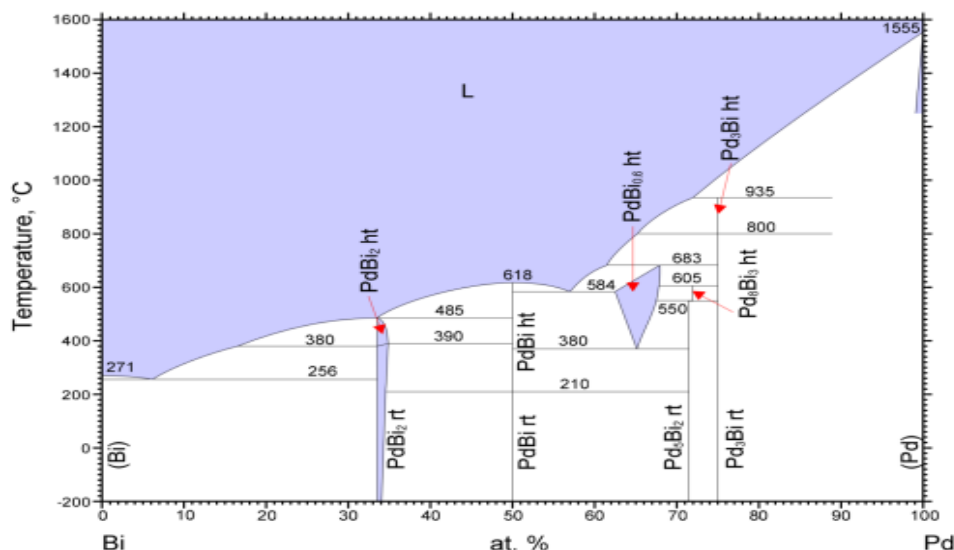


Figure 2.1: Phase diagram of the Pd-Bi system (Figure from ASM phase diagram database). L: liquid phase.

cooled to 450 °C over 30 hours. In order to retain the β -phase, the tube was then quenched in iced water directly from 450 °C. Similarly, it was attempted to grow a series of $\text{PdBi}_{2-x}\text{Pb}_x$ ($x = 0.0, 0.08, 0.15, 0.20, 0.28, 0.35, 0.40, 0.60, 0.80$, and 1.0) crystals with stoichiometric amounts of Pd, Bi, and Pb. The preparation of the Pd, Bi and Pb grains was done in the air since they are chemically stable.

In addition, the Na_xPdBi_2 compounds were grown by mixing Na and previously obtained PdBi_2 precursor, followed by the same synthetic condition but using a carbon-coated quartz tube to prevent the possible reaction of sodium with the quartz tube at high temperature. The carbon coating of the quartz tube was found to be intact after the synthesis, indicating the success of the growth. Due to the highly reactive nature of Na with moisture, the preparation procedures were carried out in

a glovebox.

2.2 Structural and chemical characterization

2.2.1 X-ray Diffraction (XRD)

XRD provides an expeditious way to identify the crystal structure and the phase impurity of bulk samples. The powdered single crystals of β -PdBi₂ and PdBi_{2-x}Pb_x were characterized by XRD at room temperature from 10 to 90 degrees using a Panalytical Xpert diffractometer with a monochromatic Cu K ($\lambda = 0.154178$ nm) radiation source. Single crystalline samples of CaFe₂As₂, (Sm, Ca)Fe₂As₂ and (Eu, Ca)Fe₂As₂ were characterized by X-ray diffraction using the Rigaku DMAX III-B diffractometer at room temperature with a Cu K ($\lambda = 0.154056$ nm) radiation source. The typical XRD (*00l*) patterns of these samples, *e.g.*, CaFe₂As₂ (as shown in Fig. 2.2), show preferred orientation along the *c* axis.

2.2.2 Wavelength Dispersive Spectroscopy (WDS)

The chemical analyses were carried out by WDS measurements to determine the compositions of the samples. A JEOL JXA-8600 electron microprobe analyzer with 15 kV accelerating voltage, a 30 nA sample current and 1 μ m spot size was used. The measurements were taken on multiple randomly chosen spots on the sample to verify the chemical homogeneity, which can be reflected by the statistical standard deviation. The precision of individual measurement is less than 0.5% relatively.

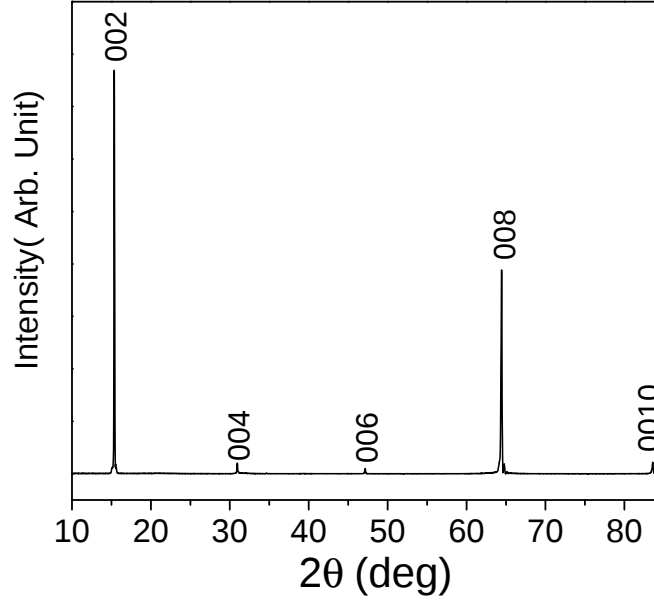


Figure 2.2: The XRD (00 l) pattern of CaFe_2As_2 single crystal.

2.3 Physical property characterization

2.3.1 Magnetic susceptibility

The magnetic susceptibilities in this work were measured using a quantum design magnetic property measurement system (MPMS). The MPMS system provides a temperature control that ranges from 2 K to 400 K and a vertical magnetic field up to 5 T. The MPMS system includes four different superconducting components: a superconducting magnet to generate large magnetic fields, a superconducting detection coil, a superconducting quantum interference device (SQUID) and a superconducting magnetic shield surrounding the SQUID. Due to the high sensitivity of the SQUID, the system can measure magnetization signal as precise as 10^{-8} emu. In order to study the magnetic behavior of materials, two principal magnetic measurements are

usually performed: $M(H)$ –magnetization as a function of applied magnetic field and $M(T)$ –magnetization as a function of temperature. The combination of these two measurements provide useful information about the magnetic behavior of materials.

To detect a magnetic transition, for example, a paramagnetic (PM) to spin-density-wave (SDW) transition, the sample is first cooled below the transition temperature (zero field cooled) and then a high magnetic field (*e.g.*, 1 T) is applied. The temperature is gradually raised above the transition temperature and the warming $M(T)$ data is taken over the whole temperature range. After that, the sample is again cooled (field cooled) to low temperature to obtain cooling $M(T)$ data. The transition can be detected as an anomaly, usually a suppression of magnetization below the transition temperature.

To detect superconductivity, the material is first cooled down below the superconducting transition temperature (T_c) and a low magnetic field is applied afterwards (zero field cooled). When the magnetic field is applied below the transition temperature of a superconductor, it expels all the magnetic flux inside and shows perfect diamagnetism. Then the temperature is raised above T_c so that the magnetic field penetrates the material as it enters the normal state. To examine the Meissner effect, the material is again cooled below the transition temperature (field cooled). Apart from the $M(T)$ data taken to determine the T_c , a $M(H)$ measurement can also be carried out to verify the diamagnetic behavior of a superconductor below the T_c .

In the practical use of MPMS, the sample is loaded inside a gel-capsule, or enclosed in a piece of small weighing paper. Then they are fixed in a transparent straw attached to the probe. The gel-capsule, the weighing paper and the straw all

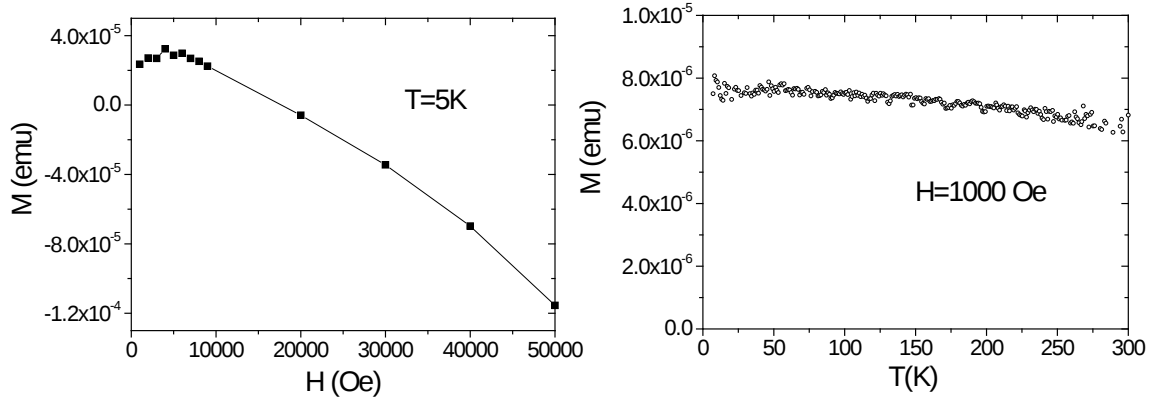


Figure 2.3: The magnetization response of a straw with a weighing paper at 5K (left) and under 1000 Oe (right).

generate background magnetic signals, particularly under high fields. Fig. 2.3 shows the background magnetic signal of a small folded paper in a straw measured at 5 K and under 1000 Oe. When the sample signal is so small that it is comparable to the background signal, precaution must be taken to subtract the corresponding background signal. Another way to solve this problem is to attach the sample to a thin quartz rod, which generates much weaker background signal than a straw/paper does.

2.3.2 Electrical resistivity

All resistivity measurements were carried out using the AC transport (ACT) option in a quantum design physical property measurement system (PPMS) or using an in-house built probe with its data acquisition (DAQ) system.

In the PPMS, the 6000 controller is able to tune the sample temperature from 1.8 K to 300 K and the applied field up to 7 T. Two samples can be mounted

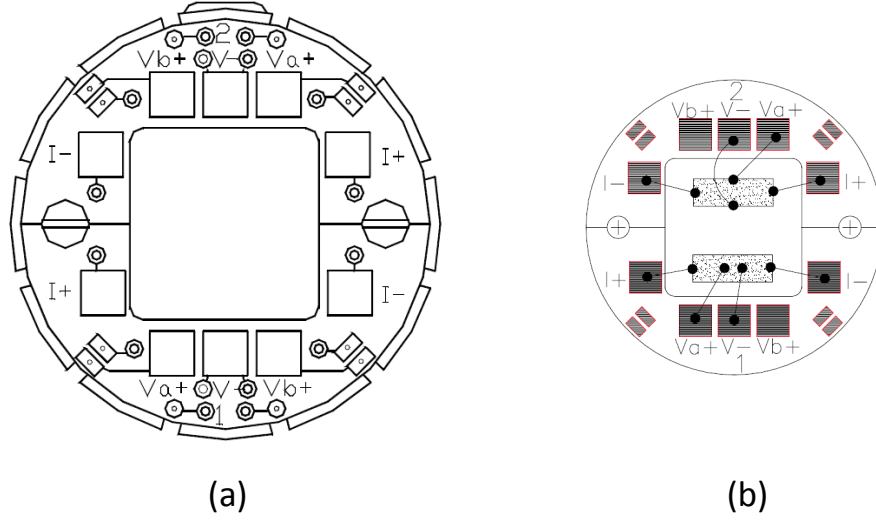


Figure 2.4: Top view of the ACT puck (left); the wiring configurations of four-lead and five-lead measurement (right). [Figure from Quantum Design user's manual]

simultaneously on the ACT puck as shown in Fig. 2.4. Then resistivity data can be acquired through the ACT option built in the PPMS, or the user option with an external resistance bridge interfaced with the PPMS.

The in-house-built DAQ system consists of a low-frequency alternating-current resistance bridge LR 400 (Linear Research), a Keithley 220 current source and a Keithley 182 voltmeter. The resistance bridge measures the sample resistance, while the current source and the voltmeter are used to measure the response of the temperature sensor near the sample. The sample attached in the probe is cooled by dipping the probe in a cryostat and the temperature can be tuned by lowering or raising the probe.

Both ways employ the four-lead measurement configuration (see Fig. 2.5) to eliminate contact resistance. Two outer leads pass a current through the sample, two

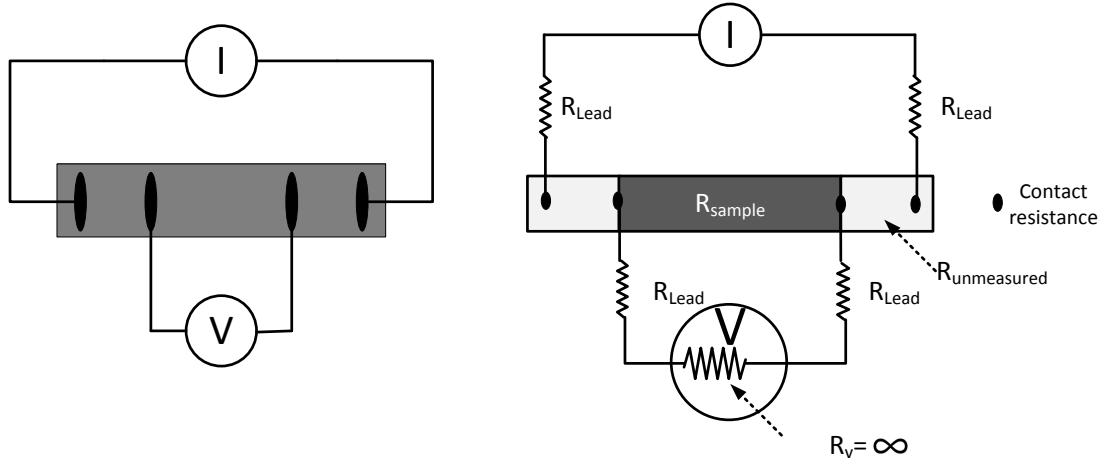


Figure 2.5: Schematic drawing of the four-lead arrangement for resistivity measurement (left); schematic drawing showing contact resistance, lead resistance and sample resistance in the four-lead arrangement(right).

inner separate leads are used to measure the voltage across them, and the resistance is calculated simply by Ohm's law. Silver paste (or silver epoxy) is used to make contact between the sample and the platinum wires, which are then soldered to the pins in the ACT puck or in the probe. Meanwhile, thermal paste is used to ensure good thermal conduction between the sample and the ACT puck (or the probe).

2.3.3 Hall-coefficient measurement

The Hall-coefficient measurement is a common method to evaluate the charge-carrier concentration of conducting materials. When charge carriers move perpendicular to a magnetic field, a Lorentz force is exerted on them perpendicular to both the field and their velocity.

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B},$$

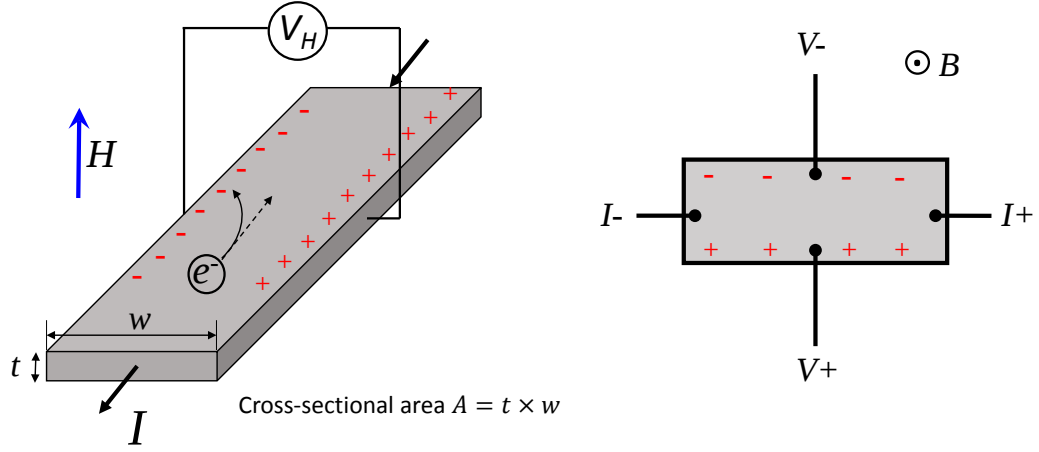


Figure 2.6: Schematics showing the Hall effect (left) and the charge-carrier distribution in the four-lead measurement (right).

where q is the charge, positive for holes and negative for electrons, $\mathbf{v}$ is the velocity of the motion, and $\mathbf{B}$ is the magnetic field.

When a longitudinal current is passed through a sample under a magnetic field perpendicular to the current, the charge carriers experience a Lorentz force and thus accumulate on one edge of the sample (Fig. 2.6). This results in a potential difference across the sample. Such a potential is therefore called Hall potential, the sign of which indicates the charge carrier type and the magnitude of which reflects the charge carrier density in the sample.

According to the Ohm's law, the Hall resistivity

$$\rho_H = \frac{E_H}{j}.$$

The Hall coefficient R_H is defined by

$$R_H = \frac{\rho_H}{B} = \frac{E_H}{jB} = \frac{V_H A}{IlB},$$

where E_H is the Hall field, V_H is the Hall potential, j is the current density given by I/A (the current divided by the cross-sectional area), and l is the separation of the transverse voltage leads. The Hall coefficient is related to the charge carrier type and charge carrier density as

$$R_H = \frac{1}{nq},$$

with n representing the charge carrier density and q representing the charge of the carrier.

Hall coefficient measurements in this work were carried out using the ACT option. The most accurate way of obtaining Hall coefficients at a certain temperature is to examine how the Hall resistivity varies with the magnetic field. According to the linear correlation of V_H and B , a plot of ρ_H versus magnetic field, $\rho_H(H)$, for a sample should yield a straight line with slope $= R_H$ (see Fig. 5.4 in Chapter 5). In a four-wire Hall coefficient measurement, the two voltage leads are not always aligned perpendicularly to the longitudinal current (see Fig. 2.7 (left)), resulting in a contribution from the longitudinal component, which is the normal electrical resistivity.

$$\rho(H) = \rho_H(H) + \rho_l(H),$$

where $\rho_H(H)$ is the Hall resistivity and $\rho_l(H)$ is the longitudinal contribution.

Therefore, the measured Hall voltage is nonzero in the absence of magnetic field, and the plot of $\rho(H)$ deviates from linearity under magnetic field due to the magnetoresistance of the longitudinal component. Here the $\rho_H(H)$ is an odd function of H while the $\rho_l(H)$ is an even function. Thus the $\rho_l(H)$ term can be eliminated by employing $R_H = (\rho(H) - \rho(-H))/2H$, which is again a linear curve. Another

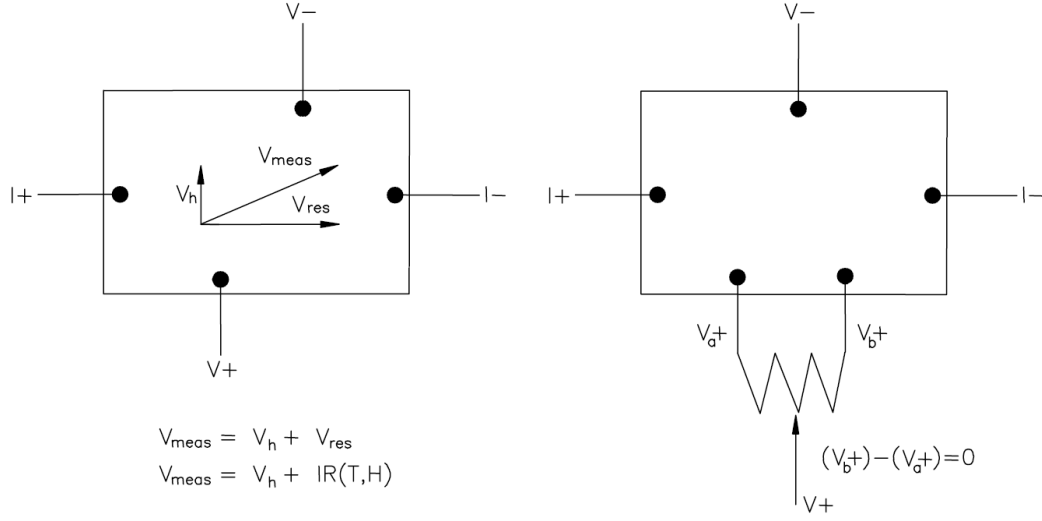


Figure 2.7: The offset with a four-lead Hall coefficient measurement (left) and offset nulling with a five-lead Hall coefficient measurement. [Figure adapted from Quantum Design user's manual]

way to further reduce the longitudinal contribution is to carry out a five-wire measurement, with an additional wire being attached in parallel to one of the other voltage leads (see Fig. 2.7). Under zero magnetic field, the potentiometer between the two leads is used to null the longitudinal resistance component. Due to the small magnitude of Hall voltage and relatively large magnetoresistance of the sample, the two methods were combined in this work. After verifying the linear correlation of $\rho(H)$, the Hall coefficient $R_H(T)$ (as a function of temperature) can be taken as $R_H(T) = [R_H(H) + R_H(-H)]/2$ at each temperature while fixing the magnetic field.

2.3.4 Heat-capacity measurements

Heat-capacity measurements in this work were carried out using the quantum design heat-capacity option. Before measuring the sample, the addenda with proper amount of N grease was measured to create an addenda table. Then the sample heat capacity was calculated by subtracting the addenda portion from the total heat capacity.

2.3.5 High-pressure study

The application of external pressure to superconductors can drive the compounds towards or away from lattice instabilities by varying the principal parameters determining the superconducting properties (the electronic density of states at the Fermi energy, $N(E_F)$, the characteristic phonon frequency, and the coupling constant of electrons and phonons), and it can be used to tune the T_c and the superconducting properties [53]. In this dissertation, high pressure studies were carried out for CaFe_2As_2 , $(\text{Sm,Ca})\text{Fe}_2\text{As}_2$, $(\text{Eu,Ca})\text{Fe}_2\text{As}_2$ and PdBi_2 compounds.

All pressure measurements were carried out using a BeCu high pressure clamp cell [54]. The clamp cell consists of a main body (part A in Fig. 2.8), which contains the piston cylinder, and a “locking cap” (part B in Fig. 2.8), which has screws to lock in the pressure. Figure 2.9 displays the schematic arrangement of all parts in the clamp cell. The sample is immersed in pressure medium that is confined within the Teflon “cup” and sealed by the BeCu “cap”. The electrical feedthrough is made by passing wires through the hole in the BeCu “cap” and sealing the hole using Stycast epoxy. Then the wires are passed through the holes in the tungsten-carbide piston,

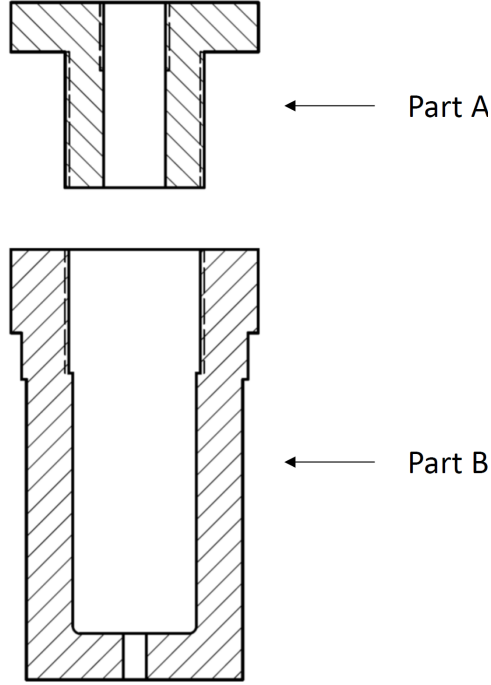


Figure 2.8: Cross-sectional view of the BeCu clamp cell (Drawn by B. Jawdat and L. Z. Deng according to C. W. Chu’s design).

the top plate, and the clamp cell body. Detailed procedures are provided below.

1. The Teflon “cup”, BeCu cap and packing rings will be deformed after each experiment and cannot be reused. Therefore the first step is to make these parts, the exact dimensions of which are shown in Fig. 2.10. All these parts can be machined using a lathe, with tools including center drills, drills with various sizes, cutting tools, and thin bits, *etc.*.

2. To prepare for the electrical feedthrough, four pairs of copper wires and one pair of thermocouple wires are passed through the tiny hole in the BeCu “cap”. Here two pairs of copper wires are used for the four-lead resistivity measurement; the other two are for a lead manometer, which is used to measure the pressure *in situ* [54]. The

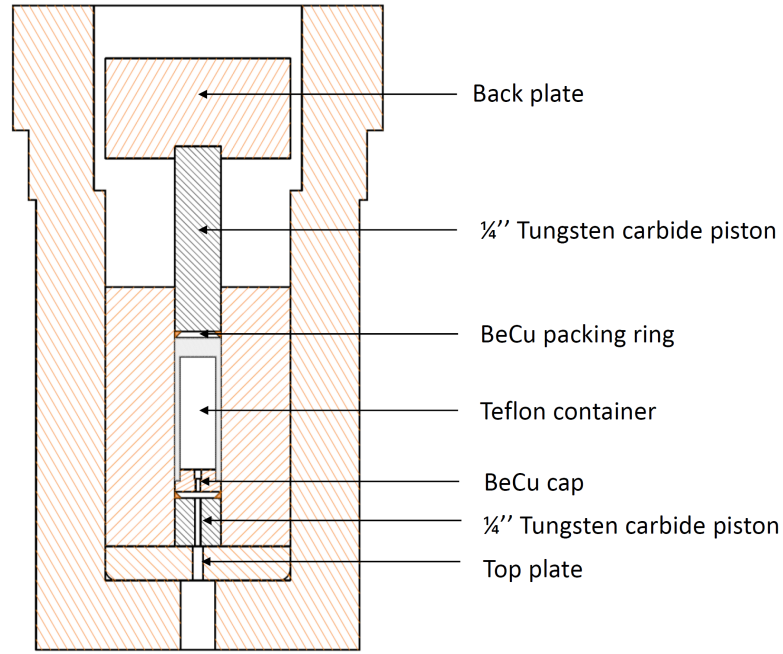


Figure 2.9: Schematic arrangement of all parts in the clamp cell (Figure prepared by B. Jawdat according to C. W. Chu's design).

thermocouple is used to monitor the sample temperature at high-temperature range, *i.e.*, $\sim 60 \text{ K} - 300 \text{ K}$. In the low-temperature regime where thermocouple becomes inaccurate, the temperature is monitored by a germanium temperature sensor, which is embedded in the wall of the BeCu clamp cell. Then the hole in the BeCu "cap" is sealed by proper amount of Stycast epoxy, which is mixed with Catalyst 9 at a weight ratio of 96% : 4%. It takes around 12 hours to cure the stycast. The entire hole should be fully filled with the stycast before being cured. Precaution must also be taken to prevent the stycast from forming sharp edges, which may break the wires after being hardened.

3. The next step is to weld a thermocouple joint and to attach the sample as well as the lead manometer to the copper wires. The sample should be seated closely

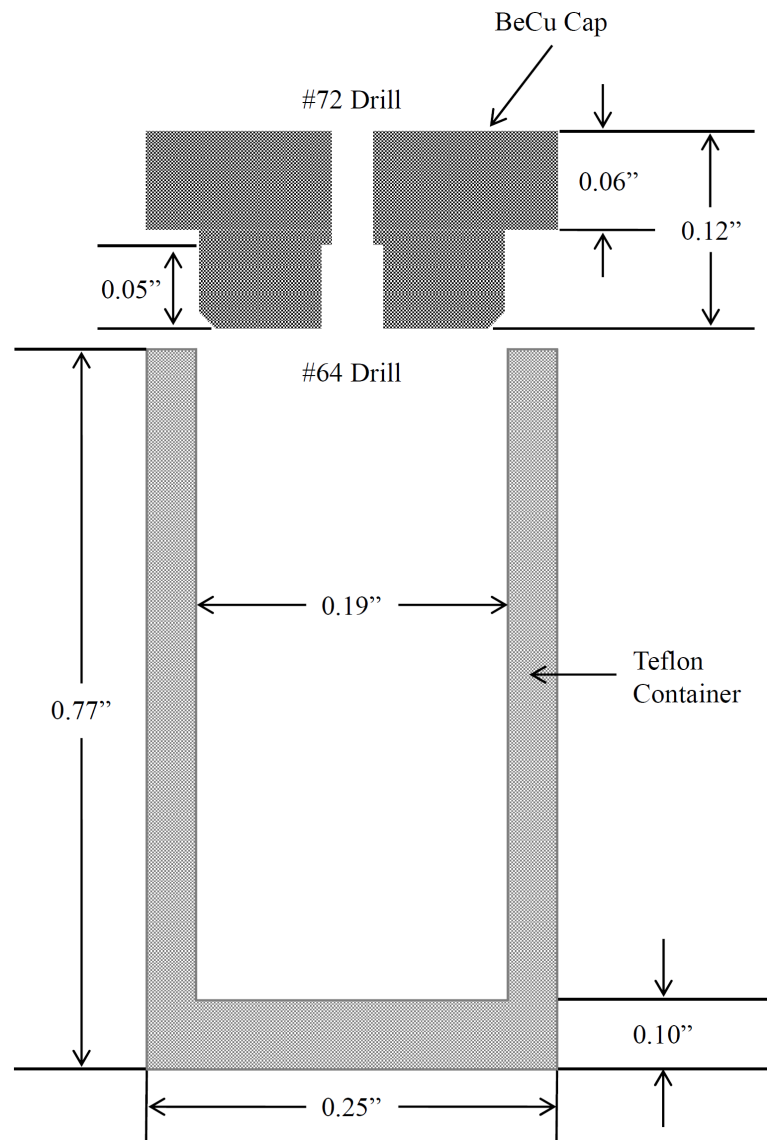


Figure 2.10: Dimensions (in inches) of the BeCu "cap" and the Teflon "cup".

on the thermocouple joint with red varnish to secure it. Care must be taken to the arrangement of the bare ends of the copper wires to avoid short circuit after being pressurized. Then the whole assembly is loaded into the Teflon “cup”, which is filled with Fluorinert (FC77) as the pressure medium.

4. As shown in Fig. 2.9, the enclosed Teflon “cup” is sandwiched by two packing rings and pistons, and loaded into the clamp cell. The four pairs of copper wires provide connections to the LR 400 Bridge for resistance and inductance measurements.

5. The pressure is applied to the system by pushing the backing plate with a hydraulic press and then squeezing the Teflon “cup” including the pressure medium that transmits the pressure. Then the pressure is locked inside the system by tightening the screws on the “locking cap”. The clamp cell can hold pressure up to 20 kbar (2 GPa). As mentioned above, the pressure is measured by a lead manometer based on the transition-temperature change of a lead under pressure:

$$\Delta T_c = 7.2 - T_c(p).$$

After assembling the pressure cell onto the probe, a glass dewar cryostat is used to cool down the system. The system temperature can reach down to 1.2 K via pumping the helium chamber of the glass dewar. The data acquisition system includes a LR 400 bridge, a Keithley 220 current source and two Keithley 181/182 voltmeters.

2.4 X-ray diffraction simulation

In chapter 3, The simulation of XRD (00 l) patterns was carried out based on a simplified intergrowth model for a mixture of two phases. Usually, the diffraction intensity of XRD peaks is determined by a structure factor (S_{hkl}), a multiplicity (M_{hkl}), Lorentz & polarization factors ($LP(\theta)$) and a temperature factor ($TF(\theta)$). The structure factor reflects the interference and position of atoms within the unit cell. The multiplicity is associated with the symmetry of the unit cell, as the d -spacings for related reflections are equivalent. The $LP(\theta)$ and $TF(\theta)$ are only angle dependent. Thus only the structure factor has been considered in our simulation model.

In the model, we consider that a crystal consists of N unit-cell layers, with p fraction of Phase 1 and $(1 - p)$ fraction of Phase 2, randomly distributed. The Bragg peaks of pure Phase 1 and pure Phase 2 can be indexed with lattice parameter c_1 and c_2 , respectively. Assuming the two phases have the same structure factor F , the (00 l) pattern can be simulated based on the following algorithm [55].

The peak intensity

$$I(\theta, p) = F \times \left| \sum_{n=1}^{n=N} e^{iS_n} \right|,$$

where

$$S_n = \frac{4\pi \sin\theta}{\lambda} [m_n c_1 + (N - m_n) c_2]$$

with m_0 being initialized as $m_0 = 0$. Then

$$m_{n+1} - m_n = 0$$

with probability $P = 1-p$;

$$m_{n+1} - m_n = 1$$

with probability $P = p$. Here m_n denotes the number of P1 layers and $N-m_n$ denotes the number of P2 layers that have been simulated.

In this work, the algorithm was modified to examine different possible layer arrangements as discussed in chapter 3. The simulation was realized under a Matlab programming environment.

Chapter 3

Interface-enhanced superconductivity with $T_c \sim 25$ K in undoped CaFe_2As_2

3.1 Background and motivation

CaFe_2As_2 , a parent compound in the large superconductor family with the well-known ThCr_2Si_2 structure, is supposed to be non-superconducting without doping [22, 23]. However, partial superconductivity with a transition temperature $T_c \leq 12$ K is induced by non-hydrostatic pressure [24, 25, 26]. Two types of interpretations have been offered: One puts the emphasis on the coexistence of different phases, *e.g.* the interface-related superconductivity [24, 25]; the other points to new phases induced by pressure, *e.g.* the so-called T' phase, an unknown tetragonal phase stabilized

at low temperature by pressure [33]. It is even more peculiar that trace superconductivity has been reported at ambient pressure, but interpreted rather differently, *e.g.*, based on the interfaces between adjacent antiferromagnetic domains [34, 35]. In addition to some intriguing features, such as the broad diffraction lines of the T' phase, a question naturally arises: could all of the observations share a common root? The answer may help to distinguish the underlying superconducting mechanism. If the key factor is the properly arranged interfaces (or domain boundaries), there would be a good chance to achieve similar ambient-pressure superconductivity through annealing, since it is well known that numerous CaFe_2As_2 “phases” can be mutually converted through post-growth thermal treatments [36, 37].

Two phases, P1 and P2, have previously been well investigated. The P1 phase (see Fig. 3.1) is tetragonal (T) and paramagnetic (PM) at room temperature but switches to an orthorhombic structure (O) with a spin-density-wave (SDW) excitation below ~ 170 K. The P2 phase (see Fig. 3.1) has a tetragonal structure (T2) with a slightly shorter lattice parameter c at room temperature, and converts to a non-magnetic collapsed-tetragonal phase (cT) below ~ 100 K [31, 32]. It should be noted that P1 and P2 are only stable ≤ 400 °C and > 800 °C, respectively [36]. Single-phase P2 crystals, for example, were obtained by quenching CaFe_2As_2 from 850 °C. The conversion between these two phases, however, can be very slow, *e.g.* it takes 24 h or longer to convert P2 to P1 at 350 °C. Both the structure and the magnetic properties of CaFe_2As_2 vary significantly with annealing and pressure. Thus, many different “phases”, *e.g.*, the T phase, have been reported [33, 36, 37]. Our XRD profile analysis and the magnetic data, however, suggest that they might be

comparable to the metastable layer-stacking components composed of P1 and P2. In this work, a systematic annealing procedure is developed to reproducibly induce (or suppress) the ambient-pressure superconductivity in CaFe_2As_2 . The systematic annealing was carried out on a P2 crystal by sealing the crystal in an evacuated quartz tube, and annealing in a preheated furnace at 350 °C for a certain time (between 3.5 and 6 hours) before quenching in ice water. A much higher $T_c \approx 25$ K with noticeable diamagnetic shielding and Meissner effect is observed. The superconductivity, however, only appears within a well-defined annealing-time window. Both the XRD profile analysis and the magnetization analysis are used to probe the mesostructure of the annealed samples. The XRD spectra, on one hand, can be reproduced as the products of randomly stacked layers of P1 and P2. Therefore heterostructures would be naturally formed by the two distinct layers (of O and cT phase at low temperature). The peak position 2θ varies systematically with the phase ratio (or the annealing time), which happens to cover the expected region for the proposed T' phase. The estimated interface density, in particular, is closely correlated with the superconducting volume fraction, as strong supportive evidence. On the other hand, we compared the P1 volume fraction (V_{P1}) extracted from the XRD result with that from the magnetization data. Although the two are in agreement for the non-superconducting crystals, a significant deficiency is observed in the magnetic volume fraction for the superconducting crystals. This suggests that the SDW excitations near the boundaries of the P1 blocks are well suppressed, possibly due to the lattice strain between P1 and P2. Thus the interfacial superconductivity may naturally be understood [56].

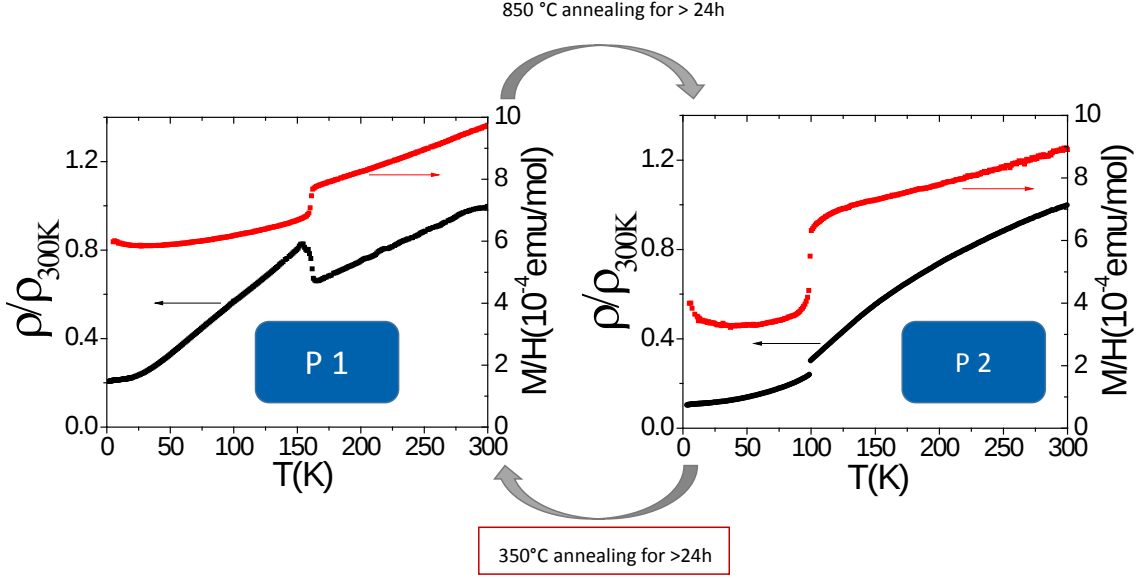


Figure 3.1: The temperature dependence of resistivity and magnetization (measured under a magnetic field of 1 T along c axis) of CaFe_2As_2 with P1 and P2 phase.

To further understand the pressure-induced superconductivity in CaFe_2As_2 , we carried out high pressure studies for a sample in the mixed phase (denoted as P3) and the sample P2. The high pressure study of P3 demonstrates two superconducting transitions, which have distinctive responses to external pressure. The lower transition resembles the observations in previous pressure studies of P1-phase CaFe_2As_2 [24, 25]. Interestingly, the higher transition is further enhanced to 30 K under a pressure of 17.05 kbar. On the other hand, no superconductivity can be induced in the sample P2 by applying pressure up to 12.50 kbar. These observations further support that the superconductivity in CaFe_2As_2 is significantly enhanced by the interfaces in the P1/P2 heterostructures.

3.2 Observation of the mixed phase and superconductivity

The indications of superconductivity of a CaFe_2As_2 sample with $t = 7.5$ h are shown in Fig. 3.2. The resistivity drop is severely suppressed by external magnetic fields. The onset transition temperature $T_c < 25$ K can be extracted as the diverging point under different fields. This value is much higher than those previously reported in CaFe_2As_2 [24, 25, 33]. The significant diamagnetic shifts below 12 K in both the zero-field-cooled and the field-cooled modes (*i.e.* the Meissner effect) confirm the interpretation (also see Fig. 3.14(b) in section 3.6), although the small $4\pi\chi$ value ~ 0.03 at 2 K suggests a non-bulk nature. Furthermore, the superconductivity under pressure survives up to 17 kbar with FC77 as the pressure medium (discussed in Section 3.6). However, the superconductivity appears only in a well-defined t window of $4 \text{ h} \leq t < 22.5 \text{ h}$ with the diamagnetic screening $\chi_{H//c}$ (2 K) peaking at $t = 14.5$ h (Fig. 3.6(d)). Samples with pure P1 or P2 phase are non-superconducting, consistent with most previous reports. The superconductivity observed, therefore, is a metastable phenomenon associated with the phase conversion from P2 to P1. Thus it seems unlikely to be due to some new stable phases.

The metastable nature of P2 at 350 °C is also evidenced by the $M(T)/H$ and the $\rho(T)$ at different stages (see Fig. 3.3(a)(b)). The anomalies ~ 100 K, which are features of the T-to-cT transition of P2, are systematically suppressed and shifted to lower temperature before $t = 14.5$ h. They are even totally eliminated after 18 h.

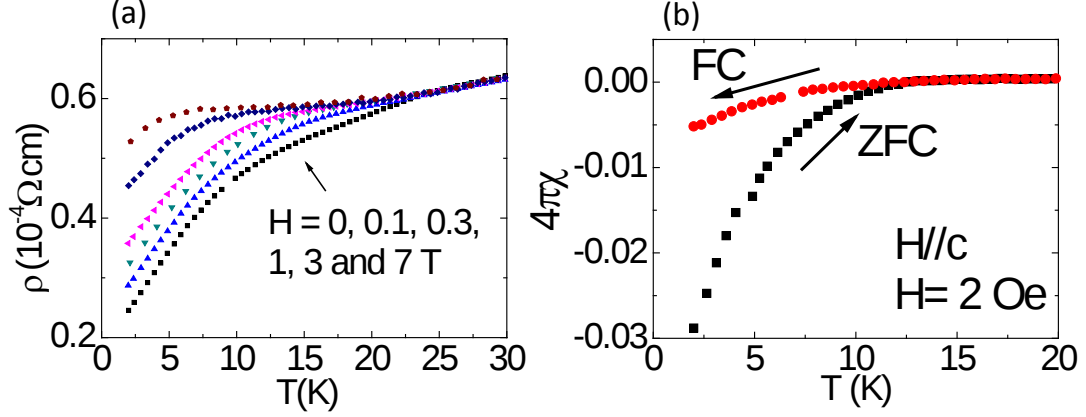


Figure 3.2: (a) The resistivity of the annealed CaFe_2As_2 with $t = 7.5$ h under magnetic fields $H = 0, 0.1, 0.3, 1, 3$ and 7 T (H/c). (b) The magnetic susceptibility of the sample with $t = 7.5$ h under a magnetic field $H = 2$ Oe (H/c).

It should be noted that the T-to-cT transition shown in $\rho(T)$ is similar to that under hydrostatic pressure, whereas it exhibits a broad decrease under non-hydrostatic pressure. Meanwhile, the anomalies at ~ 170 K, which represent the T-to-O transition of P1, appear only for $t \geq 18$ h and are enhanced with further annealing. Over the limited range of $11 \text{ h} < t < 18 \text{ h}$, weak anomalies simultaneously appear both around 100 K and 170 K, indicating the coexistence of P1 and P2. The weakening of the anomalies could be understood as a consequence of the phase-fraction variation from P2 to P1. However, the M/H drops of the 14.5 h sample at 170 K and 100 K are only 20 – 30% of the corresponding drops of the P1 and P2 samples (see Fig. 3.3(b)), which implies there exists “missing” strength in both SDW and cT transitions. In addition, the $\rho(T)$ of the superconducting samples appears as featureless above the superconducting transition temperature. These are reminiscent of the situation under non-hydrostatic pressure, where the anomalies largely disappear over the superconducting region but show up over the non-superconducting region

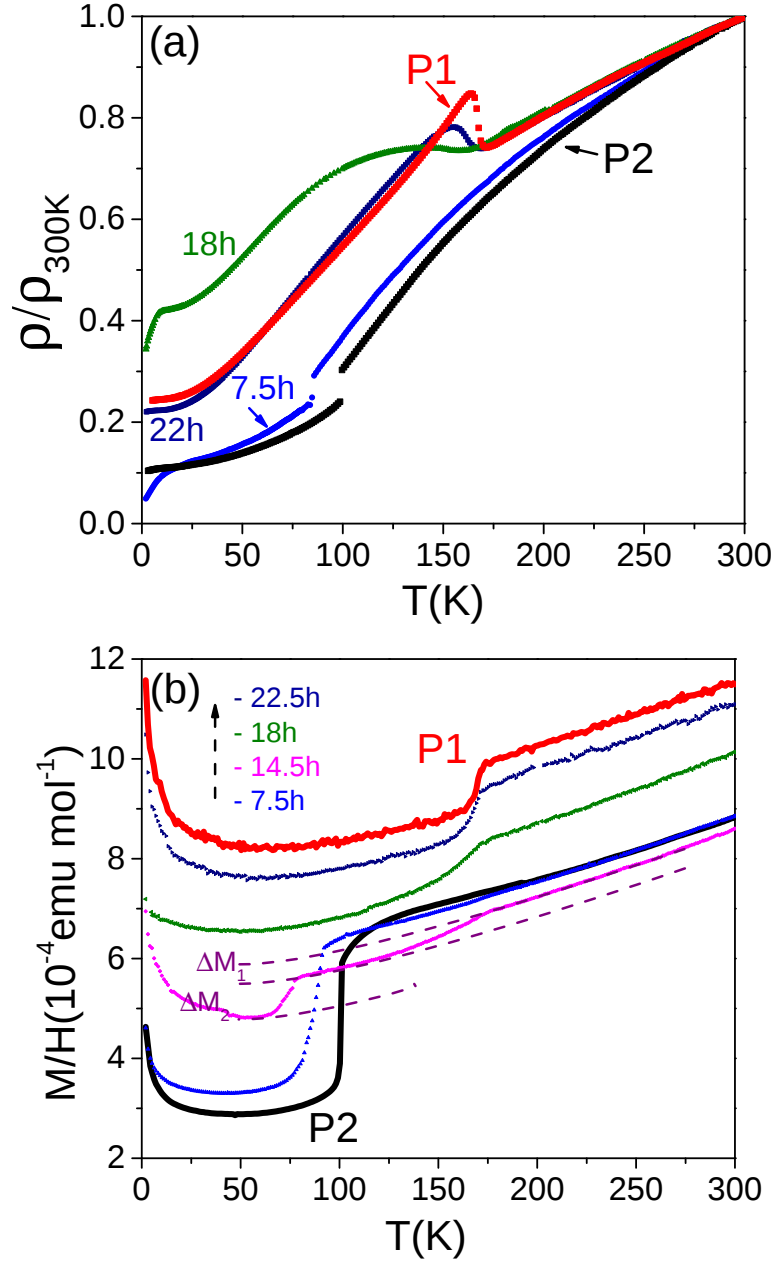


Figure 3.3: (a) Normalized resistivity of CaFe_2As_2 samples at different annealing stages. (b) Magnetization of samples at different annealing stages, measured under $H = 1 \text{ T}$ along c axis through warming (the 18, 22 and 28 h curves are all offset by a constant of $2 \times 10^{-4} \text{ emu/mol}$ for clarity).

under both the lower and the higher pressures [24, 25, 33] (See Fig. 3.4(a)(b)). These anomalies, however, are only marginally affected by the hydrostatic pressure, which mysteriously does not induce superconductivity [26] (See Fig. 3.4(c)). These may not be purely coincidental, but closely related to the underlying mechanism [49]. Furthermore, the simultaneous occurrence of superconductivity and the mixed phase indicates they are closely related. Both the mesostructure and the magnetic ground state, therefore, should be explored further.

3.3 Analysis of experimental and simulated XRD profiles as a probe for the mesostructure

An XRD study was performed to identify the phase composition and to probe the mesostructure at room temperature. If the superconductivity originates from a new phase, such as the proposed T' phase, a corresponding XRD peak should be noticeable in terms of its location, t -dependence and correlation with the superconductivity; on the contrary, if the interface mechanism dominates, the density of the interfaces should be correlated with the superconductivity. The $(00l)$ spectra of all samples show one set of peaks (Fig. 3.5(a) shows the $(00l)$ pattern for the sample with $t = 14.5$ h), which systematically shift to lower 2θ with t , a feature significantly different from that of the macroscopically mixed phases. The corresponding lattice parameter c expands upon annealing as shown in Fig 3.5(b). The (008) peaks, for example, are displayed in Fig. 3.6(a). The (008) peaks of the mixed-phase samples are located between the expected peaks of P1 and P2. Though significantly broadened, they are

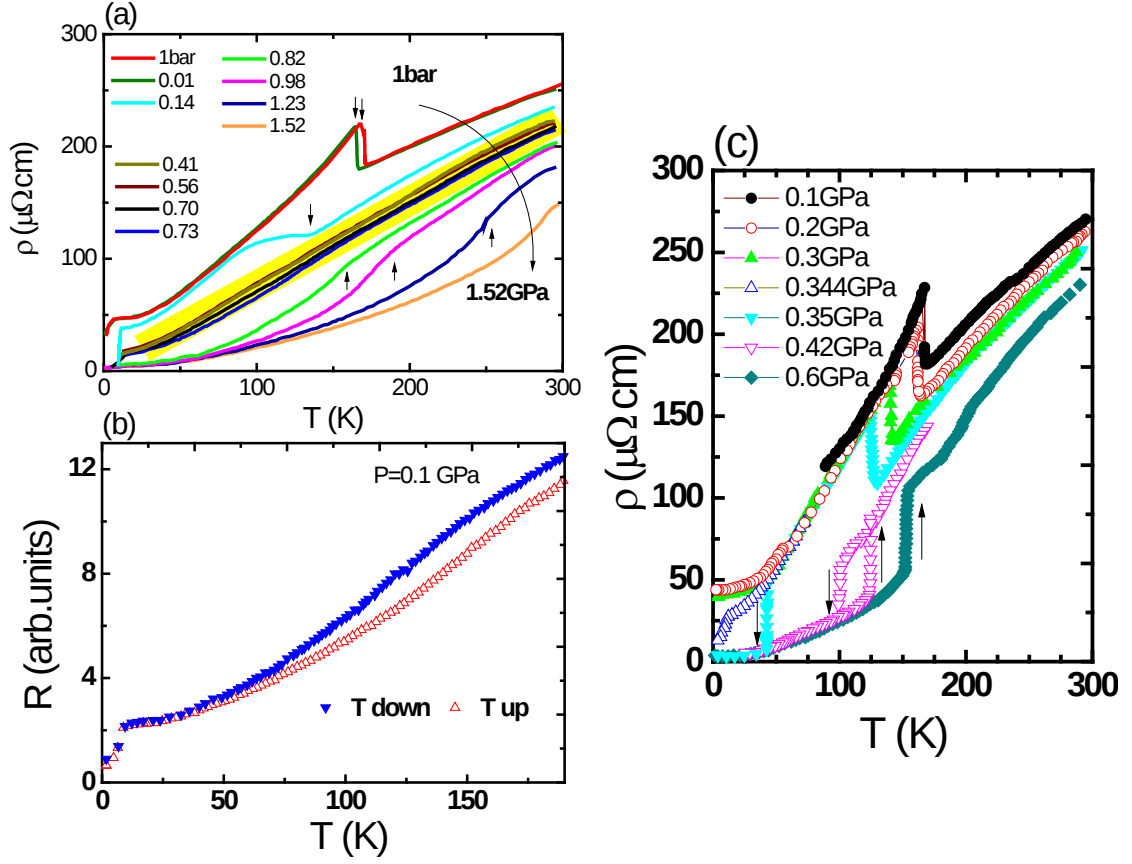


Figure 3.4: (a) The highlighted area shows the superconducting pressure regime, where the SDW and cT anomalies are suppressed in the resistivity curves of CaFe_2As_2 under non-hydrostatic pressure (adapted from [25]); (b) Resistivity curves of CaFe_2As_2 under uniaxial pressure (adapted from [33]); (c) Resistivity curves of CaFe_2As_2 under hydrostatic pressure (adapted from [26]).

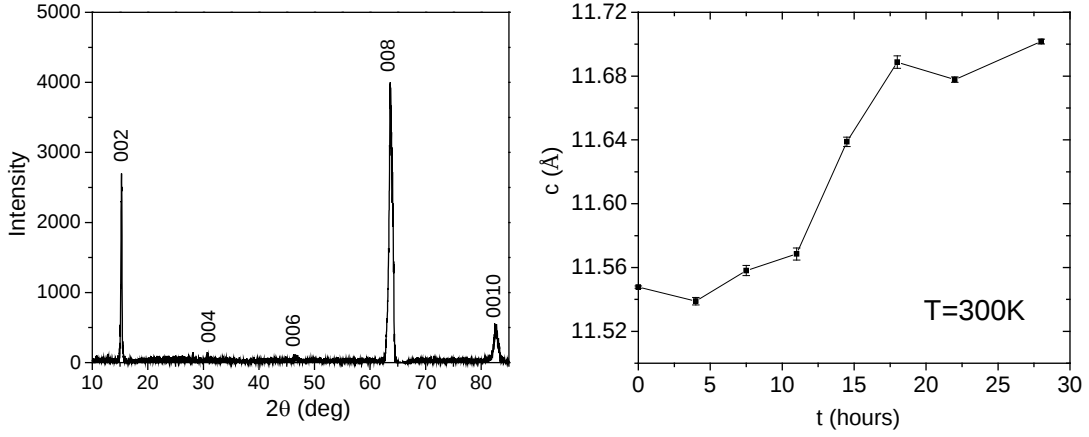


Figure 3.5: (a) The $(00l)$ XRD pattern for the sample with $t = 14.5$ h. (b) The c parameters calculated from the $(00l)$ patterns at various annealing time

well separated from the positions of the P1 and P2 peaks and cannot be divided to P1 and P2 contributions by a two-peak fitting method. Though this may imply a new phase, it seems unlikely based on its metastability as well as the smooth evolution in both the superconductivity and the magnetic transitions. The phenomenon can be better interpreted by analogy with intergrowth compounds; instead of a macroscopic mixing, the two phases are well dispersed into each other layer by layer without a strict long-range periodicity.

To verify this, an XRD profile-analysis procedure, a method widely used in the intergrowth (or the layer-stacking) compounds, was adopted [55]. In the intergrowth model, the crystals are treated as stacked unit-cell layers of the P1 and P2 phases, *i.e.* with $c_1 = 11.70$ Å and $c_2 = 11.55$ Å, respectively. The phase ratio of P1:P2 equals $p : (1 - p)$, where the p can also represent the conversion fraction from P2 to P1. Here both phases are assumed to have the same scattering amplitude. They are stacked along the c axis according to the designed sequences, which can be

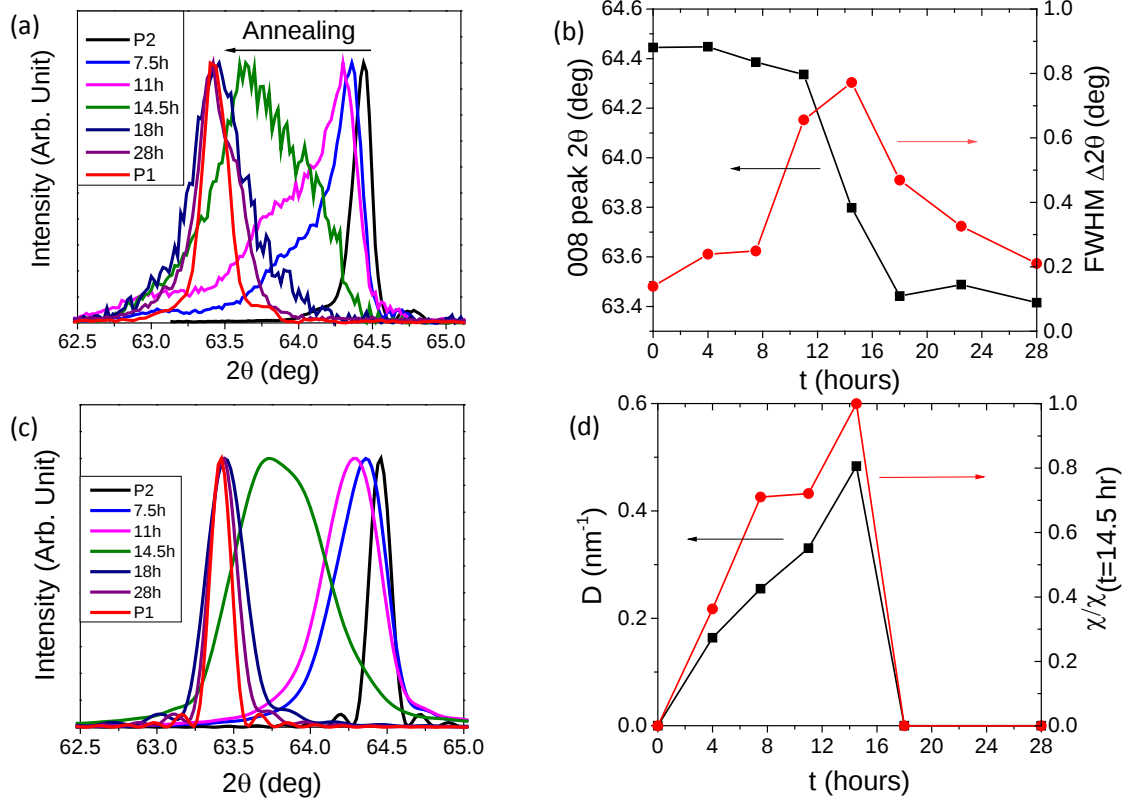


Figure 3.6: (a) The evolution of the experimental (008) peaks with normalized amplitude; (b) The (008) peak positions (squares) and corresponding FWHM (circles); (c) The simulated XRD profile of the (008) peaks; (d) The relative superconducting volume fraction (circles, measured at 2 K with $H = 2$ Oe, $H//c$) and the calculated interface density D (squares, see text for detailed definition).

manipulated to approach the best fit. For example, to simulate a random stacking case, each layer is independently assigned to be P1 (or P2) with the probability of p (or $1 - p$). It is straightforward that the lattice parameter of the whole crystal is $c = pc_1 + (1 - p)c_2$. The phase fraction, therefore, can be deduced from the $(00l)$ peak position. Additionally, the peak width can serve as a probe for the layer-by-layer arrangement. The simulation of the XRD spectra can further reveal the layer-stacking morphology.

Returning to the experimental result, the conversion fraction p can be readily deduced from the peak shift (Fig. 3.6(b)). The conversion kinetics $p(t)$ extracted can be approximately regarded as three straight sections with the starting and ending parts being horizontal. This is in good agreement with the Avrami Model of chemical decomposition [57]. The relatively flat part before 10 h represents the nucleation stage, and the jump between 11 h and 18 h corresponds to the rapid growth of P1. This growth region, however, is exactly where the superconducting volume fraction reaching maximum (Fig. 3.6(b)(d)). This seems natural for the interface scenario but rather accidental for the proposed T'-phase model. The kinetics of a new phase formation can hardly be the same as that of the P2-to-P1 conversion.

To be more quantitative, the interface density D is calculated based on the model. Starting with a P1 layer with a probability of p , the probability to have an adjacent layer being P2, *i.e.* to have an interface, will be $(1 - p)$. The expected interface density, therefore, will be $D = 2p(1 - p)/\bar{c}$ ($\bar{c}$ denotes the average lattice constant c) if there is no correlation between adjacent layers. The deduced D , shown in Fig. 3.6(d), seems to be proportional to the relative diamagnetic screening $\chi/\chi_{(t=14.5h)}$. While the

actual χ value depends on many other factors, such a correlation not only supports the interface model but also suggests that the relevant interfaces form on the ab planes.

The XRD-spectrum simulations based on differently designed layer arrangements are compared with the experimental $(00l)$ spectra. (Several possible layer-arrangement models will be discussed in details in Section 3.4.) The results show that the random stacking configuration of unit-cell P1/P2 layers may offer the best fit (Fig. 3.6(c)). Such a configuration leads to a relatively narrower single peak for the p close to both 0 and 1, but broad peak without split around $p \approx 0.5$. On the contrary, significant local aggregation of one phase will result in peak splitting. For example, an additional set of P1 peaks will emerge if five-or-more consecutive layers always share the same P1 structure. This confirms our interpretation that the two phases are mixed microscopically within a few layers rather than macroscopically in a domain-by-domain manner. Similarly, strong layer-to-layer correlation, *e.g.* large scale of alternating P1-P2-P1 arrangements, will cause corresponding satellite peaks. These possible arrangements are ruled out. The sample with $t = 14.5$ h ($p \approx 0.5$) seems rather special, exhibiting a broad (008) peak with FWHM $\approx 0.78^\circ$, which is far broader than expected. To resolve this, especially to exclude some unknown new phases, the Hall-Williamson method was used to fit all $(00l)$ peaks with $l \leq 10$ [58]. The data (see Fig. 3.7) suggest that the main factor for the broadening comes from the microstrain, which can account for a large p spread. The broadening can be reasonably reproduced by a Gauss distribution $\propto e^{\frac{-(p-0.5)^2}{\sigma^2}}$ for p with $\sigma \approx 0.032$. Such large heterogeneity in the conversion rate seems to be reasonable if the domains are

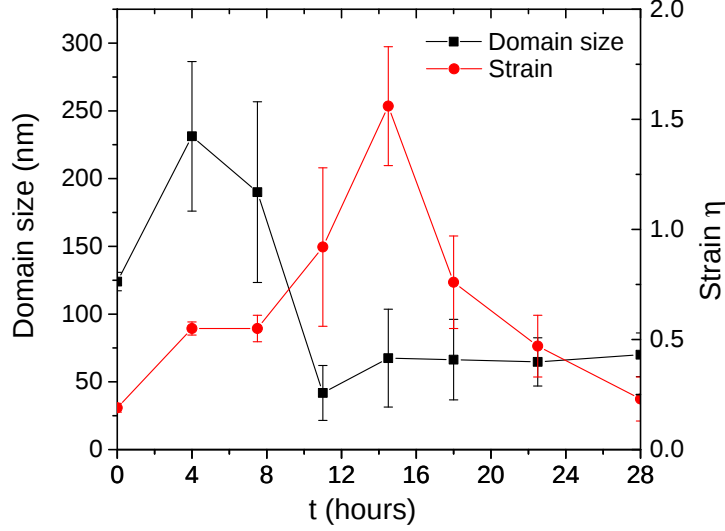


Figure 3.7: The domain size and strain calculated by using the Hall-Williamson method for all the samples at different annealing stages.

developed from different nuclei.

It is worth noting that significant shoulders have been developed at the lower 2θ side even for $t = 7.5$ h, whose main peak is otherwise much narrower (Fig. 3.6(a)). Similar shoulders also exist in other $(00l)$ peaks. Interestingly, the peak location is close to both the peak of the $t = 14.5$ h sample and that of the reported T' phase. Therefore we speculated that the $p \approx 0.5$ mesostructure might be thermodynamically preferred. While the T -phase model may offer an alternative interpretation, the conversion kinetics, the D vs. χ correlation, the distinct T_c value and the missing SDW strength suggest that the interface-associated superconductivity is a more proper interpretation.

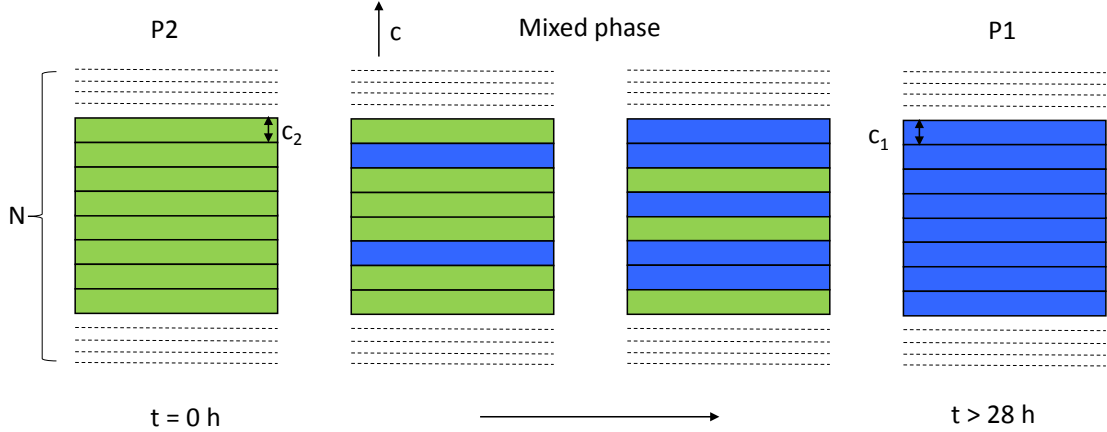


Figure 3.8: Schematic drawing of the intergrowth model through annealing from P2 phase to P1 phase.

3.4 Simulation of the $(00l)$ spectra

As we only consider the c orientation of the crystal, we assume that one crystal domain in the sample averagely consists of N unit cell layers. Ideally, at $t = 0$ h, the N single layers are all P2 phase with a lattice constant c_2 . Then according to the conversion kinetics, the single layers convert from P2 to P1 while passing the mixed-phase zone as the annealing time increases. After a sufficiently long time, all the single layers transform to P1 with a lattice constant c_1 , ending with a crystal in pure P1 phase (see Fig. 3.8). The probability for an individual layer to be P1 phase is denoted as p , which is identical to the conversion fraction. p is 0 at $t=0$ and reaches 1 when t is sufficiently long. Based on this simple model, simulations of the $(00l)$ spectra were performed through modifying the algorithm described in chapter 2. We tested several possible layer-arrangement models as discussed below.

In Model A (see Fig. 3.9(a)), we assume each single layer independently and

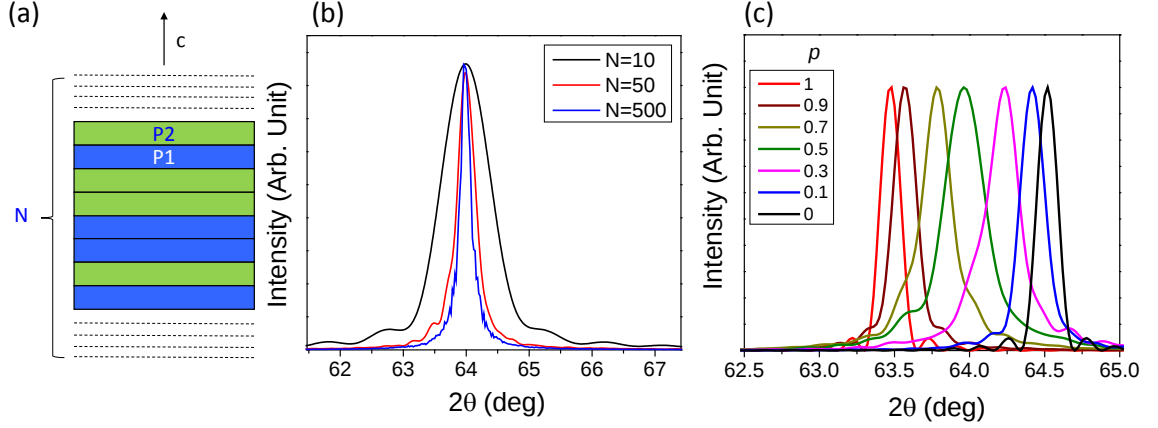


Figure 3.9: (a) Schematic drawing of the layer arrangement in Model A. (b) The simulated (008) peaks for $N = 10, 50$ and 500 with a fixed $p = 0.5$. (c) The simulated (008) peaks for p varying from 0 to 1 with a fixed $N = 50$.

randomly participates in the conversion with a probability p to be P1. There are two free parameters, the single-layer number N and the probability p . First, we examine the model by varying N while fixing $p = 0.5$ and showing how the (008) peak changes with N . The simulation result in Fig. 3.9(b) indicates that less layer numbers, which means smaller domain size, contributes to larger broadening effect. This is consistent with the Scherrer equation. Second, we fix $N = 50$ and vary the p gradually from 0 to 1 . The result in Fig. 3.9(c) illustrates that the stacking faults from the P1/P2 intergrowth lead to significant peak broadening, which supports our interpretation of the experimental data. For $p = 0.5$ where the two phases are maximally mixed, the peak width is broadest; the FWHM of $p = 0.5$ doubles that of $p = 0$ (or $p = 1$). Though the broadening level is still less than the experimental observation, the trend of the peak evolution based on the random conversion model fits well with our experimental observation.

In Model B (see Fig. 3.10(a)), we consider layer-to-layer correlations instead of

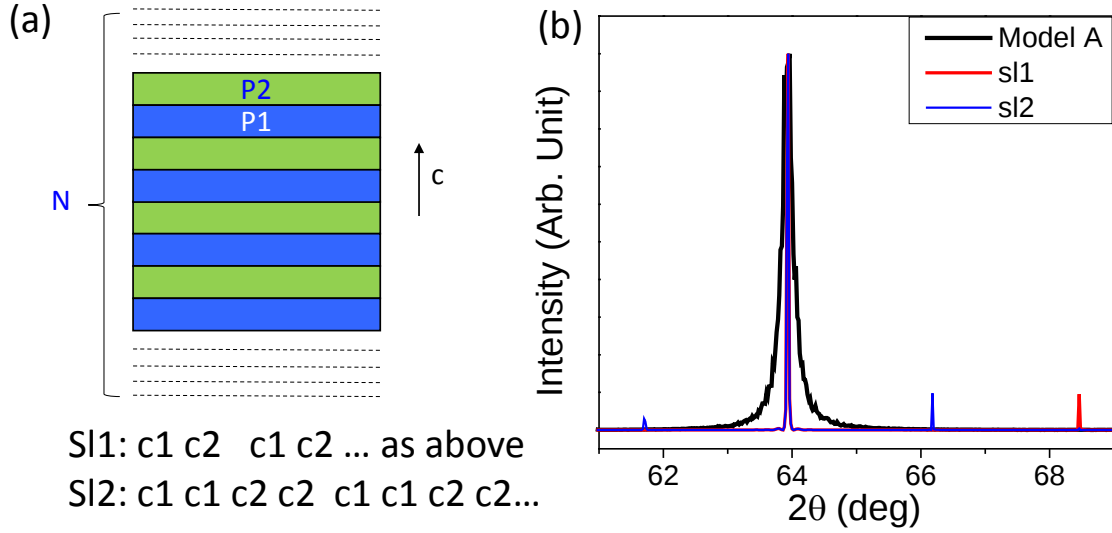


Figure 3.10: (a) Schematic drawing of the layer arrangement in Model B. (b) The simulated (008) peaks for the ordered layer arrangement sl1 and sl2 with $N = 1000$, compared with the random arrangement in Model A ($p = 0.5$).

an independent conversion for each layer. Namely, the P1 and P2 layers in the mixed phase are distributed following certain ordered sequences, for example, P1 P2 P1 P2 alternating or P1 P1 P2 P2 P1 P1 P2 P2 $\dots$. The simulation results from these two arrangements (see Fig. 3.10(b)) indicate that ordered layer arrangements will cause satellite peaks, *i.e.* forming superlattices. Since we have not observed any satellite peaks in our experimental XRD data, we can rule out Model B. The simulation of Model B suggests the conversion kinetics should be a random process, which agrees with our view.

In Model C (see Fig. 3.11(a)), we try to test the length scale of the conversion in the layers. If there exists interlayer interference, several adjacent layers may simultaneously convert and always keep in the same phase. In this model, we therefore assume that L adjacent layers always convert jointly with a probability p . Then

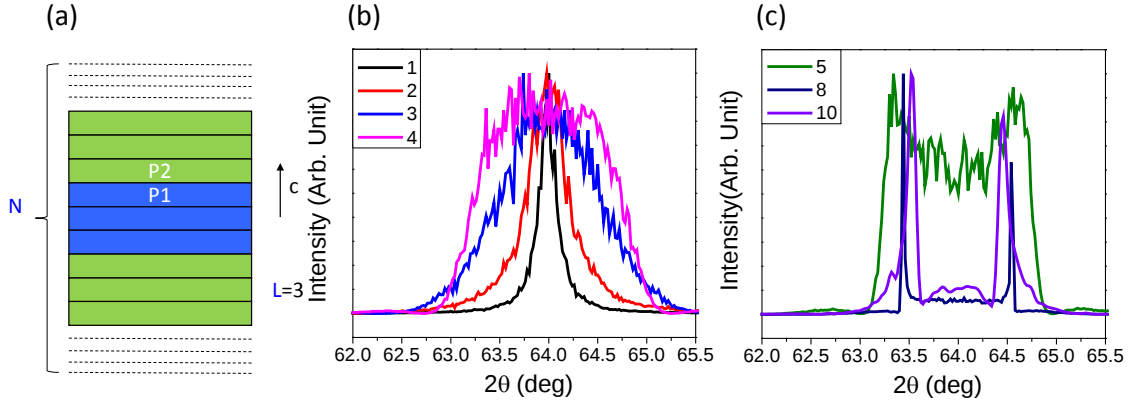


Figure 3.11: (a) Schematic drawing of the layer arrangement in Model C. (b) The simulated (008) peaks for $L = 1, 2, 3$ and 4. (c) The simulated (008) peaks for $L = 5, 8$ and 10. ($N = 1000$ and $p = 0.5$.)

we change L from 1 to 10 while fixing $p = 0.5$ in our simulation. As shown in Fig. 3.11(b), a larger L value significantly broadens the (008) peak, almost following a linear correlation. When L is greater than 5, the peak splits into two, the positions of which are corresponding to the P1 and P2 phases (see Fig. 3.11(c)). This implies the long-range periodicity for individual phase will appear if significant local aggregation ($L > 5$) of one phase occurs. The simulation of Model C indicates the mixing of P1/P2 phases must be within few-layer ($L \leq 4$) level. The two phases are well dispersed rather than distributed domain by domain. Thus, our view on the mesostructure of P1/P2 phases can be justified.

Based on the results above, Model A seems to be reasonable, while Model B and C help us rule out several other possible layer arrangements. Furthermore, we consider the heterogeneity between domains rather than assume they are homogeneous all over the crystal. The average lattice parameter of each domain is assumed to satisfy a Gaussian distribution with a deviation σ . By doing so, the broadening effect can

be reasonably reproduced and the simulated XRD ($00l$) patterns (*e.g.* (008) shown in Fig. 3.6(c)) fit well with the experimental data.

3.5 Analysis of the magnetization data as a probe for the low-temperature phase configuration

The low-temperature spin configurations in CaFe_2As_2 are affected by the structural/magnetic transitions. It is widely accepted that the appearance of superconductivity in its family, *e.g.*, $(\text{Ca},\text{Na})\text{Fe}_2\text{As}_2$, is closely related to the suppression of the SDW [59, 60]. The magnetization results above reveal that the SDW excitation may be suppressed in the mixed-phase regime. In order to understand the missing SDW strength, we analyze the magnetization data more quantitatively for all the annealed samples. The M/H drops can be used as a local gauge for phase configuration at low temperature. The M drops around the T-O and the T-cT transitions, *i.e.* ΔM_1 and ΔM_2 , are deduced through extrapolating the smooth backgrounds outside the transition regions (dashed lines in Fig. 3.3(b)). To estimate the effective volume fractions f_{M1} and f_{M2} , the drops are normalized by the corresponding drops of the P1 and P2 samples. It is expected that $f_{M1} + f_{M2} = 1$ in a macroscopic mixture, where the spin alignment of each domain is not severely affected by its neighbors; namely, the inter-domain magnetic interactions should be confined within a few unit-cell layers near the interfaces. Indeed, the extracted volume fractions follow the expectation rather well for $t > 20$ h (Fig. 3.12(a)), which agrees with above phase-conversion assumption and the XRD analysis. However, a systematic deficiency $f_{M1} + f_{M2} < 1$

appears for $5 \text{ h} < t < 20 \text{ h}$. For clarity, the difference between the f_{M1} and the XRD-derived volume fraction f_{X1} ($= p$) is shown in Fig. 3.12(b). The magnetization drop associated with the SDW excitation is largely suppressed over $t \leq 20 \text{ h}$. As discussed above, such a missing SDW moment can be found in most reported data of CaFe_2As_2 under non-hydrostatic pressure [24, 25, 33]. The difference here, however, is that the external pressure and the macroscopic strains should not exist in the annealed crystals. A plausible interpretation will be that the layer-stacking microstructure plays the role of pressure. The lattice mismatch between the stacking layers, *i.e.*, in the interfaces, may cause lateral microscopic strains that are large enough to cause the effects.

In order to further examine the interface arrangement, a rough phenomenological model is adopted as follows. The microstrain is expected to peak at the interface and to relax exponentially inward into the bulk layers. To simplify, it is assumed that the local ΔM_1 is zero within a fixed thickness of δ_1 from the interface, but recovers to bulk value outside. Surprisingly, such a rough model fits the data reasonably well with a $\delta_1 \approx 2c$ (solid line in Fig. 3.12(b)).

Based on the resistivity, magnetization, and XRD results, a phase-conversion diagram at 350°C is constructed as shown in Fig. 3.13. At room temperature, CaFe_2As_2 maintains the tetragonal structure with the lattice parameter c drastically jumping from $11.57 \text{ \AA}$ to $11.68 \text{ \AA}$ over a narrow t window of $11 \text{ h} < t < 18 \text{ h}$. The samples remain in the paramagnetic state during the annealing, with the susceptibility $M/H(300 \text{ K})$ slightly decreasing. Below 100 K , CaFe_2As_2 remains single phased only over two separated t windows of $t < 4 \text{ h}$ and $t > 18 \text{ h}$, *i.e.* being the cT phase and the

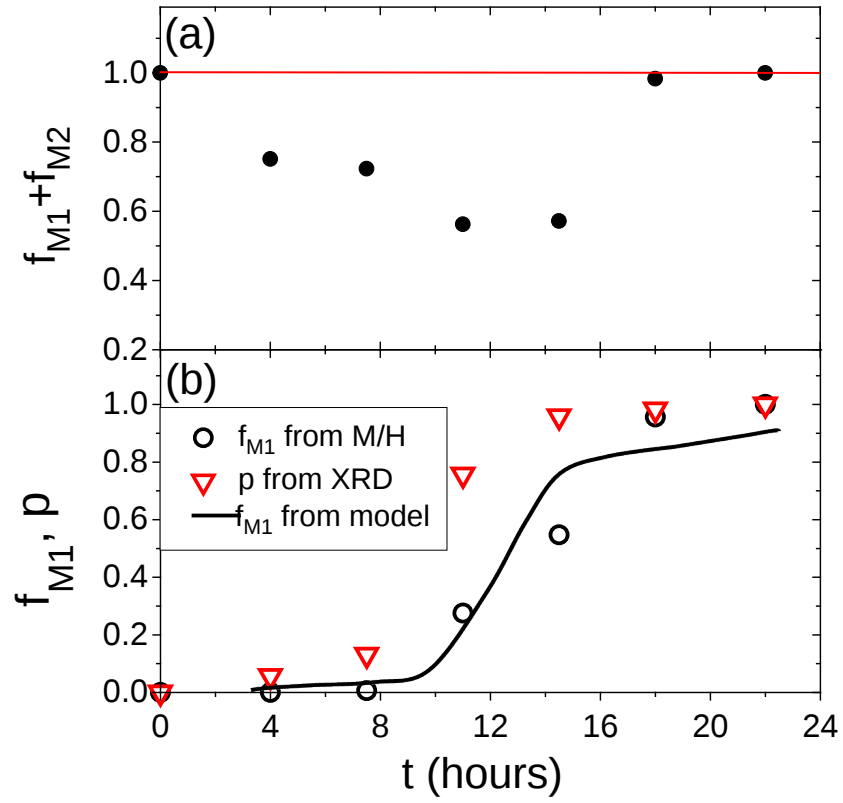


Figure 3.12: (a) The total magnetic volume fraction of M1 and M2 extracted from magnetization data; (b) The magnetic volume fraction f_{M1} extracted from magnetization data, XRD and our rough model fitting.

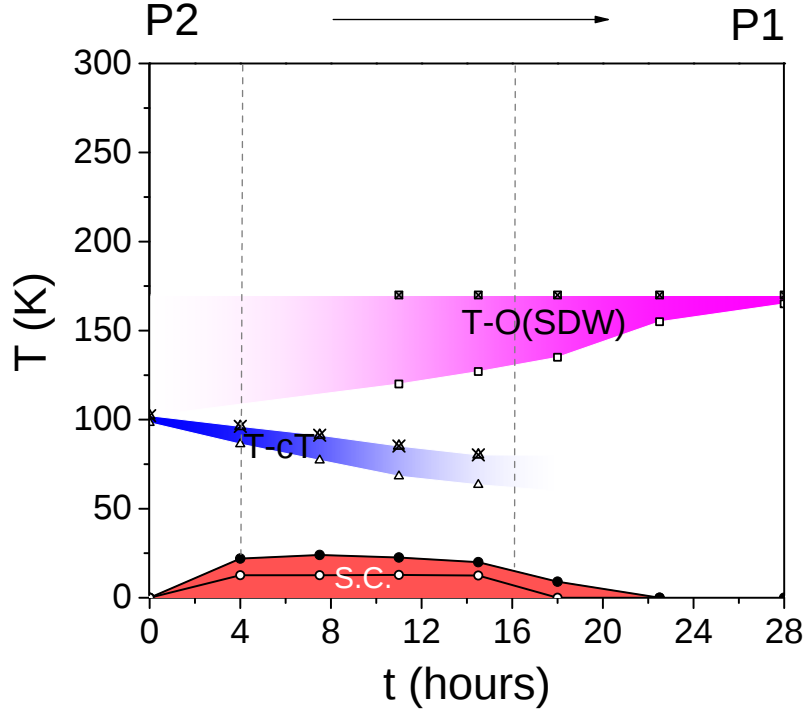


Figure 3.13: The phase conversion at 350 °C as a function of annealing time. T-O (SDW): tetragonal-to-orthorhombic transition (spin-density-wave transition); T-cT: tetragonal-to-collapsed tetragonal transition; SC: superconductivity. The structural transitions and the transition widths are determined by the magnetic data. The superconducting transition temperatures are determined by the onset T_c s from both the resistivity (solid circles) and magnetic (open circles) results. The area roughly enclosed by the dash lines indicates the metastable regime.

O phase, respectively. The crystals consist of randomly stacked P1 and P2 layers over $4 \text{ h} \leq t \leq 18 \text{ h}$. The superconductivity likely develops at the interfaces, where the SDW is suppressed by the lattice mismatch.

3.6 High-pressure studies

As clearly seen in the phase conversion diagram, CaFe_2As_2 samples in P1, P2 and the mixed phase demonstrate distinct properties at ambient pressure. A high-pressure study was carried out for a sample (denoted as P3) in the mixed phase with $T_c \sim 25$ K at ambient pressure. Sample P3 exhibits a clear Meissner effect ~ 25 K and a T-cT transition can be observed ~ 80 K (Fig. 3.14). Figure 3.15(a) shows the temperature dependence of resistivity of the sample under pressure up to 17 kbar. Surprisingly, a moderate pressure of 1.01 kbar annihilates the cT phase and the resistivity curve is not hysteretic any more (see Fig. 3.16(a)). But for pressure greater than 5.42 kbar, a downturn in resistivity at > 150 K shows up, accompanied with a clear hysteresis upon cooling and warming (see Fig. 3.16(b)), suggesting the cT phase is established again in this pressure regime. It seems that the annealing-generated cT phase and the non-hydrostatic pressure-caused cT phase are of different natures; the annealing-generated cT phase demonstrates a sharp drop in resistivity, which looks similar to the cT phase under hydrostatic pressure [26]. The elimination of the annealing-generated cT phase implies it is sensitive to non-hydrostaticity.

In the low-temperature region shown in Fig. 3.15(b), the two transitions denoted as T_{c1} and T_{c2} have distinctive responses to external pressures. The lower transition T_{c2} is initially enhanced as the transition is significantly sharpened by pressure ~ 4 kbar. Above 5.42 kbar, it is then suppressed, coinciding with the emergence of cT phase transition induced by the external pressure. The response of this transition is similar to the previous report of pressure induced superconductivity in CaFe_2As_2

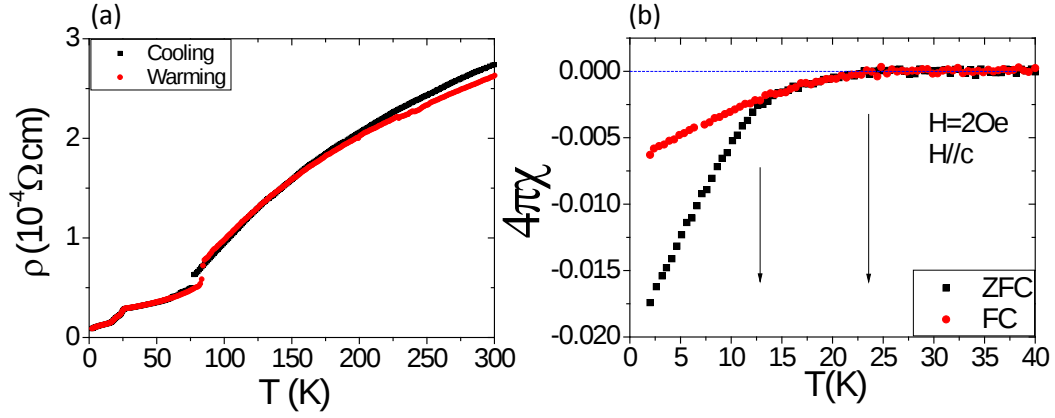


Figure 3.14: (a) The temperature dependence of resistivity for sample P3 at ambient pressure. (b) The magnetic susceptibility for sample P3 under a magnetic field of 2 Oe.

with pure P1 phase [24]. In contrast, the higher superconducting transition T_{c1} is rather continuously enhanced by pressure; it is sharpened and T_{c1} moves upwards to 30 K under 17.05 kbar. The distinctive response implies that T_{c1} may originate from a different type of interface.

In order to clarify the relation between the cT phase and superconductivity, we also carried out a pressure study on the sample P2. As shown in Fig. 3.17, no superconductivity was detected up to 12.50 kbar, indicating that the cT phase is not the superconducting phase. Such an observation directly rules out the possibility that the cT phase is responsible for superconductivity in CaFe_2As_2 , consistent with previous studies of the cT phase [31, 32]. Compared with previous high pressure studies of P1-phase CaFe_2As_2 and the non-superconducting P2 phase under pressure, the robust superconductivity of sample P3 under pressure with a further enhanced T_c suggests the superconductivity is more relevant to the interfaces than any single phases. Application of higher pressure on the sample P3 would unveil

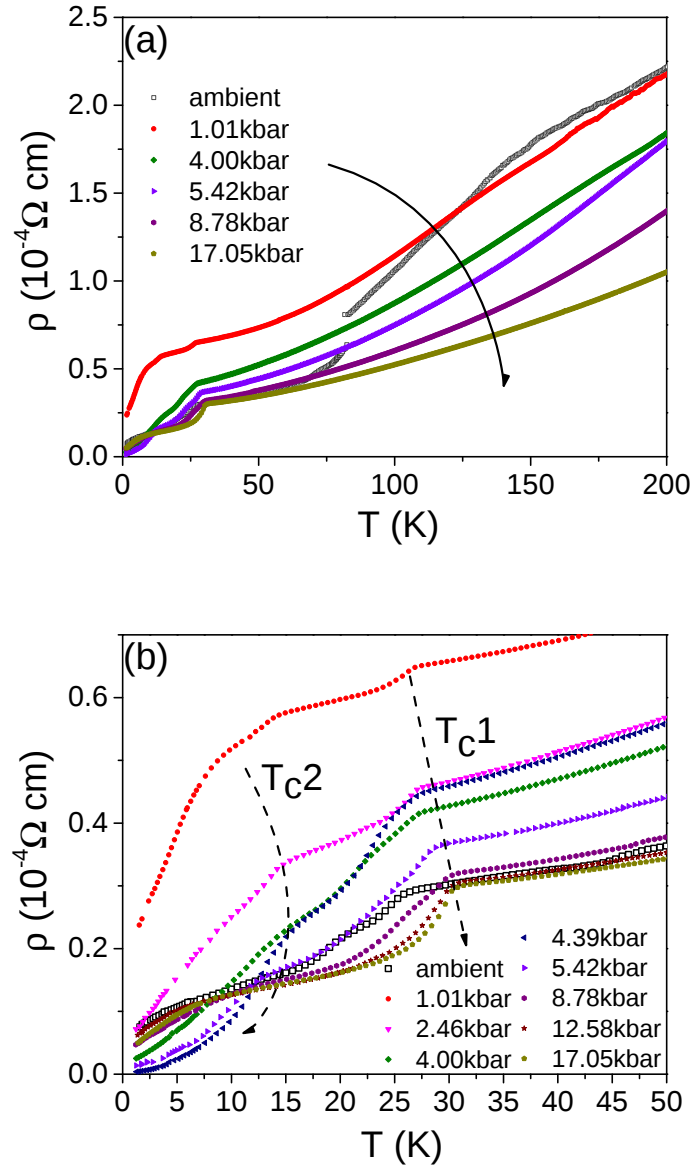


Figure 3.15: (a) The temperature dependence of resistivity for the sample P3 under pressure up to 17 kbar. (b) The zoom-in of the low temperature region of (a).

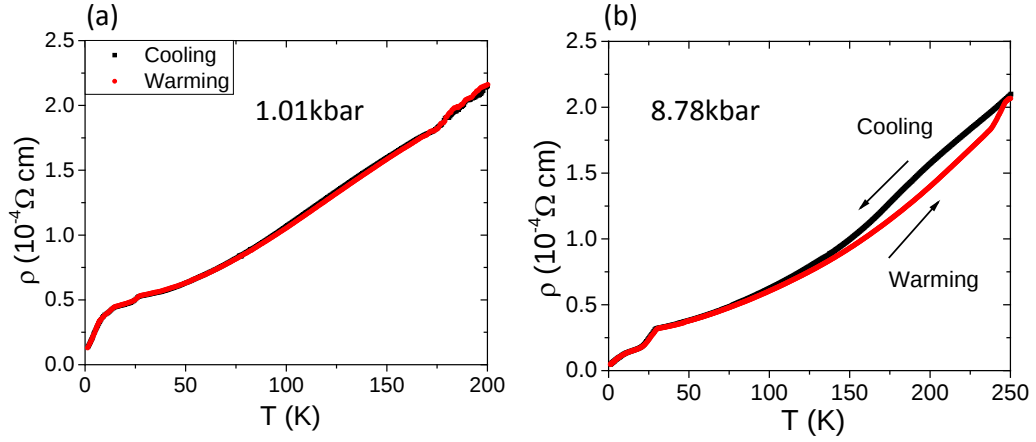


Figure 3.16: (a) The temperature dependence of resistivity up cooling and warming for the sample P3 under 1.01 kbar. (b) The temperature dependence of resistivity up cooling and warming for sample P3 under 8.78 kbar

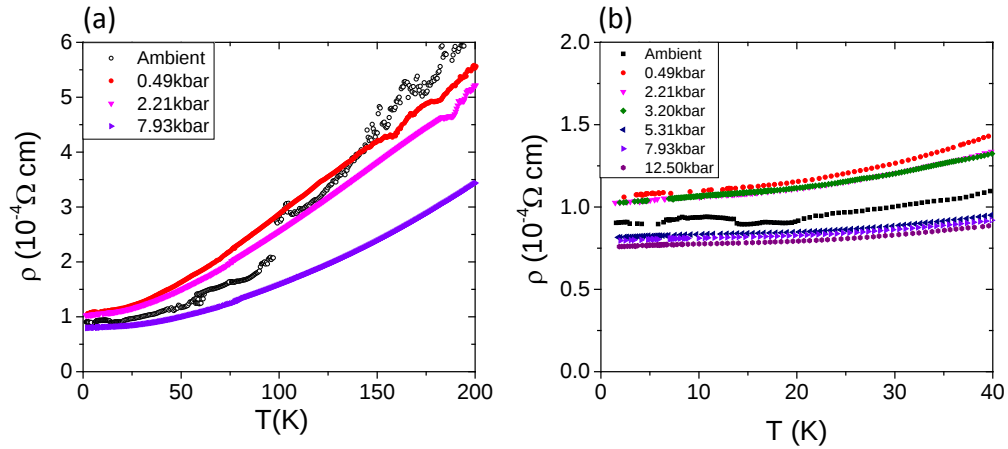


Figure 3.17: (a) The temperature dependence of resistivity for sample P2 under pressure up to 12.5 kbar. (b) The zoom-in of the low-temperature region of (a).

more information regarding the higher superconducting transition.

3.7 Summary

With the systematic annealing and high-pressure studies, we conclude the following:

1. Our annealing procedure successfully tuned the single-phased P2 crystal into a metastable layer-stacking mesostructure before converting into the single-phased P1 crystal.
2. Both the magnetization and the superconductivity along the interfaces are significantly altered. Superconductivity with $T_c < 25$ K is induced at ambient pressure in this mesostructure.
3. One of the major factors for the superconductivity seems to be the suppression of SDW along the interfaces by the lattice mismatch.
4. The enhanced T_c , the extended pressure range where CaFe_2As_2 remains superconducting, and the small superconducting volume fraction, all suggest that the superconductivity may also depend on other properties of the interfaces. Further investigations are needed.

Chapter 4

Studies on the Eu- and Sm-doped CaFe₂As₂ compounds

4.1 Background and motivation

In the CaFe₂As₂ (Ca122) family, one of the exciting observations is the unusual superconductivity with $T_c \sim 49$ K, which is first observed by our group [42]. Further investigations carried out by us reveal that non-bulk superconductivity with $T_c > 40$ K have been universally found in the RE-doped CaFe₂As₂, where RE = La, Ce, Pr and Nd, and the enhancement of T_c is possibly associated with naturally occurring interfaces [44]. In the synthesis of these compounds, the solubility of the RE elements follows a tendency of lower saturation levels for decreasing ionic radii [43]. Due to the relatively larger size mismatch between Ca²⁺ (114pm) and Sm³⁺ (109.8pm), it was believed that Sm can hardly be doped into CaFe₂As₂. On the other hand, the first

principles calculation of rare earth doped CaFe_2As_2 including Sm, which is fixed to 25%, suggests that such amount of Sm doping can induce a collapsed tetragonal phase at ambient pressure [50]. Therefore we decided to push the limit and dope Sm element into CaFe_2As_2 aiming at resolving the following questions: 1. Because the RE (La, Ce, Pr and Nd) elements doped Ca122 all demonstrate high T_c , can Sm doping also lead to an interface-enhanced high T_c ? 2. One of the interesting properties in the Ca122 system is the collapsed tetragonal (cT) phase transition, which is suggested to be detrimental to superconductivity. However, the studies in RE-doped Ca122 system have shown that the universal high T_c above 40 K is independent with the presence or absence of the cT phase. Therefore we try to experimentally verify whether Sm-doping is able to stabilize a cT phase transition (cT) at ambient pressure and to study the relation between the cT phase and superconductivity. 3. If an enhanced T_c and the cT phase can be simultaneously observed, would there be a chance to find the similar mixed-phase phenomenon as in undoped Ca122?

Thus, a series of $\text{Sm}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$ single crystals were synthesized and characterized. Unfortunately, we found out that the solubility of Sm for this system can only be up to $x = 0.046$. With such a low Sm content, the SDW transition is still not completely suppressed, nor does the cT phase take place. However, we observed a superconducting transition that reaches zero resistivity and shows partial diamagnetic shielding. The onset $T_c \sim 10$ K is close to the T_c of P1-phase CaFe_2As_2 in previous report [34]. A comparison with the other RE doped Ca122 compounds implies that the reason that Sm fails to induce the high T_c might be associated with the absence of sufficient defects needed for the interface formation due to the low solubility of

Sm.

EuFe_2As_2 itself is another interesting system in the 122 family; Eu^{2+} is magnetic and has a large spin moment of $\sim 7 \mu\text{B}$ [61]. Thus EuFe_2As_2 has two antiferromagnetic (AFM) transitions; one is a spin-density-wave (SDW) transition due to Fe moments at ~ 190 K and the other is an AFM order due to Eu^{2+} spins at ~ 20 K [62]. Superconductivity of EuFe_2As_2 is induced under doping with K [63] ($T_c \sim 32$ K) and Na [64] ($T_c \sim 35$ K) where SDW is suppressed upon hole doping. Probably due to the interference of AFM transition of local moments from Eu^{2+} ions, a broad superconducting transition and re-entrant behavior of resistivity are often observed upon chemical doping such as Co or La substitutions [65, 66, 67], or under high pressure [68] where superconductivity arises. If we can increase the interlayer As-As distance of CaFe_2As_2 by larger cation doping Eu^{2+} and prevent the appearance of the cT phase under moderate pressure, we would be able to investigate the superconducting state without the interference of the cT phase. Meanwhile, we can study the interplay of superconductivity with the SDW order and the Eu^{2+} AFM order through doping and pressure studies.

We therefore carried out a systematic study of X-ray, magnetic, resistivity and high pressure studies of $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ single crystals, and found a clear systematic evolution of the SDW order and the Eu^{2+} AFM order upon doping. Moreover, a series of temperature-dependent electrical resistance measurements at high pressure has also been carried out, and revealed both the critical pressure to induce superconductivity and the T_c increased systematically upon doping from $x = 0$ to $x = 0.45$. The maximum superconducting transition observed is ~ 19 K in $\text{Ca}_{0.55}\text{Eu}_{0.45}\text{Fe}_2\text{As}_2$

single crystal under a pressure of ~ 19 kbar [69].

4.2 Non-bulk superconductivity below 10 K in Sm-doped CaFe_2As_2

We successfully obtained $\text{Sm}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$ single crystals with actual doping level $x=0.010, 0.025, 0.043$ and 0.046 , labeled with #1–4 respectively. The actual doping levels are determined by the chemical analyses via Wavelength Dispersive Spectroscopy (WDS). The obtained Sm-doping levels are lower than the nominally prepared amount. For example, the highest doping level with nominal $x=0.2$ yields actual $x=0.043$, which suggests the solubility of Sm in Ca122 is less than 5%. The value halves the solubility of Nd (~ 0.09) in the formation of $\text{Nd}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$ [43]. This follows the trend that the solubility goes lower with larger ionic mismatch. The fact can also be supported by the scanning-electron-microscope (SEM) image of the sample #3, shown in the inset of Fig. 4.1(a), where bright spots represent undissolved Sm element. Figure 4.1(a) is the $(00l)$ diffraction pattern of $(\text{Sm,Ca})\text{Fe}_2\text{As}_2$ with $x=0.046$, showing the crystals are well oriented along the c axis. The lattice constant c for each sample is calculated from the $(00l)$ pattern and displayed in Fig. 4.1(b) with respect to doping level. As the Sm content increases, the lattice constant c is gradually contracted from $11.736 \text{ \AA}$ to $11.628 \text{ \AA}$ ($\sim 1\%$ change) for $x=0$ and $x=0.046$, respectively. The systematic change of both Sm concentration and lattice constant c indicates the successful substitution of Sm for Ca.

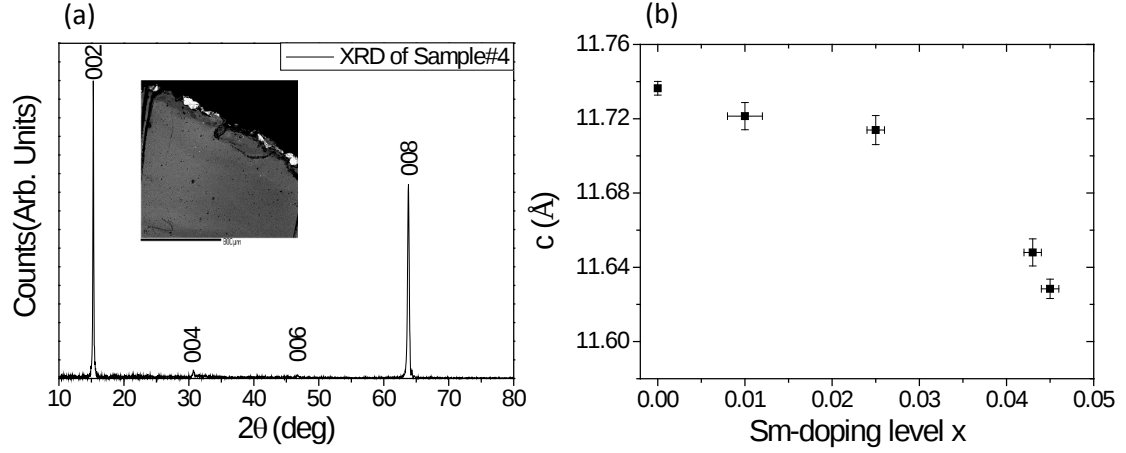


Figure 4.1: (a) The $(00l)$ diffraction pattern of sample #4; the inset shows a SEM image of the same sample. (b) The lattice constant c as a function of Sm-doping level.

For doping level $x=0.046$, the c value shows a relatively larger contraction, which agrees with the fact that Sm^{3+} has smaller ionic radius compared to Ca^{2+} . However, the c value (11.628 Å) is still larger than that ($c < 11.6$ Å) of the annealed CaFe_2As_2 possessing a cT phase transition. Thus it is unlikely that $(\text{Sm,Ca})\text{Fe}_2\text{As}_2$ with such a lattice parameter can reach a cT phase at low temperature through cooling. In other words, more doping is needed to shrink the lattice c and to induce a cT phase transition. Indeed, we have not observed a cT phase transition in any of the samples.

The temperature dependence of resistivity for all the $(\text{Sm,Ca})\text{Fe}_2\text{As}_2$ samples are shown in Fig. 4.2. The as-grown pure CaFe_2As_2 undergoes a tetragonal to orthorhombic phase transition, which is shown as a jump in resistivity at ~ 170 K. Upon Sm doping, the structural transition is continuously suppressed to lower temperature. Meanwhile, a resistivity drop emerges at ~ 10 K and the magnitude of the drop increases with Sm doping. As discussed in Chapter 3, the resistivity drop ~ 10

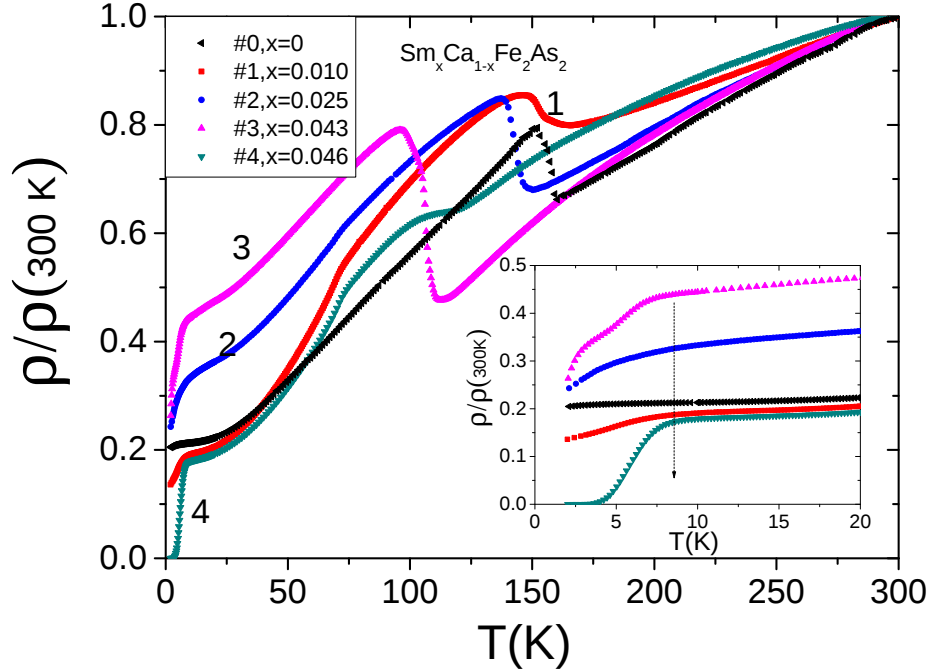


Figure 4.2: Temperature dependence of the normalized resistivity for Sm doped CaFe_2As_2 single crystals; the inset displays the superconducting transitions.

K in CaFe_2As_2 is a superconducting transition. Though the magnitude of the resistivity drop is enhanced by Sm doping, the T_c seems to be independent of the doping level (see the inset of Fig. 4.2). The independence of T_c with doping implies that electron doping provided by Sm^{3+} might not be the direct reason of superconductivity. Instead, the T_c value (~ 10 K) and its independence with doping level suggest the superconductivity might be associated with the intrinsic superconductivity in undoped CaFe_2As_2 .

With $x = 0.046$, the magnitude of the SDW transition is greatly suppressed but still observable. Interestingly, the resistivity drop at ~ 10 K is significantly

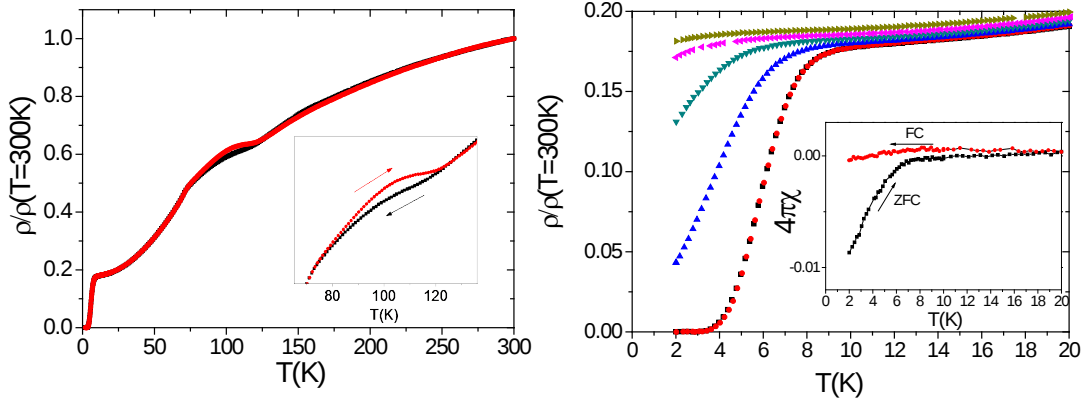


Figure 4.3: (a) Temperature dependence of the normalized resistivity for $x=0.046$. (b) The superconducting transition for sample with $x=0.046$ under magnetic fields of 0, 1, 3, 5 and 7 T; the inset shows the magnetic susceptibility of the same sample with $H//ab$.

enhanced and resistivity goes to zero ~ 4 K. Figure 4.3(a) is an individual resistivity curve of the sample with $x=0.046$ including both cooling and warming data. The SDW transition shows a conspicuous hysteresis (see the inset), implying it is a first order phase transition. To further confirm this superconducting state, a magnetic field was applied along the c axis of the sample as shown in Fig. 4.3(b), where the superconducting transition is gradually suppressed by magnetic fields. In addition, Fig. 4.3(b) inset exhibits the magnetic susceptibility of the sample with $x = 0.046$ under a magnetic field $H = 2$ Oe with H parallel to the ab plane. The zero-field-cooled (ZFC) data demonstrate a clear diamagnetic shielding below ~ 10 K. The corresponding diamagnetic shielding fraction $4\pi\chi$ is $\sim 1\%$, suggesting the non-bulk nature of the superconductivity. It is noticeable that the ZFC and FC curves slightly bifurcate, implying certain ferromagnetic signal was present, possibly due to Sm impurities or FeAs inclusions.

The superconductivity in $\text{Sm}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$ with $x=0.046$ appears with an onset $T_c < 10$ K, which is much lower than T_c s of other $\text{RE}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$ materials (where $\text{RE}=\text{La, Ce, Pr and Nd}$). It has been reported that these four compounds all show two superconducting transitions with the higher temperature transition typically above 40 K [44]. Further investigation in Pr-doped Ca122 reveals a correlation of superconductivity with defects and superparamagnetism. The high T_c emerges in Pr-doped Ca122 with the formation of superparamagnetic clusters, which are associated with the presence of Fe/As defects. The magnitude of magnetic moment in $(\text{Pr,Ca})\text{Fe}_2\text{As}_2$ is $\sim 10^3$ emu/mol at 5 K under a magnetic field higher than 1T. In contrast, the superparamagnetic signal in the Sm-doped sample (~ 100 emu/mol) is one order of magnitude lower. The magnetic moment of Sample #4 ($x = 0.047$) as a function of magnetic field at different temperatures is shown in Fig. 4.4, which indicates a weak trace of superparamagnetic signal. Thus the density of possible superparamagnetic clusters would be much lower than the proposed threshold of 0.05/Cell, a minimum level that has been simultaneously observed with high T_c . Thus we conjecture that Sm-doping at such a low level is unable to induce the same defect structure for high T_c as in other RE-doped compounds, although it still facilitates the superconductivity that occurs at ~ 10 K.

A high pressure study was carried out on another Sm-doped CaFe_2As_2 sample #5 with pressure up to 16.95 kbar (see Fig. 4.5). The sample at ambient pressure shows a broad SDW transition, which is then gradually suppressed by pressure. At 16.95 kbar, the SDW transition seems not to be totally eliminated. On the other hand, the sample at ambient pressure shows a slight resistivity drop below 10 K. At 2.51 kbar,

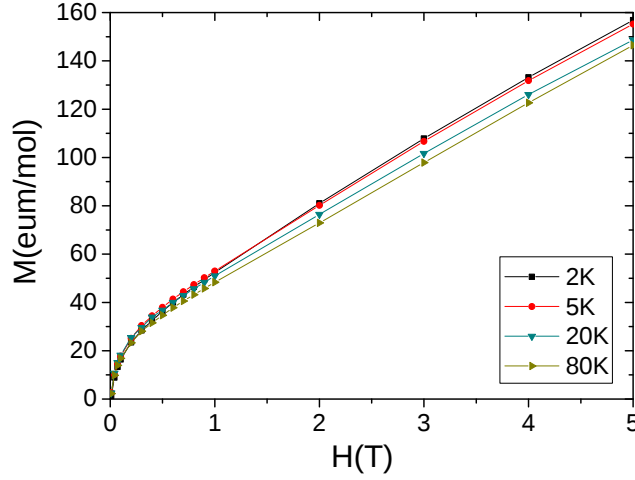


Figure 4.4: The magnetization for the sample with $x=0.046$ as a function of magnetic field at different temperatures.

the resistance drop is greatly enhanced and the resistance reaches almost zero under a pressure of 5.31 kbar. This is actually a superconducting transition, which behaves similarly to that in the P1-phase CaFe_2As_2 under non-hydrostatic pressure. As the pressure increases, the superconductivity is then suppressed at and above 8.72 kbar. However, unlike the P1-phase CaFe_2As_2 , the superconductivity appears before the SDW transition is fully suppressed and we have not observed any indications of cT phase transition under pressures up to 16.95 kbar. These unexpected observations are contradictory with the previous results in CaFe_2As_2 and further investigation is needed.

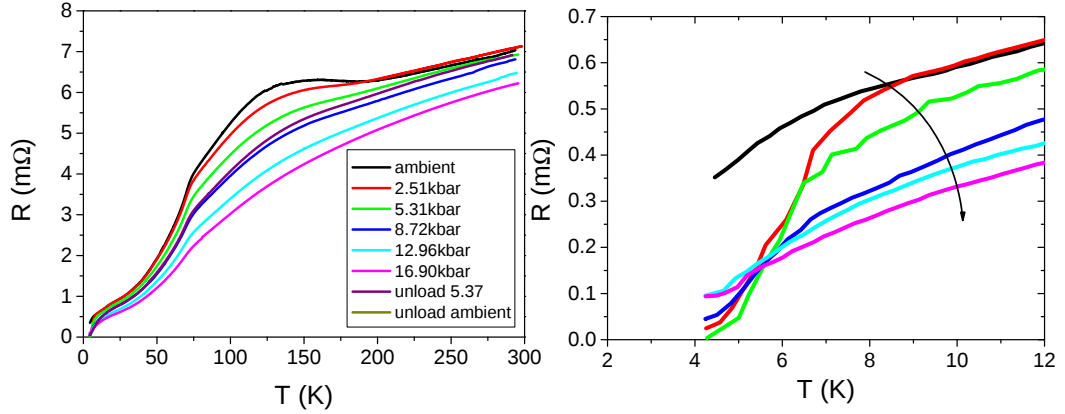


Figure 4.5: (a) Temperature dependence of resistance under pressure for the Sm-doped sample #5. (b) The zoom-in of the superconducting transition region.

4.3 Interplay of superconductivity, SDW order and Eu^{2+} AFM order in the $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ system at ambient pressure and under pressure

Large single crystals with typical dimensions of 5×5 mm were grown using the FeAs-flux technique with nominal stoichiometries of $(1-x)$: x : 4 for Ca: Eu: FeAs according to the chemical formula $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9$, and 1). A WDS chemical analysis was carried out for all the samples and actual doping levels x were found to be $x = 0.14, 0.31, 0.45, 0.58, 0.65, 0.82, 0.94$ and 1, respectively. The typical XRD patterns of single crystalline samples $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$, $x = 0.31, 0.58$ and 0.82 exhibit the expected preferred orientation along the c axis (Fig. 4.6(a)). The position of the (008) peak shifts towards lower angle with increasing x , implying that lattice parameter c increases with doping. As the ionic radius of Eu^{2+} is 125 pm and that of Ca^{2+} is 112 pm, an increase of c upon the substitution is expected.

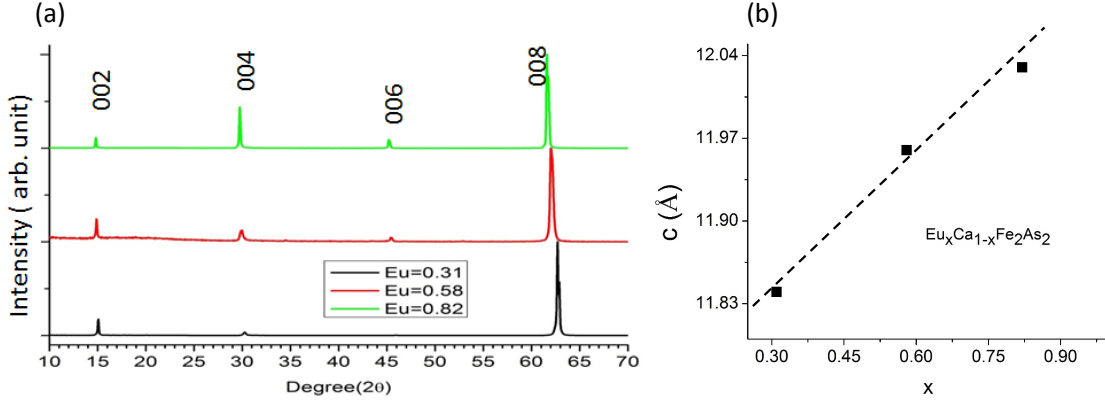


Figure 4.6: (a) (008) XRD patterns for $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ single crystals with $x=0.31$, 0.58 and 0.82; (b) The lattice parameter c as a function of doping level for the three samples.

The c -lattice parameter increases linearly with doping ($x = 0.31$, 0.58 and 0.82), indicating it follows the Vegards law. The c values for other doping levels ($x=0.14$, 0.45, 0.65, 0.94 and 1) also lie close to the straight line constructed by $x = 0.31$, 0.58 and 0.82 points in Fig. 4.6(b).

Figure 4.7(a) shows the temperature dependence of resistivity for $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ with different doping levels $x=0$, 0.14, 0.31, 0.45, 0.58, 0.65, 0.82, 0.94 and 1. For $x = 0$, the parent compound shows a SDW transition at ~ 165 K. Though the resistivity curves for Eu doped samples look similar to that of the undoped CaFe_2As_2 , the SDW transition temperature increases with a rise in x . The SDW transition temperature (T_{SDW}) is calculated by taking the midpoint of the transition and plotted as a function of doping level x , as shown in Fig. 4.7(b). The T_{SDW} is 165 K for $x = 0$, increases almost linearly up to $x = 0.45$, and saturates afterwards. T_{SDW} reaches 190 K for $x = 1$, which is consistent with previous report [61]. At low temperature, a small kink in the resistivity curve can be observed at ~ 20 K, indicated by black arrows

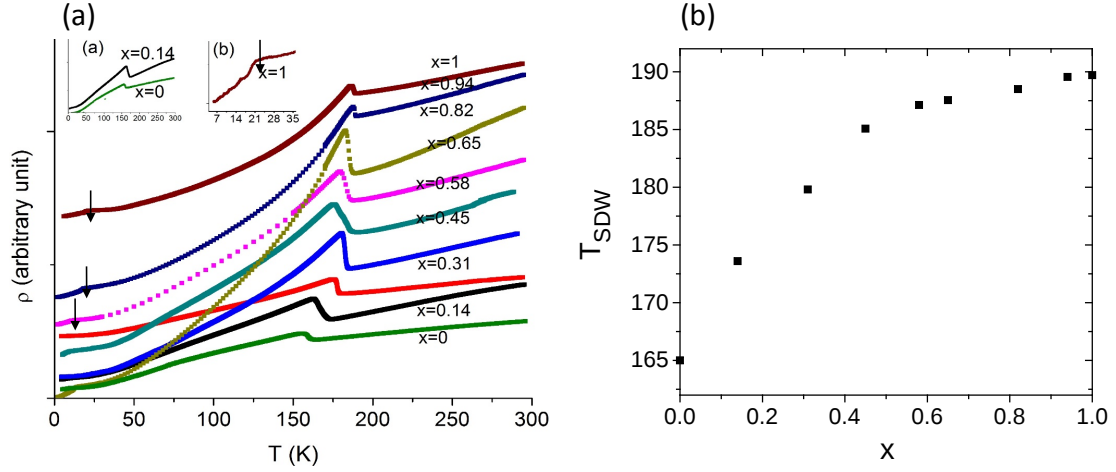


Figure 4.7: (a) Electrical resistivity versus temperature for $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ with $x=0.14, 0.31, 0.45, 0.58, 0.65, 0.82, 0.94$ and 1 (The curves are offset by a constant for clarity). Low temperature AFM transitions due to Eu^{2+} spins are marked by black arrows. Insets: (a) resistivity comparison for $x=0$ and $x=0.14$. (b) Eu^{2+} AFM order for $\text{Eu}_x\text{Fe}_2\text{As}_2$. (b) The SDW transition temperature as a function of doping x .

for samples with $x \geq 0.65$. These kinks are due to the AFM order of Eu^{2+} spins. For $x=1$ as shown in the inset (b), the Eu^{2+} AFM transition temperature (T_{AFM}) is 21 K, which is in a good agreement with previous report of pure EuFe_2As_2 [62]. T_{AFM} value is gradually lowered with a decrease in Eu doping and reaches 12 K for $x = 0.65$. The Eu^{2+} AFM order is continuously weakened with a decrease in Eu doping, resulting in that the AFM orders are not visible in resistivity measurements for $x \leq 0.58$ samples.

Figure 4.8(a) shows the temperature dependence of magnetic susceptibility for $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ samples below 50 K under a magnetic field of 1000 Oe. Though the AFM transition for Eu^{2+} is visible for doping $x \geq 0.58$, it is not clear for lower Eu doping levels ($x \leq 0.58$). In order to calculate the AFM transition temperatures

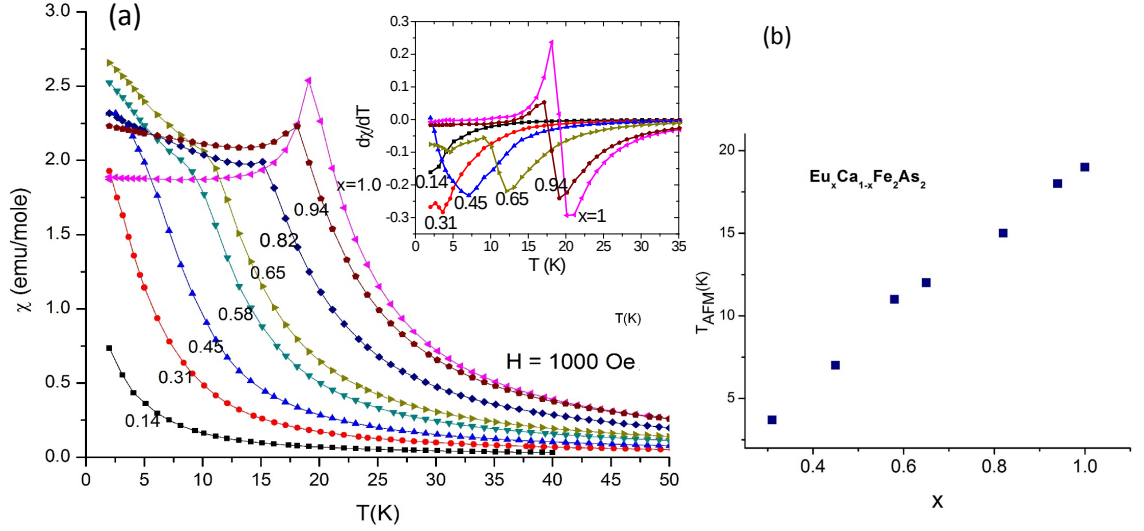


Figure 4.8: (a) Magnetic Susceptibility versus Temperature of $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ ($x=0.14, 0.31, 0.45, 0.58, 0.65, 0.82, 0.94, 1.0$); Inset: first derivatives of χ . (b) T_{AFM} versus doping x .

(T_N), we take the first derivatives of χ with respect to T as shown in the inset. The minimum in the derivative curve shows the point where the slope changes, *i.e.* the AFM transition temperature. Figure 4.8(b) shows T_{AFM} as a function of doping level x . The Eu^{2+} AFM transition starts to show up at $x=0.31$ ($T_{AFM}=3.7$ K) and increases almost linearly with increasing x , reaching 12 K for $x = 0.58$. For $x = 0.5$, T_{AFM} is expected to lie between 7 and 11 K. However, the previous report [70] of almost 80% decrease of the T_{AFM} value (from 21 K to 4 K) upon $x=0.5$ doping seems to be different from our observation. T_{AFM} reaches 19 K for $x = 1.0$ (*i.e.* pure Eu122), which is close to the value of 21 K observed in our resistivity measurement.

High-pressure experiments were carried out for samples with $x=0.14, 0.31$ and 0.45. Figure 4.9(a) shows the temperature dependence of resistance for $x = 0.14$

under various pressures. At ambient pressure, the SDW transition takes place at around 174 K and no superconductivity appears down to 4.2 K. The SDW transition is gradually suppressed by the applied pressure. As the T_{SDW} is suppressed to 120 K under a pressure of 9.75 kbar, a small drop of resistance occurs at around 12 K and the resistance decreases by $\sim 20\%$ at 4.2 K. Superconductivity with zero resistance takes place at $T_c \sim 14$ K under a pressure of 12.70 kbar. With further increase of pressure to 17.95 kbar, the T_c decreases to 11 K and again resistance value does not reach zero, which implies higher pressure might drive the sample out of the superconducting zone. We did not apply higher pressure due to the limitation of the experimental apparatus, but a complete suppression of superconductivity is expected with further increase of pressure. For pressure at and above 14.34 kbar, a strong hysteresis was observed as shown in Fig. 4.9(b). The hysteresis is usually associated with a first order transition and we conjecture that it is possibly a cT phase transition. Such a transition emerges at the pressure regime where superconductivity is being suppressed, reminiscent of the case for the P1-phase Ca122 under non-hydrostatic pressure. This is expected as the 14% Eu doping expands the lattice and thus higher pressure is needed to suppress the SDW transition and to establish the possible cT phase transition. Following the same logic, it can be understood why higher critical pressure is needed to induce the superconductivity. It should also be noted that the AFM order from Eu^{2+} seems to be minor in the sample with the low doping level $x=0.14$. However, higher doping level would lead to a significant AFM order, which competes with superconductivity under pressure. Therefore higher pressure might also be needed in order to suppress the competing AFM order. The superconductivity

forms a dome (see Fig. 4.11) with a width at least ~ 8 kbar, which is larger than that for the undoped P1-phase Ca122 (< 6 kbar) under non-hydrostatic pressure. The wider superconductivity dome and the higher T_c imply the superconductivity in 14% Eu doped Ca122 becomes more robust.

High-pressure studies were also carried out for samples with $x=0.31$ and 0.45 , in which superconductivity with maximum $T_c=16$ K and 19 K were observed under pressures of 17.26 kbar and 19.19 kbar respectively (see Fig. 4.10). Based on the results of the three different $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ ($x=0.14, 0.31$ and 0.45) and previous report of undoped CaFe_2As_2 , a phase diagram of transition temperature as a function of pressure is constructed in Fig. 4.11. As the Eu doping level increases, the critical pressure to suppress the SDW transition and to induce superconductivity also increases. Meanwhile, the T_c also increases upon Eu doping. Thus the superconductivity dome moves to higher pressure while expanding both in width and height. The SDW transition region is overlapping with the superconductivity dome for all the three samples.

4.4 Attempt to explore interface-associated superconductivity in other 122 parent compounds

The naturally assembled interface-associated superconductivity phenomenon seems to be limited within the undoped and RE doped Ca122 compounds to date. As mentioned in the introduction, there have been reports of superconductivity with

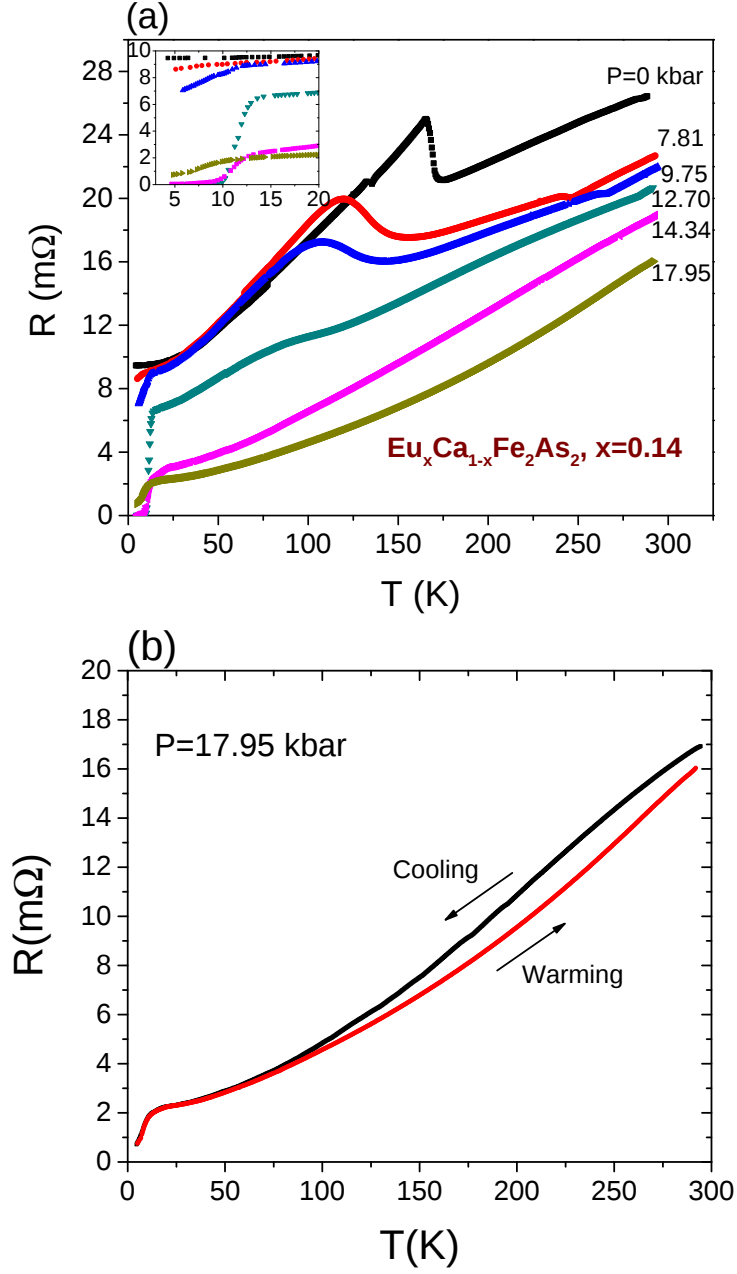


Figure 4.9: (a) Temperature dependence of resistance under pressure for the $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ with $x=0.14$; the inset shows the superconducting transitions. (b) The hysteretic feature upon warming and cooling observed under $p=17.95$ kbar.

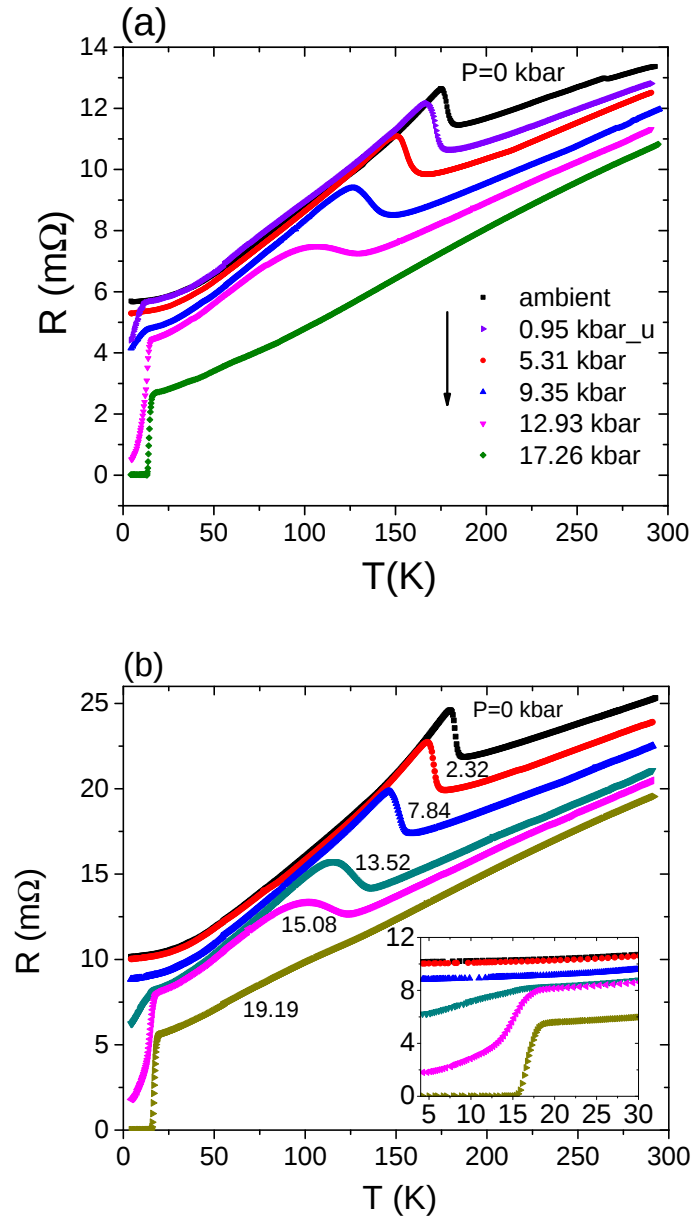


Figure 4.10: Temperature dependence of resistance under pressure for the $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ with $x=0.31$ (a) and 0.45 (b). Inset: the superconducting transitions.

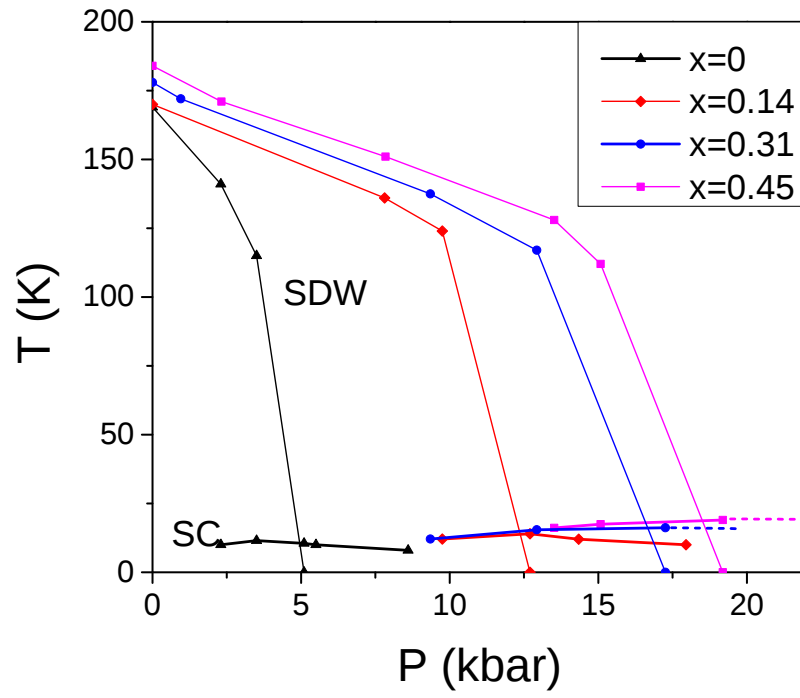


Figure 4.11: Transition temperature-pressure phase diagram for $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ with $x=0, 0.14, 0.31$ and 0.45 . (the data for $x=0$ are adapted from [24].)

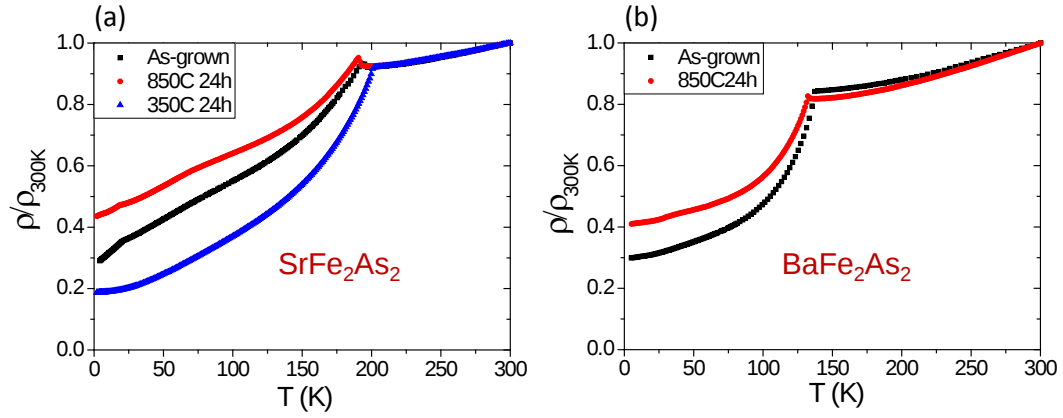


Figure 4.12: (a) The temperature dependence of resistivity for SrFe_2As_2 , as-grown, annealed at 850 °C for 24 h and 350 °C for 24 h. (b) The temperature dependence of resistivity for BaFe_2As_2 , as-grown and annealed at 850 °C for 24 h.

$T_c > 20$ K at ambient pressure in other 122 parent compounds, *i.e.* BaFe_2As_2 (22.5 K) [47] and SrFe_2As_2 (21 K) [48]. The superconductivity observed in them might share the same mechanism as the undoped CaFe_2As_2 (21 K). We therefore carried out similar annealing treatments on these two compounds (see Fig. 4.12). The annealing was only able to alter the SDW-transition temperature by less than 20 K in SrFe_2As_2 . While no cT phase was observed, a trace of superconducting transition can be detected in as-grown and high-temperature annealed SrFe_2As_2 . The annealing- and pressure-sensitivity nature seems to be unique for CaFe_2As_2 and might be related to the ionic size of the Ca^{2+} . Further investigations on those unique properties of the Ca122 system may lead to insight into possible routes for seeking, and hopefully finding, other examples of interfacial superconductivity.

4.5 Summary

We carried out systematic doping and high-pressure studies on Eu- and Sm-doped CaFe_2As_2 compounds. In $\text{Sm}_x\text{Ca}_{1-x}\text{Fe}_2\text{As}_2$, the Sm doping can only induce a superconducting transition below 10 K, which might be associated with the superconductivity in undoped CaFe_2As_2 . The reason that it fails to induce high T_c might be related to the low solubility of Sm. On the other hand, the response of Sm-doped sample to external pressure seems to be unexpected and further investigation is needed to resolve the puzzle. In the $\text{Ca}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2$ system, there is a systematic increase of the SDW-transition temperature with increasing Eu content. The AFM-transition temperature due to Eu^{2+} spins also increases systematically with the Eu doping level. The SDW is suppressed under high pressure and coexists with superconductivity; however, superconductivity with zero resistance occurs only after the SDW is eliminated completely. The constructed phase diagram suggests the Eu doped Ca122 samples with low Eu doping levels follow well with the properties demonstrated in undoped Ca122. Further studies under higher pressures will help to complete the superconductivity domes for the samples with high doping level and to reveal more information about the possible cT phase transition.

Chapter 5

Chemical doping and high-pressure studies of layered β -PdBi₂ single crystals

5.1 Background and motivation

Low-dimensional compounds, with simple structure building motifs and weak bonding force between layers, have generated much research interest within condensed matter physics over the past several decades. These low dimensional materials have displayed a variety of unusual physical phenomena such as charge density waves in transition metal chalcogenides [71, 72]; spin density waves in the parent Fe-pnictide superconductors [73, 74]; topological order in Bi₂Se₃ [75, 76]; and superconductivity in many compounds such as MgB₂ [77], doped ZrNCl [78], *etc.*. In the binary

Pd-Bi alloy family, several phases with different structures have been studied in the past [79]; in this family, the PdBi_2 is found to crystalize in two different layered structures with a low-temperature α -phase below 380 °C and a high-temperature β -phase between 380 and 490 °C [80]. The α - PdBi_2 crystalizes in a layered monoclinic ($c2/m$) structure with a six-coordinated PdBi_6 building motif, while β - PdBi_2 forms a layered tetragonal CuZr_2 -type structure ($I4/mmm$) with an eight-coordinated PdBi_8 building motif. Every four Bi-atoms in the β - PdBi_2 are face-shared with the neighboring CsCl-type PdBi_8 motif and therefore form a $\text{PdBi}_{8/4}=\text{PdBi}_2$ layer. The resulting PdBi_2 layers are packed alternately and form the body-centered tetragonal structure, as shown in the inset of Fig. 5.1(a). The interlayer spacing between the alternating PdBi_2 layers is rather large, with interlayer Bi-Bi distance of ~ 3.8 Å, indicating that there is no effective bonding between those layers.

Various phases in the Pb-Bi system have been identified as superconductors [81], such as α - PdBi with $T_c \sim 3.8$ K, α - PdBi_2 with $T_c \sim 1.73$ K, β - PdBi_2 with $T_c \sim 4.25$ K, and $\text{Pd}_{2.5}\text{Bi}_{1.5}$ with $T_c \sim 3.7\text{--}4$ K. Early studies showed that β - PdBi_2 had the highest T_c among these phases, 4.25 K, and it was recently shown that the T_c could be further raised to 5.4 K by improving the sample quality [82]. However, neither the details of the chemical doping nor the high-pressure effect are well known in β - PdBi_2 . The prior specific heat and STM studies on β - PdBi_2 suggest that it is a multi-band superconductor [82, 83], which agrees with the results from first-principles calculations [84]. Theoretical calculation shows that the density of states (DOS) around the Fermi level is dominated by the Pd 4d and Bi 6p states, and that the Fermi level is located on a positive slope below a DOS peak. Therefore, hole

doping is expected to shift the Fermi level away from the DOS peak, resulting in a decrease of the DOS at the Fermi level while electron doping will increase it. Thus one would expect a decrease of T_c upon hole doping and an increase of T_c under electron doping. Under this motivation, we decided to carry out systematic hole doping (substitution of Bi with Pb) and electron doping (Na intercalation) studies on the β -PdBi₂ system. However, we found that the T_c was suppressed in both cases, the reasons for which will be discussed in Section 5.5. Meanwhile, a high-pressure study was also carried out on the β -PdBi₂ single crystal and we observed a suppression of T_c upon applying pressure with a dT_c/dP coefficient of -0.28 K/GPa. The phase diagrams, both upon chemical doping and under high pressure, are presented [51].

The suppression of T_c in both cases leads us to examine the change of charge carrier density upon the two doping effects. In Na-intercalated PdBi₂, the charge carrier concentration at 10 K is unexpectedly decreased through the electron doping. The hump feature in the resistivity data, the large magnetoresistance and the Hall anomaly reveal evidence for a possible spin excitation associated with Fermi surface reconstruction at ~ 50 K in the Na-intercalated PdBi₂ samples. The presence of such a spin excitation, possibly a spin-density-wave (SDW) like one, could remove the electron density of states (DOS) at the Fermi level and thus contributes to the suppression of T_c .

5.2 Synthesis and characterization of a series of Pb-substituted β -PdBi₂ single crystals

β -PdBi₂ single crystals with shining metallic luster, typical size of 5 mm, and preferred orientation along the c axis after cleavage, could be obtained through the melt-growth technique, as shown in Fig. 5.1(a). The calculated lattice parameter $c=12.963(3)$ Å is consistent with previous reports [82]. A representative SEM image of the undoped β -PdBi₂ single crystal is also shown as the inset of Fig. 5.1(a). Both resistivity and magnetization measurements have shown that the superconducting transition temperature of the as-grown β -PdBi₂ crystal is 5.4 K, indicating the improved quality of the grown crystals as also pointed out by previous reports [82]. The resistivity curve exhibits a hump below 150 K and a minor downturn around 50 K, as shown in Fig. 5.1(b), suggesting possible strong electron/spin correlation in this compound.

Figure. 5.2 shows the powder XRD patterns with Miller indices of the crushed crystals for the Pb-doped PdBi_{2-x}Pb_x ($x=0.08, 0.15, 0.20, 0.28, 0.35$, and 0.40) samples. Except for a few minor peaks of the α -phase present at low doping level, namely $x=0.08$, all of the peaks are well indexed into the β -PdBi₂-type body-centered tetragonal structures in all of the samples with different doping levels. These crystals are quite stable outside the glovebox for several months. Due to the close radius sizes between Pb and Bi, the change of lattice parameter upon Pb doping is very small, and a gradual decrease of the lattice parameter from $12.963(3)$ Å for $x=0$ to $12.940(2)$ Å for $x=0.4$ is observed, but the overall lattice parameters change is less than 0.2%.

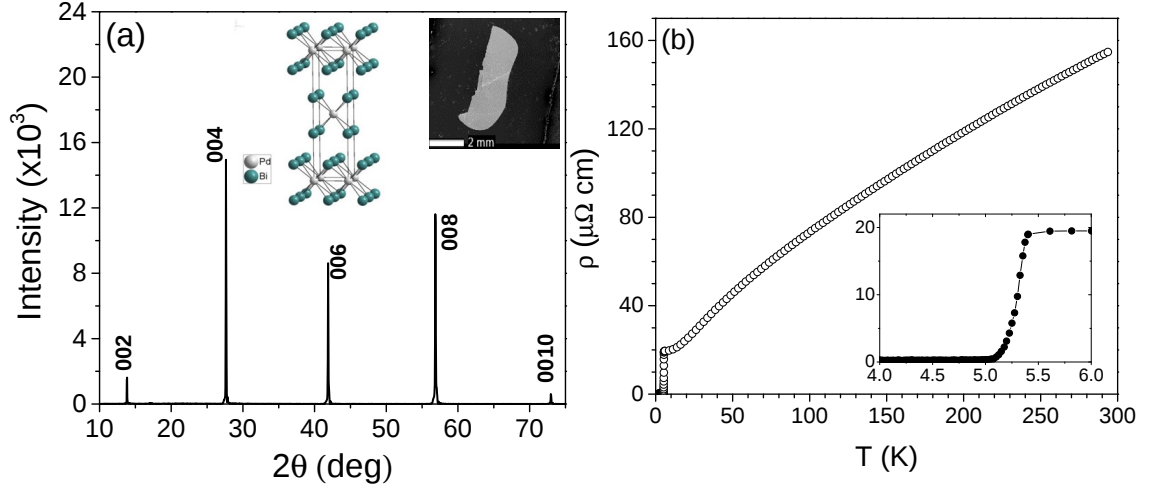


Figure 5.1: ((a) XRD pattern of β -PdBi₂ with preferred orientation along c axis; the inset shows the crystal structure and one representative crystal SEM image. (b) Resistivity of β -PdBi₂ from 2 to 300 K; the inset displays resistivity data between 4 and 6 K.

To further confirm the homogeneity of the doped samples and establish the actual doping levels, we performed chemical analyses through WDS measurements on the single crystals. The Pb-concentration is homogeneous throughout the whole sample in all cases, indicating the formation of solid solutions for these Pb-doped samples. The actual Pb doping levels are $x=0.08(2)$, $0.14(2)$, $0.19(2)$, $0.27(2)$, $0.34(1)$, and $0.39(1)$, for the nominal compositions of $x = 0.08, 0.15, 0.20, 0.28, 0.35$, and 0.40 in PdBi_{2- x} Pb _{x} , respectively. The results show that the actual doping levels are very close to the nominal compositions. Some extra impurity peaks belonging to the α -PdBi₂ monoclinic phase emerge at the doping level $x=0.60$ from X-ray powder diffraction measurements and become more dominant with further Pb doping. At the doping level of $x=1.00$, the XRD pattern shows a nearly pure phase of the α -PdBi₂-type structure with no detectable α phase, implying the solubility limit of the

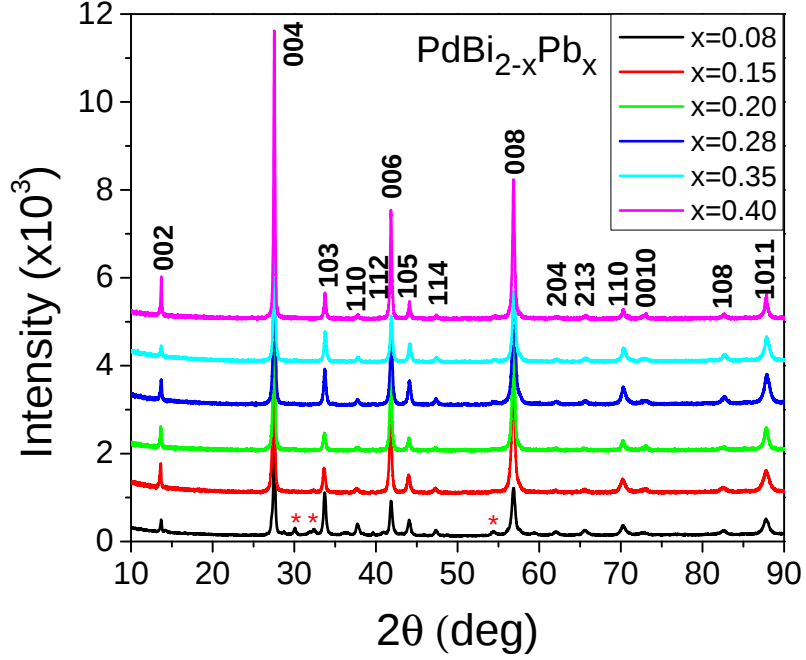


Figure 5.2: The powder x-ray diffraction patterns of $\text{PdBi}_{2-x}\text{Pb}_x$ with Miller indices. The patterns are vertically offset for better clarity. Some minor impurity peaks from the α phase are marked as *.

tetragonal β - $\text{PdBi}_{2-x}\text{Pb}_x$ phase at this high doping level.

Systematic resistivity and magnetization measurements were carried out for all samples with different doping levels. As shown in Fig. 5.3, the superconducting transition temperature T_c of $\text{PdBi}_{2-x}\text{Pb}_x$ continuously decreases upon Pb substitution, from 5.4 K for $x=0$, to 4.9 K for $x=0.08$, 4.4 K for $x=0.15$, 3.8 K for $x=0.20$, 2.5 K for $x=0.28$, and 2.2 K for $x=0.35$. The sample eventually becomes non-superconducting above 2 K when the doping level reaches $x=0.40$. The superconducting transition width (10%–90% resistivity drop) is rather narrow (less than 0.3 K) in all samples, indicating the good quality of the doped samples.

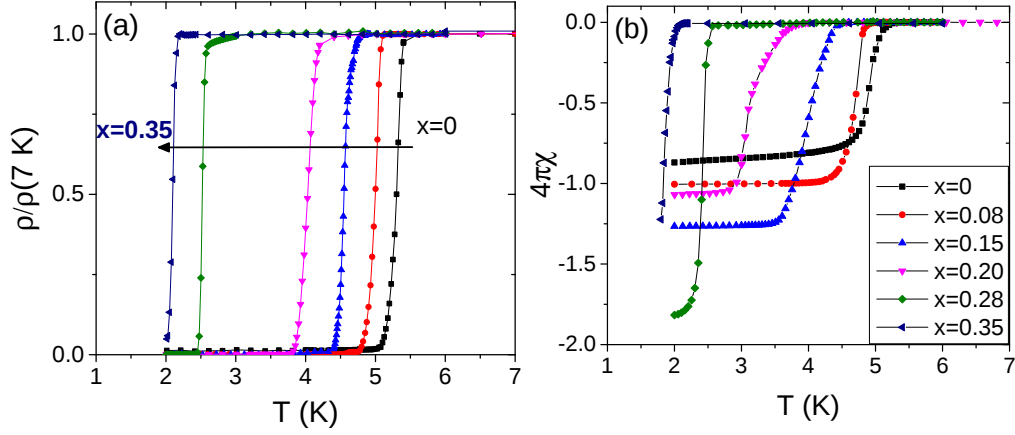


Figure 5.3: The resistivity (a) and magnetic susceptibility (b) data under $H = 2$ Oe of $\text{PdBi}_{2-x}\text{Pb}_x$ with $x = 0-0.35$ from 2 to 7 K

Similar consistent results were obtained through magnetic susceptibility measurements as shown in Fig. 5.3. The magnetization was measured under an applied magnetic field of 2 Oe on randomly oriented small crystals with typical mass ~ 20 mg packed in gelatin capsules. All of the samples with doping level $0 < x < 0.35$ exhibit substantial diamagnetic shifts at the lowest temperature. The shielding fractions $4\pi\chi$ are close to or exceed 1 without the demagnetization factor correction, which implies the bulk superconducting nature of these samples. Consistent with the resistivity data, the superconducting transition temperature systematically moves downward with doping from 5.2K for $x=0$ to 2 K for $x=0.40$.

5.3 Hole doping by Pb substitution

To confirm the effective hole doping by Pb substitution, Hall-effect measurements have been carried out to evaluate the charge-carrier concentration for the parent

compound PdBi_2 and a representative Pb-doped $\text{PdBi}_{1.8}\text{Pb}_{0.2}$ sample (Fig. 5.4). The Hall-resistivity measurements were performed in the PPMS system with field up to 5 T using the five-lead technique, which balanced the longitudinal resistance at close to zero. The raw Hall-resistivity values ρ_H are linear with the field, with negative slopes for both samples. To further eliminate the effect of possible misalignment of the Hall electrodes, the Hall coefficient R_H was taken as $R_H = [R_H(5T) + R_H(-5T)]/2$ at each temperature. The inset of Fig. 5.4 shows the Hall coefficient of PdBi_2 from 6 to 300 K. The Hall coefficient is negative over the whole temperature range and only weakly depends on temperature, suggesting that electron-type charge carriers dominate the charge transport. The value of the Hall coefficient changes by $< 30\%$ from 2 to 300 K, implying relatively minor multi-band effects, and therefore it is reasonable to evaluate the carrier concentration using the Hall coefficient R_H .

The Hall resistivities of the parent compound and the Pb-doped sample under different magnetic fields at 10 K are shown in Fig. 5.4, where one can see that the contribution from magnetoresistance is rather small. The Hall coefficients R_H , determined by the slopes of the curves, are $R_H = -4.24 \times 10^{-4} \text{cm}^3/\text{C}$ and $R_H = -1.12 \times 10^{-3} \text{cm}^3/\text{C}$ for PdBi_2 and $\text{PdBi}_{1.8}\text{Pb}_{0.2}$, respectively. The negative Hall coefficient of the Pb-doped sample indicates that the charge carriers are still dominated by electrons. By simply using the single band expression $n=1/R_H q$, we can calculate the electron concentrations: $n=1.47 \times 10^{22} \text{cm}^{-3}$ for PdBi_2 and $n=5.56 \times 10^{21} \text{cm}^{-3}$ for $\text{PdBi}_{1.8}\text{Pb}_{0.2}$. The substantial decrease of electron concentration suggests effective hole doping in the PdBi_2 system through Pb substitution at the Bi site. This effective hole doping might shift the Fermi level, resulting in a lower electronic

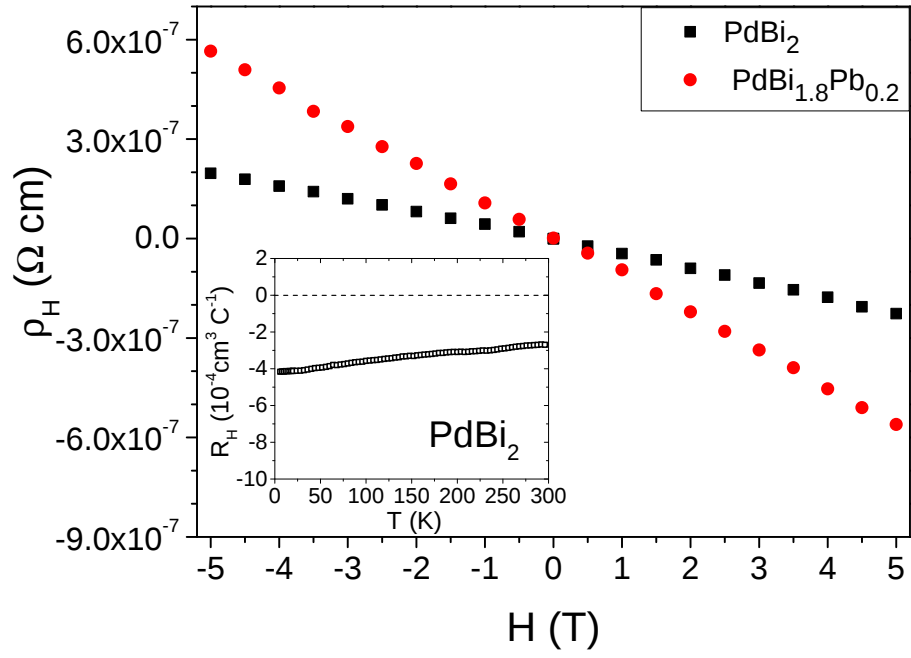


Figure 5.4: Hall resistivity of $\beta\text{-PdBi}_2$ and $\text{PdBi}_{1.8}\text{Pb}_{0.2}$ under a magnetic field at 10 K; the inset shows the Hall coefficient R_H of $\beta\text{-PdBi}_2$ from 6 to 300 K

density of states (DOS). Therefore, the lower DOS might contribute to the decrease of T_c if a rigid-band model is adopted.

5.4 Electron doping by Na intercalation

Since the hole doping by Pb substitution caused decrease of T_c , we also attempted to carry out Na intercalation, which would introduce electrons into the system. Several trials with nominal Na-concentration ranging from $x=0.1$ to $x=0.4$ on Na_xPdBi_2 have been made. X-ray powder diffraction analysis on the resulting bulk materials reveals that some small impurities (less than 10% total) of NaBi and Pd exist in the sample in addition to the formation of the β tetragonal phase. We were able to isolate smaller pure crystals from the bulk samples and carried out detailed chemical analyses and physical measurements. The isolated crystals are homogeneous from WDS analysis and have all of the three elements present. However, the actual Na content is much lower than the nominal composition. Taking the nominal $x=0.1$ as an example, the actual composition we found from the chemical analysis was Na:Pd:Bi = 0.044(3):1:2.000(5). The highest Na doping level is $\sim 0.057(2)$ determined from the chemical analysis, indicating the relatively low limit of Na intercalation into this compound compared with the Pb doping. The Na-doped crystals were moderately sensitive to air/moisture as they slowly decayed when kept outside the glovebox for one day. This also implies successful Na intercalation into the system. The superconducting T_c , on the other hand, is rapidly suppressed at such a low Na doping level, changing from 5.4 K in PdBi_2 down to 4.1 K in $\text{Na}_{0.044}\text{PdBi}_2$, and

further down to 3.9 K in $\text{Na}_{0.057}\text{PdBi}_2$, as shown in the inset of Fig. 5.5(a). However, this is in great conflict with the theoretical expectation [84], which suggests that such electron-like doping should shift the Fermi level toward the DOS peak, increasing the DOS at the Fermi level and thus the T_c .

To verify whether the DOS does increase through Na intercalation, a Hall measurement was carried out on the $\text{Na}_{0.057}\text{PdBi}_2$ sample to probe the change of charge carrier concentration. As for PdBi_2 , the Hall coefficient R_H above 50 K is T insensitive for the Na-intercalated sample, as shown in Fig. 5.5(a). Therefore, the electron concentrations for PdBi_2 and $\text{Na}_{0.057}\text{PdBi}_2$ are calculated based on the R_H at 50 K as $1.58 \times 10^{22} \text{ cm}^{-3}$ and $3.09 \times 10^{22} \text{ cm}^{-3}$, respectively. There is apparently a significant increase of the carrier concentration, which is also in line with the decrease of the room-temperature resistivity observed in Fig. 5.5(a). The deduced $d\rho/dT$ at 300 K decreases from $0.37 \mu\Omega \text{ cm/K}$ for PdBi_2 to $0.20 \mu\Omega \text{ cm/K}$ for $\text{Na}_{0.057}\text{PdBi}_2$. The Na intercalation, therefore, does introduce electrons and enhance the DOS as expected. The suppression of T_c has to be attributed to other mechanisms.

5.5 The reason for the T_c suppression upon electron doping

In order to find out other possible origins of the T_c suppression, we compared the resistivity curves of PdBi_2 , the Pb-substituted and Na-intercalated samples as shown

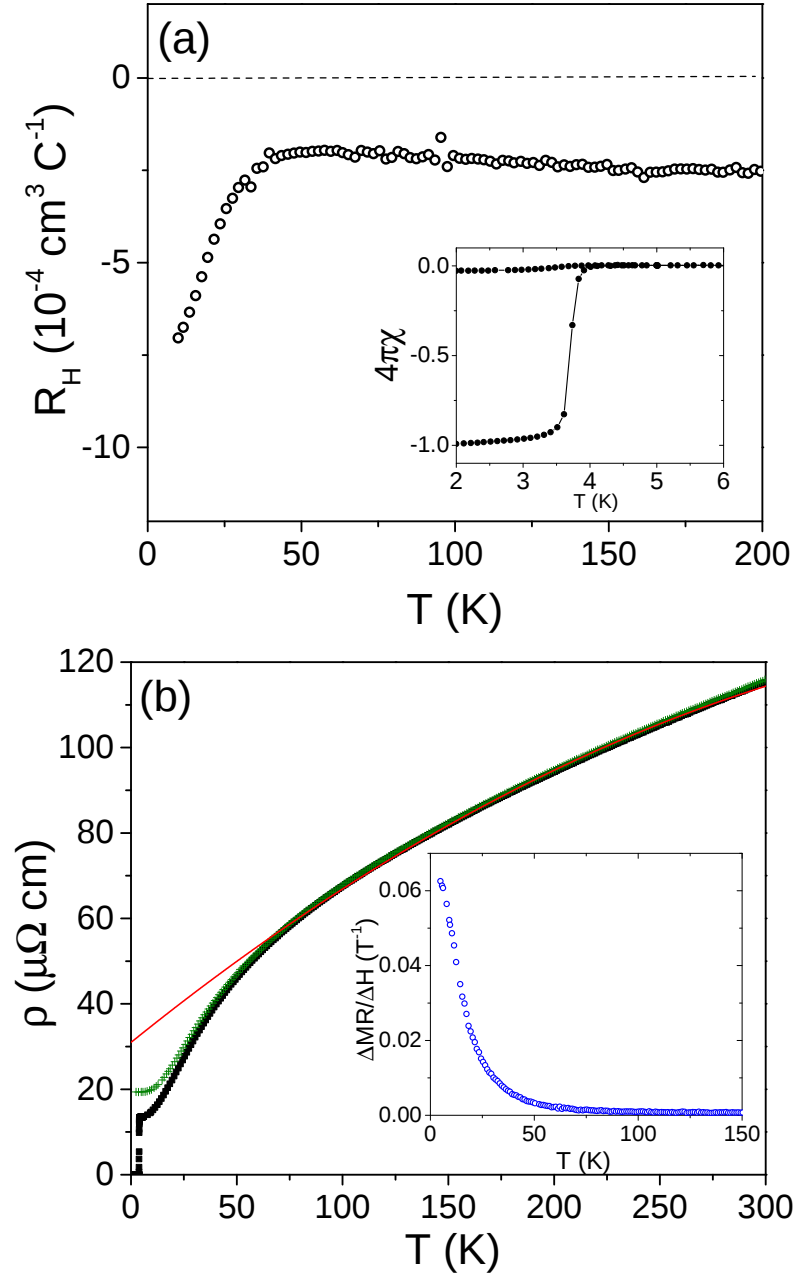


Figure 5.5: (a) The Hall coefficient R_H of $\text{Na}_{0.057}\text{PdBi}_2$ from 5 to 300 K; the inset shows the magnetic susceptibility of $\text{Na}_{0.057}\text{PdBi}_2$. (b) Magnetoresistivity of $\text{Na}_{0.057}\text{PdBi}_2$ from 2 to 300 K (solid black squares, zero field; green crosses, 7 T); The solid red line is only a guide for the eyes. The inset is the ratio of the change in the magnetoresistance $[\rho(7T) - \rho(0T)]/\rho(0T)$ to the magnetic field.

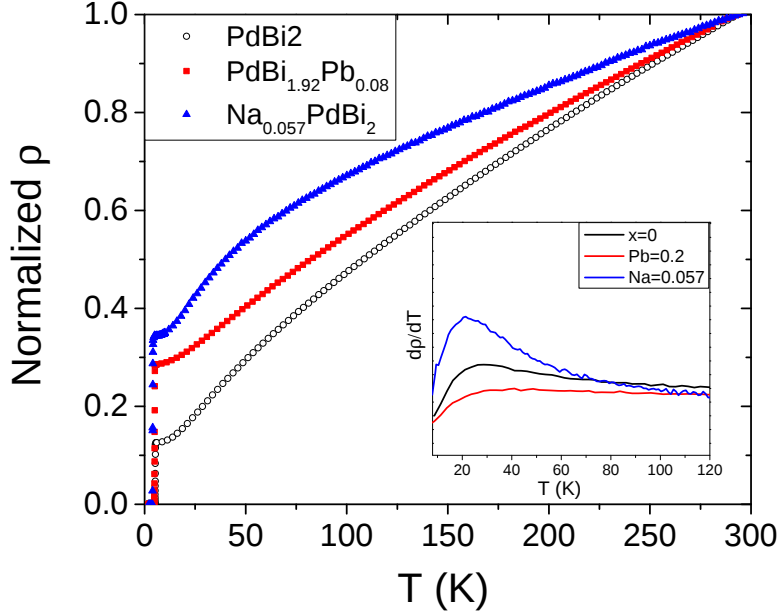


Figure 5.6: The normalized resistivity of β -PdBi₂, PdBi_{1.8}Pb_{0.2} and Na_{0.057}PdBi₂. Inset: the derivative of resistivity over temperature.

in Fig. 5.5. The hump feature starting ~ 50 K is suppressed by hole doping but enhanced by electron doping, which can be clearly seen in the $d\rho/dT$ (Fig. 5.6 inset). The different responses imply a certain scattering effect is influenced by charge doping. Such an effect is magnified by means of electron doping, and might be associated with the T_c suppression.

It is well known that both the competing excitations and the impurity scattering (especially pair-broken scattering) may suppress superconductivity. To explore the issue, both the magnetoresistance and the R_H are investigated (Fig. 5.5). The Hall coefficient R_H is enhanced almost by a factor of 3 upon cooling below 50 K (Fig. 5.5a). As demonstrated previously (Fig. 5.4 inset), the multiband effect has trivial interference effects on the R_H for the undoped PbBi₂. The unexpected enhancement of

the R_H in the Na-intercalated sample can hardly be attributed to the multiband effect, but is more likely caused by certain spin-related scattering/excitations. Spin-density-waves (SDW) under field, for example, may create a local magnetic moment. This consequentially produces a Hall component similar to the anomalous Hall effect in the ferromagnetic materials but quasi-linear on H and unusually large below the SDW transition temperature. Similar situations have been reported in some pnictides. Han *etal.* have observed that the R_H of SrFeAsF significantly increased with cooling below 150–160 K with the spin-density-wave (SDW) transition around 173 K [85]. Such an interpretation seems to be supported by both the resistivity and the magnetoresistivity data(Fig. 5.5(b)).

Following this speculation, we carried out magnetization and specific heat measurements to seek features of SDW excitation. The SDW transition is usually characterized by a decrease in the magnetization at high field and an jump in the specific heat. [85, 86] Due to the small magnitude of the magnetic susceptibility, the crystal was attached to a thin quartz rod in order to reduce the background signal. The high field magnetization data of PdBi₂ and Na_{0.057}PdBi₂ are shown in Fig. 5.7 for comparison. In the parent compound PdBi₂, there is no anomaly from room temperature down to 2 K as the curve follows the Curie-Weiss fitting. In Na_{0.057}PdBi₂, we were merely able to observe an upturn in magnetic susceptibility, which is inconsistent with other well-known SDW system (such as Fe-pnictides). The upturn anomaly in magnetic susceptibility, however, suggests a possible spin ordering occurs ~ 50 K. Besides, we also carried out a specific heat measurement for Na_{0.057}PdBi₂. The

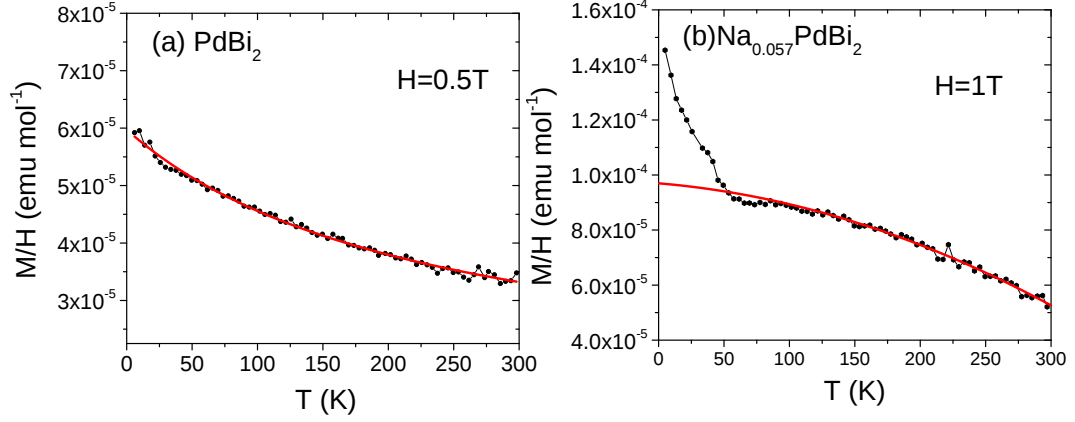


Figure 5.7: (a) The magnetization of PdBi_2 under a magnetic field of 0.5 T; (b) The magnetization of $\text{Na}_{0.057}\text{PdBi}_2$ under a magnetic field of 1 T. (The red line in (b) is a guide for the eyes.)

superconducting transition is exhibited as a jump at ~ 4 K (see Fig. 5.8), confirming the bulk nature. However, we were unable to detect an anomaly ~ 50 K when seeking evidence for the possible SDW transition. As we applied a magnetic field of 7 T, the specific heat curve demonstrated no observable change.

However, it should be noted that these are rather general characteristics of all spin orderings. For instance, an anomalous Hall effect and colossal magnetoresistance are observed in the manganites such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [87, 88]. To explore the situation in $\text{Na}_{0.057}\text{PdBi}_2$, the $R(T)$ above 70 K is fitted as a quadratic function of T (the solid red line in Fig. 5.5(b)), where the R -drop below 50 K is evident. The $R(T)$ under magnetic field of 7 T, in particular, is much higher than that under 0 T (Fig. 5.5(b), inset) with the deduced $\partial \ln R / \partial H \approx 0.05/T$ at 10 K. The enhanced hump feature, the large magnetoresistance, and the increased amplitude of the Hall coefficient below 50 K suggest a Fermi surface reconstruction and an ordering in the spin section

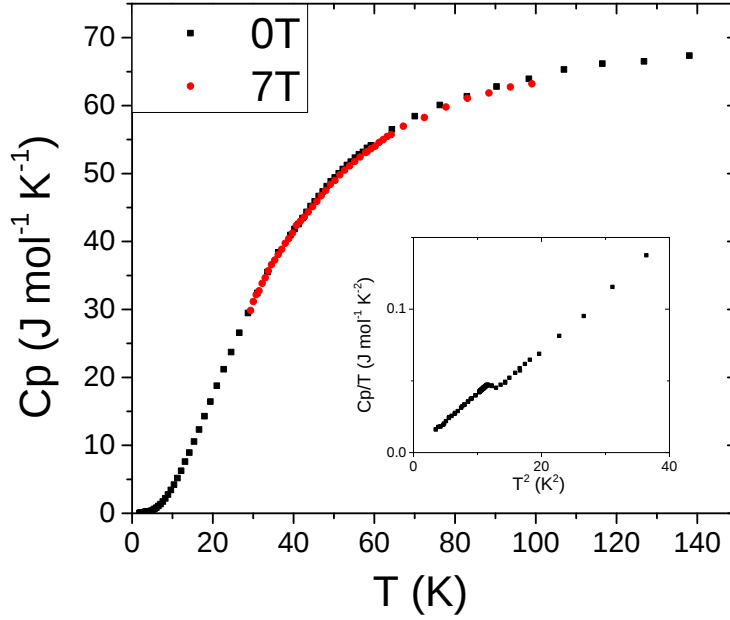


Figure 5.8: The specific heat of $\text{Na}_{0.057}\text{PdBi}_2$. Inset: the anomaly due to the superconducting transition.

around 50 K induced by Na doping. Thus the suppressed superconductivity in Na-intercalated PdBi_2 could be attributed to the competing spin ordering associated with the Fermi surface reconstruction, although the exact nature of this spin ordering needs further investigation.

Based on the above data, we were able to construct the phase diagram of T_c as a function of doping level (both hole and electron doping) as shown in Fig. 5.9. At the right side of the phase diagram (hole doping), the T_c decreases continuously with Pb doping. The suppression of T_c can be understood as a decrease of the DOS at the Fermi level caused by hole doping. At the left side of the figure, we demonstrate that the T_c is also quickly suppressed by a small amount of Na-intercalation. The cause of this T_c suppression might be attributed to the emergence of possible spin ordering,

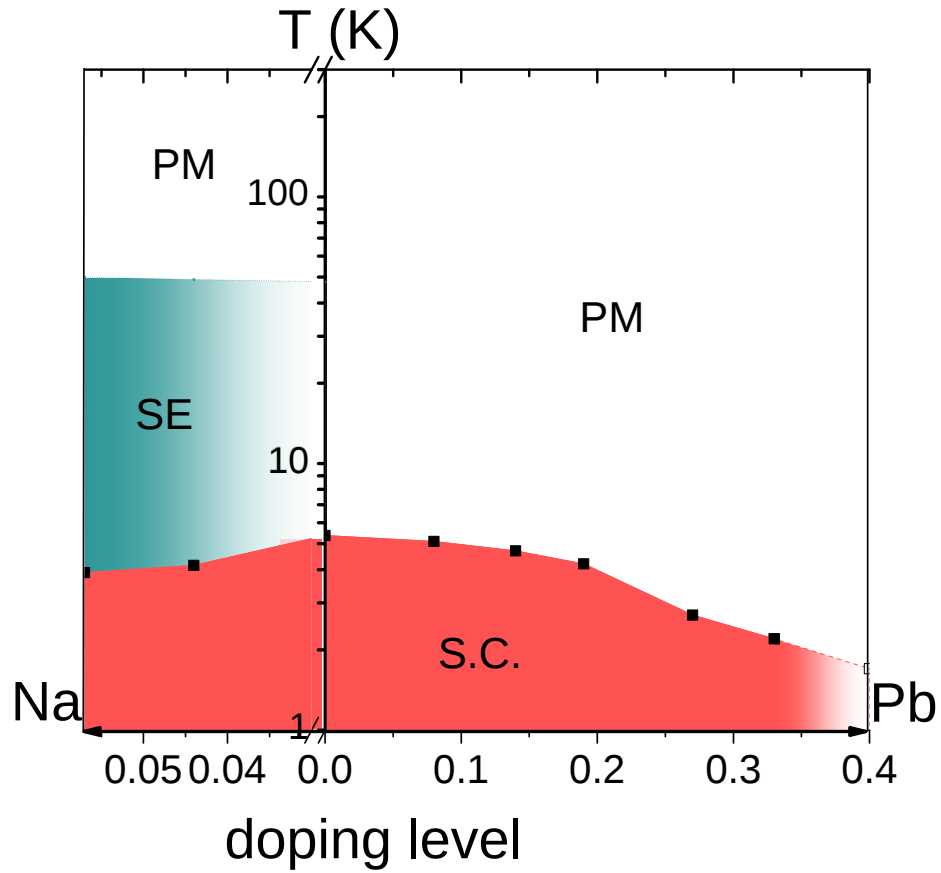


Figure 5.9: The phase diagram for both hole- and electron-doped PdBi₂. SC, superconducting transition temperature determined by resistivity data; PM, paramagnetic state; "SE", possible spin excitation(ordering) induced by Na intercalation.

which may compete for the ground state and be counterproductive in stabilizing the superconducting state.

5.6 High-pressure study on undoped PdBi_2

To further examine the above conjectures based on doping, we investigated the pressure effect on the undoped PdBi_2 with the highest T_c of this series by measuring the temperature dependence of resistivity under pressures up to 16.63 kbar, as shown in Fig. 5.10(a). As the applied pressure increases, the normal-state resistivity considerably decreases. A closer look at the low-temperature part, as shown in Fig. 5.10(b), reveals that the superconducting transition becomes slightly sharper, and is gradually suppressed, upon applying pressure at a linear suppression rate of $dT_c/dP = -0.28\text{K/GPa}$. At 16.63 kbar, the T_c is reduced to 4.9 K. To verify the stability of the sample, the pressure cell was unloaded to lower and ambient pressure. The corresponding data are denoted as (u) in Fig. 5.10(b). We observed that superconducting transition T_c values measured upon loading and unloading the pressure cell fell along the same line, proving the stability of the sample in the pressure cycle. The corresponding phase diagram of T_c versus pressure is shown in the inset of Fig. 5.10(b). The suppression of T_c by pressure appears to be consistent with the doping experiment.

5.7 Summary

In summary, we have systematically grown large single crystals of the layered compounds $\beta\text{-PdBi}_2$, the hole-doped $\text{PdBi}_{2-x}\text{Pb}_x$ and the electron-doped Na_xPdBi_2 , and studied their magnetic and transport properties. Hall measurements on PdBi_2 ,

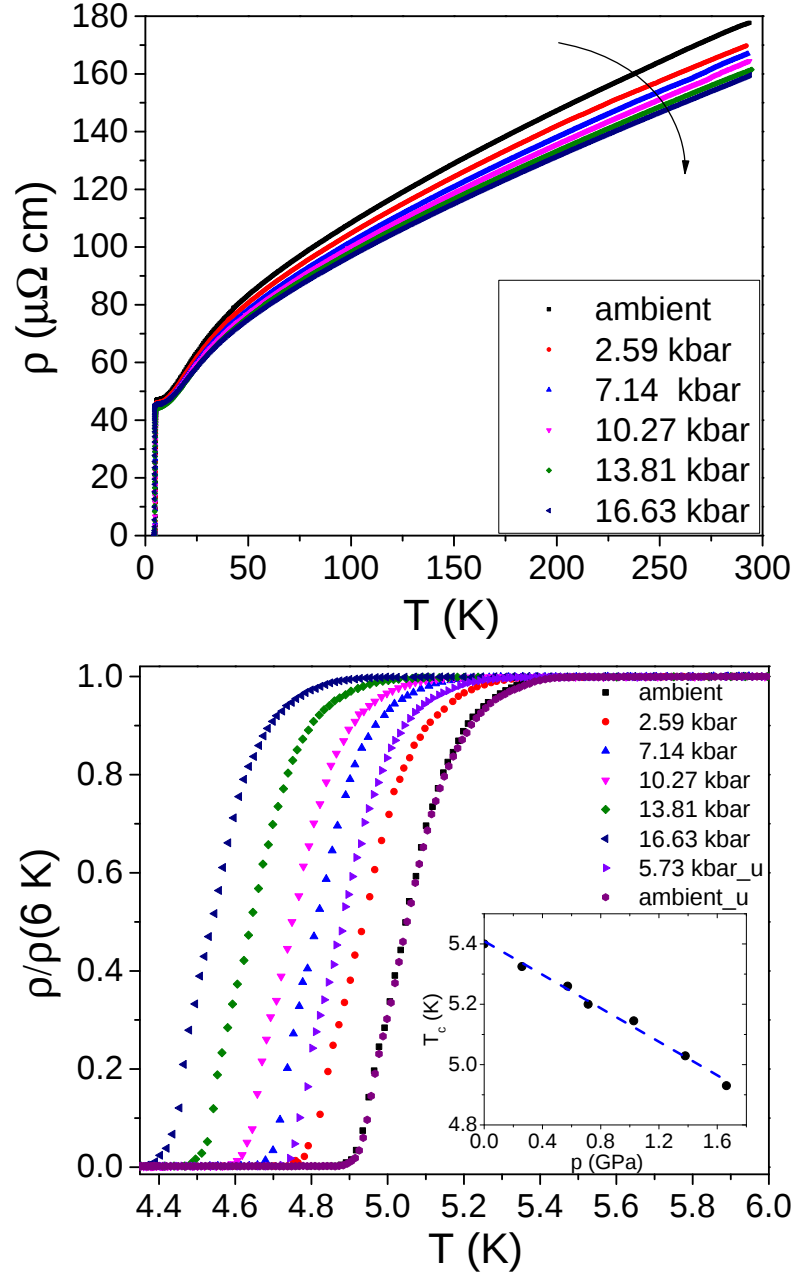


Figure 5.10: (a) The resistivity of β -PdBi₂ from 1.2 to 300 K under high pressure. (b) The normalized resistivity under different pressures, where u denotes the unloaded pressure run. The inset shows the shift of T_c with pressure for β -PdBi₂.

$\text{PdBi}_{1.8}\text{Pb}_{0.2}$, and $\text{Na}_{0.057}\text{PdBi}_2$ show that the charge transport is dominated by electrons in all of the samples. The electron concentration is substantially reduced upon Pb doping in $\text{PdBi}_{2-x}\text{Pb}_x$ and increased upon Na intercalation in Na_xPdBi_2 , indicating effective hole doping by Pb and electron doping by Na. In Pb-doped PdBi_2 , we observed a monotonic decrease of T_c from 5.4 K in undoped PdBi_2 to less than 2 K for $x > 0.35$. The monotonic decrease of the T_c upon doping can be explained by the reduced DOS at the Fermi level. In Na-intercalated samples, a rapid decrease of T_c with a slight Na-intercalation level is also observed, which is in contradiction with the theoretical expectation. Both the magnetoresistance and Hall measurements further reveal evidence for a possible competing spin ordering at ~ 50 K, which could contribute to the suppression of the T_c in Na-intercalated samples. Meanwhile, application of external pressure up to 16.63 kbar on the undoped PdBi_2 also suppresses the superconducting transition linearly with a dT_c/dP coefficient of -0.28 K/GPa, consistent with the doping experiments.

Chapter 6

Conclusions

We successfully achieved ambient-pressure superconductivity in the undoped Ca122 through the post-growth thermal treatments. The resistivity and magnetization studies indicate that a $T_c \sim 25$ K with partial diamagnetic shielding and Meissner effect was induced only in the annealing-time regime where the two phases (P1 and P2) coexist. As suggested by the experimental XRD results and verified by the simulations, the single-phased P2 crystal was tuned into a metastable layer-stacking mesostructure before being converted into the single-phased P1 crystal. These observations imply that the superconductivity with an enhanced T_c might be associated with the dense interfaces forming in the heterostructures, which are composed of O and cT phase at low temperature. In addition, as a supportive evidence, the superconducting volume fraction exhibits a correlation with the interface density calculated based on our intergrowth model. The magnetic data further suggest that the spin-density-wave excitations in the P1 phase are largely suppressed along the

interfaces. The microstrain along the interfaces, therefore, may play a crucial role in the interface-associated superconductivity.

The mixed-phase sample P3 unexpectedly exhibits two superconducting transitions with distinctive responses to the external pressure. As a result, the higher transition is continuously enhanced up to 30 K under a pressure of 17 kbar. On the contrary, no trace of superconductivity has been detected upon applying pressure to the sample in the P2 phase. The pressure studies further support our interpretation of the interfacial superconductivity. The enhanced T_c , the small superconducting volume fraction and the extended pressure range, where the superconductivity is even enhanced, all suggest that the superconductivity may also depend on other properties of the interfaces.

Further investigations are needed to visualize the exact morphology of the interfaces. For example, a low-temperature XRD experiment would give more accurate evaluations of the phase compositions in the ground state. In this work, the analyses of the mesostructure are limited to the c axis. A study with the assistance of electron microscopes, *e.g.*, a transmission electron microscopy (TEM), would reveal more information of the mesostructure on the ab plane.

Similar phenomena were not observed through our systematic studies of the Eu and Sm doped Ca122 compounds. Sm doping can only induce a superconducting transition below 10 K, which might be associated with the superconductivity in undoped Ca122. On the other hand, the response of Sm-doped sample to pressure seems to be unexpected and further study is needed. In the Eu doped Ca122 system, both the SDW-transition temperature and the AFM-transition temperature due to

Eu^{2+} spins increase systematically with Eu doping. The SDW is suppressed under high pressure and coexists with superconductivity. However, superconductivity with zero resistance occurs only after the SDW is eliminated completely. The phase diagram suggests that the Eu doped Ca122 samples with low Eu-doping level may follow the properties demonstrated by the undoped P1-phase Ca122 under non-hydrostatic pressure. Further studies under higher pressures would help to characterize the possible cT phase transition and to complete the superconductivity domes for other samples.

The interface-enhanced superconductivity in the heterostructures naturally formed by the two distinct phases seems to be unique in the Ca122 system to date. Further investigations on those unique properties of the Ca122 system may provide insight into possible routes for searching for, and hopefully finding, other examples of interfacial superconductivity.

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