Study of superconducting and magneto transport properties of REFeAsO$_{1-x}$Fx (RE=La and Ce)

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STUDY OF SUPERCONDUCTING AND MAGNETO TRANSPORT PROPERTIES OF $RE\text{FeAsO}_{1-x}F_x$
($RE=$La and Ce)

Thesis submitted in fulfilment of the requirement
for the award of the degree

Master

From the
University of Wollongong

By

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Institute for Superconducting &
Electronic Materials

Faculty of engineering

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Abstract

Iron-based superconductors are the most recently discovered superconductors which could be suitable for a variety of applications. The high upper critical fields and relatively high critical current density in this group are good evidence that these compounds can be competitive with MgB$_2$ and even high critical temperature ($T_c$) cuprates. Moreover, the first high temperature superconductors, cuprates, have been studied intensively for more than 20 years, but scientists still don’t know exactly how these materials work. Finding the first non-cuprate high temperature superconductors can help to unveil the mystery of superconductivity. It is possible that the clues to how these materials work could lead to the design of room temperature superconductors.

The first iron-based superconductor compound, LaFeAsO$_{1-x}$F$_x$, shows superconductivity at 26 K. However, the transition temperature is increased by replacing La by other rare earth elements with smaller atomic radii, such as Ce, Sm, Nd, Pr, and Gd, resulting in an increase of up to 56 K for GdFeAsO$_{1-x}$F$_x$ compound. The parent compounds show antiferromagnetic spin density wave order, and superconductivity appears by introducing charge carriers, either through electron or hole doping.

Six families of iron based superconductors have been discovered so far. The first family has the formula $RE$OFeAs, in which $RE$ stands for rare earth element. These compounds have a tetragonal layered ZrCuSiAs structure with the P4/nmm space group. The second family has the formula AFe$_2$As$_2$, in which A is alkali- Rear elements. They have the ThCr$_2$Si$_2$ structure with space group I4/mmm. The next family is LiFeAs, which has an infinite layered structure and crystallizes into the CuPb-type tetragonal structure. The next category, FeSe, presents a tetragonal structure, the simplest crystal structure among
the iron-based superconductors. The latest families discovered so far are (Ca,Sr)FFeAs and Sr₄Sc₂Fe₂As₂O₆. (Ca,Sr)FFeAs has the ZrCuSiAs type structure with P4/nmm space group. Sr₄Sc₂Fe₂As₂O₆ has a layered structure with the space group I4/mmm.

For practical application of the Fe-based superconductors, two of the most important parameters are the upper critical field, \(H_{c2}\), and the critical current density, \(J_c\). The upper critical field is an intrinsic property, which has been approximated to be higher than 55 or 64 T in LaFeAs O₁₋ₓFₓ, 70 T in PrFeAsO₀.₈₅F₀.₁₅, over 100 T in SmFeAsO₀.₈₅F₀.₁₅, and 230 T in high-pressure (HP) fabricated NdFeAsO₀.₈₂F₀.₁₈. The \(J_c\) is sample dependent and controlled by the flux pinning behaviour. However, the available data for critical current density and pinning force in LaFeAsO₁₋ₓFₓ compound are very limited so far. As La is non-magnetic, LaFeAsO₁₋ₓFₓ was selected for study in this thesis, as it should be an ideal sample to study the flux pinning related properties. This is because all the other \(RE\) compounds contain a magnetic \(RE\). Compared to LaFeAsO₁₋ₓFₓ, where Fe is the only possible ion carrying a significant magnetic moment, a rare-earth oxypnictide with a paramagnetic ion such as Ce\(^{⁺³}\) in CeFeAsO₁₋ₓFₓ also offered a unique opportunity to study the interplay between the rare-earth element and the Fe magnetic ions.

Our results show that the critical current density for both compounds, LaFeAsO₁₋ₓFₓ and CeFeAsO₁₋ₓFₓ, depends on the level of fluorine doping. For LaFeAsO₁₋ₓFₓ compound, with increasing fluorine doping from \(x = 0.05\) to \(x = 0.15\), \(J_c\) is increased. After that, with further increases in \(x\), the \(J_c\) is reduced. For CeFeAsO₁₋ₓFₓ, \(J_c\) is decreased with increasing fluorine doping. Both compounds show a superior \(J_c\) field dependence at low temperature. A peak effect was observed in the CeFeAsO₁₋ₓFₓ samples with \(x = 0.1\) at T
= 20 K. The peak effect was also detected at 5 K, 10 K and 15 K for LaFeAsO$_{0.85}$F$_{0.15}$ compound. $J_c$ shows weak magnetic field dependence at $T < 20$ K for both compounds.

By using the Ginzburg-Landau equation and the Werthamer-Helfand-Hohenberg (WHH) theory, we estimate $H_{c2}^{ab}(0) = 122$ T and 185 T for LaFeAsO$_{0.85}$F$_{0.15}$ and CeFeAsO$_{0.9}$F$_{0.1}$, respectively.

The pinning potential scales as $U_o/\kappa_B \propto B^n$, where $U_o$ is the pinning potential energy, $\kappa_B = $ Boltzmann’s constant, and $n = 0.2$ for $B < 3$ T and $n = 0.7$ for $B > 3$ T for CeFeAsO$_{0.9}$F$_{0.1}$, and $n = 0.13$ for $B < 1$ T and $n = 0.68$ for $B > 1$ for LaFeAsO$_{0.85}$F$_{0.15}$. So, it is expected that single-vortex pinning may coexist with collective creep in low field. The value of $U_o$ for the CeFeAsO$_{0.9}$F$_{0.1}$ doped sample is two times higher than for the LaFeAsO$_{0.95}$F$_{0.05}$.

The $H_{c2}$ values of these compounds have the potential to be increased even more, through proper chemical doping and physical approaches, due to the two-gap superconductivity in the new iron-based superconductors. As the $J_c$ values are still considerably lower than those of individual grains, the challenge is to produce these materials with more texture and connectivity, in order to allow these new superconductors to carry a high critical current density in low and high magnetic fields.
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Chapter 1

1 Introduction

The discovery of the iron-based superconductor \( \text{LaFeAsO}_{1-x}\text{F}_x \) on 23 February, 2008 has attracted enormous attention in condensed-matter physics, due to the presence of superconductivity in a compound which contained the ferromagnetic element iron. This family is regarded as the second class of high temperature superconductors since the discovery of the cuprates. The first compound, \( \text{LaFeAsO}_{1-x}\text{F}_x \), shows superconductivity at 26 K. By replacing La with other rare earth elements, such as Sm, Ce, Nd, Pr, and Gd, the critical temperature could be doubled, resulting in an increase of up to 55 K for Sm. The parent compounds show antiferromagnetic spin density wave order, and the superconductivity appears as a result of doping with charge carriers, either electrons or holes. Six different crystal structures of iron based superconductors have been reported so far: the first one is \( \text{REFeAsO} \) with the ZrCuSiAs structure, where \( \text{RE} \) stands for a rare earth element. The second iron pnictide family has the \( \text{ThCr}_2\text{Si}_2 \) type structure, which has the formula \( \text{AFe}_2\text{As}_2 \) where \( \text{A} \) represents an alkali metal. The third structure reported is \( \text{LiFeAs} \), with the \( \text{Cu}_2\text{Sb} \) type crystal structure. The next family is \( \alpha\text{-FeSe} \) compound with the \( \alpha\text{-PbO} \) type structure. Recently, superconductivity has been reported in \( \text{CaFeAsF} \) and \( \text{Sr}_2\text{Sc}_2\text{Fe}_2\text{As}_2\text{O}_6 \). Similar to the cuprates, iron-based superconductors have layered structures, a small coherence length, and unconventional pairing. On the other hand, iron-based superconductors have metallic parent compounds, and their electronic anisotropy is smaller than for the cuprate high temperature superconductors and does not depend on the level of doping. The very high upper critical fields in iron-based
superconductors have demonstrated that these materials can be competitive with MgB$_2$
and even high critical temperature, $T_c$, cuprates.

The structure of this thesis consists of five chapters. Following this brief introduction, a
review of the most recent literature available on the new iron-based superconductors
appears in Chapter 2. The material preparation, and characterisation method and
facilities are described in Chapter 3. The crystal structure, microstructure, critical
current density, and flux pinning properties of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15 and 0.20)
compound will be discussed in Chapter 4. The crystal structure, morphology, and
superconductivity in the CeFeAsO$_{1-x}$F$_x$ compound will be investigated in Chapter 5.
CHAPTER 2

2 Literature Review

2.1 Fundamental properties of superconductivity

Many metals, alloys, and ceramic compound, undergo a phase transition below a critical temperature, to a state having zero electrical resistance. This phenomenon, which known as superconductivity[1], was initially discovered by Heike Kamerlingh Onnes in Holland in 1911. He observed that the electrical resistance of mercury will drop to zero when it is cooled to any temperature below 4.2K [2] (Fig. 2. 1). His further study on other materials showed that the transition from the normal to the superconducting state occurred at different temperatures for different material. Therefore, the temperature at which a material changes from the normal state to the superconducting state was called the transition temperature ($T_c$).

![Figure 2-1: Experimental data obtained on mercury by Kamerling Onnes showing the superconducting transition for the first time[1].](image)
He also realised that a huge current density could flow through the mercury sample in its superconducting state. However, there was a particular maximum value for the current density above which the sample returned to the normal state, even though it might be below its transition temperature. This maximum value was called the critical current density, $J_c$. As discovered later, above $J_c$, the DC current breaks the Cooper pairs of electrons and thus, destroys the superconducting state.

It was also observed that the superconducting state can be destroyed not only by too high a DC current, but also by a magnetic field higher than some threshold value, $B_c$, can simply destroy the superconductivity. This magnetic field is called the critical field.

In 1933, W. Meissner and R. Oeschsenfeld observed that when a superconducting material is cooled below its critical temperature ($T_c$) magnetic fields are excluded from the material and the material act as a perfect diamagnet, as shown in Fig. 2-2. This has become known as the Meissner effect[3]. The Meissner effect has implications for making powerful superconducting magnets for magnetic resonance imaging (MRI). It is also used for high speed magnetically levitated trains.

![Figure 2-2: The Meissner effect, the expulsion of external magnetic field from inside the superconductor. The field is applied at (a) $T > T_c$ and (b) $T < T_c$.](image-url)
In 1950, the Ginzburg-Landau theory of superconductivity was devised by Landau and Ginzburg. This theory had great success in explaining the macroscopic properties of superconductors. The microscopic theory of superconductivity was proposed in 1957 by Bardeen, Cooper and Schrieffer and is known as BCS theory. This theory explained the superconducting current as a superfluid of Cooper pairs, pairs of electrons interacting through the exchange of phonons.

In 1958, Abrikosov divided superconducting materials into two groups by their behaviour in magnetic fields: type I and type II superconductors. The magnetization of type I and type II superconductors is shown in Fig. 2.3.

![Phase diagram for magnetic field vs. temperature for type I (left) and type II (right) superconductors.](image)

In the early superconductors, including all of the elemental superconductors, the superconductivity is quenched in relatively low magnetic field. In contrast, type II superconductors have two critical field strengths for a given temperature, a lower critical field \(B_{c1}\) and an upper critical field \(B_{c2}\). Below \(B_{c1}\), these materials act exactly like type I superconductors and magnetic field can not penetrate inside the material, and above the \(B_{c2}\), they act like normal materials at low temperature. However, between \(B_{c1}\) and \(B_{c2}\) the superconductors have a unique property. They have a resistance of zero, but
allow a certain amount of flux penetration in the form of vortices. Each vortex can be approximated by a long cylinder with its axis parallel to the external magnetic field. Inside the cylinder, the superconducting order is zero. These vortices are surrounded by a superconducting region. The radius of the cylinder is of the order of the Ginzburg-Landau coherence length $\xi_{GL}[3]$. The supercurrent circulates around the vortices within an area of radius $\sim \lambda$, and it forms a regular triangular lattice under ideal conditions, as shown in Figure 2.4. However, the ideal triangular vortex lattice can only occur in a homogeneous superconductor. In fact, the material structure has a great influence on the vortex pattern[3]. For example, a vortex can be pinned or trapped by defect or impurities in the material. This phenomenon is called flux pinning. Flux pinning is only possible when there are defects in the crystalline structure of the superconductor, such as grain boundaries, impurity particles, and or crystal imperfections. This phenomenon is used in high temperature superconductors in order to prevent flux creep, which can create resistance and decrease the critical current density and upper critical field.

Figure 2-4: Vortices in the mixed state of type II superconductor. The gray area is the normal state at the centre of vortices, and the arrows show the supercurrent circulating around the vortices.
In 1962, Brian Josephson demonstrates the existence of a superconducting current through a tunnelling device made from two superconductors separated by a thin insulating layer. The effect known as Josephson effect and has had practical applications in the development of miniature electronics, winning him the 1973 Nobel Prize.

Before the discovery of superconductivity in cuprates, the highest temperature of 23.2 K was observed in Nb$_3$Ge. However, the real history of high temperature superconductivity began in 1986 when Bednorz and Müller discovered superconductivity in La-Ba-Cu-O ceramic at 30 K. In 1987, superconductivity at 93 K was discovered in Y-Ba-Cu-O (YBCO). Just a year later Bi and Tl based superconducting cuprates were discovered with $T_c = 110$ K and 125 K, respectively. Finally, Hg–based cuprate with the highest $T_c = 135$ K was discovered in 1993 [3].

Figure 2-5: Superconducting critical temperatures of several superconductors as a function of year of discovery.

Magnesium diboride was discovered in March 2001 with critical temperature of 39 K. In February 2008 an iron-based family of high temperature superconductors was discovered. Hideo Hosono of the Tokyo Institute of Technology discovered that
lanthanum oxygen fluorine iron arsenide becomes a superconductor at 26 K. Following research by other groups suggested that replacing the lanthanum by other rare earth elements, such as cerium, samarium, neodymium, and praseodymium, can lead to superconductivity up to 56 K. Figure 2.5 shows the superconducting critical temperature of different superconductors as a function of year of discovery.

Magnesium diboride is a conventional superconductor because its superconducting properties can be explained by BCS theory, while cuprate and the new iron-based superconductors are unconventional superconductors.

Scientists are excited about the discovery of the new iron-based superconductors because now they have an opportunity to study the electrical and magnetic properties in a different high temperature superconductor (HTS) system, to hopefully understand the nature of superconductivity in unconventional superconductors. Clues to how these high temperature superconductor materials work will lead to the design of new materials with zero resistance at higher temperature. These materials would be good candidates for use in electricity generators, cheaper medical imaging scanners, and extremely fast levitating trains because superconducting materials with higher $T_c$ would not require expensive coolants to reach the superconducting transition temperature.

### 2.2 Iron based superconductors

Cuprate superconductors were the only known superconductors that worked far above liquid-helium temperatures for more than 20 years. Two years ago, scientists discovered the first non-cuprate high-temperature superconductors, which were based on iron. These new materials could help unveil the mystery of superconductivity.
Hideo Hosono and his colleagues were looking to improve the property of transparent oxide semiconductors, but they ended up discovering superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ [4]. Superconductivity in the iron based compound surprised scientists, as they thought that the magnetic nature of iron would disrupt the pairing of electrons in superconducting compounds. After only one month the critical temperature of these compounds was doubled by replacing La by other rare earth elements with smaller atomic radius.

Table 2.1 shows transition temperature of some well-known superconductors in comparison with the boiling points of liquid nitrogen and hydrogen.

**Table 2-1: Transition temperature of some well-known superconductors.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition temperature (K)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgBa$_2$Ca$_2$Cu$<em>3$O$</em>{6+δ}$</td>
<td>134</td>
<td>Copper-oxide superconductors</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{6+δ}$ (YBCO)</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td><strong>Boiling point of liquid nitrogen at 77 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SmFeAsO$_{1-x}$F$_x$</td>
<td>55</td>
<td>Iron-based superconductors</td>
</tr>
<tr>
<td>Gd$_{1-x}$Th$_x$FeAsO</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Sr$_2$VO$_3$FeAs</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td><strong>Boiling point of liquid hydrogen at 20 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb$_3$Sn</td>
<td>18</td>
<td>Metallic low-temperature</td>
</tr>
<tr>
<td>Hg(Mercury)</td>
<td>4.2</td>
<td>superconductors</td>
</tr>
</tbody>
</table>

New iron-based superconductors share similar characteristics with cuprate superconductors, such as the layered structure, the small coherence length, and
unconventional pairing. Also, in both families, the metallic layer is responsible for superconductivity and the insulator layer provides charge carrier. On the other hand, the new iron based superconductors have metallic parent compounds, and their electronic anisotropy is generally smaller than for cuprate superconductors [5].

2.2.1 Crystal structure of iron pnictide superconductor

The family of iron based superconductors has been extended quickly, and it can be divided into six categories. The first category, with the formula $R$FeAsO [6], where $R$ stands for rare earth element, is described as FeAs-1111 phase. These compounds crystallize with the tetragonal layered ZrCuSiAs structure, in the space group P4/nmm. The interlayer chemical bonding is covalent, and the interlayer chemical bonding has an ionic character[6]. Electron carriers can be introduce by replacing oxygen by fluorine or by oxygen deficiency[4,6-10], which results in superconductivity in these compounds. Also, superconductivity can be triggered through hole doping in this system by partial substitution of the rare earth element[11]. The second class has the general formula $A$Fe$_2$As$_2$, where $A$ represents an alkaline earth element. It is symbolized as FeAs-122 and has the ThCr2Si2 structure with space group I4/mmm. These compounds have a more simple crystalline structure compared to the 1111-FeAs family, and the FeAs layers separated by $A$ layers. Superconductivity has been found in hole doped Sr$_{1-x}$K$_x$Fe$_2$As$_2$ [12], Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ [13], and Eu$_{1-x}$K$_x$Fe$_2$As$_2$ [14], as well as electron doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [15] and Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [16]. There is also pressure induced superconductivity in the parent compounds CaFe$_2$As$_2$ [16], SrFe$_2$As$_2$ [17], and BaFe$_2$As$_2$ [17].
Figure 2-6: Structures of different families of iron based superconductors.

$L_nP_nAsO$  $T_{c,\text{max}}=55$ K [18]
$L_n=\text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy}
P_n=P, \text{As, Sb}$

$A_{1-x}\text{Me}_x\text{Fe}_2\text{As}_2$  $T_{c,}\text{max}=38$ K [18]
$A=\text{Ca, Sr, Ba}
\text{Me}=\text{K, Cs, Rb}$

$\text{Li}_{1-\delta}\text{FeAs}$  $T_{c}=18$ K [19]

$\alpha\text{FeSe}$  $T_{c}=8$ K [20]

$\text{CaFFe}_{1-x}\text{Co}_x\text{As}$  $T_{c}=22$ K [21]

$\text{Sr}_2\text{VO}_3\text{FeAs}$  $T_{c}=37$ K [22]
These discoveries were followed by the announcement of other new parent compounds: LiFeAs, FeSe, and SrFeAsF with a maximum $T_c$ of 18 K [23], 8 K [24] and 56 K [25], respectively. LiFeAs has an infinite layered structure and is denoted as FeAs-111. LiFeAs crystallizes into the Cu$_2$Pb-type tetragonal structure containing, FeAs layers with an average iron valence of +2. The crystal structure of FeSe presents a tetragonal structure, the simplest crystal structure in an iron based family. Recently, superconductivity was discovered in Ca$_{1-x}$RE$_x$FeAsF and Sr$_4$Sc$_2$Fe$_2$As$_2$O$_6$ with $T_c$ of 57 K for $RE = Pr$ [26] and 17 K [27], respectively. CaFeAsF has the ZrCuSiAs type structure with P4/nmm space group. Sr$_4$Sc$_2$Fe$_2$As$_2$O$_6$ has a layered structure with the space group I4/mmm.

Table 2.2 gives summary of the reported iron based superconductors and their transition temperatures. Experimental facts have revealed that FeAs-1111 and the oxygen free Ca$_{1-x}$RE$_x$FeAsF family exhibit the highest $T_c$ above 40 K in the iron based superconductor family.

Table 2-2: Transition temperatures of some iron-based superconductors.

<table>
<thead>
<tr>
<th>compound</th>
<th>$T_c$ (K)</th>
<th>$a=b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1111-FeAs Family</strong></td>
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</tr>
<tr>
<td>LaFeAsO$<em>{0.89}$F$</em>{0.11}$ [28]</td>
<td>28.2</td>
<td>4.0277</td>
<td>8.7125</td>
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<tr>
<td>LaFeAsO$<em>{0.89}$F$</em>{0.11}$ [7] (HP)</td>
<td>43</td>
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</tr>
<tr>
<td>La$<em>{0.87}$Sr$</em>{0.13}$FeAsO [11]</td>
<td>25</td>
<td>4.0350</td>
<td>8.7710</td>
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<tr>
<td>La$<em>{0.85}$Na$</em>{0.15}$FeAsO$<em>{0.85}$F$</em>{0.15}$</td>
<td>30.9</td>
<td></td>
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</tr>
<tr>
<td>LaFeAs$<em>{0.95}$Sb$</em>{0.05}$O$<em>{0.8}$F$</em>{0.2}$ [29]</td>
<td>30.1</td>
<td>4.02017</td>
<td>8.701</td>
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<tr>
<td>Compound</td>
<td>30.3</td>
<td>4.018</td>
<td>8.713</td>
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<tr>
<td>La$<em>{0.8}$Th$</em>{0.2}$FeAsO [30]</td>
<td>10.5</td>
<td>4.0359</td>
<td>8.6944</td>
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<td>LaFe$<em>{0.9}$Ir$</em>{0.1}$AsO [31]</td>
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<tr>
<td>LaNiAsO [32]</td>
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<td>4.0240</td>
<td>8.7132</td>
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<tr>
<td>LaFe$<em>{0.89}$Co$</em>{0.11}$AsO [33]</td>
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<td>3.994</td>
<td>8.598</td>
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<tr>
<td>La$<em>{0.2}$Ce$</em>{0.8}$FeAsO$<em>{0.9}$F$</em>{0.1}$ [34]</td>
<td>9.5</td>
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<tr>
<td>La$<em>{0.7}$Pb$</em>{0.3}$FeAsO [34]</td>
<td>41</td>
<td>3.988</td>
<td>8.607</td>
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<td>CeFeAsO$<em>{0.8}$F$</em>{0.2}$ [35]</td>
<td>11.3</td>
<td>3.9918</td>
<td>8.603</td>
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<tr>
<td>CeFe$<em>{0.9}$Co$</em>{0.1}$AsO [36]</td>
<td>48.6</td>
<td>3.9654</td>
<td>8.5803</td>
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<td>Ce$<em>{0.6}$Y$</em>{0.4}$FeAsO$<em>{0.8}$F$</em>{0.2}$ [37]</td>
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<td>SmFe$<em>{0.9}$Co$</em>{0.1}$FeAs [39]</td>
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<td>TbFeAsO$_{0.85}$ [41]</td>
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<td>Tb$<em>{0.8}$Th$</em>{0.2}$FeAsO [42]</td>
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<td>YFeAsO$<em>{0.9}$F$</em>{0.1}$ [43]</td>
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<td>EuAsFeO$<em>{0.85}$F$</em>{0.15}$</td>
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<td>PrFeAsO$<em>{0.89}$F$</em>{0.11}$</td>
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<td>3.99</td>
<td>8.65</td>
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<td>Pr$<em>{0.8}$Sr$</em>{0.2}$FeAsO [44]</td>
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<td>Nd$<em>{0.8}$Th$</em>{0.2}$FeAsO [46]</td>
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<td>HoFeAsO$_{1.4}$ [47]</td>
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<td>HoFeAsO$<em>{0.9}$F$</em>{0.1}$ [48]</td>
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<td>Compound</td>
<td>TbFeAsO$_{1-\delta}$ [47]</td>
<td>GdFeAsO$<em>{0.8}$F$</em>{0.2}$ [49]</td>
<td>Gd$<em>{0.8}$Y$</em>{0.2}$FeAsO$<em>{0.8}$F$</em>{0.2}$ [49]</td>
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<tr>
<td></td>
<td>48.5</td>
<td>43.9</td>
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<td>3.878</td>
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<td>8.354</td>
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122-FeAs family

<table>
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<tr>
<th>Compound</th>
<th>EU$<em>{0.5}$K$</em>{0.5}$Fe$_2$As$_2$ [14]</th>
<th>EU$<em>{0.7}$Na$</em>{0.3}$Fe$_2$As$_2$ [52]</th>
<th>KFe$_2$As$_2$ [53]</th>
<th>CaFe$<em>{1.9}$Rh$</em>{0.1}$As$_2$ [54]</th>
<th>CsFe$_2$As$_2$ [53]</th>
<th>Cs$<em>{0.4}$Sr$</em>{0.6}$Fe$_2$As$_2$ [53]</th>
<th>K$<em>{0.4}$Sr$</em>{0.6}$Fe$_2$As$_2$ [55]</th>
<th>SrFe$<em>{1.8}$Co$</em>{0.2}$As$_2$ [16]</th>
<th>Ba$<em>{0.6}$K$</em>{0.4}$Fe$_2$As$_2$ [56]</th>
<th>Ba$<em>{0.85}$La$</em>{0.15}$Fe$_2$As$_2$ [56]</th>
<th>BaFe$<em>{1.8}$Co$</em>{0.2}$As$_2$ [15]</th>
<th>BaFe$<em>2$(As$</em>{0.68}$P$_{0.32}$)$_2$</th>
<th>Ba$<em>{0.8}$Rb$</em>{0.1}$Sn$_{0.09}$Fe$<em>2$As$</em>{1.96}$</th>
<th>Ba(Fe$<em>{0.943}$Rh$</em>{0.057}$)$_2$As$_2$ [57]</th>
<th>BaFe$<em>{1.9}$Rb$</em>{0.1}$As$_2$ [58]</th>
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<td>FeSe family</td>
<td>AFeAsF family (A=Ca, Sr)</td>
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<td>Ba(Fe$<em>{0.95}$Pd$</em>{0.043}$)$_2$As$_2$ [57]</td>
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<td>LiFeAs [23]</td>
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<td>3.77</td>
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<td>FeSe$_{0.88}$ [24]</td>
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<tr>
<td>Mn$<em>{0.2}$Fe$</em>{0.8}$Se$_{0.85}$ [61]</td>
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<td>FeTe$_{0.92}$ [62]</td>
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<td>CaFe$<em>{0.9}$Co$</em>{0.1}$AsF [64]</td>
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<tr>
<td>Sr$<em>{0.56}$Nd$</em>{0.44}$FeAsF [65]</td>
<td>52</td>
<td></td>
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<tr>
<td>Sr$<em>{0.5}$Sm$</em>{0.5}$FeAsF [25]</td>
<td>56</td>
<td>3.918</td>
<td>8.956</td>
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<tr>
<td>Sr$<em>{0.8}$La$</em>{0.2}$FeAsF [66]</td>
<td>36</td>
<td>3.997</td>
<td>8.961</td>
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<tr>
<td>SrFe$<em>{0.875}$Co$</em>{0.125}$AsF [67]</td>
<td>4</td>
<td>4.0018</td>
<td>8.943</td>
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<tr>
<td>Other compounds</td>
<td>29.2</td>
<td>3.9003</td>
<td>15.8376</td>
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<tr>
<td>Sr$<em>2$Cr$</em>{0.8}$Ti$_{1.2}$O$_6$Fe$_2$As$_2$ [68]</td>
<td></td>
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<tr>
<td>Fe$_2$As$<em>2$Sr$<em>4$Mg$</em>{1+y}$Ti$</em>{1.6}$O$_6$ [69]</td>
<td>39</td>
<td>3.935</td>
<td>15.952</td>
<td></td>
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<tr>
<td>Sr$<em>2$VO$</em>{2.9}$FeAs [70]</td>
<td>40</td>
<td>3.928</td>
<td>15.669</td>
<td></td>
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<tr>
<td>Sr$_4$Sc$_2$O$_6$Fe$_2$P$_2$ [71]</td>
<td>17</td>
<td>4.016</td>
<td>15.543</td>
<td></td>
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<tr>
<td>Sr$_2$VO$_3$FeAs [72]</td>
<td>37.2</td>
<td>3.9296</td>
<td>15.6732</td>
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</table>

The electronic structures and physical properties of the pnictide compound families \( \text{REFeAsO} \) \((\text{RE} = \text{La, Ce, Pr, Nd, Sm})\), \( \text{AFe$_2$As$_2} \) \((\text{A} = \text{Ca, Sr, Ba, Eu})\), \text{LiFeAs}, \text{and FeSe} are quite similar. However, the 1111-FeAs family shows the highest transition temperature and the most anisotropic upper critical field. Also, its fan-shaped resistivity transition is similar to those in cuprates, while the 122 family has lower transition temperature compared to 1111-FeAs compounds and it is much less anisotropic with a sharper resistive transition, as in low temperature superconductors [5].

### 2.2.2 Synthesis methods

#### 2.2.2.1 Polycrystalline

Compare to cuprates, synthesising iron based superconductors is very complicated due to the toxicity and low vaporization temperature of arsenic, as well as the high reactivity of rare-earth, alkali metal, and alkaline earth elements, so the synthesis needs strict handling and care.

For the starting material, rare-earth elements, alkali elements, arsenic, iron, and \( \text{Fe}_2\text{O}_3 \) can be directly used. \( \text{REF}_3 \) and \( \text{FeF}_2 \) can be used for fluorine doping. A safe, simple, and easy one-step sintering method has been realised for iron-based compounds, in which
all of the starting materials are mixed together and sintered in a solid-state reaction method in an inert atmosphere or in vacuum [73]. However, the sample quality is poor. A two-step process is preferred, which can involve either solid state reaction or high-pressure sintering. In these methods, the metal pieces (La, Ba, etc) and the arsenic powder are first reacted together at about 600-1000°C. This process prevents the loss of As in the final step and also makes a fine powder of all the starting materials. Then, the stoichiometric fine powders are mixed, ground, and pressed into pellets. For solid state reaction, the pellets are sealed in an evacuated quartz tube and sintered at high temperatures to produce high quality samples.

For the high pressure method, the prepared pellets are sealed in boron nitride crucibles, and then placed inside a graphite heating tube and mounted into a six-anvil high-pressure sintering machine. Then, the samples are sintered under the pressure of 6 GPa at a temperature of 1300°C for 2 hours. The high pressure sintering technique was found to be more suitable for the synthesis of the fluorine containing superconductors [10]. This technique can help to make a very dense and high quality sample. Also the pressure-sealing of the boron nitride cell prevents fluorine loss. However, producing a single-phase sample is difficult due to the short synthesis time and unstable conditions [10].

2.2.2.2 Single crystals

For single crystal growth, two methods have been reported: the flux method and high-pressure sintering. Jaroszynski et al. used the flux method to grow NdFeAsO$_{0.7}$F$_{0.3}$ single crystals. In this method, neodymium and arsenic were first mixed, ground, and pressed into a pellet. The
resulting pellet was sealed in an evacuated quartz tube and sintered at 800°C for 10 h. The pellet was ground and mixed with NdF$_3$, Fe$_2$O$_3$, and Fe. The resultant powder was then pressed into a pellet, and placed in an evacuated quartz tube with NaCl as flux and reacted at 1050°C for 10 days. Then, it was cooled down to 800°C at a very slow rate of less than 10°C/h. This was followed by quick furnace cooling to room temperature [74]. Instead of NaCl as flux, tin and FeAs can be used as the flux. Tin flux can introduce impurities into the compound, but FeAs flux can promote more pure single crystals because it contains only elements that are in the final crystal.

Figure 2.7 is a schematic diagram of the equipment used to grow single crystals of BaFe$_{1.87}$Co$_{0.13}$As$_2$ [75].

![Schematic diagram of the equipment used to grow single crystals of BaFe$_{1.87}$Co$_{0.13}$As$_2$](image)

For high pressure sintering, a mixture of REAs, FeAs, Fe$_2$O$_3$, Fe, and REF$_3$ powders was used as the starting material and NaCl / KCl as flux. The starting material was mixed and pressed into a pellet. The resulting pellet and flux were placed in a boron nitride crucible inside a propylite cube with a graphite heater. Six tungsten carbide anvils generated pressure on the whole assembly. Pressure of 3 GPa was applied at
room temperature. Then, the temperature was increased within 1 h to the maximum value of 1350-1450°C, kept at that temperature for 4-48 h, and decrease to room temperature in 1-24 h [18].

Figure 2-8: (a) Single crystals of BaFe$_2$As$_2$ obtained at the bottom of ZrO$_2$ crucible. (b) Typical separated single crystals showing a partly opened top layer (001) and well developed crystallographic faces [76].

A batch of typical BaFe$_2$As$_2$ single crystals produced by this method is shown in Fig. 2-8(a). Fig. 2-8(b) shows the as-grown crystals with a surface layer seen partly cleaved off and separated from the c plane due to the layered structure.

2.2.2.3 **LaFeAsO$_{0.9}$F$_{0.1}$ wire**

It was reported that the LaFeAsO$_{0.9}$F$_{0.1}$ wire was prepared by the powder-in-tube method using La, As, LaF$_3$, Fe, and Fe$_2$O$_3$ as starting materials[77]. The raw materials were ground and packed into an iron tube. An inner titanium sheath was first placed in the tube to prevent a reaction between the raw material and the iron tube. Then, the tube
was rotary swaged and drawn to wires 2 mm in diameter. The wire was then cut into pieces 4 to 6 cm in length, sealed in an iron tube, and sintered at 1150°C for 40 h.

Figure 2-9: (a) LaFeAsO$_{0.8}$F$_{0.1}$ wire; SEM images for (b) transverse and (c) longitudinal cross-sections after sintering [77].

Fabrication of Fe(Se,Te) wire [78] and Ta-sheathed SmFeAsO$_{0.8}$F$_{0.2}$ wire with $T_c = 52.5$ K [79] have also been reported using the powder-in-tube method.

### 2.2.3 $\textit{REFeAsO (RE = La, Ce, Pr, Nd, Sm, ...)}$ system

#### 2.2.3.1 Superconductivity and electrical properties

The parent $\textit{REFeAsO}$ compound is metallic and shows anomalies around 140-150 K for LaFeAsO in both resistivity and dc magnetic susceptibility [4]. These anomalies are related to spin density wave (SDW) instability [80] and the structural phase transition from tetragonal with space group $P4/nmm$ to orthorhombic with space group $P112/n$ at
low temperature [81]. However, superconductivity can occur when the SDW is suppressed, either through chemical doping (e.g. fluorine doping) or pressure. Also, oxygen vacancies can create more electron carriers and favour lattice shrinkage, allowing realization of superconductivity in this class of materials [6]. However, comparing the oxygen deficient superconductors LaFeAsO$_{1-x}$ with the F-doped samples shows that the F-doped samples have better superconducting properties, because F-doping can help form a more stable structural phase than oxygen vacancies in this La-based system due to the large atomic radius of La [82]. There have also been reports of Co-doping at Fe sites, which results in superconductivity at a lower transition temperature [36] [36,83].

![Graph showing temperature dependence of resistivity for nominal REFeAsO$_{0.85}$ samples synthesized by the HP method.](image)

Figure 2.10: The temperature dependence of resistivity for nominal REFeAsO$_{0.85}$ samples synthesized by the HP method [84].

Figure 2.10 shows the temperature dependences of resistivity for the nominal REFeAsO$_{0.85}$ samples synthesized by the hot pressing (HP) method. For most of these compounds, $T_c$ varies in the range of 40-50 K, while LaFeAsO stands out with its
significantly lower transition temperature of 26 K. However, in reference [7], a synthesis of this system under high pressure was reported, making samples with $T_c$ of 41 K.

Figure 2.11: Temperature dependence on the value of the lattice parameter $a$ [84].

Figure 2.11 shows changes in the critical temperature for the different Re in $RE$FeAsO. The critical temperature increases by the substitution of smaller $RE$ element ions in $RE$FeAsO, due to further shrinkage of the crystalline lattice by chemical pressure [6].

Figure 2-12: Temperature dependence of resistivity for a series of CeFeAsO$_{1-x}$F$_x$ samples [9].

26
Figure 2.12 shows the temperature dependence of the resistivity for CeFeAsO$_{1-x}$F$_x$ compounds. The pure CeFeAsO shows an anomaly at about 145 K which was ascribed to the spin density wave instability. Fluorine doping suppresses the anomaly, leading to superconductivity. The highest $T_c = 41$ K was obtained at $x = 0.16$ [9]. The interplay between the superconducting phase and the SDW instability suggests that the magnetic fluctuation play a key role in the superconducting pairing mechanism [9].

2.2.3.2 Magnetic structure and phase diagram

It was confirmed by neutron scattering experiments that as the temperature decreases, undoped LaFeAsO undergoes a phase transition from tetragonal ($P4/nmm$) to orthorhombic ($Cnma$) phase at ~160 K, as well as an antiferromagnetic transition at ~140 K [85]. Fig. 2.13 shows the phase diagram of the LaFeAsO$_{1-x}$F$_x$ system [86]. It is clear that the temperatures of structural and magnetic transitions are separated, while the superconductivity region does not overlap with the antiferromagnetic region.

![Phase diagram of LaFeAsO$_{1-x}$F$_x$]

*Figure 2-13: electronic phase diagram of LaFeAsO$_{1-x}$F$_x$. $T_s$ is the temperature of the structural transition [86].*
Figure 2.14 shows the structural and magnetic phase diagram of CeFeAsO$_{1-x}$F$_x$. With increasing fluorine doping, the structural phase transition decreases steadily, while the antiferromagnetic order is suppressed before superconductivity occurs [87].

2.2.3.3 Upper critical field

In term of potential applications, the upper critical field is one of the most important topics of research on the new superconductors. The upper critical field is an intrinsic property, which has been reported to be over 65 T in LaFeAsO$_{0.9}$F$_{0.1}$ [88], 150 T in SmFeAsO$_{0.85}$F$_{0.15}$ [82], and 230 T in NdFeAsO$_{0.82}$F$_{0.18}$ [89] bulk samples.
Figure 2.15: (a) Field-reduced temperature dependence of different samples. The solid lines are only guides to the eyes. (b) Theoretical value of $H_{c2}$ based on GL theory.

Figure 2.15 shows the upper critical field as a function of reduced temperature for MgB$_2$ ($T_c = 39$ K), LaFeAsO$_{0.89}$F$_{0.11}$ ($T_c = 27$ K) [88,90], SmFeAsO$_{0.89}$F$_{0.11}$ ($T_c = 45$ K) [91], and NdFeAsO$_{0.82}$F$_{0.18}$ ($T_c = 51$ K) [89]. The upper critical field values of $H_{c2}(0)$ can go over 80–230 T for NdFeAsO$_{0.82}$F$_{0.18}$, similar to high temperature cuprate superconductors and surpassing the values of all low temperature superconductors and MgB$_2$ [89]. This
value has the potential to be increased even more by proper chemical doping and through physical approaches, due to the two gap superconductivity in the new iron based superconductor class.

2.2.3.4 Critical current density

In the term of applications, the critical current density, $J_c$, is one of the most important topics of research on the new iron-based superconductors. The $J_c$ is sample dependent and controlled by flux pinning behaviour[89]. Critical current density for single crystals must be estimated by magnetization measurements and use of the Bean model along the $ab$ and $c$ directions. This is always possible for field parallel to the $c$-axis but much less achievable for field parallel to the $ab$-plane, due to the small size of crystals, large anisotropy, and the difficulty in aligning crystals accurately with the field axis[5]. The $J_c$ in a single crystal SmFeAsO$_{0.8}$F$_{0.2}$ sample has been reported to be $10^{10}$ A/m$^2$ at 5 K and nearly field independent in fields up to 7 T (Figure 2.16) [18]. It can be seen that the critical current density slightly increases for higher magnetic field, possibly due to the increase in the effectiveness of pinning centres with increasing magnetic field [92].

In many cuprates [93] and in some low temperature superconductors such as MgB$_2$ [94] a magnetization peak effect has been observed, and several models have been proposed to explain the increased pinning as the magnetic field increases to the peak field. The first observation of a peak effect in an iron based family was reported by Senatore et al. in SmFeAsO$_{0.85}$F$_{0.15}$ compound [91].
2.2.3.5 Flux pinning behaviour and thermally activated energy

Figure 2.17 shows the magnetic field dependence of the activation energy, $U_o$, of NdFeAsO$_{0.82}$F$_{0.18}$. The value of the thermally activated energy drops very weakly with applied magnetic field for $B < 0.4$ T and then decreases very slowly for $B > 0.4$ T. We can see that the values of $U_o$ are 2-3 times greater than that for Bi$_{2212}$ in both low and high magnetic field [95]. However, the $U_o$ for NdFeAsO$_{0.82}$F$_{0.18}$ is lower than that of MgB$_2$ thin film [96] for $H < 8$ T, but higher than MgB2 for $H > 8$ T. This indicates that the NdFeAsO$_{0.82}$F$_{0.18}$ has strong pinning characteristics in high magnetic field [97].
Figure 2-17: Magnetic field dependence of the activation energy of NdFeAsO$_{0.82}$F$_{0.18}$, MgB$_2$, and Bi-2212 [97].

2.2.3.6 Pressure effects

Figure 2-18: (a) Temperature dependence of resistance at different pressures for SmFeAsO$_{0.85}$; (b) transition temperature as a function of pressure for the same sample [98].
Figure 2.18 presents the electrical resistance of a SmFeAsO$_{0.85}$ sample as a function of pressure. The $T_c$ of the sample is 55 K at ambient pressure. The transition temperature shifts to lower temperature with increasing pressure[98]. The same behaviour was observed for NdFeAsO$_{0.85}$ [98] and CeFeAsO$_{0.88}$F$_{0.12}$ [99]. On the other hand, a transition temperature of 43 K was obtained under pressure of 4GPa for LaFeAsO$_{1-x}$F$_x$ [7]. ($T_c = 28$ at ambient pressure.)

2.2.4 $A$Fe$_2$As$_2$ ($A =$ Ba, Sr, …) system

2.2.4.1 Superconductivity and electrical properties

A simpler family of iron based superconductors was discovered by Rotter et. al. by synthesis of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ compound with critical temperature of 38 K for $x = 0.4$. The 122 iron-arsenide family has the general formula of $A$Fe$_2$As$_2$ where $A =$ Ba, Sr, Ca, and Eu. It has been reported that the superconductivity is achieved through hole doping with alkali metals such as Na [52], K [14], Rb [100] or Cs [12] or by electron doping from replacing a small fraction of the Fe with a larger transition metal element, such as Co [15], Ni [101], Rh [57], Ru[102], Rb [100], Ir [103] and Pd [57]. Figure 2.19 shows the temperature dependence of the resistance for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ compound. It can be seen that the parent compound of this family, BaFe$_2$As$_2$, shows typical metallic behaviour with an anomaly in the resistivity at about 140 K, which is associated with SDW and a structural phase transition [104]. Replacing Ba$^{+2}$ with K$^+$ ions leads to hole doping,
which suppresses the SDW transition, resulting in superconductivity [104]. Similar behaviour was observed in Sr$_{1-x}$K$_x$Fe$_2$As$_2$ with $T_c = 38$ K [55].

Figure 2-19: DC resistance as a function of temperature for BaFe$_2$As$_2$ [104].

2.2.4.2 Magnetic structure and phase diagram

Figure 2-20: Composition-temperature phase diagram of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [105] $T_s$ is the temperature of the antiferromagnetic ordering and structural transition, and $T_c$ is the superconducting transition temperature.
The superconducting transition temperature and the temperature of antiferromagnetic order for Ba_{1-x}K_xFe_2As_2 are illustrated in Fig. 2.20. It can be seen that the SDW order from the Ba end and the superconductivity from the K end overlap in the intermediate composition range. The antiferromagnetic ordering decreases with increasing potassium doping, and superconductivity occurs at 14 K for \( x = 0.2 \). The \( T_c \) increased with further potassium doping, reaching a maximum of 37.5 K at \( x = 0.5 \). After that, with increasing potassium, the \( T_c \) decreased. At \( x = 1 \), \( T_c \) is 3.8 K for the KFe_2As_2 sample [105].

### 2.2.4.3 Upper critical field and anisotropy value

#### Table 2-3: Superconducting parameters of 122 iron-based single crystals.

<table>
<thead>
<tr>
<th>sample</th>
<th>( T_c ) (K)</th>
<th>( H_{c2}^{ab} ) (T)</th>
<th>( H_{c2}^{c} ) (T)</th>
<th>( \delta_H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba_{0.6}K_{0.4}Fe_2As_2 [106]</td>
<td>36.5</td>
<td>235</td>
<td>135</td>
<td>2-3</td>
</tr>
<tr>
<td>Ba_{0.55}K_{0.44}Fe_2As_2 [107]</td>
<td>30</td>
<td>( \geq 75 )</td>
<td>( \geq 75 )</td>
<td>1.2-3.5</td>
</tr>
<tr>
<td>Ba_{0.84}Rb_{0.1}Sn_{0.09}Fe_2As_2 [100]</td>
<td>23</td>
<td>120</td>
<td>70</td>
<td>2.4-3</td>
</tr>
<tr>
<td>BaFe_2As_2 [108]</td>
<td>22.5</td>
<td>~88</td>
<td>~31</td>
<td>~2.8</td>
</tr>
<tr>
<td>Ba(Fe_{0.9}Co_{0.1})_2As_2 [109]</td>
<td>22</td>
<td>~70</td>
<td>~50</td>
<td>1.5-2</td>
</tr>
<tr>
<td>Ba(Fe_{0.92}Co_{0.08})_2As_2 [110]</td>
<td>23</td>
<td>55</td>
<td>50</td>
<td>1.1-3.4</td>
</tr>
<tr>
<td>SrFe_2As_2 [111]</td>
<td>21</td>
<td>~70</td>
<td>~24</td>
<td>~2.6</td>
</tr>
<tr>
<td>Sr_{0.6}K_{0.4}Fe_2As_2 [112]</td>
<td>35.5</td>
<td>185.4</td>
<td>93.1</td>
<td>2</td>
</tr>
<tr>
<td>KFe_2As_2 [113]</td>
<td>2.79</td>
<td>4.47</td>
<td>1.25</td>
<td>3.5-6.8</td>
</tr>
<tr>
<td>BaFe_2(As_{0.68}O_{0.32})_2 [114]</td>
<td>30.9</td>
<td>77.4(3.66)</td>
<td>36.4(1.72)</td>
<td>2.13</td>
</tr>
</tbody>
</table>
Table 2.3 summarizes the upper critical field and anisotropy values of different 122 iron based superconducting single crystals. Compare to the electron-doped system, the hole-doped system has higher critical field values of over 100 T. The anisotropy ratios of 122 iron based superconductors are lower than 4, which is lower than what has been reported for the 1111 iron based family [115].

2.2.4.4 Critical current density

![Figure 2-21: Magnetic field dependence of the critical current density $J$ of Ba (Fe$_{1-x}$Co$_x$)$_2$As$_2$. Triangles indicates broad maximum positions [109].](image)

Several single crystal results were reported in the 122-FeAs system, because large crystal can be easily grown. Yang et al. reported a very big fishtail peak effect and large $J_c$ of $5 \times 10^6$ A/cm$^2$ at 4.2 K in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ single crystal [116]. Prozorov et al. deduced $J_c$ of $2.6 \times 10^5$ A/cm$^2$ at 5 K for Ba(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$ single crystal, as well as the presence of a fishtail peak [117]. The critical current density estimated from the
width of the hysteresis loops using the Bean model for a Co-doped BaFe$_2$As$_2$ sample, is shown in Fig. 2.21. Similar to the 1111-FeAs family, $J_c$ decreased rapidly at low fields and then became relatively field independent at high magnetic field for $T < 10$ K. The self-field $J_c$ is $4 \times 10^5$ A/cm$^2$ at 4.2 K, which is quite high for single crystal [109].

### 2.2.4.5 Pressure effects

The superconducting transition temperature of Ba$_{0.55}$K$_{0.45}$Fe$_2$As$_2$ as a function of pressure is shown in Figure 2.22. The superconducting transition temperature decreases with increasing pressure [118].

![Figure 2-22](image)

**Figure 2-22**: Reduced resistivity as a function of temperature for Ba$_{0.55}$K$_{0.45}$Fe$_2$As$_2$ at different pressures. The inset shows the superconducting transition temperature as a function of pressure [118].

Also, pressure induced superconductivity occurs in single crystal BaFe$_2$As$_2$ around 1.5 GPa [119]. The $T_c$ is increased up to a pressure of about ~1.5 GPa and then decreases
monotonically beyond this pressure [119]. The spin density wave transition temperature decreases rapidly with increasing pressure.

2.2.5 LiFeAs family

The search for new iron based superconductors with simpler structure has resulted in the discovery of superconductivity at 18 K in LiFeAs. LiFeAs crystallizes into a Cu$_2$Sb type tetragonal structure with $a = 3.77$ Å and $c = 6.36$ Å. Compared with the 1111-FeAs and 122-FeAs families, the $c$-axis parameter is smaller for LiFeAs [23].

![Figure 2-23: DC susceptibility of LiFeAs in both ZFC and FC [120].](image)

Tapp et al. reported superconductivity in LiFeAs compound with the elemental ratio of 1:1:1. This result is in contrast to the report from Wang et.al., who observed no superconductivity in stoichiometric LiFeAs compound [23]. Figure 2.23 shows the dc susceptibility of LiFeAS with zero field cooling (ZFC) and field cooling (FC) with $H = 10$ Oe [120]. It has been reported that NaFeAs with the 111 structure shows superconductivity at 9 K [121].
An upper critical field of over 80 T at zero temperature has been reported in this compound [120].

2.2.5.1 Pressure effects

Figure 2.24: Normalized inductance of LiFeAs at different pressures [122].

Figure 2.24 shows the temperature dependence of the inductance at different pressures for LiFeAs compound. With increasing pressure, the inductance curves shift to be nearly parallel at lower temperature. The $T_c$ of LiFeAs decreases linearly with increasing pressure at the rate of 1.56 K/GPa, as shown in the inset of Figure 2.24.

LiFeAs compound reveals superconductivity even in ambient pressure, because lithium is the smallest ion in the alkali metal series, which makes for a significant compression of the LiFeAs structure as compared with the 1111-FeAs and 122-FeAs families.

Also, no spin density waves have been reported in the LiFeAs family due to the compressed structure of this compound compared to other families [122].
2.2.6 FeSe family

2.2.6.1 Superconductivity and electrical properties

Hsu et al. reported superconductivity at 8 K in tetragonal FeSe [24], which was followed by pressure studies that revealed a $T_c$ of 27 K for a pressure of 15 kbar [123]. The critical temperature at ambient pressure temperature is increased up to 15 K with S and Te substitution [59], as shown in Fig. 2.25. Compared to the 1111-FeAs family, FeSe is less toxic and has a simpler structure, but it is difficult to make a single phase FeSe sample. Also, the crystal structure is changed easily from superconducting $\alpha$-FeSe phase to non-superconducting hexagonal phase.

![Graph](image)

Figure 2-25: Temperature dependence of normalized resistance for FeSe$_{1-x}$Te$_x$ [60]. The inset shows an enlargement of the low temperature region.

2.2.6.2 Upper critical field and anisotropy

Figure 2.26 shows the upper critical field versus temperature phase diagram for the points where resistivity drops to 90%, 50%, and 10% of $\rho_n$ for FeTe$_{0.6}$Se$_{0.4}$ single
crystal, where $\rho_n$ is the normal state resistivity. The values of upper critical field are 184 T, 88 T, and 69 T for 90%, 50%, and 10% of resistivity in the normal state at 16 K, respectively [124], as shown in the inset of Figure 2-26. Note that the lower critical field shows a positive curvature in both the $ab$ and $c$ directions. The anisotropy parameter was estimated to be 4 at 1.8 K.

Figure 2-26: Upper critical field versus temperature of FeTe$_{0.6}$Se$_{0.4}$ single crystal [124]. The inset shows the lower critical field measured for $H_{c1c}$ and $H_{c1ab}$.

2.2.6.3 Critical current density

Figure 2-27: Magnetic field dependence of critical current density for FeTe$_{0.61}$Se$_{0.39}$ single crystal [125].
Critical current density versus magnetic field for FeTe$_{0.61}$Se$_{0.39}$ single crystal is shown in Figure 2.27. The maximum value of the critical current density is estimated to be $1 \times 10^5$ A/cm$^2$ at 5 K in zero magnetic fields. Although this value of critical current density is much less than for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystal [126], it is still in the range for practical application. The fishtail effect is clearly seen for this sample [125].

2.2.6.4 **Thermally activated energy**

![Image: Arrhenius plot of resistivity for FeTe$_{0.6}$S$_{0.4}$ single crystal for magnetic field up to 14 T. The inset shows the magnetic field dependence of $U_o$ [124].]

The activation energy, $U_o$, for FeTe$_{0.6}$S$_{0.4}$ is estimated from the slope of the Arrhenius curve in the linear part using the formula $\rho(T, H) = \rho_o \exp(U_o/K_B T)$. The magnetization field dependence of the activation energy is shown in the inset of Figure 2.28. The activation energy changes linearly from 710 K to 1490 K for magnetic field of 14 T and 0 T, respectively [124].
2.2.6.5 **Pressure effects**

An enormous enhancement of the superconducting transition temperature was observed in the tetragonal FeSe superconductor under high pressure. An onset transition temperature of 27 K was obtained at 1.48 GPa and the upper critical field was estimated to be 72 T at this pressure [123].

![Figure 2.29: Pressure dependence of $T_c^{onset}$, $T_c^{mid}$, and $T_c^{zero}$ for FeSe](image)

Figure 2.29 shows the transition temperature as a function of pressure for an FeSe sample. $T_c^{onset}$ and $T_c^{zero}$ increase significantly with increasing pressure and reach the maximum value of 27 K and 13.5 K, respectively [123].

The transition temperature as function of pressure for FeSe$_{0.25}$Te$_{0.75}$ and FeSe$_{0.8}$S$_{0.2}$ samples is shown in Figure 2.30. The transition temperature of FeSe$_{0.25}$Te$_{0.75}$ monotonically increases with increasing pressure; on the other hand, FeSe$_{0.8}$S$_{0.2}$ shows dome-shaped behaviour. This results show that the physical pressure effect and the chemical pressure effect are not equivalent in the FeSe system [127].
2.2.7 \textit{AeFeAsF (Ae = Ca, Sr, and Eu) family}

2.2.7.1 Superconductivity and electrical properties

Figure 2-30: Transition temperature as a function of pressure for FeSe [127].

Figure 2-31: Temperature dependence of resistivity for CaFe$_{1-x}$Co$_x$AsF compound [64].
Figure 2.31 shows the temperature dependence of the resistivity for CaF_{1-x}Co_xeAsF compound. The undoped CaFeAsF shows an anomaly in the resistivity at about 120 K. Similar anomalies were observed for the 1111-FeAs and 122-FeAs families, which is related to a structural and/or magnetic transition. With 10% Co doping, this anomaly is suppressed, and superconductivity appears at 22 K for \( x = 0.1 \) [64].

Also, superconductivity was observed with rare earth element doping in Ca\(_{0.4}\)Nd\(_{0.6}\)FeAsF and Ca\(_{0.4}\)Pr\(_{0.6}\)FeAsF with \( T_c \) of 57.4 K and 52.8 K [128], respectively.

2.2.7.2 Magnetic structure and phase diagram

Figure 2.32 summarizes the superconducting transition temperature (\( T_c \)), low temperature magnetic ordering (\( T_N \)), and SDW transition temperature (\( T_{SDW} \)) as functions of Nd doping (\( x \)) for Sr\(_{1-x}\)Nd\(_x\)FeAsF. At \( x = 0.36 \), the SDW anomaly is completely suppressed but no evidence of superconductivity was observed. Superconductivity only occur above \( x = 0.4 \) Nd-doping, and the highest \( T_c \) of 52 K was obtained at \( x \geq 0.46 \) [65].

![Figure 2-32: Phase diagram giving a summary of the SDW transition temperature(\( \bullet \)), low temperature magnetic ordering (\( T_N \)) temperature (\( \bullet \)), and superconducting transition temperature(\( \bigtriangleup \)) as functions of Nd doping for Sr\(_{1-x}\)Nd\(_x\)FeAsF compound [65].](image-url)
2.2.7.3 **Critical current density**

The critical current density as function of applied magnetic field at 6.5 K for 
Nd$_{0.57}$Sr$_{0.43}$FeAsF is shown in Figure 2.33. The intragrain J$_c$ in this compound is about $10^5$A/cm$^2$, which is comparable with the other iron based superconductors [65].

![Critical current density versus magnetic field for Nd$_{0.57}$Sr$_{0.43}$FeAsF compound](image)

Figure 2-33: Critical current density versus magnetic field for Nd$_{0.57}$Sr$_{0.43}$FeAsF compound [65].

The inset shows a magnetic hysteresis loop.

**2.2.8 Sr$_4$Sc$_2$Fe$_2$As$_2$O$_6$ family**

2.2.8.1 **Superconductivity and electrical properties**

Recently, a new series of iron based superconductors with a thick perovskite layer were discovered [71,72].
The electrical resistance of Sr$_2$VO$_{3-\delta}$FeAs as a function of temperature is shown in Figure 2.34. The transition temperature decreases with the increasing oxygen deficiency. The highest transition temperature of 40 K is obtained near the stoichiometric formula Sr$_2$VO$_{3-\delta}$FeAs, as shown in the inset to Figure 2.34. However, it is possible to say that superconductivity in this compound is not induced by oxygen deficiency [70]. Ogino et al. have reported superconductivity at 17 K in Sr$_2$ScFePO$_3$, which is the highest $T_c$ in the FeP system [71].

2.2.8.2 Upper critical field

A very large slope of $(dH_c^2/dT)_{T=T_c} = -11.3$ T/K is obtained for Sr$_4$V$_2$O$_6$Fe$_2$As$_2$ compound. This value is larger than that achieved for other iron based superconductors [129]. The upper critical field value is 302 T, which is determined by using the
Werthamer-Helfand-Hohenberg formula [72]. An upper critical field of 337 T is obtained for Sr$_2$VO$_{2.9}$FeAs compound [70].

![Graph showing upper critical field and irreversibility field as a function of temperature for Sr$_4$V$_2$O$_6$Fe$_2$As$_2$](image)

**Figure 2-35**: Upper critical field and irreversibility field ($H_{irr}$) as a function of temperature for Sr$_4$V$_2$O$_6$Fe$_2$As$_2$ [72].

### 2.2.8.3 Pressure effects

![Graph showing pressure dependence of superconducting critical temperature](image)

**Figure 2-36**: Pressure dependence of superconducting critical temperature of Sr$_2$VFeAsO$_3$ [130].
Figure 2.36 shows the variation in the superconducting transition temperature as a function of pressure for Sr$_2$VFeAsO$_3$ compound [130]. The $T_c$ of Sr$_2$VFeAsO$_3$ increases considerably with increasing pressure.

### 2.2.9 Comparing resistivity and upper critical field in the 1111-FeAs, 122-FeAs, and FeSe families

Figure 2.37 shows the temperature dependences of the magnetoresistance of three single crystal samples of Nd-1111 [131], Ba-122 [109], and Fe-11 in magnetic field applied parallel to the $c$-axis. For Nd-1111, the transition becomes wider with increasing magnetic field, but for Ba-122, the broadening of the transition is field independent. For Fe-11 the situation is intermediate, although this compound has lower $T_c$ compare with Nd-1111 and Ba-122.
Figure 2-37: the temperature dependence of magnetoresistance of three single crystal samples of Nd-1111 (top) [131]; Fe-11 (middle); and Ba-122 (bottom) [109] in magnetic field applied parallel to the c-axis.
Figure 2.38 shows $H_{c2}$ in the ab plane and c directions determined by the 90% criterion. The three materials are different not only in transition temperature and values of $H_{c2}$, but also in their temperature dependence of $H_{c2}$. Nd-1111 single crystal has linear behaviour in both directions, while Ba-122 and Fe-11 show an almost linear dependence in the c direction, but exhibit a downward curvature in the ab direction. The $H_{c2}$ anisotropy, in particular, is changed by the different temperature dependences in the two directions. For Nd-1111 compound, the anisotropy is almost constant and equal to 5, while in Ba-122 and Fe-11, it decreases with decreasing temperature. For example, the anisotropy close to $T_c$ is about 2 for Fe-11, but because of the downward curvature in the ab direction, the anisotropy becomes 1 at the lowest temperature [5].
Chapter 3

3 Experimental techniques

3.1 Sample preparation

Polycrystalline samples with nominal composition of LaFeAsO$_{1-x}$F$_x$ ($x = 0.10, 0.15, 0.20$) were synthesized by a conventional two-step solid state reaction at ambient pressure. In the first step, La (99.9% purity, 0.5–1 mm size, Leico), Fe (99.98% purity, 0.2–0.5 mm, Aldrich), and As (99.999% purity, Lump, Alfa-Aesar) were mixed in a ratio of 1:3:3 to prepare LaAs, Fe$_2$As, and FeAs by using an agate mortar and pestle. The powder was pressed into a pellet and sealed in an evacuated quartz tube in Argon atmosphere. The sealed silica tube was heated at 900°C for 12 hours. In the second step, the mixture of LaAs, Fe$_2$As and FeAs was ground in a mortar and mixed with La$_2$O$_3$ (99.99% purity, 0.1–0.2 mm size, Aldrich), La, and LaF$_3$ (99.9% purity, 0.1–0.2 mm size, Aldrich) in the stoichiometric ratio. The final stoichiometry is $(1+x)$ La + $(1-x)$ La$_2$O$_3$ + $x$LaF$_3$ + 3FeAs, $x=0.05, 0.15, 0.2$, for different fluorine doped samples. The resulting powder was pressed into a pellet and sealed in an evacuated silica tube. Then, it was sintered at 1150°C for 60 h, followed by furnace cooling to room temperature. All the grinding was carried out in a glove box containing P$_2$O$_5$ and NaOH under argon atmosphere[132]. All the samples were made and provided for the thesis work by Drs. C. Shekhar and O.N. Srivastava at the Centre for Advanced Studies of the Physics of Materials, Department of Physics in Banaras Hindu University in India.
3.2 Sample characterization

3.2.1 X-ray diffraction

The x-ray diffraction technique was used to determine the microstructure and phase formation of the sample. The XRD patterns were used for the calculation of lattice parameters and strain in the lattice.

The X-ray measurement was performed using a GBC instrument with Cu-Kα radiation in the 2θ range of 20° to 80°, with a step interval of 0.02°. All X-ray diffraction patterns were obtained on powder samples fixed on a glass slide with a drop of ethanol.

Peaks in the XRD patterns were indexed using Bragg’s law:

\[ 2d \sin \theta = n \lambda \]  

where \( n \) is an integer determined by the order given, \( \lambda \) is the wavelength of the X-rays, \( d \) is the space between the plans in the atomic lattice and \( \theta \) is the angle between the incident ray and the scattering planes.

Figure 3-1 Schematic diagram showing X-ray diffraction.
3.2.2 Rietveld refinement

The Rietveld refinement method is a powerful method for extracting the details of the crystal structure. Here, we used the Rietica software package to do the refinement. The x-ray diffraction pattern for each compound shows special peaks with particular heights, widths, and positions for different reflections. The height, width and position for each of these reflections can be used to calculate many details of the materials structure such as lattice parameters and strain in the lattice. The Rietveld refinement matches the theoretical data with the observed data by using a least squares approach.

3.2.3 Scanning electron microscopy

A scanning electron microscope (SEM) is a microscope that uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. These signals reveal information about the sample, such as texture, chemical composition, crystalline structure and orientation of grains in the sample. The combination of higher magnification, larger depth of field, and greater resolution makes the SEM one of the most heavily used instruments in many research areas today.

In this work, the microstructures of the samples and their morphology were studied using scanning electron microscopy and field emission scanning electron microscopy (FE-SEM, JEOL7500), operated at 50 kV. The best way to observe the morphology and microstructure of an iron based bulk sample is to examine the freshly broken surface. Figure 3.2 shows a schematic diagram of SEM.
3.3 Transport and magnetic properties measurements

The transport and magnetic properties were measured over a wide range of temperature and magnetic field up to 14 T using a Quantum Design Physical Properties Measurement System (PPMS).

The four probe technique was used for resistivity measurements of the samples. This method consists of attaching current and voltage contacts to the sample by silver paste. The resistivity versus temperature curves were measured in magnetic fields up to 14 T. For a long sample with rectangular cross-section with dimensions $l \times w$, critical current density ($J_c$) can be calculated using the extended Bean model:

$$J_c = 20 \times \frac{\Delta m}{V} \left( l \left(1 - l/3w \right) \right) \quad l<w$$

(3-2)
where $V$ is the sample volume and, $\Delta m = m^+ - m^-$, where $m^+$ and $m^-$ are values of $m$ as an applied field decreasing and increasing, respectively.

Upper critical field in the $ab$ plane and $c$ directions is defined from the resistivity versus temperature curves collected at different fields using the following relation:

$$
\rho(\ H_{c2}^{ab}) = 0.9 \rho(T_c) \text{ and } \rho(\ H_{c2}^c) = 0.1 \rho(T_c)
$$

(3-3)
Chapter 4

4 Superconductivity, critical current density, and thermally activated flux flow in 
LaFeAsO$_{1-x}$F$_x$ superconductor

4.1 Introduction

The discovery of iron-based layered superconductors with transition temperature of 26 in LaFeAsO$_{1-x}$F$_x$ ($x = 0.05-0.12$) [4] compounds has attracted great interest in the scientific community. This is partly because the new superconductor containing the ferromagnetic atom “iron” shows superconductivity at the relatively high temperature of 26 K in LaFeAsO$_{0.89}$F$_{0.11}$ [133]. This new family of REFeAsO$_{1-x}$F$_x$ compounds, where RE is a rare earth element, reveals quite high critical temperature, when compared to all except the cuprate superconductors.

For practical application of the Fe-based superconductors, two of the most important parameters are the upper critical field, $H_{c2}$, and the critical current density, $J_c$. The upper critical field is an intrinsic property, which has been approximated to be higher than 55 or 64 T [115] [115,134] in LaFeAsO$_{0.9}$F$_{0.1}$, 70 T in PrFeAsO$_{0.85}$F$_{0.15}$, over 100 T in SmFeAsO$_{0.85}$F$_{0.15}$ [91], and 230 T in high-pressure (HP) fabricated NdFeAsO$_{0.82}$F$_{0.18}$
[89]. The $J_c$ is sample dependent and controlled by the flux pinning behaviour. However, the available data for critical current density and pinning force in LaFeAsO$_1$$_x$F$_x$ compound are very limited so far. As La is non-magnetic, LaFeAsO$_{1-x}$F$_x$ should be an ideal sample to study the flux pinning related properties. This is because all the other 1111- compounds contain a magnetic RE element.

In this chapter, I will explain the structures, microstructures, flux pinning, $J_c$, and upper critical fields in LaFeAsO$_{1-x}$F$_x$. My results show that the $J_c$ is sensitive to the fluorine concentration. $J_c$ increases with increasing fluorine doping from $x = 0.05$ to $x = 0.15$.

Beyond that, with further increases in $x$, the $J_c$ is reduced. Thermally activated flux flow is responsible for the broadening of the transition at $T_c$ in high magnetic field. An upper critical field of 122 T is obtained for LaFeAsO$_{0.85}$F$_{0.15}$ at low temperature.

4.2 Experimental details

Polycrystalline samples with the nominal composition of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15, and 0.20) were prepared by conventional solid state reaction. The details of the preparation process can be found in Chapter 3. XRD, SEM, and FE-SEM were employed for phase analysis. The microstructural characterization was carried out by high resolution transmission electron microscopy (HRTEM, FEI Technai 20G$^2$, operated at 200 kV). The transport and magnetic properties were measured over a wide range of temperature and magnetic fields up to 13 T using a physical properties measurement system (PPMS, Quantum Design). The critical current density was
calculated using the Bean model. The crystal structures were refined using Rietveld refinement.

### 4.3 Result and discussion

#### 4.3.1 Structures

Typical X-ray diffraction (XRD) patterns of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15, and 0.20) are shown in Fig. 4.1. It can be seen that the as-prepared samples are nearly single phase LaFeAsO$_{1-x}$F$_x$ compound.

![X-ray diffraction patterns of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15, and 0.20).](image)

Figure 4-1: X-ray diffraction patterns of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15, and 0.20).

The Rietveld refinement results show that the LaFeAsO$_{0.85}$F$_{0.15}$ crystallized in a tetragonal structure with space group $P4/nmm$ and lattice parameters $a = 4.011$ Å and $c$...
= 8.681 Å (derived from Rietveld refinement of XRD pattern in Fig. 4.2). Table 1 summarizes the lattice parameters and atomic positions of LaFeAsO$_{1-x}$F$_x$ for $x = 0.05$, 0.15, and 0.20. These values are quite comparable with the reported lattice constants of LaFeAsO$_{1-x}$F$_x$, with $a = 4.0229$ Å and $c = 8.7142$ Å for $x = 0.08$ [135] [135,136]. The lattice parameters were reduced with increasing fluorine doping, which indicates successful chemical doping.

![LaFeAsO$_{0.95}$F$_{0.05}$](image1)

![LaFeAsO$_{0.85}$F$_{0.15}$](image2)

Figure 4-2: Observed (symbols) and calculated (solid line) XRD patterns of LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$ (top panel) and 0.15 (bottom panel)), with the bottom traces showing the difference. The blue lines indicate the peak positions in the standard. Inset in top panel shows the crystal structure of the LaFeAsO$_{1-x}$F$_x$. 

60
Table 4-1 Properties of LaFeAsO$_{1-x}$F$_x$.

**a) Refined structure parameters** ($x = 0.05$ (first line), $0.15$ (second line) and $0.20$ (third line)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.1442</td>
</tr>
<tr>
<td>Fe</td>
<td>0.7500</td>
<td>0.2500</td>
<td>0.5000</td>
</tr>
<tr>
<td>As</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.6527</td>
</tr>
<tr>
<td>F/O</td>
<td>0.7500</td>
<td>0.2500</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**b) selected interatomic distances**

\[
\begin{array}{ccc}
    x &=& 0.05 & 0.15 & 0.20 \\
    \text{La-As} & 4.2801 \text{ Å} & 4.2669 \text{ Å} & 4.1942 \text{ Å} \\
    \text{La-As} & 3.3500 \text{ Å} & 3.3388 \text{ Å} & 3.2911 \text{ Å}
\end{array}
\]
Table 4.1: Interatomic Distances in LaFeAsO_\textsubscript{1-x}F_\textsubscript{x} (\text{Å})

<table>
<thead>
<tr>
<th></th>
<th>x = 0.05</th>
<th>x = 0.15</th>
<th>x = 0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{La-O}</td>
<td>4.6701</td>
<td>4.6561</td>
<td>4.5905</td>
</tr>
<tr>
<td>\text{La-O}</td>
<td>2.3713</td>
<td>2.3646</td>
<td>2.3291</td>
</tr>
<tr>
<td>\text{Fe-Fe}</td>
<td>2.8449</td>
<td>2.8362</td>
<td>2.7971</td>
</tr>
<tr>
<td>\text{Fe-As}</td>
<td>4.6906</td>
<td>4.6765</td>
<td>4.6150</td>
</tr>
<tr>
<td>\text{Fe-As}</td>
<td>2.4114</td>
<td>2.4044</td>
<td>2.3771</td>
</tr>
</tbody>
</table>

Microstructure

Figure 4.3 shows a field emission scanning electron micrograph (FE-SEM) and scanning electron microscope (SEM) images of the fractured surface of LaFeAsO_{1-x}F_x. The SEM image (Fig. 4.4(a)) shows plate-like grains which are densely placed, although with some voids between them. The FE-SEM image (Fig. 4.4(b)) reveals clearly that this sample has a typical layered structure.
Figure 4-3: FE-SEM image of LaFeAsO$_{1-x}$F$_x$ ($x = 0.15$).

Figure 4-4: SEM images of LaFeAsO$_{1-x}$F$_x$ ($x = 0.15$).
HRTEM images of the LaFeAsO$_{1-x}$F$_x$ ($x = 0.20$) are shown in Fig. 4.5. One outstanding feature in these images is the presence of layered structure. Several layers forming a block can be easily seen in Figure 4.5(a) and (b). These layered blocks are indicated by arrows in Fig. 4.5(b). The layered blocks are shifted with respect to each other, forming a stair-like structure. It appears that a group of LaO(F)-FeAs layers becomes shifted with respect to the second such block. This suggests rather weak bonding between two LaO(F)-FeAs layers. These features are indicative of a layer growth mechanism for the formation of La-O(F)FeAs phase. Figure 4.5(c) is the selected area diffraction (SAED) pattern corresponding to the microstructure shown in Fig. 4.5(b). As can be seen from Figure 4.5(c), the diffraction spots are arranged on a square grid corresponding to (101) and (011) spots. This reveals that the (011) and (101) planes are in the most preferred direction of layered growth. In addition, a typical HRTEM micrograph is shown in Figure 4.5(d). Careful analysis of lattice fringes shows the presence of a regular $c$ lattice parameter of ~8.73 Å. We have collected SAED patterns with the electron beam along the [100] or [010] direction. A representative diffraction pattern is shown in Figure 4.5(e). (00l) type diffraction spots are observed, whose indexing is outlined in the figure. Analysis of the bright (00l) spots revealed the standard $c$ spacing of ~8.73 Å.
Figure 4-5: TEM (a) and HRTEM (b) micrographs of as-synthesised fluorine doped LaFeAsO$_{1-x}$F$_x$ with $x = 0.2$. The presence of layers in (b) is indicated by arrows. (c) shows the SAED pattern corresponding to the microstructure in (b), showing the [101] and [011] directions. The HRTEM image in (d) shows the lattice fringes with ~8.73 Å fringe width, and the same width (8.73 Å) is indicated in the corresponding SAED pattern in (e). Note that the same width (8.73 Å) is indicated in the SAED pattern in (c).

We noted that the lattice parameter $c$ for the $x = 0.2$ sample determined from XRD refinement is indeed different from what was measured using HRTEM. We have no clear answers as to what caused the difference. However, it is likely that lattice
expansion might have taken place as a result of surface degradation and high energy electron radiation during the TEM examination. This is a common effect in TEM experiments for most of the FeAs based superconductors. However, our results from Rietveld refinements shows a strong trend for both the $a$ and $c$ parameters towards decreasing with increasing F doping level.

From our XRD refinement results, we have shown that our samples are almost single phase, and they only contain a tiny amount of magnetic impurities. It is interesting obtain information on the flux pinning behaviour for these compounds, which only incorporate a small amount of magnetic phase. The Bean model should still stand, as we have successfully extracted the ferromagnetic background from the small amount of magnetic impurity. This method has also been reported for a SmFeAsO$_{0.85}$F$_{0.15}$ sample [10]. The peak at 27$^\circ$ is from an unknown impurity which is expected to contribute to the ferromagnetic background of the $M$-$H$ loops.

Magnetic moment versus field was measured at 5, 10, 15, 20, 25, 30, and 35 K in fields up to 5 T. Figure 4.6(a) shows typical $M$-$H$ loops at 5 K and 35 K for the $x = 0.05$, 0.15 and 0.20 fluorine doped samples. Such an $M$-$H$ loop can be understood as the superposition of the superconducting contribution and a ferromagnetic background. Measurements performed above the superconducting transition temperature, $T_c$, show no hysteresis at all.
Figure 4-6(a): Magnetic moment as a function of the applied field at $T = 5$ K with the ferromagnetic background for the 5%, 15%, and 20% fluorine doped samples. (b) Magnetic moment as a function of applied magnetic field at $T = 35$ K for the same samples.
Figure 4-7: Superconducting contribution to the magnetic moment as a function of field at $T = 5$, 10, and 15 K for 5% and 15% fluorine doped samples.

The superconducting contribution to the $M$-$H$ loop of each compound can be obtained by subtracting the ferromagnetic signal of Fe (and/or Fe$_2$O$_3$) from the whole loop. The resulting curves for $T \leq 15$ K are shown in Fig. 4.7. The low value of the superconducting magnetic moment for the examined samples suggests the presence of weak links, i.e. the current does not circulate through the entire sample [91,137].
The $J_c$ values were calculated from the $M-H$ loops at different temperatures by using the extended Bean model:

$$J_c = 20 * \frac{\Delta m}{V} \frac{l}{l-3w}, \text{ with } l < w$$

where $l$ and $w$ are the sample dimensions perpendicular to the applied field, $V$ is the sample volume, and $\Delta m$ the width of the magnetization loop.

The critical current density ($J_c$) vs. magnetic field at different temperatures is shown in Fig 4.8. At 5 K for the $x = 0.15$ sample, the $J_c$ is approximately $10^3$ A/cm$^2$ at zero field and then decreases to 320 A/cm$^2$ at 1.2 T. The $J_c$ increases slightly with increasing magnetic field above 1.2 T to a maximum of 330 A/cm$^2$ at about 2.2 T (Fig. 4.8). The same peaks can be seen at 10 K and 15 K, but in lower magnetic fields. A similar peak
effect has been detected for the $x = 0.05$ sample. This peak effect has also been observed in SmFeAsO$_{1-x}$F$_x$ [91,137] and NdFeAsO$_{1-x}$F$_x$ [138] compounds.

Figure 4.9 shows the normalized pinning force $(F/F_{\text{max}} \propto J_c^*B)$ versus magnetic field at different temperatures. For all the curves at different temperatures, the pinning force increases with increasing magnetic field and then decreases after reaching a maximum. The peak position shifts to higher field with decreasing temperature and increasing fluorine concentration for both samples. The field applied is not high enough to observe the peak of the pinning force at 5 K.

Figure 4-9: Normalized pinning force vs. field for LaFeAsO$_{1-x}$F$_x$ ($x = 0.05, 0.15$) samples at different temperatures.

Figure 4.10 shows the temperature dependence of the resistance of the samples for different magnetic fields up to 13 T. The resistance starts to drop at the temperature of 27.5 K and 26 K, and then vanishes below 25.5 K and 24 K for the 5% and 15% fluorine doped sample in zero magnetic fields, respectively. The resistance for the $x =$
0.05 sample decreases linearly with decreasing temperature down to $T_c$, whereas the resistance for the $x = 0.15$ sample decreases down to 70 K and then increases again, reaching a maximum at the onset of $T_c$. The residual resistivity ratio ($RRR = R_{300K}/R_{28K}$) = 7.98, 2.67, and 8.72 for the 5%, 15% and 20% fluorine doped samples, respectively, which indicates that the 20% doped sample has less impurity scattering than the other two samples. The onset of the transition temperature, $T_c$, decreases very slowly with increasing magnetic field. The $\Delta T_c (T_c (90\%) - T_c (10\%))$ for zero magnetic field is only 2 K and 1.8 K for the 5% and 15% fluorine doped samples, respectively, which is much smaller than the 4.5 K reported for LaFeAsO$_{1-x}$F$_x$ with $x = 0.11$ [139].

![Figure 4-10: Temperature dependence of the resistance of the LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$, 0.15, and 0.2) up to room temperature.](a)
Figure 4-11: Temperature dependence of the resistance of the LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$ (a), $0.15$ (b), and $0.2$ (c)) at different magnetic fields up to 13 T.
As the $J_c$ drops to zero at a temperature of about 20 K in $H > 2T$, the 90% and 10% points of normal state resistance can be regarded as the upper critical field, $H_{c2}^{ab}$ and $H_{c2}^{c}$, respectively. The estimated slope $dH_{c2}^{ab}/dT$ for $H_{\text{max}}$ (90% $R_n$) is -4.1, -6.8, and -3.55 TK$^{-1}$ for the 5%, 15%, and 20% fluorine doped sample, respectively. The value obtained from our LaFeAsO$_{0.85}$F$_{0.15}$ sample is larger than for LaFeAsO$_{0.89}$F$_{0.11}$ ($dH_{c2}/dT = 2$ TK$^{-1}$) and for NdOFeAs$_{0.82}$F$_{0.18}$ ($dH_{c2}/dT = 5.8$ TK$^{-1}$) [89]. The slope $dH_{c2}^{c}/dT$ for $H_{\text{min}}$ (10% $R_n$) is -1.8, -2.1, and -1.5 TK$^{-1}$, for the 5%, 15%, and 20% fluorine doped sample, respectively. $H_{c2}(0)$ can be estimated using the Werthamer-Helfand-Hohenberg (WHH) formula: $H_{c2}(0) = -0.693 \frac{T_c}{dH_{c2}/dT} \approx 78, 122, \text{ and } 69$ T for the 90% $R_n$ fields, and $H_{c2}(0)$ is 34.3, 37.8, and 29 T for the 10% $R_n$ fields for the 5%, 15%, and 20% fluorine doped sample, respectively, using the Ginzburg-Landau equation:

$$H_{c2}(T) = H_{c2}(0) \times (1-t^2) / (1+t^2)$$

where $t=T/T_c$ is the reduced temperature and $H_{c2}(0)$ is the upper critical field at zero temperature. Figure 8(b) shows the fit of the Ginzburg-Landau equation to the experimental data for the high temperature range. $H_{c2}^{ab}(0)$ is estimated to be 89.2 and 121.5 T for the 5% and 15% fluorine doped sample, respectively. $H_{c2}^{c}(0)$ is about 35 T for both samples. These values are much greater than the highest value of 60 T which was reported earlier [140].

We have taken into account the possible Pauli paramagnetic limiting (PL) effect for our samples. It has been reported that the Pauli limiting effect is responsible for the $H_{c2}$ values in high fields in As-deficient LaFeAs$_{1-x}$O$_{0.9}$F$_{0.1}$ superconductor [141]. The $H_{c2}$ due to the PL effect is lower than what is estimated using the WHH formula and can be calculated using: $H_{c2}^{p}(0) = H_{c2}^{*}(0) / \sqrt{1+\alpha^2}$
where $\alpha$ is the Maki parameter. The $\alpha$ values are sample dependent and can vary between 0.25 and 3 for the La-1111 and Nd-1111 compounds [141,142] $\alpha = 1.31$ for the As-deficient LaFeAs$_{1.5}$O$_{0.5}$F$_{0.1}$ [141]. As our samples are not As deficient and showed a small value of $\alpha = 0.25$, as reported for La-1111 sample, the $H_{c2}^p (0)$ values should be almost the same as that from the WHH estimation.

Using the value of $H_{c2}^{ab} (0)$, we calculated the Ginzburg Landau coherence length, $\xi_{GL}$, by the formula $\xi_{GL} = (\varphi_0/2\pi H_{c2}^{ab})^{1/2}$ where $\varphi_0 = 2.07 \times 10^{-7}$ Oe.cm$^2$. The obtained zero temperature coherence lengths are $\xi_{GL} = 2.0$ nm, 1.6 nm, and 2.2 nm for the 5%, 15%, and 20% fluorine doped sample, respectively. These values are smaller than the reported values for LaFeAsO$_{0.89}$F$_{0.11}$ compound. [139]. According to our data, the estimated anisotropy for LaO$_{0.85}$F$_{0.15}$FeAs is $\gamma = H_{c2}^{ab}/H_{c2}^c = 2.3, 3.2, \text{and} 2.4$ for the 5%, 15%, and 20% fluorine doped sample, respectively, for the temperature range of $17 < T < 28$ K. These values are smaller than what have been reported for the same compounds[143].
Figure 4-12: Upper critical field - temperature phase diagram of LaFeAsO$_{1-x}$F$_x$ (a) and an extrapolation of the phase diagram down to 0 K using the Ginzburg-Landau equation.

It has been reported that the broadening of the superconducting transition in magnetic field is caused by the thermally activated flux flow in NdFeAsO$_{1-x}$F$_x$ superconductor.
Thus we use the same model to discuss the broadening of resistance in our samples. The resistance in the broadened region is caused by the creep of vortices. According to the thermally activated flux flow model the resistance is \( R(T, B) = R_0 \exp \left[-U_o/k_B T\right] \), where \( U_o \) is the flux-flow activation energy, which can be obtained from the slope of the linear part of an Arrhenius plot, \( R_0 \) is a parameter, and \( k_B \) is Boltzmann’s constant. In Fig. 4-13, we plot the data as \( \log R \) vs. \( T^{-1} \). The thermally activated behaviour of the resistance is immediately apparent. The slope of the curve is the activation energy \( U_o \). The best fit to the experimental data yields values of the activation energy ranging down from \( U_o/k_B = 1130 \text{ K} \) and \( 910 \text{ K} \) in the low field of \( 0.1 \text{ T} \) for the 5% and 15% fluorine doped sample, respectively. The value of the activation energy is lower than in a previous report for a polycrystalline \( \text{NdFeAsO}_{0.82}\text{F}_{0.18} \) sample \((U_o/k_B \approx 2000 \text{ K} \) for a magnetic field of \( 0.1 \text{ T} \) [97].

![Figure 4-13: Arrhenius plot of the electrical resistance of \( \text{LaFeAsO}_{1-x}\text{F}_x \) with \( x = 0.05 \) (top) and 0.15 (bottom). The activation energy \( U_o \) is given by the slope from a linear fitting.](image)
Figure 4.14: Magnetic field dependence of the activation energy $U_o$ of $\text{LaFeAsO}_{1-x}\text{F}_x$ ($x = 0.05, 0.15,$ and 0.20).

Figure 4.14 shows the magnetic field dependence (up to 13 T) of the activation energy $U_o$ for all samples. We can see that the values of $U_o$ for $\text{LaFeAsO}_{0.85}\text{F}_{0.15}$ drop very weakly with field for $B < 1$ T, scale as $B^{-0.13}$, and then decrease as $B^{-0.68}$ for $B > 1$ T. The 5% and 20% fluorine doped samples show a similar trend with field. The field dependence of the $U_o$ in our samples is the same as what we have found in an $\text{NdFeAsO}_{1-x}\text{F}_x$ sample [97] indicating that the vortices should have the same nature in both La1111 and the Nd1111 polycrystalline superconductors. As the $U_o$ is not constant, as has been observed in $\text{NdFeAsO}_{1-x}\text{F}_x$ single crystal[131], and it decreases weakly with field, it is expected that single-vortex pinning may coexist with collective creep in low field ($< 1$ T), and the collective creep then dominates for $H > 1$ T for all our La1111 samples with various F concentrations.
4.4 Conclusion

LaFeAsO$_{1.3}$F$_x$ shows a superior $J_c$ field dependence at low temperature. A peak effect was observed in the LaFeAsO$_{1.3}$F$_x$ samples with $x = 0.05$ and 0.15. LaFeAsO$_{0.85}$F$_{0.15}$ exhibits exceptionally high $H_{c2}^{ab}$, given the $dH_{c2}^{ab}/dT$ of 6.8 TK$^{-1}$, and the estimated $H_{c2}^{ab}(0) = 122$ T from the Ginsberg-Landau equation. The $H_{c2}$ values of these compounds have the potential to be increased even more, through proper chemical doping and physical approaches, due to the two-gap superconductivity in the new iron based superconductors. As the $J_c$ values are still considerably lower than those of individual grains, the challenge is to produce these materials with more texture and connectivity, in order to allow these new superconductors to carry a high critical current density in low and high magnetic fields. The pinning potential scales as $U_o/k_B \propto B^n$ with $n = 0.13$ for $B < 1$ T and $n = 0.68$ for $B > 1$ T in the $x = 0.15$ sample.
Chapter 5

5 Superconductivity and thermally activated flux flow studies on electron doped CeFeAsO$_{1-x}$F$_x$ superconductors

5.1 Introduction

Shortly after the discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ compounds, the critical temperature, $T_c$, was increased by replacing La with other rare earth elements such as Ce, Pr, Sm, Nd, and Gd. The $T_c$ reached as high as 55 K for SmFeAsO$_{0.9}$F$_{0.1}$ [144] and 56 K for Gd$_{1-x}$Th$_x$FeAsO [50].

It has been reported that electron-doped cerium iron oxypnictide superconductors have many features similar to LaFeAsO$_{1-x}$F$_x$ compounds [9]. Compared to LaFeAsO$_{1-x}$F$_x$, where Fe is the only possible ion carrying a significant magnetic moment, the rare-earth oxypnictides with paramagnetic ions such as Ce$^{3+}$ in CeFeAsO$_{1-x}$F$_x$ offer a unique opportunity to study the interplay between the rare-earth and Fe magnetic ions.

A transition temperature around 30 K for 10% fluoride doping in CeFeAsO$_{1-x}$F$_x$ has been reported, which is increased to 40 K for 20% doping, with an upper critical field of 48.8 T[145]. Another group has reported $T_c = 42.5$ K for 20% fluoride doping in
CeFeAsO_{1-x}F_x and enhancement of the upper critical field (H_{c2}) to 94T for 10% fluoride[146].

Another important parameter to characterise superconductivity is the upper critical field, $H_{c2}(0)$. In Chapter 4, we already found a rather high upper critical field of $H_{c2}(0) = 122$ T [147] for LaFeAsO_{0.85}F_{0.15} superconductor. Here, we would expect much higher $H_{c2}(0)$ in Ce-based compounds due to higher $T_c$.

In this chapter, we discuss the structures, flux pinning, $J_c$, and upper critical field in CeFeAsO_{1-x}F_x for $x = 0.1$ and 0.2 composition.

### 5.2 Experimental Details

Polycrystalline samples with nominal composition of CeFeAsO_{1-x}F_x with $x = 0.1$ and 0.2 were synthesized by the conventional solid state reaction method using Ce, CeO_2, CeF_3, and FeAs with purities of 99.9% as the starting materials. FeAs was obtained by reacting Fe chips and As powder at 900°C for 24 h. The raw materials were mixed according to the stoichiometric ratio, and then sealed in evacuated silica ampoules and heated at 1000°C for 48 h. The powder was then pressed into pellets, wrapped in Ta foil, and then sealed in evacuated silica ampoules and heated at 1180°C for 48 hours.

X-ray diffraction of the samples was performed with Cu-Kα radiation in the 2θ range of 20° to 80°, with a step interval of 0.02°. The microstructures of the as-obtained samples and their morphology were studied using field emission scanning electron microscopy (FE-SEM, JEOL7500), operated at 50 kV. The transport and magnetic properties were
measured over a wide range of temperature and magnetic fields up to 13 T using a Physical Property Measurement System (PPMS, Quantum Design).

**Results and Discussion**

Figure 5.1 shows a typical X-ray diffraction (XRD) pattern of CeFeAsO$_{1-x}$F$_x$ ($x = 0.1, 0.2$). It can be seen that the as-prepared samples are nearly single phase CeFeAsO$_{1-x}$F$_x$ compound. The Rietveld refinement results show that the CeFeAsO$_{1-x}$F$_x$ ($x = 0.1, 0.2$) was crystallized in a tetragonal structure with space group $P4/nmm$ and lattice parameters of $a = 3.9877 \, \text{Å}$ and $c = 8.6203 \, \text{Å}$ for $x = 0.10$ and $a = 3.9632 \, \text{Å}$ and $b = 8.5699 \, \text{Å}$ for $x = 0.20$, respectively. These results indicate that with increasing fluorine doping, the lattice parameters are reduced due to the fluorine atom size, which is smaller than oxygen atom size. The lattice parameters are smaller than in the parent compound CeFeAsO ($a = 3.996 \, \text{Å}$ and $c = 8.652 \, \text{Å}$) reported earlier[87].
Figure 5-1: Observed (symbols) and calculated (solid line) XRD patterns of CeFeAsO$_{1-x}$F$_x$ ($x = 0.1$, 0.2) at 300 K, with the bottom trace showing the difference. The blue lines indicate the peak position.

Table 5-1: Properties of CeFeAsO$_{1-x}$F$_x$ ($x = 0.1$ (first line), and $x = 0.2$ (second line)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.1449</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1487</td>
</tr>
<tr>
<td>Fe</td>
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<td>0.2500</td>
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<td></td>
<td></td>
<td></td>
<td>0.5000</td>
</tr>
<tr>
<td>As</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.6561</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6568</td>
</tr>
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</table>
b) selected interatomic distances

<table>
<thead>
<tr>
<th></th>
<th>X=0.10</th>
<th></th>
<th>X=0.20</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-As</td>
<td>4.2116 Å</td>
<td></td>
<td>4.2150 Å</td>
<td></td>
</tr>
<tr>
<td>Ce-As</td>
<td>3.3000 Å</td>
<td></td>
<td>3.2606 Å</td>
<td></td>
</tr>
<tr>
<td>Ce-O</td>
<td>4.6300 Å</td>
<td></td>
<td>4.6105 Å</td>
<td></td>
</tr>
<tr>
<td>Ce-O</td>
<td>2.3526 Å</td>
<td></td>
<td>2.3559 Å</td>
<td></td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>2.8198 Å</td>
<td></td>
<td>2.8024 Å</td>
<td></td>
</tr>
<tr>
<td>Fe-As</td>
<td>4.6575 Å</td>
<td></td>
<td>4.6303 Å</td>
<td></td>
</tr>
<tr>
<td>Fe-As</td>
<td>2.4064 Å</td>
<td></td>
<td>2.3944 Å</td>
<td></td>
</tr>
</tbody>
</table>

c) lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>x=0.10</th>
<th></th>
<th>x=0.20</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a = b</td>
<td>3.9877 Å</td>
<td></td>
<td>3.9632 Å</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>8.6203 Å</td>
<td></td>
<td>8.5699 Å</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5.2 and Fig. 5.3 show the scanning electron microscope (SEM) and field emission SEM (FE-SEM) images of the fractured surface of CeFeAsO$_{1-x}$F$_x$ superconductor. The SEM image shows densely spaced plate-like grains, although there are some voids between them, which strongly reveal the typical layered structure of these superconductors.
Figure 5-2: SEM image of CeFeAsO$_{1-x}$F$_x$ ($x = 0.10$).

Figure 5-3: FE-SEM images of CeFeAsO$_{1-x}$F$_x$ ($x = 0.10$).
Figure 5-4: Magnetic moment as a function of applied magnetic field at $T = 5$ K (a) and 30 K (b) with the ferromagnetic and paramagnetic background for the 10% and 20% doped samples.
Figure 5.5: Superconducting contribution to the magnetic moment as a function of field at $T =$ 5, 10, and 20 K for both samples.

Magnetic moment versus field was determined at different temperatures (5, 10, 15, 20, 25, and 30 K) in fields up to 5 T. Figure 5-4 shows two typical $M$-$H$ loops at 5 K (a) and 30 K (b) for the $x =$ 0.10 and 0.20 samples. The $M$-$H$ loops can be understood as the superposition of the superconducting contribution and the paramagnetic background.

Measurements performed close to the superconducting transition temperature, $T_c$, show a paramagnetic curve with no sign of saturation, possibly due to the paramagnetic effect of the Ce$^+$ ions. For a long sample with rectangular cross-section $l \times w$ (with $l < w$) perpendicular to the applied field, it is convenient to use the expression $J_c = 20\Delta m/V \left(1 - \frac{l}{3w}\right)$, where $V$ is the sample volume, $\Delta m = m - m^+$, and $m^+(m^-)$ is the magnetization associated with increasing (decreasing) field.

The critical current density ($J_c$) vs. magnetic field at different temperatures is shown in Fig 5.6. At 20 K for the $x =$ 0.10 sample, the $J_c$ is approximately 400 A/cm$^2$ at low
magnetic field and then decreases dramatically to 40 A/cm$^2$ at 0.4 T. The $J_c$ increases slightly with increasing magnetic field above 0.4 T to a maximum of 55 A/cm$^2$ at about 1 T. This peak effect has been observed in SmFeAsO$_{1-x}$F$_x$ [91] and NdFeAsO$_{1-x}$F$_x$ [138] compounds. No peak effect was observed at low temperature in the CeFeAsO$_{0.9}$F$_{0.1}$ or in the CeFeAsO$_{0.3}$F$_{0.2}$ samples.

The zero-field $J_c$ for the 10% doped sample is $2 \times 10^3$ A/cm$^2$, which is slightly higher than $J_c$ for the 20% doped sample. $J_c$ decreases dramatically with increasing applied magnetic field up to 1 T, and after that, it has a very weak dependence on magnetic field and remains nearly constant for $B > 1$ T and $T = 5$ and 10 K, which is very similar to the $J_c$ performance in Nd or Sm based oxypnictides[89,138,148].

![Figure 5-6: Magnetic field dependence of the critical current density at different temperatures.](image)

It should be noted that the zero field $J_c$ is low, which is very likely due to the interfaces between grains. As the field is applied, these interfaces are dramatically changed, and $J_c$ goes down to a very low value. As $J_c$ is determined from magnetization experiments,
the small hysteresis is due to individual grains that are more or less completely disconnected. Therefore, it is expected that the real $J_c$ of individual grains should be higher than $J_c$ calculated using the sample dimension.

Figure 5-7 shows the temperature dependence of the resistivity of the samples for different magnetic fields up to 13 T. The resistivity starts to drop at the temperature of 38.6 K and 40.4 K, and then vanishes below 35.1 K and 30.5 K for the 10% and the 20% fluorine doped samples in zero magnetic field, respectively. The onset of the transition temperature shifts gradually with magnetic field, while the zero resistance temperature varies significantly. The transition width $\Delta T_c$, determined by adopting the criterion of 10-90% of the normal-state resistivity is 2.3 K and 6.9 K for the 10% and 20% fluorine doped samples, respectively, for zero magnetic field, which is in good agreement with what has been reported for CeFeAsO$_{1-x}$F$_x$ ($x = 0.1$ and 0.2)[146].
Figure 5-7: Temperature dependence of the resistance of the CeFeAsO$_{1-x}$F$_x$ (x=0.10, 0.20) samples at different magnetic fields up to 13 T. (a) is a comparison of the samples in zero field from 4 to 50 K, while (b) and (c) show the detailed responses for 10% and 20% fluorine doping, respectively, from 15 to 40 K in different magnetic fields.

Near $T_c$, the data show considerable flux-flow broadening, as shown in Fig. 5-7(b) and (c), where the magnetic field was varied from 0 to 13 T. The transition width indicates a
broad region of flux-flow resistivity of possibly thermally activated origin near the offset.

The resistive transition widths are quite large between 2.3 and 6.9 K. As the $J_c$ drops to zero at a temperature of about 20 K for $H > 4$ T, the fields at 90% and 10% of normal state resistance, $R_n$, can be regarded as the upper critical fields, $H_{c2}^{ab}$ and $H_{c2}^{c}$, respectively. The estimated slope, $dH_{c2}^{ab}/dT$, for $H_{max}$ (90% $R_n$) is 5.9 and 2.4 TK$^{-1}$ for the 10% and the 20% fluorine doped sample, respectively. This value obtained from our CeFeAsO$_{0.9}$F$_{0.1}$ sample, is larger than that reported for CeFeAsO$_{0.9}$F$_{0.1}$ ($dH_{c2}^{ab}/dT = 3.52$ TK$^{-1}$) and NdFeAsO$_{0.82}$F$_{0.18}$ ($dH_{c2}^{ab}/dT = 5.6$ TK$^{-1}$) [89]. The slope $dH_{c2}^{c}/dT$ for $H_{min}$ (10%) is 1.9 and 1.3 TK$^{-1}$, for the 10% and the 20% fluorine doped sample, respectively. Using the Ginzburg-Landau equation:

$$H_{c2}(T) = H_{c2}(0) \frac{(1-t^2)}{(1+t^2)}$$

(1)

where $t = T/T_c$ is the reduced temperature and $H_{c2}(0)$ is the upper critical field at zero temperature. Figure 5-8(b) shows the fit of the Ginzburg-Landau equation to the experimental data for the high temperature range. $H_{c2}^{ab}(0)$ is estimated to be 185 and 70 T for the 10% and the 20% fluorine doped sample, respectively. Likewise, $H_{c2}^{c}(0)$ is about 47 T and 30 T for the 10% and the 20% doped sample, respectively. It should be noted that the $H_{c2}$ value using both equations is usually far below the real experimental data [115].
Figure 5-8: Upper critical field- temperature behaviour of CeFeAsO$_{1-x}$F$_x$: (a) $dH_{c2}/dT$ vs. $T$; (b) $H_{c2}$ vs. $T$; (c) upper critical field vs. reduced temperature for CeFeAsO$_{1-x}$F$_x$ in comparison with LaFeAsO$_{1-x}$F$_x$ samples. The 90% and 10% in (c) refer to the fields at 10% and 90% of the normal state resistance.
Using the value of $H_{c2}^{ab}(0)$, we calculated the Ginzburg Landau coherence length by the formula

$$\xi_{GL} = \left(\frac{\varphi_0}{2\pi H_{c2}^{ab}}\right)^{1/2}$$

where $\varphi_0 = 2.07 \times 10^{-7}$ Oe·cm$^2$. The obtained zero temperature coherence lengths are $\xi_{GL} = 3.34$ nm and 5.43 nm for $H_{c2}^{ab}(0)$ for the 10% and the 20% fluorine doped samples, respectively. These values are larger than the reported values for CeFeAsO$_{1-x}$F$_x$ ($x = 0.1$ and 0.2) compounds[146].

As a comparison, $H_{c2}^{ab}$ and $H_{c2}^{c}$ for LaFeAsO$_{1-x}$F$_x$ ($x = 0.05$ and 0.15)[147] are also plotted as a function of reduced temperature in Fig. 5-8-(c). The CeFeAsO$_{0.5}$F$_{0.1}$ sample clearly shows the highest values of both $H_{c2}^{ab}$ and $H_{c2}^{c}$, but the CeFeAsO$_{0.3}$F$_{0.2}$ sample shows the lowest value.

According to our data, the estimated anisotropy for CeFeAsO$_{0.85}$F$_{0.15}$ is $\Gamma = (H_{c2}^{ab} / H_{c2}^{c}) = 3.9$ and 2.3 for the 10% and the 20% fluorine doped sample, respectively, for the temperature range of 17 K $< T <$ 40 K.
The broadening of the transition with magnetic field has been reported to be caused by the thermally activated flux flow for NdFeAsO$_{1-x}$F$_x$ single crystals and polycrystalline bulks[97,131]. Therefore, we use the same model to discuss the broadening of the resistivity transition in our CeFeAsO$_{1-x}$F$_x$ samples. The resistivity in the broadened region is caused by the creep of vortices, so according to the thermally activated flux flow model, the resistivity is $\rho (T, B) = \rho_o \exp \left[ -U_o / k_B T \right]$, where $U_o$ is the flux-flow...
activation energy, which can be obtained from the slope of the linear part of an
Arrhenius plot, $\rho_o$ is a parameter, and $k_B$ is Boltzmann’s constant. $U_o$ can be deduced
only from the limited temperature interval below $T_c$, where the data from the Arrhenius
plot of $\rho(T)$ yield a straight line. In Fig. 5-9, we plot the data as $\log \rho$ vs. $T^{-1}$. The
thermally activated behaviour of the resistivity is immediately apparent. The slope of
the curve is the activation energy $U_o$. The best fit to the experimental data yields values
of the activation energy ranging down from $U_o/k_B = 2000$ K and 530 K in the low field
of 0.1 T for the 10% and the 20% fluorine doped samples, respectively. The value of the
activation energy for the 10% doped sample is in good agreement with a previous report
for a polycrystalline NdFeAsO$_{0.82}$F$_{0.18}$ sample ($U_o/k_B \approx 2000$ K for magnetic field of 0.1
T) [97]. This agrees very well with the granular behaviour of the samples, but could also reflect
inhomogeneity in the stochiometry of the sample. Therefore the tail in the resistive
transition is not mainly due to an intrinsic flux flow mechanism. However, the intrinsic
flux flow mechanism has been well demonstrated in a high quality NdFeAsO$_{1-x}$F$_x$ single
crystal [131]. Therefore, both the intrinsic and extrinsic factors coexist, causing the
tails in the resistivity. This is the reason why the curve in Fig. 5.9(a) deviates from
linear at low temperature.
Figure 5-10 shows the magnetic field dependence (up to 13 T) of the activation energy $U_o$ for both samples. We can see that the values of $U_o$ drop weakly with field for $B < 3$ T and are scaled as $B^{-0.2}$, so it is expected that single-vortex pinning may coexist with collective creep in low field and then decrease slowly as $B^{-0.71}$, as collective creep dominates for $B > 3$ T for the 10% doped sample. The 20% fluorine doped sample shows a similar trend with magnetic field. The value of $U_o$ for the 10% doped sample is two times higher than for the LaFeAsO$_{0.95}F_{0.05}$ that we reported previously [147]. However, $U_o$ for CeFeAsO$_{0.9}F_{0.1}$ is lower than for MgB$_2$ thin film for $H < 8$ T, but higher than that of MgB$_2$ for $H > 8$ T [96].

### 5.3 Conclusion

CeFeAsO$_{1-x}F_x$ shows a superior $J_c$ field dependence at low temperature. A peak effect was observed in the CeFeAsO$_{1-x}F_x$ samples with $x = 0.1$ at $T = 20$ K. CeFeAsO$_{0.9}F_{0.1}$
exhibits exceptionally high $H_{c2}^{ab}$, given the $dH_{c2}^{ab}/dT$ of 5.9 TK$^{-1}$, and the estimated $H_{c2}^{ab}(0) = 161.5$ T from the Ginsberg-Landau equation. The $H_{c2}$ values of these compounds have the potential to be increased even more, through proper chemical doping and physical approaches, due to the two-gap superconductivity in the new iron based superconductors. $J_c$ of $2 \times 10^3$ A/cm$^2$ at 5 K in low magnetic field was estimated, and the $J_c$ shows a weak magnetic field dependence. As the $J_c$ values are still considerably lower than those of individual grains, the challenge is to produce these materials with more texture and connectivity, in order to allow these new superconductors to carry a high critical current density in low and high magnetic fields. The pinning potential scales as $U_o/k_B \propto B^n$ with $n = 0.2$ for $B < 3$ T and $n = 0.7$ for $B > 3$ T in the $x = 0.10$ sample.
In summary, $REFeAsO_{1-x}F_x$ ($RE$=La and Ce) with different fluorine concentration, show superior $J_c$ field dependence at low temperature. CeFeAsO$_{1-x}F_x$ show higher critical current density compared to LaFeAsO$_{1-x}F_x$ at low magnetic fields, probably due to higher transition temperature. Also different sample quality can cause different values of critical current density. Magnetisation is found to be enhanced with increasing magnetic field continuously for CeFeAsO$_{1-x}F_x$ which is related to the paramagnetic effect of Ce. On the other hand, magnetisation increases at low magnetic fields for LaFeAsO$_{1-x}F_x$ and becomes almost field independent due to non-magnetic effect of La. The critical current density decreases with increasing magnetic field for low field and shows weak magnetic field dependence for high fields. Peak effect is also observed for both LaFeAsO$_{1-x}F_x$ ($x$=0.05 and 0.15) and CeFeAsO$_{1-x}F_x$($x$=0.1).

The pinning mechanism is almost the same for both LaFeAsO$_{1-x}F_x$ and CeFeAsO$_{1-x}F_x$ compounds. In low fields, the value of pinning potential, $U_o$, drop weakly with field for both compounds due to single vortex pinning coexisting with collective creep in low magnetic field. The activation energy decreases slowly with increasing magnetic field, as collective vortex pinning dominates for higher magnetic fields. The value of $U_o$ for CeFeAsO$_{0.9}F_{0.1}$ is two times higher than LaFeAsO$_{0.95}F_{0.05}$ at low magnetic fields.

The $H_{c2}$ values of both LaFeAsO$_{1-x}F_x$ and CeFeAsO$_{1-x}F_x$ compounds have the potential to be increased further through proper chemical and physical approaches because of multigap superconductivity in the iron based superconductors. As the $J_c$ values are still considerably lower than those of individual grains, the challenge is to produce these materials with excellent grain texture and connectivity in order to allow these new superconductors to carry a high critical current density in low and high magnetic field.
6 References

1 J.B.Ketterson and S.N.Song, *superconductivity* (Cambridge University, 1999).
3 A. Mourachkine, *room temperature superconductivity* (Cambridge international science publishing.


