



Title	Experimental Studies on Electronic States of Iron Pnictide Superconductors RFe(P, As)(0, F) (R = La, Pr, Nd)
Author(s)	竹森, 章
Citation	大阪大学, 2015, 博士論文
Version Type	VoR
URL	<a href="https://doi.org/10.18910/52313">https://doi.org/10.18910/52313</a>
rights	
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Dissertation for Doctoral Degree

Experimental Studies on Electronic States  
of Iron Pnictide Superconductors  
 $R\text{Fe}(\text{P}, \text{As})(\text{O}, \text{F})$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ )

Department of Physics, Graduate School of Science, Osaka University

Akira Takemori

February 2, 2015



# Abstract

The iron-based superconductors show unconventional superconductivity with high superconducting transition temperature ( $T_c$ ). Several experimental studies have suggested that  $T_c$  is strongly correlated with the local structural parameters around Fe site such as pnictogen - Fe - pnictogen bond angle and pnictogen height from Fe layer. However, it is not clear yet what electronic parameter is modified by these structural parameters. On the other hand, some theories suggest that the antiferromagnetic (AFM) fluctuation plays an important role for the appearance of superconductivity in the iron-based superconductors, but there is no direct experimental evidence that  $T_c$  is correlated with the strength of antiferromagnetic fluctuation. Therefore, in order to clarify the mechanism of superconductivity in this system, it is necessary to find a microscopic parameter that scales with  $T_c$ , comparing various physical properties of various iron pnictides with different  $T_c$ .

In this work, I focus on  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ , where  $R$  are La, Pr, and Nd. First advantage of this system is that P and As are isovalent elements and thus a carrier number is kept constant in principle. The change in physical properties with  $x$  is considered to be induced by a structural change due to chemical pressure. The second advantage is that I can cover a wide range of  $T_c$  from  $\sim 3$  to  $\sim 50$  K by changing  $x$ . This helps us to find a physical quantity that scales with  $T_c$ . The third advantage is that the strength of antiferromagnetic fluctuation can be controlled by varying  $x$ .  $R\text{FeAsO}$  is an antiferromagnetic metal. With F doping, the magnetic order is suppressed and the superconductivity appears above F concentration of  $\sim 0.08$ . Therefore, the end material in the present study,  $R\text{FeAsO}_{0.9}\text{F}_{0.1}$  shows superconductivity, but has large antiferromagnetic fluctuation. In contrast, the other end material  $R\text{FeP}(\text{O}, \text{F})$  are superconducting at lower temperature and shows a paramagnetic metallic behavior in the normal state. Therefore, the antiferromagnetic fluctuation is expected to be controllable by changing  $x$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ . In the present study, I have investigated the transport properties and

---

angle resolved photoemission spectroscopy (ARPES) in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  with various  $T_c$ , lattice constants and presumably antiferromagnetic fluctuation strength to find a relationship among  $T_c$ , crystal structure and electronic properties in iron pnictides.

First, I have studied the transport properties of the polycrystalline samples and single crystals, and searched the parameters correlating to  $T_c$ . The present results have revealed that there are two distinct regions of  $x$ . In the low  $x$  region ( $x < 0.6 - 0.8$ ),  $T_c$  linearly increases from  $\sim 3$  to  $\sim 30$  K with decreasing the power  $n$  in  $\rho = \rho_0 + AT^n$  from 2 at  $x = 0$  to 1 around  $x = 0.6 - 0.8$ . This strongly suggests that some bosonic fluctuation such as antiferromagnetic one is a primary factor to enhance  $T_c$ . The universal  $T_c - n$  relation holds for all the  $R$  systems with  $x < 0.6 - 0.8$ . In addition to the  $T$ -linear resistivity,  $R_H$ ,  $\rho_0$ , and  $A$  are strongly enhanced near  $x = 0.6 - 0.8$ , suggesting some critical change of the electronic state. In the high  $x$  region ( $x > 0.6 - 0.8$ ), on the other hand,  $T_c$  becomes strongly  $R$ -dependent and further increases with  $x$ , but shows no clear correlation with  $n$ . The compounds with  $x > 0.6 - 0.8$  seem to approach another universal  $T_c - n$  relation which holds for  $R\text{FeAsO}_{1-y}$ . The presence of two distinct  $T_c - n$  relations could be the evidence that there are two  $T_c$ -rising mechanisms and related two different Fermi surface states in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

Next, I have investigated the ARPES using single crystals of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  with  $x = 0.4, 0.8$  and  $1.0$  in order to clarify  $x$ -dependent changes of band structures and Fermi surfaces (FSs). The ARPES results indicate the existence of three hole and two electron FSs in  $x = 0.4$ , and two hole and two electron FSs in  $x = 0.8$  and  $1.0$  samples. The orbital characters of these FSs have been assigned by the measurements of polarization dependence of incident light. The  $d_{xz}$  hole FS exists around  $\Gamma$  point at  $x = 0.4$ . The  $d_{xz}$  band sinks down with increasing  $x$ , and the top of this band touches  $E_F$  around  $\Gamma$  point in the  $x = 0.8$  sample. With further increasing  $x$ , the hole FS with  $d_{xz}$  character disappears at  $x = 1.0$ . The  $T_c$ ,  $n$  and other transport properties distinctly change around  $x = 0.6 - 0.8$ . The clear difference of FSs below and above  $x = 0.6 - 0.8$  may be related with the change of transport properties, and support the scenario of two  $T_c$ -rising mechanisms and two different Fermi surface states in this system.

# Contents

<b>I</b>	<b>Introduction</b>	<b>6</b>
<b>1</b>	<b>Introduction</b>	<b>7</b>
1.1	Fundamental facts of iron-based superconductors . . . . .	7
1.1.1	Discovery of iron pnictide superconductors . . . . .	7
1.1.2	1111-type iron pnictides . . . . .	7
1.1.3	122-type iron pnictides . . . . .	10
1.1.4	111-type iron pnictides . . . . .	12
1.1.5	42622-type iron pnictides . . . . .	13
1.2	Theoretical studies on iron pnictide superconductors . . . . .	14
1.2.1	Band structure and Fermi surfaces of 1111-type iron pnictides . . . . .	14
1.2.2	Spin fluctuation theory . . . . .	16
1.3	Experimental studies on iron pnictide superconductors . . . . .	16
1.3.1	Correlations between crystal structural parameters and $T_c$ . . . . .	16
1.3.2	Superconducting gap structure of various iron pnictide superconductors .	17
1.3.3	P/As substitution studies on 1111-type iron pnictides . . . . .	22
1.3.4	ARPES measurements in 1111 system . . . . .	24
<b>2</b>	<b>Objective</b>	<b>28</b>
<b>II</b>	<b>Studies on Polycrystalline <math>R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}</math> (<math>R = \text{La, Pr, Nd}</math>)</b>	<b>30</b>
<b>3</b>	<b>Experimental methodology</b>	<b>31</b>
3.1	Synthesis . . . . .	31
3.1.1	Synthesis of precursors $R\text{As}$ and $RP$ ( $R = \text{La, Pr, Nd}$ ) . . . . .	31
3.1.2	Synthesis of polycrystalline $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ( $R = \text{La, Pr, Nd}$ ) . . . .	32

## CONTENTS

---

3.2	Measurements . . . . .	34
3.2.1	Crystal structural analysis . . . . .	34
3.2.2	Magnetic susceptibility . . . . .	34
3.2.3	Electrical resistivity . . . . .	35
3.2.4	Hall effect . . . . .	35
<b>4</b>	<b>Experimental results</b>	<b>38</b>
4.1	Crystal structural analysis . . . . .	38
4.1.1	Powder X-ray diffraction . . . . .	38
4.1.2	Synchrotron X-ray diffraction . . . . .	40
4.2	Magnetic susceptibility . . . . .	41
4.3	Electrical resistivity . . . . .	43
4.4	Hall effect . . . . .	48
4.4.1	Hall resistivity . . . . .	48
4.4.2	Hall coefficient . . . . .	54
<b>5</b>	<b>Discussion</b>	<b>56</b>
5.1	Crystal structural parameters and $T_c$ . . . . .	56
5.1.1	Bond angle $\alpha$ dependence of $T_c$ . . . . .	56
5.1.2	Pnictogen height $h_{Pn}$ dependence of $T_c$ . . . . .	57
5.2	Transport properties . . . . .	57
5.2.1	$x$ dependences of $T_c$ and $n$ . . . . .	57
5.2.2	$x$ dependences of $\rho_0$ and $A$ . . . . .	60
5.2.3	$x$ dependence of $R_H$ at $T = 50$ K . . . . .	60
5.2.4	Correlation between $T_c$ and $n$ . . . . .	63
<b>III</b>	<b>Studies on Single-crystalline NdFeP<sub>1-x</sub>As<sub>x</sub>(O, F)</b>	<b>67</b>
<b>6</b>	<b>Experimental methodology</b>	<b>68</b>
6.1	Single crystal growth of NdFeP <sub>1-x</sub> As <sub>x</sub> (O, F) by high pressure synthesis . . . . .	68
6.1.1	Previous studies of single crystal growth . . . . .	68
6.1.2	Procedure of high pressure synthesis of NdFeP <sub>1-x</sub> As <sub>x</sub> (O, F) . . . . .	69
6.2	Measurements . . . . .	72

## CONTENTS

---

6.2.1	Composition analysis . . . . .	72
6.2.2	Magnetic susceptibility and transport measurements . . . . .	72
6.2.3	ARPES measurement . . . . .	73
<b>7</b>	<b>Experimental results</b>	<b>79</b>
7.1	Single crystals of $\text{NdFeP}_{1-x}\text{As}_x(\text{O, F})$ grown by high pressure synthesis . . . . .	79
7.2	Magnetic susceptibility . . . . .	81
7.3	Electrical resistivity . . . . .	81
7.4	Hall effect . . . . .	83
7.4.1	Hall resistivity . . . . .	83
7.4.2	Hall coefficient . . . . .	84
7.5	Magnetoresistance . . . . .	84
7.6	ARPES . . . . .	87
7.6.1	$k_z$ dependence of FS mapping . . . . .	87
7.6.2	Band dispersion . . . . .	88
7.6.3	Hole and electron FSs around $\Gamma$ and M Points . . . . .	92
<b>8</b>	<b>Discussion</b>	<b>98</b>
8.1	Transport properties . . . . .	98
8.1.1	$x$ dependences of $T_c$ and $n$ . . . . .	98
8.1.2	$x$ dependence of $\rho_0$ and $A$ . . . . .	98
8.1.3	$x$ dependence of $R_H$ at $T = 50$ K . . . . .	101
8.1.4	Correlation between $T_c$ and $n$ . . . . .	103
8.2	ARPES measurement . . . . .	103
8.2.1	Comparison with band calculation . . . . .	103
8.2.2	$x$ dependence of FSs . . . . .	104
<b>IV</b>	<b>Conclusion</b>	<b>108</b>
<b>9</b>	<b>Conclusion</b>	<b>109</b>

## Part I

# Introduction

# Chapter 1

## Introduction

### 1.1 Fundamental facts of iron-based superconductors

#### 1.1.1 Discovery of iron pnictide superconductors

The first iron-based superconductor LaFePO having  $T_c = 4$  K was discovered by Kamihara *et al.* in Tokyo Institute of Technology in 2006 [1]. Two years later, LaFeAs(O, F) ( $T_c = 26$  K) was also reported by them [2] and studies on iron-based superconductors have been activated in all the world.  $T_c$  immediately increased to 55 K by substituting La with Sm whose ionic radius is smaller than that of La [3]. Additionally, new iron-based superconductors having different crystal structures were also discovered, such as  $AeFe_2As_2$  (122-type), FeSe (11-type) and so on. Iron-based superconductors have the second highest  $T_c$  following cuprates. Both of them are unconventional superconductors and do not follow the BCS theory, which explains the generation mechanism of Cooper pair mediated by electron-phonon coupling. Some common features between iron-based superconductors and cuprates are confirmed, such as (i) they have 2-dimensional layered structure constructed of conduction and insulation layers, (i) superconductivity emerges by suppression of the AFM order of mother compounds, and so on. On the other hand, there is a difference that the mother compounds of cuprates are Mott-insulators and those of iron-based superconductors are AFM metals.

#### 1.1.2 1111-type iron pnictides

1111-type iron pnictides  $RFePnO$  ( $R$  = rare earth and  $Pn$  = P, As) is one of representative iron-based superconductors. They are called 1111 system from the compositional ratio of  $R$  :

$\text{Fe} : \text{Pn} : \text{O} = 1 : 1 : 1 : 1$ . The crystal structure of  $R\text{FePnO}$  is ZrCuSiAs-type (tetragonal,  $P4/nmm$ ) and illustrated in Figure 1.1  $R\text{FePnO}$  has the layered structure constructed of  $\text{FePn}$

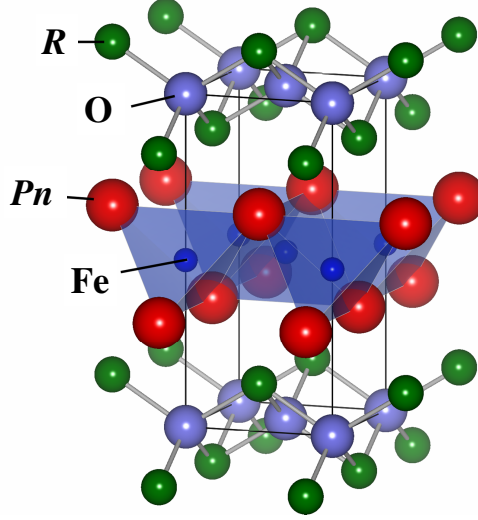


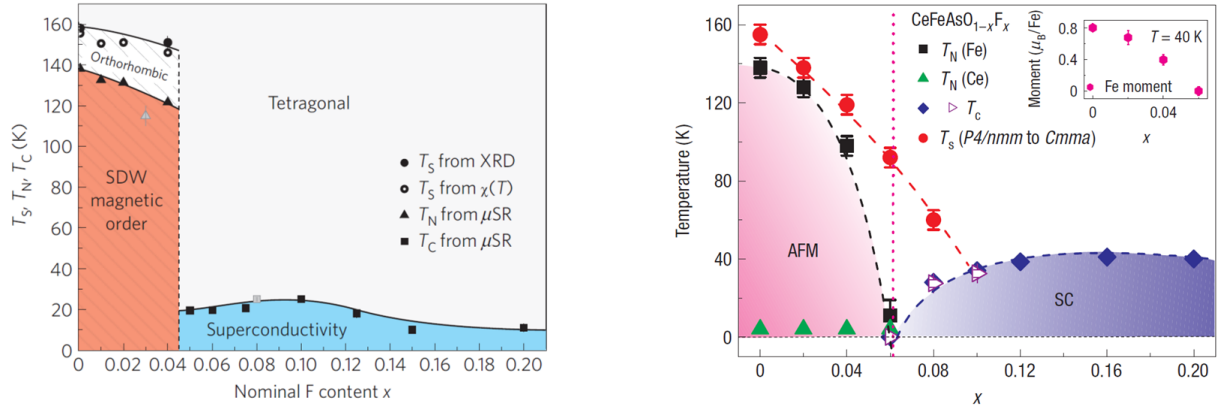
Figure 1.1: Crystal structure of  $R\text{FePnO}$ .

conduction layers and  $RO$  insulation layers. Therefore, physical properties of  $R\text{FePnO}$ , such as electrical resistivity and the critical magnetic field, show strong 2-dimensionality.  $\text{SmFeAs}(\text{O}, \text{F})$  [3] and  $(\text{Gd}, \text{Th})\text{FeAsO}$  [4] in this system shows superconductivity at  $T_c \sim 55$  K, which is the highest in all iron-based superconductors. Almost all experimental studies on this system are performed by using polycrystalline samples because of the difficulty to grow large single crystals. Then clarification of physical properties of 1111 system is not advanced compared with other systems, such as 122 and 11 ones.

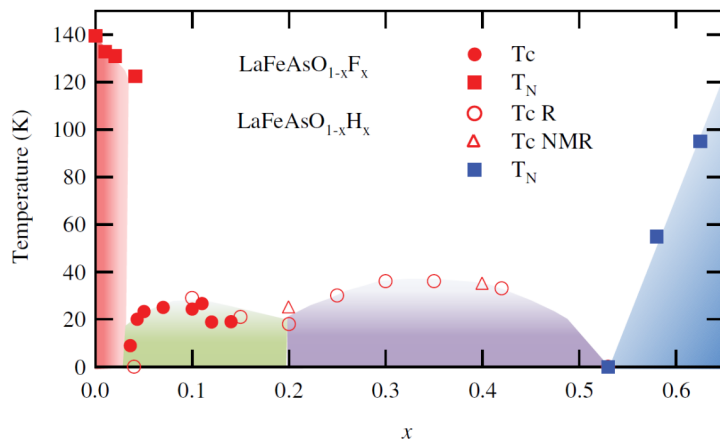
The emerging process of superconductivity is different between the cases of  $R\text{FeAsO}$  and  $R\text{FePO}$ . In the case of  $R\text{FeAsO}$ , the structural phase transition from a tetragonal lattice to an orthorhombic one and the magnetic phase transition to a spin density wave (SDW) -type AFM order occurs at  $T_s$  and  $T_N \sim 150\text{K}$ . Superconductivity emerges by electron doping to FeAs-layers, which is often accomplished by substituting O with F. The electronic phase diagrams of  $\text{LaFeAsO}_{1-x}\text{F}_x$  and  $\text{CeFeAsO}_{1-x}\text{F}_x$  are shown in Figure 1.2 [5, 6]. The AFM order is gradually suppressed and the superconducting state is enhanced for O/F substitution in both cases of  $\text{LaFeAsO}_{1-x}\text{F}_x$  and  $\text{CeFeAsO}_{1-x}\text{F}_x$ . The maximum  $T_c$  reaches 26 K ( $R = \text{La}$ ) - 55 K ( $R = \text{Sm}$ ) in the case of O/F substitution and the F concentration is about 10 - 15%.

Not only O/F substitution, but also O/H substitution, O deficiency and Fe/Co substitution are electron doping ways. The O/H substitution limit is much higher than the O/F substitu-




 Figure 1.2: Electronic phase diagrams of  $\text{LaFeAsO}_{1-x}\text{F}_x$  and  $\text{CeFeAsO}_{1-x}\text{F}_x$  [5, 6].

tion one. The electronic phase diagrams of  $\text{LaFeAsO}_{1-x}\text{H}_x$  is shown in Figure 1.3 [7]. Two superconducting domes are coupled and a new AFM order emerges at  $x \sim 0.6$ . The new AFM order seems to be caused by the nesting between electron FSs. O deficiency causes similar effect to O/F substitution [8]. Fe/Co substitution also shows superconductivity, but the  $T_c$  is much lower than that of O/F substitution [9]. This may be caused by the substitution in the FeAs conduction layers. On the other hand,  $\text{RFePO}$  does not have the above structural and magnetic transitions [1]. Superconductivity emerges without carrier doping and  $T_c$  is 2 - 5 K. Exceptionally,  $\text{CeFePO}$  shows heavy fermion-like behavior [10].


 Figure 1.3: Electronic phase diagram of  $\text{LaFeAsO}_{1-x}\text{H}_x$  [7].

### 1.1.3 122-type iron pnictides

122-type iron pnictides  $AeFe_2As_2$  ( $Ae = Ca, Sr, Ba$  of alkaline-earth metals or  $Eu$ ) are also one of representative iron-based superconductors and called 122 system from the compositional ratio of  $Ae : Fe : As = 1 : 2 : 2$ . The crystal structure of  $AeFe_2As_2$  is  $ThCr_2Si_2$ -type (tetragonal,  $I4/mmm$ ) and illustrated in Figure 1.4.  $AeFe_2As_2$  also shows the structural and

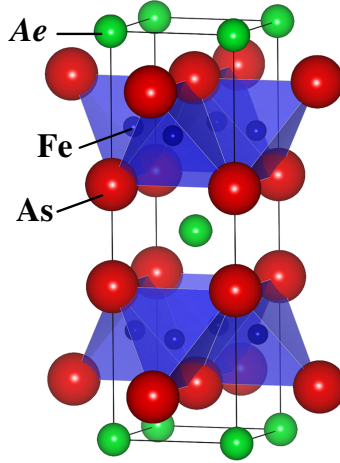
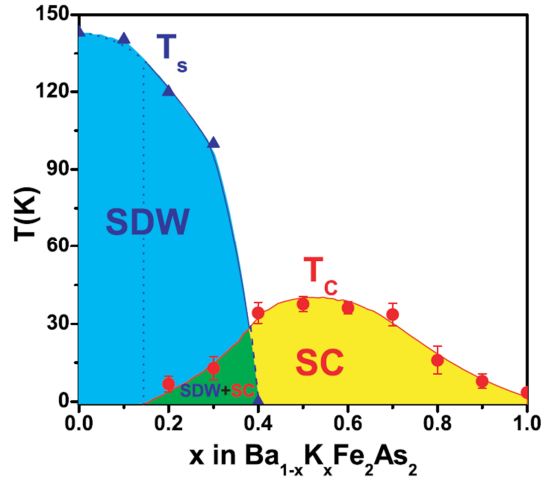


Figure 1.4: Crystal structure of  $AeFe_2As_2$ .

the AFM transitions at low temperatures.  $T_s$  and  $T_N$  changes from  $\sim 200$  K ( $Ae = Sr$ ) to  $\sim 140$  K ( $Ae = Ba$ ) [11, 12]. Superconductivity emerges by substituting each element, such as  $Ae \rightarrow Na$  or  $K$  (hole doping),  $Fe \rightarrow Co$  or  $Ni$  (electron doping) and  $As \rightarrow P$  (chemical pressure inducing). Large single crystals are obtained by using a self flux method in this system. Then experimental studies on 122 system is the most advanced in all iron pnictide superconductors.

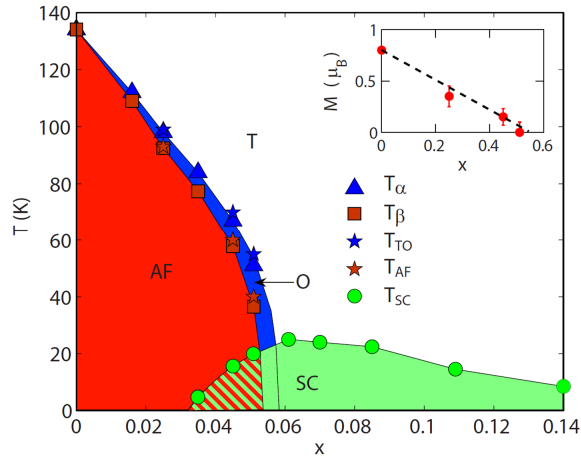
#### Hole-doped system

Hole doping is mainly accomplished by substituting  $Ae$  with alkali metal  $A = Na, K$ , and so on. The electronic phase diagram of  $Ba_{1-x}K_xFe_2As_2$  is shown in Figure 1.5 [13]. Superconductivity emerges in the wide region of  $x = 0.2 - 1.0$ .  $T_c$  reaches 38 K at  $x = 0.4$ , which is the highest in 122 systems except for a non-bulk superconductor  $Ca_{1-x}R_xFe_2As_2$  [14].


 Figure 1.5: Electronic phase diagram of  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  [13].

### Electron-doped system

Electron doping is mainly accomplished by substituting Fe with transition metal  $TM = \text{Co}$ , Ni, and so on. The electronic phase diagram of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  is shown in Figure 1.6 [15]. The  $T_c$  of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  is lower than that of  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  and  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ . This seems to be caused by the disorder to 3d electron of Fe.


 Figure 1.6: Electronic phase diagram of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  [15].

### Pressure-induced system

Chemical pressure inducing is accomplished by substituting As with P. The temperature dependence of the electrical resistivity and the electronic phase diagram of  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  are presented in Figure 1.7 [16]. The maximum  $T_c$  reaches 30 K at  $x = 0.33$ . Temperature

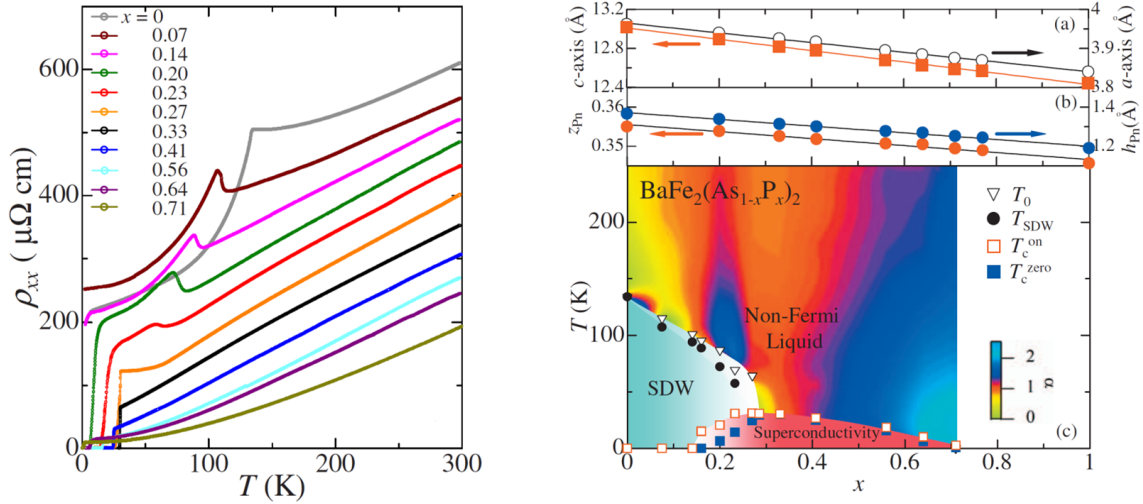


Figure 1.7: Temperature dependence of electrical resistivity (Left) and electronic phase diagram (Right) of  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  [16].

dependence of electrical resistivity shows the  $T$ -linear behavior and  $|R_H|$  is enhanced at  $x = 0.33$ . These behaviors suggest that  $x \sim 0.3$  is the quantum critical point (QCP) which shows non-Fermi liquid-like behaviors.  $T_c$  disappears and temperature dependence of electrical resistivity shows  $\sim T^2$  behavior at  $x \sim 0.7$ . Not only chemical pressure but also physical pressure promotes superconductivity.  $T_c$  reaches 30 K under 4 GPa in the case of  $\text{BaFe}_2\text{As}_2$  [17].

#### 1.1.4 111-type iron pnictides

111-type iron pnictides are composed of  $\text{AFePn}$  ( $A = \text{Li, Na}$  and  $Pn = \text{P, As}$ ). The crystal structure of  $\text{AFePn}$  is  $\text{PbClF}$ -type (tetragonal /  $P4/nmm$ ) and illustrated in Figure 1.8 [18]. They have to be taken in inert gas to avoid reaction with air.  $\text{LiFeAs}$  and  $\text{LiFeP}$  are stoichiometric superconductors and  $T_c$  is 18 K and 5 K, respectively [19, 20]. Temperature dependence of electrical resistivity of both  $\text{LiFeAs}$  and  $\text{LiFeP}$  shows  $\sim T^2$  behavior [21].

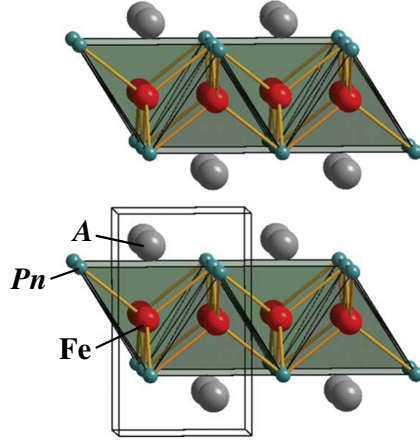


Figure 1.8: Crystal structure of  $AFePn$  [18]

### 1.1.5 42622-type iron pnictides

Representative 42622-type iron pnictides are  $Sr_4V_2O_6Fe_2As_2$  ( $T_c = 37$  K) [22],  $Sr_4Sc_2O_6Fe_2P_2$  ( $T_c = 17$  K) [23] and  $Ca_4Al_2O_6Fe_2Pn_2$  ( $Pn = As, P$ ) ( $T_c = 28$  K and 17 K) [24], which are stoichiometric superconductors. The crystal structure of  $Sr_4Sc_2O_6Fe_2P_2$  (tetragonal,  $P4/nmm$ ) is illustrated in Figure 1.9.  $T_c = 17$  K of  $Sr_4Sc_2O_6Fe_2P_2$  and  $Ca_4Al_2O_6Fe_2P_2$  is the highest in

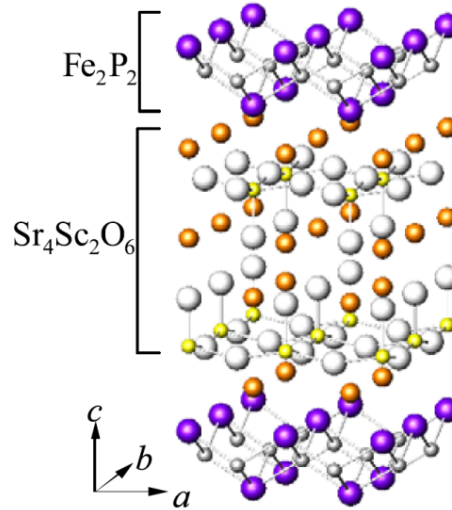


Figure 1.9: Crystal structure of  $Sr_4Sc_2O_6Fe_2P_2$  [23].

pure iron phosphide superconductors.

P/As substitution effect is studied in  $Ca_4Al_2O_6Fe_2Pn_2$  [25]. The electronic phase diagram of  $Ca_4Al_2O_6Fe_2(As_{1-x}P_x)_2$  is shown in Figure 1.10. Interestingly, a new AFM order is discovered

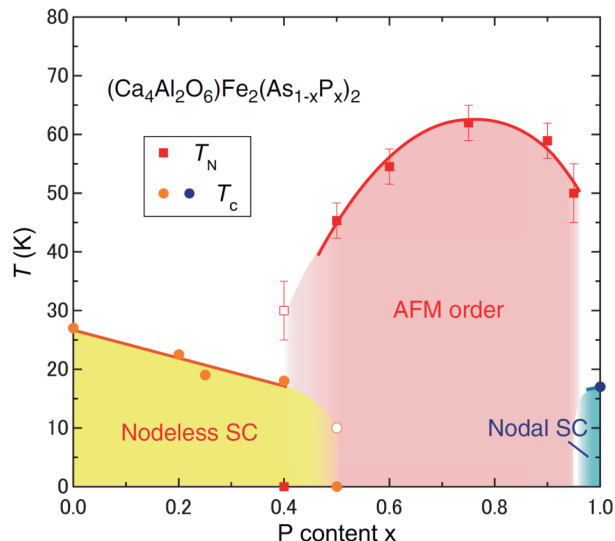


Figure 1.10: Electronic phase diagram of  $\text{Ca}_4\text{Al}_2\text{O}_6\text{Fe}_2(\text{As}_{1-x}\text{P}_x)_2$  [25].

at  $x = 0.5 - 0.95$  by the NMR measurement. The AFM order may be an essential one between nodal and nodeless superconducting states for many iron pnictide superconductors.

## 1.2 Theoretical studies on iron pnictide superconductors

### 1.2.1 Band structure and Fermi surfaces of 1111-type iron pnictides

The electronic states of  $\text{LaFeAsO}$  and  $\text{LaFePO}$  are predicted by band calculation [26]. As a result, five  $3d$  electron bands per 1 Fe locate in the vicinity of Fermi level ( $E_F$ ). Calculated band structures of  $\text{LaFeAsO}$  and  $\text{LaFePO}$  are shown in Figure 1.11. The unit cell is defined as that for 2 Fe atoms. In both cases of  $\text{LaFeAsO}$  and  $\text{LaFePO}$ , two hole bands (around  $\Gamma - Z$ ) and two electron bands (around  $M - A$ ) having  $d_{xz}$  and  $d_{yz}$  orbital characters cross  $E_F$ . Additionally, the 2-dimensional hole band having  $d_{xy}$  orbital character also crosses  $E_F$  around  $\Gamma - Z$  in  $\text{LaFeAsO}$ . On the other hand, the 3-dimensional band having  $d_{z^2}$  orbital character also crosses  $E_F$  around  $Z$  in  $\text{LaFePO}$ . This difference is not caused by the lattice constant  $a$  or  $c$  but the local crystal structural parameters of  $Pn$  around Fe. Calculated 3-dimensional Fermi surfaces (FSs) of  $\text{LaFeAsO}$  and  $\text{LaFePO}$  are illustrated in Figure 1.12. The unit cell is defined as that for 2 Fe atoms. 2-dimensional cylindrical FSs are predicted in both of  $\text{LaFeAsO}$  and  $\text{LaFePO}$ , which reflect strong 2-dimensionality of 1111 system. Three cylindrical hole FSs around  $\Gamma - Z$  and two cylindrical electron FSs around  $M - A$  are observed in  $\text{LaFeAsO}$ . On the

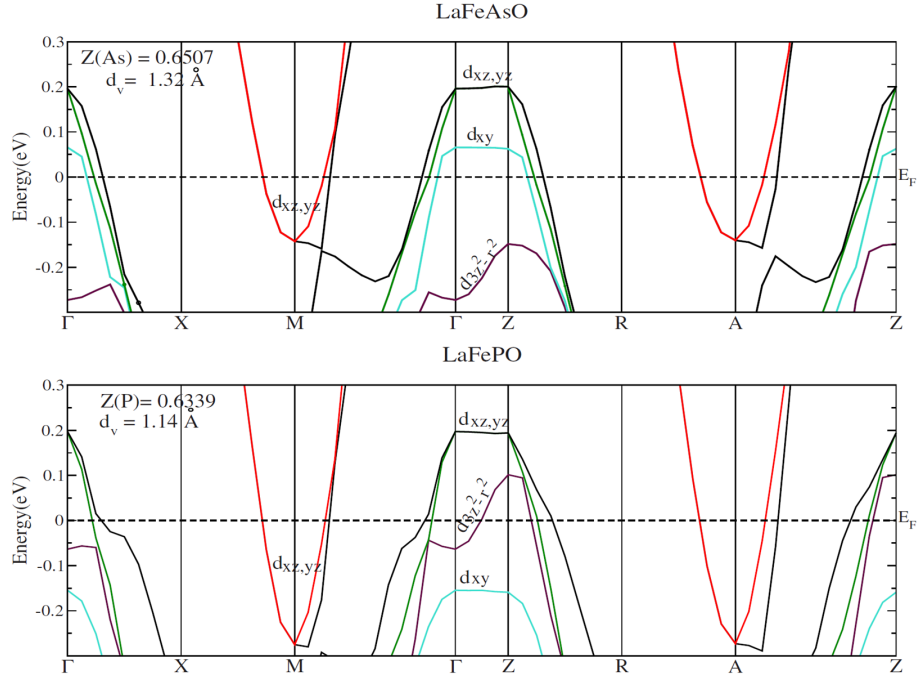


Figure 1.11: Calculated band structures of LaFeAsO (above) and LaFePO (below) [26]. The unit cell is defined as that for 2 Fe atoms.

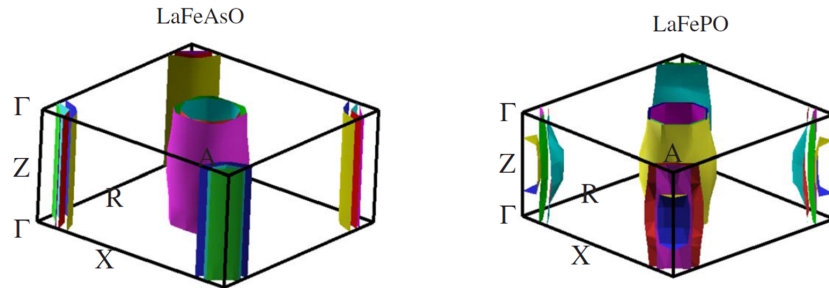


Figure 1.12: Calculated 3-dimensional FSs of LaFeAsO and LaFePO [26]. The unit cell is defined as that for 2 Fe atoms.

other hand, two cylindrical hole FSs around  $\Gamma$  - Z, two cylindrical electron FSs around M - A and one closed hole FS around Z are observed in LaFePO. 2-dimensionality of LaFeAsO is stronger than that of LaFePO. This tendency of FSs warping in iron phosphides confirmed in comparison between BaFe<sub>2</sub>As<sub>2</sub> and BaFe<sub>2</sub>P<sub>2</sub>.

### 1.2.2 Spin fluctuation theory

The Cooper pair formation mechanism in iron based superconductors is not electron-phonon coupling because of the high  $T_c$ . Then the other superconducting mechanism mediated by spin fluctuation is discussed.  $s_{\pm}$  superconducting gap state, whose sign is different between hole and electron FSs, is suggested by Kuroki *et al* [27]. 2-dimensional FSs of 1111 system and superconducting gap state are shown in Figure 1.13. The unit cell is defined as that for 1 Fe atom. In the case of RFeAsO, the FSs are shown in Figure 1.13 (Left). Nesting vectors are

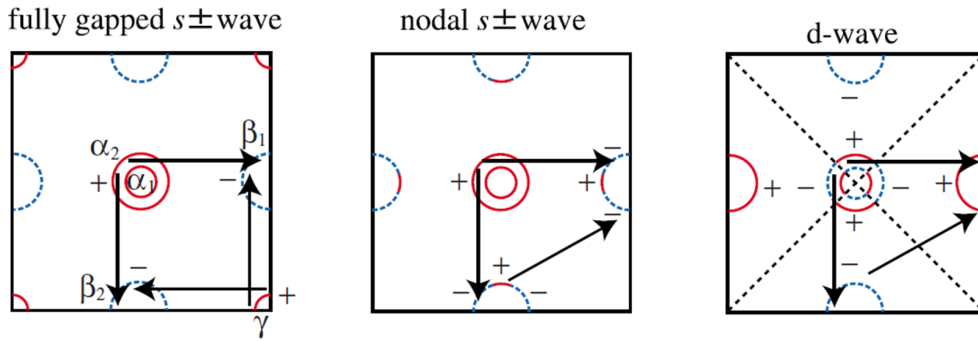


Figure 1.13: 2-dimensional FSs of 1111 system and nesting vectors between FSs [27]. The unit cell is defined as that for 1 Fe atom.

mediated to the direction of  $(\pi, 0)$  and  $(0, \pi)$ . In the case of RFePO, the FSs are shown in Figure 1.13 (Center and Right). Nesting vectors are mediated to the direction of  $(\pi, 0)$  and  $(\pi, \pi)$ .

## 1.3 Experimental studies on iron pnictide superconductors

### 1.3.1 Correlations between crystal structural parameters and $T_c$

The mechanism to determine  $T_c$  of iron based superconductor is not clear yet. Phenomenologically, the correlation between  $Pn$ -Fe- $Pn$  bond angle  $\alpha$  and  $T_c$  is suggested by Lee *et al* [28].  $\alpha$  dependence of  $T_c$  (so-called ‘Lee-plot’) is presented in Figure 1.14. This plot suggests that



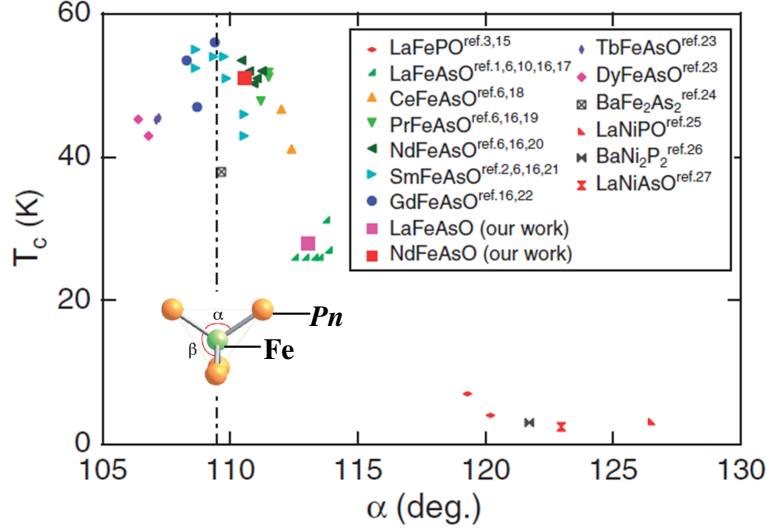


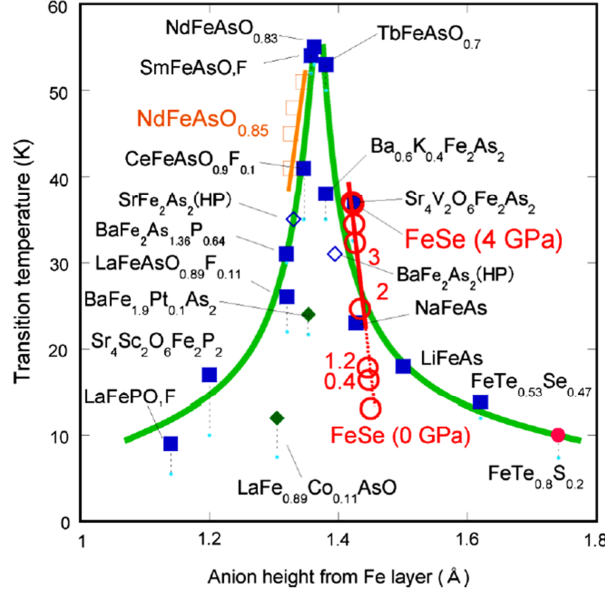
Figure 1.14:  $Pn$ -Fe- $Pn$  bond angle  $\alpha$  dependence of  $T_c$  [28].

$T_c$  reaches the maximum value when  $\alpha$  approaches  $109.47^\circ$ , namely when  $\text{FeAs}_4$  approaches regular tetrahedra.  $T_c$  increases from  $\text{LaFeAsO}$  to  $\text{SmFeAsO}$  and decreases from  $\text{SmFeAsO}$  to  $\text{DyFeAsO}$  in 1111 system. The bond angle  $\alpha$  is regarded as the most important parameter by many researchers because of the clear correlation. However, iron phosphides, such as  $\text{LiFeP}$ , do not follow this plot. As a result, Lee-plot looks correct only in the special case that targets for comparison are iron arsenides and have the same crystal structure.

The other parameter to determine  $T_c$  was suggested by Kuroki *et al.* They suggest the pnictogen height from Fe-layer  $h_{Pn}$  is the key parameter to change FSs, nesting condition and superconducting gap structure.  $h_{Pn}$  dependence of  $T_c$  is presented in Figure 1.15. In this plot, iron arsenides with large  $h_{Pn}$  have higher  $T_c$  than iron phosphides with small  $h_{Pn}$ . This  $h_{Pn}$  plot is appropriate to explain the difference between  $\text{FeAs}$  and  $\text{FeP}$  systems in the same system.

### 1.3.2 Superconducting gap structure of various iron pnictide superconductors

According to the suggestion by Kuroki *et al.*, the local crystal structural parameter of  $Pn$  around Fe can be a key parameter to determine  $T_c$  and superconducting gap symmetry. The local crystal structural parameter is quite different between the cases of  $Pn = \text{P}$  and As. Then previous studies on the superconducting gap structure are summarized below in order to compare those of iron arsenide and iron phosphide superconductors. The superconducting gap symmetry


 Figure 1.15:  $h_{Pn}$  dependence of  $T_c$  [29].

and size are often determined by measurements of magnetic penetration depth (MPD), angle-resolved photoemission spectroscopy (ARPES) and point-contact Andreev reflection (PCAR).

### Magnetic penetration depth

Temperature dependence of MPD gives the information on superconducting gap symmetry. In the case of nodeless superconductors, the temperature dependence of MPD is described as

$$\frac{\Delta\lambda(T)}{\lambda(0)} \approx \sqrt{\frac{\pi\Delta}{2k_B T}} \exp\left(-\frac{\Delta}{k_B T}\right) \quad (1.1)$$

where  $\Delta$  is superconducting gap size and  $\Delta\lambda(T) = \lambda(T) - \lambda(0)$ .  $\Delta\lambda(T)$  hardly shows temperature dependence at very low temperatures. On the other hand, in the case of nodal superconductors with line nodes, it is described as

$$\frac{\Delta\lambda(T)}{\lambda(0)} \approx \frac{\ln 2}{\Delta} k_B T. \quad (1.2)$$

Then  $\Delta\lambda(T)$  shows  $T$ -linear behavior.

Temperature dependence of MPD of 1111-type, 122-type and 111-type iron pnictide superconductors are presented in Figures 1.16, 1.17 and 1.18 (Left) [30, 31, 32, 33]. Temperature dependence of  $\Delta\lambda(T)$  of LaFePO, BaFe<sub>2</sub>(As<sub>0.67</sub>P<sub>0.33</sub>)<sub>2</sub> and LiFeP shows  $T$ -linear behavior at very low temperatures. Therefore, nodal superconducting gap state arises in these iron phosphide

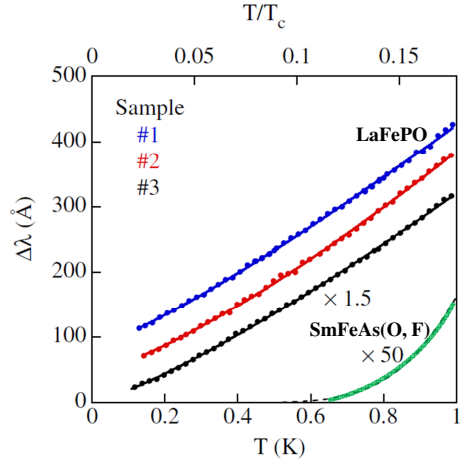


Figure 1.16: Temperature dependence of MPD of 1111-type iron pnictide superconductors [30, 31].

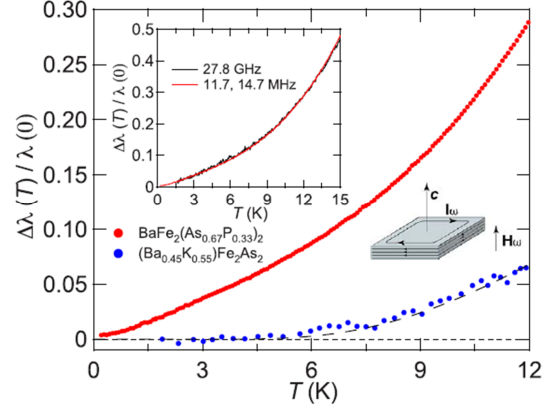


Figure 1.17: Temperature dependence of MPD of 122-type iron pnictide superconductors [32].

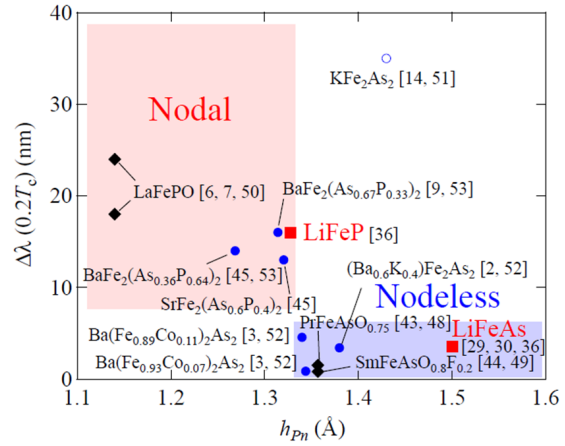
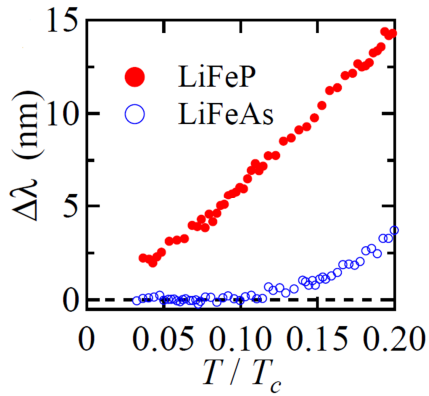


Figure 1.18: Temperature dependence of MPD of 111-type iron pnictide superconductors (Left) and the correlation between  $h_{Pn}$  and  $\Delta\lambda(T)$  at  $T = 0.2T_c$  (Right) [33].

superconductors. On the other hand,  $\Delta\lambda(T)$  of  $\text{SmFeAs}(\text{O}, \text{F})$ ,  $\text{Ba}_{0.45}\text{K}_{0.55}\text{Fe}_2\text{As}_2$  and  $\text{LiFeAs}$  hardly shows temperature dependence and it is nearly zero. Then, nodeless superconducting gap state arises in these iron arsenide superconductors.

The correlation between  $h_{P_n}$  and  $\Delta\lambda(T)$  at  $T = 0.2 T_c$  is presented in Figure 1.18 (Right) [33]. According to the plot, iron arsenide superconductors with large  $h_{P_n}$  have small  $\Delta\lambda(T)$  and it reflects the nodeless superconducting gap state, except for heavily hole-doped  $\text{KFe}_2\text{As}_2$ . On the other hand, iron phosphide superconductors with low  $h_{P_n}$  have large  $\Delta\lambda(T)$  and it suggests the nodal superconducting gap state.  $h_{P_n} = 1.34 \text{ \AA}$  is the boundary of nodal and nodeless states in this plot.

### Angle-resolved photoemission spectroscopy

Superconducting gap causes the decrease of the density of state (DOS) on the energy distribution curve (EDC) spectrum in ARPES measurements. Superconducting gap size is estimated by the difference between Fermi level and the edge of EDC spectrum. Superconducting gap symmetry is determined by the measurement of the superconducting gap size of each position on the FS. Superconducting gap of  $\text{NdFeAsO}_{0.85}\text{F}_{0.15}$  and  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$  are shown in Figures 1.19 and 1.20 [34, 35]. One nodeless superconducting gap with  $\Delta = 15 \text{ meV}$  on the hole FS is

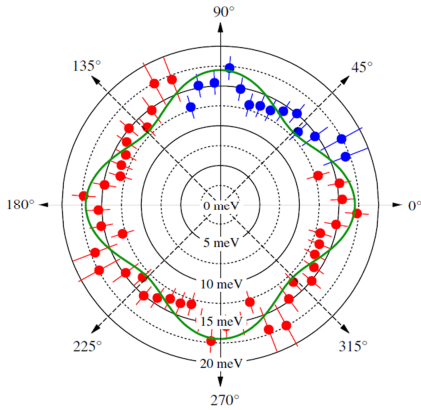


Figure 1.19: Superconducting gap of  $\text{NdFeAsO}_{0.85}\text{F}_{0.15}$  [34].

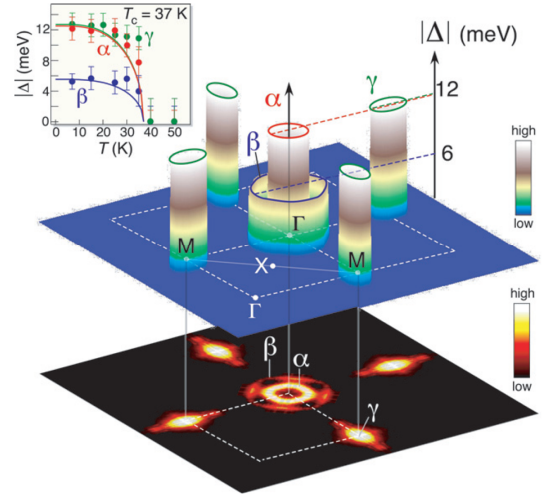


Figure 1.20: Superconducting gap of  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$  [35].

observed in  $\text{NdFeAsO}_{0.85}\text{F}_{0.15}$ . Two nodeless superconducting gap with  $\Delta = 12 \text{ meV}$  on inner hole and electron FSs and one nodeless superconducting gap with  $\Delta = 6 \text{ meV}$  on outer hole FS are observed in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ .

On the other hand, superconducting gap structures of pure iron phosphide superconductors, such as  $R\text{FePO}$ ,  $\text{LiFeAs}$  and  $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{P}_2$ , are not observed in ARPES measurements because of the low  $T_c$  or the difficulty to obtain large single crystals. Instead of pure iron phosphides, superconducting gap structure of  $\text{BaFe}_2(\text{As}, \text{P})_2$  is measured by some groups. According to the ARPES measurement by Feng *et al.*, the superconducting gap on the outer hole FS goes to zero around Z, namely horizontal line nodes are suggested on the outer hole FS around Z [36]. However, the nodal loop structure on electron FSs is suggested by the angle-resolved thermal conductivity measurement [37]. Then the location of the superconducting gap node has not been consented.

### Point-contact Andreev reflection

PCAR is also a tool to determine the gap structure. If one incident electron with the energy  $E < \Delta$  is shot from a metal to a superconductor with the superconducting gap energy  $\Delta$ , one Cooper pair is formed in the superconductor and one hole is reflected on the interface between the metal and the superconductor (Andreev reflection). In principle, the electrical conductivity is enhanced twice than the normal conductivity. If  $E > \Delta$ , Andreev reflection does not occur and the electrical conductivity does not change. These behaviors are analyzed by the Blonder, Tinkham and Klapwijk (BTK) model and the superconducting gap size and symmetry are calculated. Unlike MPD and ARPES measurements, PCAR can be measured by using polycrystalline samples.

In the studies on iron-based superconductors, similar results on the superconducting gap structure to MPD and ARPES measurements are observed in many 1111 and 122 systems. As the original achievement of PCAR spectroscopy, polycrystalline  $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{P}_2$  is measured [38]. As a result, a zero-bias conduction peak, which is the evidence of nodal superconducting gap, is observed in the measurement.

### Summary

Almost all experiments of MPD, ARPES and PCAR suggest that nodeless superconductivity emerges in iron arsenide superconductors and nodal superconductivity emerge in iron phosphide superconductors. This difference between iron arsenides and iron phosphides seems to be caused by the difference of local crystal structural parameters of  $Pn$  around Fe, such as  $h_{Pn}$  and  $\alpha$ . In addition to that fact, the existence of the AFM order between nodal and node-

less superconducting states is also suggested by Mukuda *et al.* from the NMR measurement of  $\text{Ca}_4\text{Al}_2\text{O}_6\text{Fe}_2(\text{As}_{1-x}\text{P}_x)_2$  [25]. The AFM order, the nodal and nodeless superconducting states, which are plotted in the 2-dimensional plane of structural parameters of the nearest-neighbor Fe-Fe distance  $a_{\text{Fe-Fe}}$  and  $h_{Pn}$ , is shown in Figure 1.21.

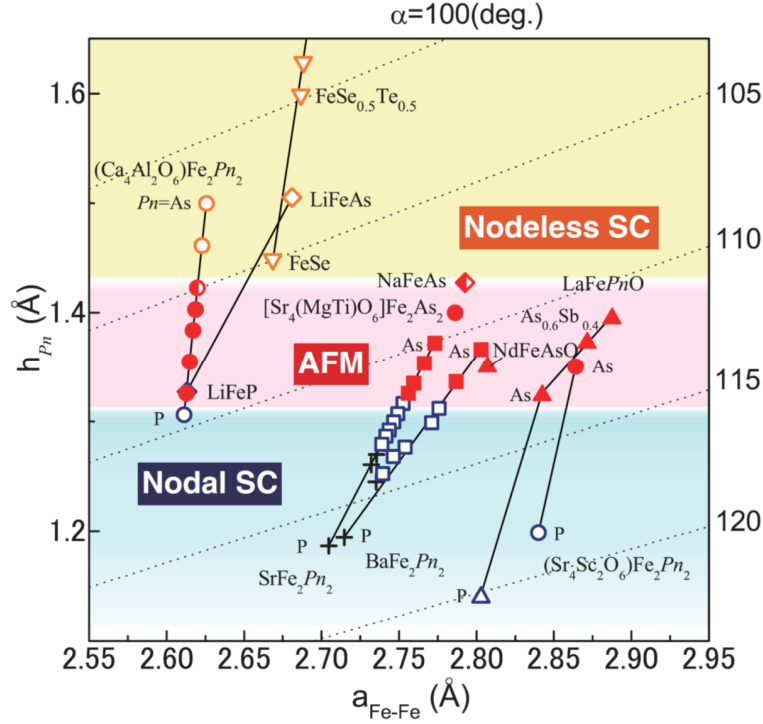


Figure 1.21: The AFM order, the nodal and nodeless superconducting states in iron-based superconductors. They are plotted in the 2-dimensional plane of structural parameters of the nearest-neighbor Fe-Fe distance  $a_{\text{Fe-Fe}}$  and  $h_{Pn}$  [25].

### 1.3.3 P/As substitution studies on 1111-type iron pnictides

P/As substitution changes the local crystal structural parameters around Fe effectively. There are several reports on P/As substitution effect in 1111-type iron pnictides.



The electronic phase diagram of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{1-y}\text{F}_y$  ( $y = 0, 0.05, 0.1$ ) is presented in Figure 1.22, where the result of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  is my data in this thesis. In the case of  $y = 0$ , two superconducting domes (SC1 and SC2) are observed and SC1 dome seems to occur in the vicinity of QCP. Additionally, a new AFM order (AFM2) between SC1 and SC2 is also detected

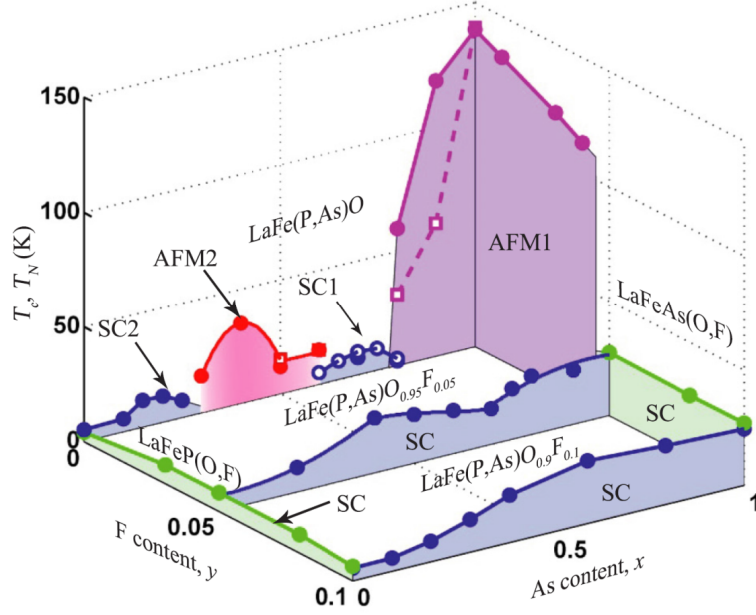


Figure 1.22: Electronic phase diagram of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{1-y}\text{F}_y$  ( $y = 0, 0.05, 0.1$ ) [39].

by the NMR measurement. The emergence of the new AFM order in P/As substitution system is also observed in  $\text{Ca}_4\text{Al}_2\text{O}_6\text{Fe}_2(\text{As}_{1-x}\text{P}_x)_2$ . In the case of  $y = 0.05$ , superconductivity emerges in all  $x$  region. The maximum  $T_c$  is observed at  $x = 0.4$  and  $1.0$ , where AFM order exists at  $y = 0$ . Therefore, the correlation between superconductivity and AFM fluctuation is suggested. In the case of  $y = 1.0$ ,  $T_c$  increases with  $x$  in the region of  $x = 0 - 0.6$  and does not change in the region of  $x = 0.6 - 1.0$  at  $y = 0.1$ .

### **$\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ and $\text{CeFeAs}_{1-x}\text{P}_x\text{O}_{0.95}\text{F}_{0.05}$**

Electronic phase diagrams of  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  and  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}_{0.95}\text{F}_{0.05}$  are shown in Figure 1.23 [40, 41]. As for  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ , in the case of  $\text{CeFeAsO}$ , structural and magnetic phase transitions occur at  $T_s$  and  $T_N \sim 140\text{K}$  and AFM order caused by  $4f$  electron of Ce emerges at  $T_N = 4\text{K}$ . On the other hand,  $\text{CeFePO}$  is the heavy fermion system. The AFM order caused by  $3d$  electron of Fe disappears at  $x = 0.4$  and FM order emerges at  $x = 0.35 - 0.9$ . The disappearance of structural and magnetic phase transitions is confirmed by the neutron scattering measurement. Then  $x = 0.4$  is regarded as QCP.

As for  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}_{0.95}\text{F}_{0.05}$ , superconductivity emerges at  $x = 0 - 0.55$  and FM order of Ce emerges at  $x = 0.45 - 1.0$ .

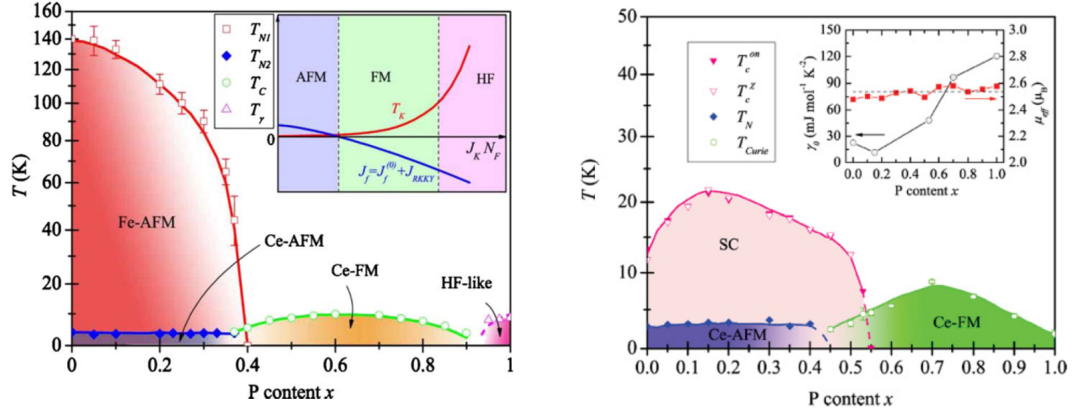


Figure 1.23: Electronic phase diagrams of  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$  (Left) and  $\text{CeFeAs}_{1-x}\text{P}_x\text{O}_{0.95}\text{F}_{0.05}$  (Right) [40, 41].

### $\text{SmFeAs}_{1-x}\text{P}_x\text{O}$

Temperature dependence of electrical resistivity of  $\text{SmFeAs}_{1-x}\text{P}_x\text{O}$  is shown in Figure 1.24 [42]. Superconductivity emerges at  $x = 0.565$ . This behavior is similar to  $\text{LaFeP}_{0.3}\text{As}_{0.7}\text{O}$ .

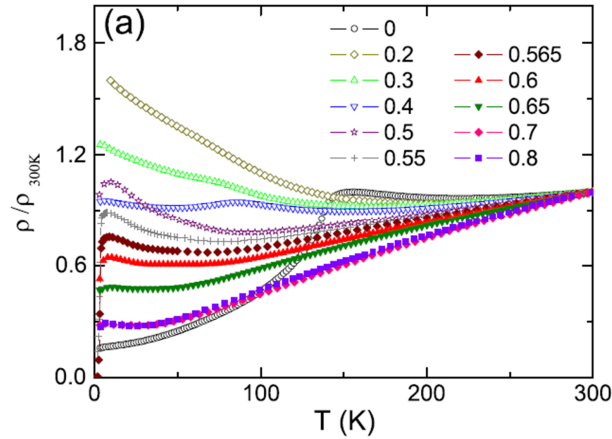


Figure 1.24: Temperature dependence of electrical resistivity of  $\text{SmFeAs}_{1-x}\text{P}_x\text{O}$  [42].

### 1.3.4 ARPES measurements in 1111 system

#### LaFePO and LaFeAsO

FS mapping at  $k_z = 0$  of LaFePO and LaFeAsO is presented in Figure 1.25 [43, 44]. As for LaFePO, one large hole FS and two small hole FSs are observed around  $\Gamma$ . The two small FSs are nearly degenerated. Two electron FSs are observed around M. The positions and the



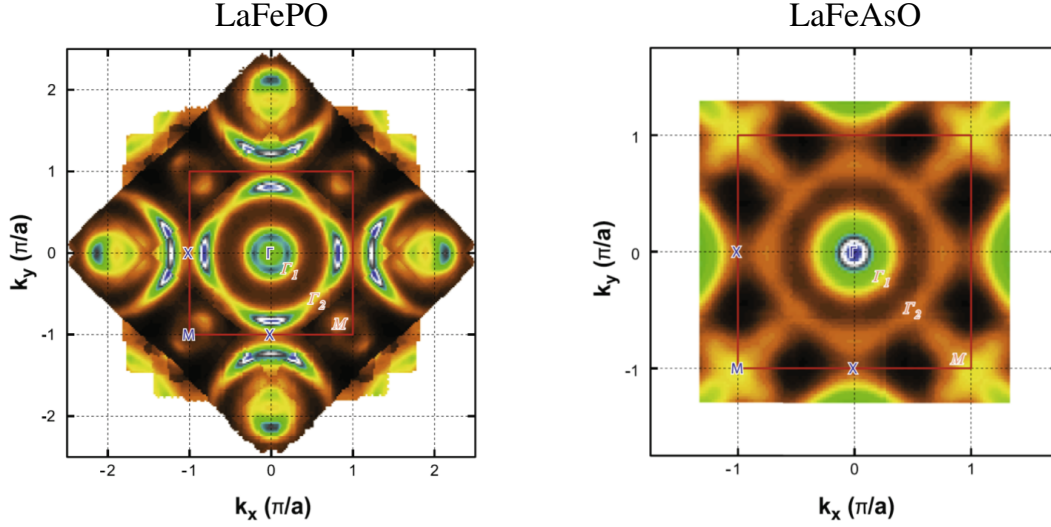


Figure 1.25: FS mapping at  $k_z = 0$  of LaFePO (Left) and LaFeAsO (Right) [43, 44]

sizes of the two small hole FSs and the two electron FSs are nearly consistent with theoretical calculation. As for LaFeAsO, one large hole FS, one small hole FS and one pseud-hole FS are observed around  $\Gamma$ . Two electron FSs are observed around  $M$ . The largest hole FS is observed in all ARPES measurements of 1111 system, but the enlargement of the hole FS is quite unlikely because of the electrical neutrality.

FSs of LaFePO is also observed by the measurement of the de Haas-van Alphen (dHvA) effect [45]. The FSs of LaFePO determined by the dHvA measurement is shown in Figure 1.26. Two hole FSs and two electron FSs are detected, but one small 3-dimensional hole FS around  $Z$  is not observed. The large hole FS in the ARPES measurements is not detected. Therefore, the large hole FS may be caused by the surface effect.

### PrFeAsO<sub>0.7</sub>

FS mapping at  $k_z = 0$  of PrFeAsO<sub>0.7</sub> is shown in Figure 1.27 [46]. Three hole FSs around  $\Gamma$  and clover-shaped electron FSs around  $M$  are reported. The clover-shaped electron FSs are also reported in heavily hole-doped KFe<sub>2</sub>As<sub>2</sub>. This suggests that the electronic neutrality may be not obtained in the cleaved surface and the reconstruction of electronic state may occur on the sample surface.

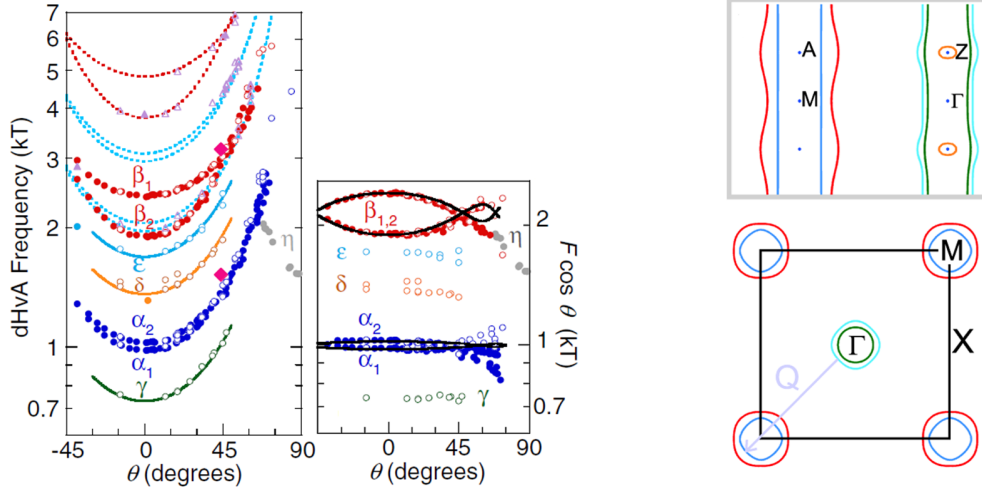


Figure 1.26: FSs of LaFePO observed in the dHvA measurement [45].

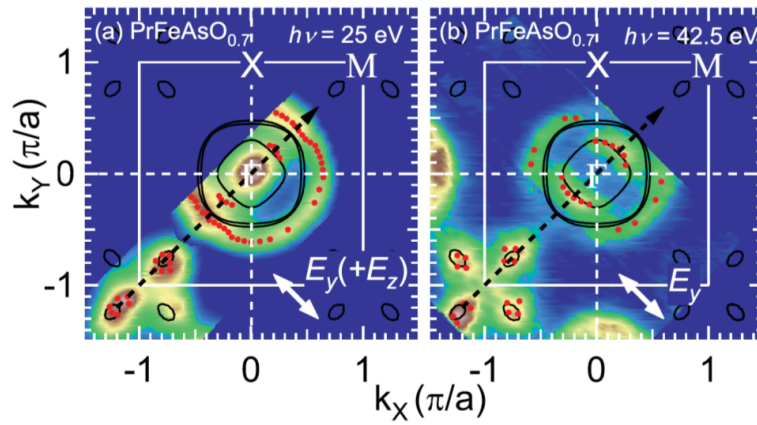


Figure 1.27: FS mapping at  $k_z = 0$  of  $\text{PrFeAsO}_{0.7}$  [46].

### NdFeAsO<sub>0.85</sub>F<sub>0.15</sub>

FS mapping at  $k_z = 0$  of NdFeAsO<sub>0.85</sub>F<sub>0.15</sub> is shown in Figure 1.28 [34]. One large hole FS around  $\Gamma$  and one electron FS around M are observed. The nodeless superconducting gap with  $\Delta = 15$  meV is reported on the hole FS.

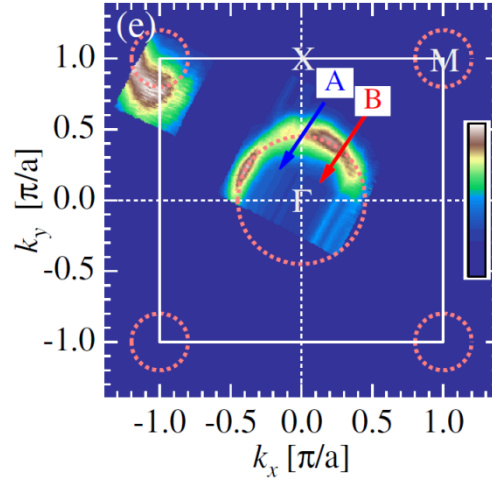


Figure 1.28: FS mapping at  $k_z = 0$  of NdFeAsO<sub>0.85</sub>F<sub>0.15</sub> [34].

### SmFeAsO

FS mapping at  $k_z = 0$  of SmFeAsO is shown in Figure 1.29 [47]. The large hole FS around  $\Gamma$  is also reported and it is ascribed to the surface effect.

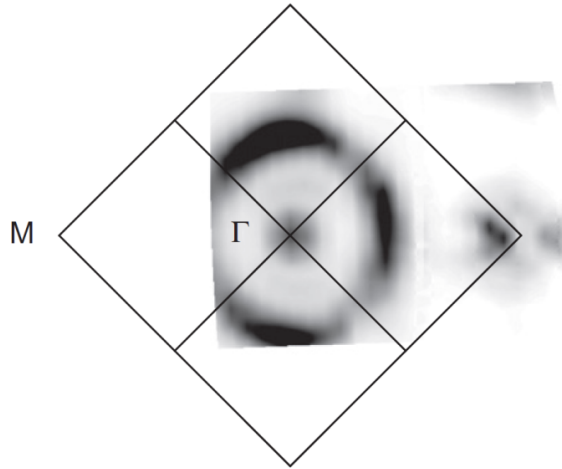


Figure 1.29: FS mapping at  $k_z = 0$  of SmFeAsO [47].

## Chapter 2

# Objective

Recently discovered iron-based superconductors have the second highest  $T_c$  following cuprates. They are important substances to clarify the superconducting mechanism with high  $T_c$ . In 1111-type iron pnictide superconductors  $R\text{FePnO}$ ,  $T_c$ , the structural and magnetic properties are different between  $R = \text{As}$  and  $R = \text{P}$ . In the case of  $R\text{FeAsO}$ , superconductivity emerges together with the suppression of the structural and magnetic transitions by F doping or F deficiency, and the maximum  $T_c$  reaches  $\sim 55$  K, which is the highest in iron-based superconductors. On the other hand, no structural and magnetic transitions exist and  $T_c$  is  $\sim 5$  K in the case of  $R\text{FePO}$ . Some empirical rules are proposed to explain the difference of  $T_c$  from the view point of the local crystal structural parameters around Fe, such as bond angle  $\alpha$  and pnictogen height  $h_{\text{Pn}}$ . However, it is not clear yet what electronic parameter is modified by these structural parameters. Although, some theories suggest that the antiferromagnetic fluctuation plays an important role for the appearance of superconductivity in the iron-based superconductors, there is no direct experimental evidence that  $T_c$  is correlated with the strength of antiferromagnetic fluctuation.

In order to find the key parameter to determine the  $T_c$  of iron-based superconductors, I studied P/As substitution effect of 1111-type iron pnictide superconductors by using transport and ARPES techniques. This P/As substituted 1111 system is appropriate to study the above relationship because (i) superconductivity emerges in both of  $R\text{FeAs}(\text{O}, \text{F})$  and  $R\text{FeP}(\text{O}, \text{F})$ , (ii)  $T_c$ , the local crystal structural parameters around Fe and perhaps strength of antiferromagnetic fluctuation drastically change with the substitution.

In part II, I present the studies on polycrystalline  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ). The purpose is to study the relationship among crystal structural parameters,  $T_c$  and transport properties in various  $R$  systems having various  $T_c$ , and to find the key parameter for supercon-

ductivity. The composition dependence of the crystal structural parameters,  $T_c$  and transport properties are discussed and several suggestive results are obtained. As results of the electrical resistivity measurements, two different superconducting  $x$  regions are suggested from  $x$  dependence of  $T_c$  and  $n$ , which is defined from  $\rho(T) = \rho_0 + AT^n$ . In the region of  $x < 0.6 - 0.8$ ,  $T_c$  and  $n$  correlate and  $T_c$  increases by the enhancement of AFM fluctuation. On the other hand, in the region of  $x > 0.6 - 0.8$ , no clear relationship between  $T_c$  and  $n$  is observed. Two scaling lines are also observed in the correlation between  $T_c$  and  $n$  and the different scaling lines may reflect the different FSs and nesting vectors.

In part III, I studied on single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O, F})$ . There are mainly three objectives to launch this study. First, I would like to establish the single crystal growth method of 1111-type iron pnictide superconductors because it is very difficult to obtain large-sized single crystals in 1111 system and successful examples are few in the world. Second, the transport properties including the anisotropy and no grain boundary effect can be measured by using the single-crystalline samples. The results also tell us whether the polycrystalline results in part II are intrinsic or not. Third, the band dispersion and the FSs are directly observed by the ARPES measurement. The third is the most important in this P/As substitution study. I would like to clarify the difference of the FS configuration between below and above  $x = 0.6 - 0.8$  where  $T_c$  and  $n$  show distinct  $x$  dependences.

## Part II

### Studies on Polycrystalline

$R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ )

## Chapter 3

# Experimental methodology

### 3.1 Synthesis

All processes of weighting and mixing the raw materials in this study were performed in an Ar-filled glove box. Both concentrations of O<sub>2</sub> and H<sub>2</sub>O in the glove box were kept less than 10 ppm.

#### 3.1.1 Synthesis of precursors *R*As and *RP* (*R* = La, Pr, Nd)

*R* ( = La, Pr, Nd) (3N, KOJUNDO CHEMICAL LABORATORY CO.,LTD (KCL.)), As (6N, FURUKAWA DENSHI CO.,LTD.) and P (5N, KCL.) were used to synthesize the precursors of *R*As and *RP*. First, *R* chips held in spindle oil were cleaned with hexane in order to remove the oil before the synthesis. This procedure was operated by using an ultrasonic cleaning device in the sequence of 10 min × 3 times. The mixture of *R* and hexane was filtered with a filtering paper. The remnant hexane around *R* was vaporized in vacuum and the cleaned *R* chips were stored in the globe box. Next, *R* and As (P) were mixed with the stoichiometric ratio of 1 : 1 and sealed in an evacuated silica tube ( $\sim 10^{-6}$  Torr) with the external diameter of 13 mm and the internal diameter of 11 mm. To prevent the explosion of the silica tube during heating, the length of sealed silica tubes should be 16 - 18 cm and the weights of As and P should be less than 1.0 g and 0.4 g, respectively. The *R* and As (P) in the sealed silica tube were heated and reacted at 900 °C (850 °C) in an electrical furnace. Temperature conditions for synthesis of *R*As and *RP* are illustrated in Figures 3.1 and 3.2, respectively.

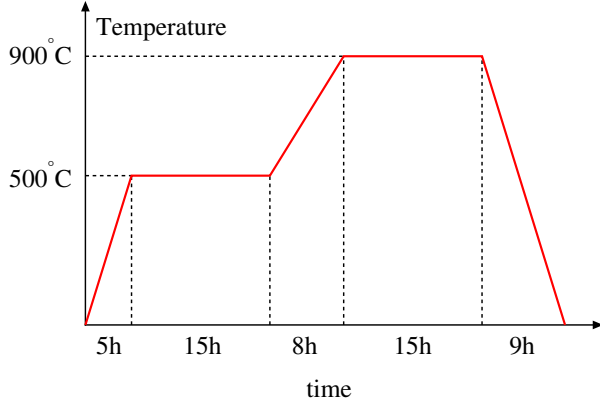


Figure 3.1: The temperature condition for synthesis of  $RAs$ .

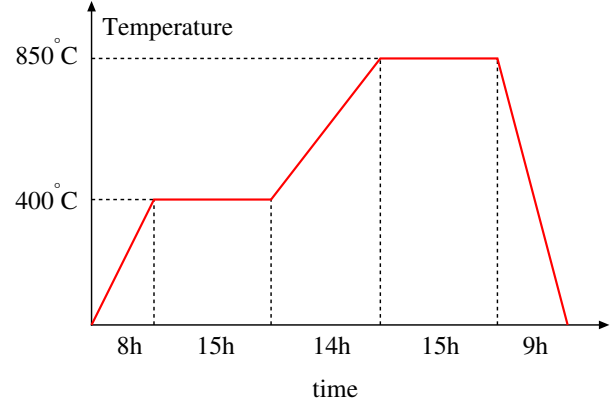
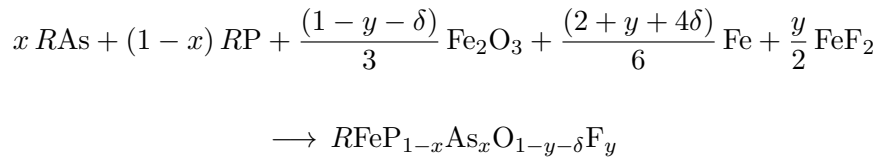


Figure 3.2: The temperature condition for synthesis of  $RP$ .

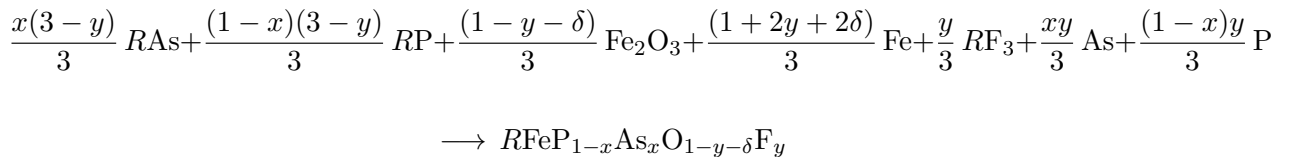
### 3.1.2 Synthesis of polycrystalline $RFeP_{1-x}As_xO_{0.9}F_{0.1}$ ( $R = La, Pr, Nd$ )

$RAs$ ,  $RP$ ,  $Fe_2O_3$  (4N, KCL.),  $Fe$  (5N, KCL.),  $FeF_2$  (2N, RARE METALLIC Co.,LTD.) and  $RF_3$  (5N, KCL.) were used as starting materials to synthesize polycrystalline  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$ . Each starting material was weighted with a composition of  $RFeP_{1-x}As_xO_{1-y-\delta}F_y$ . The O deficiency  $\delta$  was introduced to the samples in order to make F substitution easy and subtract excess O introduced during the synthesis process. The  $\delta$  value ( $\sim 0.1$ ) is not noted in the later chapters and sections. Many researchers who studies on P/As substituted iron pnictides often define iron arsenides as main phases and  $x$  as P substitution ratio for As site, such as  $BaFe_2(As_{1-x}P_x)_2$  and  $Ca_4Al_2O_6Fe_2(As_{1-x}P_x)_2$ . In my thesis, however, I defined iron phosphides as main phases and  $x$  as As substitution ratio for P site (e.g.  $P_{1-x}As_x$ ) because my experimental results showed systematic changes with  $x$  in the vicinity of iron phosphides.

The chemical reaction formula of  $RFeP_{1-x}As_xO_{1-y}F_y$  in the case of using  $FeF_2$  is



The chemical reaction formula in the case of using  $RF_3$  is





### Chapter 3 Experimental methodology

In this study,  $\text{FeF}_2$  was used in the cases of  $R = \text{Pr}$  and  $\text{Nd}$ , while  $\text{RF}_3$  was used in the case of  $R = \text{La}$ .

Materials of  $\text{RAs}$ ,  $\text{RP}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}$ ,  $\text{FeF}_2$  or  $\text{RF}_3$  were weighted, following the ratio in the above formula and mixed in an agate mortar for 20 minutes. Then the mixture was pressed into a pellet (1.0 - 1.5 g) under the pressure of 20 MPa. The pellet was sealed in an evacuated silica tube and reacted at 1100 °C. The pellet sealed in the evacuated silica tube is shown in Figure 3.3. Temperature conditions for the synthesis of  $\text{RFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  is illustrated in Figure 3.4.

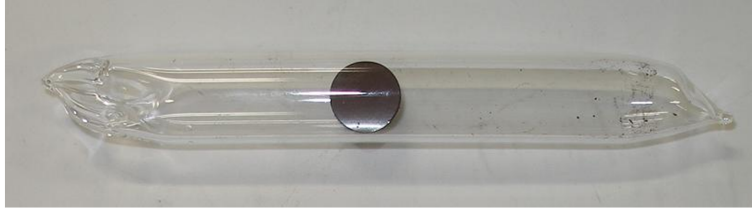


Figure 3.3: The pellet ( $\phi = 10$  mm) sealed in the evacuated silica tube.

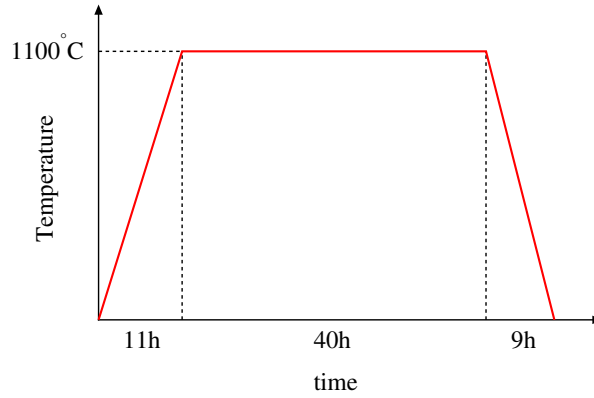


Figure 3.4: The temperature condition for the synthesis of  $\text{RFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

Polycrystalline samples with the following nominal compositions were synthesized.

- $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$ )
- $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x = 0, 0.2, 0.4, 0.6, 0.8, 0.9, 1.0$ )
- $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x = 0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0$ )

Hereafter, I use the nominal concentrations of F (0.1) and As ( $x$ ).

### 3.2 Measurements

#### 3.2.1 Crystal structural analysis

##### Powder X-ray diffraction in Laboratory

Powder X-ray diffraction is a standard tool to evaluate lattice parameters and impurity concentrations of a polycrystalline sample. It was measured by using MiniFlex and RINT-2000 (Rigaku Co.).

First, a piece of a polycrystalline sample was crushed and powdered with an agate mortar. Then the powder of the sample was stuck on a glass plate and they were set up on the above machines. Bragg peaks were detected by  $\theta - 2\theta$  scan in the range of  $2\theta = 20 - 100^\circ$ . X-ray source was Cu and  $K_{\alpha 1}$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) without  $K_{\alpha 2}$  one was used for analysis. The lattice constants were obtained by the least squares fitting of the X-ray diffraction profile.

##### Synchrotron X-ray diffraction

Synchrotron X-ray diffraction using X-ray with strong intensity is able to determine accurate crystal structural parameters including atomic positions and atomic occupancies. They are essential information for iron-based superconductors where  $T_c$  is sensitive to those parameters. Synchrotron X-ray diffraction was measured at the beam line BL-8A in Photon Factory (PF) in KEK, Tsukuba, Japan.

A piece of a polycrystalline sample was powdered over 1 hour and then inserted into a glass capillary tube with the internal diameter of  $200 \mu\text{m}$ . The powder X-ray diffraction measurements were performed at 300 K by using X-ray with the energy of 15 keV. Crystal structural parameters were determined by Rietveld analysis [48].

#### 3.2.2 Magnetic susceptibility

Magnetic susceptibility measurement is an appropriate tool to detect  $T_c$  and superconducting volume fraction because it is dramatically changed by diamagnetism of superconductivity. Temperature dependence of magnetic susceptibility was measured by using MPMS-7 (Quantum Design, Inc.) under the magnetic field of 10 Oe in both conditions of zero field cooling (ZFC) and field cooling (FC). The  $\chi$  value was defined as the averaged measurement value in three times.

### 3.2.3 Electrical resistivity

Electrical resistivity measurement is also an appropriate tool to detect  $T_c$  through zero-resistivity of superconductivity. The detail of temperature dependent resistivity in the normal state was also studied in this work. It was measured by using conventional four-probe method. A sample was shaped to about  $1 \times 1 \times 3 \text{ mm}^3$  cuboid by polishing with a sand paper. Au wires ( $\phi = 25 \text{ }\mu\text{m}$ , The Nilaco Co.) were connected on the sample with DOTITE (FUJIKURA KASEI CO.,LTD.) silver paste as electrodes. The configuration of sample and electrodes for electrical resistivity measurement is shown in Figure 3.5. Cooling temperature for the measurement was

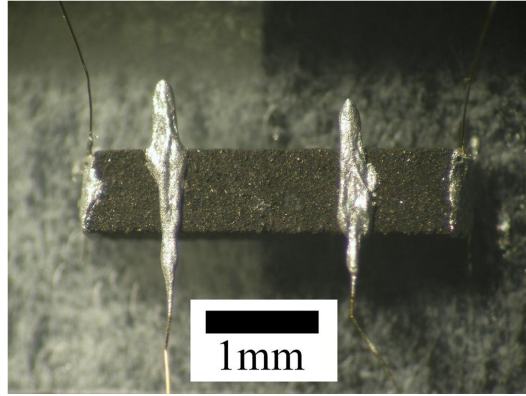


Figure 3.5: The configuration of sample and electrodes for electrical resistivity measurement (inner: voltage probes, outer: current probes).

controlled in He vessel. Electrical resistivity  $\rho$  was calculated by the equation

$$\rho = R \frac{S}{l} \quad (3.1)$$

where  $R$ ,  $S$  and  $l$  are the resistance, the sample cross-section area and the distance between voltage probes, respectively.

### 3.2.4 Hall effect

Hall effect measurement is a tool to determine a sign of carriers and carrier density. Hall effect was measured by using MPMS to control magnetic field. Sample probe holder was specially designed for four-probe method to detect Hall resistivity. A sample was shaped to about  $1.5 \times 1.5 \times 0.25 \text{ mm}^3$ . Current and voltage probes were made with the same method of the measurement of electrical resistivity. The configuration of sample and electrodes for Hall effect measurement

is shown in Figure 3.6.

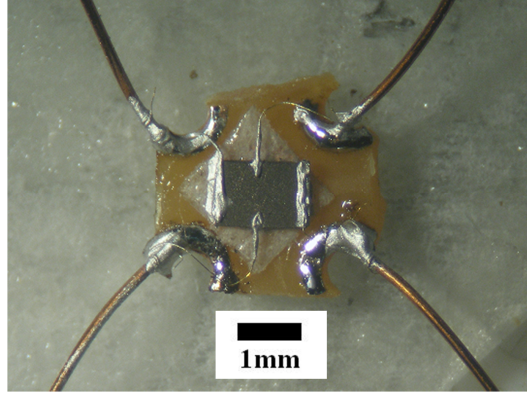


Figure 3.6: The configuration of sample and electrodes for Hall effect measurement (top and bottom: voltage probes, left and right: current probes).

When the magnetic field  $H$  is applied, the resistance  $R(H)$  contains not only Hall resistance  $R_{xy}(H)$  but also a part of the normal resistance  $R_{xx}(H)$ . Then  $R(H)$  is written as

$$R(H) = R_{xx}(H) + R_{xy}(H). \quad (3.2)$$

On the other hand,  $R(-H)$  is written as

$$\begin{aligned} R(-H) &= R_{xx}(-H) + R_{xy}(-H) \\ &= R_{xx}(H) - R_{xy}(H). \end{aligned} \quad (3.3)$$

From the above two equations, Hall resistance  $R_{xy}(H)$  is written as

$$R_{xy}(H) = \frac{R(H) - R(-H)}{2}. \quad (3.4)$$

Hall resistivity  $\rho_{xy}$  is calculated by the equation,

$$\rho_{xy}(H) = R_{xy}(H) \frac{Wd}{l}. \quad (3.5)$$

where  $W$ ,  $d$  and  $l$  are the sample width, the sample thickness and the distance of voltage probes, respectively. When voltage probes are putted on lateral side,  $l \approx W$ . Then  $\rho_{xy}(H)$  is written as

$$\rho_{xy}(H) \approx R_{xy}(H) d. \quad (3.6)$$

### Chapter 3 Experimental methodology

---

From above equation, the thickness  $d$  should be small to obtain large  $R_{xy}(H)$  signal.  $\rho_{xy}(H)$  was fitted with the formula

$$\rho_{xy}(H) = c_1 H + c_2 H^3 \quad (3.7)$$

and Hall coefficient  $R_H$  was determined as the first gradient to the magnetic field, namely

$$c_1 = R_H. \quad (3.8)$$

The typical measurement current was  $I = 10$  mA and magnetic field was changed from  $H = -7$  T to 7 T. The accurate  $R(H)$  value was defined as the average value for 10 times measurements.

## Chapter 4

# Experimental results

### 4.1 Crystal structural analysis

#### 4.1.1 Powder X-ray diffraction

Powder diffraction patterns of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  measured by MiniFlex or RINT-2000 are shown in Figures 4.1, 4.2 and 4.3. Positions and in-

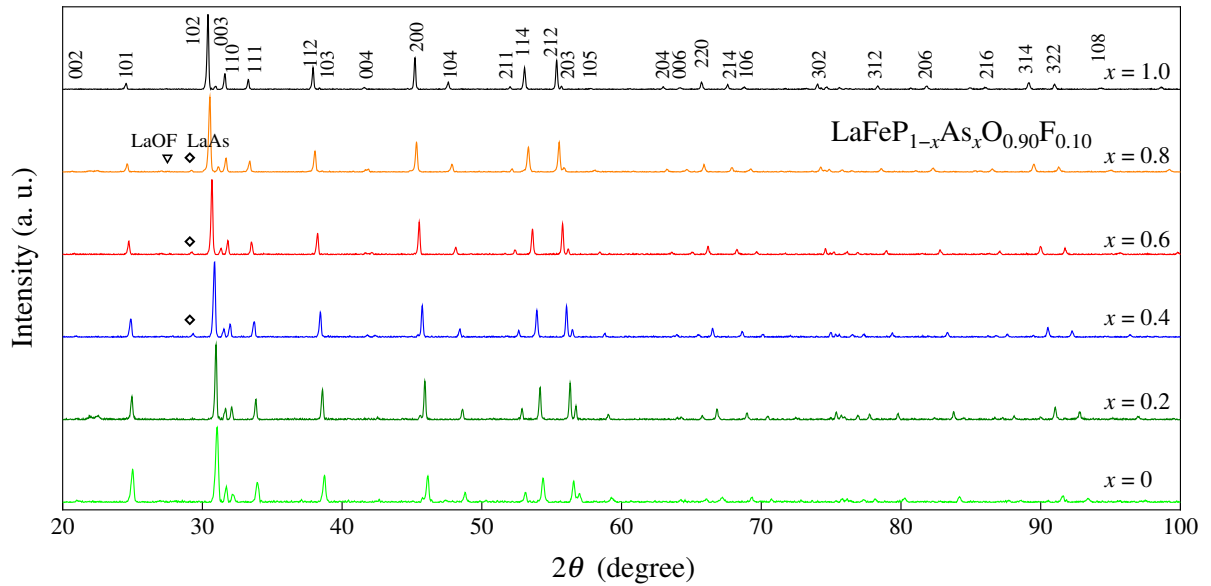


Figure 4.1: Powder X-ray diffraction patterns of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

tensities of Bragg peaks are consistent with the previous reports on 1111 system. As shown in Figures 4.1, 4.2 and 4.3, almost all the diffraction peaks are indexed assuming the tetragonal structure with the  $P4/nmm$  symmetry. Bragg peaks systematically shift to lower angle with

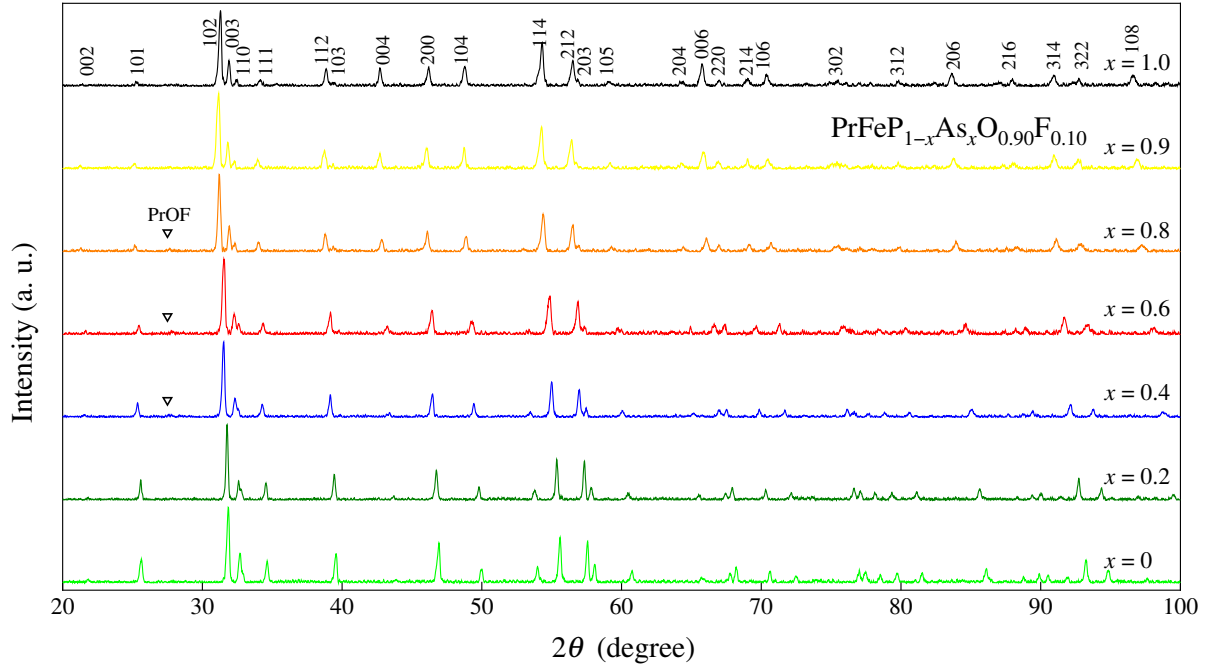


Figure 4.2: Powder X-ray diffraction patterns of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.90}\text{F}_{0.10}$ .

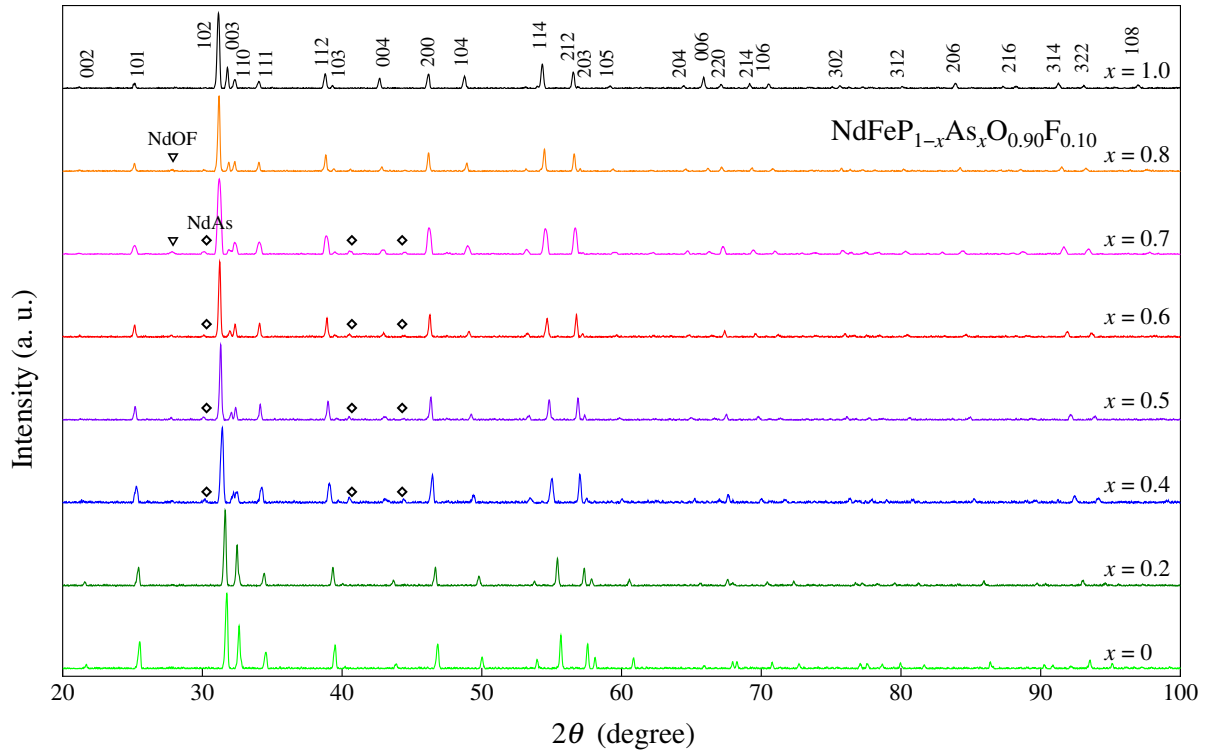


Figure 4.3: Powder X-ray diffraction patterns of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.90}\text{F}_{0.10}$ .

increasing  $x$ . This suggests that lattice constants  $a$  and  $c$  increase with  $x$  and P/As substitution in 1111 system is succeeded. A little impurities of  $RAs$  and  $ROF$  are detected, but they do not seriously affect magnetic and transport properties.

#### 4.1.2 Synchrotron X-ray diffraction

Powder diffraction patterns measured at BL-8A in PF are analyzed by Rietveld method [48]. They are well fitted with the symmetry of  $P4/nmm$  in the tetragonal lattice. The  $x$  dependences of lattice constants ( $a$  and  $c$ ), pnictogen height from Fe-layer ( $h_{Pn}$ ) and  $Pn$ -Fe- $Pn$  bond angle ( $\alpha$ ) of  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$  ( $R = La, Pr, Nd$ ) are plotted in Figure 4.4. Lattice parameters of  $x$

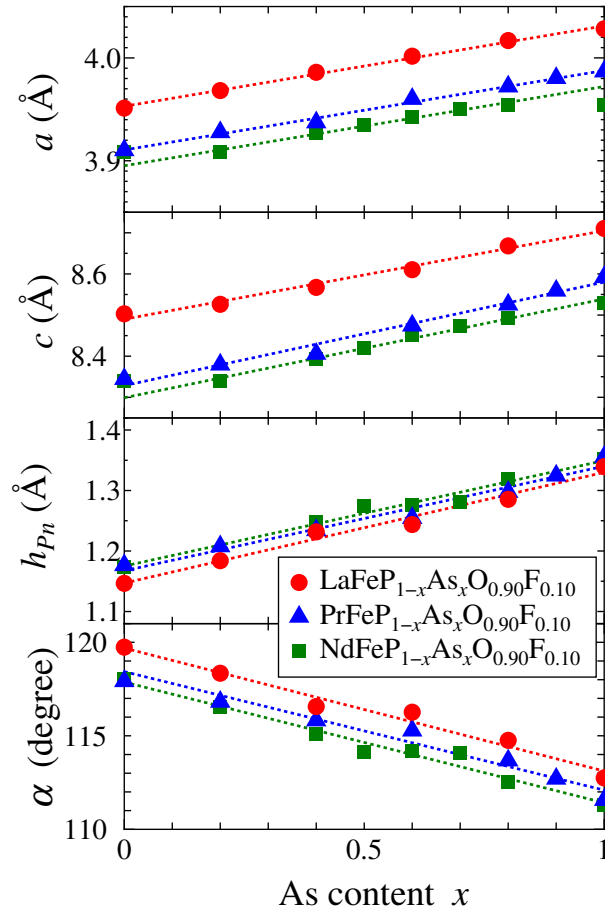


Figure 4.4:  $x$  dependence of  $a$ ,  $c$ ,  $h_{Pn}$  and  $\alpha$  of  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$  ( $R = La, Pr, Nd$ ).

$x = 0$  and  $1.0$  are consistent with the previous studies [49] - [53].  $a$  and  $c$  linearly increase with  $x$ , following Vegard's law. It proves that P/As substitution in  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$  is successfully prepared.  $h_{Pn}$  and  $\alpha$ , which are the key parameters for iron-based superconductors, are also



linearly changed with  $x$ . The 10 % F substitution causes the disappearance of structural and magnetic transitions in 1111 system. Therefore, above crystal structural parameters do not change at low temperatures.

## 4.2 Magnetic susceptibility

Temperature dependences of magnetic susceptibility of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are presented in Figures 4.5, 4.6 and 4.7. Sharp superconducting transition and bulk superconductivity are observed in most of the samples.

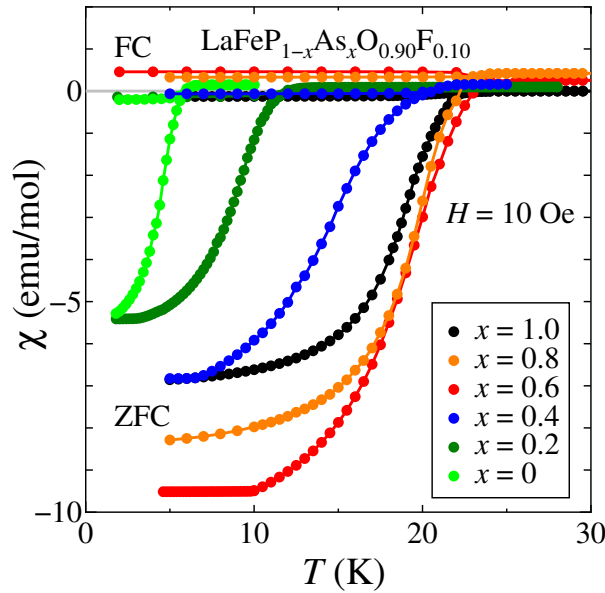


Figure 4.5: Temperature dependence of magnetic susceptibility of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

$T_c$  of  $x = 0$  and  $x = 1.0$  are consistent with the previous studies [1, 2, 5, 54, 55]. The superconducting volume fraction is sufficiently large in most samples.  $T_c$  and the absolute value of  $\chi$  are most enhanced at  $x = 0.6$  in the case of  $R = \text{La}$ . On the other hand,  $T_c$  gradually increases with  $x$  in Pr and Nd systems.

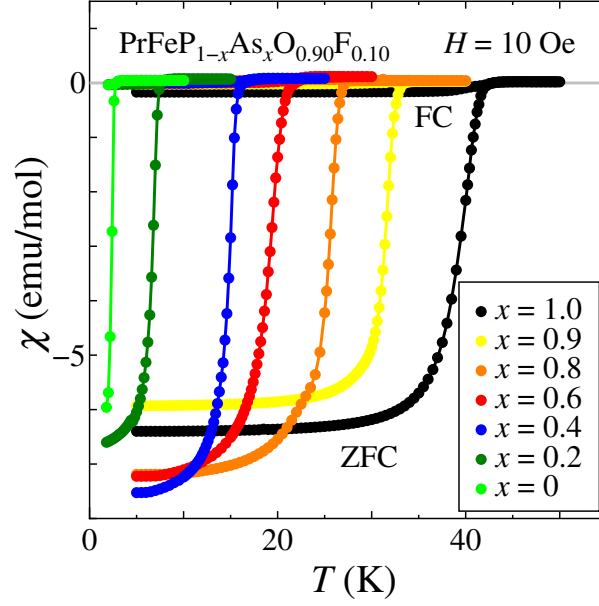


Figure 4.6: Temperature dependence of magnetic susceptibility of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

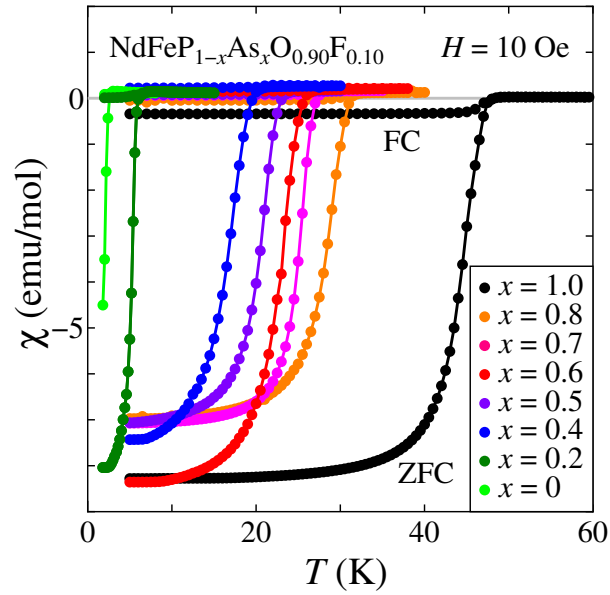


Figure 4.7: Temperature dependence of magnetic susceptibility of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

### 4.3 Electrical resistivity

Temperature dependences of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are presented in Figures 4.8, 4.11 and 4.14. Absolute values of  $\rho$  of my polycrystalline samples are about ten times larger than that of single crystals in the previous works [56]. This is caused by a grain boundary effect. However, the temperature dependence profiles of  $\rho$  is not so different between polycrystalline and single-crystalline samples. Therefore, it is meaningful to discuss transport properties of polycrystalline samples. The anisotropic factor  $\Gamma$  of a metal is described as

$$\Gamma = \frac{H_{c2}^{ab}}{H_{c2}^c} = \left( \frac{m_c^*}{m_{ab}^*} \right)^{\frac{1}{2}} = \left( \frac{\rho_c}{\rho_{ab}} \right)^{\frac{1}{2}} \quad (4.1)$$

where  $H_{c2}^{ab}$  ( $H_{c2}^c$ ),  $m_{ab}^*$  ( $m_c^*$ ),  $\rho_{ab}$  ( $\rho_c$ ) are in-plane (out-of-plane) upper critical magnetic field, effective mass and electrical resistivity, respectively.  $\rho_c/\rho_{ab}$  is  $\sim 25$  when  $\Gamma$  is  $\sim 5$  as reported previously [56]. Therefore, it is expected that electrical current mainly flows in the in-plane direction and electrical resistivity of polycrystalline samples mainly reflects in-plane one in 1111 system.

In spite of different  $R$ , some common behaviors are observed as follows.

- (i) No indication of structural and magnetic transitions is observed in all samples.
- (ii) At  $x = 0$ ,  $\rho$  shows a conventional Fermi liquid behavior  $\rho \sim T^2$  and the absolute value of  $\rho$  is the smallest.
- (iii) At  $x \sim 0.6$ ,  $\rho$  shows  $T$ -linear behavior and the absolute value of  $\rho$  is the largest.

In order to analyze and discuss the above behaviors, I fit the resistivity  $\rho(T)$  with the formula

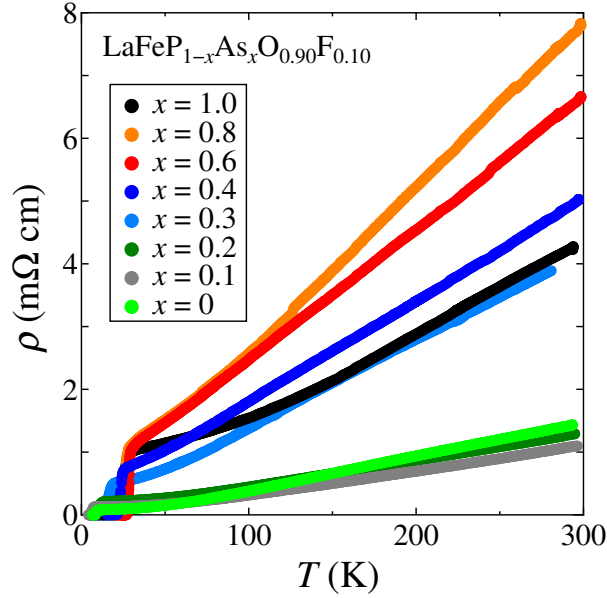
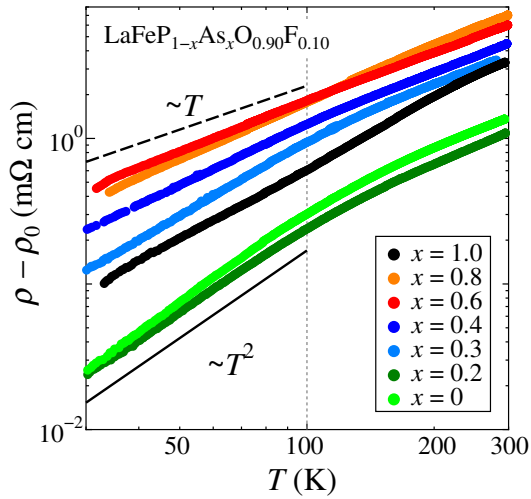
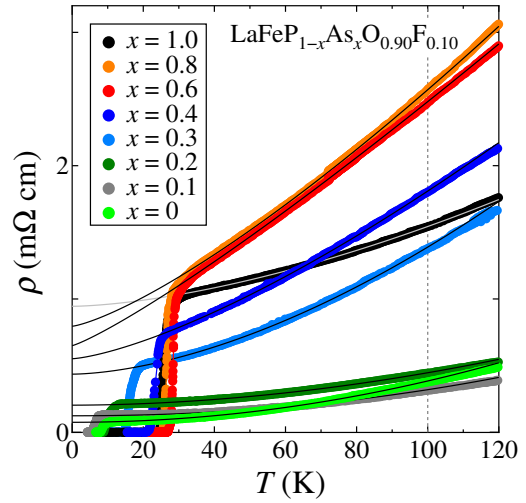
$$\rho(T) = \rho_0 + AT^n \quad (4.2)$$

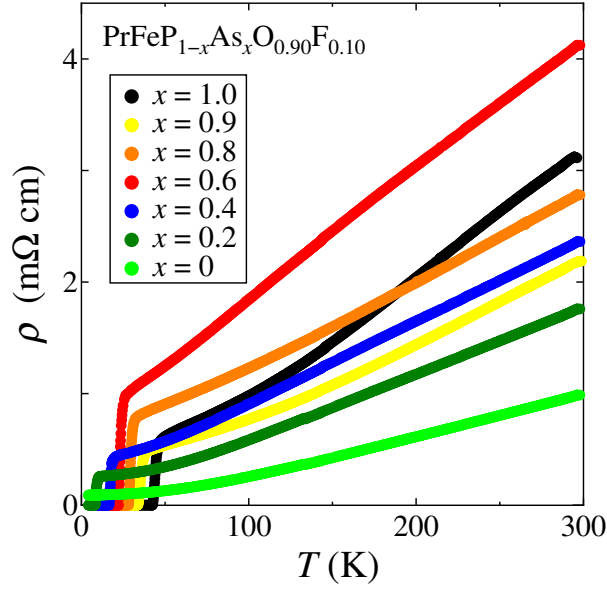
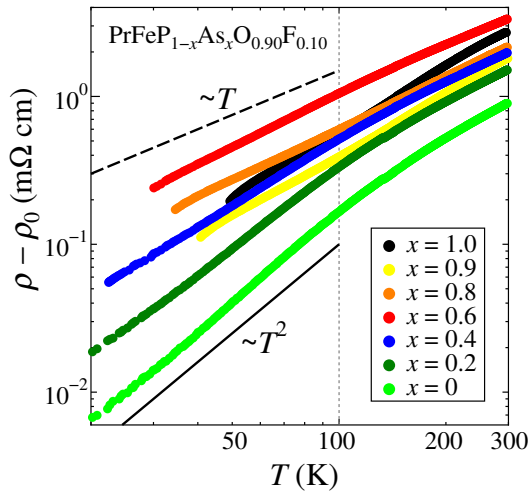
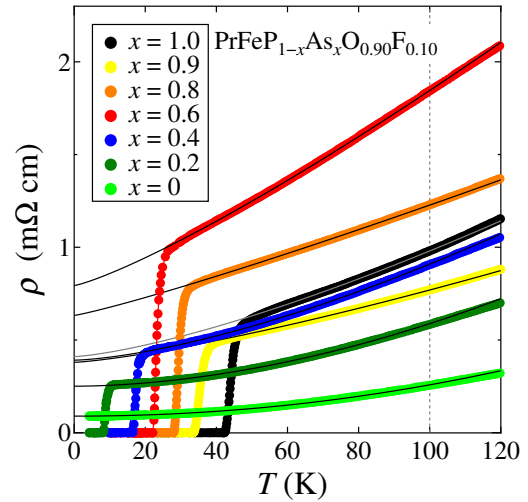
in the temperature range between  $T_c$  and 100 K, where  $\rho_0$ ,  $A$  and  $n$  are the residual resistivity, the slope and the power law exponent of  $T$ , respectively. The present fitting range is defined to subtract the scattering effect by phonon at high temperatures and focus on the essential behaviors of strongly correlated electron system at low temperatures. I note that  $\rho(T)$  is exponent at  $T < 100$  K because  $\log(\rho - \rho_0)$  is always linear to  $\log T$  at  $T < 100$  K. Double logarithmic plots of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and

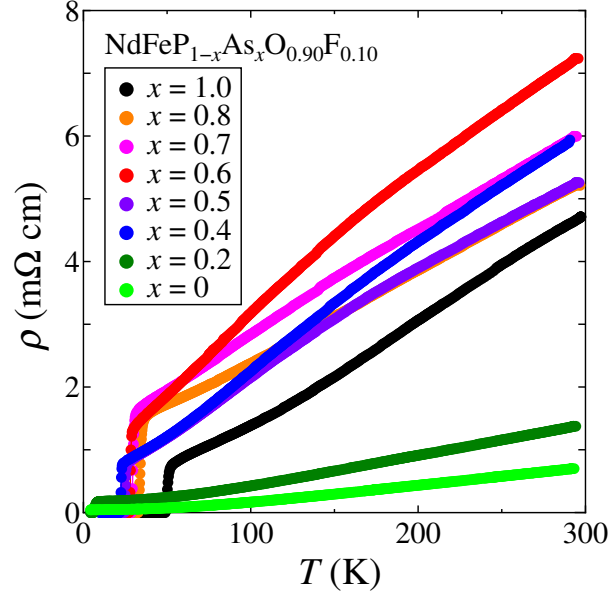
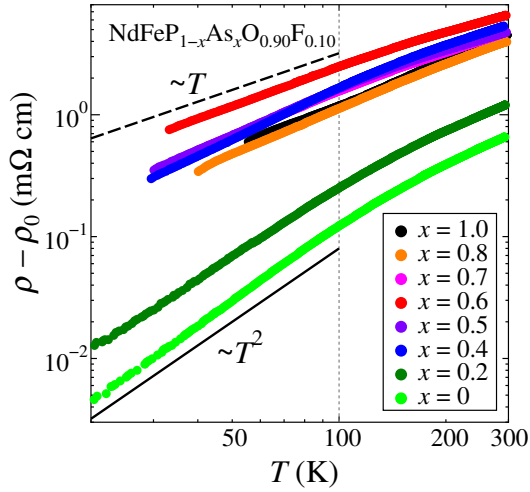
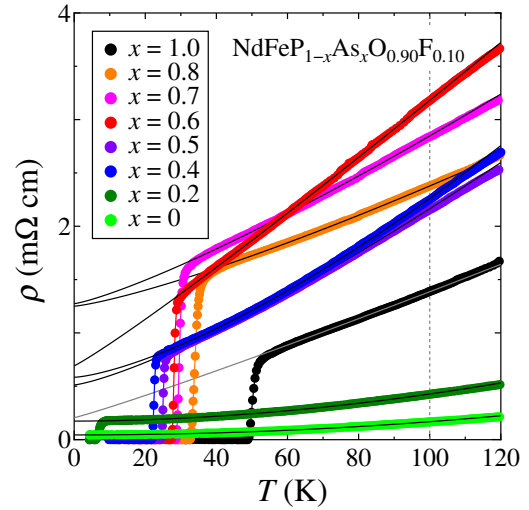
## Chapter 4 Experimental results

---

$\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are presented in Figures 4.9, 4.12 and 4.15. Fitting curves of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are presented in Figures 4.10, 4.13 and 4.16. Details of fitting parameters are discussed in Chapter 5.


 Figure 4.8: Temperature dependence of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.90}\text{F}_{0.1}$ .

 Figure 4.9: Double logarithmic plot of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.90}\text{F}_{0.1}$ .

 Figure 4.10: Experimental results (dots) and fitting curves (solid line) of electrical resistivity of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.90}\text{F}_{0.1}$ .


 Figure 4.11: Temperature dependence of electrical resistivity of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.12: Double logarithmic plot of electrical resistivity of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.13: Experimental results (dots) and fitting curves (solid line) of electrical resistivity of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .


 Figure 4.14: Temperature dependence of electrical resistivity of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.15: Double logarithmic plot of electrical resistivity of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.16: Experimental results (dots) and fitting curves (solid line) of electrical resistivity of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

## 4.4 Hall effect

### 4.4.1 Hall resistivity

#### LaFeP<sub>1-x</sub>As<sub>x</sub>O<sub>0.9</sub>F<sub>0.1</sub>

Magnetic field dependences of Hall resistivity  $\rho_{xy}$  in LaFeP<sub>1-x</sub>As<sub>x</sub>O<sub>0.9</sub>F<sub>0.1</sub> with various  $x$  are shown in Figures 4.17 - 4.22. In multi-carrier system having hole and electron as carriers,  $\rho_{xy}(H)$  shows magnetic field dependence and it is described as

$$\rho_{xy}(H) = \frac{1}{|e|} \frac{n_h \mu_h^2 - n_e \mu_e^2 + (\mu_h \mu_e)^2 (n_h - n_e) H^2}{(n_h \mu_h + n_e \mu_e)^2 + (\mu_h \mu_e)^2 (n_h - n_e)^2 H^2} H \quad (4.3)$$

where  $n_h$  ( $n_e$ ) and  $\mu_h$  ( $\mu_e$ ) are hole (electron) carrier density and mobility [57]. This system is regarded as a nearly compensated metal because the F concentration is only 10 %. When  $n_h \approx n_e$  is assumed,  $(n_h \mu_h + n_e \mu_e)^2 \gg (\mu_h \mu_e)^2 (n_h - n_e)^2 H^2$  holds. Then  $\rho_{xy}(H)$  is fitted with the formula  $\rho_{xy}(H) = c_1 H + c_2 H^3$  and  $c_1$  is defined as  $R_H$ . Dots and lines in Figs 4.17 - 4.37 indicate the experimental results and the fitting curves of  $\rho_{xy}(H) = c_1 H + c_2 H^3$ , respectively. When superconductivity is broken by high magnetic fields,  $\rho_{xy}$  cannot be fitted with the above formula. So below  $T_c$ ,  $\rho_{xy}$  is fitted with  $\rho_{xy}(H) = c_1 H$  only in the low magnetic field in order to describe the superconducting state in  $H \rightarrow 0$ .

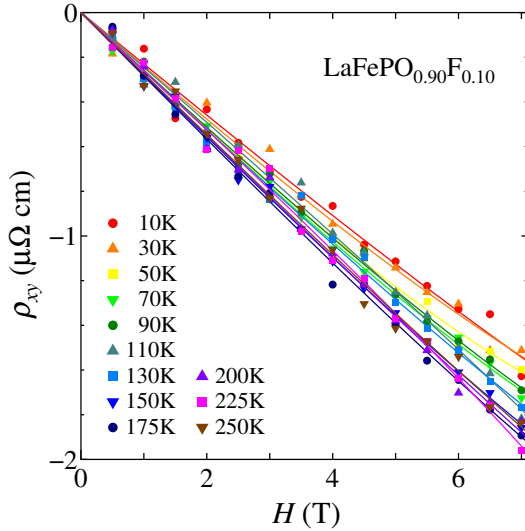


Figure 4.17: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of LaFePO<sub>0.9</sub>F<sub>0.1</sub>.

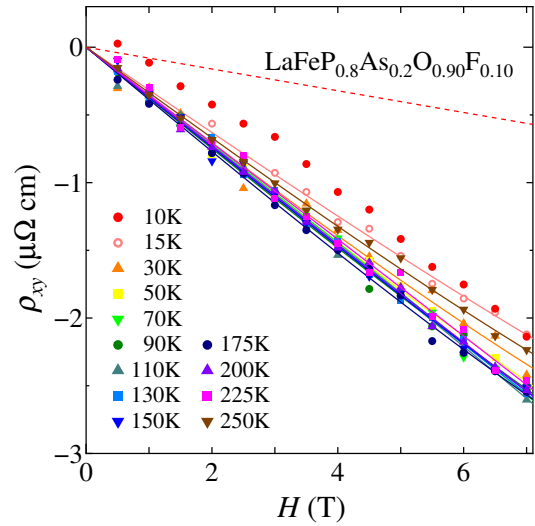


Figure 4.18: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of LaFeP<sub>0.8</sub>As<sub>0.2</sub>O<sub>0.9</sub>F<sub>0.1</sub>.



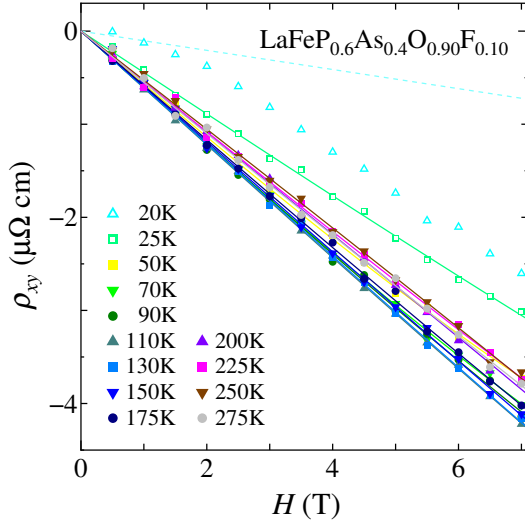


Figure 4.19: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{LaFeP}_{0.6}\text{As}_{0.4}\text{O}_{0.9}\text{F}_{0.1}$ .

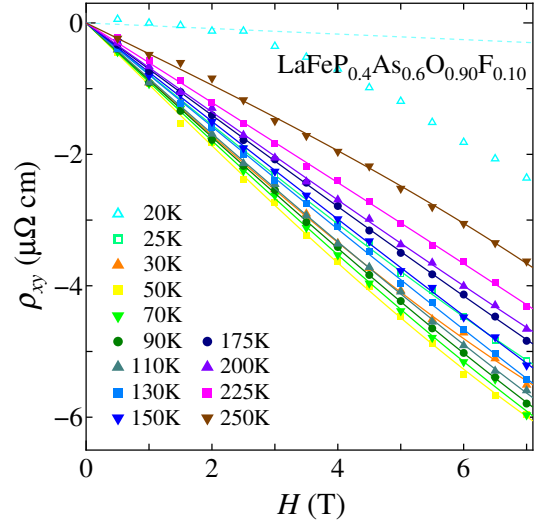


Figure 4.20: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{LaFeP}_{0.4}\text{As}_{0.6}\text{O}_{0.9}\text{F}_{0.1}$ .

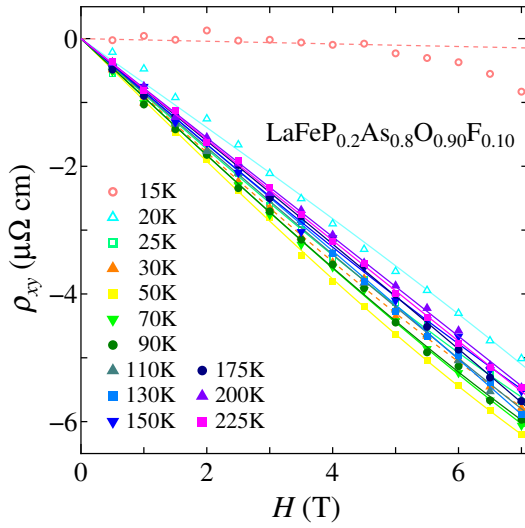


Figure 4.21: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{LaFeP}_{0.2}\text{As}_{0.8}\text{O}_{0.9}\text{F}_{0.1}$ .

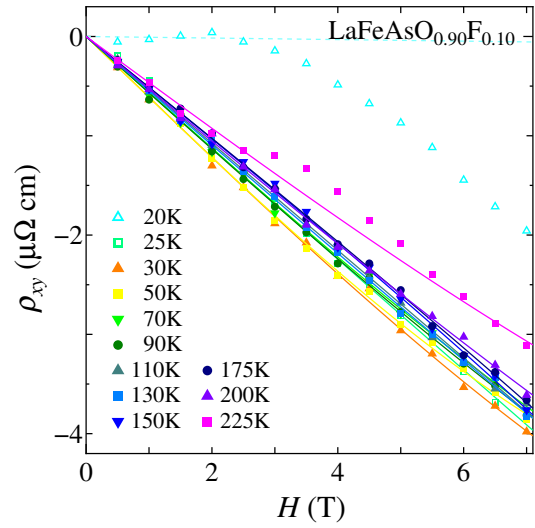


Figure 4.22: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ .

### $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$

Magnetic field dependences of Hall resistivity  $\rho_{xy}$  in  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  with various  $x$  are shown in Figures 4.23 - 4.29.

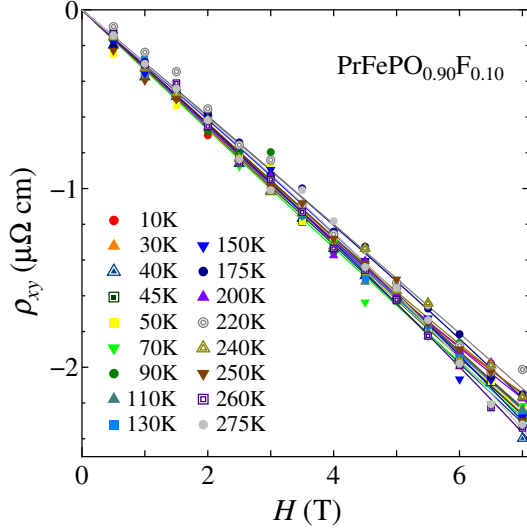


Figure 4.23: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFePO}_{0.9}\text{F}_{0.1}$ .

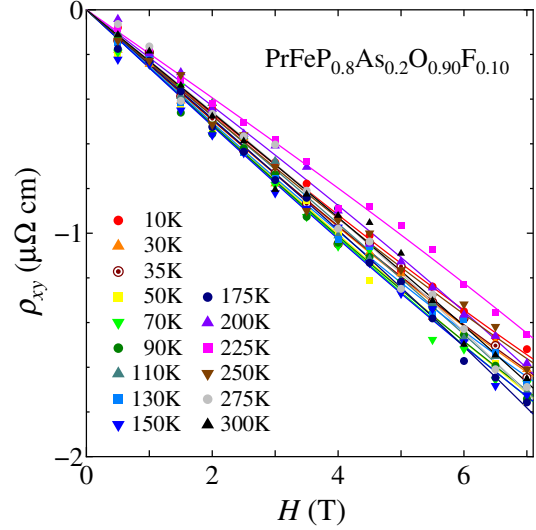


Figure 4.24: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeP}_{0.8}\text{As}_{0.2}\text{O}_{0.9}\text{F}_{0.1}$ .

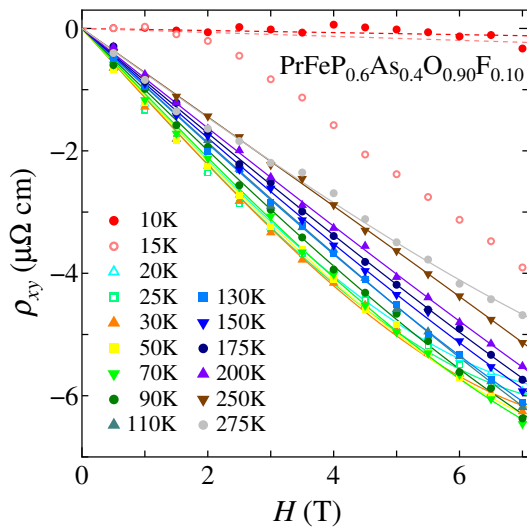


Figure 4.25: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeP}_{0.6}\text{As}_{0.4}\text{O}_{0.9}\text{F}_{0.1}$ .

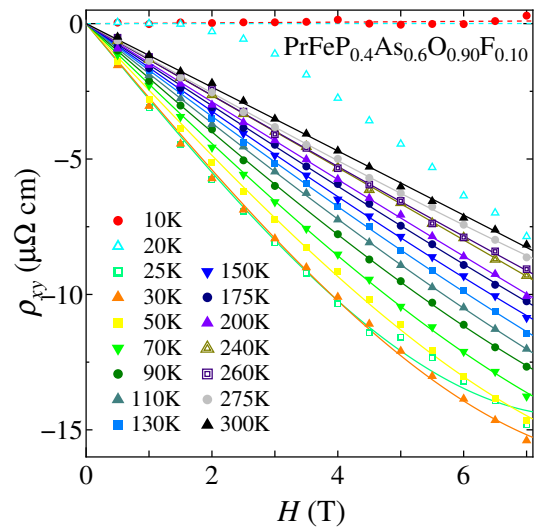


Figure 4.26: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeP}_{0.4}\text{As}_{0.6}\text{O}_{0.9}\text{F}_{0.1}$ .

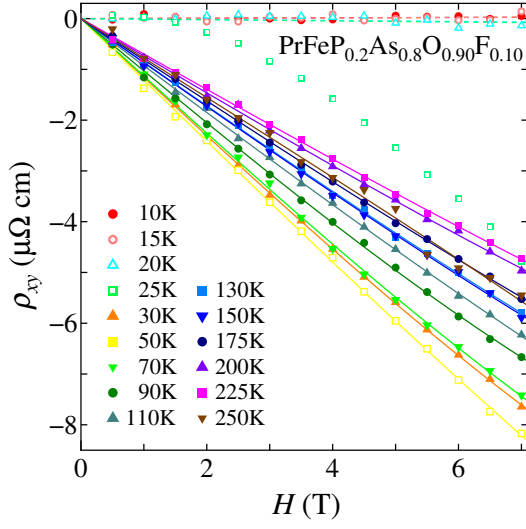


Figure 4.27: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeP}_{0.2}\text{As}_{0.8}\text{O}_{0.9}\text{F}_{0.1}$ .

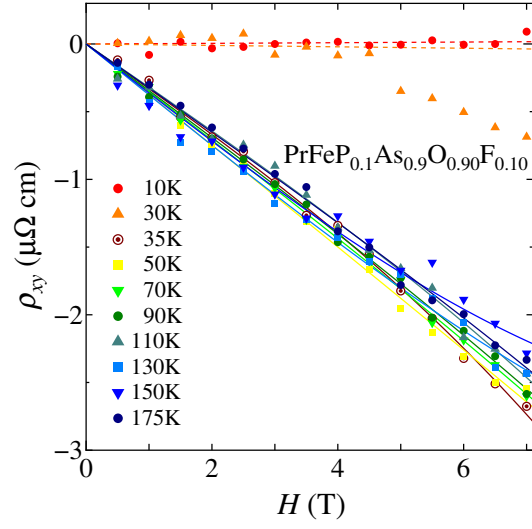


Figure 4.28: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeP}_{0.1}\text{As}_{0.9}\text{O}_{0.9}\text{F}_{0.1}$ .

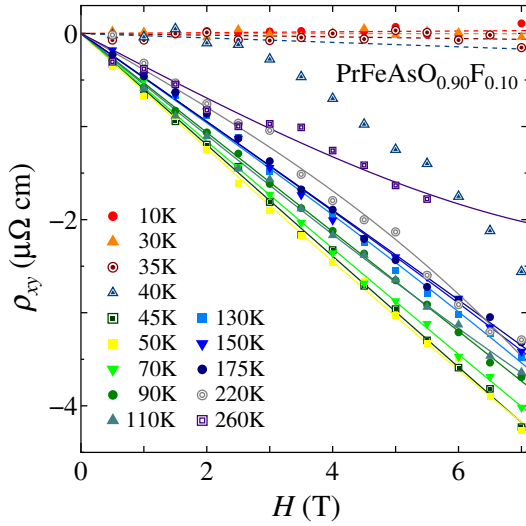


Figure 4.29: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{PrFeAsO}_{0.9}\text{F}_{0.1}$ .

### $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$

Magnetic field dependences of Hall resistivity  $\rho_{xy}$  in  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  with various  $x$  are shown in Figures 4.30 - 4.37.

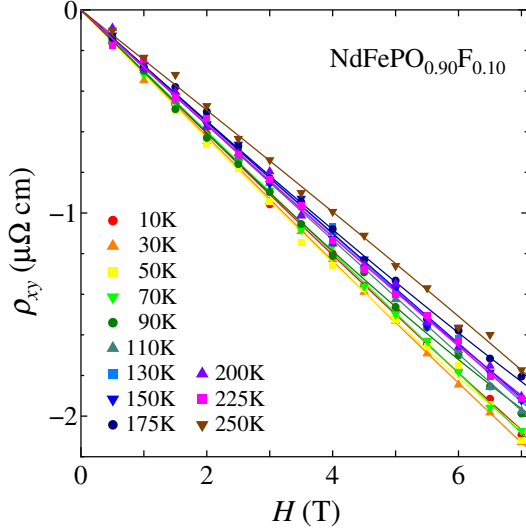


Figure 4.30: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFePO}_{0.9}\text{F}_{0.1}$ .

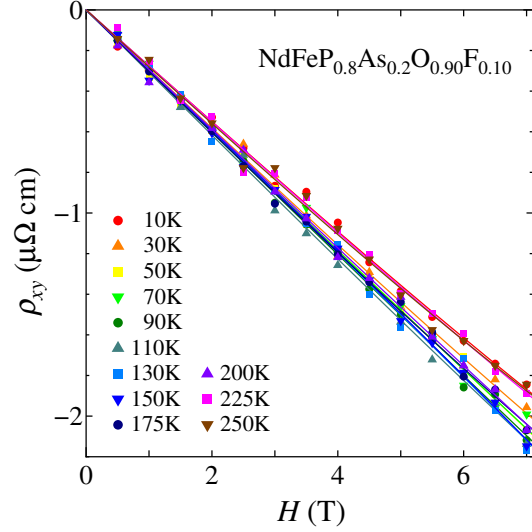


Figure 4.31: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.8}\text{As}_{0.2}\text{O}_{0.9}\text{F}_{0.1}$ .

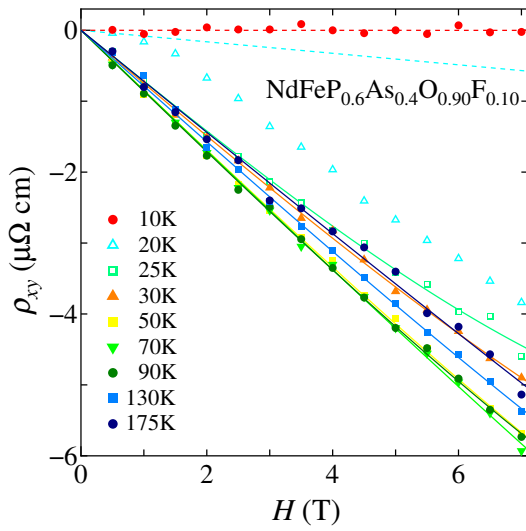


Figure 4.32: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.6}\text{As}_{0.4}\text{O}_{0.9}\text{F}_{0.1}$ .

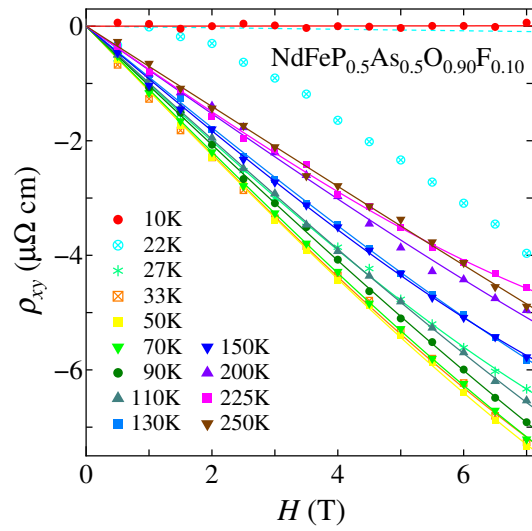
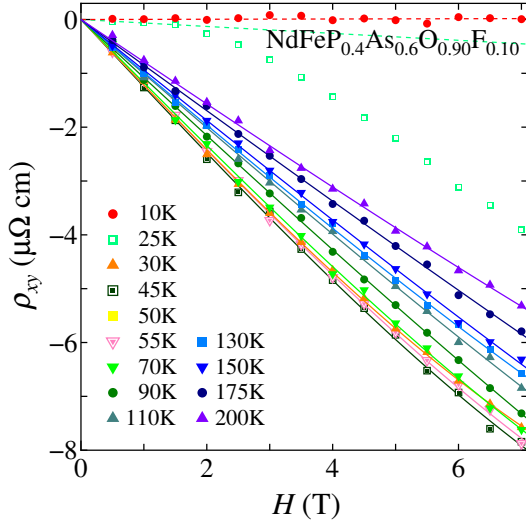
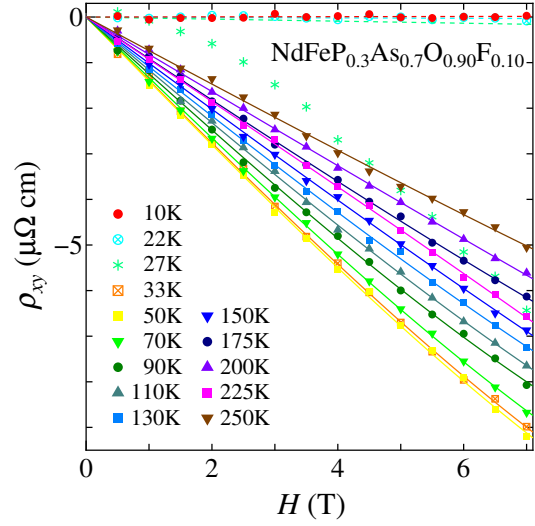
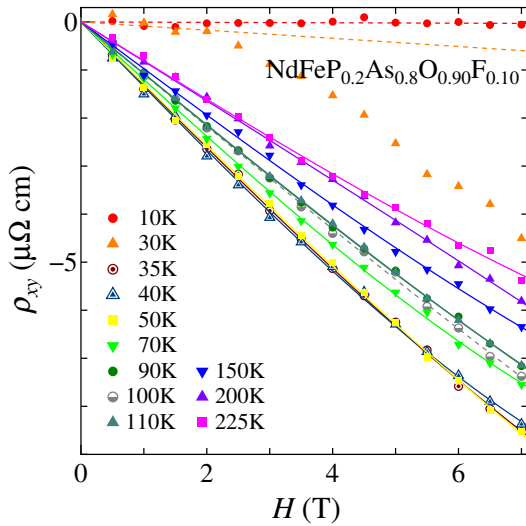
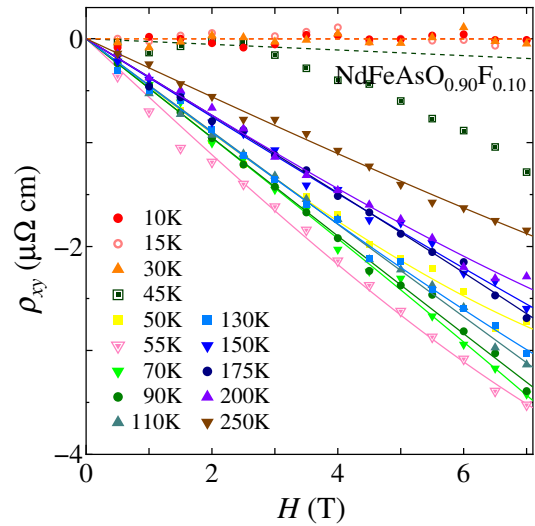


Figure 4.33: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.5}\text{As}_{0.5}\text{O}_{0.9}\text{F}_{0.1}$ .


 Figure 4.34: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.4}\text{As}_{0.6}\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.35: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.3}\text{As}_{0.7}\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.36: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeP}_{0.2}\text{As}_{0.8}\text{O}_{0.9}\text{F}_{0.1}$ .

 Figure 4.37: Magnetic field dependence of Hall resistivity  $\rho_{xy}$  of  $\text{NdFeAsO}_{0.9}\text{F}_{0.1}$ .

### 4.4.2 Hall coefficient

Temperature dependences of Hall coefficient  $R_H$  of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ,  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are presented in Figures 4.38, 4.39 and 4.40. The value of  $R_H$  in

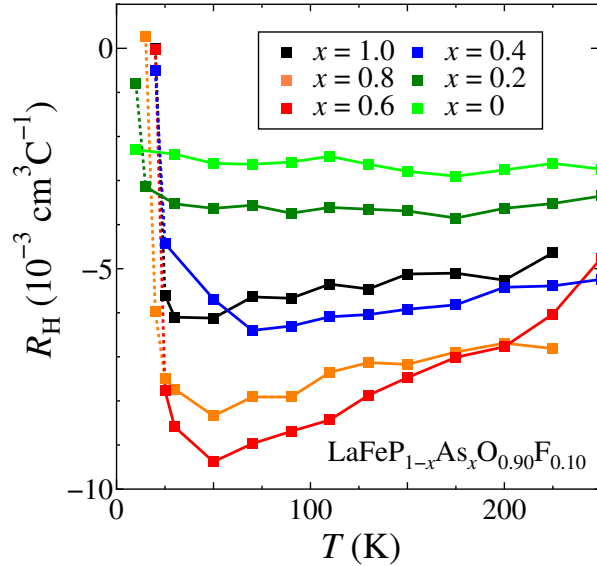


Figure 4.38: Temperature dependence of Hall coefficient of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

the normal state is negative for all compositions, and the dominant carriers are electrons in this system. At  $x = 0$ , the absolute value of  $R_H$  ( $|R_H|$ ) is small ( $\sim 3 \times 10^{-3} \text{ cm}^3/\text{C}$ ) and almost temperature-independent for all  $R$  systems. On the other hand,  $|R_H|$  is large and strongly temperature dependent at  $x \sim 0.6$ . At  $x = 1.0$ ,  $|R_H|$  is smaller and shows weaker temperature dependence than that of  $x \sim 0.6$ . The results suggest the change of the electronic structure around  $x \sim 0.6$ . The details are discussed in the next chapter.

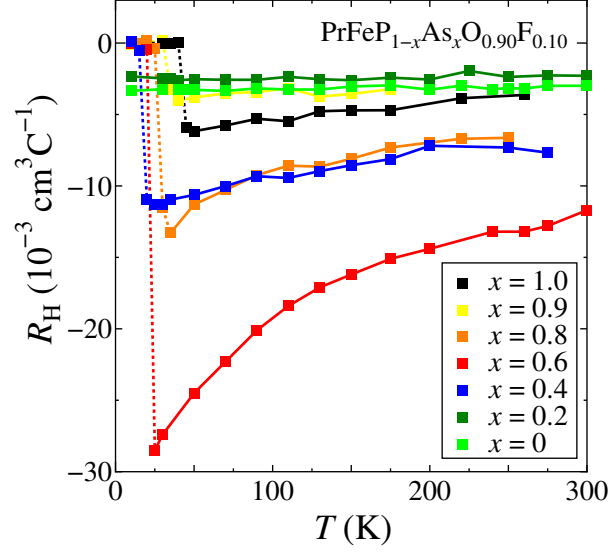


Figure 4.39: Temperature dependence of Hall coefficient of  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

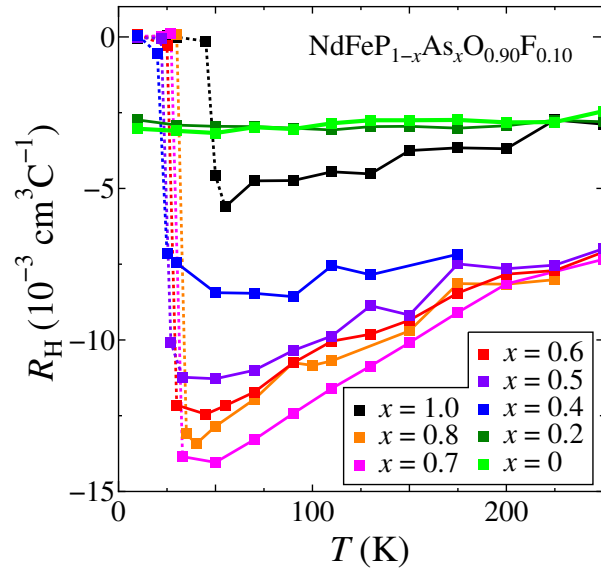


Figure 4.40: Temperature dependence of Hall coefficient of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .

## Chapter 5

# Discussion

### 5.1 Crystal structural parameters and $T_c$

#### 5.1.1 Bond angle $\alpha$ dependence of $T_c$

$Pn$ -Fe- $Pn$  bond angle  $\alpha$  dependence of  $T_c$  in  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$  ( $R = La, Pr, Nd$ ) is plotted in Figure 5.1. The reported results of  $RFeAsO_{1-y}$  are also plotted together. My results of  $\alpha$  and

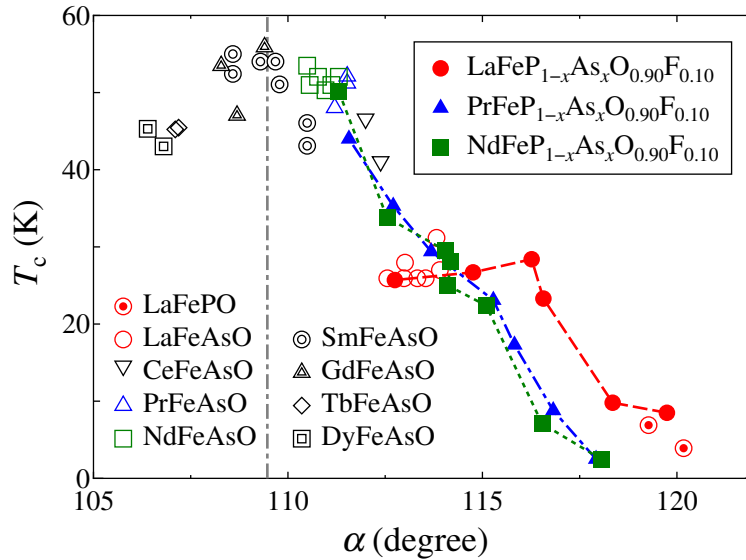


Figure 5.1:  $Pn$ -Fe- $Pn$  bond angle  $\alpha$  dependence of  $T_c$  in  $RFeP_{1-x}As_xO_{0.9}F_{0.1}$  ( $R = La, Pr, Nd$ ) (solid symbols). The reported results of  $RFePO$  and  $RFeAsO_{1-y}$  are also plotted (open symbols) [28].

$T_c$  at  $x = 0$  and 1.0 are consistent with those in the previous studies.  $T_c$  gradually increases to 44 K and 50 K with decreasing  $\alpha$  in Pr and Nd systems. On the other hand,  $T_c$  increases from



$\alpha = 120^\circ$  to  $116^\circ$  and keeps 26 - 28 K from  $116^\circ$  to  $113^\circ$  in La system. Additionally,  $T_c$  of La system is much higher than that of Pr and Nd systems at the same  $\alpha$ , where  $\alpha = 115 - 120^\circ$ . Therefore, variations of  $T_c$  cannot be ascribed to only those of  $\alpha$ .

### 5.1.2 Pnictogen height $h_{Pn}$ dependence of $T_c$

Pnictogen height from Fe-layer  $h_{Pn}$  versus  $T_c$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ) is plotted in Figure 5.2. The reported results of other iron pnictide superconductors are also plotted together.  $h_{Pn}$  and  $T_c$  at  $x = 0$  and 1.0 are consistent with the previous studies.  $T_c$

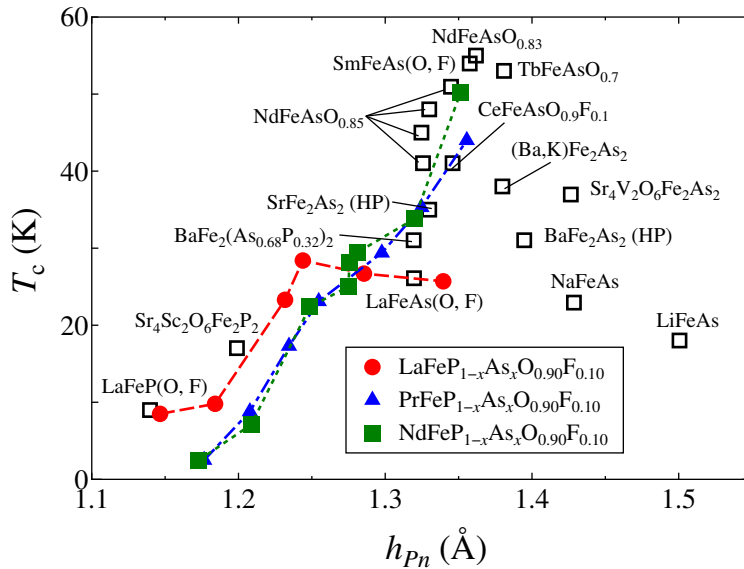


Figure 5.2: Pnictogen height from Fe-layer  $h_{Pn}$  dependence of  $T_c$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ) (solid symbols). The reported results of other iron pnictide superconductors are also plotted (black open squares) [29].

gradually increases with  $h_{Pn}$  in Pr and Nd systems. On the other hand,  $T_c$  increases from  $h_{Pn} = 1.15 \text{ \AA}$  to  $1.24 \text{ \AA}$  and does not change much from  $1.24 \text{ \AA}$  to  $1.35 \text{ \AA}$  in La system. As a result, variations of  $T_c$  cannot be ascribed to only those of  $h_{Pn}$ .

## 5.2 Transport properties

### 5.2.1 $x$ dependences of $T_c$ and $n$

Temperature dependence of electrical resistivity is fitted with the formula  $\rho(T) = \rho_0 + AT^n$ .  $x$  dependences of  $T_c$  and  $n$  of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ) are presented in Figure

5.3. In almost all samples, the superconducting transitions are sharp enough to determine  $T_c$  from the middle temperature of the resistive transition. In  $\text{PrFePO}_{0.9}\text{F}_{0.1}$  and  $\text{NdFePO}_{0.9}\text{F}_{0.1}$ ,  $T_c < 4.2$  K is defined as an onset temperature in magnetic susceptibility.

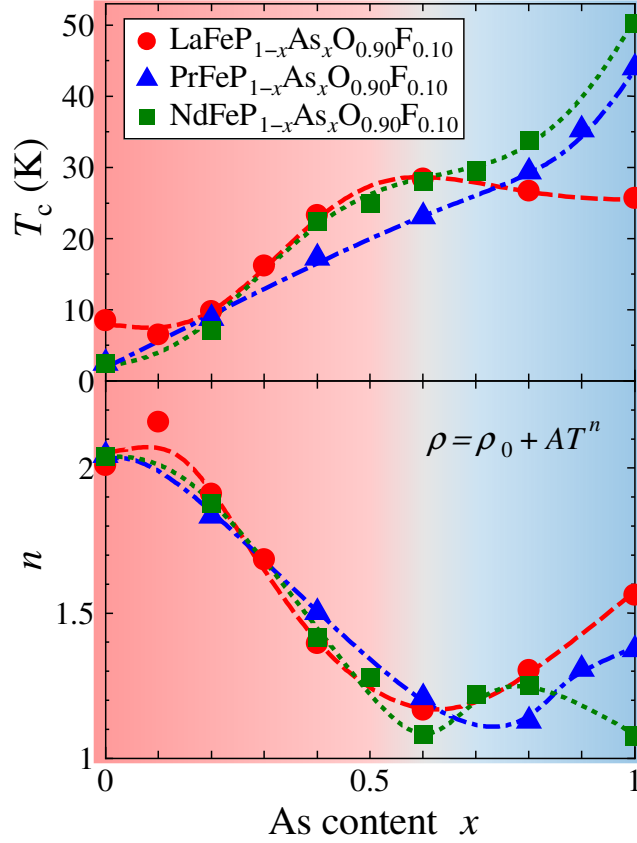


Figure 5.3:  $x$  dependences of  $T_c$  and  $n$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ). Two different composition regions of  $x < 0.6 - 0.8$  (red) and  $x > 0.6 - 0.8$  (blue) are also illustrated.

$T_c$  and  $n$  change non-linearly with  $x$  while crystal structural parameters change linearly with  $x$ , as shown in Figure 4.4. This suggests the existences of other hidden parameters beyond the crystal structural parameters. When  $x$  dependences of  $T_c$  and  $n$  are simultaneously focused on, two different composition regions of  $x < 0.6 - 0.8$  (red area in Figure 5.3) and  $x > 0.6 - 0.8$  (blue area) are extracted.

In the region of  $x < 0.6 - 0.8$ , both of  $T_c$  and  $n$  show nearly the same behaviors in all  $R$  systems. They are affected by neither  $\alpha$  nor  $h_{Pn}$  that are significantly different between La and the other systems.  $T_c$  increases from  $\sim 3$  K to  $\sim 30$  K with  $x$  in the region of  $x < 0.6 - 0.8$ .  $n$  is  $\sim 2$  at  $x = 0$ , namely  $\rho \sim T^2$ . This behavior can be explained as a conventional Fermi liquid behavior.  $n$  decreases from  $\sim 2$  to  $\sim 1$  with increasing  $x$  and then  $\rho$  shows  $T$ -linear behavior

at low temperatures around  $x = 0.6$ . In 2-dimensional AFM compounds,  $\rho$  decreases linearly with  $T$  in the vicinity of QCP [58]. As for QCP, it is confirmed with  $T$ -linear resistivity at  $x = 0.3$  in P/As substituted  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ . As for AFM fluctuation, NMR measurements using my polycrystalline samples of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x = 0, 0.2, 0.6$ ) are performed by Mukuda *et al.* [59]. Their results of  $1/T_1T$  are shown in Figure 5.4. The peak of  $1/T_1T$  at

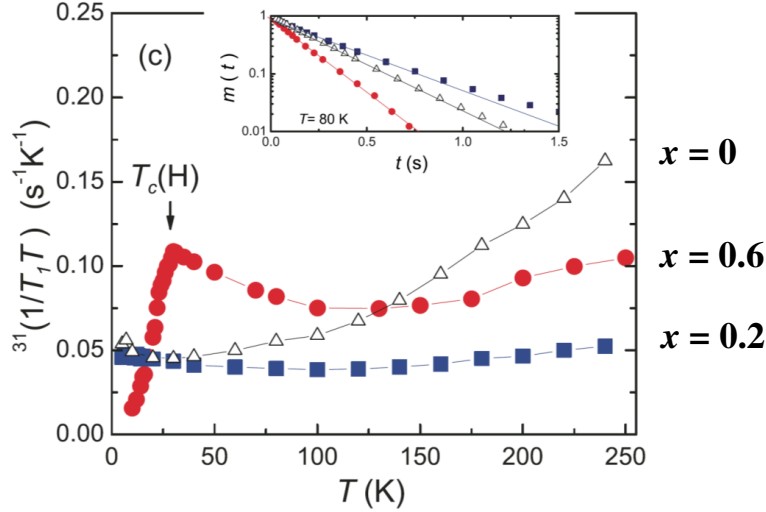


Figure 5.4: Temperature dependence of  $1/T_1T$  [59]

$x = 0.6$  suggests the enhancement of the AFM fluctuation. As a result, the  $T$ -linear behavior of electrical resistivity in the present systems indicates the enhancement of AFM fluctuation around  $x = 0.6 - 0.8$ . These experimental facts that  $T_c$  and AFM fluctuation increase and AFM fluctuation is enhanced with  $x$  mean that AFM fluctuation enhanced  $T_c$  to about 30 K in this composition region. This conclusion is consistent with many theoretical and experimental studies on iron-based superconductors.

In the region of  $x > 0.6 - 0.8$ ,  $T_c$  is affected not only by  $x$  but also  $R$ .  $x$  dependence of  $T_c$  shows different behaviors among different  $R$  systems. In the case of  $R = \text{La}$ ,  $T_c$  does not change significantly with  $x$ . In the case of  $R = \text{Pr}$  and  $\text{Nd}$ ,  $T_c$  increase with  $x$ . No clear correlation between  $T_c$  and  $n$  is observed except for  $x = 1.0$ . At  $x = 1.0$ ,  $T_c$  increases and  $n$  decreases with the decreasing ionic radius of  $R$  ( $\text{La} \rightarrow \text{Pr} \rightarrow \text{Nd}$ ). The similar behaviors of  $T_c$  and  $n$  were observed in  $R\text{FeAsO}_{1-y}$  system, and the details is discussed later.

### 5.2.2 $x$ dependences of $\rho_0$ and $A$

$x$  dependence of  $\rho_0$  and  $A$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ) is presented in Figure 5.5. It is impossible to obtain accurate absolute values of  $\rho_0$  and  $A$  because the sintered density of

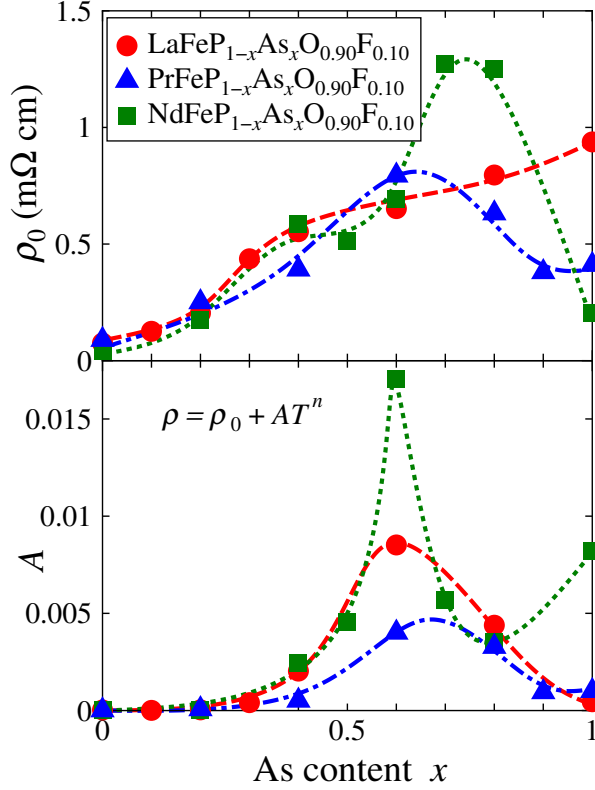


Figure 5.5:  $x$  dependence of  $\rho_0$  and  $A$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ).

polycrystalline samples is not constant. However, rough tendencies that  $\rho_0$  and  $A$  are enhanced at  $x \sim 0.6 - 0.8$  are observed in all  $R$  systems.

### 5.2.3 $x$ dependence of $R_H$ at $T = 50$ K

To clarify the  $x$  dependence of Hall coefficient at low temperatures,  $x$  dependences of  $R_H$  at  $T = 50$  K and  $n$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr, Nd}$ ) are presented in Figure 5.6. Both of P and As have the valence of -3 in the present systems. Therefore, P/As substitution should not change the carrier density of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ . However,  $|R_H|$  is enhanced and shows strong temperature dependence at  $x \sim 0.6 - 0.8$ , where  $n$  approaches 1. They seem to be ascribed to (i) band crossing on  $E_F$  and/or (ii) inherent behaviors of strongly correlated electron system.

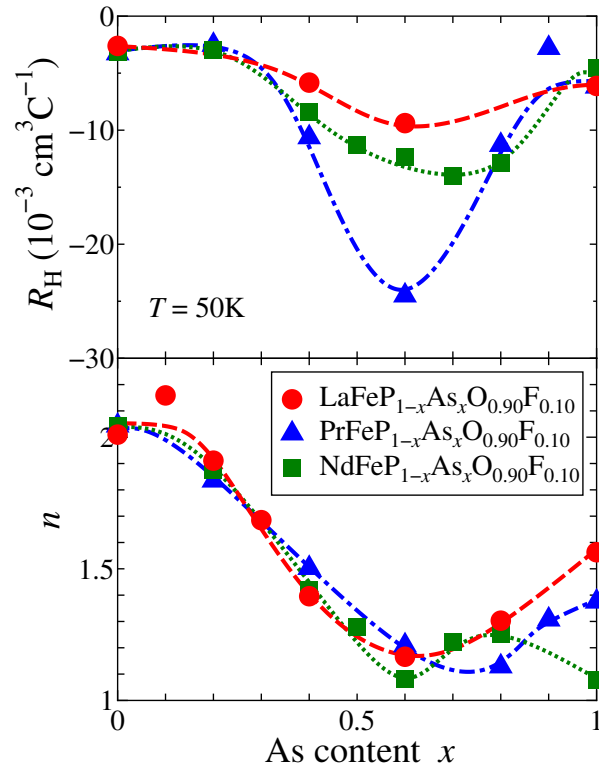


Figure 5.6:  $x$  dependence of  $R_H$  at  $T = 50 \text{ K}$  and  $n$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ).

As for the case (i),  $R_H$  of normal single-band metal is described as

$$R_H = \begin{cases} \frac{1}{n_h e} & (\text{hole}) \\ -\frac{1}{n_e e} & (\text{electron}) \end{cases} \quad (5.1)$$

On the other hand, iron pnictides have both hole and electron carriers (multiband). Then  $R_H$  of a multiband metal is described as

$$R_H = \frac{1}{e} \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2} \quad (5.2)$$

where  $n_h$  ( $n_e$ ) and  $\mu_h$  ( $\mu_e$ ) are hole (electron) carrier density and mobility, respectively. Theoretical calculations of band dispersions and FSs of NdFeAsO and LaFePO are shown in Figure 5.7. The theoretical study has demonstrated that the 3-dimensional hole FS with  $d_{Z^2}$  orbital

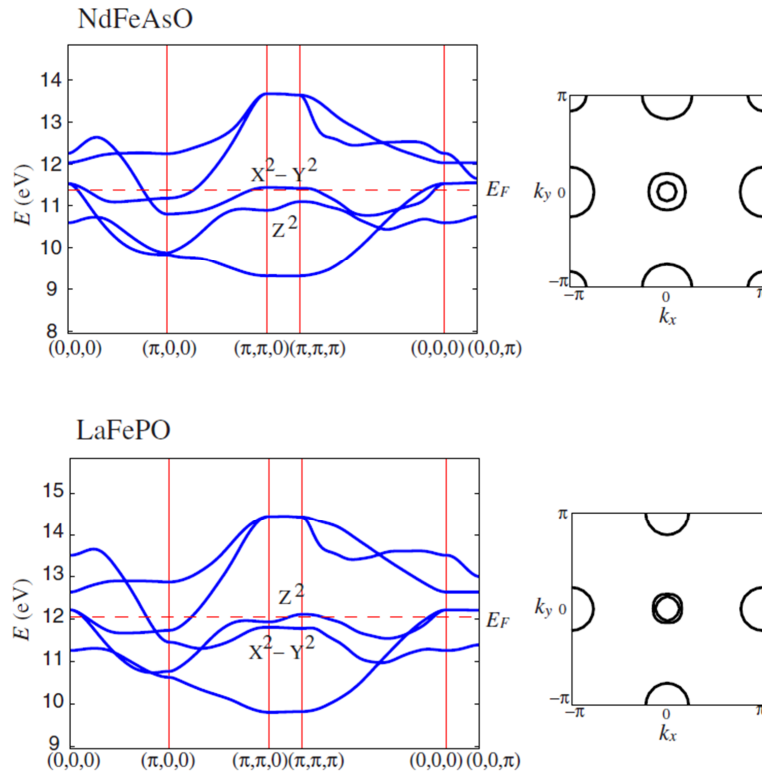


Figure 5.7: Theoretical calculation of band dispersions and FSs of NdFeAsO and LaFePO [27]

character exists around  $(\pi, \pi, \pi)$  in LaFePO, while the 2-dimensional hole FS with  $d_{X^2-Y^2}$  orbital character exists around  $(\pi, \pi, 0)$  in NdFeAsO. Both of the bands of  $d_{Z^2}$  and  $d_{X^2-Y^2}$  may sink below  $E_F$  at  $x \sim 0.6 - 0.8$ . In that case, a decrease of  $n_h$  and the enhancement of  $|R_H|$  are

expected.

As for the case (ii), similar behaviors are also observed in  $\text{Ce}TM\text{In}_5$  ( $TM = \text{Co}, \text{Rh}, \text{Ir}$ ) in heavy fermion system [60]. Not only the enhancement of  $R_H$  but also  $T$ -linear resistivity and breaking the Kohler's law are suggested as characteristic behaviors of strongly correlated electron system.

If the scenario (ii) is adopted and the AFM fluctuation affects superconductivity in the region of  $x > 0.6 - 0.8$ ,  $|R_H|$  should show a different behavior for each  $R$  system having different  $T_c$ . Nevertheless,  $|R_H|$  monotonically decreases with increasing  $x$  and reaches nearly the same value ( $\sim -5 \times 10^{-3} \text{ cm}^3\text{C}^{-1}$ ) at  $x = 1.0$  in all  $R$  systems. Therefore, the scenario (i) is more likely than the scenario (ii).

#### 5.2.4 Correlation between $T_c$ and $n$

##### Correlation between $T_c$ and $n$ in $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ( $R = \text{La}, \text{Pr}, \text{Nd}$ )

In the region of  $x < 0.6 - 0.8$ ,  $T_c$  increases from  $\sim 3 \text{ K}$  to  $\sim 3$  and  $n$  decreases from  $\sim 2$  to  $\sim 1$  with increasing  $x$ . In this region, the enhancement of AFM fluctuation causes the increase of  $T_c$ . For further understanding,  $n$  is plotted against  $T_c$  in Figure 5.8. In the region of  $x <$

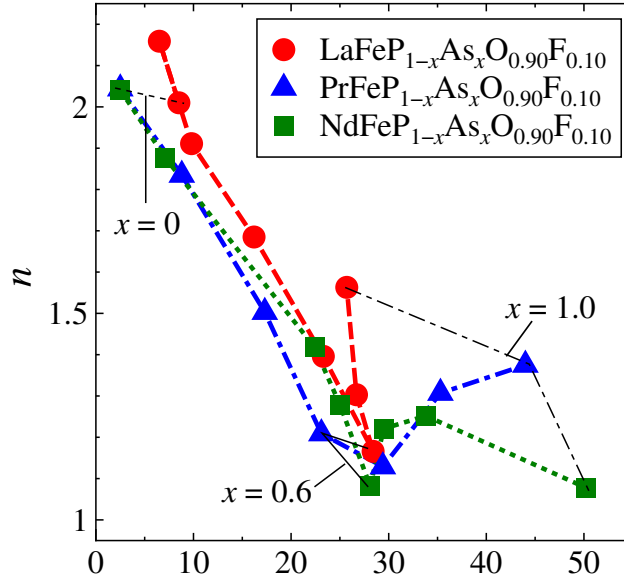


Figure 5.8: Correlation between  $T_c$  and  $n$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ).

0.6 - 0.8,  $T_c$  and  $n$  are on the same scaling line in spite of different  $R$  systems with different

lattice parameters. This scaling line demonstrates the correlation between the AFM fluctuation and  $T_c$ .  $T_c$  and  $n$  change with  $x$  on this line, therefore, As content  $x$  is an important parameter in this region. In the region of  $x > 0.6 - 0.8$ , however, the different behaviors of  $T_c$  and  $n$  are observed for different  $R$  systems.

### Correlation between $T_c$ and $n$ in various iron pnictide superconductors

The other correlation between  $T_c$  and  $n$  is also reported by Ishida *et al.* [61]. They discuss the relationship between  $T_c$  and  $n$  in 1111-type  $R\text{FeAsO}_{1-y}$  ( $R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ ), 122-type  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ,  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  and  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ . As shown in Figure 5.9, the new scaling line is found, where  $n$  decreases from  $\sim 2$  to  $\sim 1$  and  $T_c$  increases from  $\sim 20$  K to  $\sim 50$  K.  $T_c$  and  $n$  of  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  ( $x = 0.3 - 0.7$ ), 111-type  $\text{LiFeAs}$  and  $\text{LiFeP}$  by Kasahara *et al.* are also plotted with them in Figure 5.9. My and Ishida's scaling lines are indicated by red and blue bands, respectively.

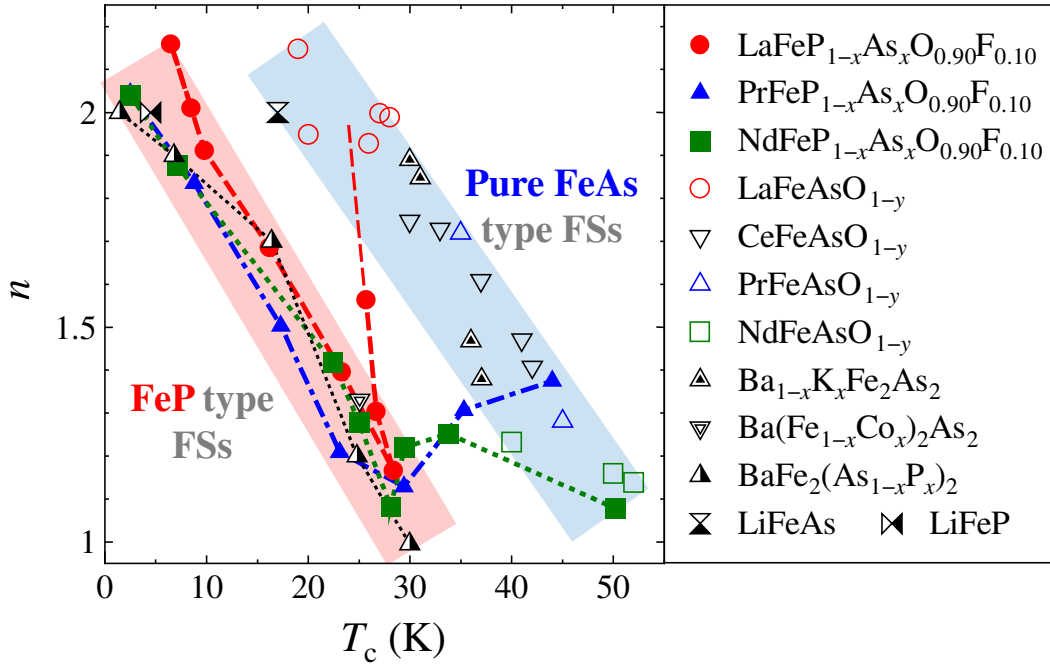


Figure 5.9: Correlation between  $T_c$  in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ) and various iron pnictide superconductors [16, 21, 56, 61].

My scaling line changes from  $T_c \sim 0$  K /  $n \sim 2$  to  $T_c \sim 30$  K /  $n \sim 1$ . This scaling line contains not only the data for  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x = 0 - 0.6$ ) but also those for  $\text{BaFe}_2\text{P}_2$  and  $\text{LiFeP}$ . As for  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ , the hole FS with  $d_{X^2-Y^2}$  orbital character is expected to appear only



in the vicinity of  $x = 1.0$  by band calculation. The hole FS generates different nesting vectors in spin fluctuation theory. Therefore, the correlation between  $T_c$  and  $n$  of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $x < 0.6 - 0.8$ ) may mean the enhancement of AFM fluctuation in the nesting situation without the  $d_{x^2-y^2}$  hole FS. 3-dimensionality of FSs, such as warping or decreasing of the contribution of the  $d_{xy}$  orbital character compared with iron arsenides, is also suggested in  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  and  $\text{LiFeP}$ . As a result, my scaling line suggests the enhancement of AFM fluctuation in FeP-type FSs.

Ishida's scaling line in Figure 5.9 changes from  $T_c \sim 20 \text{ K} / n \sim 2$  to  $T_c \sim 50 \text{ K} / n \sim 1$ . This scaling line is constructed of compounds having pure FeAs-type FSs, such as  $R\text{FeAsO}_{1-y}$  ( $R = \text{La, Ce, Pr, Nd}$ ),  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  and  $\text{LiFeAs}$ . The present results of  $\text{PrFeAsO}_{0.9}\text{F}_{0.1}$  and  $\text{NdFeAsO}_{0.9}\text{F}_{0.1}$  are located on this second scaling line.

My scaling line indicates the enhancement of  $T_c$  with decreasing  $n$  in FeP-type FSs, while Ishida's line indicates a similar  $T_c$  behavior in pure FeAs-type FSs. The difference of  $T_c$  between the two scaling lines is  $\sim 20 \text{ K}$ . This difference of  $T_c$  may be caused by (i) the difference of FSs and nesting vectors or (ii) the difference between spin fluctuation and other new fluctuation.

### Correlation among $T_c$ , $n$ and superconducting gap structure

Crystal structural parameters in iron-based superconductors affect not only  $T_c$  but also superconducting gap structure. Nodeless superconducting gap was reported in  $R\text{FeAsO}_{0.9}\text{F}_{0.1}$ , ( $R = \text{La, Pr, Nd}$ ),  $R\text{FeAsO}_{1-y}$  ( $R = \text{La, Ce, Pr, Nd}$ ),  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ,  $\text{LiFeAs}$ . On the other hand, nodal superconductivity was reported in  $R\text{FePO}_{0.9}\text{F}_{0.1}$ , ( $R = \text{La, Pr, Nd}$ ),  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  and  $\text{LiFeP}$ . Correlation between  $T_c$  and  $n$  together with superconducting gap structure (Nodeless / Nodal) for various iron pnictide superconductors is presented in Figure 5.10.

The present results for  $x < 0.6 - 0.8$  of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are on the same scaling line with the results of  $\text{LiFeP}$  and  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  having a nodal gap.  $R\text{FePO}_{0.9}\text{F}_{0.1}$  is suggested to have a nodal gap on the electron FS with  $s\pm$  wave symmetry or that on the hole FS with  $d$  wave symmetry. My experimental results of  $x = 1.0$  of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  are on the same scaling line with  $R\text{FeAsO}_{1-y}$  ( $R = \text{La, Ce, Pr, Nd}$ ) having a nodeless gap.  $R\text{FeAsO}_{0.9}\text{F}_{0.1}$  is suggested to have a nodeless gap in  $s\pm$  wave symmetry.

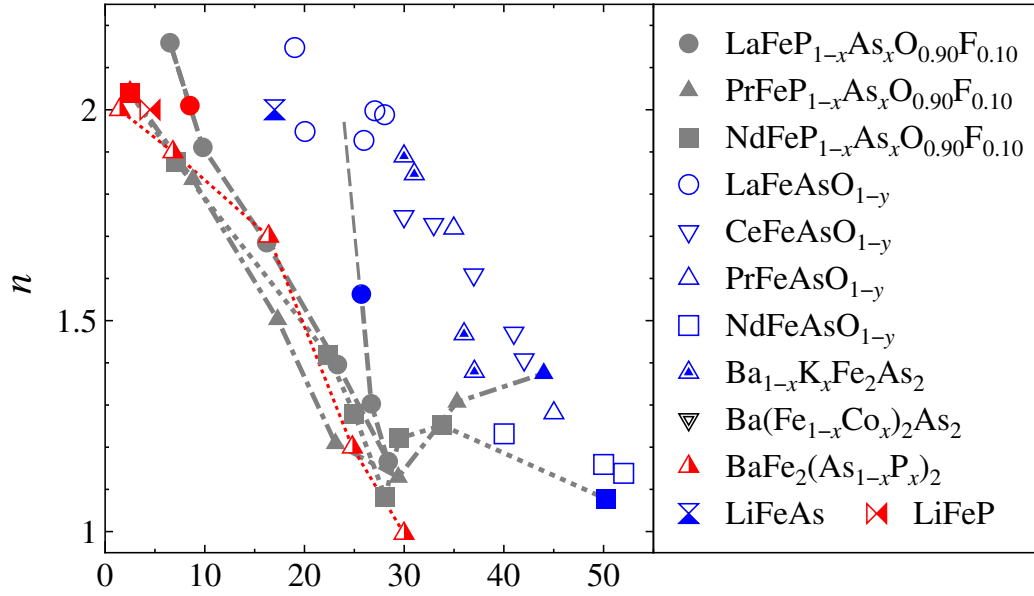
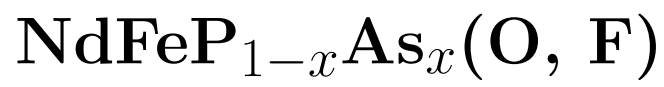


Figure 5.10: Correlation between  $T_c$  and  $n$  together with superconducting gap structure (Nodeless / Nodal) for various iron pnictide superconductors [16, 21, 56, 61].

## Part III

### Studies on Single-crystalline



## Chapter 6

# Experimental methodology

### 6.1 Single crystal growth of $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ by high pressure synthesis

#### 6.1.1 Previous studies of single crystal growth

There are a few reports on single crystal growth of 1111-type iron pnictide. Only two groups constantly succeed in the synthesis of  $\sim 1$  mm sized superconductive single crystals. Both of them use a high pressure technique.

Single crystals of O-deficient  $\text{PrFeAsO}_{1-y}$  have been obtained by Ishikado *et al.* in National Institute of Advanced Industrial Science and Technology (AIST), Japan [56]. A flat-belt type press machine was used to apply pressure and single crystals were grown by a self flux method using  $\text{PrAs}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}$  and  $\text{As}$ . Their synthesis conditions such as applied pressure, heating temperature and heating time are 2 GPa, 1300 - 1400 °C and 2 hours, respectively. A short heating time of 2 hours and the water-cooling press efficiently realized a large temperature gradient in the sample space like Bridgman-method. Reported sample size and  $T_c$  were 0.5 - 0.8 mm and 44 K, respectively. Single-crystalline  $\text{PrFeAsO}_{1-y}$  synthesized by them were provided to various measurements, such as ARPES, magnetic penetration depth measurements and so on.

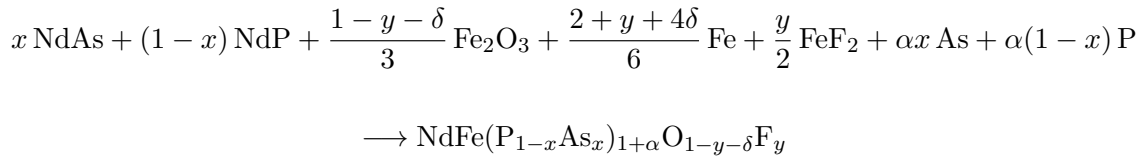
Single crystals of  $R\text{FeAs}(\text{O}, \text{F})$  ( $R = \text{Pr}, \text{Nd}$ ) have been obtained by Zhigadlo *et al.* in Eidgenössische Technische Hochschule Zürich (ETHZ) [62]. A cubic anvil type press machine is used to apply pressure. They adopted the  $\text{NaAs/KAs}$  flux method and their synthesis condition were slightly different from that in AIST group. In their synthesis, the temperature gradient in

the sample space is smaller than that in AIST group. Applied pressure and heating temperature in their crystal growth are 3 GPa and 1350 - 1450 °C. The holding time at the maximum temperature and slow-cooling time are 2 - 5 hours and 35 -90 hours. The reported sample size and  $T_c$  were 0.4 - 1 mm, 30 K for PrFeAs(O, F) and 39 K for NdFeAs(O, F), respectively.

In the present work, single crystal growth was performed by using a high pressure technique and the self flux method. Our press machine is cubic anvil type and our assembling parts without pyrophyllite are similar to those in AIST group. I grew the single crystals of NdFeP<sub>1-x</sub>As<sub>x</sub>(O, F) in order to clarify the detail of transport properties and the FSs by ARPES measurements.

### 6.1.2 Procedure of high pressure synthesis of NdFeP<sub>1-x</sub>As<sub>x</sub>(O, F)

Precursors NdAs and NdP were synthesized by following the processes described in Chapter 3. A composition of NdFe(P<sub>1-x</sub>As<sub>x</sub>)<sub>1+α</sub>O<sub>1-y-δ</sub>F<sub>y</sub> was determined as a target of weighting calculation, where  $x$ ,  $y$ ,  $δ$  and  $α$  were As substitution ratio for P site, F substitution ratio for O site, O deficiency ratio for O site and additional (P, As) ratio, respectively. The additional (P, As) was introduced to drop the melting point. The  $δ$  and  $α$  values are not noted in later chapters and sections. The raw materials are mixed with the below ratio,



The compositional ratio was often Nd : Fe : (P, As) : O : F = 1 : 1: 1.3 : 0.6 : 0.3 (namely  $y = 0.3$ ,  $δ = 0.1$  and  $α = 0.3$ ). The starting materials of NdAs, NdP, Fe<sub>2</sub>O<sub>3</sub>, Fe, FeF<sub>2</sub>, As and P were weighted with the above ratio and mixed in an agate mortar for 20 minutes. The mixture was pressed into a pellet (~ 2.5 g) under the pressure of 20 MPa.

High pressure synthesis was performed by using cubic anvil type press machine. Assembling parts for high pressure synthesis are shown in Figure 6.1 and Table 6.1. Pyrophyllites of 1 and 2 in Figure 6.1 have the chemical formula of Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> and play an important role as pressure media. The pyrophyllite is insulated and moderately soft to deform under pressure. Therefore, it is often used in high pressure synthesis. Stainless steel (SUS) of 3 and molybdenum of 4 in Figure 6.1 are electrodes to connect between the anvil and carbon. Carbons of 5 and 6 in Figure 6.1 are heaters to generate Joule heat by electrical conduction. Boron nitrides (BN) of 7 and 8 in Figure 6.1 construct a sample room and avoid the reaction between the sample

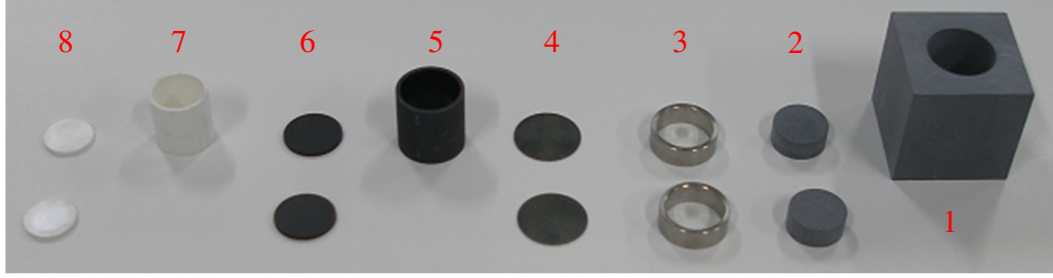


Figure 6.1: Assembling parts for high pressure synthesis.

Table 6.1: The list of assembling parts for high pressure synthesis.

Number	Material	size	No. of pcs.
1	Pyrophyllite	$21 \times 21 \times 21 \text{ mm}^3$	1
2	Pyrophyllite	$\phi 10 \times 4 \text{ mm}^2$	2
3	SUS	$\phi 12 \times \phi 10 \times 4 \text{ mm}^3$	2
4	Molybdenum	$\phi 12 \times 0.3 \text{ mm}^2$	2
5	Carbon	$\phi 12 \times \phi 10.5 \times 12.2 \text{ mm}^3$	1
6	Carbon	$\phi 10.5 \times 0.8 \text{ mm}^2$	2
7	BN	$\phi 10.5 \times \phi 9 \times 10.6 \text{ mm}^3$	1
8	BN	$\phi 9 \times 0.8 \text{ mm}^2$	2

and the carbon. Pyrophyllite and BN were dehydrated at  $600^\circ\text{C}$  for 24 hours. The schematic procedure of assembling parts for high pressure synthesis is illustrated in Figure 6.2.

First, six insulated sheets made of polytetrafluoroethylene (Teflon) were attached to the anvils in order to insulate among anvils and to conduct electrical current through carbon and only two anvils. All the parts were assembled and set into cubic anvils. The high pressure synthesis machine and the assembled parts on the anvils are shown in Figure 6.3. The weight applied to the press was often 260 t and it corresponds to the pressure of 3.8 GPa in the sample room. The calibrated relationship between the pressure and the weight is shown in Table 6.2.

Table 6.2: The calibrated relationship between the pressure and the weight.

Pressure (GPa)	Weight (t)
2	70
3	175
4	280
5	390
6	500
7	605

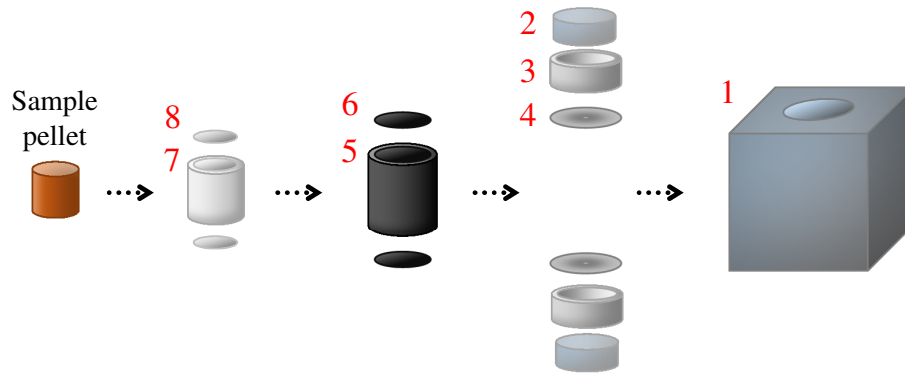


Figure 6.2: Procedure of assembling parts for high pressure synthesis.



Figure 6.3: The high pressure synthesis machine (Left) and the assembled parts on the anvils (Right).

The electronic power of  $\sim 2000$  W applied to the carbon heater, and the sample was heated up to  $\sim 1400$  °C. One example of the power condition to grow single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  is illustrated in Figure 6.4. Single crystals are expected to grow in the in-plane direction in the

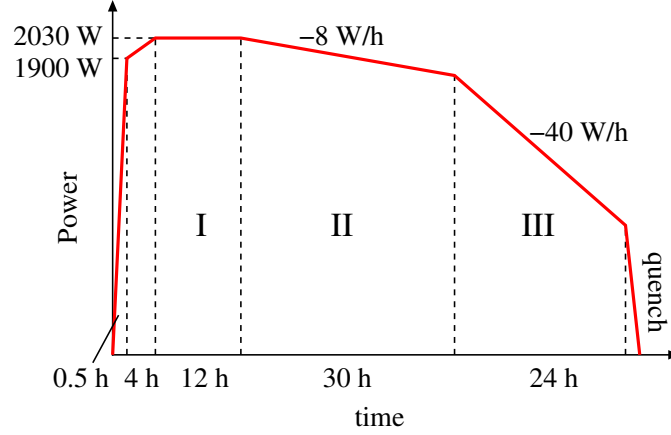


Figure 6.4: One example of the power condition to grow single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

region I and to grow in the out-of-plane direction in the region II in Figure 6.4. F is introduced into the single crystals in the region III. All anvils were air-cooled during the synthesis in order to avoid breaking anvils and to generate a large temperature gradient in a sample space. In fact, the probability to obtain single crystals in the case of anvil air-cooling was ten times larger than that without air-cooling. Therefore, temperature gradient in the sample space is plays an important factor in the present crystal growth process.

## 6.2 Measurements

### 6.2.1 Composition analysis

Composition analysis was performed by using electron probe microanalyzer (EPMA) in The Institute of Scientific and Industrial Research (ISIR), Osaka University and energy dispersive X-ray spectrometry (EDX) in Ashida Lab, Osaka University. 3 - 6 samples were measured by EDX and the composition was defined as the average value.

### 6.2.2 Magnetic susceptibility and transport measurements

Magnetic susceptibility, electrical resistivity, Hall effect and magnetoresistance were measured in order to discuss physical properties. The measurement procedures for single crystals



were almost the same as the case of polycrystalline samples. Magnetic susceptibility was measured in the magnetic field of 10 Oe parallel to the  $c$ -axis. In-plane electrical resistivity and magnetoresistance were measured by using the current perpendicular to the  $c$ -axis. Hall coefficient was measured in the magnetic field parallel to  $c$ -axis.

### 6.2.3 ARPES measurement

ARPES is a powerful technique, which can directly observe the dispersion of valence bands and Fermi surfaces. I performed APRES measurements to clarify the  $x$ -dependent change of the electronic structure and FSs in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  single crystals. Below, I describe the sample preparation, condition of measurement and analysis of ARPES measurement.

#### Sample preparation

Processes of the sample preparation for ARPES measurement are the following. First, all samples for ARPES measurements were confirmed to have a uniform  $T_c$  and show a sharp superconducting transition by magnetic susceptibility measurement. All of them were also confirmed to be a single-domain crystal by taking Laue photograph. Next, parts of the sample holder for the ARPES measurement, which are the base and the sample mount, were prepared. The base and the sample mount were made of Cu and BeCu, respectively. The edge of the sample mount was chipped off with a sand paper to cut off the reflected light from the surface of the sample mount. The top of the sample mount was also scratched to make adhesion between it and Ag paste easy. The sample was attached to the top of the sample mount with Ag paste. They were heated at 120 °C for 30 minutes to harden Ag paste (I confirmed that this heating procedure did not change the temperature dependence of magnetic susceptibility and  $T_c$  of the sample). The base and the sample mount were assembled into the sample holder. Interspaces between them was filled with an indium wire ( $\phi$  1 mm  $\times$   $\sim$  5 mm). The indium wire was used in order to make thermal contact good and to cool the sample down to low temperature. The sample mount was stabilized to the base like the configuration, as illustrated in the left panel of Figure 6.5. In this configuration, the hole and electron FSs can be observed by changing only the tilt angle in the ARPES measurement. The sample alignment was confirmed by taking Laue photograph again (See the right panel of Figure 6.5). At last, an alumina pole ( $\phi$  1 mm  $\times$  4 mm) for cleaving was stuck to the sample surface with Torr Seal (Pascal Co.) (See the left panel of Figure 6.6). They were heated at 120 °C for 30 minutes to harden Torr Seal.

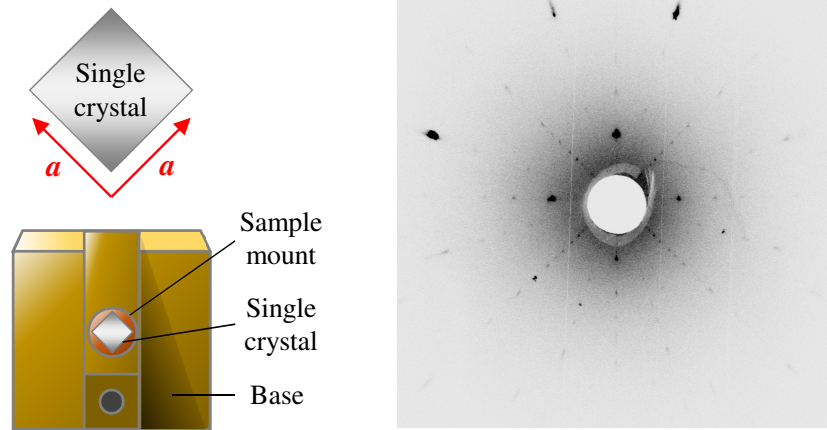


Figure 6.5: The sample location (Left) and the Laue photograph (Right).

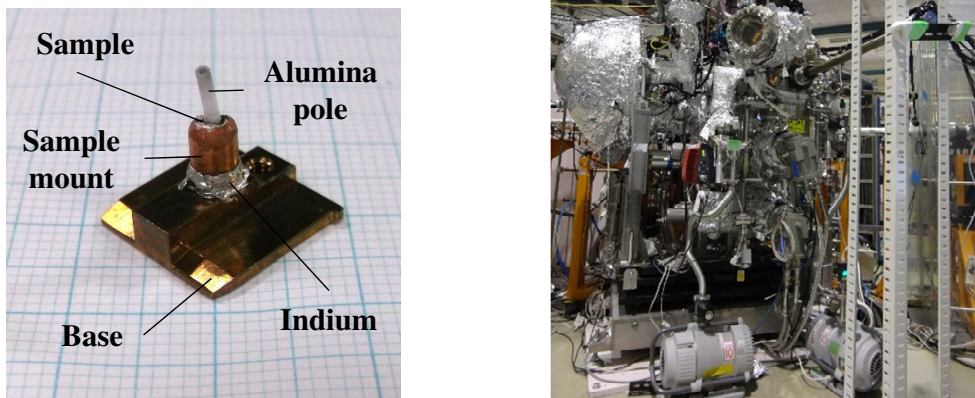


Figure 6.6: The sample holder (Left) and the instrument of the ARPES measurement at BL-7U in UVSOL (Right).

Further processes of the sample preparation performed at BL-7U in UVSOR (the right panel of Figure 6.6) are the following. The sample holder was coated by aero-duck (The Nilaco Co.) to cut off the reflected light. The sample holder was inserted into the cryostat in the vacuum space using a transfer rod. The sample was cooled below 20 K and cleaved to get a clean surface.

### Measurements and analysis

In general, the ARPES experiments are performed to detect the energy and momentum distribution of electron in occupied states. The electron is excited by absorption of photons from monochromatized light source. The photoemission processes can be understood by the three step model.

- (i) The photon is absorbed and the electron in bulk sample is excited.
- (ii) The excited electron moves to the surface through the sample without scattering.
- (iii) The electron overcomes the potential of work function  $\Phi$  and escapes into the vacuum with a kinetic energy  $E_{\text{kin}}$ .

In the photoemission process, the momentum of electron perpendicular to sample surface is partially lost because of the work function, when the excited electron escapes into the vacuum. On the other hand, its momentum parallel to surface is conserved due to the transition symmetry. Figure 6.7 illustrates a schematic process of photoemission spectroscopy. When the electron in the sample absorbs a photon with sufficiently high energy  $h\nu$ , it is emitted as a photoelectron. According to the energy conservation and momentum one, the kinetic energy and the momentum are written as follows.

$$E_{\text{kin}} = h\nu - \Phi - |E_{\text{B}}|. \quad (6.1)$$

$$p_{//} = \hbar k_{//} = \sqrt{2mE_{\text{kin}}} \sin\theta. \quad (6.2)$$

Here,  $E_{\text{B}}$ ,  $p$ ,  $\theta$ , and  $m$  are binding energy, momentum of electron in vacuum, pole angle, and electron mass, respectively. The work function is the energy difference between Fermi level  $E_{\text{F}}$  and vacuum energy  $E_{\text{vac}}$ , i.e.  $\Phi = E_{\text{vac}} - E_{\text{F}}$ . In actual experiment, the kinetic energy measured from  $E_{\text{F}}$  rather than  $E_{\text{vac}}$  is observed. Then, it is convenient to write

$$E_{\text{kin}} = h\nu - |E_{\text{B}}|. \quad (6.3)$$

By measurement of kinetic energy of the electron together with the position of detector, the binding energy and the momentum of electron on the 2-dimensional Fe plane can be determined.

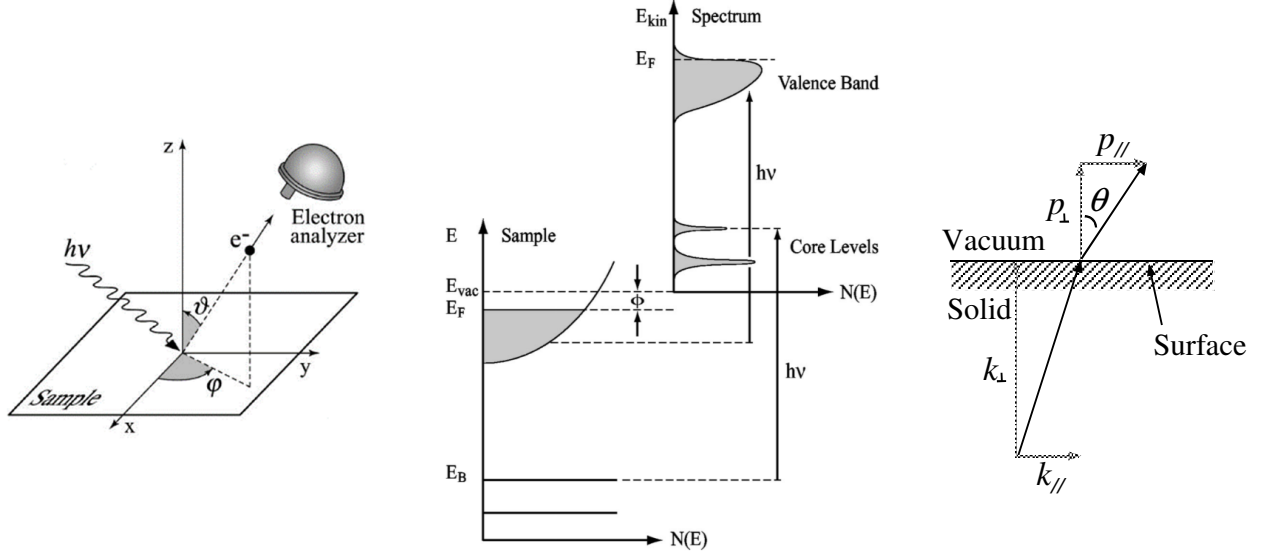


Figure 6.7: Geometry on ARPES measurement (Left) and the photoemission of electrons (Center) and the geometry of a photoelectron on the sample surface (Right) [63].

Figure 6.8 shows the schematic procedure of band mapping by ARPES. By detecting all the electrons with different kinetic energy but with same momentum, we can get the energy distribution curve (EDC). In contrast, the momentum distribution curve (MDC) can be gotten by collecting the electrons with same energy but different momentum. EDC includes the information of density of state. I measured the EDC along several directions on Brillouin zone, and determined the band dispersion. On the other hand, I performed the MDC measurement under the condition of constant energy around  $E_F$  along many cuts on Brillouin zone, and got the FS mapping.

The iron-based superconductors are multi-band systems, and have several hole- and electron-FSs with different  $d$ -orbital characters of Fe. These FSs are expected to have different nesting conditions and different contribution to superconductivity. Therefore, it is important to clarify the orbital characters of each FS (or band) in the present system. When the symmetry of  $3d$  orbitals in real space is considered, the photoemission signal of certain orbitals depends on the polarization of incident light generally. In the present ARPES measurement, I used two linear polarization geometries,  $P$  and  $S$  polarizations. Figure 6.9 shows the experimental setup for polarization dependent ARPES. In  $P$  polarization (or  $S$  polarization) configuration, the electric

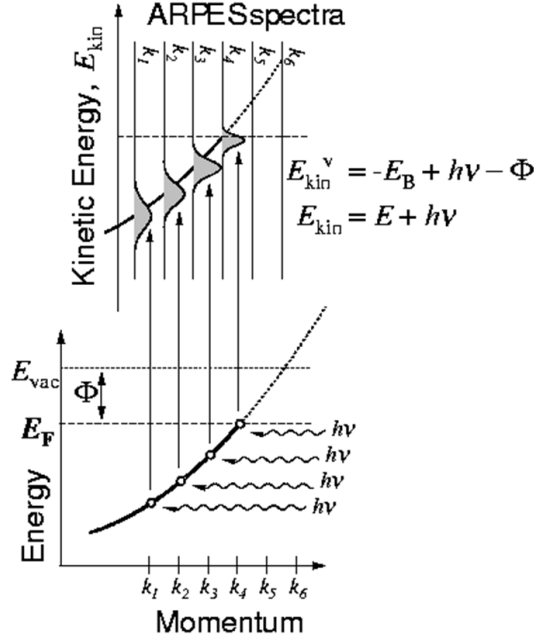


Figure 6.8: The relationship between the ARPES spectra and the band dispersion.

field direction of the incident light is parallel (or perpendicular) to the mirror plane defined by the analyzer slit and sample surface. By measuring the polarization dependence of ARPES along  $\Gamma$ -M with high symmetry, we could determine the orbital character of bands. The bands with  $d_{xz}$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$  characters can be observed in the  $P$  polarization configuration, while those with  $d_{yz}$  and  $d_{xy}$  can be detected in the  $S$  polarization configuration.

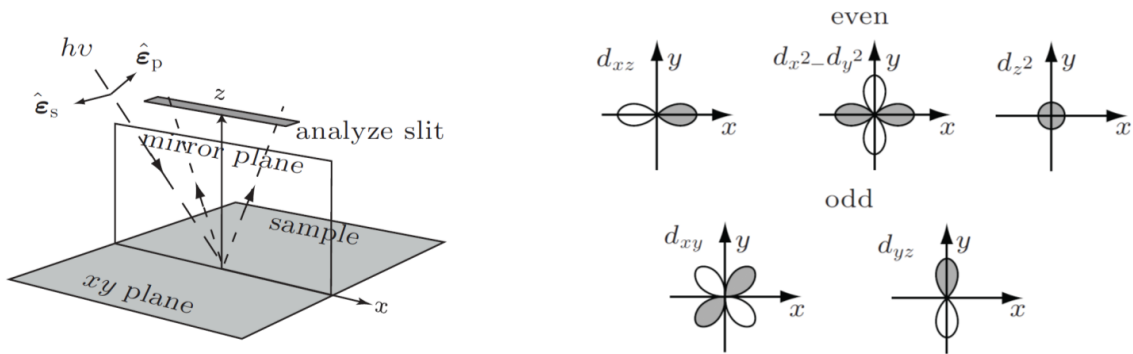


Figure 6.9: The polarized directions of  $P$  and  $S$  (Left) and the orbital characters of  $3d$  electrons (Right) [64].

The ARPES measurement was performed at the SAMURAI end-station of the undulator beamline BL-7U in UVSOR-III in the Institute for Molecular Science. Measurement samples were single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x$  ( $\text{O, F}$ ) ( $x = 0.4, 0.8$  and  $1.0$ ). The measurement temperature is

## Chapter 6 Experimental methodology

---

about 12 K. The light source energy ( $h\nu$ ) is 12 eV - 40 eV. The energy resolution was about 15 meV. The angular resolution was about  $0.17^\circ$ .  $E_F$  was calibrated using an evaporated Au film.

## Chapter 7

# Experimental results

### 7.1 Single crystals of $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ grown by high pressure synthesis

The single crystals of  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  were grown within the sintered pellet. The pellet separated into two pieces and an extracted single crystal of  $\text{NdFeP}_{0.4}\text{As}_{0.6}(\text{O}, \text{F})$  are shown in Figure 7.1.

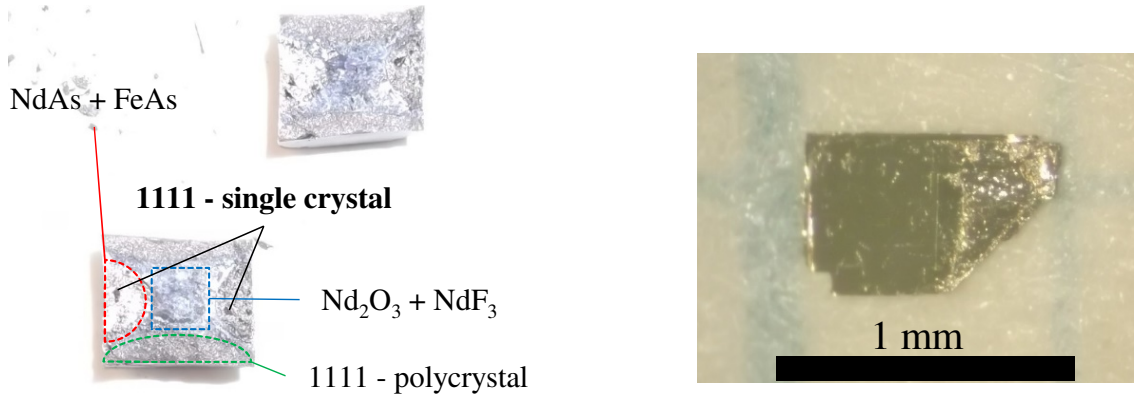


Figure 7.1: A sintered pellet separated into two pieces along the perpendicular direction (Left) and a single crystal of  $\text{NdFeP}_{0.4}\text{As}_{0.6}(\text{O}, \text{F})$  (Right).

The sintered pellet is mainly separated into three regions of (i) NdAs and FeAs, (ii)  $\text{Nd}_2\text{O}_3$  and  $\text{NdF}_3$  and (iii) 1111-type polycrystals. The compositions of each region are measured by using EDX. Single crystals were discovered in the region of (i). A typical single crystal size was about  $1 \times 1 \times 0.03 \text{ mm}^3$ .

The F concentration estimated by EPMA was  $\sim 0.05$  in a whole  $x$  region. In the As end material ( $x = 1.0$ ), no structural transition was observed in the temperature dependence of electrical resistivity and  $T_c$  is lower than that of an optimal doped sample. According to above facts in the  $x = 1.0$  sample, the F concentration is also expected to be 5 - 10 %, which is close to that of EPMA values.

The nominal F content  $y$  was 0.3 in most cases. However, the  $y$  value cannot be determined by EDX, because the energy of the X-ray absorption peak for Fe is close to that for F. Then only As content  $x$  was determined by EDX measurements. The result of the EDX measurements is shown in Figure 7.2 and Table 7.1.

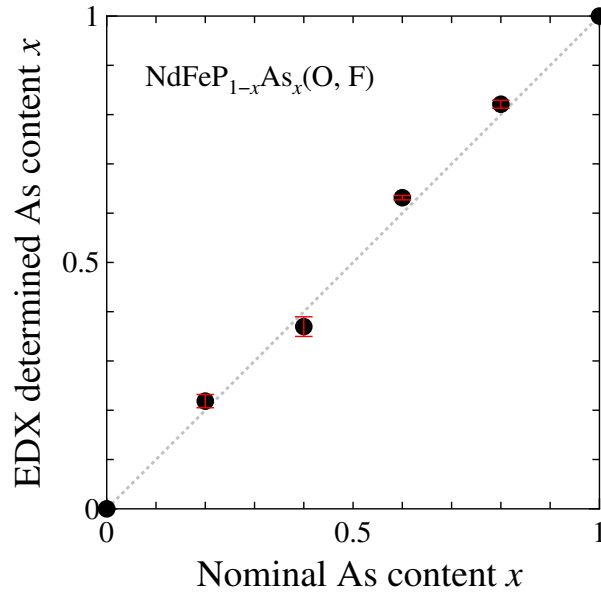


Figure 7.2: The actual As content  $x$  determined by the EDX measurement.

Table 7.1: The actual As content  $x$  determined by the EDX measurement.

Nominal	EDX
0	0
0.2	0.219(13)
0.4	0.370(20)
0.6	0.631(4)
0.8	0.821(8)
1.0	1

Hereafter, I use the nominal As content as  $x$ , because  $x$  determined by the EDX measure-



ments is nearly same to the nominal one.

## 7.2 Magnetic susceptibility

Temperature dependence of magnetic susceptibility of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  is presented in Figure 7.3.  $T_c$  of grown single crystals in the same batch are almost same. Bulk superconductivity emerged at  $x = 0.4 - 1.0$ . The  $T_c$  of  $\text{NdFeAs}(\text{O}, \text{F})$  was 43.5 K, which is higher than that of the crystals grown by the ETHZ group.

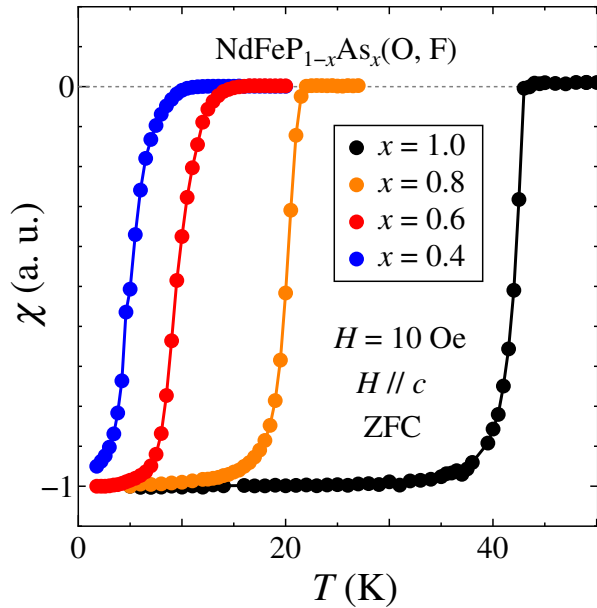


Figure 7.3: Temperature dependence of magnetic susceptibility of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

## 7.3 Electrical resistivity

Temperature dependence, double logarithmic plots and fitting curves of electrical resistivity of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  are presented in Figures 7.4, 7.5 and 7.6.  $T_c$  and the temperature dependence of electrical resistivity hardly changed in the same batch. The residual resistivity ratio ( $RRR$ ) defined as  $\rho_{300\text{K}}/\rho_{0\text{K}}$  of  $\text{NdFeAs}(\text{O}, \text{F})$  was  $\sim 5$ , which is higher than that of the crystals without annealing of the AIST group. The  $x$  dependence of  $T_c$ ,  $n$ ,  $A$  and  $\rho_0$  are discussed in Chapter 9.

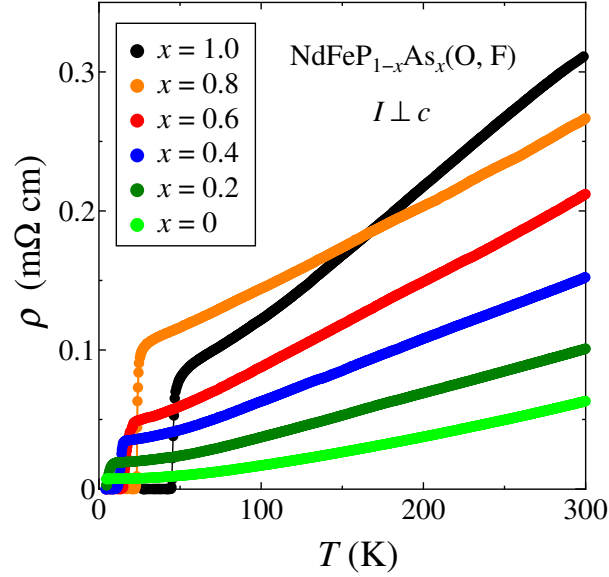


Figure 7.4: Temperature dependence of electrical resistivity of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

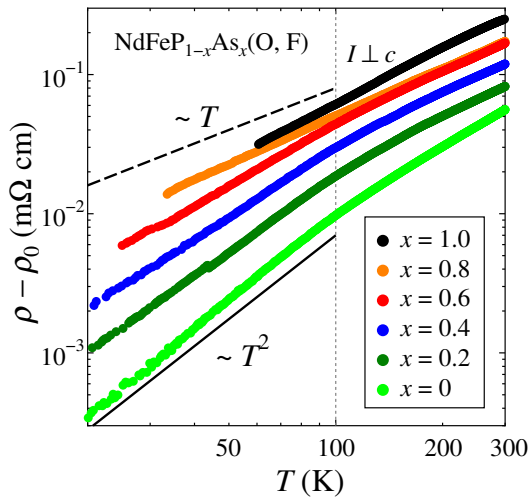


Figure 7.5: Double logarithmic plot of electrical resistivity of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

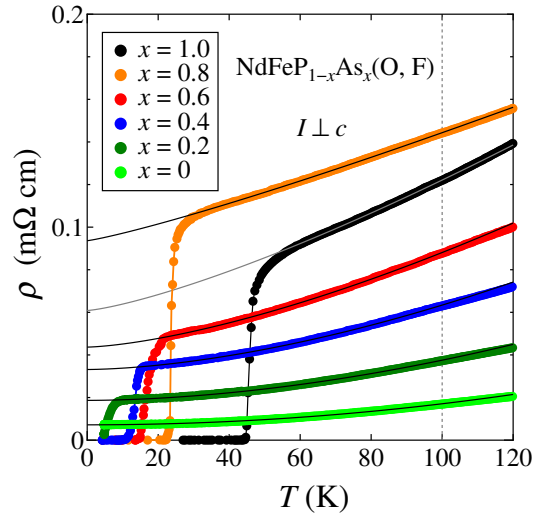


Figure 7.6: Fitting curves of electrical resistivity of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

## 7.4 Hall effect

### 7.4.1 Hall resistivity

Magnetic field dependences of Hall resistivity  $\rho_{xy}$  in single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  with various  $x$  at various temperature are plotted in Figures 7.7 - 7.12.  $\rho_{xy}$  is fitted with the formula  $\rho_0 = c_1 H + c_2 H^3$  and  $c_1$  is defined as  $R_H$ .

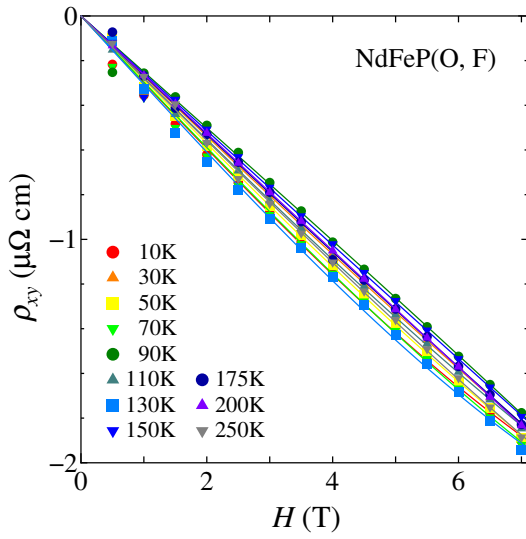


Figure 7.7: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeP}(\text{O}, \text{F})$ .

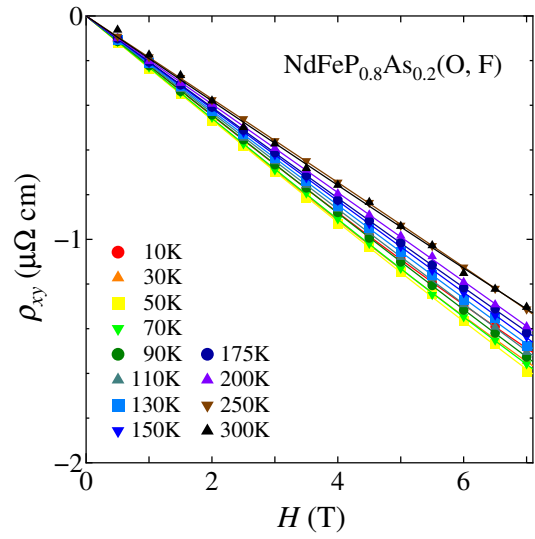


Figure 7.8: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeP}_{0.8}\text{As}_{0.2}(\text{O}, \text{F})$ .

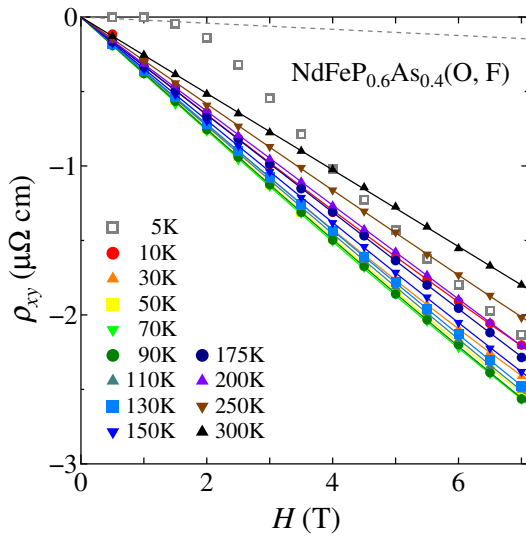


Figure 7.9: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeP}_{0.6}\text{As}_{0.4}(\text{O}, \text{F})$ .

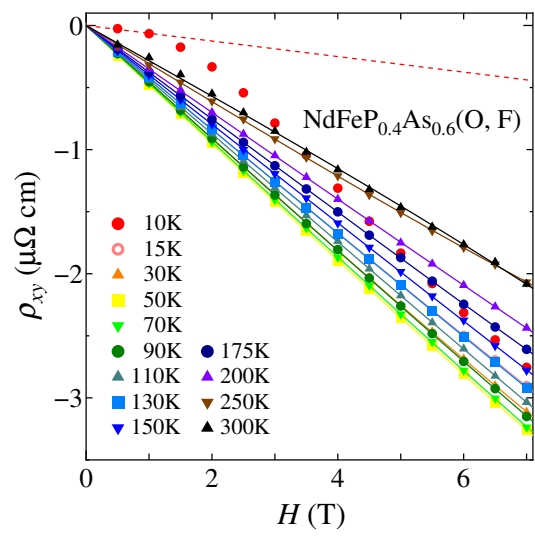


Figure 7.10: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeP}_{0.4}\text{As}_{0.6}(\text{O}, \text{F})$ .

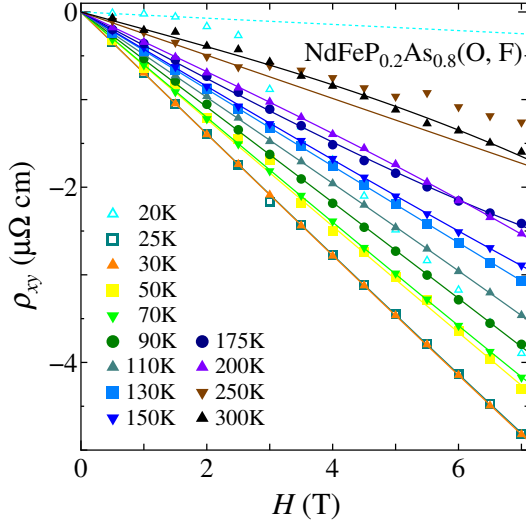


Figure 7.11: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeP}_{0.2}\text{As}_{0.8}(\text{O}, \text{F})$ .

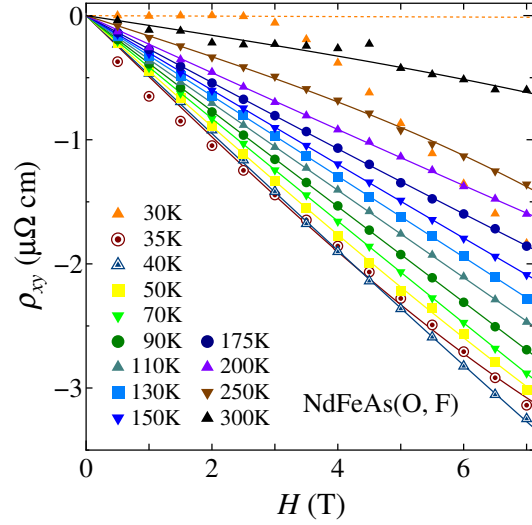


Figure 7.12: Magnetic field dependence of  $\rho_{xy}$  of single-crystalline  $\text{NdFeAs}(\text{O}, \text{F})$ .

#### 7.4.2 Hall coefficient

Temperature dependence of Hall coefficient of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  with various  $x$  shown in Figure 7.13. Temperature dependence of  $R_H$  of single-crystalline samples is similar to that of polycrystalline samples.  $R_H$  hardly change with temperature at  $x = 0$  and  $0.2$ .  $R_H$  gradually shows a temperature dependence with increasing  $x$  and the strong temperature dependence at  $x = 0.8$  and  $1.0$ .  $|R_H(T = 300\text{K})| / |R_H(50\text{K})| \sim 5$  at  $x = 1.0$  is much smaller than that ( $\sim 2$ ) of the polycrystalline sample. This result is consistent with the previous report of single-crystalline  $\text{NdFeAsO}_{0.82}\text{F}_{0.18}$  [65].

### 7.5 Magnetoresistance

Temperature dependences of magnetoresistance of  $\text{NdFeAs}(\text{O}, \text{F})$  are shown in Figures 7.14 and 7.15.  $\rho(T)$  is normalized at 55 K. With applying magnetic field, the resistive transition to superconducting state is broaden, and the suppression of  $T_c$  by magnetic field is more remarkable in the case of  $H // c$  than the case of  $H \perp c$ .

Upper critical magnetic field  $H_{c2}$  of  $\text{NdFeAs}(\text{O}, \text{F})$  is presented in Figure 7.16.  $H_{c2}$  is defined as the magnetic field where  $\rho(T)$  drops to 90 %, 70% and 50 % of  $\rho(55 \text{ K})$ , and anisotropic parameter  $\Gamma$  is estimated as 7.7, 4.4, and 4.0, respectively. The  $\Gamma$  values are consistent with those of the previous studies [56].

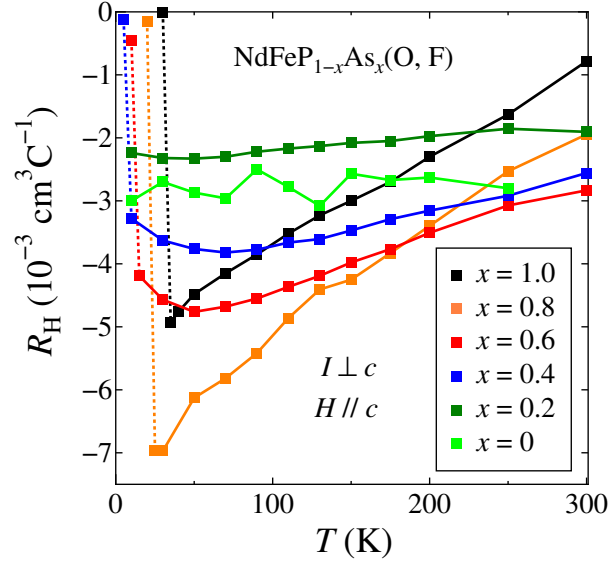


Figure 7.13: Temperature dependence of Hall coefficient  $R_H$  of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

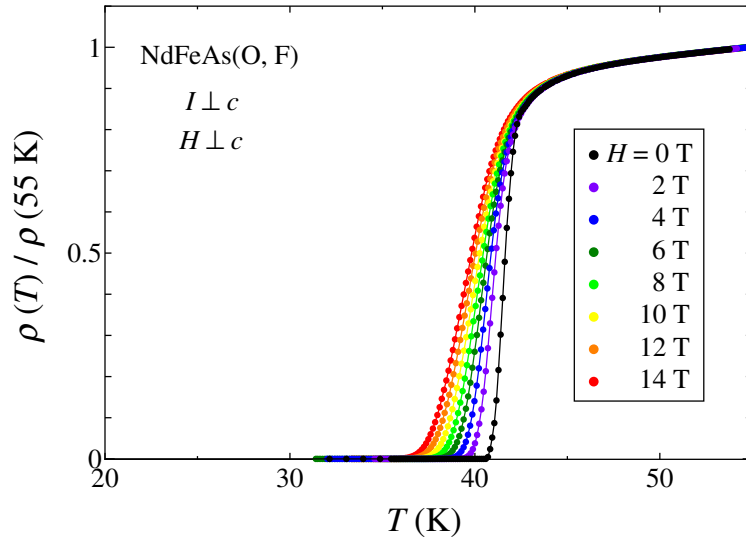


Figure 7.14: Temperature dependences of magnetoresistance of  $\text{NdFeAs}(\text{O}, \text{F})$ . The magnetic field was applied in the direction perpendicular to the  $c$ -axis.

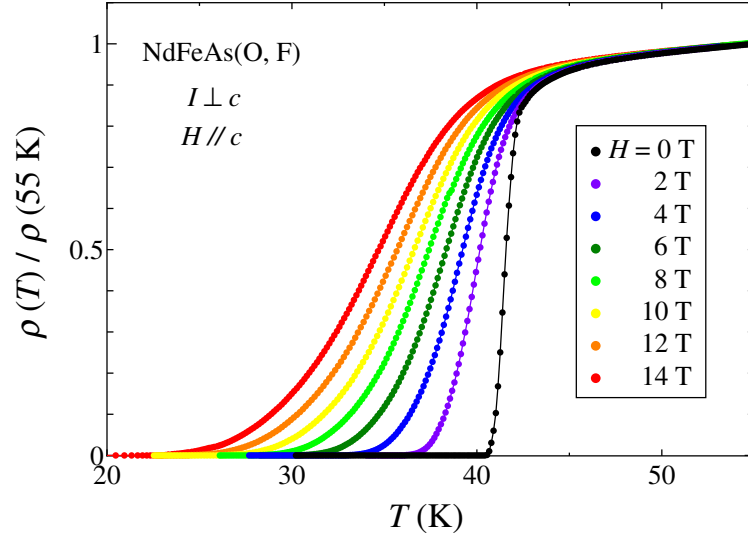


Figure 7.15: Temperature dependences of magnetoresistance of NdFeAs(O, F). The magnetic field was applied in the direction parallel to the  $c$ -axis.

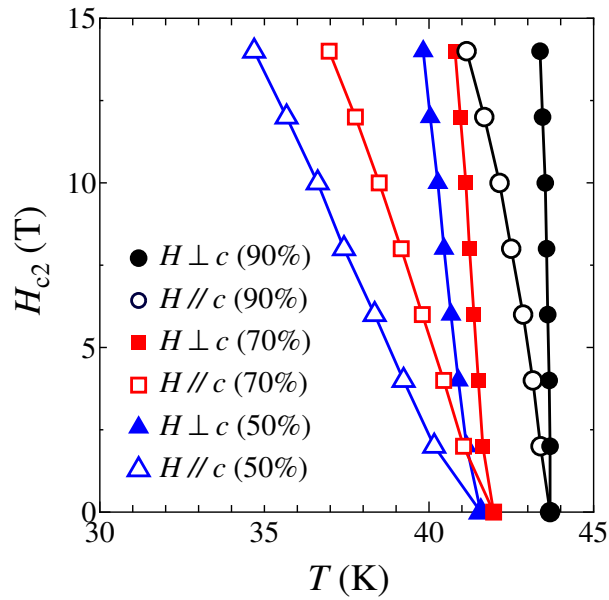


Figure 7.16: Upper critical magnetic field  $H_{c2}$  of NdFeAs(O, F).

## 7.6 ARPES

### 7.6.1 $k_z$ dependence of FS mapping

The energies of incident light corresponding to  $\Gamma$  and Z points in reciprocal lattice have to be determined by the measurement of the energy dependence of FS mapping. First, the band dispersion along  $\Gamma$  - M direction was measured by using the incident light with the energies of  $h\nu = 12 - 40$  eV. Next, the intensity of the MDCs at  $E_F$  were measured by using incident light with various energies. The energy dependence of the intensity of MDCs was changed to its  $k_z$  dependence by the analysis. FS mapping on  $k_x - k_z$  plane in  $P$  polarization of  $\text{NdFeP}_{0.2}\text{As}_{0.8}(\text{O}, \text{F})$  is shown in Figure 7.17. There is a cylindrical hole FS around  $k_x \sim \pm 0.4$ , indicated by

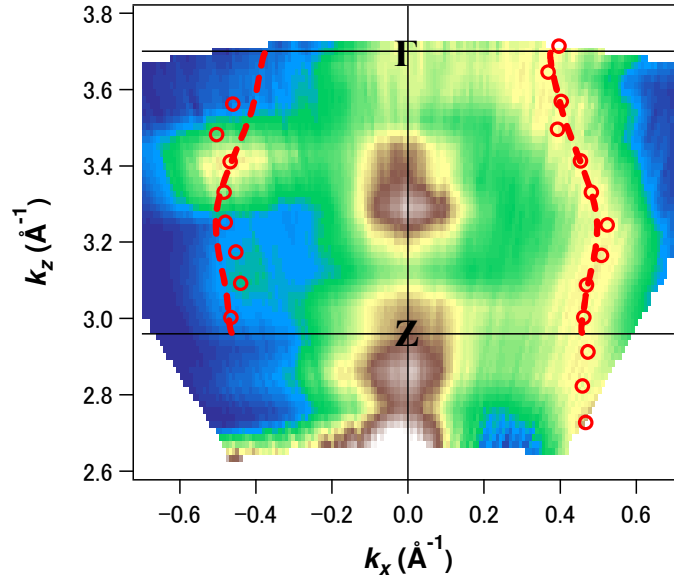


Figure 7.17: FS mapping on  $k_x - k_z$  plane in  $P$  polarization of  $\text{NdFeP}_{0.2}\text{As}_{0.8}(\text{O}, \text{F})$ .

red broken lines in Figure 7.17 (This FS has  $d_{z^2}$  orbital character. The detail of assignment of orbital character is described later.). This FS are slightly 3-dimensional and bent. The FS with  $d_{z^2}$  orbital character is expected to have a large shrinkage around  $\Gamma$  point. Then I determined that  $\Gamma$  point is located at  $k_z = 3.7$ , corresponding to the incident energy of 36 eV of incident light. The shape of this FS is similar to that of  $x = 0.4$ . Lattice constant  $c$  of  $x = 0.4$  and 1.0 is only 1.1 % smaller and 0.4 % larger than that of  $x = 0.8$ , and their Brillouin zone sizes along  $k_z$  are almost same. Therefore, 36 eV is determined as the energy to detect  $\Gamma$  point in all the samples of the present system.

### 7.6.2 Band dispersion

Band dispersion along  $\Gamma$  - M direction of  $\text{NdFeP}_{0.6}\text{As}_{0.4}(\text{O}, \text{F})$ ,  $\text{NdFeP}_{0.2}\text{As}_{0.8}(\text{O}, \text{F})$  and  $\text{NdFeAs}(\text{O}, \text{F})$  are presented in Figures 7.18 - 7.23.



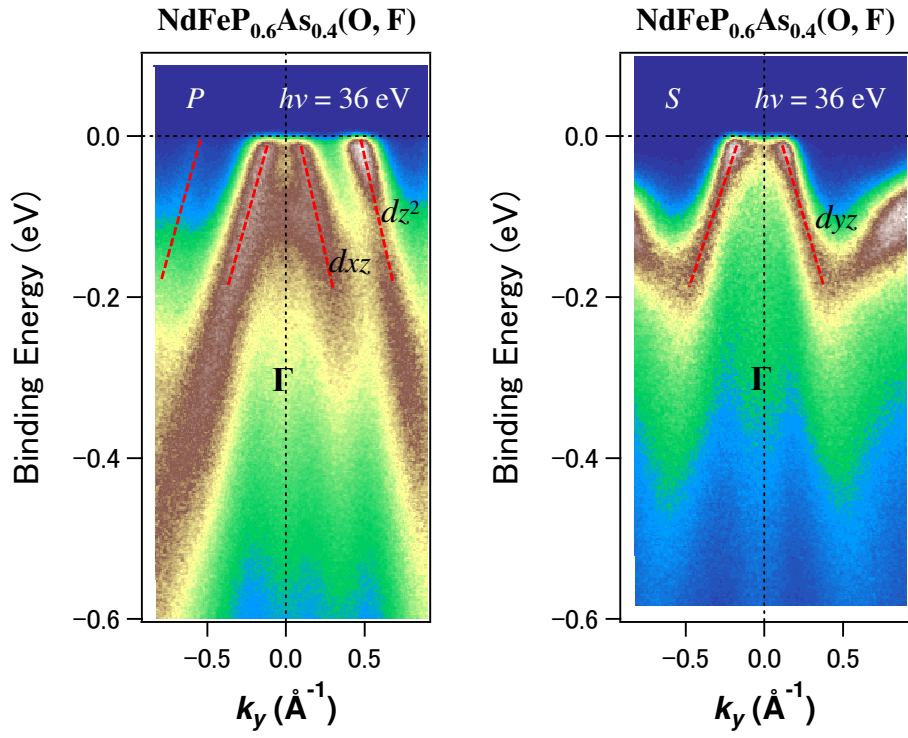


Figure 7.18:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around  $\Gamma$  point of NdFeP<sub>0.6</sub>As<sub>0.4</sub>(O, F).

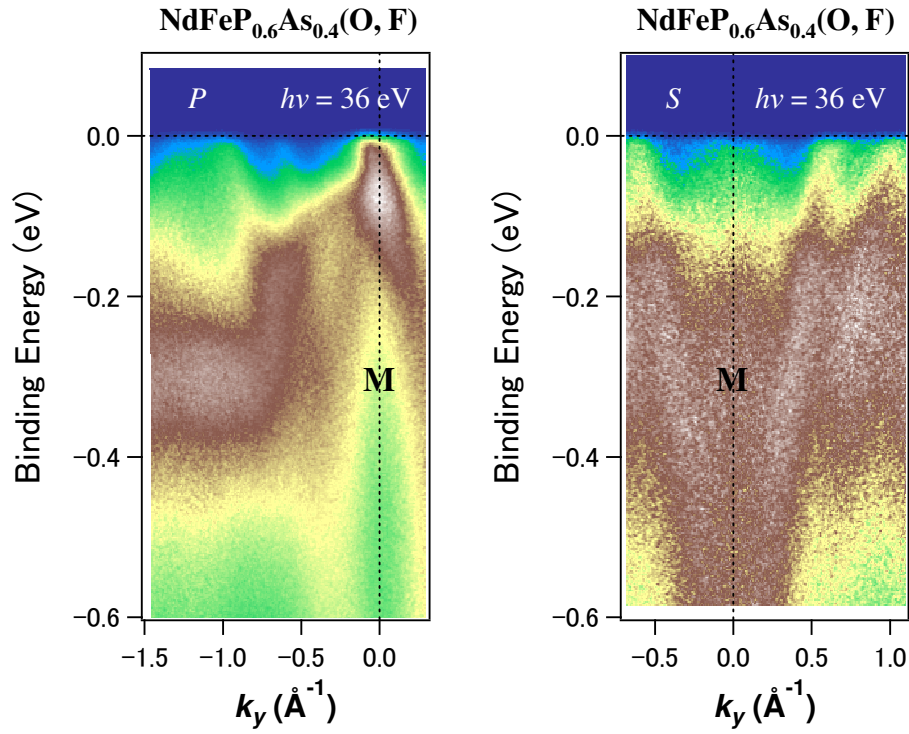


Figure 7.19:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around M point of NdFeP<sub>0.6</sub>As<sub>0.4</sub>(O, F).

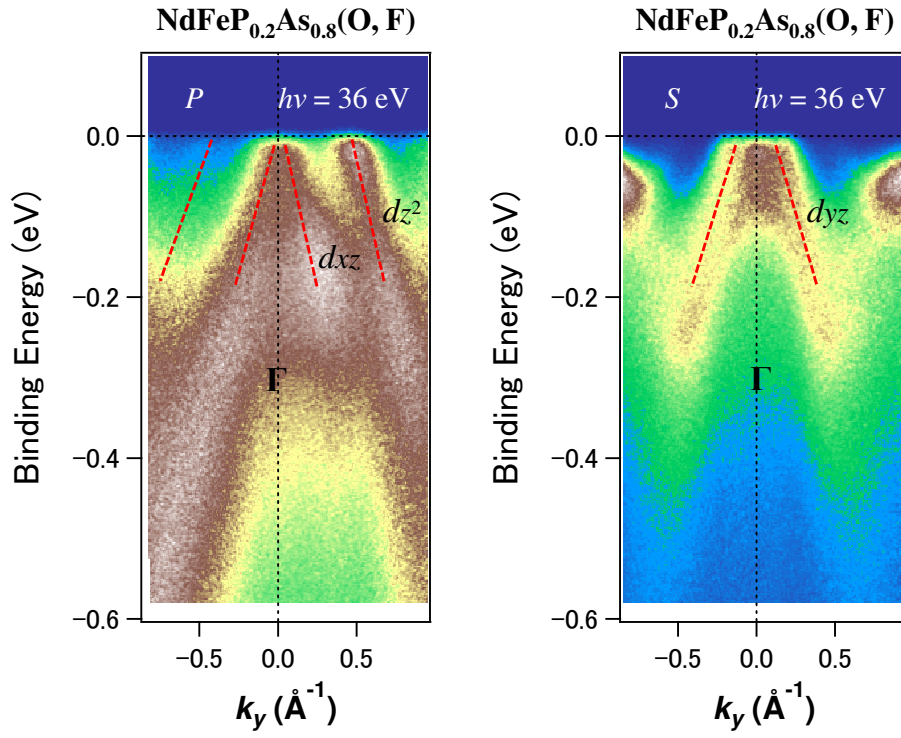


Figure 7.20:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around  $\Gamma$  point of NdFeP<sub>0.2</sub>As<sub>0.8</sub>(O, F).

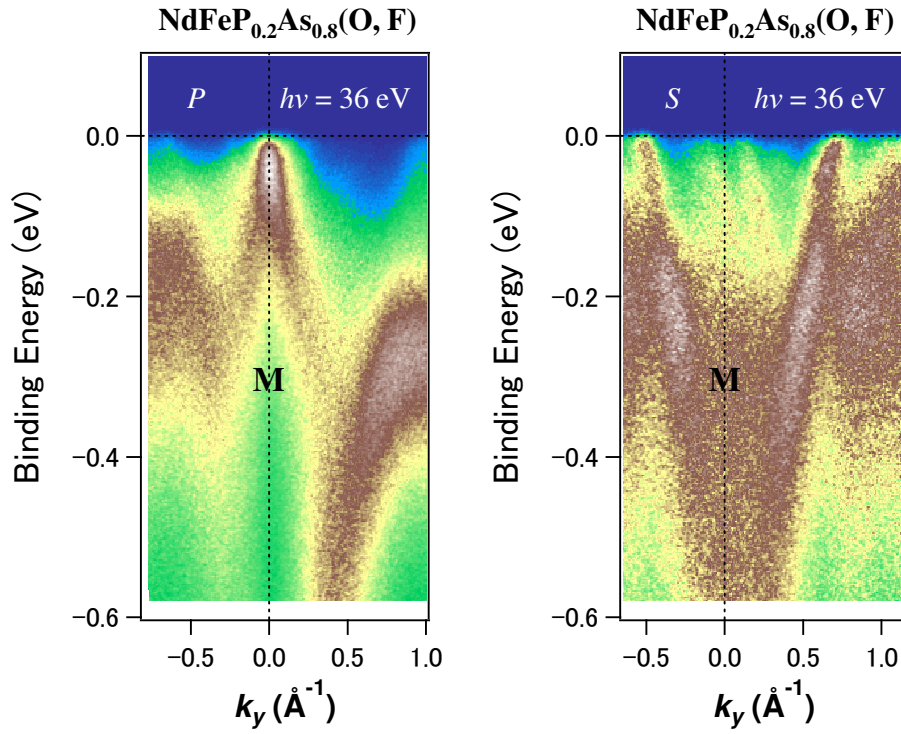


Figure 7.21:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around  $M$  point of NdFeP<sub>0.2</sub>As<sub>0.8</sub>(O, F).

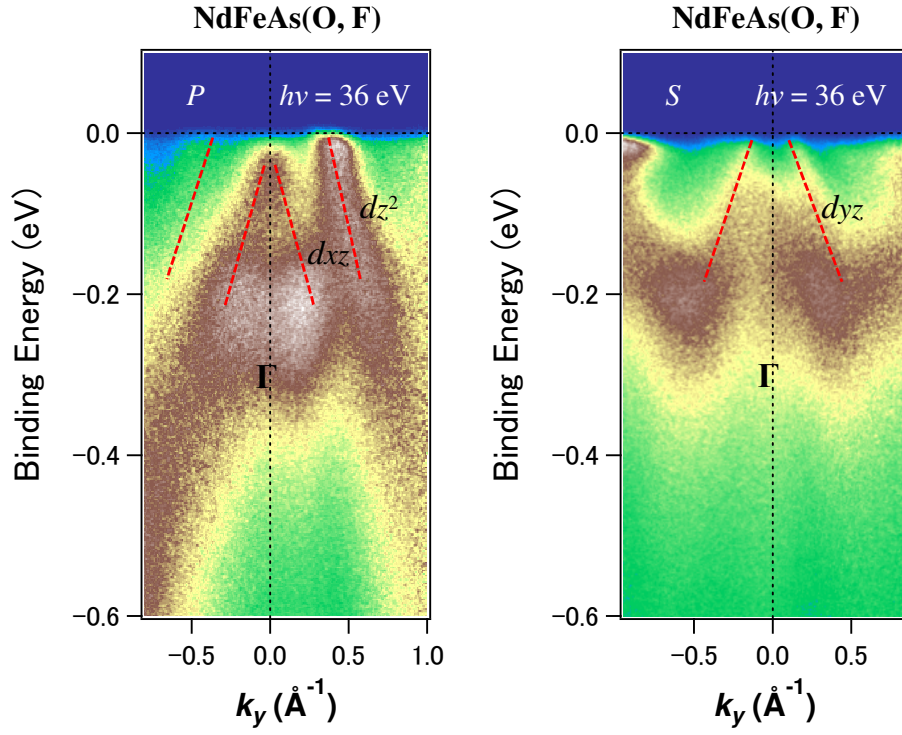


Figure 7.22:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around  $\Gamma$  point of  $\text{NdFeAs}(\text{O}, \text{F})$ .

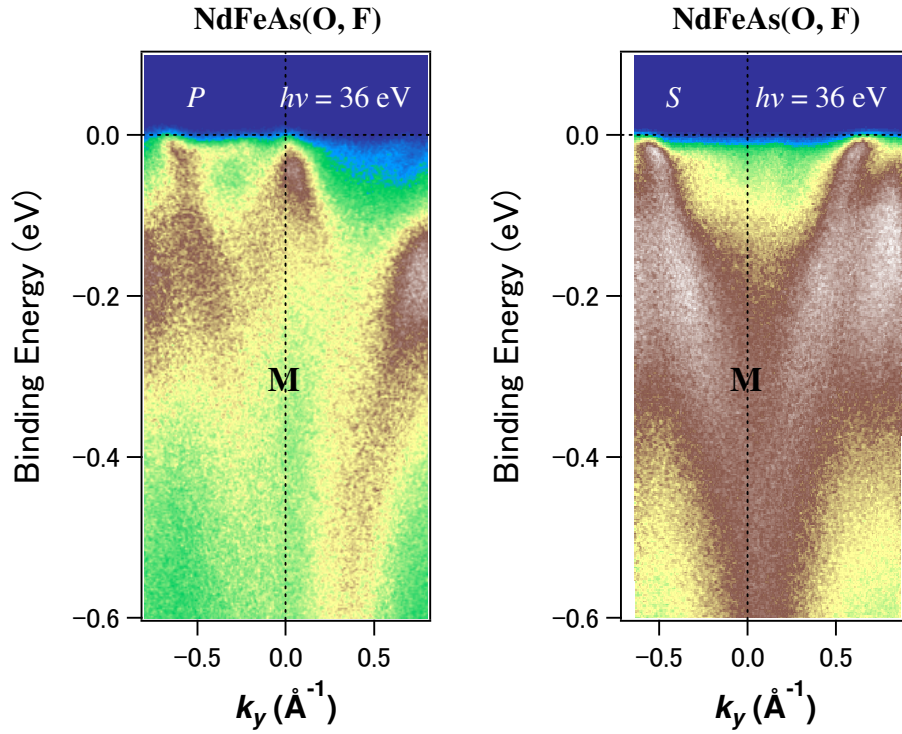


Figure 7.23:  $P$ - (Left) and  $S$ - (Right) polarized band dispersion around  $M$  point of  $\text{NdFeAs}(\text{O}, \text{F})$ .

As shown in the right panels of Figures 7.18, 7.20 and 7.22, one hole band is observed around  $\Gamma$  point in  $S$  polarization configuration. Along  $\Gamma$  - M direction in the  $S$  polarization, the bands with  $d_{yz}$  and  $d_{xy}$  orbital characters can be detected around  $\Gamma$  point. This band has a bottom around  $k_y = \pm 0.4$  and upturns near M point. This dispersion is consistent with the  $d_{yz}$  band in the theoretical study [26]. Resultantly, the present results indicate that the band observed around  $\Gamma$  point in  $S$  polarization has  $d_{yz}$  orbital character.

As shown in the left panels of Figures 7.18, 7.20 and 7.22, several bands are observed around  $\Gamma$  point in  $P$  polarization configuration. In this polarization, the bands with  $d_{xz}$  and  $d_{z^2}$  characters can be observed. The  $d_{x^2-y^2}$  band can be also observed in this polarization, but the theoretical studies have predicted that the bands with the  $d_{xz}$  and  $d_{z^2}$  orbital characters exist and the  $d_{x^2-y^2}$  band does not appear. The band calculation also has demonstrated that the  $d_{xz}$  and  $d_{yz}$  bands almost degenerated around  $\Gamma$  point. Therefore, the band most near  $\Gamma$  point in the  $P$  polarization is assigned to one with  $d_{xz}$  orbital character. This  $d_{xz}$  band sinks with increasing As content  $x$ . Other broad band around  $\Gamma$  point have been observed in all the samples. This band may have  $d_{z^2}$  orbital character, but the existence of this broad band is not consistent with the theoretical studies. In LaFePO, the previous ARPES study has clarified the appearance of the same broad band around  $\Gamma$  point. The surface effect may be related with the appearance of this band. The band dispersion and related large FS with  $d_{z^2}$  character, described later, suggest that the sample surface is hole-doped and the top layer on the sample surface may be  $\text{FePn}$  layer.

Figures 7.19, 7.21 and 7.23 show the band dispersion around M point in the  $P$  and  $S$  polarization configuration in the  $x = 0.4, 0.8$  and  $1.0$  samples. The band calculation indicates the existence of two electron-like bands around M point. Around M point, the present ARPES intensity has finite values, suggesting the existence of density of states at  $E_F$ . The finite intensity of ARPES is due to the electron-like bands with  $d_{xz}$  and  $d_{yz}$  characters predicted by the theoretical study.

### 7.6.3 Hole and electron FSs around $\Gamma$ and M Points

In  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  with  $x = 0.4, 0.8$  and  $1.0$ , I measured the MDCs at  $E_F$  along many cutting lines on Brillouin zone, and mapped FSs on  $k_x - k_y$  plane at  $k_z = 0$ , which include  $\Gamma$  and M points. Figures 7.24, 7.25 and 7.26 show the maps of FSs on  $k_x - k_y$  plane at  $k_z = 0$  by using  $P$  and  $S$  polarization configurations in the  $x = 0.4, 0.8$  and  $1.0$  samples, respectively. The MDCs have several peaks, revealing the finite value of density of state at  $E_F$ , i.e. the existence

of FS. I fitted these peaks of MDCs by using Lorentz model, and the open circles indicate the positions of peak center of MDCs in Figures 7.24, 7.25 and 7.26. I connected these circles by the broken lines with circle shapes. In other words, the broken lines show the FSs. In principle, the FSs should be almost isotropic. However, the intensity of EDCs and FSs are anisotropic. This is due to measurement setting. In the EDC measurements, I fixed the direction of incident light and the position of the detector, while the samples was rotated and tilted. These rotations and tilting of the sample cause the anisotropic intensity of EDCs and FSs.

I briefly explain the relation between the band dispersion shown in Figures 7.18 - 7.23 and the map of FSs in Figures 7.24 - 7.26. In Figures 7.18 - 7.23, I show the band dispersions along  $k_y$  ( $\Gamma$  - M direction). This  $k_y$  direction corresponds to the vertical  $\Gamma$  - M one in Figures 7.24 - 7.26.

First, please see the lower panels in Figures 7.24 - 7.26. There are small and large FSs around  $\Gamma$  point. The analysis of band dispersion, described in previous section, indicates the existence of one hole FS with  $d_{yz}$  orbital character. The small FS around  $\Gamma$  point in the map for  $S$  polarization configuration corresponds to hole FS with  $d_{yz}$  character. As shown in the lower panel of Figure 7.24, other small FS is drawn by broken line around  $\Gamma$  point. This is the small hole FS with  $d_{xz}$  orbital character, observed in the  $P$  polarization and shown in the upper panel in Figure 7.24. For comparison, I show this  $d_{xz}$  FS in the lower panel in Figure 7.24. I also represent the larger FS with  $d_{z^2}$  character around  $\Gamma$  point observed in the  $P$  polarization configuration in the lower panels in Figures 7.24 - 7.26.

In the lower panels of Figures 7.24 - 7.26, there are larger FSs. The origin of these FSs is not clear. These FSs' area is similar to that of the  $d_{z^2}$  FS. In the  $S$  polarization, however, the  $d_{z^2}$  FS cannot be observed. The surface effect may affect not only the  $d_{z^2}$  but also  $d_{xy}$  bands. The larger FS may have the  $d_{xy}$  orbital character and be caused by the surface effect.

Around M point in the lower panels in Figures 7.24 - 7.26, there is one FS. The theoretical study indicates the existence of electron-like FSs with  $d_{xz}$  and  $d_{yz}$  characters. This FS around M point observed in the  $S$  polarization can be assigned to the electron FS with  $d_{yz}$  character. In the lower panels in Figures 7.24 - 7.26, I also show the small FSs around M point, which are observed in the  $P$  polarization configuration and represented in the upper panels of these figures.

Next, please see the upper panels in Figures 7.24 - 7.26. The FSs observed in the  $S$  polarization are also shown in these panels for comparison. As shown in the upper panel of Figure

7.24, there are small and large hole FSs around  $\Gamma$  point. From the analysis of band dispersion in the previous section, the small and large FSs in the  $x = 0.4$  sample have  $d_{xz}$  and  $d_{z^2}$  orbital characters, respectively. As shown in the upper panels of Figures 7.25 and 7.26, the small FS with  $d_{xz}$  character disappears and the area of large FS shrinks with increasing As concentration  $x$ . The detail of these FSs' behaviors is discussed later. Around M point, there is one FS. Perhaps, this FS is electron on with  $d_{xz}$  character.

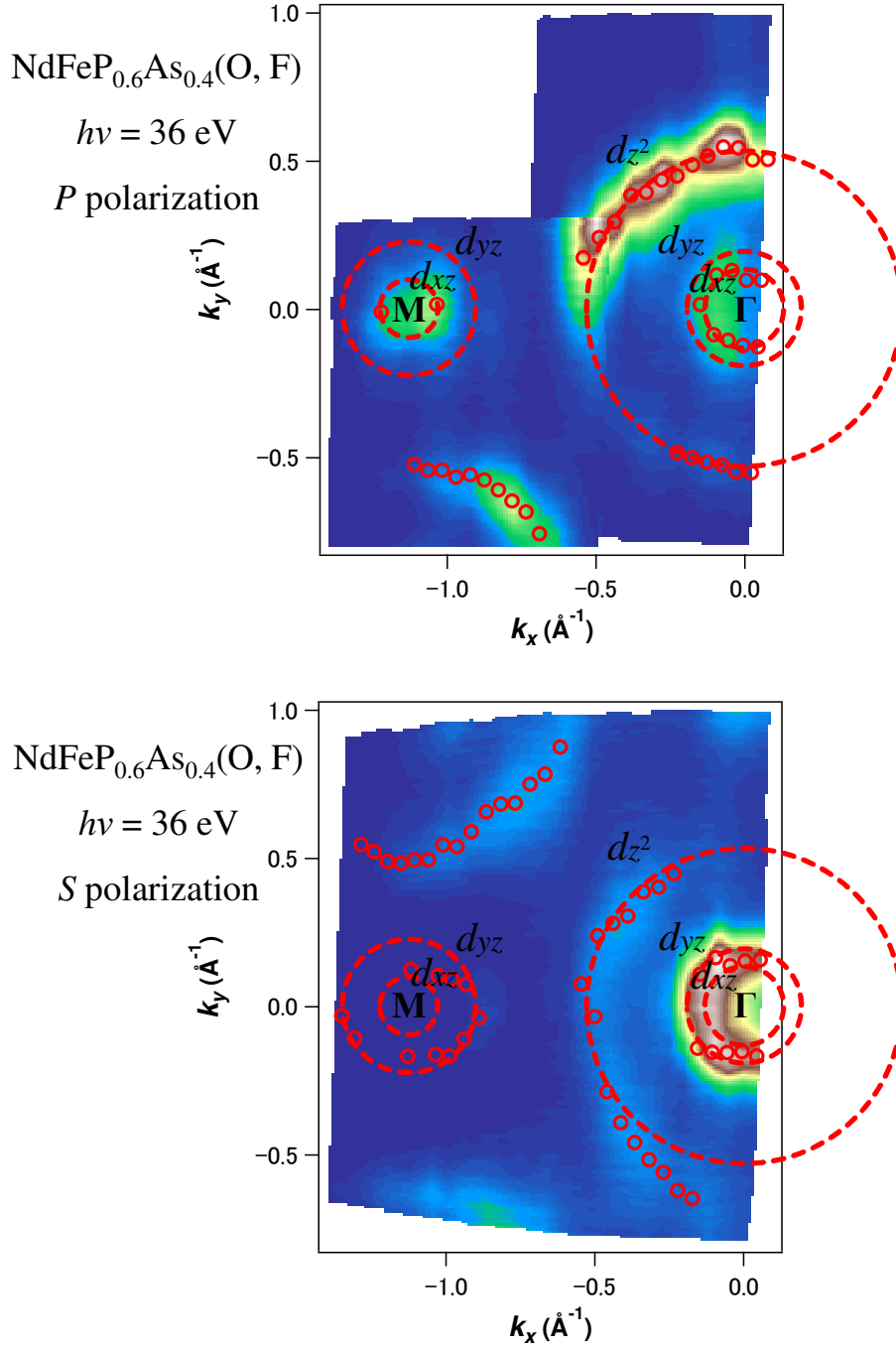


Figure 7.24: Maps of intensity of MDCs on  $k_x$  -  $k_y$  plane at  $k_z = 0$  and at  $E_F$  in  $\text{NdFeP}_{0.6}\text{As}_{0.4}(\text{O}, \text{F})$ . Upper and lower panels show the results in  $P$  and  $S$  polarization configurations, respectively. The energy of incident light is 36 eV. The bright and dark colors indicate the higher and lower intensities of MDCs.

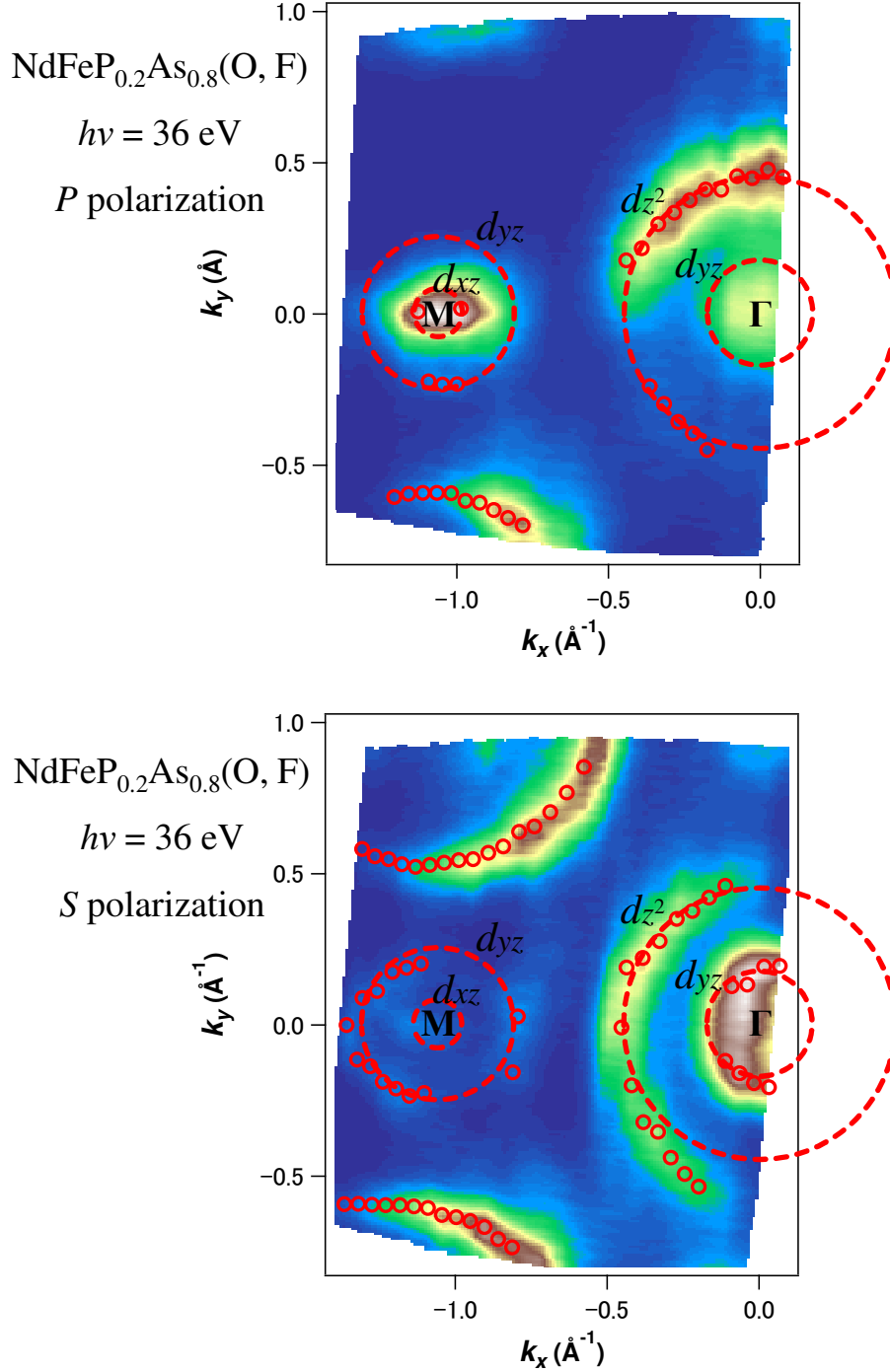


Figure 7.25: Maps of intensity of MDCs on  $k_x - k_y$  plane at  $k_z = 0$  and at  $E_F$  in NdFeP<sub>0.2</sub>As<sub>0.8</sub>(O, F). Upper and lower panels show the results in *P* and *S* polarization configurations, respectively. The energy of incident light is 36 eV. The bright and dark colors indicate the higher and lower intensities of MDCs.



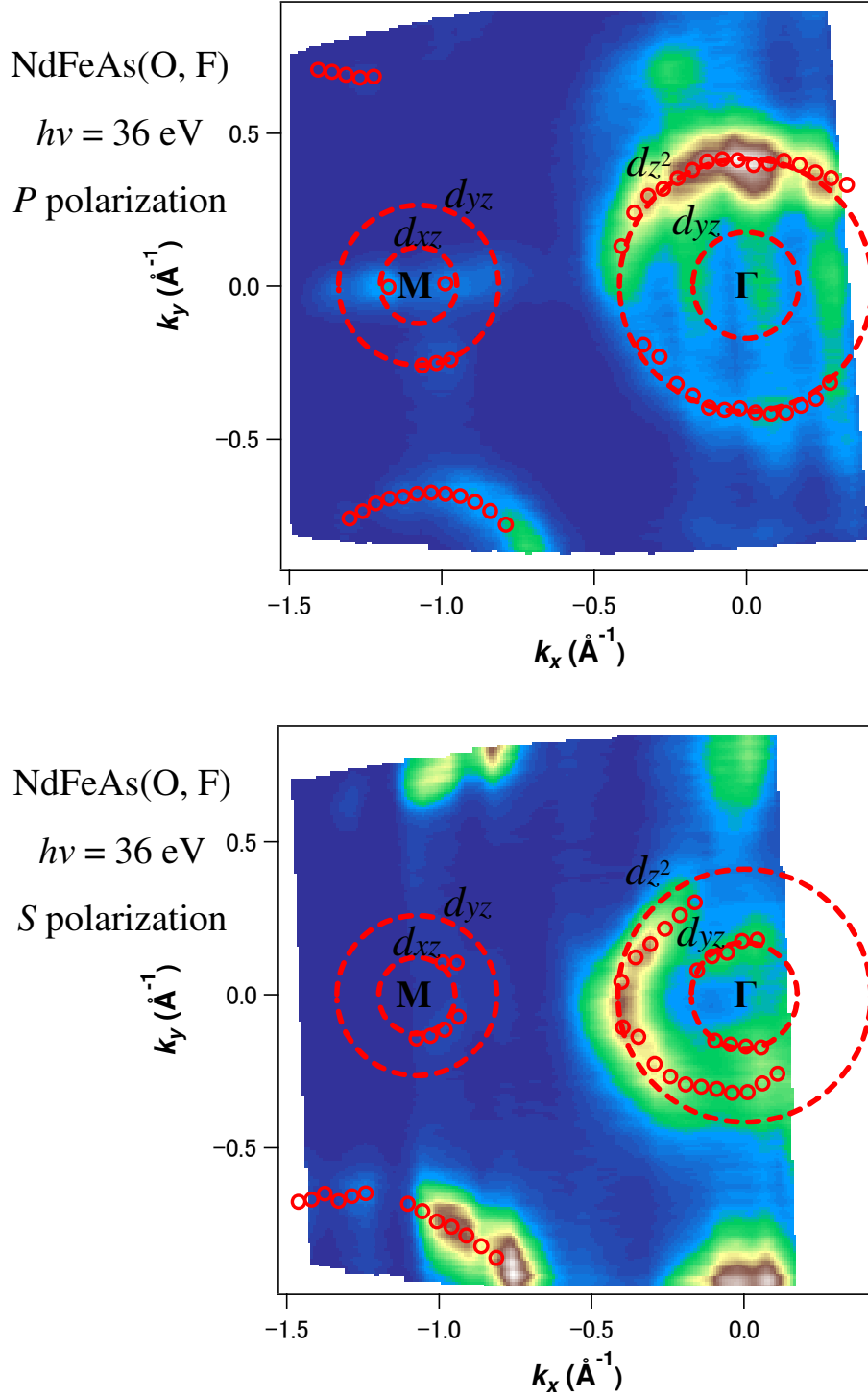


Figure 7.26: Maps of intensity of MDCs on  $k_x$  -  $k_y$  plane at  $k_z = 0$  and at  $E_F$  in NdFeAs(O, F). Upper and lower panels show the results in *P* and *S* polarization configurations, respectively. The energy of incident light is 36 eV. The bright and dark colors indicate the higher and lower intensities of MDCs.

## Chapter 8

# Discussion

### 8.1 Transport properties

#### 8.1.1 $x$ dependences of $T_c$ and $n$

$T_c$  and the power  $n$  are determined in the same way as the case of polycrystalline samples.  $T_c$  and  $n$  are plotted as a function of As content  $x$  in Figure 8.1.  $T_c$  of single-crystalline  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  (red) is lower than that of polycrystalline  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  (gray) for all  $x$ . This is caused by the lower F concentration of single-crystalline samples than that of polycrystalline ones. The nonmonotonous  $x$  dependence of  $n$  is also observed in single-crystalline samples. Therefore,  $x$  dependence of  $n$  in polycrystalline samples is caused by not the grain boundary effect but an essential physical property. The  $x$  dependence of  $T_c$  and  $n$  for single crystals indicates a correlation between  $T_c$  and  $n$  in the region of  $x = 0 - 0.8$  but no correlation above  $x > 0.8$ .  $T_c$  increases from  $\sim 0$  K to 23.6 K and  $n$  decreases from 2.0 to 1.16 in the region of  $x = 0 - 0.8$ . This suggests that  $T_c$  is enhanced by the AFM fluctuation in this region. On the other hand, no relationship is observed in the region of  $x = 0.8 - 1.0$ . The boundary  $x$  composition changes from  $x = 0.6$  in polycrystalline samples to  $x = 0.8$  in single crystals. This may be caused by the difference of their carrier concentration. In fact, the electronic phase diagrams and the boundary composition are different in  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{0.95}\text{F}_{0.05}$ .

#### 8.1.2 $x$ dependence of $\rho_0$ and $A$

The  $x$  dependences of  $\rho_0$  and  $A$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  are shown in Figure 8.2.  $\rho_0$  and  $A$  cannot be discussed rigorously in the cases of polycrystalline samples because of the grain

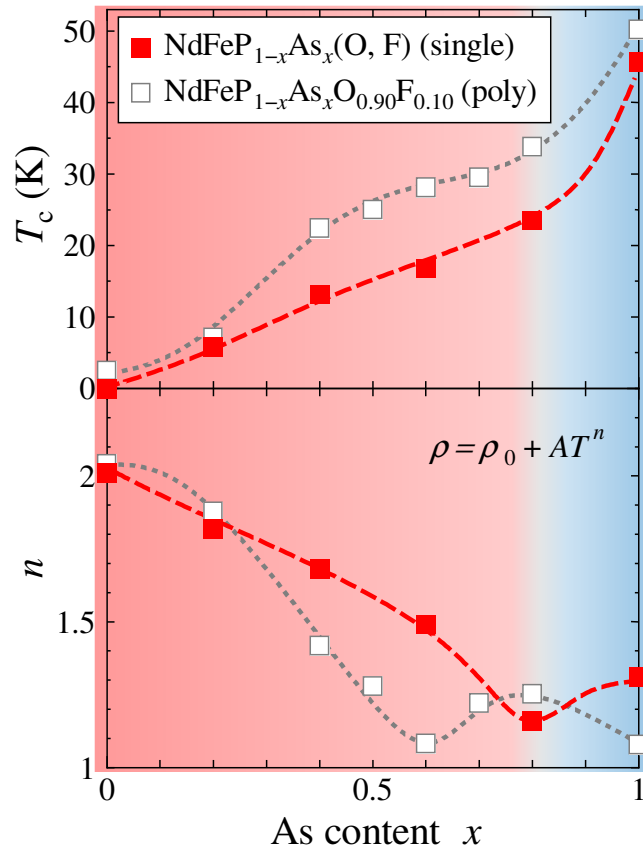
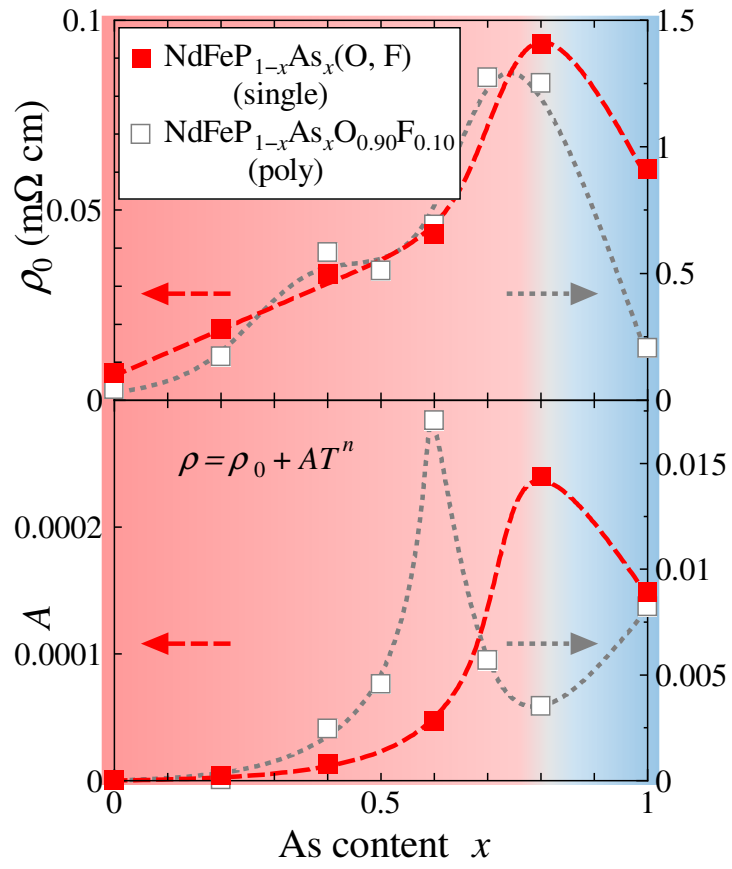


Figure 8.1:  $x$  dependences of  $T_c$  and  $n$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O, F})$ .

Figure 8.2:  $x$  dependence of  $\rho_0$  and  $A$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ .

boundary effect. However, in the cases of single-crystalline samples, there is no grain boundary effect, and  $\rho_0$  and  $A$  can be discussed. Both of  $\rho_0$  and  $A$  change systematically and they are enhanced at  $x = 0.8$ , where  $n$  approaches  $\sim 1$ .  $\rho_0$  and  $A$  increase with  $x$  in the region of  $x = 0 - 0.8$  and decrease with  $x$  in the region of  $x = 0.8 - 1.0$ . The  $x$  dependences of  $\rho_0$  and  $A$  of single crystals are similar to that of polycrystals. Therefore, the results of polycrystals are also valid for discussion. As well as  $T_c$  and  $n$ , the enhancements of  $\rho_0$ ,  $A$  and  $|R_H|$  around  $x = 0.6 \sim 0.8$  may be also connected with non-Fermi liquid behavior in the present system. I point out that similar enhancements of  $R_H$ ,  $\rho_0$ ,  $A$ , and  $T_c$  together with  $T$ -linear resistivity were observed in  $\text{CeCu}_2(\text{Si, Ge})_2$  [66, 67, 68]. Apart from a magnetic quantum critical point in the pressure- $T$  phase diagram, this heavy fermion compound shows another critical behavior at a higher pressure where the  $T_c$  reaches the highest value. The observed anomalies were interpreted as a result of the rapid change of the Ce valence. Watanabe *et al.* successfully explained these anomalies by the microscopic theory for valence fluctuation based on an extended Anderson model [69]. In the case of the present iron based superconductor, the P/As substitution is an isovalent substitution in a chemical sense. However, it is likely that the exchange of band energy with  $x$  (the band with some  $d$  orbital character is lifted up above  $E_F$  or other band shifts down below  $E_F$ .) causes valence (charge) fluctuation near the critical composition  $x = 0.6 - 0.8$ . Below  $x = 0.6 - 0.8$ , not only the AFM fluctuation but also this charge fluctuation gradually may increase with  $x$  and cause the enhancement of  $T_c$ . Actually, the ARPES results indicate that the FS with  $d_{xz}$  orbital character disappears around  $x \sim 0.8$ . This change of FS may be related with the anomalous transport properties around  $x \sim 0.8$ .

### 8.1.3 $x$ dependence of $R_H$ at $T = 50$ K

As reported in the previous paper, the absolute values of  $R_H$  in single crystals are lower than those in polycrystalline samples. However, the single crystals and polycrystalline samples show similar  $x$  dependence of  $R_H$ , i.e.  $|R_H|$  is enhanced at  $x = 0.6 - 0.8$ , where  $n$  approaches to  $\sim 1$ .  $x$  dependences of  $R_H$  at  $T = 50$  K and  $n$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O, F})$  are plotted in Figure 8.3.  $|R_H|$  is enhanced at  $x = 0.8$ , where  $n$  approaches  $\sim 1$ . Therefore, the band crossing of  $d_{Z^2}$  and  $d_{X^2-Y^2}$  are suggested like polycrystalline  $\text{RFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ .  $x$  dependence of  $R_H$  of single-crystalline samples is more gradual than that of polycrystalline ones. This may be related to the anisotropy of the crystals.

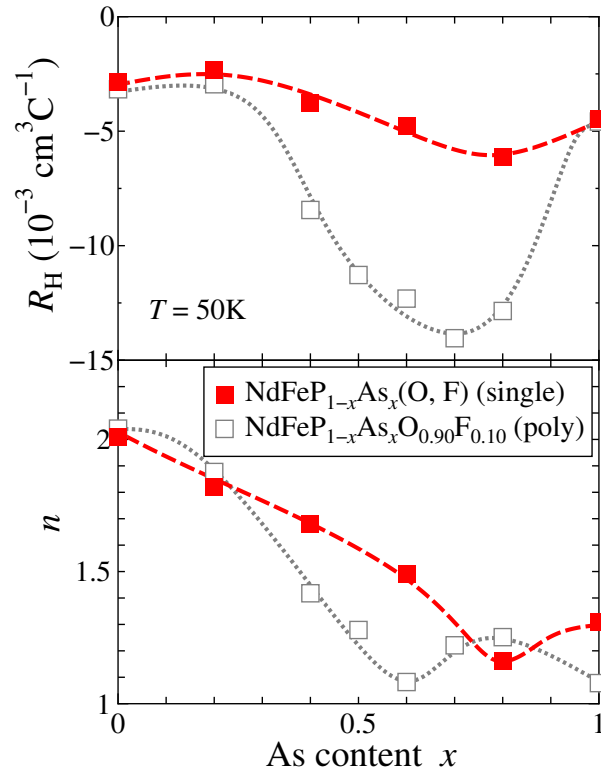


Figure 8.3:  $x$  dependence of  $R_H$  at  $T = 50$  K and  $n$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$

### 8.1.4 Correlation between $T_c$ and $n$

Correlation between  $T_c$  and  $n$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  is presented in Figure 8.4. The data point for  $x = 0 - 0.8$  of  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$  are on the same scaling line for  $x = 0 - 0.6$  of polycrystalline samples. The present results indicate that the AFM and/or other fluctuations enhance  $T_c$  in lower  $x$  region, and the end point for  $T_c - n$  correlation in lower  $x$  region is located at  $x \sim 0.8$ . All the results of transport measurements are qualitatively the same in poly- and single crystals. This guarantees my discussions systematic.

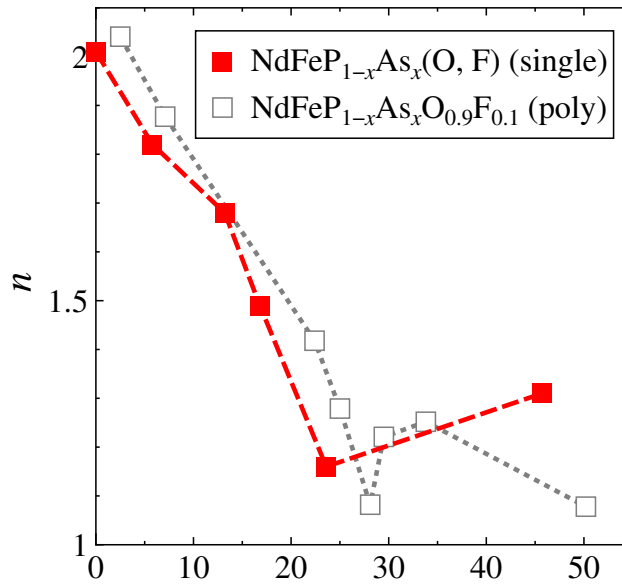


Figure 8.4: Correlation between  $T_c$  and  $n$  in  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$

## 8.2 ARPES measurement

### 8.2.1 Comparison with band calculation

Three or two hole FSs around  $\Gamma$  and two electron FSs around M are observed in all samples. Especially, two small hole FSs and two electron FSs observed in  $x = 0.4$  are consistent with the band calculation result of 1111 system. However, the largest hole FS constructed of the  $d_{z^2}$  band (and perhaps with the  $d_{xy}$  one) is not predicted by band calculation. It is not also detected by dHvA measurements of  $\text{LaFePO}$ . On the other hand, the large hole FS is observed in all ARPES measurements of 1111 system, where  $R$  is La, Pr, Nd or Sm and  $Pn$  is P or As. The nodeless

superconducting gap of  $\Delta = 15$  meV is also reported on this FS in NdFeAs(O, F). However, if the extremely large hole FS exists in truth, the system should be heavily hole-doped one. It is quite unlikely, then the other explanation is needed.

One possible explanation of the large hole FS is the surface effect. If a single-crystalline  $RFePnO$  is cleaved,  $RO$  or  $FePn$  layer seems to appear on the surface. Both of  $RO$  and  $FePn$  layers do not obtain electronic neutrality, therefore a new electronic state seems to emerge on the surface. Even if the observed FS mapping at  $k_z = 0$  is hole doped state on the surface, the shapes of all hole and electron FSs hardly change. As a result, differences from the original states seem to be nearly the same for all samples. Therefore, the discussion of substitution effect in NdFeP<sub>1-x</sub>As<sub>x</sub>(O, F) is meaningful.

On the other hand, the hole FS constructed of the band with  $d_{xy}$  orbital character is predicted by band calculation for NdFeAs(O, F). It is considered as the trigger of high  $T_c$  nodeless superconductivity in spin fluctuation theory. However, it is not observed in all  $x$ . Recently, it is suggested that the  $d_{xy}$  band shows the strong dependence of photon energy of the incident light in K<sub>0.8</sub>Fe<sub>1.6</sub>Se<sub>2</sub> in the ARPES measurements. In the present system, the  $d_{xy}$  band in the bulk electronic state may also be strongly dependent on the energy of the incident light, and the selected photon energy may be too inadequate to observe the  $d_{xy}$  band or FS.

### 8.2.2 $x$ dependence of FSs

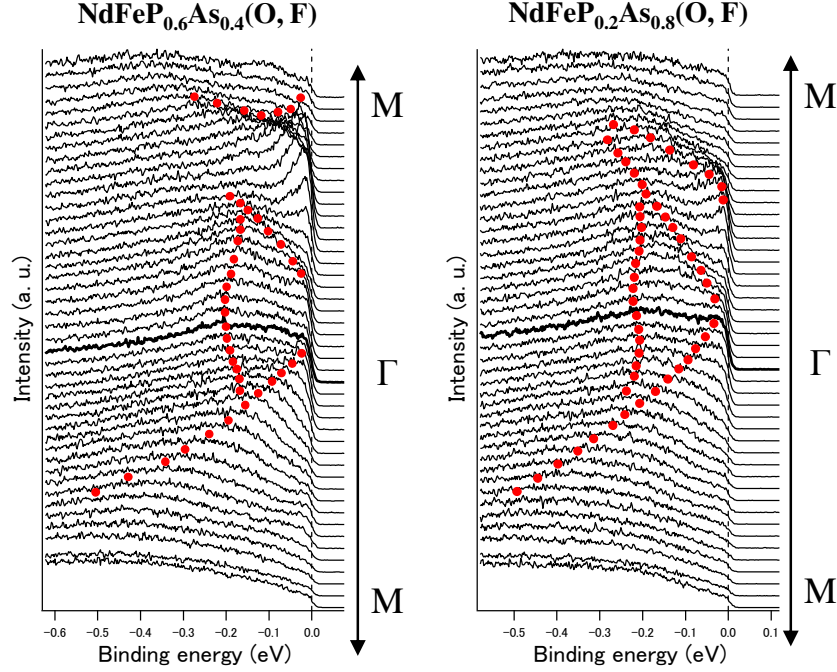
Following two characteristic features of  $x$  dependence are observed in the results of ARPES measurements.

- (i) The largest hole FS gradually shrinks with increasing  $x$ .
- (ii) The smallest hole FS disappears at  $x \sim 0.8$ .

As for (i), the size of the largest hole FS is  $1.06 \text{ \AA}^{-1}$  at  $x = 0.4$ ,  $0.90 \text{ \AA}^{-1}$  at  $x = 0.8$  and  $0.82 \text{ \AA}^{-1}$  at  $x = 1.0$ , which corresponds to about 47 %, 40 % and 37 % for first Brillouin zone, respectively. According to the band calculation,  $d_{z^2}$  band makes a hole FS at Z in  $RFePO$  and the band sinks below  $E_F$  with increasing As content  $x$ . Therefore, the shrinkage of the hole FS with  $x$  is consistent with the band calculation (though the hole FS exists in all  $x$ ). This is the first experimental report of the systematic  $x$  dependence of the  $d_{z^2}$  band.

As for (ii), EDCs for  $P$  polarization of  $x = 0.4$  and  $0.8$  are shown in Figure 8.5. The smallest hole FS constructed of  $d_{xz}$  band disappears at  $x \sim 0.8$ . To compare the feature (ii) in my



Figure 8.5: EDCs for  $P$  polarization of  $x = 0.4$  and  $0.8$ .

experimental result with the previous studies, the band dispersions and FS mappings at  $k_z = 0$  of LaFePO, LaFeAsO and NdFeAsO<sub>0.85</sub>F<sub>0.15</sub> [43, 44, 46, 70] are shown in Figure 8.6. In the case of LaFePO, a large hole FS ( $\Gamma_2$  in the left panel of Figure 8.6) and double degenerated hole FSs ( $\Gamma_1$ ) are observed. In LaFeAsO, a large hole FS ( $\Gamma_2$ ) and a small non-degenerated hole FS are observed. In PrFeAsO<sub>0.7</sub> (shown in chapter 1), a large hole FS and a small FS are also reported, though the assignment of the orbital character is different from mine [46]. In NdFeAsO, only a large hole FS is observed and a hole-like-band exists below  $E_F$  around  $\Gamma$  point.

If the above previous studies are explained from the suggestion (ii) in NdFeP<sub>1-x</sub>As<sub>x</sub>(O, F), the degenerated hole FSs ( $\Gamma_1$ ) in LaFePO seems to be resolved and they are separated to the small hole FS and a pseud-hole FS in LaFeAsO. In widely, the small hole band seems to gradually sinks below  $E_F$  with decreasing bond angle  $\alpha$  (or the increasing  $h_{Pn}$ ) in LaFePO, LaFeAsO and NdFeAsO<sub>0.85</sub>F<sub>0.15</sub> (and perhaps PrFeAsO<sub>0.7</sub>).

The band calculation where the bond angle  $\alpha$  is virtually changed has been performed [71]. The band calculation result for the bond angle  $\alpha$  variations of  $120^\circ$ ,  $110^\circ$  and  $100^\circ$  in LaFeAsO is shown in Figure 8.7. The two hole bands around  $\Gamma$  are nearly degenerated at  $\alpha = 120^\circ$ , which is similar to the experimental result of LaFePO. The degeneracy is resolved following decreasing  $\alpha$  and it is similar situation to  $x = 0.4$ . The degeneracy is completely resolved at  $\alpha = 110^\circ$

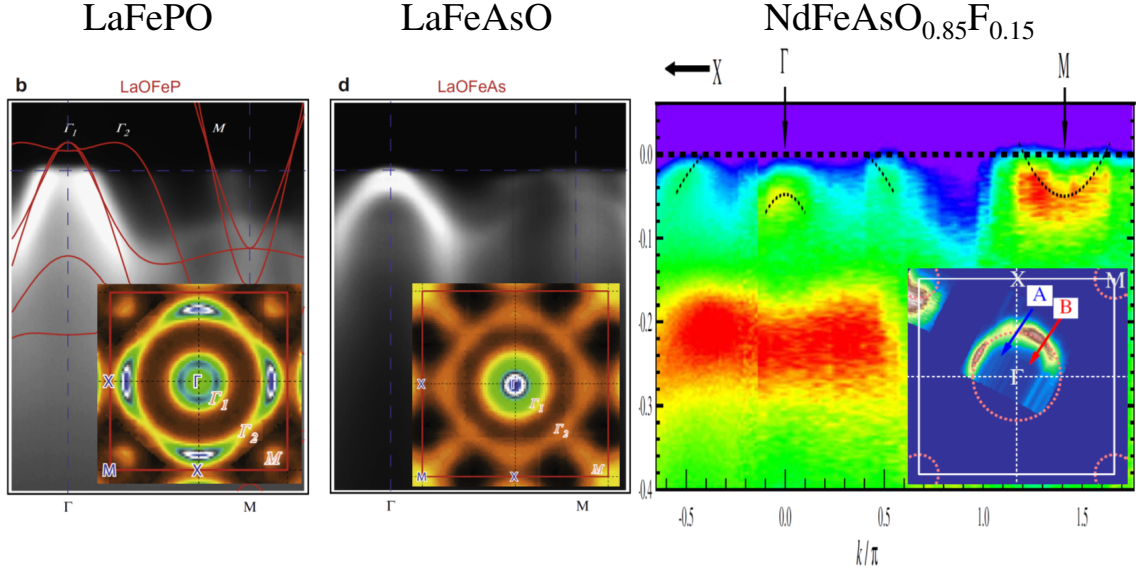


Figure 8.6: Band dispersions and FS mappings at  $k_z = 0$  of LaFePO (Left), LaFeAsO (Center) and NdFeAsO<sub>0.85</sub>F<sub>0.15</sub> (Right) [43, 44, 46, 70].

°. One hole FS gradually decreases with decreasing  $\alpha$  and completely disappears  $\alpha = 100$  °. As a result, the tendency to disappear the hole FS constructed of  $d_{xz}$  band is similar to band calculation, however, the difference of  $\alpha$  is  $\sim 10$  °.

In the present system, the  $d_{xz}$  band sinks down with increasing  $x$ , and the top of this band touches  $E_F$  around  $\Gamma$  point at  $x \sim 0.8$ . Below  $x \sim 0.8$ , the hole FS with  $d_{xz}$  is observed around  $\Gamma$  point, while it disappears above  $x \sim 0.8$ . The  $x$  dependence of  $T_c$  and  $n$ , their relationship and other transport properties are distinctly changed around  $x = 0.6 \sim 0.8$ . As described before, I think that these nonmonotonic changes of  $T_c$  and transport properties are caused by the transformation of FS from the FeP type to the FeAs one, i.e., the 3-dimensional hole FS with  $d_{z^2}$  orbital character disappears and the cylindrical  $d_{xy}$  FS appears. Unfortunately, I could not observe the above-mentioned FS changes perhaps because of the surface effect and other problems. However, I found the clear change of  $d_{xz}$  band around  $x \sim 0.8$ , and think that the change of this FS induces the nonmonotonic changes of  $T_c$  and transport properties.

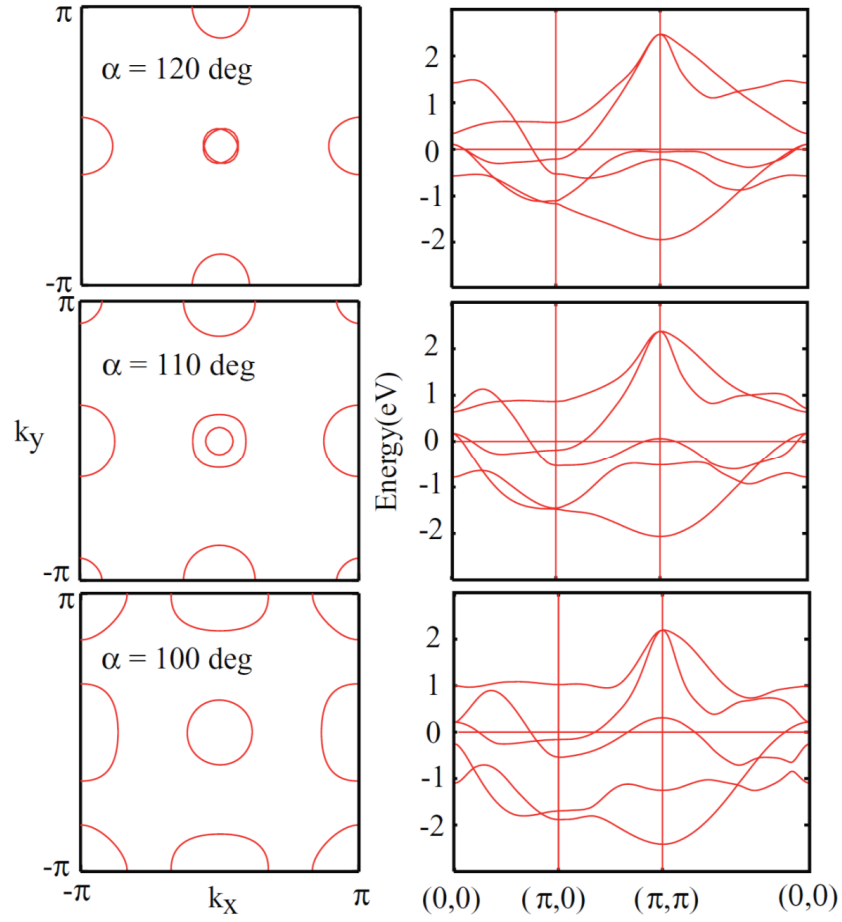


Figure 8.7: The band calculation result for bond angle  $\alpha$  variations of 120 °, 110 ° and 100 ° in LaFeAsO [71].

## Part IV

# Conclusion

## Chapter 9

# Conclusion

In this work, I have investigated the transport properties and ARPES in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{1-y}\text{F}_y$  in order to find a key parameter determining  $T_c$  in iron pnictides. From my work, the following experimental results and conclusions are obtained.

(i) I have studied the transport properties of the polycrystalline samples of  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La, Pr and Nd}$ ), and clarified the relation between  $T_c$  and the transport properties by changing the P/As ratio in this system. The present results have revealed that there are two distinct regions of  $x$ . In the low  $x$  region ( $x < 0.6 - 0.8$ ),  $T_c$  linearly increases from  $\sim 3$  to  $\sim 30$  K with decreasing the power  $n$  in  $\rho = \rho_0 + AT^n$  from  $\sim 2$  at  $x = 0$  to  $\sim 1$  around  $x = 0.6 - 0.8$ . This strongly suggests that some bosonic fluctuation such as AFM one is a primary factor to enhance  $T_c$ . The universal  $T_c - n$  relation holds for all the  $R$  systems with  $x < 0.6 - 0.8$  in the present study as well as  $\text{AeFe}_2(\text{As, P})_2$  ( $\text{Ae} = \text{Ba and Sr}$ ). In addition to the  $T$ -linear resistivity,  $R_H$ ,  $\rho_0$ , and  $A$  are strongly enhanced near  $x = 0.6 - 0.8$ , suggesting some critical change of the electronic state. In the high  $x$  region ( $x > 0.6 - 0.8$ ), on the other hand,  $T_c$  becomes strongly  $R$ -dependent and further increases with  $x$ , but shows no clear correlation with  $n$ . The compounds with  $x > 0.6 - 0.8$  seem to approach another universal  $T_c - n$  relation which holds for  $R\text{FeAsO}_{1-y}$  and  $(\text{Ba, K})\text{Fe}_2\text{As}_2$ . The presence of two distinct  $T_c - n$  relations could be the evidence that there are two  $T_c$ -rising mechanisms and related two different FS states in the iron pnictides.

(ii) I have synthesized the single crystals of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  and investigated the transport properties and ARPES of them. I have succeeded in the single crystal grown of this system by high pressure technique. The transport properties of these single crystals without the grain

boundary effect are consistent with those of polycrystalline samples. The present results of single crystals strongly indicate the existence of two  $T_c$ -rising mechanism and two different FS states.

(iii) I have performed the ARPES measurement using single crystals of  $\text{NdFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  with  $x = 0.4, 0.8$  and  $1.0$  in order to clarify  $x$ -dependent changes of band structures and FSs. The ARPES results indicate the existence of three hole and two electron FSs in  $x = 0.4$ , and two hole and two electron FSs in  $x = 0.8$  and  $1.0$  samples. The orbital characters of these FSs have been assigned by the measurements of polarization dependence of incident light. The  $d_{xz}$  hole FS exists around  $\Gamma$  point at  $x = 0.4$ . The  $d_{xz}$  band sinks down with increasing  $x$ , and the top of this band touches  $E_F$  around  $\Gamma$  point in the  $x = 0.8$  sample. With further increasing  $x$ , the hole FS with  $d_{xz}$  character disappears at  $x = 1.0$ . The  $T_c$ ,  $n$  and other transport properties distinctly change around  $x = 0.6 - 0.8$ . The clear difference of FSs below and above  $x = 0.6 - 0.8$  may be related with the change of transport properties, and support the scenario of two  $T_c$ -rising mechanisms and two different FS states in this system.

### Future works

In this work, I succeeded in the observation of several FSs and the systematic doping dependence of band structure by ARPES study. As described in the main content, I think that the nonmonotonic changes of  $T_c$  and transport properties are caused by the transformation of FS from FeP type to FeAs one, i.e., the 3-dimensional hole FS with  $d_{z^2}$  orbital character disappears and the cylindrical  $d_{xy}$  FS appears. Unfortunately, I could not observe such FS changes perhaps because of the surface effect and other problems. Particularly, the  $d_{xy}$  FS perhaps plays an important role for the appearance of high  $T_c$  superconductivity but it is missing in my spectra. This  $d_{xy}$  FS must be searched and its behavior must be clarified by ARPES measurements using the incident lights with various photon energy. In addition, I could not observe the superconducting gap of each FS by ARPES because of the time limitation. They also must be observed in future works to clarify the superconducting feature in this system.

# Bibliography

- [1] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *J. Am. Chem. Soc.* **128**, 10012 (2006).
- [2] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [3] Z. Ren, W. Lu, J. Yang, W. Yi, X. Shen, Z. Li, G. Che, X. Dong, L. Sun, F. Zhou, and Z. Zhao, *Chin. Phys. Lett.* **25**, 2215 (2008).
- [4] C. Wang, L. Li, S. Chi, Z. Zhu, Z. Ren, Y. Li, Y. Wang, X. Lin, Y. Luo, S. Jiang, X. Xu, G. Cao, and Z. Xu, *Euro. Phys. Lett.* **83**, 67006 (2008).
- [5] H. Luetkens, H.-H. Klauss, M. Kraken, F. J. Litterst, T. Dellmann, R. Klingeler, C. Hess, R. Khasanov, A. Amato, C. Baines, M. Kosmala, O. J. Schumann, M. Braden, J. Hamann-Borrero, N. Leps, A. Kondrat, G. Behr, J. Werner, and B. Buchner, *Nature Mater.* **8**, 305 (2009).
- [6] J. Zhao, Q. Huang, C. de la Cruz, S. Li, J. W. Lynn, Y. Chen, M. A. Green, G. F. Chen, G. Li, Z. Li, J. L. Luo, N. L. Wang, and P. Dai, *Nature Mater.* **7**, 953 (2008).
- [7] N. Fujiwara, S. Tsutsumi, S. Iimura, S. Matsuishi, H. Hosono, Y. Yamakawa and H. Kon-tani, *Phys. Rev. Lett.* **111**, 097002 (2013).
- [8] K. Miyazawa, K. Kihou, P. M. Shirage, C. H. Lee, H. Kito, H. Eisaki, and A. Iyo, *J. Phys. Soc. Jpn.* **78**, 034712 (2009).
- [9] S. Matsuishi, Y. Inoue, T. Nomura, Y. Kamihara, M. Hirano, and H. Hosono, *New J. Phys.* **11**, 025012 (2008).
- [10] E. M. Brüning, C. Krellner, M. Baenitz, A. Jesche, F. Steglich, and C. Geibel, *Phys. Rev. B* **101**, 117206 (2008).
- [11] J.-Q. Yan, A. Kreyssig, S. Nandi, N. Ni, S. L. Bud'ko, A. Kracher, R. J. McQueeney, R. W. McCallum, T. A. Lograsso, A. I. Goldman, and P. C. Canfield, *Phys. Rev. B* **78**, 024516 (2008).
- [12] X. F. Wang, T. Wu, G. Wu, H. Chen, Y. L. Xie, J. J. Ying, Y. J. Yan, R. H. Liu, and X. H. Chen, *Phys. Rev. Lett.* **102**, 117005 (2009).
- [13] H. Chen, Y. Ren, Y. Qiu, Wei Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang, and X. H. Chen, *Euro. Phys. Lett.* **85**, 17006 (2009).

- [14] S. R. Saha, N. P. Butch, T. Drye, J. Magill, S. Ziemak, K. Kirshenbaum, P. Y. Zavalij, J. W. Lynn, and J. Paglione, *Phys. Rev. B* **85**, 024525 (2012).
- [15] C. Lester, J. Chu, J. G. Analytis, S. C. Capelli, A. S. Erickson, C. L. Condon, M. F. Toney, I. R. Fisher, and S. M. Hayden, *Phys. Rev. B* **79**, 144523 (2009).
- [16] S. Kasahara, T. Shibauchi, K. Hashimoto, K. Ikada, S. Tonegawa, R. Okazaki, H. Shishido, H. Ikeda, H. Takeya, K. Hirata, T. Terashima, and Y. Matsuda, *Phys. Rev. B* **81**, 184519 (2010).
- [17] S. A. J. Kimber, A. Kreyssig, Y. Zhang, H. O. Jeschke, R. Valenti, F. Yokaichiya, E. Colombier, J. Yan, T. C. Hansen, T. Chatterji, R. J. McQueeney, P. C. Canfield, A. I. Goldman, and D. N. Argyriou, *Nature Mater.* **8**, 471 (2009).
- [18] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu, and A. M. Guloy, *Phys. Rev. B* **78**, 060505(R) (2008).
- [19] O. Heyer, T. Lorenz, V. B. Zabolotnyy, D. V. Evtushinsky, S. V. Borisenko, I. Morozov, L. Harnagea, S. Wurmehl, C. Hess, and B. Büchner, *Phys. Rev. B* **84**, 064512 (2011).
- [20] K. Mydeen, E. Lengyel, Z. Deng, X. C. Wang, C. Q. Jin, and M. Nicklas, *Phys. Rev. B* **82**, 014514 (2010).
- [21] S. Kasahara, K. Hashimoto, H. Ikeda, T. Terashima, Y. Matsuda, and T. Shibauchi, *Phys. Rev. B* **85**, 060503 (2012).
- [22] X. Zhu, F. Han, G. Mu, P. Cheng, B. Shen, B. Zeng, and H. Wen, *Phys. Rev. B* **79**, 220512(R) (2009).
- [23] H. Ogino, Y. Matsumura, Y. Katsura, K. Ushiyama, S. Horii, K. Kishio, and J. Shimoyama, *Supercond. Sci. Technol.* **22**, 075008 (2009).
- [24] P. M. Shirage, K. Kihou, C. H. Lee, H. Kito, H. Eisaki, and A. Iyo, *Physica C* **484**, 12 (2012).
- [25] H. Kinouchi, H. Mukuda, Y. Kitaoka, P. M. Shirage, H. Fujihisa, Y. Gotoh, H. Eisaki, and A. Iyo, *Phys. Rev. B* **87**, 121101(R) (2013).
- [26] V. Vildosola, Leonid Pourovskii, Ryotaro Arita, Silke Biermann, and Antoine Georges, *Phys. Rev. B* **78**, 064518 (2008).
- [27] K. Kuroki, H. Usui, S. Onari, R. Arita, and Hideo Aoki, *Phys. Rev. B* **79**, 224511 (2009).
- [28] C. H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, *J. Phys. Sci. Jpn.* **77**, 083704 (2008).
- [29] Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou, and Y. Takano, *Supercond. Sci. Technol.* **23**, 054013 (2010).
- [30] J. D. Fletcher, A. Serafin, L. Malone, J. G. Analytis, J.-H. Chu, A. S. Erickson, I. R. Fisher, and A. Carrington, *Phys. Rev. B* **102**, 147001 (2009).
- [31] L. Malone, J. D. Fletcher, A. Serafin, and A. Carrington, *Phys. Rev. B* **79**, 145501(R) (2009).



- [32] K. Hashimoto, M. Yamashita, S. Kasahara, Y. Senshu, N. Nakata, S. Tonegawa, K. Ikada, A. Serafin, A. Carrington, T. Terashima, H. Ikeda, T. Shibauchi, and Y. Matsuda, *Phys. Rev. B* **81**, 220501(R) (2010).
- [33] K. Hashimoto, S. Kasahara, R. Katsumata, Y. Mizukami, M. Yamashita, H. Ikeda, T. Terashima, A. Carrington, Y. Matsuda, and T. Shibauchi, arXiv: 1107.4505v1 (2011).
- [34] T. Kondo, A. F. Santander-Syro, O. Copie, C. Liu, M. E. Tillman, E. D. Mun, J. Schmalian, S. L. Bud'ko, M. A. Tanatar, P. C. Canfield, and A. Kaminski, *Phys. Rev. Lett.* **101**, 147003 (2008).
- [35] H. Ding, P. Richard, K. Nakayama, K. Sugawara, T. Arakane, Y. Sekiba, A. Takayama, S. Souma, T. Sato, T. Takahashi, Z. Wang, X. Dai, Z. Fang, G. F. Chen, J. L. Luo, and N. L. Wang, *Euro. Phys. Lett.* **83**, 47001 (2008).
- [36] Y. Zhang, Z. R. Ye, Q. Q. Ge, F. Chen, Juan Jiang, M. Xu, B. P. Xie, and D. L. Feng, *Nature Phys.* **4**, 2248 (2012).
- [37] M. Yamashita, Y. Senshu, T. Shibauchi, S. Kasahara, K. Hashimoto, D. Watanabe, H. Ikeda, T. Terashima, I. Vekhter, A. B. Vorontsov, and Y. Matsuda, *Phys. Rev. B* **84**, 060507(R) (2011).
- [38] K. A. Yates, T. M. Usman, K. Morrison, J. D. Moore, A. M. Gilbertson, A. D. Caplin, L. F. Cohen, H. Ogino and J. Shimoyama, *Supercond. Sci. Technol.* **23**, 022001 (2010).
- [39] K. T. Lai, A. Takemori, S. Miyasaka,<sup>1</sup> F. Engetsu, H. Mukuda, and S. Tajima, *Phys. Rev. B* **90**, 064504 (2014).
- [40] Y. Luo, Y. Li, S. Jiang, J. Dai, G. Cao, and Z. Xu, *Phys. Rev. B* **81**, 134422 (2010).
- [41] Y. Luo, H. Han, S. Jiang, X. Lin, Y. Li, J. Dai, G. Cao, and Z. Xu, *Phys. Rev. B* **83**, 054501 (2011).
- [42] Y. Li, X. Lin, T. Zhou, J. Shen, Y. Luo, Q. Tao, G. Cao, Z. Xu, *Physica C* **470**, 493 (2009).
- [43] D. H. Lu, M. Yi, S. -K. Mo, A. S. Erickson, J. Analytis, J.-H. Chu, D. J. Singh, Z. Hussain, T. H. Geballe, I. R. Fisher, and Z.-X. Shen, *Nature* **455**, 07263 (2008).
- [44] D. H. Lu, M. Yi, S. -K. Mo, J. G. Analytis, J. -H. Chu, A. S. Erickson, D. J. Singh, Z. Hussain, T. H. Geballe, I. R. Fisher, and Z. -X. Shen, *Physica C* **469**, 452 (2009).
- [45] A. I. Coldea, J. D. Fletcher, A. Carrington, J. G. Analytis, A. F. Bangura, J.-H. Chu, A. S. Erickson, I. R. Fisher, N. E. Hussey, and R. D. McDonald, *Phys. Rev. Lett.* **101**, 216402 (2008).
- [46] I. Nishi, M. Ishikado, S. Ideta, W. Malaeb, T. Yoshida, A. Fujimori, Y. Kotani, M. Kubota, K. Ono, M. Yi, D. H. Lu, R. Moore, Z. -X. Shen, A. Iyo, K. Kihou, H. Kito, H. Eisaki, S. Shamoto, and R. Arita, *Phys. Rev. B* **84**, 014504 (2011).
- [47] L. X. Yang, B. P. Xie, Bo Zhou, Yan Zhang, Q. Q. Ge, Fan Wu, X. F. Wang, X. H. Chen, and D. L. Feng, *J. Phys. Chem. Solids* **72**, 460 (2011).
- [48] F. Izumi, and K. Momma, *Solid. State. Phenom.* **130**, 15 (2007).

- [49] T.M. McQueen, M. Regulacio, A. J. Williams, Q. Huang, J. W. Lynn, Y.S. Hor, D. V. West, M.A. Green, and R. J. Cava, *Phys. Rev. B* **78**, 024521 (2008).
- [50] A. S. Sefat, A. Huq, M. A. McGuire, R. Jin, B. C. Sales, D. Mandrus, L. M. D. Cranswick, P. W. Stephens, and K. H. Stone, *Phys. Rev. B* **78**, 104505 (2008).
- [51] B.I. Zimmer, W. Jeitschko, J. H. Albering, R. Glaum, and M. Reehuis, *J. Alloys Compds.* **229**, 238 (1995).
- [52] P. Quebe, L. Terbuchte, and W. Jeitschko, *J. Alloys Compd.* **302**, 70 (2000).
- [53] Y. Xiao, Y. Su, R. Mittal, T. Chatterji, T. Hansen, S. Price, C. M. N. Kumar, J. Persson, S. Matsuishi, Y. Inoue, H. Hosono, and Th. Brueckel, *Phys. Rev. B* **81**, 094523 (2010).
- [54] R. E. Baumbach, J. J. Hamlin, L. Shu, D. A. Zocco, N. M. Crisosto, and M. B. Maple, *New J. of Phys.* **11**, 025018 (2009).
- [55] Z. Ren, J. Yang, W. Lu, W. Yi, X. Shen, Z. Li, G. Che, X. Dong, L. Sun, F. Zhou, and Z. Zhao, *Euro. Phys. Lett.* **82**, 57002 (2008).
- [56] M. Ishikado, S. Shamoto, H. Kito, A. Iyo, H. Eisaki, T. Ito, and Y. Tomioka, *Physica C* **469**, 901 (2008).
- [57] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, 240 (1976).
- [58] T. Moriya, *Spectroscopy of Mott Insulators and Correlated Metals*, eds. A. Fujimori and Y. Tokura, p.66-79 (Springer, Berlin, 1995).
- [59] H. Mukuda, F. Engetsu, K. Yamamoto, K. T. Lai, M. Yashima, Y. Kitaoka, A. Takemori, S. Miyasaka, and S. Tajima, *Phys. Rev. B* **89**, 064511 (2014).
- [60] Y. Nakajima, H. Shishido, H. Nakai, T. Shibauchi, K. Behnia, K. Izawa, M. Hedo, Y. Uwatoko, T. Matsumoto, R. Settai, Y. Onuki, H. Kontani, and Y. Matsuda, *J. Phys. Soc. Jpn.* **76**, 024703 (2007).
- [61] S. Ishida, M. Nakajima, Y. Tomioka, T. Ito, K. Miyazawa, H. Kito, C. H. Lee, M. Ishikado, S. Shamoto, A. Iyo, H. Eisaki, K. M. Kojima, and S. Uchida, *Phys. Rev. B* **81**, 094515 (2010).
- [62] N. D. Zhigadlo, S. Weyeneth, S. Katrych, P. J. W. Moll, K. Rogacki, S. Bosma, R. Puzniak, J. Karpinski, and B. Batlogg, *Phys. Rev. B* **86**, 214509 (2012).
- [63] A. Damascelli, Z. Hussain, and Z. X. Shen, *Rev. Mod. Phys.* **75**, 473 (2003).
- [64] Z. R. Ye, Y. Zhang, B. P. Xie, and D. L. Feng, *Chin. Phys. B* **22**, 087407 (2013).
- [65] P. Cheng, H. Yang, Y. Jia, L. Fang, X. Zhu, G. Mu, and H. Wen, *Phys. Rev. B* **78**, 134508 (2008).
- [66] H. Q. Yuan, F. M. Grosche, M. Deppe, C. Geibel, G. Sparn, and F. Steglich, *Science* **302**, 2104 (2003).
- [67] H. Q. Yuan, F. M. Grosche, M. Deppe, G. Sparn, C. Geibel, and F. Steglich, *Phys. Rev. Lett.* **96**, 047008 (2006).

- [68] G. Seyfarth, A. -S. Ruetschi, K. Sengupta, A. Georges, and D. Jaccard, Phys. Rev. B **85**, 205105 (2012).
- [69] S. Watanabe, M. Imada, and K. Miyake, J. Phys. Soc. Jpn. **75**, 043710 (2006).
- [70] C. Liu, T. Kondo, A. D. Palczewski, G. D. Samolyuk, Y. Lee, M. E. Tillman, N. Ni, E. D. Muna, R. Gordon, A. F. Santander-Syro, S. L. Bud'ko a, J. L. McChesney, E. Rotenberg, A. V. Fedorov, T. Valla, O. Copie, M. A. Tanatar, C. Martin, B. N. Harmon, P. C. Canfield, R. Prozorov, J. Schmalian, and A. Kaminski, Physica C **469**, 461 (2009).
- [71] H. Usui and K. Kuroki, Phys. Rev. B, **84**, 024505 (2011).

# Acknowledgment

I would like to appreciate following people who supported me to accomplish this study. Without their help, this dissertation would not have materialized.

## **Tajima Laboratory**

Prof. Setsuko Tajima, Prof. Shigeki Miyasaka, Prof. Masamichi Nakajima, Prof. Takahiko Masui, Mr. Shinnosuke Suzuki, Mr. Satoshi Saijo, Mr. Wataru Hirata, Mr. Ryuichiro Fukuta, Mr. Tyler Miyake, Dr. Kwing To Lai, Mr. Tatsuya Kobayashi, Mr. Kazuhiro Henmi, Mr. Tohru Adachi, Mr. Taichi Tokuhisa, Mr. Masahiro Uekubo, Mr. Takahiro Yamamoto and Ms. Yoshiko Ishimoto

## **Graduate school of science, Osaka University**

Prof. Kazuhiko Kuroki, Prof. Hidetomo Usui, Prof. Katsuhiko Suzuki, Prof. Masayuki Hagiwara and Prof. Takanori Kida

## **Graduate school of engineering science, Osaka University**

Prof. Yoshio Kitaoka, Prof. Hidekazu Mukuda, Prof. Masaaki Ashida, Prof. Masayoshi Ichimiya, Prof. Akira Sekiyama, Prof. Takayuki Kisu, Prof. Hidenori Hujiwara and Mr. Kohei Yamagami

## **UVSOR Facility, Institute for Molecular Science (IMS) and Nagoya University**

Prof. Tetsuya Hajiri, Prof. Kiyohisa Tanaka and Prof. Masaharu Matsunami

**International Superconductivity Technology Center (ISTEC) - Superconductivity Research Laboratory (SRL)**

## Acknowledgment

---

Dr. Keiichi Tanabe, Dr. Sergey Lee, Dr. Noriko Chikumoto and Dr. Seiji Adachi

### **High Energy Accelerator Research Organization (KEK)**

Prof. Youichi Murakami, Prof. Hironori Nakao, Prof. Akiko Nakao and Prof. Reiji Kumai

# List of publications

1. A. Takemori, S. Saijo, S. Suzuki, S. Miyasaka, S. Tajima, A. Nakao, H. Nakao, R. Kumai, and Y. Murakami, “Correlation between  $T_c$  and Transport Properties in  $\text{PrFeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$ ”, J. Phys. Soc. Jpn. **81**, SB043 (2012).
2. A. Takemori, S. Miyasaka, S. Tajima, S. Lee, S. Adachi, N. Chikumoto, and K. Tanabe, “Single crystal growth of Nd-1111 iron pnictide superconductors by high pressure synthesis”, JPS Conf. Proc. **1**, 012111 (2014).
3. S. Miyasaka, A. Takemori, S. Saijo, S. Suzuki, and S. Tajima, “Search for Key Parameter for Determining  $T_c$  in Fe-based Superconductors: Study of As/P Substitution in  $R\text{Fe}(\text{As}, \text{P})(\text{O}, \text{F})$  [ $R = \text{La}$  and  $\text{Nd}$ ]”, J. Phys. Chem. Solid **72**, 414 (2011).
4. T. Okuda, W. Hirata, A. Takemori, S. Suzuki, S. Saijo, S. Miyasaka, and S. Tajima, “Thermoelectric Properties of  $\text{LaFePO}_{1-x}\text{F}_x$  and  $\text{LaFeAsO}_{1-x}\text{F}_x$  –Possibility of the Hidden Mass Enhancement of  $\text{LaFeAsO}_{1-x}\text{F}_x$ –”, J. Phys. Soc. Jpn. **80**, 044704 (2011).
5. S. Adachi, T. Shimode, M. Miura, N. Chikumoto, A. Takemori, K. Nakao, Y. Oshikubo, and K. Tanabe, “Pulsed laser deposition of  $\text{BaFe}_2(\text{As}, \text{P})_2$  superconducting thin films with high critical current density”, Supercond. Sci. Technol. **25**, 105015 (2012).
6. M. Miura, S. Adachi, T. Shimode, K. Wada, A. Takemori, N. Chikumoto, K. Nakao, and K. Tanabe, “Anisotropy and Superconducting Properties of  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  Films with Various Phosphorus Contents”, Appl. Phys. Express. **6**, 093101 (2013).
7. S. Miyasaka, A. Takemori, T. Kobayashi, S. Suzuki, S. Saijo and S. Tajima, “Two Fermi Surface States and Two  $T_c$ -Rising Mechanisms Revealed by Transport Properties in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}$ , and  $\text{Nd}$ )”, J. Phys. Soc. Jpn. **82**, 124706 (2013).

8. H. Mukuda, F. Engetsu, K. Yamamoto, K. T. Lai, M. Yashima, Y. Kitaoka, A. Takemori, S. Miyasaka and S. Tajima, “Enhancement of superconducting transition temperature due to antiferromagnetic spin fluctuations in iron-pnictides  $\text{LaFe}(\text{As}_{1-x}\text{P}_x)(\text{O}_{1-y}\text{F}_y)$ :  $^{31}\text{P}$ -NMR Studies”, Phys, Rev. B **89**, 064511 (2014).
9. K. T. Lai, A. Takemori, S. Miyasaka, F. Engetsu, H. Mukuda, and S. Tajima, “Evolution of the phase diagram of  $\text{LaFeP}_{1-x}\text{As}_x\text{O}_{1-y}\text{F}_y$  ( $y = 0 - 0.1$ )”, Phys, Rev. B **90**, 064504 (2014).

# List of presentation at international conferences

1. “Search for Key Parameter for Determining  $T_c$  in Fe-based Superconductors: Study of As/P Substitution in  $R\text{Fe}(\text{As}, \text{P})(\text{O}, \text{F})$  [ $R = \text{La}$  and  $\text{Nd}$ ]”, The 9th International Conference on Spectroscopies of Novel superconductors 2010, in Shanghai in 2010 (Poster).
2. “P/As Substitution Effect on 1111 Iron Pnictide Superconductors”, International Workshop on Novel Superconductors and Super Materials 2011, in Tokyo in 2011 (Poster).
3. “Correlation between  $T_c$  and Transport Properties in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{1-y}\text{F}_y$ ”, TOKIMEKI 2011 -International workshop on heavy fermions-, in Osaka in 2011 (Poster).
4. “Two Different Superconducting Mechanisms in  $R\text{Fe}(\text{P}, \text{As})(\text{O}, \text{F})$  [ $R = \text{rare earth}$ ]”, Materials and Mechanisms of Superconductivity 2012, in Washington, D.C. in 2012 (Poster).
5. “Single crystal growth of  $\text{NdFeAs}(\text{O}, \text{F})$  by high pressure synthesis”, IRON-SEA, in Osaka in 2013, (Poster).
6. “Single crystal growth of Nd-1111 iron pnictide superconductors by high pressure synthesis”, Asia Pacific Physics Conference 12, in Chiba in 2013 (Poster).
7. “Band Structure Change with P/As Substitution in  $\text{NdFe}(\text{P}, \text{As})(\text{O}, \text{F})$ ”, The 1st International Symposium on Cadet Program, in Osaka in 2014 (Poster).



# List of presentation at the Japan physical society meetings

1. “P/As substitution effect in 1111-type iron pnictide superconductors”, The Japan physical society fall meeting, in Osaka in 2010 (Oral).
2. “P/As substitution effect in 1111-type iron pnictide superconductors II”, The Japan physical society spring meeting, in Niigata in 2011 (Oral).
3. “Transport properties in  $R\text{FeP}_{1-x}\text{As}_x\text{O}_{0.9}\text{F}_{0.1}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ )”, The Japan physical society fall meeting, in Toyama in 2011 (Oral).
4. “Single crystal growth and physical properties measurement of 1111 iron pnictide superconductor  $\text{NdFe}(\text{P},\text{As})(\text{O},\text{F})$ ”, The Japan physical society fall meeting, in Aichi in 2014 (Oral).
5. “Composition-dependent ARPES on  $\text{NdFeP}_{1-x}\text{As}_x(\text{O}, \text{F})$ ”, The Japan physical society spring meeting, in Tokyo in 2015 (Oral).