

Thesis

Nuclear Magnetic Resonance Studies of Iron Pnictides $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

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Abstract

In this thesis, we demonstrate our nuclear magnetic resonance (NMR) studies of iron-based superconductor (iron pnictide) $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, which have clarified the following anomalous properties from microscopic point of view: quantum criticality, spatial coexistence of magnetism and superconductivity, and orbital nematicity.

Static and dynamic magnetic properties of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.07 \leq x \leq 0.33$ were investigated by the measurement of ^{31}P -NMR spectrum and the nuclear spin-lattice relaxation time T_1 , respectively. The averaged magnetic ordered moment $\langle m \rangle$ at the zero-temperature limit, which is estimated from the ^{31}P -NMR spectrum shows a continuous decrease toward $x \sim 0.35$ with increasing P concentration x , verifying that a second-order quantum phase transition occurs at $x \sim 0.35$. Both of the SDW gap Δ_S derived from temperature dependence of $(T_1T)^{-1}$ below T_N and the characteristic temperature of antiferromagnetic (AFM) spin fluctuations θ estimated from the Curie-Weiss behavior of $(T_1T)^{-1}$ above T_N decrease toward $x \sim 0.35$ with increasing x as well as $\langle m \rangle$. All these results indicate the existence of an AFM QCP at $x \sim 0.35$, suggesting that AFM quantum critical spin fluctuations play an important role in the pairing mechanism in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

The coexisting state of magnetism and superconductivity is one of the most intriguing subject to study since the mechanism of unconventional superconductivity is expected to be highly related to magnetism. ^{31}P -NMR measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $x = 0.25$ at ambient pressure and $x = 0.20$ at hydrostatic pressure of $p \sim 2$ GPa were performed. These samples locate at the intermediate region between AFM ordered phase and superconducting state because both of them show superconducting (SC) transition in the AFM ordered state. $(T_1T)^{-1}$ measurement of ^{31}P at the magnetically ordered site revealed that SC transitions occur in magnetic ordered region of the sample for both $x = 0.25$ and $x = 0.20$ ($p \sim 2$ GPa). This is the direct evidence of spatial coexistence of superconductivity and antiferromagnetism in the microscopic scale. Moreover, ^{31}P -NMR spectrum found to become narrow below T_c , indicative of the suppression of internal magnetic field due to the competition between SC and AFM order parameters. Our results strongly suggest that antiferromagnetism and superconductivity occur at the same Fermi surfaces but they compete with each other.

In the recent research field of iron pnictides, the electronic nematic state has been a hot topic in which the electronic state spontaneously breaks the fourfold lattice symmetry in the tetragonal phase thus making various physical properties two-fold symmetric in the plane. Motivated by this, we measured in-plane field orientation dependence of ^{75}As -NMR of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ single crystal for $x = 0.04$ above T_S . A large difference in the linewidth between $H \parallel [100]_o$ and $H \parallel [110]_o$ in the orthorhombic basis revealed that in-plane anisotropy of the electric field gradient is present even in the tetragonal phase. This in-plane anisotropy arises from population imbalance between As- $4p_x$ and $4p_y$ orbitals, which reaches $|n_x - n_y| \sim 0.004$ electron at $T \rightarrow T_S$. The occupation imbalance in As- $4p$ orbitals is expected to be highly related to the orbital ordering of Fe- $3d_{xz}$ and d_{yz} electrons. In addition, this orbital polarization is already static near room temperature, suggesting that it is caused by the pinning of orbital nematic fluctuations by disorder. The orbital polarization is found to be further enhanced below ~ 150 K, which is consistent with the emergence of nematicity in torque and photoemission measurements. This result indicates either a crossover in the magnitude/length of the orbital-nematic correlations, or a phase transition.

This thesis is organized as follows: We will first provide the necessary background knowledge of the iron-based superconductors and then will review the research material $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ in Chapter 1. Chapter 2 will serve as the introduction to our experimental technique Nuclear Magnetic Resonance (NMR). Basic physics and principles of NMR will be discussed. Chapter 3 will deal with experimental details including NMR measurement setup, properties of the samples,

and experimental conditions for NMR measurements. In Chapter 4, a short review of the previous NMR studies of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ will be given. Chapter 5, 6 and 7 are the main contents of the thesis. In Chapter 5, we will discuss magnetic quantum criticality through the results of ^{31}P -NMR measurement for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ polycrystalline samples which show AFM transitions. In Chapter 6, we will present ^{31}P -NMR measurement for coexisting phase of AFM and superconductivity. Coexisting nature, whether spatially coexisting or phase-separated, will be discussed as well as the competing nature. Finally in Chapter 7, we will focus on ^{75}As -NMR study of a single crystalline sample of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Then, we will summarize our experimental results and make conclusions in Chapter 8. To improve the readability of this thesis, details on some calculations, analyses, and experimental techniques will be given in the appendices.

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List of Symbols and Abbreviations

(θ, ϕ)	Polar and azimuthal angles
μ	Nuclear magnetic moment
I	Nuclear spin angular momentum
k	Wave vector
l	Electron orbital angular momentum
q	Momentum vector
s	Electron spin angular momentum
v	Spin-wave velocity
χ	Susceptibility
χ'	Real part of susceptibility
χ''	Imaginary part of susceptibility
χ_P	Pauli paramagnetic susceptibility
χ_{spin}	Spin susceptibility
χ_{VV}	Van Vleck susceptibility
δH	a resonance field measured from the peak field of the paramagnetic ^{31}P -NMR spectra above T_N
δ	Tilting angle of the principal axis (z -axis) of electric field gradient from the crystalline c -axis
ϵ_0	Vacuum permittivity
η	In-plane EFG anisotropy
γ	Nuclear gyromagnetic ratio
γ_∞	Anti-shielding factor
γ_e	Gyromagnetic ratio of electron
$\hbar$	Reduced Planck constant
Δ	Superconducting gap

κ	Thermal conductivity
λ	Penetration depth
$\langle H_{\text{int}} \rangle$	Average of the internal magnetic field
$\langle m \rangle$	Average of magnetic moment at Fe site
$\mathcal{H}$	Hamiltonian
μ	Magnetic permeability
μ_0	Vacuum permeability
μ_{n}	Nuclear magneton
ν_{α}	α component of the electric quadrupole frequency
$\nu_{\alpha}^{\text{lat}}$	Off-site contribution to electric quadrupole parameter from the surrounding charge ions in the lattice
ν_{α}^{on}	On-site contribution to electric quadrupole parameter from an imbalance of occupation numbers of each electron orbitals
Ω	Solid angle
$\omega_{\mathbf{k}}$	Angular frequency of wave vector $\mathbf{k}$
ω_{L}	Larmor frequency
ϕ_{d}	Diameter of copper wire
ψ	Wave function
ρ	Electrical resistivity
θ	Characteristic temperature of antiferromagnetic spin fluctuations
ξ_{fill}	Filling factor
$^{31}\mathbf{A}_{\text{hf}}$	Hyperfine coupling tensor between P and Fe site
$^{31}A_{\text{hf}}^{\text{dia}}$	Average of diagonal components of hyperfine coupling tensor between P and Fe site
$^{31}A_{\text{hf}}^{\text{off}}$	Average of off-diagonal components of hyperfine coupling tensor between P and Fe site
$^{31}I(\delta H)$	^{31}P -NMR intensity as a function of δH
a, b, c	Crystal lattice parameters
AE	Alkaline earth metal
AM	Alkali metal
C	Capacitance
C_{coh}	The relaxation via the coherent gapped spin-wave excitations
C_{inc}	The relaxation via the incoherent gapless particle-hole excitations

C_M	Matching capacitor
C_T	Tuning capacitor
Ch	Chalcogen
E	Energy
e	Elementary charge
E_F	Fermi energy
f	frequency
$g(\omega), g(H)$	Number density of P nuclei as a function of angular frequency and magnetic field
$g(H_{\text{int}})$	Volume fraction of the magnetic ordered region with H_{int} in the sample
g_n	Effective g -factor of the nucleus
H	Magnetic field strength
h	Planck constant
H_1	Excitation pulse field
H_{ext}	Amplitude of external magnetic field
H_{int}	Internal magnetic field
h_{P_n}	the pnictogen height from the iron plane: $h_{P_n} = (z_{P_n} - 0.25) \times c$
I	Nuclear spin quantum number
I_+	Raising operator
I_-	Lowering operator
K	Knight shift
k_B	Boltzmann constant
K_{chem}	Chemical shift
K_{core}	Core polarization shift
K_{dia}	Diamagnetic shift
K_{dip}	Dipolar shift
K_{Fermi}	Fermi contact shift
K_{orb}	Orbital part of Knight shift
K_{spin}	Spin part of Knight shift
L	Inductance
l	Length of an NMR coil
M	Nuclear magnetization

m^*	Effective mass of carriers
m_0	Free electron mass
N	Total occupation number of electron for As-4 <i>p</i> orbitals
$N(E)$	Density of states as a function of energy
N_{spin}	The number of spins in the unit volume
n_i	Occupation number of electron for As-4 <i>p_i</i> orbital
P	Pressure
Pn	Pnictogen
Q	Electric quadrupole moment
R	Resistance
R_H	Hall coefficient
RE	Rare earth metal
RR	Residual resistivity
RRR	Residual resistivity ratio
S	Cross section area of an NMR coil
T	Temperature
T^*	Electronic nematic transition temperature
T_1	Nuclear spin-lattice relaxation time
T_2	Nuclear spin-spin relaxation time
T_B	Bose-Einstein condensation temperature
T_C	Curie temperature
T_c^*	Superconducting transition temperature of antiferromagnetic ordered site
T_F	Effective Fermi temperature
T_N	Néel temperature
TM	Transition metal
V	Unit cell volume
$V_{\alpha\alpha}$	Diagonalized electric field gradient tensor component
V_{As}	Electrostatic potential at As site
Z	Impedance
z_{Pn}	<i>z</i> coordinate of pnictogen atoms in the unit cell
Δ_S	Spin-density-wave gap in the spin excitation spectrum

$\text{Li}_n(z)$	n -th polylogarithm of z
2D	Two-dimensional
3D	Three-dimensional
T_c	Superconducting transition temperature
T_N	Long-range antiferromagnetic ordering temperature
T_S	Tetragonal-to-orthorhombic structural phase transition temperature
AFM	Antiferromagnetic
APRES	Angle-resolved photoemission spectroscopy
APW	Augmented plane wave
BCS	Bardeen, Cooper, and Schrieffer
BPF	Band pass filter
CW	Curie-Weiss
DBM	Double balanced mixer
DFT	Density-functional theory
dHvA	de Haas-van Alphen
DOS	Density of states
DSO	Digital storage oscilloscope
EFG	Electric field gradient
FL	Fermi liquid
FM	Ferromagnetic
FS	Fermi surface
FWHM	Full width at half maximum
GL	Ginzburg-Landau
HF	Heavy fermion
LDA	Local density approximation
LPF	Low pass filter
NMR	Nuclear magnetic resonance
NN	Nearest-neighbor
NNN	Next-nearest-neighbor
PG	Pseudogap
PM	Paramagnetic

PSD	Phase sensitive detector
QAM	Quadrature amplitude modulation
QCP	Quantum critical point
RX	Receiver
SC	Superconducting
SCR	Self-consistent renormalization
SG	Signal generator
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
TX	Transmitter
VTI	Variable temperature insert
XRD	X-ray diffraction

Chapter 1

Introduction

In this chapter, an introduction will be given to the recently discovered iron-pnictide superconductors in general and to the studied materials $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ in specific. First, a short historical summary of the discovery is given. Iron pnictide superconductors have much variety of crystal structure, phase diagrams, and superconducting gap structures and hence the unified picture for describing their physics has yet to be established. It is clearly beyond the scope of this study to overview the research progress accumulated in the past six years for all iron pnictides. Therefore, after having touched on the basic properties of the iron pnictides and having sketched the current status of understanding of this family of superconductors, we will focus on the overview of the research material of this study, $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, including the crystals structure, band structure, magnetic ordered state and superconductivity.

1.1 Historical Overview of Superconductivity

One of the most fascinating phenomena in condensed matter physics is superconductivity, which is the ability of a material to lose its electrical resistivity completely below a certain temperature, and expel any external magnetic field. From a practical application point of view, for example, the prospect of superconducting transmission lines without energy dissipation is appealing. The existing superconductors have been utilized as superconducting magnets, SQUID (Superconducting QUantum Interference Device), maglev trains that levitate above a magnetic field, and so on. The superconductivity is still a mysterious topic although one hundred years has already passed from its discovery by Heike Kamerlingh Onnes in April 1911 in Leiden [1]. Effectively, the lifetime of the superconducting (SC) current can be considered as infinite. Zero resistivity alone does not make a material a superconductor. The formation of ring currents on the surface of a superconductor enables it to counter external magnetic fields perfectly, resulting in zero net magnetic field inside the superconductor. This so-called Meissner effect, which was discovered by Meissner's student Ochsenfeld, leads (in type II superconductors) to levitation of a superconductor above a magnet.

Nearly half a century had to pass by until its mechanism in the conventional superconductors with rather low SC transition temperatures (T_c) could be explained consistently within the theory by Bardeen, Cooper and Schrieffer (BCS), published in 1957 [2]. However, most of the unconventional superconductors such as heavy fermions, discovered in 1979 [3], and the famous high temperature cuprate superconductors, discovered in 1986 [4], are far from being understood completely up to now although the latter is very attractive for the practical application because of its high T_c (The highest T_c defined by the onset of SC transition in resistivity reaches up to 166 K in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ under a pressure of 23 GPa [5], while the highest T_c defined by zero-resistivity is 153 K in the same compound under a pressure of 15 GPa [6]). The history of the discovery of new superconductors with higher T_c 's is summarized in Fig. 1.1(a).

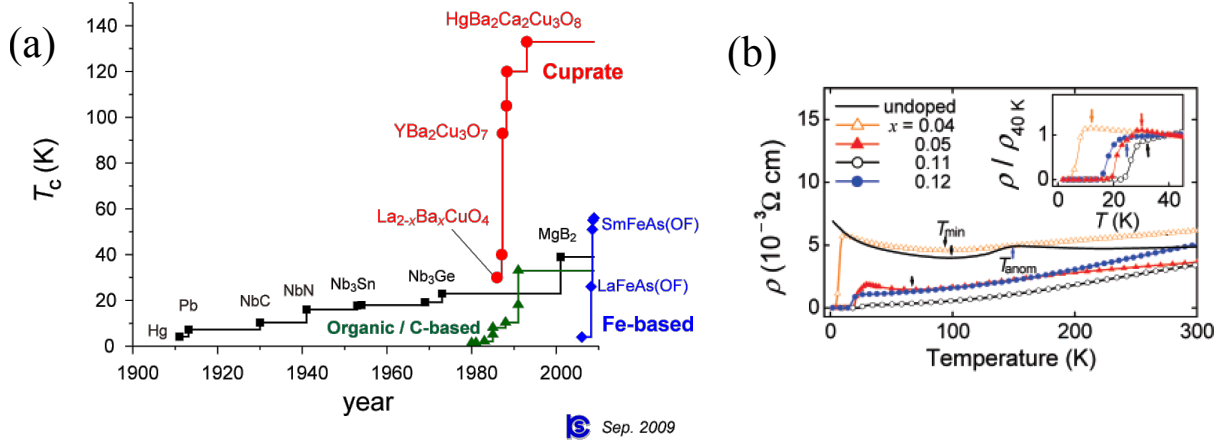


Figure 1.1: (a) Discovery of superconducting materials with successively higher T_c 's over the last century. All T_c 's denoted here are obtained at ambient pressure. This figure is cited from Shunichiro Kittaka's homepage. (b) Electrical resistivity ρ versus temperature T for undoped LaFeAsO and doped LaFeAs(O_{1-x}F_x): $x = 0.04, 0.05, 0.11$, and 0.12 . Inset shows expanded $\rho - T$ curves for $x = 0.04, 0.05, 0.11$, and 0.12 . Arrows show the onset transition temperatures. Figure reprinted from Ref. [7].

At the end of February 2008, iron-based superconductors LaFeAs(O_{1-x}F_x) with a relatively high maximum T_c of 26 K at $x = 0.11$ have been newly discovered by Dr. Kamihara in Prof. Hosono's group in Tokyo Institute of Technology [7]. The undoped LaFeAsO does not show superconductivity but exhibits a tetragonal-to-orthorhombic structural phase transition at $T_S \sim 160$ K and a long-range antiferromagnetic (AFM) spin ordering below $T_N \sim 145$ K. By substituting fluorine for a part of oxygen (corresponding to electron doping), LaFeAs(O_{1-x}F_x) exhibits relatively high- T_c superconductivity as shown in Fig. 1.1(b). Soon after the discovery, a series of different rare-earth element analogue superconductors $RE\text{FeAs}(\text{O}_{1-x}\text{F}_x)$ (RE : rare-earth elements such as La, Ce, Pr, Nd, Sm, and Gd) are reported to have T_c up to ~ 55 K [8], which is the highest record of T_c other than the high- T_c cuprate superconductors at present [8; 9; 10; 11; 12; 13; 14; 15]. Since iron is usually associated with ferromagnetism rather than with superconductivity, the new iron-based superconductors which exhibit surprisingly high T_c imply an intimate relationship between magnetism originating from Fe-3d electrons and the high- T_c superconductivity. Moreover, their crystal structures are two-dimensionally layered and are similar to the high- T_c cuprates. Both of the iron pnictides and the cuprates have d -electrons which play a key role for superconductivity, and possess a layered structure. Such similarities between the two systems have been attracting the interest of many researchers since antiferromagnetism and superconductivity are observed in both systems.

1.2 Iron-Based Superconductor

1.2.1 Crystal Structure

Iron-based superconductors can be divided into several structural families. The six representative ones are depicted in Fig. 1.2¹. They are frequently called as “11”, “111”, “122”, “1111”, “32522”, and “42622” systems according to the stoichiometries of their parent compounds as typified by FeSe, LiFeAs, BaFe₂As₂, LaFeAsO, Sr₃Sc₂O₅Fe₂As₂, and Sr₂VO₃FeAs. All these families commonly possess a tetragonal layered structure with the two-dimensional (2D) FeP_n or

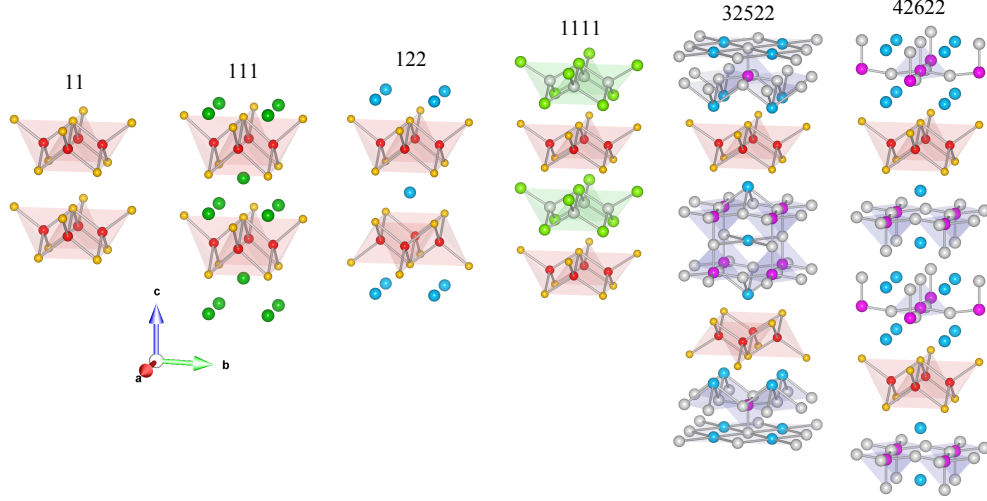


Figure 1.2: The iron-pnictogen layer (red-orange) is intercalated by nothing in the case of the so-called “11” (e.g. FeSe [16; 17]), by an alkali element (green) in the “111” family (e.g. LiFeAs [18; 19]), by an alkaline earth element (blue) in the case of the “122” (e.g. BaFe₂As₂ [20]), by an *RE*-oxygen layer (skyblue-white) in the case of the “1111” family (e.g. LaOFeAs [7]) or a block layer (violet-skyblue-white) in the case of the “32522” (e.g. Sr₃Sc₂O₅Fe₂As₂ [21]) and “42622” (e.g. Sr₂VO₃FeAs [22]).

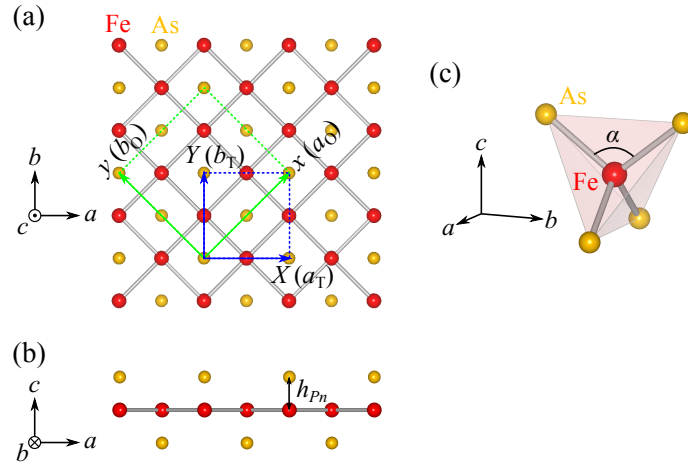


Figure 1.3: (a) FeAs-layer viewed from *c*-axis direction. (b) FeAs-layer viewed from *b*-axis direction. (c) FeAs₄-tetrahedron with As-Fe-As bond angle α .

¹Quite recently, another new type of iron pnictide superconductors having “112” crystal structure have been reported [23; 24; 25].

FeCh layers, in which Fe atoms are arrayed on a square lattice forming metallic bonds (Fig. 1.3). Because of the tetrahedral coordination of As, there are two Fe atoms per unit cell. These conducting layers, where superconductivity takes place, are intercalated by some alkali metals *AM* in “111” (*AMFeAs*), alkaline earth metals *AE* or *AM* in “122” (*AEFe₂As₂*, *AM_xFe_{2-y}Se₂*), rare earth-oxygen layers *REO* in “1111” (*REOFeAs*), or perovskite block layers in “32522” (*AE₃TM₂O₅Fe₂As₂*) and “42622” (*AE₄TM₂O₆Fe₂As₂*). *Pn* ions are arranged above and below the Fe-plane in a tetrahedral symmetry as shown in Fig. 1.3.

1.2.2 Electronic Structure

A knowledge of the electronic structure is essential for understanding the physical properties of these materials. Detailed band structure calculations for all classes of these compounds have been performed [26; 28; 29; 30; 31; 32; 33; 34]. The obtained results are similar in all studies. In pnictides (formally, Fe²⁺: 3d⁶), all five Fe-3d orbitals cross the Fermi level and add charge carriers. Pnictides feature a high density of states (DOS) at the Fermi energy, $N(E_F)$, dominated by Fe-3d bands moderately hybridizing with As-4p bands (Fig. 1.4(a)). Thanks to their high DOS at the Fermi level, the non-SC parent compounds of pnictides are itinerant (bad) metals [33].

The Fermi surfaces (FSs) composed of several electron and hole pockets which are disconnected from each other: three hole pockets at the center of the Brillouin zone (Γ point) and two electron pockets centered at its corners (M points) (see Fig. 1.4(b) for the FS topology in the folded² Brillouin zone). The hole-like cylinders at the Γ point and electron-like ones at the M point are nearly nested (overlapped) by nesting vector $\mathbf{Q} = (\pi, \pi)$ for folded Brillouin zone (two Fe atoms in the unit cell). Therefore, electronic transitions from the hole pockets to the electron pockets with momentum vector $\mathbf{q} \sim (\pi, \pi)$ should lead to a broad (because the electron pockets are oval rather than circular) peak in the susceptibility $\chi(\mathbf{q}, \omega \rightarrow 0) = \frac{f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \omega - i\delta}$ at $\mathbf{Q} = (\pi, \pi)$. The enhancement of susceptibility leads to the spin fluctuations at this finite nesting vector $\mathbf{Q}$. Sufficiently strong spin fluctuations can cause a stripe-type AFM ordering, which is indeed observed as ground states for the parent materials [35; 36].

Also, as shown in Fig. 1.5, the low energy band structure of LaFeAsO is quite sensitive to the pnictogen height h_{Pn} [27]. The topology of the FS changes when going from $h_{Pn} = 1.32$ Å (experimental value of h_{Pn} of LaFeAsO) to $h_{Pn} = 1.17$ Å (that of LaFePO), with a tube-like hole pocket with d_{xy} orbital character of 2D dispersion in the former case transforming into a 3D pocket with $d_{3z^2-r^2}$ orbital character in the latter. The physical origin of this sensitivity to h_{Pn} is the covalency of the iron-pnictogen bond, leading to strong hybridization effects.

The main effect of charge-carrier doping is a change in the relative sizes of the electron and hole FSs, which causes a bad nesting condition in the FS. The change of the lattice constants by elemental substitution or applying pressure also results in the bad nesting between the electron and hole FSs due to the change in dimensionality of FSs nevertheless electron and hole FS volumes are compensated because of no carrier doping. One of the differences among the existing structural families of pnictides is energy dispersion of the electronic bands along the k_z direction. The “122”, “111”, and “11” systems have more 3D FSs than that of the “1111” system.

Qualitatively similar FSs to the ones predicted from theories are observed experimentally. The observed FS indeed consists of three hole pockets and two electron pockets [37].

²The folded Brillouin zone corresponds to the crystallographic unit cell containing two Fe ions (and two As ions), to account for the fact that As ions are located above and below the FeAs-plane (Fig. 1.3(c)). The wave vector (π, π) in the folded Brillouin zone corresponds to $(\pi, 0)$ in the unfolded Brillouin zone with one Fe atom per unit cell [28].

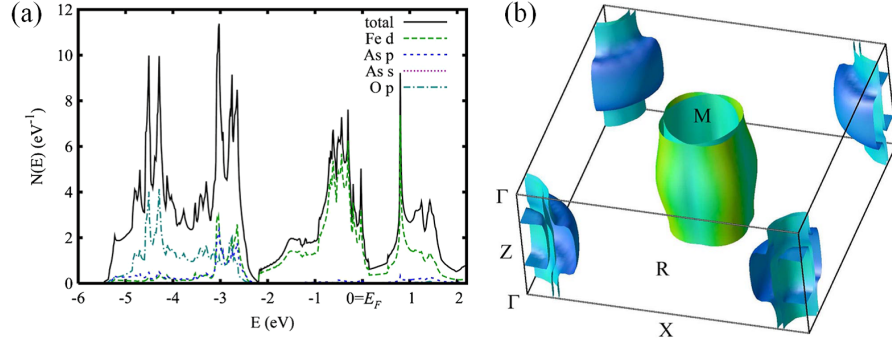


Figure 1.4: (a) Local density approximation (LDA) density of states $N(E_F)$ of LaFeAsO and projections onto the LAPW spheres on a per formula unit both spins basis [26]. (b) LDA Fermi surface of LaFeAsO shaded by velocity [darker (blue) is low velocity]. The symmetry points are $\Gamma = (0, 0, 0)$, $Z = (0, 0, 1/2)$, $X = (1/2, 0, 0)$, $R = (1/2, 0, 1/2)$, $M = (1/2, 1/2, 0)$, $A = (1/2, 1/2, 1/2)$ [26].

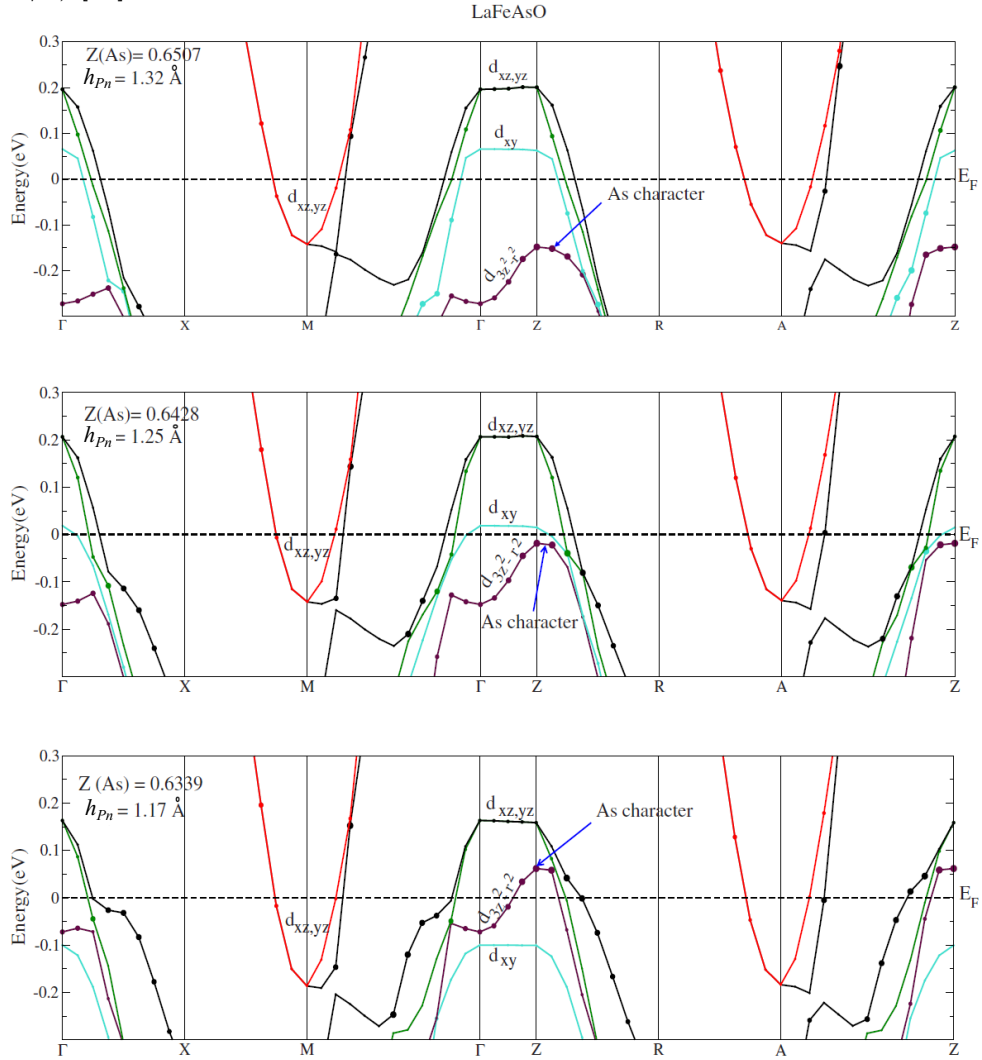


Figure 1.5: Sensitivity of the low-energy band structure for LaFeAsO to h_{Pn} (As height with respect to the Fe plane) for fixed lattice constants a and c . The considered h_{Pn} values are indicated in each plot. This figure is reproduced from Ref. [27].

1.2.3 Ground States and Phase Diagram

Most of the undoped parent compounds of iron-based superconductors undergo a magnetic phase transition to an antiferromagnetic (AFM) ordered state on cooling at around 140 - 200 K, which is accompanied or preceded by a structural phase transition from a tetragonal to an orthorhombic symmetry. Upon hole-/electron-doping or upon applying physical/chemical pressure, these transitions get suppressed and superconductivity emerges. A notable exception is the “111” compound LiFeAs, which is a stoichiometric superconductor [19; 38; 39].

Electron-doping in the “1111” family is achieved by substituting oxygen (O^{2-}) by fluorine (F^-), leading to $(RE)FeAsO_{1-x}F_x$ [7], by introducing oxygen deficiencies: $(RE)FeAsO_{1-\delta}$ [40] or by substituting cobalt for iron: $(RE)Fe_{1-x}Co_xAsO$ [41]. As shown in Fig. 1.6(a), for $LaFeAsO_{1-x}F_x$, the AFM ordering temperature (T_N) is weakly suppressed by doping and abruptly disappears at $x \sim 0.04$ followed by the emergence of superconductivity with SC transition temperatures (T_c). Once superconductivity appears, T_c exhibits a broad dome-like shape against x with a maximum T_c of 26 K. In the overdoped regime ($x \geq 0.2$), $LaFeAsO_{1-x}F_x$ undergoes a second SC dome with a maximum T_c of 36 K [42]. A further doping suppresses the second SC phase and induces another new AFM ordering phase of which detailed character is unknown [43]. On the other hand, $SmFeAsO_{1-x}F_x$ shows a bit different phase diagram from La-1111 system (Fig. 1.6(b)) [44]. In the region $0.10 \leq x \leq 0.15$ of the phase diagram of $SmFeAsO_{1-x}F_x$, the magnetism and the superconductivity show coexistence, while that of $LaFeAsO_{1-x}F_x$ suggests phase separation of these two orders.

In the “122” family, electron-doping is achieved by substituting Fe partially with Co leading to $AE(Fe_{1-x}Co_x)_2As_2$ with alkaline earth element $AE = Ba, Ca, Sr$ [45]. Hole-doping in the “122” families is done by partially substituting the divalent AE with a monovalent alkali element ($AM = K, Cs, Na$), leading to $AE_{1-x}AM_xFe_2As_2$ with the famous example of $Ba_{1-x}K_xFe_2As_2$ [20]. Superconductivity can be also induced by isovalent substitution of P for As [46; 47]. Due to the isovalency, this substitution does not introduce extra charge carriers but only introduce chemical pressure effect. The emergence of superconductivity by pressurizing without carrier doping suggests the importance of optimization of the crystal structure in iron pnictides. The phase diagram of $BaFe_2As_2$ -based materials with the three different chemical substitution is summarized in Fig. 1.6(c) [48].

In the “111” family, there are two parent compounds: LiFeAs and NaFeAs. Despite their similarities of crystal structure, they exhibit quite different physical properties. As for LiFeAs, there are neither structural transition nor AFM ordering but it only shows superconductivity below $T_c \approx 17$ K. By substituting Ni for Fe (corresponding to electron doping), superconductivity is continuously suppressed and system becomes metallic [49] as shown in Fig. 1.7(a). Increasing the ratio of Fe against Li, however, induces fluctuating itinerant moments that freeze at low temperatures. On warming, the AFM fluctuations is appears to show crossover to ferromagnetic fluctuations. Co doping to the parent NaFeAs suppresses both structural and AFM transitions with the enhancement of T_c [50]. T_c shows maximum where T_S and T_N are suppressed, which resembles the phase diagrams of “122” system.

Finally, we introduce the phase diagrams of “11” system. In the chalcogenide $Fe_{1+y}Se_xTe_{1-x}$ system, the Néel temperature drops rapidly for $x \leq 0.1$ and superconductivity appears from $x \sim 0.2$ up to $x = 1$ with mediating in-between state of spin glass for $0.1 \leq x \leq 0.3$ (Fig. 1.7(c)) [51]. The pressure versus temperature phase diagram of FeSe is fairly unconventional (Fig. 1.7(d)). By applying hydrostatic pressure, T_c goes up first, and after the emergence of AFM ordering at higher temperatures, T_c starts to decrease by competing with magnetism [52]. However, upon applying further pressure, T_c goes up again and superconductivity becomes to show coexistence with antiferromagnetism.

As presented above, iron pnictides have a large variety of the electronic phase diagram and

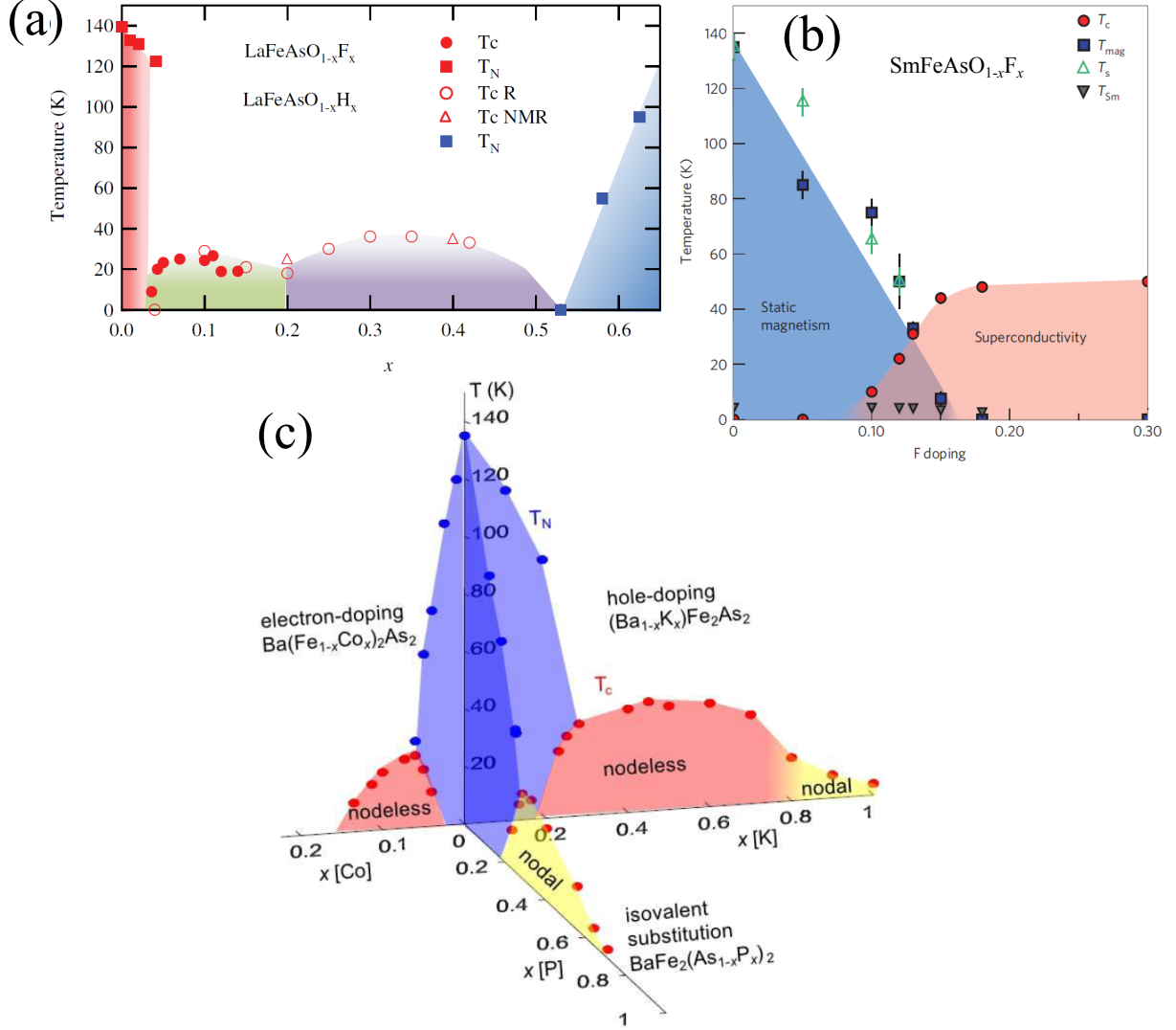


Figure 1.6: (a) Phase diagrams of $\text{LaFeAsO}_{1-x}\text{F}_x$ and $\text{LaFeAsO}_{1-x}\text{H}_x$ [43]. Especially, the one for $\text{LaFeAsO}_{1-x}\text{H}_x$ forms a symmetric alignment of AFM and SC phases, which is highly unconventional. (b) Phase diagram of $\text{SmFeAsO}_{1-x}\text{F}_x$ having a region of coexistence of antiferromagnetism and superconductivity [44]. (c) AFM and SC phase diagram of BaFe_2As_2 -based materials. Superconductivity emerges when the AFM order is suppressed via either hole doping in $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ (right), electron doping in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (left), or isovalent substitution in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ (bottom) [48]. In the P substituted system and in the overdoped region of K-doped system, the SC gap has line nodes [48].

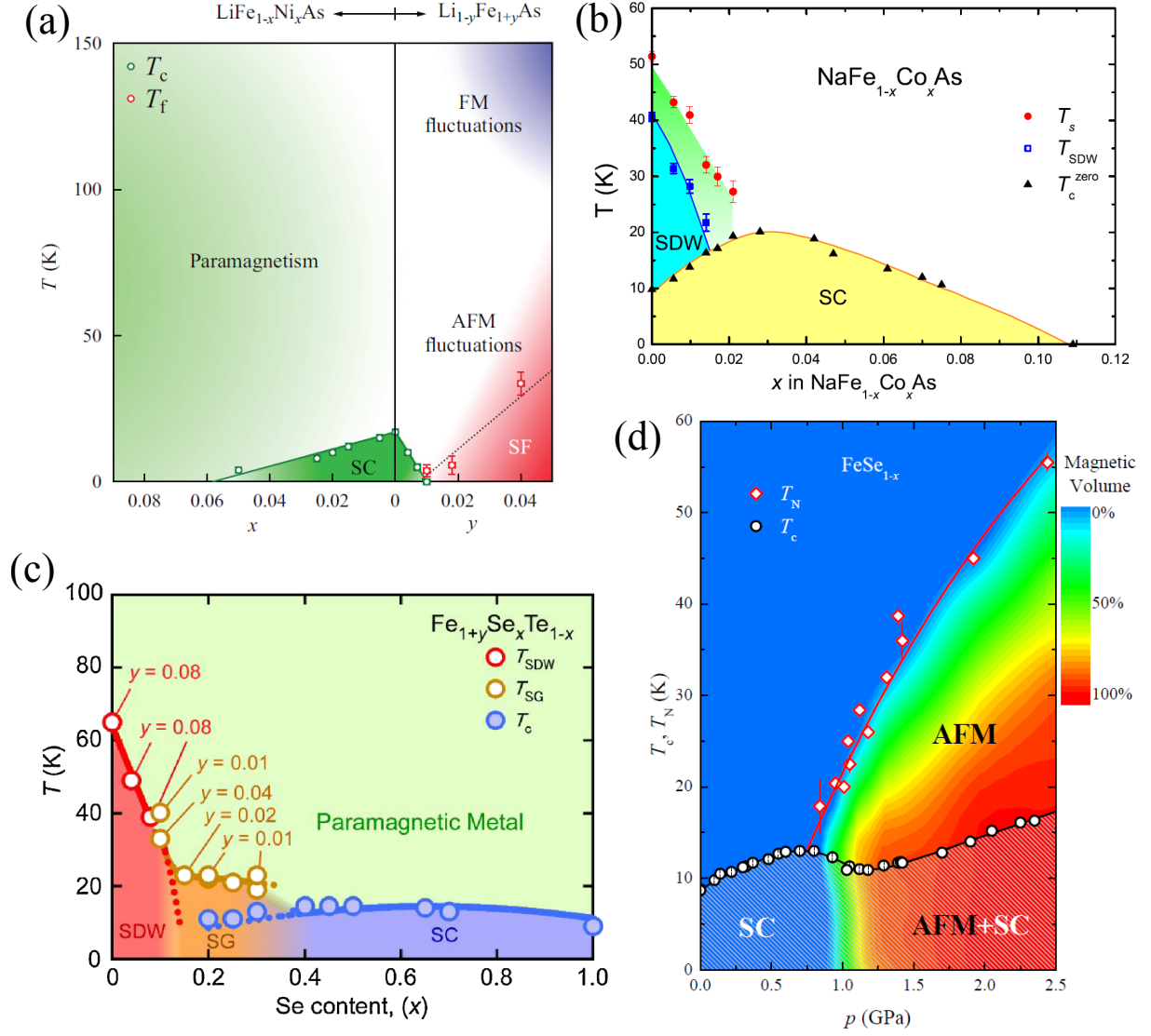


Figure 1.7: (a) Phase diagram for the $\text{Li}_{1-y}\text{Fe}_{1+y}\text{As}$ and $\text{LiFe}_{1-x}\text{Ni}_x\text{As}$ series, showing regions of superconductivity (SC), spin freezing (SF), as well as (anti)ferromagnetic fluctuations [49]. (b) Phase diagram of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ [50]. (c) Phase diagram of $\text{Fe}_{1+y}\text{Se}_x\text{Te}_{1-x}$ with $y \sim 0$ [51]. The nominal Fe content, y , is $y = 0$ unless it is specified. SG represents “spin glass”. (d) Pressure dependence of the T_c , T_N , and the SC and AFM volume fractions of FeSe_{1-x} . The SC volume is determined to be 100 % for all pressures and the AFM volume is represented by the color scale [52].

thus it seems very difficult to establish the unified picture for understanding all of these phase diagrams. Therefore, it is important first of all to focus on the specific system (“122” system, in this study) to understand.

1.2.4 Magnetism

The first direct evidence of AFM ordering in LaFeAsO is reported from neutron powder diffraction measurements [35]. LaFeAsO undergoes an abrupt structural transition at ~ 155 K from high-temperature tetragonal ($a = b$) to low-temperature orthorhombic ($a > b$) phase, and then long-range stripe-type AFM order develops at ~ 140 K with a small magnetic moment (Figs. 1.8(a) and 1.8(b)). The observed magnetic moment of $0.36 \mu_B$ per iron atom at 8 K is rather smaller than the theoretical value of $2.3 \mu_B$ per iron atom predicted from *ab initio* studies [53; 54]. This indicates that there should be factors which reduce the ordered moment such as magnetic frustration or strong spin fluctuations. Subsequently, the detailed magnetic structure is clarified to be with AFM alignment along longer *a*-axis and ferromagnetic (FM) alignment along shorter *b*-axis [55] as shown in Fig. 1.8(c). These tetragonal-to-orthorhombic distortion and stripe-type AFM ordering are observed in the parent compounds of iron pnictides except for FeTe [56].

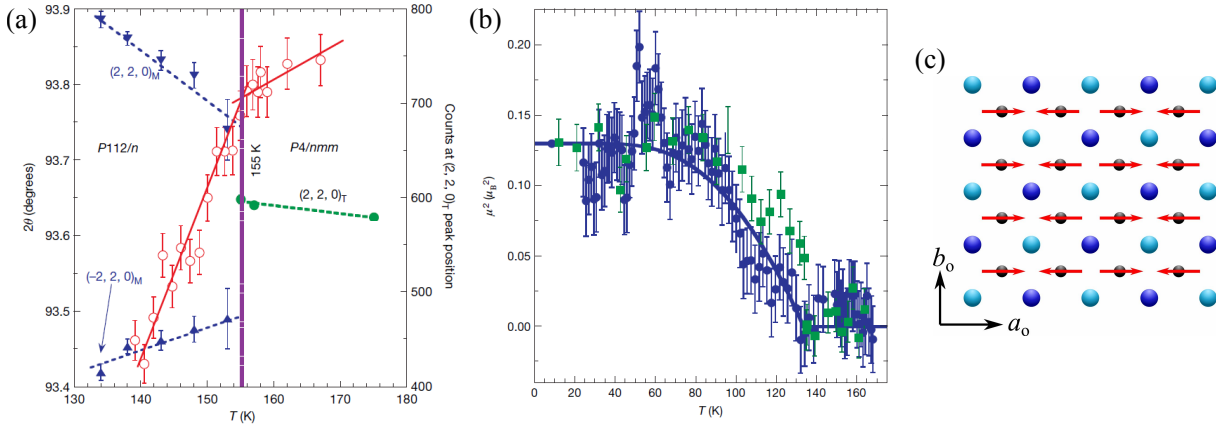


Figure 1.8: (a) Temperature dependence of the (2, 2, 0) nuclear reflection indicative of a structural phase transition at ~ 155 K in LaFeAsO [35]. (b) Temperature dependence of magnetic Bragg intensity measured at the wave vector $\mathbf{Q} = 1.53 \text{ \AA}^{-1}$ [35]. (c) The spin configuration in the AFM ordered state of LaFeAsO. The iron ordered moment represented by red arrow is aligned antiferromagnetically along longer *a*-axis and ferromagnetically along shorter *b*-axis.

1.2.5 Superconductivity

In general, the Cooper-pairing mechanism in high- T_c superconductors is one of the most challenging problems in solid state physics. Investigation of the SC order parameter is important for clarifying the mechanism of unconventional superconductivity. Up to now, various experiments and theoretical studies have been performed [57; 58; 59; 60; 61; 62; 63].

NMR Knight shift measurements are crucial to determine the spin part of SC order parameter. In iron-based superconductors, it is a common feature that Knight shift decreases in the SC state, indicative of a realization of a spin-singlet state [64; 65] (Fig. 1.9(a))

As for the orbital part, various experiments such as ARPES [67; 69], penetration depth [70; 71], specific heat [72], point contact spectroscopy [73], and thermal transport [74] suggest nodeless SC gap in $R\text{FeAs}(\text{O}_{1-x}\text{F}_x)$, $R\text{FeAsO}_{1-\delta}$, $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$, and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$.

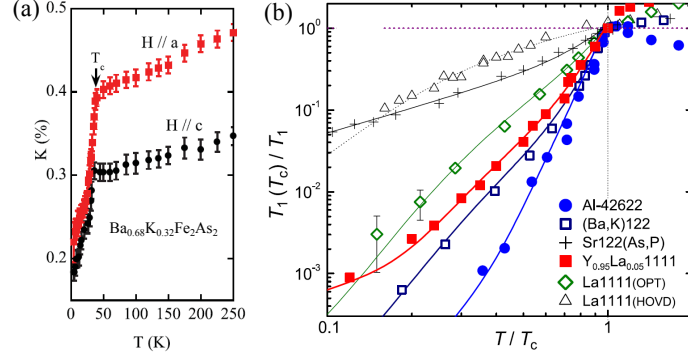


Figure 1.9: (a) Temperature dependence of the Knight shift for $\text{Ba}_{0.68}\text{K}_{0.32}\text{Fe}_2\text{As}_2$ with $H \parallel a$ axis and $H \parallel c$ axis, respectively. The arrow indicates T_c for $H \parallel a$ [65]. (b) Temperature dependence of normalized $T_1(T_c)/T_1$ for various iron-based superconductors [66].

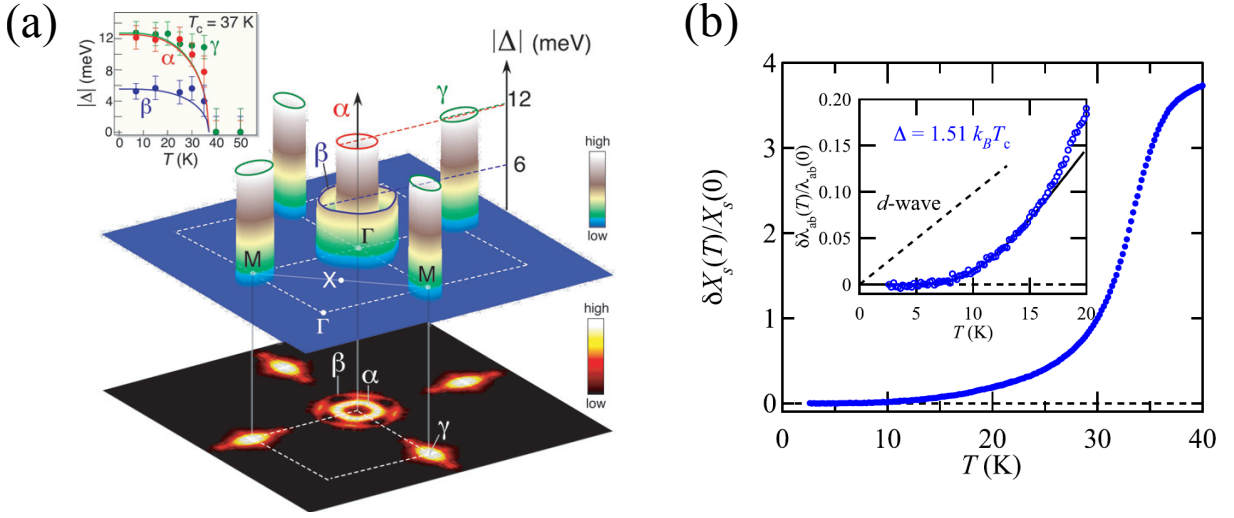


Figure 1.10: (a) 3D plot of the SC gap size (Δ) of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ measured at 15 K on the three observed FS sheets (shown at the bottom as an intensity plot) and their temperature evolutions (inset) [67]. (b) Temperature dependence of $\delta X_s(T)/X_s(0)$, which corresponds to $\delta \lambda_{ab}(T)/\lambda_{ab}(0)$ in the SC state for $\text{PrFeAsO}_{1-\delta}$.

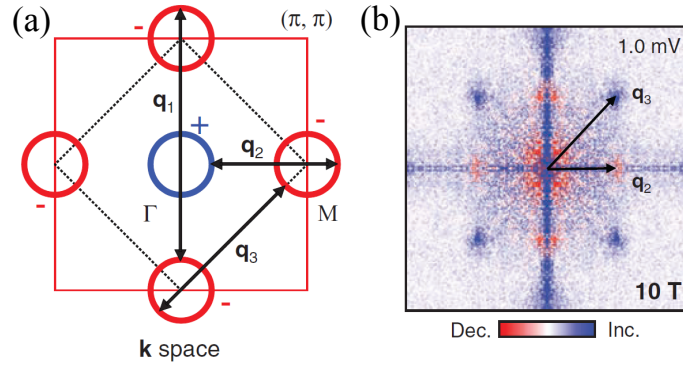


Figure 1.11: (a) A schematic drawing of FSs and inter-Fermi-pocket scatterings in k space. There are two hole cylinders and two electron cylinders around Γ and M points, respectively. Signs of the SC gap expected for $s_{\pm}$ -wave symmetry are shown by different colors. The arrows denote inter-Fermi-pocket scatterings. $\mathbf{q}_2$ and $\mathbf{q}_3$ connect different pockets, whereas $\mathbf{q}_1$ is an umklapp process. (b) Magnetic field-induced change in quasi-particle scattering interference intensities in $\text{Fe}(\text{Se}_{1-x}\text{Te}_x)$ [68].

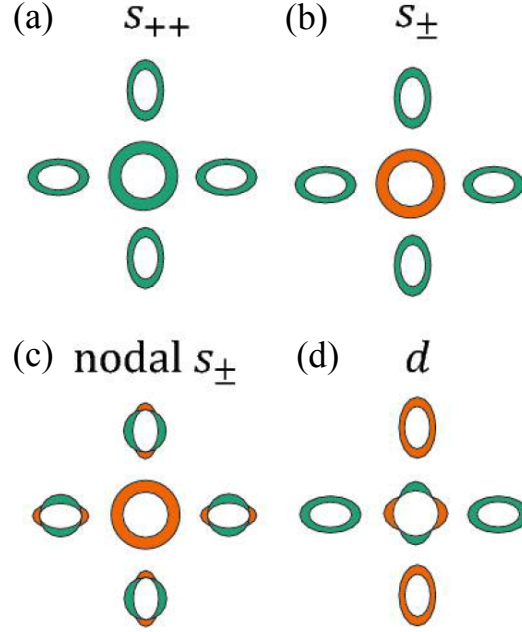


Figure 1.12: Schematic pictures of the proposed SC order parameters in the iron-based superconductors represented in the 2D, one iron Brillouin zone. Different colors stand for different signs of the gap. (a) s_{++} -wave symmetry, (b) $s_{\pm}$ -wave symmetry, (c) nodal $s_{\pm}$ -wave symmetry, (d) d -wave symmetry.

Figure 1.10(a) shows the FS dependence of the SC gaps for $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ revealed by ARPES: large gaps of $\Delta \approx 12$ meV on the inner hole and electron FSs and small gap of $\Delta \approx 6$ meV on the outer hole FS, where all of the observed gaps are nearly isotropic without nodes [67]. The in-plane microwave penetration depth λ_{ab} in single crystals of $\text{PrFeAsO}_{1-\delta}$ ($T_c = 35$ K) shows a flat dependence at low temperatures, suggestive of the nodeless SC gap as shown in Fig. 1.10(b) [71]. Moreover, the nuclear spin-lattice relaxation rate $1/T_1$ probed by NMR shows a sharp drop just below T_c , indicating no sign of Hebel-Slichter coherence peak [66; 75] (Fig. 1.9(b)). This suggests SC gap structure has a sign change. Scanning tunneling spectroscopy (STS) also detected the sign change of the SC gap [68]. Figure 1.11 shows the magnetic field induced change in quasi-particle scattering interference intensities in $\text{Fe}(\text{Se}_{1-x}\text{Te}_x)$. It is clear that signals at the momentum vectors $\mathbf{q}_2$ and $\mathbf{q}_3$ exhibit totally opposite behavior, indicating that these two scatterings have different characters. This pattern can be explained only if the SC gap possesses $s_{\pm}$ -wave symmetry.

There are two theoretical candidates of SC gap symmetry in iron-based superconductors: $s_{\pm}$ -wave and s_{++} -wave symmetries. Soon after the discovery of the iron-based superconductors, Mazin *et al.*, Kuroki *et al.*, and Cvetkovic *et al.* independently proposed that spin fluctuations arising from nesting between the hole and electron FSs might give rise to the $s_{\pm}$ -wave superconductivity with sign-reversing SC gaps as shown in Fig. 1.12 with unfolded Brillouin zone [31; 32; 76]. The $s_{\pm}$ -wave can explain the relationship between T_c and Pn height from Fe plane and the variation in SC gap symmetry. When Pn height is high, the γ hole pocket appears at Γ' point and the fully-gapped $s_{\pm}$ wave is stabilized. On the other hand, γ hole pocket disappears and the nodal $s_{\pm}$ wave or d wave gap gets an advantage when Pn height becomes lower. T_c in low Pn height is lower than that in high Pn height due to the frustration [77]. Although the $s_{\pm}$ -wave pairing is plausible from the theoretical and some experimental points of view, Sato *et al.* threw doubt on the $s_{\pm}$ -pairing state on the basis of their experimental

studies on $\text{La}(\text{Fe}_{1-y}\text{Co}_y)\text{As}(\text{O}_{1-x}\text{F}_x)$ and $\text{Nd}(\text{Fe}_{1-y}\text{Ru}_y)\text{As}(\text{O}_{1-x}\text{F}_x)$ [78]. They claimed that T_c suppression rates by Co and Ru substitution are much lower than the rate expected for superconductors with opposite signs of the order parameters. Following this stream, Onari and Kontani have theoretically proposed the s_{++} -wave symmetry mediated by orbital fluctuations. In s_{++} -wave, SC gaps are isotropic and have no sign change (Fig. 1.12). Kontani *et al.* has explained that many experimental results, which suggest the $s_{\pm}$ SC gap symmetry, e.g., observation of a resonance peak below T_c by neutron scattering measurements and the absence of a coherence peak in $1/T_1$, can be understood by s_{++} -wave model [79; 80; 81; 82]. Therefore, the one of the most important issues in iron-based superconductors is to experimentally identify their SC gap structures and pairing symmetries including a sign of SC gap.

1.3 BaFe₂(As_{1-x}P_x)₂

1.3.1 Normal State

Transport Properties

The first report on the iron-pnictide superconductor BaFe₂(As_{1-x}P_x)₂ has been given by Jiang *et al.* in 2009 [47]. BaFe₂(As_{1-x}P_x)₂ has the “122” type structure shown in Fig. 1.2. Since P ion is isovalent to As ion, the substitution of P for As does not dope any extra charge carriers and the system satisfies the compensation condition. Therefore, we can only tune magnetic character without nominally changing charge-carrier concentrations. Soon after the first report, Kasahara *et al.* reported the resistivity, x-ray diffraction (XRD) and the Hall effect measurements with high-quality single crystals over the entire phase diagram ($0 \leq x \leq 0.71$) [83; 84]. Figure 1.13(a) represents the temperature dependence of in-plane resistivity ρ_{xx} measured by Kasahara *et al.* The linear doping evolutions of lattice parameters a , c , and h_{Pn} is represented in Figs. 1.13(b) and 1.13(c). The systematic change of physical properties with P substitution is thus driven not by charge doping but by chemical pressure. The electronic phase diagram of BaFe₂(As_{1-x}P_x)₂ derived from the results of resistivity is shown in Fig. 1.13(d).

The parent compound BaFe₂As₂ shows the simultaneous structural and magnetic transitions in the resistivity at $T_S = T_N = 137$ K followed by the sharp reduction just below 137 K and saturation at low temperature. With increasing P dopant concentration x , a sudden jump due to the tetragonal-to-orthorhombic structural transition appears below T_S followed by a peak at T_N and the resistivity goes down. The low resistivity below T_N for $0 \leq x \leq 0.23$ indicates that BaFe₂(As_{1-x}P_x)₂ becomes an itinerant electron magnet in the AFM ordered state. The increase in x leads the suppressions of T_S and T_N and, in the region $0.20 \leq x \leq 0.28$ where the

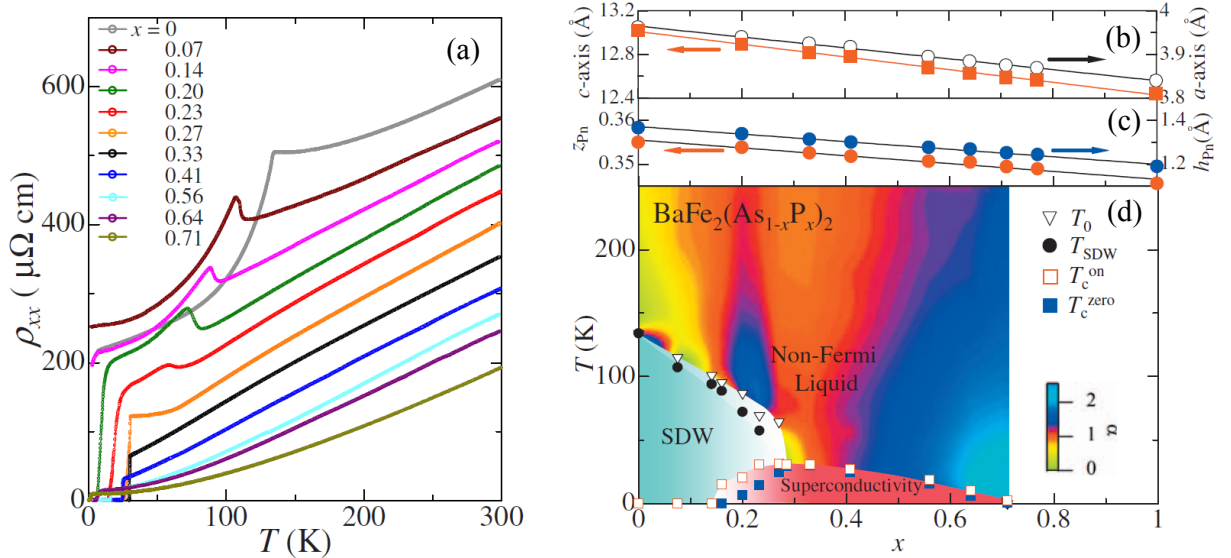


Figure 1.13: (a) Temperature dependence of in-plane resistivity ρ_{xx} in BaFe₂(As_{1-x}P_x)₂. (b) The P-concentration dependence of lattice parameters a and c and (c) the z coordinate of pnictogen atoms in the unit cell z_{Pn} and the pnictogen height from the iron plane $h_{Pn} = (z_{Pn} - 0.25) \times c$ determined from x-ray measurements. (d) The electronic phase diagram of BaFe₂(As_{1-x}P_x)₂. T_0 corresponds to T_S in the main text. The color scale of the background represents the exponent α in the following fitting equation to ρ_{xx} in the normal state: $\rho_{xx} = \rho_0 + AT^\alpha$. These figures are adopted from Ref. [83].

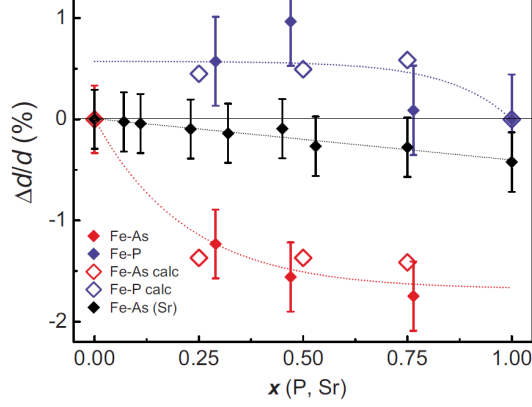


Figure 1.14: Changes in the normalized Fe-As and Fe-P bond lengths d in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ from single-crystal XRD data and in $(\text{Ba}_{1-x}\text{Sr}_x)\text{Fe}_2\text{As}_2$ from powder diffraction [88]. Open symbols represent Fe- Pn bond lengths predicted by DFT structure optimizations of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

ortho-AFM and SC phases overlap on the phase diagram, the resistivity shows zero even below T_N . T_c becomes highest with $T_c = 31$ K at $x \sim 0.30$. For further doped region $x \geq 0.33$, T_c starts to decrease and almost completely suppressed at $x = 0.71$. The temperature dependence of the normal-state resistivity exhibits characteristic change from T -linear ($\propto T$) at $x = 0.33$ to T -superlinear ($\propto T^2$) behavior at $x = 0.71$, indicating the evolution from Non-Fermi-liquid to Fermi-liquid property of the system. Such a systematic variation in power-index of T has been also reported in other unconventional superconductors like cuprates and heavy fermions, which could be related to AFM spin fluctuations originating from the proximity to the magnetic instability.

The Hall coefficient R_H defined as the field derivative of Hall resistivity ρ_{xy} , $R_H \equiv d\rho_{xy}/dH$ at $\mu_0 H \rightarrow 0$ T is negative indicating that not holes but electrons are dominant to the transport in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [83].

Nakajima *et al.* reported the improvement of the method for synthesizing $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ single crystals [85]. They used $\text{Ba}_2\text{As}_3/\text{Ba}_2\text{P}_3$ as self flux instead of the conventionally used FeAs and obtained large single crystals ($\sim 7 \times 7$ mm²). They also found that the quality of the as-grown crystals is improved by post-annealing, as evidenced by the increase in T_c and T_N , as well as the significant increase in residual resistivity ratio (RRR) from 3 to 30 for $x = 0$ and 35 to 75 for $x = 1.0$. This indicates that the post-annealing reduces the lattice defects and/or disorders. Subsequently, they reported combined measurements of in-plane resistivity and optical conductivity over the entire range $0 \leq x \leq 1$ disentangling coherent and incoherent components of charge dynamics [86; 87]. They revealed that the isovalent P substitution increases the “effective” coherent carrier number, which stems from the weakening of electronic correlations via chemical pressure. The role of P substitution is to expand the region of the coherent quasiparticle states in the momentum space.

Crystal structure

Rotter *et al.* investigated the detailed crystal structural parameters of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ by high-resolution XRD measurements and density-functional theory (DFT) calculations [88]. They found that As and P atoms are statistically distributed, but at different coordinates z_{As} and z_{P} , which is necessary to obtain reasonable Fe-P and Fe-As bond lengths. Fe-As bonds contract strongly at low doping and converges to ≈ 236 pm at higher doping levels. This behavior is almost quantitatively reproduced by DFT calculations using ordered model structures of

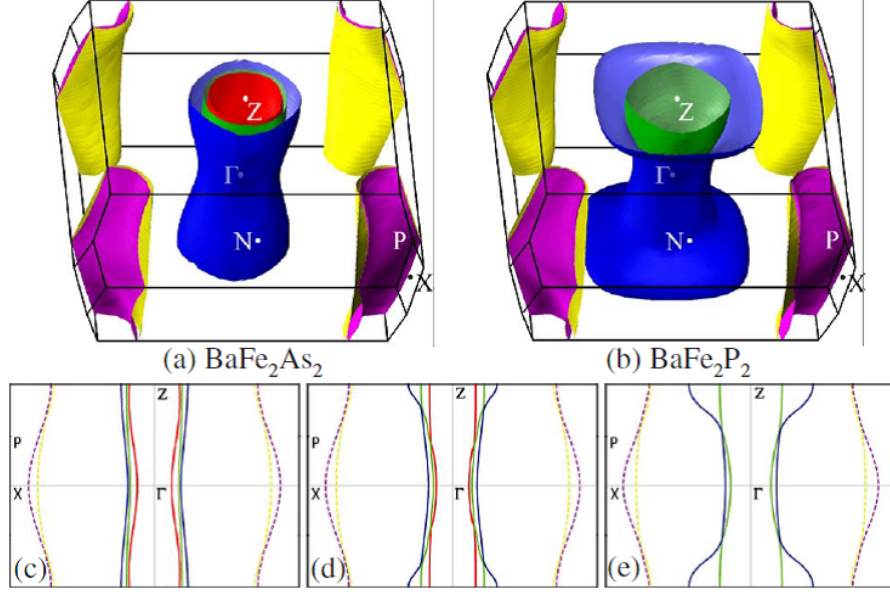


Figure 1.15: Fermi surfaces of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ (a) for $x = 0$ and (b) $x = 1$. Cross-section views along $[110]$ plane are also shown for (c) $x = 0$, (d) $x = 0.3$, and (e) $x = 1$ [83]. Experimental atomic positions are used as the structural parameters for the calculation.

$\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ as shown in Fig. 1.14. These results indicate that tiny but finite local distortion is introduced at the P(As) dopant site in $0 < x < 0.5$ ($0.5 < x < 1$) in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system, whereas the dopants does not act as strong scatterers in the FeAs conducting layer as evidenced by the observation of quantum oscillation signals in wide x range $0.41 \leq x \leq 1$.

Electronic structure

Fermi surfaces (FSs) for $x = 0, 0.3$, and 1.0 derived from the band calculation by density functional theory implemented in the WIEN2K code [89] are shown in Fig. 1.15 [83]. There are three hole pockets around $\Gamma - Z$ line in $x = 0$ and 0.3 while one of them is absent in $x = 1$. On the other hand, two electron pockets, which are the dominant carriers for the transport, exist around $X - P$ and remains almost unchanged for the entire x range. The dimensionality of hole FSs are quite sensitive to the pnictogen height h_{Pn} . h_{Pn} is expected to be linearly reduced by substituting P for As resulting in an increase in interlayer hopping and the promotion of three dimensionality of hole sheets. The enlarged hole FS warping upon P-substitution is considered to weaken the nesting between hole and electron pockets along the (π, π) ($\Gamma - X$) direction.

de Haas-van Alphen (dHvA) effect is the phenomenon that the magnetic susceptibility shows quantum oscillation against magnetic field. This is a powerful technique to investigate the detailed structure of FSs and the effective mass of the quasiparticle. To observe the dHvA effect, the extreme conditions such as ultra-low temperatures, high magnetic field, and extremely clean single crystals having very small impurity scattering are indispensable. Shishido *et al.* observed quantum oscillations in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.41 \leq x \leq 1$ and discussed x dependence of FSs [90]. The observation of the dHvA effect in the mixed crystal system is quite rare indicating that $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is very clean samples. As shown in Fig. 1.16(a), the shrink of the volume of electron FSs from $x = 1.0$ to 0.41 is demonstrated. Since the number of charge carrier does not change with x , the size of hole FSs is expected to shrink equally to the electron FSs maintaining electroneutrality although the dHvA signals from hole pockets are not observed in

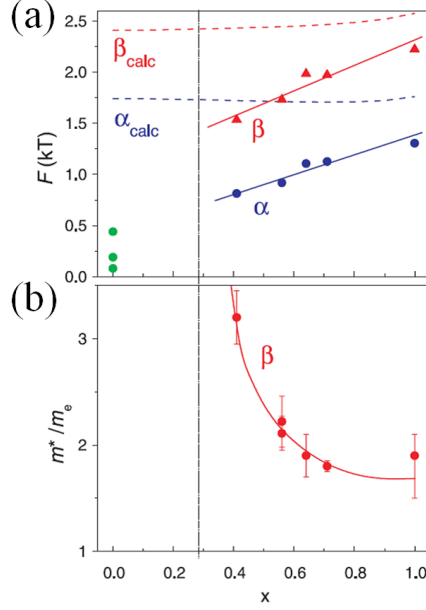


Figure 1.16: P-concentration dependence of (a) dHvA frequencies of electron FS sheets (α and β) $F(kT)$ related to the FS cross-sectional area and (b) the effective mass of the quasiparticle [90]. The dotted line in Fig. 1.16(a) represents the x -dependence of the frequencies expected from the band calculation. The green point indicates the data for $x = 0$ from Ref. [91].

this report. Together with the shrink of electron FSs, the enhancement of the effective mass of the quasiparticle are observed, whereas such an enhancement is not expected from the band structure. These results suggest the enhancement of many-body effects such as AFM spin fluctuations.

Following this, Analytis *et al.* reported the observation of one hole FS and two electron FSs for $x = 0.63$ by dHvA measurement [92]. It is clarified that the stronger nesting than expected by the band calculation exists even at $x = 0.63$ from the observation of equally warped hole FS and inner electron FS. They also indicated that the effective mass on the hole FS is about twice as much as that on the electron FS.

dHvA signals from all of the FS sheets were firstly reported by Arnold *et al.* for BaFe_2P_2 ($x = 1$) [93]. They observed that even for the non-SC composition $x = 1$, one of the hole sheets is almost perfectly nested with the inner electron FS, similar to that found for $x = 0.63$. The results for $x = 0.63$ and 1 suggest that the nesting is probably a necessary but not sufficient ingredient for superconductivity.

Another powerful experimental probe with unique capability to resolve in energy-momentum space and image electronic structures of materials is ARPES (Angle-Resolved Photoemission Spectroscopy). Yoshida *et al.* investigated the three dimensionality of the FSs of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with nearly optimal $x = 0.38$ via ARPES [94]. The effective mass enhancement is 2-3 on the electron FS and 2.5-4 on the hole FS, consistent with the results of dHvA measurements [90; 92]. One of the observed hole FS β is 2D with $d_{zx/yz}$ orbital character, resulting in the good nesting with the outer 2D electron FS δ with d_{xy} as shown in Fig. 1.17(b), whereas the orbital character of each FS is different. On the other hand, another hole FS γ is three-dimensional (3D) with $d_{3z^2-r^2}$, resulting in the bad and partial nesting with electron FSs. These results suggest that the three dimensionality and the difference in orbital character of FSs make the nesting condition worse.

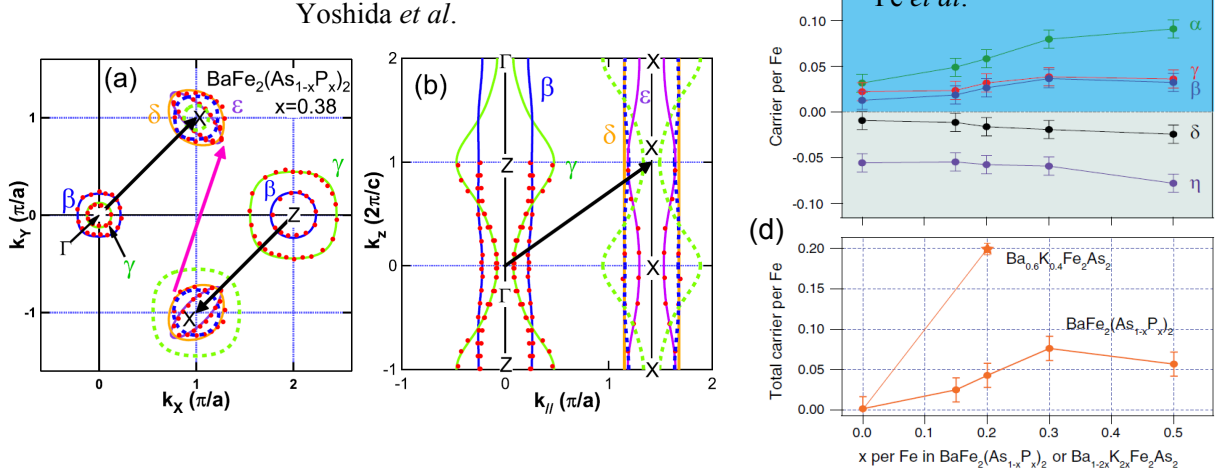


Figure 1.17: A cross section of FSs of $\text{BaFe}_2(\text{As}_{0.62}\text{P}_{0.38})_2$ (a) for $k_X - k_Y$ (b) for $k_z - k_{||}$ investigated by ARPES [94]. These FSs have different orbital characters: $d_{zx/yz}$ for the β FS, d_{xy} for the δ FS, and $d_{3z^2-r^2}$ for γ FS around the Z point, while $d_{3z^2-r^2}$ orbital character is almost absent in the electron FSs. Dotted line represents hole FSs shifted by the AFM nesting vector (black arrows). Partial nesting between adjacent electron FSs δ is indicated by a pink arrow. (c) The carrier density contributed by individual bands. (d) The total carrier density in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ for comparison.

Ye *et al.* reported ARPES experimental results that P substitution induces significant changes in dimensionality and orbital character of the FS, together with an expanding behavior of both hole and electron pockets and a suppression of electron correlation [95], which are consistent with the previous dHvA measurements [90]. They also found the sizable increase of holes with P substitution from $x = 0$ to 0.5 (Fig. 1.17) by counting the FS volume, which is not expected in the ordinary picture of isovalent doping. One possibility for hole doping they raised is that, for lightly P-doped case, the local lattice distortion induced by P dopant localize electrons [96] and thus introduces extra holes into the system. An alternative possibility is that the hole doping effect is extrinsic: The actual composition of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ they used for their experiments is not stoichiometric but $\text{Ba} : \text{Fe} : (\text{AsP}) = 1 : 2.1 : 1.9$ instead, indicating that there are some vacancies or interstitial ions in the system that could induce carriers.

Chemical Pressure versus Physical Pressure

Since P substitution results in the contraction of lattice constants, i.e., chemical pressure without carrier-doping [83], it is important to compare this effect with physical pressure effect. Measurements of T_c on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system under hydrostatic pressure via bulk AC susceptibility were reported from Klintberg *et al.* [97]. The pressure dependence of several P concentrations in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ranging from $0 \leq x \leq 0.48$ all point toward an identical maximum T_c of 31 K as shown in Fig. 1.18. This demonstrates that P substitution and physical pressure result in similar SC phase diagram, and that P substitution does not induce suppression of T_c due to substantial impurity scattering.

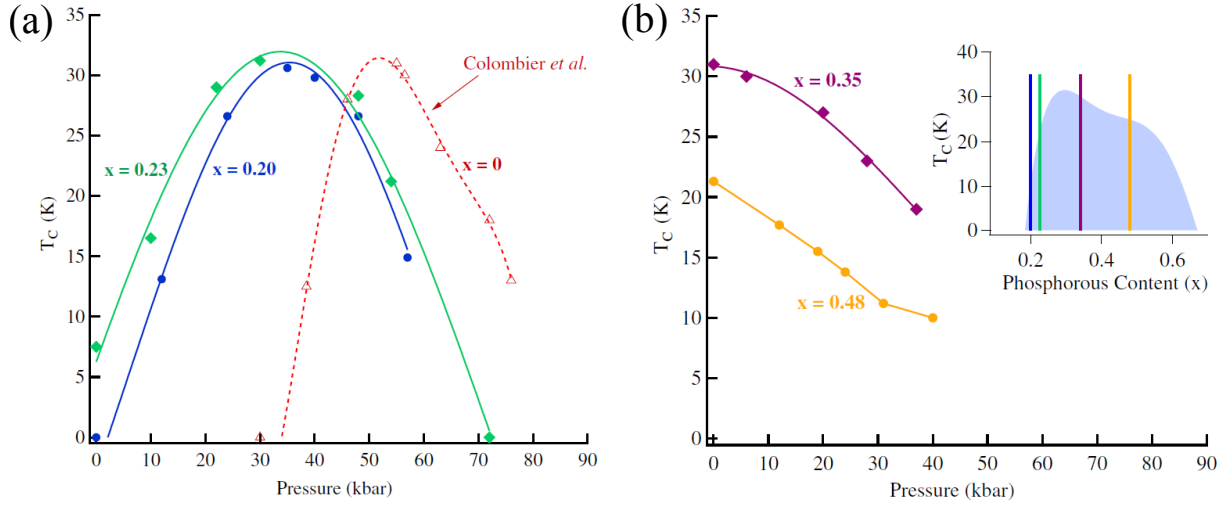


Figure 1.18: T_c -pressure phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ at P contents of (a) $x = 0.20$ [97] and 0.23 [97] together with $x = 0$ of which data are taken from resistivity measurements for comparison [98] and (b) $x = 0.35$ [99], 0.48 [97]. Inset of the right figure shows a schematic of the four chosen P contents in relation to the SC dome with T_c vs x data taken from Ref. [100].

1.3.2 Antiferromagnetic State

There are few experimental reports focusing on the AFM ordered phase of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ so far. Ishida *et al.* referred to the physics of AFM phase in their report of systematic resistivity measurements for Ba122 family [101]. The resistivity of the parent BaFe_2As_2 exhibits an abrupt decrease below $T_S = T_N = 143$ K associated with the transition from the tetragonal paramagnetic (PM) phase to the orthorhombic AFM phase. The decrease in the resistivity despite the loss of carrier density is due to a reconstruction of the FS in the AFM phase that generates high-mobility carriers, which dominate the charge transport. They investigated the comparative study of Co, P, and K doping effects by tracing the doping evolution of the in-plane resistivity and its anisotropy. As shown in Fig. 1.19(a)-(f), they observed the doping evolution of residual resistivity (RR) that, for all the three cases, RR initially increases with increasing doping x whereas the increasing ratio of RR against x represents a large difference. These results indicate that the magnitude of RR , or the strength of the impurity scattering by dopant atoms, gets smaller as the dopant site moves further away from the Fe plane. From comparison of the suppression rate of T_N and increasing rate of RR , they concluded that a disorder effect plays a substantial role in the suppression of the AFM phase. Considering the fact that the AFM ordering is also suppressed by the application of hydrostatic pressure [98], a change in the lattice parameters with doping could be another driving force. However, with further doping, RR starts to decrease, accompanied by the appearance of superconductivity as can be seen in Fig. 1.19(a)-(c). In addition, they measured the in-plane anisotropy of resistivity for each compounds (Fig. 1.19(g)-(i)). Originally, the resistivity anisotropy was considered to arise directly from the intrinsically anisotropic electronic state of the AFM ordered phase. For the Co-doped system, the resistivity along the shorter b -axis (ρ_b) with FM spin alignment is always higher than that along the longer a -axis (ρ_a) with AFM spin alignment (Fig. 1.19(g) and Ref. [102]). They found that the resistivity anisotropy at low temperatures almost vanishes for post-annealed clean BaFe_2As_2 . These results suggest that the resistivity anisotropy originates from the anisotropic impurity scattering by doped Co atoms/crystal defects. Extended measurements of in-plane anisotropy to P- and K-doped compounds clarified a sizable anisotropy for P-doped one and almost no anisotropy for K-doped one as

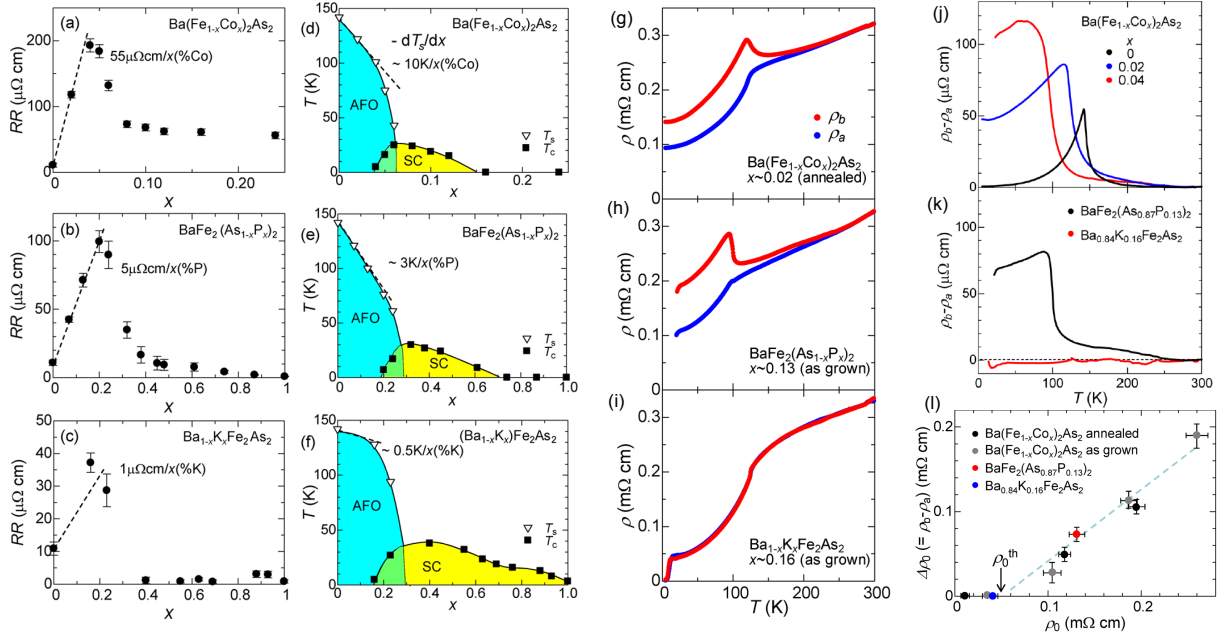


Figure 1.19: Doping dependence of the residual resistivity (RR) of (a) $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, (b) $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, and (c) $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. Dashed lines indicate the increases in RR upon doping. The increasing rates (indicated by the slopes) are also shown. (d)-(f) Phase diagrams for the three compounds based on the in-plane resistivity measurements. Also shown are the suppression rates of AFO (antiferromagnetic orthorhombic) ordering ($-dT_S/dx$). (g)-(i) In-plane resistivity anisotropies of selected compounds: (g) post-annealed $\text{Ba}(\text{Fe}_{0.98}\text{Co}_{0.02})_2\text{As}_2$; (h) as-grown $\text{BaFe}_2(\text{As}_{0.87}\text{P}_{0.13})_2$; (i) as-grown $\text{Ba}_{0.84}\text{K}_{0.16}\text{Fe}_2\text{As}_2$. (j)-(k) Resistivity anisotropy $\Delta\rho = \rho_b - \rho_a$ plotted as a function of temperature for (j) $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0, 0.02$, and 0.04 and (k) $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with $x = 0.13$ and $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with $x = 0.16$. (l) Difference in the residual component of the in-plane resistivity ($\Delta\rho_0 = \rho_b - \rho_a$) at low temperature as a function of the RR . ρ_0^{th} indicates the threshold value of the RR at which the resistivity anisotropy appears.

shown in Fig. 1.19(g)-(k). From these measurements, they summarized the relationship between RR , as a measure of disorder introduced by dopant atoms and lattice defects, and the in-plane anisotropy of resistivity $\Delta\rho_0 \equiv \rho_b - \rho_a$ in Fig. 1.19(l). With increasing RR above the threshold residual resistivity $\rho_0^{\text{th}} \sim 50 \mu\Omega\text{cm}$, $\Delta\rho_0$ increases linearly. This supports their scenario that the in-plane anisotropy is induced by disorder in FeAs-layer, and gives the new insight that when the impurity potential is too weak, the unusual anisotropic impurity state is not formed.

1.3.3 Superconducting State: Gap Structure

One of the most important question concerning the iron-based superconductors is what is the interaction that glues the electrons into Cooper pairs. Conventional phonon-mediated pairing leads to the SC gap opening all over the FS, while unconventional pairing mechanisms, such as spin-fluctuation-mediated one, can lead to a gap which has opposite signs on some regions of the FS. The sign changing is a result of the anisotropic pairing interaction which is repulsive in some momentum directions. In iron pnictides, the FS has disconnected hole and electron sheets and hence the condition for a sign-changing gap can be fulfilled without nodes. In fact, a simple picture based on spin fluctuations predicts a distinct type of unconventional order parameter

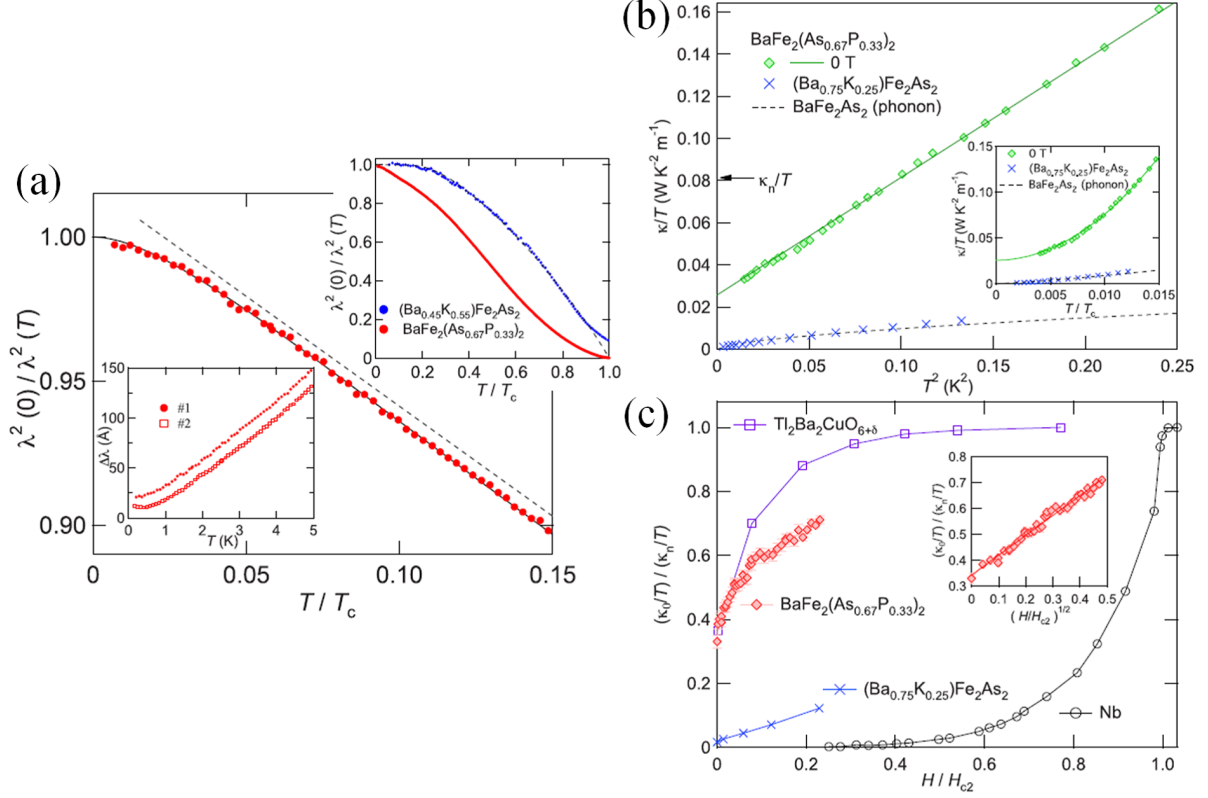


Figure 1.20: (a) The temperature dependence of the normalized superfluid density $\lambda^2(0)/\lambda^2(T)$ for $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ [103]. The linear dependence (broken line) can be seen up to $T/T_c \sim 0.05$. The temperature dependence including the deviation from linear dependence below $T/T_c \leq 0.05$ is fitted with the line node model considering the contribution from the disorder. The upper inset displays the data Upton T_c . $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ indicates apparently different behavior from full gap behavior of $(\text{Ba}_{0.45}\text{K}_{0.55})\text{Fe}_2\text{As}_2$. The lower inset shows $\Delta\lambda(T) \equiv \lambda(T) - \lambda(0)$ at low temperatures for two different samples of $x = 0.33$ (shifted vertically for clarity). (b) Thermal conductivity divided by temperature κ/T is plotted against T^2 at zero field (main panel) and on a linear T axis (inset). The solid lines are the fit to the T^2 dependence. The reported data of $(\text{Ba}_{0.75}\text{K}_{0.25})\text{Fe}_2\text{As}_2$ ($T_c \approx 30$ K (Ref. [74]) and the phonon contribution estimated in BaFe_2As_2 (Ref. [104]) are also shown. (c) Residual $\kappa_0(H)/T$ vs H/H_{c2} . Also shown are the results for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Ref. [105]), $(\text{Ba}_{0.75}\text{K}_{0.25})\text{Fe}_2\text{As}_2$ (Ref. [74]), and Nb (Ref. [106]). Inset shows the same data in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ plotted against $(H/H_{c2})^{1/2}$. The line represents the $\sqrt{H}$ dependence.

with a sign change between the sheets, known as an $s_{\pm}$ state [31; 77]. In this case, each FS is fully gapped, preventing low-energy excitations of quasiparticles. Thus, knowledge of the SC gap structure is a major step toward identification of the pairing interactions.

Penetration depth

The penetration depth λ is related to the superfluid density n_s : $n_s \propto \lambda^{-2}$. The information of the SC gap structure can be obtained from the temperature dependence of the superfluid density. Hashimoto *et al.* investigated the SC state of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with optimal concentration $x = 0.33$ by measuring the penetration depth. They showed the linear temperature dependence

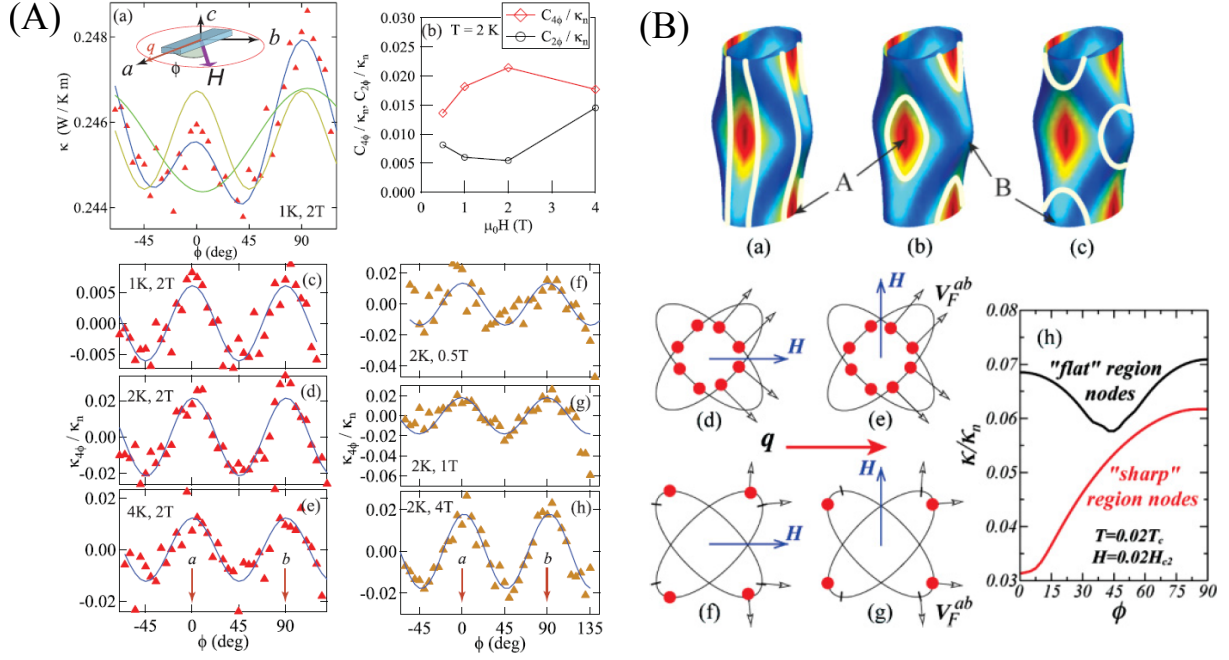


Figure 1.21: Panel (A): (a) Angular variation of $\kappa(\phi)$ in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ with a fit to $\kappa(\phi) = \kappa_0 + \kappa_{2\phi} + \kappa_{4\phi}$ (solid line). The sinusoidal curves with one minimum (two minima) represent the twofold (fourfold) term obtained by the fitting. The inset illustrates the measurement configuration. (b) The magnitudes of $\kappa_{2\phi}$ and $\kappa_{4\phi}$ at 2 K are plotted against the field magnitude H . (c)-(e) The fourfold term $\kappa_{4\phi}$ at $\mu_0 H = 2$ T. (f)-(h) $\kappa_{4\phi}$ at $T = 2$ K. Panel (B): (a)-(c) Electron FSs of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The shading represents the in-plane Fermi velocity v_F^{ab} . Note that the flat parts of the outer electron sheets near point A have high v_F^{ab} values. Possible node positions are indicated by white lines. For $k_z = 0$ and $\pm 2\pi/c$, electron surface cross sections are approximately elliptical, as (d)-(g). (d), (e) When the nodes are on the flat part, the field-induced states near all nodes (filled red circles) have a comparable contribution to the heat current for $\mathbf{H} \parallel \mathbf{q}$ (d) and for $\mathbf{H} \perp \mathbf{q}$ (e), so that the twofold component of κ is nearly absent. (f), (g) When the nodes are on the sharp ends, the field-induced DOS is small for nodes with $\mathbf{v}_F$ nearly parallel to $\mathbf{H}$ (crosses). The nodes with more quasiparticles (filled circles) have a different angle between $\mathbf{v}_F$ and $\mathbf{q}$ for the two field orientations, leading to a dominant twofold anisotropy. (h) Comparison of $\kappa(\phi)$ for the two cases with the scattering rate $\gamma = \Gamma/2\pi T_c = 0.01$, phase shift of scattering $\delta = 60^\circ$, and the ratio of interband to intraband scattering $\delta v = 0.9$. These figures are taken from Ref. [107]

of the superfluid density indicative of the existence of line nodes in the SC gap as shown in Fig. 1.20(a) [103].

Thermal conductivity

Hashimoto *et al.* also measured the thermal conductivity of $x = 0.33$ in zero-field and revealed the existence of the finite residual density of states (RDOS) at zero-temperature which corresponds to 30 % of the density of states in the normal states as shown in Fig. 1.20(b). Moreover, they observed the sublinear field dependence of the RDOS $N(H) \propto \sqrt{H}$ due to Doppler shift of quasiparticle as shown in Fig. 1.20(c) expected in case where the SC gap has line nodes.

Qiu *et al.* performed thermal conductivity measurements on a heavily underdoped $x = 0.18$ sample and observed a large residual linear term at κ_0/T at zero field and a $\sqrt{H}$ dependence of

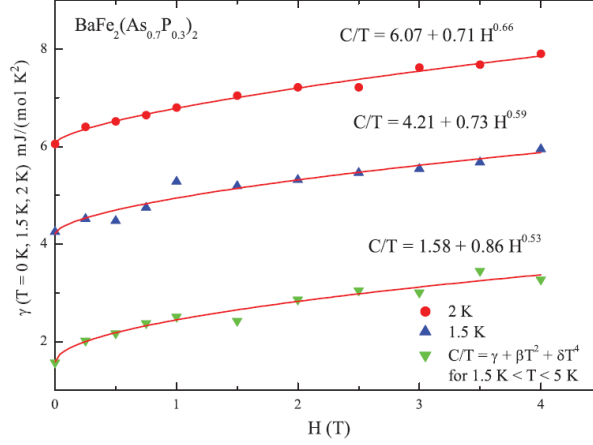


Figure 1.22: Field dependence of $\gamma(= C/T)$ of $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ at 2 K, 1.5 K, and 0 K determined by the extrapolation of the finite temperature data over the range $1.5 < T < 5$ K. The fitting functions of the data are labeled beside the curves. This figure is taken from Ref. [109].

$\kappa_0(H)/T$ as the ones reported by Hashimoto *et al.* Taking into account these results, the nodal superconductivity seems to be robust at least in the underdoped regime.

Yamashita *et al.* provided a possible answer to the question that which part of the FSs has the line nodes [107]. They surveyed in-plane field-angle dependence of thermal conductivity for optimal concentration $x = 0.33$ and found distinct fourfold oscillations with minima when the field is directed at $\pm 45^\circ$ with respect to the tetragonal a -axis. Combined with the results of the superfluid density ρ_s [103], specific heat C [108], the band-structure calculation, and guided by comparison with the theoretical predictions for angular variations of κ for different FS shapes and nodal structures, they concluded that the nodal lines form closed loops at the flatter part of the outer electron pocket near the intersection of the electron pockets with the $\Gamma - X$ line as shown in Fig. 1.21.

Specific heat

Kim *et al.* reported the results of specific heat measurement for the single crystal from the same batch which Hashimoto *et al.* used for penetration depth and thermal conductivity measurements. The low-temperature specific heat C/T related to RDOS $N(0)$ indicates H -linear dependence indicating that $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ is a fully gapped superconductor. This result seems to be inconsistent with the results of penetration depth and thermal conductivity measurements. However, more precise measurements at low fields by Wang *et al.* revealed the presence of a Volovik-like $\sqrt{H}$ term which persists roughly over a range of 4 T, crossing over to a linear behavior above this scale (Fig. 1.22) [109]. The crossover from sublinear to linear H dependence can be understood by a multiband calculation in the quasiclassical approximation assuming gaps with different momentum dependence on the hole- and electron-like FSs and thus, does not compete with the other experimental results suggesting the nodal gap structure but rather supports those claims.

Neutron Scattering

The first inelastic neutron scattering measurement on polycrystalline sample with $x = 0.35$ ($T_c = 30$ K) was reported by Ishikado *et al.* [111]. The spin resonance which is theoretically expected

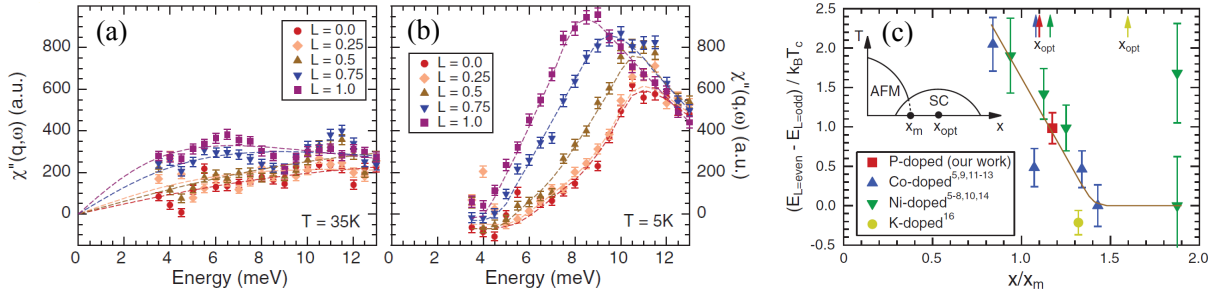


Figure 1.23: Energy spectra of $\chi''(\mathbf{q}, \omega)$ (a) above and (b) below T_c . The dashed lines in (a) are fits obtained using $\chi''(\mathbf{q}, \omega) = \chi_0 \Gamma \hbar \omega / [\Gamma^2 + (\hbar \omega)^2]$, and those in (b) are guides to the eye. (c) Doping dependence of the bandwidth of the resonance dispersion along L for various iron-based superconductors (see references in Ref. [110]). Energies are normalized by $k_B T_c$, and the doping levels are normalized by the levels where AFM disappears (x_m). The x_m values are assumed to be 29%, 5.6%, 4%, and 25% for P-, Co-, Ni-, and K-doped samples, respectively. The optimum doping level (x_{opt}) is depicted by arrows. These figures are taken from Ref. [110].

to appear in the $s_{\pm}$ -wave iron-based superconductor without line nodes [28; 112] is observed at $Q = (0.5, 0.5)$ in the tetragonal notation below T_c . In addition, the resonance enhancement (the enhancement of dynamical spin susceptibility at the resonance energy $\chi''(E_{\text{res}} = 12 \text{ meV})$), which is a measure of the area of sign reversal between the hole and electron FSs, is a factor of ~ 1.7 . This value is comparable to those of other iron-pnictide system without line nodes [113; 114]. These facts indicate that the sign reversal between the FSs is still dominant and the line nodes create only a limited area of sign reversal on a single FS. However, the interpretation of the enhancement of magnetic signal is also given by s_{++} -wave gap symmetry in terms of the absence of inelastic quasiparticle scattering just on the gap [80; 115]. Therefore, determination of SC gap symmetry from inelastic neutron scattering is considered to be difficult, although this experimental technique provides many of important information.

Quite recently, Lee *et al.* also reported an inelastic neutron scattering measurement on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with $x = 0.34$ single crystals ($T_c = 29.5 \text{ K}$) [110]. In the normal state, well-defined commensurate magnetic signals are observed at $(\pi, 0)$ ($(0.5, 0.5, L)$ in tetragonal notation), which is consistent with the nesting vector of the FS. Once the system goes below T_c , a clear spin gap with resonance energies dispersing along the c -axis is observed as shown in Fig. 1.23(b). They found that the resonance dispersion becomes larger with approaching the AFM ordered phase universally in all SC BaFe_2As_2 , indicating that this dispersive feature is attributed to the 3D AFM correlations (Fig. 1.23(c)). Their results suggest a strong relationship between magnetism and superconductivity.

ARPES

The pairing mechanism will be reflected in the momentum dependence of the SC gap properties. Spin fluctuation mechanism predicts strongly orbital-dependent SC gap magnitude [32; 77], while orbital fluctuations eliminate such orbital dependence [79; 119; 120]. Because each FS sheet in iron pnictides has a distinct d -orbital character, probing the FS dependence of the SC gap magnitude will be a test for identifying the contribution of the orbital fluctuations in the electron pairing. Shimojima *et al.*, reported the FS dependence of the SC gap magnitude of $\text{BaFe}_2(\text{As}_{0.65}\text{P}_{0.35})_2$ by using bulk-sensitive laser-ARPES [117; 121]. As shown in Fig. 1.24(a), the FS angle dependence of SC gap Δ indicates the fully gapped nature of the three hole FSs in $\text{BaFe}_2(\text{As}_{0.65}\text{P}_{0.35})_2$. Considering the nodal SC gap symmetry proposed by the penetration

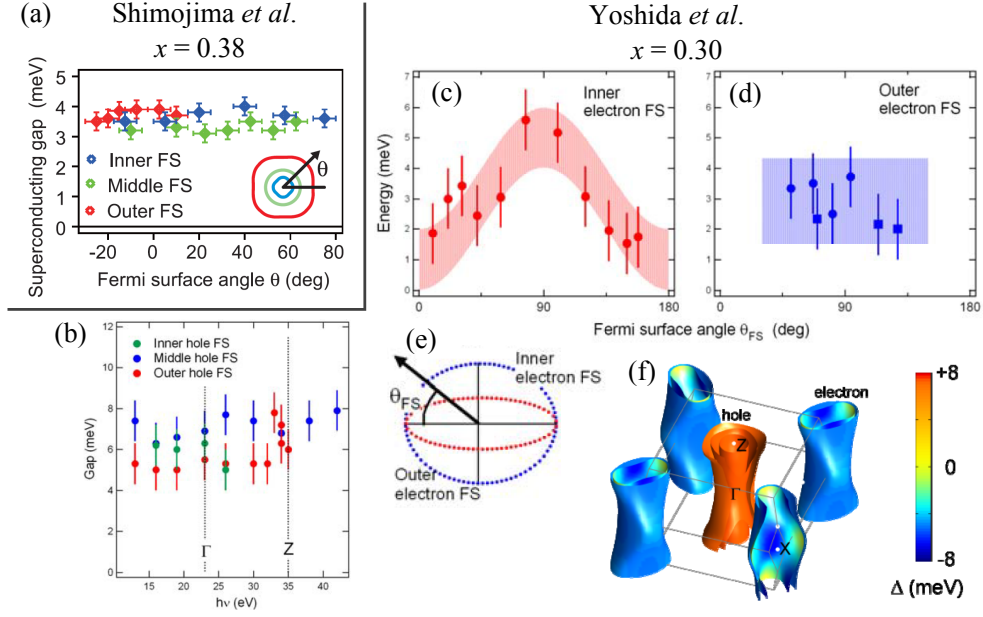


Figure 1.24: (a) FS angle dependence of the SC gap magnitude in each hole FS for $x = 0.35$. Inset shows the definition of the FS angle θ . (b) SC gap observed on the hole FSs with various k_z in $x = 0.30$. (c) SC gap anisotropy observed in $x = 0.30$ taken at $h\nu = 40$ eV for (c) inner and (d) outer electron FSs around the X point. (e) The Fermi surface angle is defined so that the direction from X to Γ is $\theta_{FS} = 0$. (f) SC gap value Δ determined from ARPES experiment of Ref. [116] for all the FSs of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. These figures are adopted from Refs. [116; 117].

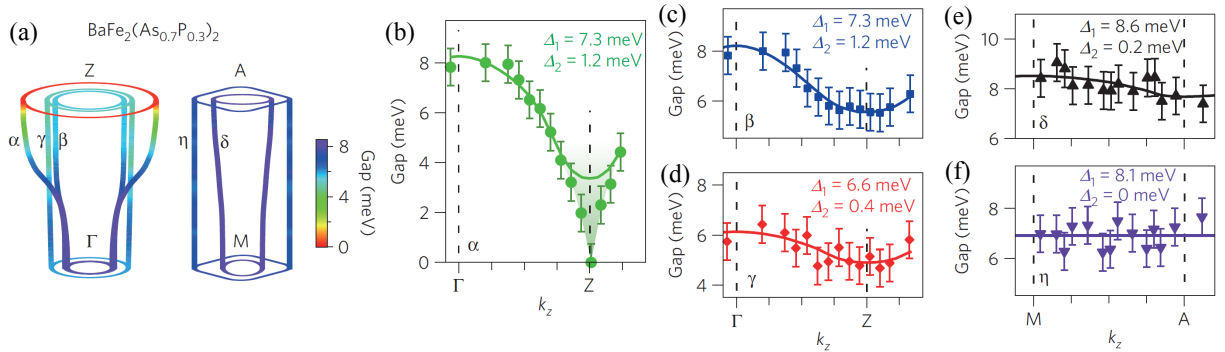


Figure 1.25: (a) False-colour plots of the gap distribution on the FSs of $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$. The SC gap of $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ versus on (b) the α , (c) β and (d) γ hole FSs and on (e) the δ and (f) η electron FSs for $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ as functions of k_z . The solid lines are fits to $\Delta_1 |\cos(k_x a) \cos(k_y a)| + \Delta_2 \cos(k_z c)$. These figures are adopted from Ref. [118].

depth, thermal conductivity [103] and NMR [122], their results rule out d -wave symmetry and imply the possible presence of line nodes in electron FSs around zone corners. This result is consistent with the angle-resolved thermal conductivity measurement which showed the presence of looped line nodes on electron FS [107]. The Δ of each hole FS is comparable to the common reduced gap value of $2\Delta/k_B T_c \sim 3.0$. The remarkable feature is the coincidence of Δ in the three hole FSs. The size and this characteristic behavior in SC gaps are observed independently of the k_z values, indicating SC gaps are almost orbital-independent.

Yoshida *et al.* have done more systematic ARPES measurements on $x = 0.30$, revealing a

peculiar momentum-dependent anisotropy in the SC gap. The large anisotropy found only in the electron FS (Figs. 1.24(c) and 1.24(d)) and the nearly isotropic gap on the entire hole FSs (Fig. 1.24(b)) are together consistent with modified $s_{\pm}$ gap with nodal loops.

On the other hand, the direct observation of a horizontal circular line node on the largest hole Fermi surface around the Z point at the Brillouin zone boundary has been reported by Zhang *et al.* as shown in Fig. 1.25 [118]. In addition, they did not find any nodes on electron FSs despite their extensive survey. Their results are inconsistent with the angle-resolved thermal conductivity results [107] and the above ARPES results [116; 117; 121] this problem is not fully settled at present.

Theoretical Works on Nodal Gap Structures

Both vertical loop nodes and horizontal nodes are supported by theories [123; 124; 125; 126; 127].

Especially, Suzuki *et al.* investigated the SC gap structure within the spin-fluctuation-mediated pairing mechanism [126]. They found that the gap is basically $s_{\pm}$, but when the hole FS around Z point having a strong $3z^2 - r^2$ orbital character becomes larger by P substitution, the SC gap on that FS exhibits 3D nodal structures. Since the $3z^2 - r^2$ orbital does not play an important role in spin-fluctuation-mediated superconductivity, this explains why T_c in the isovalent P doping system is relatively high despite the presence of nodes. This picture is consistent with the above ARPES results by Zhang *et al.* [118]

On the other hand, Saito *et al.* obtained a nodal s -wave state in the crossover region between the orbital-fluctuation-mediated s_{++} -wave and spin-fluctuation-mediated $s_{\pm}$ -wave states. They showed the appearance of loop-shaped nodes on the electron FSs by considering the competition between orbital and spin fluctuations [125]. This picture is consistent with the results of angle-resolved thermal conductivity and recent ARPES studies by Yoshida *et al.* [107; 116]

Therefore, in case the nodes exist on hole FSs, the superconductivity is spin-fluctuation-mediated type, while in case the nodes exist on electron FSs, the superconductivity would be induced by cooperation or competition between spin and orbital fluctuations.

1.3.4 Superconducting State: Quantum Criticality

In two families of high-temperature superconductors, cuprates and iron-pnictides, superconductivity emerges in close proximity to an antiferromagnetically ordered state, and T_c has a dome-shaped dependence on doping or pressure [59; 62; 131]. What happens inside this SC dome is still a matter of debate. In particular, elucidating whether a quantum critical point (QCP) is hidden inside it may be key to understanding high- T_c superconductivity. A QCP marks the position of a quantum phase transition, a zero-temperature second-order phase transition driven by quantum fluctuations.

Hashimoto *et al.* have reported a sharp peak in the x -dependence of the London penetration depth λ_L at zero temperature in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ at $x = 0.30$, where T_c reaches a maximum as displayed in Fig. 1.26(a) [128]. This structure may arise from quantum fluctuations associated with a QCP even existing inside the SC dome (Fig. 1.26(c)). The ratio of T_c/T_F at $x = 0.30$ is enhanced, implying a possible crossover toward the Bose-Einstein condensate limit driven by quantum criticality (Fig. 1.26(d)) [48; 128; 129], where T_F is the Fermi temperature..

Following the report by Hashimoto *et al.*, Walmsley *et al.* also reported the existence of a peak structure at $x = 0.3$ in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ by a combined study of specific heat and dHvA effect as shown in Fig. 1.26(b) and ensured that the sharp peak in the inverse superfluid density [128] in this system results from a strong increase in the quasiparticle mass at the QCP.

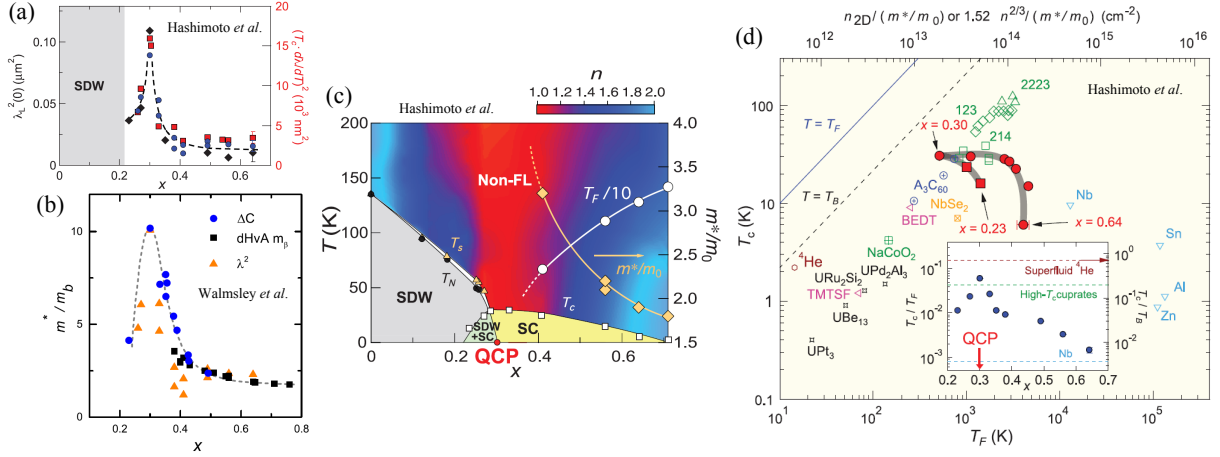


Figure 1.26: (a) penetration depth $\lambda_L^2(0)$ in the zero-temperature limit determined by three different methods: aluminum coating method (black diamonds), microwave cavity perturbation technique (blue circles), and the low-temperature slope of the change of the penetration depth with temperature (red squares, right-hand scale) [128]. Different points for the same x correspond to different crystals from the same batch, but for some of the microwave and the low-temperature slope data we used the same crystals. Error bars shown for $x = 0.64$ represent typical experimental errors largely resulting from uncertainties in the determination of geometrical factors. (b) Mass enhancements as derived from specific heat, dHvA, and microwave magnetic penetration depth measurements [129]. (c) Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. With increasing x , T_N decreases down to zero at $x = 0.30$. The red shaded region at around $x = 0.30$ represents the region where the resistivity, $\rho(T) = \rho(0) + aT^n$, is close to unity, which is a hallmark of a non-FL. The composition dependence of the effective Fermi temperature T_F and renormalized mass m^*/m_0 determined by dHvA oscillations [90] are also plotted. (d) Uemura plot. T_c is plotted as a function of T_F for various superconductors [130]. They used an average of the Al coating and microwave data for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The data for $x \geq 0.30$ (red circles) and for $x < 0.30$ (red squares) bridge a gap between the conventional superconductors such as Nb and cuprate high- T_c superconductors such as $(\text{La},\text{Sr})_2\text{CuO}_4$ (214), $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (123), and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223). $x = 0.30$ represents the data at the QCP. The dashed line is the BEC temperature for the ideal 3D boson gas. (Inset) Composition dependence of T_c/T_F (left axis) or BEC temperature (right axis). Green and light blue dashed lines mark the T_c/T_F values for underdoped cuprates 123 and for the conventional superconductor Nb. Brown arrow represents $T_c/T_B = 0.7$ for superfluid ^4He .

1.3.5 Electronic Nematic State

Quite recently, unexpected in-plane anisotropy have been observed even above T_S , i.e., in the tetragonal phase in some “122”-type iron pnictides [133; 134; 135; 136]. Such state is called “electronic nematic state” by an analogy from nematic phase of liquid crystal, in which the rotational symmetry is broken into twofold while the translational symmetry remains unbroken. However, the resistivity measurements were performed in the tetragonal phase under uniaxial stress, which itself breaks the 90° rotational C_4 symmetry. Therefore, the question remains open whether the nematicity can exist above T_S without an external driving force. Kasahara *et al.* reported magnetic torque measurements of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ without any uniaxial stress, showing that the nematicity develops well above T_S and, moreover, persists to the non-magnetic SC regime. They extracted the finite twofold oscillation component in in-plane field angle dependence of torque $\tau_{2\phi}$. The extracted amplitude of the twofold oscillation $|A_{2\phi}|$ grows rapidly

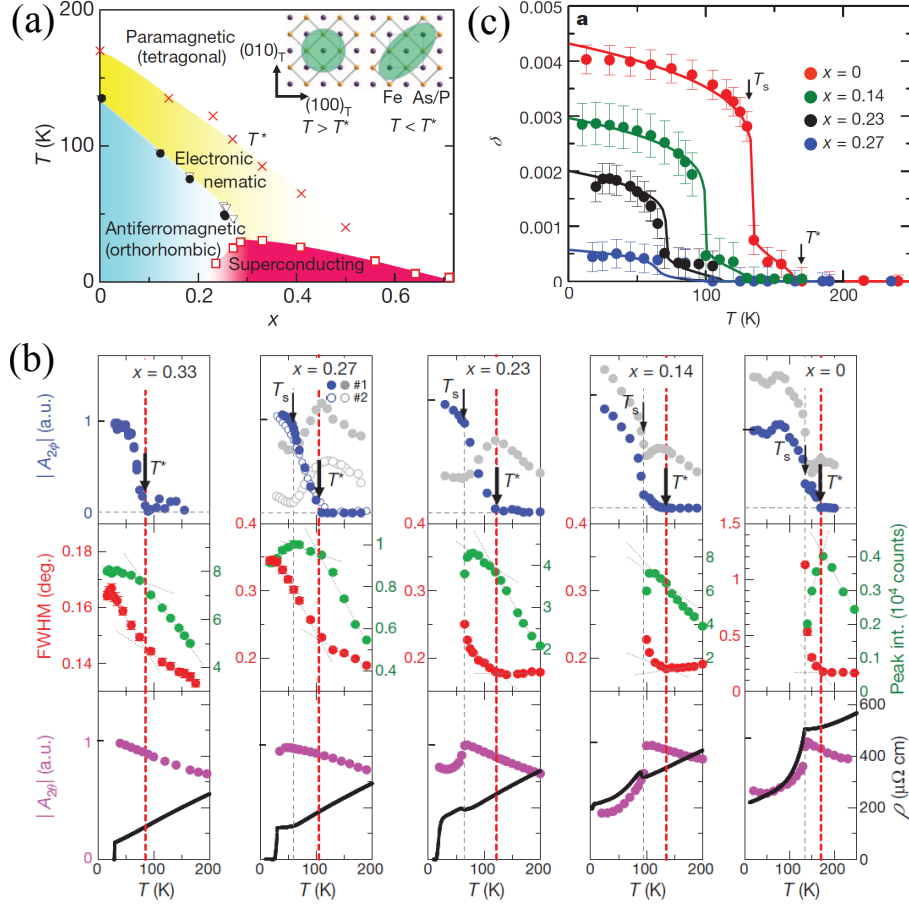


Figure 1.27: (a) Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Crosses indicate the nematic transition temperature T^* determined by the torque and synchrotron X-ray diffraction measurements. (b) Temperature dependence of the twofold oscillation amplitude $|A_{2\phi}|$ of the torque (blue circles in upper panels), the FWHM and peak intensity (red and green circles in middle panels, respectively) of the synchrotron X-ray Bragg reflection, the in-plane resistivity ρ (black lines in lower panels), and the torque amplitude for θ rotation (pink circles in lower panels) are shown for x values of 0.33, 0.27, 0.23, 0.14 and 0. The nematic transition temperature T^* and the meta-nematic transition temperature T_S are defined by red and grey vertical dashed lines, respectively, as well as by arrows in the upper panels. (c) Temperature dependence of lattice distortion $\delta = (a - b)/(a + b)$. These figures are taken from Ref. [132].

below T^* as shown in Fig. 1.27(c). They also determined the direction of nematicity to be along $[110]_T$ direction in the tetragonal basis, that is, Fe-Fe bond direction (Fig. 1.27(b), inset). Anomalies at T^* can also be seen in the synchrotron X-ray diffraction measurements, in which the full width at half maximum (FWHM) of the higher-order Bragg peaks grows below T^* (middle panel of Fig. 1.27(c), red circles), accompanied by the suppression of the peak intensity (middle panel of Fig. 1.27(c), green circles). They quantified the orthorhombicity $\delta = (a - b)/(a + b)$ in

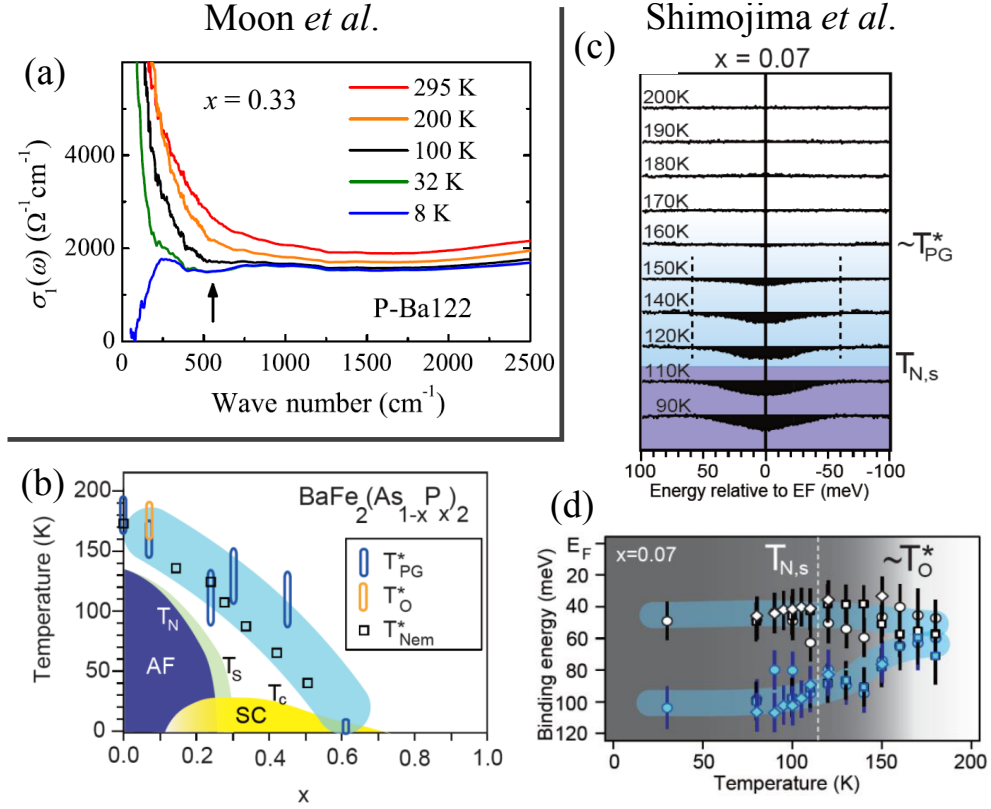


Figure 1.28: (a) Temperature-dependent $\sigma_1(\omega)$ of $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ [137]. The arrow denotes the frequency above which $\sigma_1(\omega)$ displays slight increase due to pseudogap (PG). (b) Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with the critical temperatures of the PG formation T_{PG}^* (blue markers) and inequivalent energy shift in zx/yz orbitals T_O^* (an orange marker) obtained by laser-ARPES. Square symbols represent nematic transition temperature T_{Nem}^* obtained by torque magnetometry [132]. (c) Symmetrized and normalized energy distribution curves for $x = 0.07$. The temperature-dependent depression of the spectral weight is indicated by the black shaded area. (d) Temperature dependence of the energy position of the two hole-bands. Critical temperature T_O^* where the two hole-bands start to shift is estimated to be $160 \sim 180$ K.

the nematic state by fitting the X-ray data with two-peak procedure and found $\delta \sim 0.0004$ as shown in the upper panel of Fig. 1.27(d).

Subsequently, Moon *et al.* reported the formation of a pseudogap (PG) in the excitation spectrum of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $x = 0.33$ below ~ 100 K from infrared studies of charge dynamics (Fig. 1.28(a)) [137]. Correspondingly, recent ARPES experiments revealed the appearance of PG from T_{PG}^* well above T_S (Fig. 1.28(c)) as well as its evolution with P substitution (Fig. 1.28(b)). In addition, the PG is accompanied by inequivalent energy shifts in zx/yz orbitals of iron atoms, indicative of a peculiar iron orbital ordering which breaks the fourfold rotational symmetry.

At this moment, the rotational symmetry breaking in the so-called “nematic” state has been already reported in spin [132], lattice [132], and Fe-3d orbital degrees of freedom [138] together with the pseudogap formation [137; 138]. Their observations suggest that different degrees of freedom are highly entangled with each other in this $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system and hence it is important to take all of them into account for understanding physics in iron pnictides.

Chapter 2

Nuclear Magnetic Resonance

In this chapter, the fundamental principles of our experimental technique, Nuclear Magnetic Resonance (NMR), are briefly explained.

2.1 An Isolated Single Nuclear Spin

Most of the elements on the periodic table possess a nuclear spin angular momentum $\mathbf{I}$. The nuclear spin causes a nuclear magnetic moment $\boldsymbol{\mu}$ as follows:

$$\boldsymbol{\mu} = g_n \mu_n \mathbf{I} = \gamma \hbar \mathbf{I}. \quad (2.1)$$

Here, g_n denotes an effective g -factor of the nucleus, $\mu_n = 5.05 \times 10^{-27} \text{ JT}^{-1}$ is the nuclear magneton, and $\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ Js}$ represents the reduced Planck constant. The nuclear gyromagnetic ratio γ combines all the prefactors of Eq. (2.1) to an isotope-specific constant. The nuclear magnetic moment couples to an external magnetic field $\mathbf{H}$ via the Zeeman interaction, given by the following Hamiltonian:

$$\mathcal{H}_Z = -\mu_0 \boldsymbol{\mu} \cdot \mathbf{H} = -\gamma \hbar \mu_0 \mathbf{I} \cdot \mathbf{H}, \quad (2.2)$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ TmA}^{-1}$ is the vacuum permeability. In quantum mechanics, $\mathbf{I}$ should be replaced by the operator $\hat{I}$ with the eigenvalues $m\hbar$. Assuming that the external field is aligned along the z -direction: $\mathbf{H} = H\mathbf{e}_z$, one arrives at:

$$\mathcal{H}_z = -\gamma \hbar \mu_0 \hat{I}_z H \quad (2.3)$$

$$E_m = -\gamma \hbar \mu_0 H \langle I, m | \hat{I}_z | I, m \rangle = -m \gamma \hbar \mu_0 H \quad (m = I, I-1, \dots, -I+1, -I), \quad (2.4)$$

and obtains the corresponding $(2I+1)$ equidistantly split energy levels as shown in Fig. 2.1. Since the matrix elements between states $|I, m\rangle$ and $|I, m'\rangle$ of the operator $\hat{I}_z$ vanish unless $m' = m \pm 1$, transitions between these levels are allowed only for $\Delta m = \pm 1$. To undergo such transitions, the system has to absorb the energy $\Delta E = \hbar \omega_L$, where $\omega_L = \gamma \mu_0 H$ is the so-called Larmor frequency.

2.2 Collective Spin System

Since the observation of a radio frequency absorption by a single nuclear spin is unrealistic, we have to discuss the circumstances of collective spins in materials. In thermodynamic equilibrium, the nuclear magnetic energy levels E_m given by Eq. (2.4) are occupied obeying the Boltzmann distribution $p(m) = \exp\left(\frac{-E_m}{k_B T}\right)$, where k_B is Boltzmann constant. The resulting unequal occupation of the energy levels leads to a nuclear spin polarization $\langle \hat{I}_z \rangle$ and hence to a nuclear magnetization M_z :

$$M_z = N_{\text{spin}} \gamma \langle \hat{I}_z \rangle = N_{\text{spin}} \gamma \frac{\sum_{m=-I}^{m=+I} \hbar m \exp(-E_m/k_B T)}{\sum_{m=-I}^{m=+I} \exp(-E_m/k_B T)} \approx \frac{N_{\text{spin}} \gamma^2 \hbar^2 I(I+1)}{3k_B T} \mu_0 H, \quad (2.5)$$

where N_{spin} represents the number of spins in the unit volume. The intensity of NMR signal is directly related to M_z . NMR spectra can be obtained by tracking the change of the signal intensity by sweeping excitation energy $\hbar\omega$ around $\hbar\omega_L$. The spectral shape provides various information of electronic states at around target nuclei.

2.3 Nuclear Spin Hamiltonian

Hereafter, we consider the interactions among the nuclear spins and with their electronic environment which cause shifts and broadenings of the nuclear magnetic energy levels E_m . In other words, such interactions shift the resonance frequency. The total Hamiltonian is expressed as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{n-e} + \mathcal{H}_{n-n} + \mathcal{H}_Q, \quad (2.6)$$

where $\mathcal{H}_Z$ denotes Zeeman interaction between a nucleus and a static magnetic field, $\mathcal{H}_{n-e}$ is the interaction between the nuclear and the electron spins and between the nuclear spins and orbital momenta, $\mathcal{H}_{n-n}$ is the interaction between nuclear spins, and $\mathcal{H}_Q$ is the electric quadrupole interaction. Each of the interactions except the already introduced Zeeman interaction is discussed in the following part.

2.3.1 Magnetic Hyperfine Interaction: $\mathcal{H}_{n-e}$

$\mathcal{H}_{n-e}$ includes the interaction of the nuclear spin with the spins and the orbital moments of the electrons via hyperfine coupling mechanisms. Together with the first term (the Zeeman term) of Eq. (2.6), one obtains:

$$\mathcal{H}_Z + \mathcal{H}_{n-e} = -\gamma\hbar\mathbf{I}(\hat{\mathbf{1}} + \hat{\mathbf{K}})\mu_0H, \quad (2.7)$$

with $\hat{\mathbf{K}}$ being the Knight shift tensor and $\hat{\mathbf{1}}$ being the unit tensor. Here, we assume that the quantization axis is along the principal axis of the EFG tensor. The different contributions to the Knight shift K are divided into the spin shift K_{spin} , the orbital shift K_{orb} , and the diamagnetic shift K_{dia} :

$$K = K_{\text{spin}} + K_{\text{orb}} + K_{\text{dia}}. \quad (2.8)$$

K_{spin} and K_{orb} come from the hyperfine interaction $\mathcal{H}_{\text{hf}}$ between a nuclear spin $\mathbf{I}$ and the electron spin $\mathbf{s}$ and the orbital angular momentum $\mathbf{l}$ of an electron being at a distance $\mathbf{r}$ from the nucleus:

$$\mathcal{H}_{\text{hf}} = \gamma\gamma_e\hbar^2\mathbf{I} \cdot \left[\frac{1}{r^3} \left(\frac{3(\mathbf{s} \cdot \mathbf{r})\mathbf{r}}{r^2} - \mathbf{s} \right) + \frac{8\pi}{3}\mathbf{s}\delta(\mathbf{r}) + \frac{8\pi}{3} \sum_i \{ |\psi_i^\uparrow(0)|^2 - |\psi_i^\downarrow(0)|^2 \} \mathbf{s} + \frac{\mathbf{l}}{r^3} \right]. \quad (2.9)$$

Here, γ_e represents the gyromagnetic ratio of electron, $\psi_i^\uparrow(0)$ and $\psi_i^\downarrow(0)$ indicate wave functions at $\mathbf{r} = 0$ for up and down spins of i -th electron, respectively.

The Spin Shift

The first term in Eq. (2.9) describes the dipolar interaction between the nuclear spin and the electronic spin leading to a dipolar shift K_{dip} . A (point) dipolar approximation can however only be made if the distance between the nuclear spin and the electronic spin is large enough. This is the case for p -, d -, and f -orbitals, but not for s -electrons, which exhibit a finite spin density at the nuclear site.

The direct coupling between the nuclear spin and the spin of unpaired s -electrons is described by the second term in Eq. (2.9) which is called the Fermi contact interaction. The shift resulting from this interaction, K_{Fermi} , is proportional to the existence probability of the s -electron at the nuclear site, expressed by the squared modulus of the electronic wave function at $\mathbf{r} = 0$: $|\psi(\mathbf{r} = 0)|^2$. Spins from unfilled outer electronic shells will polarize closed s -shells, leading to the so-called core polarization term K_{core} , which acts in the same way as the Fermi contact contribution does, but with opposite sign. K_{core} is negative, while K_{Fermi} is positive. Both terms are isotropic, while the dipolar interaction and the resulting K_{dip} depend on the relative orientation of the crystal to the applied magnetic field and are therefore anisotropic. K_{Fermi}

and K_{core} are subsumed into the isotropic part of the NMR shift, K_{iso} , since they are usually not distinguishable one from another. All three contributions K_{dip} , K_{Fermi} , and K_{core} are only caused by the interactions between the spin of the nucleus $\mathbf{I}$ and the spin of the electron $\mathbf{s}$. No angular momentum $\mathbf{l}$ is involved in these three shifts. They are therefore combined to form the spin part of the NMR shift:

$$K_{\text{spin}} = K_{\text{dip}} + K_{\text{Fermi}} + K_{\text{core}}. \quad (2.10)$$

The spin parts of the Hamiltonian (2.9), combining interactions between a nuclear spin at site i , $\mathbf{I}_i$, and an electron spin at site j , $\mathbf{s}_j$ (and thus referring to K_{spin}), can be expressed as:

$$\mathcal{H}_{\text{spin}} = -\mathbf{I}_i \hat{\mathbf{A}}_{ij} \mathbf{s}_j, \quad (2.11)$$

where $\hat{\mathbf{A}}_{ij}$ is the hyperfine coupling tensor. To be more general, $\mathbf{s}$ can be replaced by its expectation value $\langle \mathbf{s} \rangle = \chi_{\text{spin}} H$. It follows, that the spin part of the NMR shift K_{spin} is proportional to the static spin susceptibility $\chi_{\text{spin}}(\mathbf{q} = 0, \omega = 0)$:

$$K_{\text{spin}} = \frac{A_{\text{hf}}}{N_A \mu_B} \chi_{\text{spin}}. \quad (2.12)$$

In the metallic state, the static spin susceptibility χ_{spin} corresponds to the temperature-independent Pauli spin susceptibility of the conduction electrons $\chi_P = 2\mu_B^2 N(E_F)$, where $N(E_F)$ denotes the electronic density of states at Fermi energy.

The Orbital Shift

The last term of Eq. (2.9) represents the orbital interaction between the nuclear spin $\mathbf{I}$ and the angular momentum $\mathbf{l}$ of the electron. In contrast to the diamagnetic shift, originating from current loops in inner orbitals, where the angular momentum is quenched, the orbital shift K_{orb} is due to current loops from electrons which possess a static angular momentum $\mathbf{l}$. For transition metal ions in crystal fields, the orbital moment of the conduction electrons is also quenched. An external magnetic field can however partially reconstruct an orbital moment by mixing the ground state with low lying excited states. This is the so-called Van Vleck paramagnetism which leads to an orbital shift of the form:

$$K_{\text{orb}} = 2\langle r^{-3} \rangle \chi_{\text{VV}}, \quad (2.13)$$

where χ_{VV} is the temperature-independent Van Vleck paramagnetic susceptibility. K_{orb} is thus temperature-independent.

The Diamagnetic Shift

The diamagnetic shift K_{dia} stems from the diamagnetism of the closed inner electronic shells (ion cores) and the Landau diamagnetism of the conduction electrons. It is temperature-independent and rather small (of the order of $\Delta\omega/\omega \approx 10^{-5}$). In solid state NMR of magnetic and conducting materials, other contributions to the Knight shift are usually much larger and the diamagnetic shift can be neglected.

2.3.2 Interaction between Nuclear Spins: $\mathcal{H}_{\text{n-n}}$

The coupling between two nuclear spins $\mathbf{I}_i$ and $\mathbf{I}_j$, $\mathcal{H}_{\text{n-n}}$, can be divided into two parts, a direct dipolar coupling between nuclear spins and an indirect coupling:

$$\mathcal{H}_{\text{n-n}} = \mathcal{H}_{\text{n-n}}^{\text{dir}} + \mathcal{H}_{\text{n-n}}^{\text{indir}} = \sum_{i < j}^N \left\{ \frac{\hbar^2 \gamma^2}{r_{ij}^3} \left[\mathbf{I}_i \cdot \mathbf{I}_j - 3 \frac{(\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right] + \mathbf{I}_i \hat{\mathbf{a}}_{ij} \mathbf{I}_j \right\}, \quad (2.14)$$

where $\mathbf{r}_{ij}$ represents a vector from $\mathbf{I}_i$ to $\mathbf{I}_j$.

The first term is the direct dipolar Hamiltonian giving rise to a homogeneous broadening of the resonance line. The dipolar broadening width is typically of the order of a few Gauss [139] and independent of the applied magnetic field.

The second term is the indirect coupling between nuclei mediated via electrons although the exact expression of the coupling tensor $\hat{\mathbf{a}}_{ij}$ depends on the detailed mechanism. The typical example of the indirect coupling is so-called RKKY (Ruderman, Kittel, Kasuya and Yosida) interaction. In this case the prefactor a_{ij} of the scalar part of Hamiltonian becomes:

$$a_{\alpha\alpha}(\mathbf{r}_{ij}) = \frac{1}{(\hbar\gamma_e)^2} \sum_{\mathbf{q}} \chi'_{\alpha}(\mathbf{q}) |A_{\alpha\alpha}(\mathbf{q})|^2 \exp(-i\mathbf{q} \cdot \mathbf{r}_{ij}), \quad (2.15)$$

with $\alpha = x, y, z$. It is proportional to the real part of the static, $\mathbf{q}$ -dependent susceptibility $\chi'_{\alpha}(\mathbf{q})$ of the electronic system, which mediates the coupling between the nuclear spins via the hyperfine coupling $A_{\alpha\alpha}(\mathbf{q})$.

The analysis of the spin-spin relaxation rate $(1/T_{2G})^2 \propto |a(\mathbf{r}_{ij})|^2$ in conductors (especially for cuprate superconductors, one can obtain $(1/T_{2G})^2 \propto |a(\mathbf{r}_{zz})|^2 \propto (\chi'_z(\mathbf{q}))^2$ for $H_0 \parallel z$) is therefore a measure of $\chi'_{\alpha}(\mathbf{q})$ and thus complementary to measurements of the spin-lattice relaxation rate $1/T_1$, which itself yields information about the imaginary part of the dynamic, $\mathbf{q}$ -dependent susceptibility $\chi''(\mathbf{q}, \omega)$ (for detail, see Section 2.6).

2.3.3 Electric Quadrupole Interaction: $\mathcal{H}_Q$

The last term of Eq. (2.6), $\mathcal{H}_Q$ describes the electric quadrupole interaction between the quadrupole moment of the nucleus, Q , and the electric field gradient (EFG) $V_{\alpha\beta}$:

$$\mathcal{H}_Q = \frac{1}{6} \sum_{\alpha\beta} V_{\alpha\beta}^i Q_{\alpha\beta}^i. \quad (2.16)$$

$V_{\alpha\beta}$ is caused by the surrounding charge distribution of the nucleus. It is given by $V_{\alpha\beta} = \frac{\partial^2 V}{\partial \alpha \partial \beta} \big|_{r=0}$, where V is the electrostatic potential and $\alpha, \beta = x, y, z$. In its principal axes system (X, Y, Z) the tensor $V_{\alpha\beta}$ can be described by its diagonal elements V_{XX} , V_{YY} , and V_{ZZ} . Since the potential V has to fulfill Laplace's equation: $\nabla^2 V = 0$, the EFG is traceless:

$$V_{XX} + V_{YY} + V_{ZZ} = 0. \quad (2.17)$$

It can therefore be described by using only two parameters. It is common to use the convention $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$ and then take $V_{ZZ} \equiv eq$ and the asymmetry parameter:

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad 0 \leq \eta \leq 1, \quad (2.18)$$

for the adequate description of the EFG. Then, Eq. (2.16) becomes:

$$\mathcal{H}_Q = \frac{1}{6} \sum_{\alpha} V_{\alpha\alpha} Q_{\alpha\alpha}. \quad (2.19)$$

In a cubic symmetry as well as for a spherically symmetric charge distribution (s -electrons for instance), $V_{XX} = V_{YY} = V_{ZZ} = 0$. The quadrupole interaction vanishes in these cases.

The quadrupole moment of the nucleus, $Q_{\alpha\alpha}$, describes deviations of the nuclear charge distribution from a spherically symmetric distribution. It is defined as:

$$Q_{\alpha\alpha} = \int \rho(\mathbf{r}) (3\alpha^2 - r^2) d^3r, \quad (2.20)$$

where $\rho(\mathbf{r})$ is the charge density at a distance $\mathbf{r}$ away from the origin of the nucleus. Q is finite only for nuclei with $I \geq 1$ in a non-cubic environment.

The Hamiltonian of the quadrupole interaction, $\mathcal{H}_Q$, can be written as:

$$\mathcal{H}_Q = \frac{h\nu_Z}{6} \left[(3I_Z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2) \right], \quad (2.21)$$

where Z refers to the Z -axis in the principle axis system of the EFG, I_+ and I_- are raising and lowering operators, respectively, and ν_Z is the quadrupole frequency defined as:

$$\nu_Z = \frac{3eQV_{ZZ}}{2I(2I-1)h} = \frac{3e^2qQ}{2I(2I-1)h}. \quad (2.22)$$

In a strong magnetic field H , where $\nu_Z \ll \omega_L/2\pi$, $\mathcal{H}_Q$ can be treated as a perturbation of $\mathcal{H}_Z$.

In first order, the change of the m -th energy level is given by:

$$E_m^{(1)} = \frac{eQV_{zz}}{4I(2I-1)} [3m^2 - I(I+1)] \quad \left(I \neq \frac{1}{2} \right), \quad (2.23)$$

where V_{zz} is the component of the EFG parallel to the direction of the applied magnetic field. Expressing V_{zz} in the principal axis system of the EFG by using the polar and azimuthal angles θ and ϕ which describe the orientation of the principle axis system of the EFG with respect to the laboratory axis system of the external magnetic field:

$$V_{zz} = V_{XX} \sin^2 \theta \cos \phi + V_{YY} \sin^2 \theta \sin \phi + V_{ZZ} \cos^2 \theta, \quad (2.24)$$

and inserting the definitions of η and ν_Z given in Eqs. (2.18) and (2.22), one arrives at [140]:

$$E_m^{(1)}(\theta, \phi, \eta) = \frac{h\nu_Z}{4} (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi) \left[m^2 - \frac{1}{3} I(I+1) \right]. \quad (2.25)$$

These energy changes result in a splitting of the NMR resonance line into $2I$ resonance lines, where adjacent lines are separated by a frequency proportional to ν_Z , whose absolute value depends on the orientation of the principle axes of the EFG relative to the direction of the applied magnetic field. This first-order quadrupole shift is given by the difference $E_m/h - E_{m-1}/h$ [140]:

$$\Delta^{(1)}\nu_m(\theta, \phi, \eta) = \frac{\nu_Z}{2} \left(m - \frac{1}{2} \right) (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi). \quad (2.26)$$

Note that the resonance frequency of the central transition ($m = -\frac{1}{2} \leftrightarrow +\frac{1}{2}$) remains unaffected in first-order, and according to Eq. (2.25) both levels ($m = \pm\frac{1}{2}$) are shifted by the same amount of energy. The intensity of each of the $2I$ resonance lines depends on m .

The change of the m -th energy level in second order, $E_m^{(2)}$, can be found for instance in Ref. [140]. For $\eta = 0$, $E_m^{(2)}$ is odd in m , which means that the distance between the satellites does not change even when considering second-order effects. Only the resonance frequency of the central transition shifts.

Finally, Fig. 2.1 summarizes all possible interactions introduced above and their influence on the energy levels.

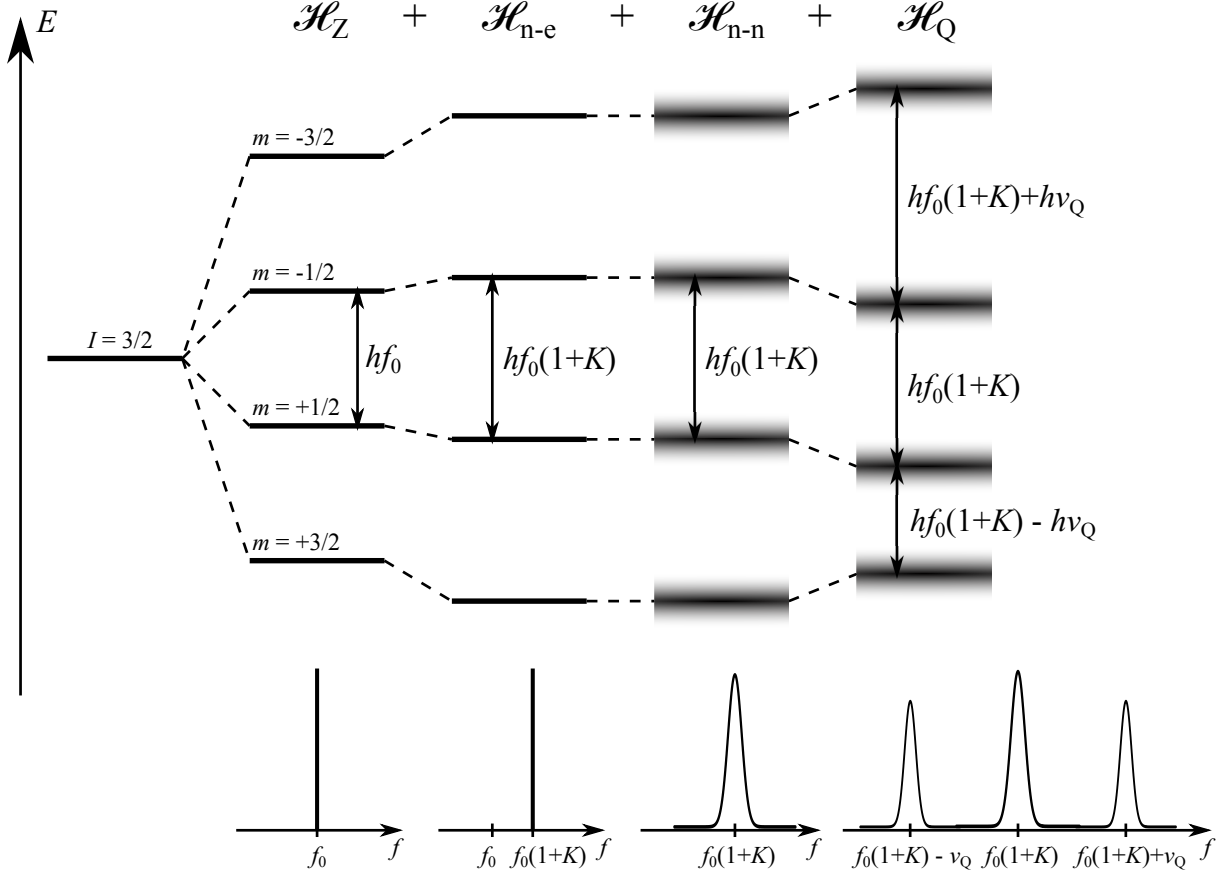


Figure 2.1: Summary of all possible interactions, their influence on the nuclear magnetic energy levels and the resulting NMR spectra for $I = 3/2$, $\eta = 0$, $\theta = 0^\circ$ and $V_{zz} \neq 0$ under the condition that $\mathcal{H}_Q \ll \mathcal{H}_Z$. Note that the choice of a positive Knight shift K is arbitrary.

2.4 Resonance Frequency

Including the second-order quadrupole shift, the resonance frequency corresponding to the $m \leftrightarrow m - 1$ transition can be generally written as [140]:

$$\begin{aligned}
 f_{m \leftrightarrow m-1}(\theta, \phi) = & f_0(1 + K_{\text{iso}}) && \text{(Isotropic Knight shift)} \\
 & + \frac{f_0}{2} [K_1(3 \cos^2 \theta - 1) + K_2 \sin^2 \theta \cos 2\phi] && \text{(Anisotropic Knight shift)} \\
 & + \frac{\nu_Z}{2} \left(m - \frac{1}{2}\right) (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi) && \text{(1st-order quadrupole shift)} \\
 & + \frac{\nu_Z^2}{f_0(1 + K_{\text{iso}})} \left\{ \frac{1}{32} \sin^2 \theta (C \cos^2 \theta - B) \right. \\
 & + \frac{\eta}{48} \sin^2 \theta (C \cos^2 \theta + B) \cos 2\phi && \text{(2nd-order quadrupole shift)} \\
 & \left. + \frac{\eta^2}{72} \left[A - (A + B) \cos^2 \theta - \frac{C}{4} \sin^4 \theta \cos^2 2\phi \right] \right\}. && (2.27)
 \end{aligned}$$

$$\left(\begin{array}{ll} f_0 = \frac{\gamma \mu_0 H}{2\pi} & \\ K_{\text{iso}} = \frac{K_X + K_Y + K_Z}{3} & A = 24m(m-1) - 4I(I+1) + 9 \\ K_1 = \frac{2K_Z - K_X - K_Y}{3} & B = 6m(m-1) - 2I(I+1) + 3 \\ K_2 = K_X - K_Y & C = 4A + B \end{array} \right) \quad (2.28)$$

In this study, we use ^{31}P nuclei with $I = 1/2$ and ^{75}As nuclei with $I = 3/2$. It is useful to express Eq. (2.27) for specific cases of ^{31}P ($I = 1/2$) as

$${}^{31}f_{\frac{1}{2} \leftrightarrow -\frac{1}{2}}(\theta, \phi) = f_0 (1 + K_X \sin^2 \theta \cos^2 \phi + K_Y \sin^2 \theta \sin^2 \phi + K_Z \cos^2 \theta) \quad (2.29)$$

$$= f_0 \left(1 + K_{\text{iso}} + K_1 \frac{3 \cos^2 \theta - 1}{2} + K_2 \frac{\sin^2 \theta \cos 2\phi}{2} \right), \quad (2.30)$$

and of ^{75}As ($I = 3/2$) as

(Center line: $m = \frac{1}{2}$)

$$\begin{aligned}
 {}^{75}f_{\frac{1}{2} \leftrightarrow -\frac{1}{2}}(\theta, \phi) = & f_0 \left(1 + K_{\text{iso}} + K_1 \frac{3 \cos^2 \theta - 1}{2} + K_2 \frac{\sin^2 \theta \cos 2\phi}{2} \right) \\
 & + \frac{\nu_Z^2}{f_0(1 + K_{\text{iso}})} \left[\frac{3}{16} \sin^2 \theta (1 - 9 \cos^2 \theta) - \frac{\eta}{8} \sin^2 \theta (1 + 9 \cos^2 \theta) \cos 2\phi \right. \\
 & \left. - \frac{\eta^2}{48} (8 - 12 \cos^2 \theta - 9 \sin^4 \theta \cos^2 2\phi) \right] \quad (2.31)
 \end{aligned}$$

(Electric quadrupole frequency defined as a half of satellite peak splitting)

$$\nu(\theta, \phi) = \frac{{}^{75}f_{\frac{3}{2} \leftrightarrow \frac{1}{2}}(\theta, \phi) - {}^{75}f_{-\frac{1}{2} \leftrightarrow -\frac{3}{2}}(\theta, \phi)}{2} = \frac{\nu_Z}{2} (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi). \quad (2.32)$$

2.5 Spin-Echo

Experiments in this study were performed with Hahn spin-echo technique. Every magnetic moments $\boldsymbol{\mu} = \gamma \mathbf{I}$ exposed to a static magnetic field $\mathbf{H}_0$ parallel to z -axis experiences a torque $\mathbf{T}$:

$$\mathbf{T} = \frac{d\mathbf{I}}{dt} = \mu_0 \boldsymbol{\mu} \times \mathbf{H}_0. \quad (2.33)$$

For the nuclear magnetization $\mathbf{M} = N\boldsymbol{\mu} = N\gamma\mathbf{I}$, the equation of motion results in:

$$\frac{d\mathbf{M}(t)}{dt} = \mu_0\gamma(\mathbf{M}(t) \times \mathbf{H}_0). \quad (2.34)$$

Its solution is a precession of $\mathbf{M}$ around $\mathbf{H}_0$ with the precession angular frequency $\omega_L = \mu_0\gamma H_0$. By applying a circularly polarized field $\mathbf{H}_1$ with the rotation frequency ω perpendicular to $\mathbf{H}_0$ by the NMR coil, the total magnetic field during the application of $\mathbf{H}_1$ becomes:

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1 = H_1 \cos \omega t \mathbf{x} + H_1 \sin \omega t \mathbf{y} + H_0 \mathbf{z}. \quad (2.35)$$

It is convenient to go from the fixed laboratory reference frame $\mathbf{S}$ to a new frame $\mathbf{S}'$ rotating with the frequency ω around $z' = z$ axis. We consider without loss of generality in the following that $\mathbf{H}_1$ is fixed along $\mathbf{x}'$. Then, the effective magnetic field in $\mathbf{S}'$ is given by:

$$(\mathbf{H})_{\mathbf{S}'} = H_1 \mathbf{x}' + \left(H_0 + \frac{\omega}{\mu_0\gamma} \right) \mathbf{z}'. \quad (2.36)$$

Now The magnetization precesses around this effective field. In the case of $\omega = -\omega_L = -\mu_0\gamma H_0$, the effective field becomes $(\mathbf{H})_{\mathbf{S}'} = H_1 \mathbf{x}'$ and the magnetization precesses around $\mathbf{H}_1$ with the precession frequency $\omega' = -\mu_0\gamma H_1$ in $\mathbf{S}'$ frame. The angle of tilt of the magnetization by applying $\mathbf{H}_1$ is given by $\alpha = \omega' t_p = -\mu_0\gamma H_1 t_p$. If we choose the pulse duration time t_p and the pulse field strength H_1 carefully, it is possible to flip the magnetization from the thermal equilibrium state $\mathbf{M} = M_0 \mathbf{z}$ into the $\mathbf{y}'$ -($-\mu_0\gamma H_1 t_p = \pi/2$) or $\mathbf{z}$ -direction ($-\mu_0\gamma H_1 t_p = \pi$). These are called 90° -($\pi/2$ -) and 180° -(π -)pulse, respectively. After the disturbance by the radio frequency pulse, M_z reduces while M_x and M_y appear, and then they relax back to its thermodynamic equilibrium $\mathbf{M} = (0, 0, M_z)$. The decay of M_x and M_y can be described by the spin-spin (transverse) relaxation time T_2 , while the recovery of M_z back to M_0 can be characterized by the spin-lattice (longitudinal) relaxation time T_1 . The relaxation equations in the laboratory system $\mathbf{S}$ are:

$$\begin{aligned} \frac{dM_x(t)}{dt} &= -\frac{M_x(t)}{T_2} \\ \frac{dM_y(t)}{dt} &= -\frac{M_y(t)}{T_2} \\ \frac{dM_z(t)}{dt} &= -\frac{M_z(t) - M_0}{T_1}. \end{aligned} \quad (2.37)$$

Putting Eq. (2.37) together with Eq. (2.34) describing the precession of $\mathbf{M}$ around $\mathbf{H}$, one can obtain the Bloch equations [141]:

$$\begin{aligned} \frac{dM_x(t)}{dt} &= \mu_0\gamma(\mathbf{M}(t) \times \mathbf{H})_x - \frac{M_x(t)}{T_2} \\ \frac{dM_y(t)}{dt} &= \mu_0\gamma(\mathbf{M}(t) \times \mathbf{H})_y - \frac{M_y(t)}{T_2} \\ \frac{dM_z(t)}{dt} &= \mu_0\gamma(\mathbf{M}(t) \times \mathbf{H})_z - \frac{M_z(t) - M_0}{T_1}. \end{aligned} \quad (2.38)$$

After emitting a short pulse and rotating $M_0\mathbf{z}$ to $\mathbf{y}'$ -direction, the derived signal of $M_0\mathbf{y}'$, which is a so-called free-induction-decay (FID) signal, decays very fast in most cases because of local inhomogeneities of the magnetic field.

In this study, however, the following Hahn spin echo method having some advantages over detecting FID signal was employed. The pulse sequence of this method is shown in Fig. 2.2. A first 90° -pulse applied along the $\mathbf{x}'$ -axis flips the magnetization from its equilibrium position into the $x'y'$ -plane (Fig. 2.2(b)). Due to spin-spin interactions and local field inhomogeneities the individual moments rotate with different speeds within the $x'y'$ -plane and thus begin to dephase (Fig. 2.2(c)). This induces the FID signal in the coil. Subsequently the transverse magnetization M_{xy} decreases. After a time τ , a 180° -pulse is applied to the system again along $\mathbf{x}'$ (Fig. 2.2(d)). It flips the different components of the transverse magnetization within the $x'y'$ -plane, such that they will refocus at the time 2τ and give rise to the spin echo, whose intensity is related to the magnitude of $M_{xy}(2\tau)$ (Fig. 2.2(e)-(g)). There are two big advantages of the Hahn spin echo versus the direct observation of the FID. Firstly, the influences of local field inhomogeneities, which are static on the time scale of the measurement, cancel out due to the refocusing. Only intrinsic effects of spin-spin interactions remain as a source for the reduction of $M_{xy}(2\tau)$. The FID decays with the time T_2^* , containing intrinsic spin-spin interactions and the effects of inhomogeneities of the static magnetic field and electric field gradient (EFG). On the contrary, the intensity of the Hahn spin echo can be used to measure the spin-spin relaxation time T_2 . Secondly, since the spin echo appears at a time distance τ away from the last pulse, it is not superimposed by possible tails of the pulses during their fall time and its observation is not hindered by the dead time of the detection electronics.

In this study, the saturation recovery method was used for the measurement of T_1 . In this method, first, the nuclear magnetization is saturated by applying a number of saturation 90° -pulses. Then, by changing the interval time P_1 between saturation pulse and first 90° -pulse, the time evolution of $M(P_1)$ is recorded. The obtained $M(t)$ recovery curve is fitted to the equation for specific nuclear spin I , which will be introduced in subsection 3.2.2 in detail.

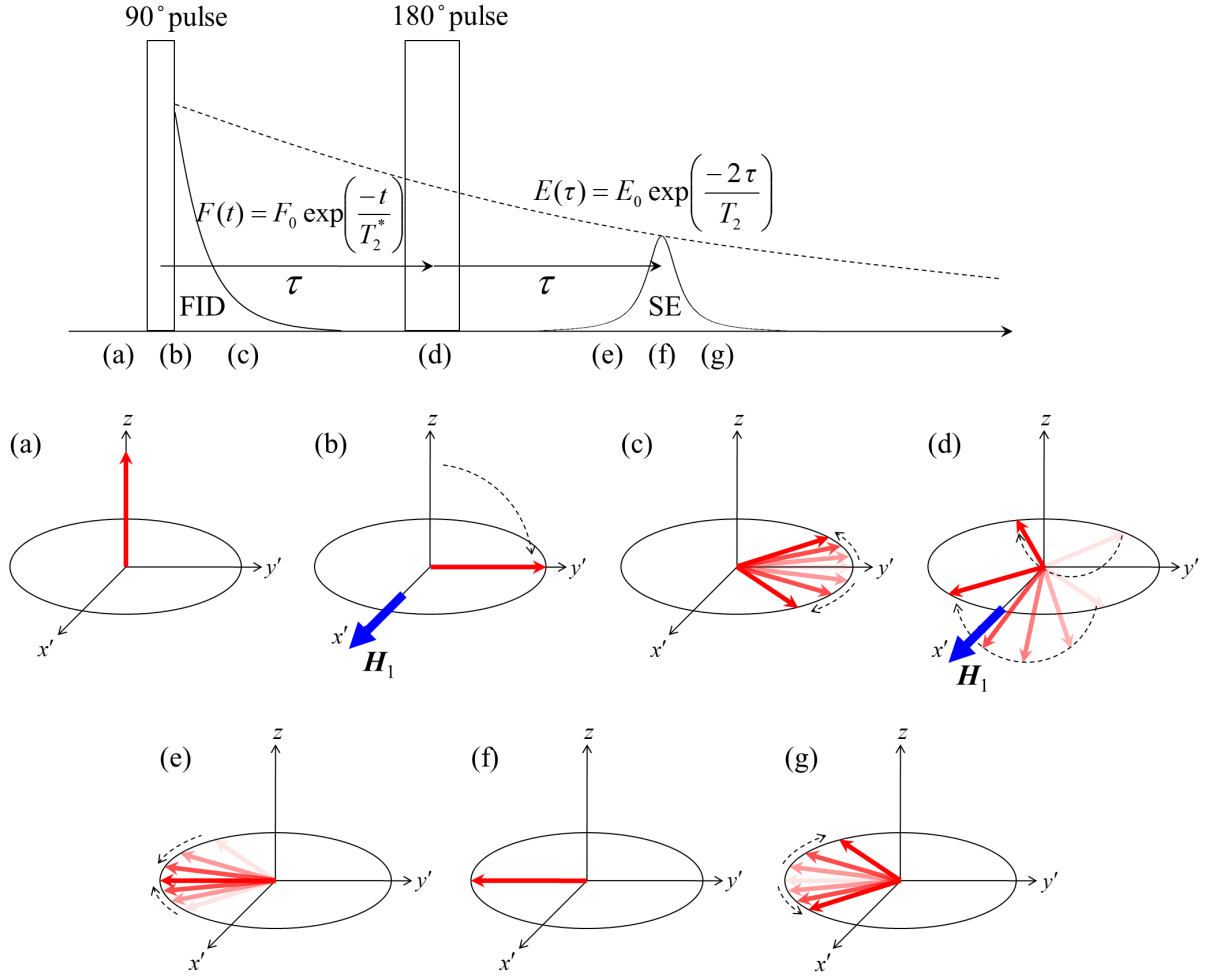


Figure 2.2: Sketch of the Hahn spin echo pulse sequence on a time scale (upper panel) and the corresponding movement of the nuclear magnetization in the rotating frame system S' (lower panel).

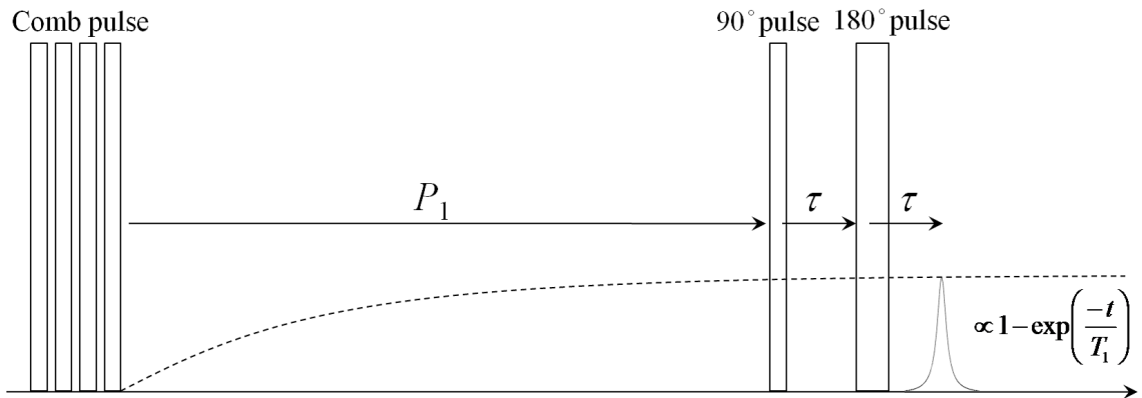


Figure 2.3: Pulse sequence of saturation recovery method for the measurement of T_1 .

2.6 Nuclear Spin-Lattice Relaxation

The nuclear spin system has weak thermal coupling with the electronic system. Through the coupling, heat supplied to the nuclear spin system by radio-frequency pulses flows into the electronic system, and the excited nuclear spin system relaxes for a characteristic time scale T_1 . The nuclear spin-lattice relaxation rate $1/T_1$ contains important information concerning with the dynamics of the electrons at the FS.

When the nuclear spin system is relaxed by the magnetic fields induced by the electronic spins δH , the transition probability is formulated by using the Fermi's golden rule as:

$$W_{m,\nu \leftrightarrow m+1,\nu'} = \frac{2\pi}{\hbar} |\langle m, \nu | \gamma \hbar \mathbf{I} \cdot \delta \mathbf{H} | m+1, \nu' \rangle|^2 \delta(E_m + E_\nu - E_{m+1} - E_{\nu'}). \quad (2.39)$$

With this transition probability, $1/T_1$ is defined as:

$$\frac{1}{T_1} = \sum_{\nu, \nu'} \frac{2W_{m,\nu \leftrightarrow m+1,\nu'}}{(I-m)(I+m+1)} = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} dt \cos \omega_0 t \left\langle \frac{\delta H_+(t) \delta H_-(0) + \delta H_-(t) \delta H_+(0)}{2} \right\rangle. \quad (2.40)$$

When fluctuation-dissipation theorem is adopted to Eq. (2.40), the general representation for $1/T_1$ is obtained:

$$\frac{1}{T_1} = \frac{2\gamma^2 k_B T}{(\gamma_e \hbar)^2} \sum_{\mathbf{q}} A_{\mathbf{q}} A_{-\mathbf{q}} \frac{\chi''_{\perp}(\mathbf{q}, \omega_0)}{\omega_0}. \quad (2.41)$$

Here, $A_{\mathbf{q}}$, $\chi''_{\perp}(\mathbf{q}, \omega_0)$, and ω_0 are the hyperfine coupling constant in $\mathbf{q}$ space, the imaginary part of dynamical susceptibility, and the NMR frequency, respectively.

The $\mathbf{q}$ dependence of $A_{\mathbf{q}}$ is weak, when $1/T_1$ is measured at the site where electronic spins locate. However, it should be taken into account, when $1/T_1$ is measured at ligand nuclei. The hyperfine field from the neighboring sites is expressed as:

$$A_{\mathbf{q}} = \sum_n A_n \exp(i\mathbf{q} \cdot \mathbf{r}_n), \quad (2.42)$$

where n and $\mathbf{r}_n$ represents the neighboring nuclear sites, and the position of them, respectively. For instance, the calculated result of the form factor for the As site in the FeAs layer of iron pnictides is shown in Sec. 4.1.2.

The temperature dependence of $1/T_1$ has been studied by using the self-consistent renormalization (SCR) theory. The SCR theory is available when the electronic system is close to a magnetic instability. The dynamical susceptibility assumed in this theory is formulated as:

$$\chi(\mathbf{Q} + \mathbf{q}, \omega) = \frac{\chi(\mathbf{Q})}{1 + \mathbf{q}^2 A \chi(\mathbf{Q}) - i\omega \mathbf{q}^{-\theta} C \chi(\mathbf{Q})}. \quad (2.43)$$

The dynamical susceptibility is expanded in $\mathbf{q}$ space around $\mathbf{Q}$, which represents the ordering wave vector. When the magnetic ordering is ferromagnetic ($\mathbf{Q} = 0$), $\theta = 1$ is used to calculate $\chi(\mathbf{q}, \omega)$, and when it is antiferromagnetic ($\mathbf{Q} > 0$), $\theta = 0$. The parameters A and C are determined self-consistently to minimize the free energy. The temperature dependence of $1/T_1$ above the magnetic transition is derived using the renormalized dynamical susceptibility. The results depend on the dimensionality and the θ values. The temperature dependence anticipated from the SCR theory is listed in Table 2.1.

Table 2.1: Temperature dependence of $1/T_1T$ of two- and three-dimensional itinerant magnets anticipated from the SCR theory. T_C indicates Curie temperature of ferromagnets and T_N is Néel temperature of antiferromagnets.

	2D	3D
FM	$\frac{1}{T_1T} \propto \frac{1}{(T-T_C)^{3/2}}$	$\frac{1}{T_1T} \propto \frac{1}{T-T_C}$
AFM	$\frac{1}{T_1T} \propto \frac{1}{T-T_N}$	$\frac{1}{T_1T} \propto \frac{1}{\sqrt{T-T_N}}$

2.7 NMR in the Superconducting State

In a superconducting (SC) state, thermally excited quasiparticles contribute to the Knight shift K and the nuclear spin-lattice relaxation rate $1/T_1$. If an SC order parameter Δ exhibits $\mathbf{k}$ -dependence which becomes zero for some directions, the density of states for quasiparticle is given by,

$$N_{\text{sc}}(E) = \frac{N_0 E}{4\pi} \int_0^{2\pi} \int_0^\pi \frac{\sin \theta d\theta d\phi}{\sqrt{E^2 - \Delta^2(\theta, \phi)}} \quad (2.44)$$

where E is the quasiparticle energy, which is determined as $E^2 = \epsilon^2 + \Delta^2$ (ϵ is the energy of a single electron), and N_0 is the density of states in the normal state. The angle dependence of the SC gap for each type of symmetry is schematically shown in Fig. 2.4 and listed below:

$$\begin{aligned} \text{(s-wave)} \quad \Delta(\theta, \phi) &= \Delta_0 & N_{\text{sc}}(E) &= \begin{cases} \frac{N_0 E}{\sqrt{E^2 - \Delta_0^2}} & (E \geq \Delta_0) \\ 0 & (E < \Delta_0) \end{cases} \end{aligned} \quad (2.45)$$

$$\begin{aligned} \text{(axial } p\text{-wave)} \quad \Delta(\theta, \phi) &= \Delta_0 \sin \theta e^{i\phi} & N_{\text{sc}}(E) &= \frac{N_0 E}{2\Delta_0} \ln \left| \frac{E + \Delta_0}{E - \Delta_0} \right| \end{aligned} \quad (2.46)$$

$$\begin{aligned} \text{(polar } p\text{-wave)} \quad \Delta(\theta, \phi) &= \Delta_0 \cos \theta & N_{\text{sc}}(E) &= \begin{cases} \frac{N_0 E}{\Delta_0} \sin^{-1} \frac{\Delta_0}{E} & (E \geq \Delta_0) \\ \frac{\pi N_0 E}{2\Delta_0} & (E < \Delta_0) \end{cases} \end{aligned} \quad (2.47)$$

$$\begin{aligned} \text{(2D } d\text{-wave)} \quad \Delta(\theta, \phi) &= \Delta_0 \cos 2\phi & N_{\text{sc}}(E) &= \frac{N_0 E}{2\pi} \int_0^{2\pi} \frac{d\phi}{\sqrt{E^2 - \Delta_0^2 \cos 2\phi}} \end{aligned} \quad (2.48)$$

The resulting energy dependence of N_{sc} is also shown in Fig. 2.5(a) for each case. The temperature dependence of the Knight shift (or, spin susceptibility χ_{spin}) and the relaxation rate in the SC state can be computed from the following equations with using $N(E)$ calculated above:

$$K_{\text{spin}} = \frac{A_{\text{hf}}}{N_A \mu_B} \chi_{\text{spin}} = -\frac{4\mu_B A_{\text{hf}}}{N} \int_{\Delta(T)}^\infty N_{\text{sc}}(E) \frac{\partial f(E)}{\partial E} dE, \quad (2.49)$$

$$\chi_{\text{spin}} = -4\mu_B^2 \int_{\Delta(T)}^\infty N_{\text{sc}}(E) \frac{\partial f(E)}{\partial E} dE, \quad (2.50)$$

$$\frac{1}{T_1} = \frac{\pi A_{\text{hf}}^2}{\hbar N^2} \int_{\Delta(T)}^\infty \left(1 + \frac{\Delta_0^2}{E^2} \right) N_{\text{sc}}(E)^2 f(E) (1 - f(E)) dE. \quad (2.51)$$

Here, $f(E)$ is the Fermi distribution function. The term $\left(1 + \frac{\Delta_0^2}{E^2} \right)$ in Eq. (2.51) is referred to as the coherence factor, which is derived from the spin flip process of unpaired electrons through the interactions between the unpaired electrons and Cooper pairs. Since the single-particle DOS $N_{\text{sc}}(E)$ has a singularity at the gap edge $E = \Delta$ and the existence of the coherence factor, Eq. (2.51) leads to a singularity of $1/T_1$ at $T = T_c$. This is the so-called Hebel-Slichter coherence peak. In general, the coherence peak is absent except for conventional s -wave superconductivity with isotropic gap.

In the case of $s\pm$ -wave superconductivity often discussed in the gap symmetry of iron-based superconductors, however, the coherence peak can be severely suppressed due to the opposite of gap sign between the hole and electron FSs although the existence of isotropic gaps [142]. For simplicity, we assume the SC gaps of the electron and hole FSs have an identical amplitude with opposite sign, $\Delta_e = -\Delta_h = \Delta_0$, and also assume the same s -wave DOS between the electron and hole FSs, $N_{\text{sc}}^e = N_{\text{sc}}^h = \frac{E}{\sqrt{E^2 - \Delta_0^2}}$. We further assume that inter-band scatterings due to the

nesting give dominant contributions to $1/T_1$. Then, we can express Eq. (2.51) as:

$$\frac{1}{T_1} \propto \int_{\Delta(T)}^{\infty} \left(1 + \frac{\Delta_e \Delta_h}{EE'}\right) \frac{E^2}{E^2 - \Delta_0^2} f(E)(1 - f(E')) dE \quad (2.52)$$

$$= \int_{\Delta(T)}^{\infty} \frac{E^2 - \Delta_0^2}{E^2 - \Delta_0^2} \text{sech}^2\left(\frac{E}{2T}\right) dE \quad (2.53)$$

$$= \int_{\Delta(T)}^{\infty} \text{sech}^2\left(\frac{E}{2T}\right) dE. \quad (2.54)$$

As T decreases, the integral decreases monotonically, resulting in a reduced Hebel-Slichter coherence peak. In principle, measurements of the temperature dependence of $1/T_1$ at low temperatures can help to distinguish types of SC pairing. For s -wave superconductivity, $1/T_1$ exhibits an activated temperature dependence, as expected from the existence of an isotropic gap. For point-node superconductors, $N_{\text{sc}}(E) \propto E^2$ for $E \ll \Delta_0$, leading to $1/T_1 \propto T^5$. For line-node superconductors, $N_{\text{sc}}(E) \propto E$ for $E \ll \Delta_0$, leading to $1/T_1 \propto T^3$. For line-node superconductors with a finite residual density of states (RDOS) induced by disorder, $N_{\text{sc}}(E) \approx \text{const.}$ for $E \ll \Delta_0$, leading to $1/T_1 \propto T$. These differences arise from quasiparticle excitations near the gap nodes, and are summarized in Fig. 2.5(b) and in what follows:

$$\frac{1}{T_1} \propto \begin{cases} \exp(-\Delta_0/k_B T) & \text{for } s\text{-wave isotropic gap} \\ T^5 & \text{for point-nodal gap} \\ T^3 & \text{for line-nodal gap} \\ T & \text{for line-nodal gap with RDOS} \end{cases} \quad (2.55)$$

In iron pnictide superconductors, however, the above discussion cannot be adopted easily. Since iron pnictides are multi-band system having two electron-like and three hole-like FSs and each of them can possibly have different gap structures, i.e. nodal/nodeless and isotropic/anisotropic gaps, the temperature dependence of $1/T_1$ below T_c is expected to show complicated behavior contributed from summation of these different gaps with different weight and gap amplitudes. In the case of an anisotropic SC gap model incorporated with impurities or a multi-SC gap effect [143; 144; 145], the behavior of $1/T_1$ at low temperatures changes from T^5 to T^2 . Therefore, it is very difficult or almost impossible to decide gap structures from the exponent of temperature dependence of $1/T_1$ at low temperatures, while $1/T_1 \propto T$ and the coherence peak just below T_c can nevertheless be seen as the direct evidence of the existence of RDOS and the isotropic gap with no nodes, respectively [142; 146].

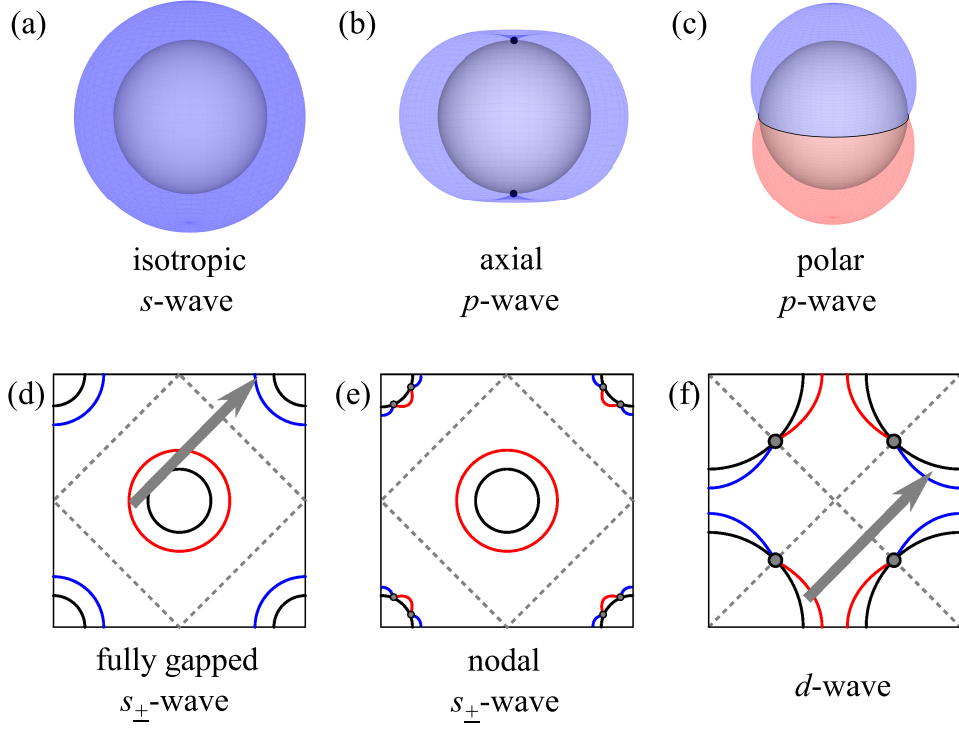


Figure 2.4: Schematic images of various SC gap symmetry. Red and blue lines indicate the SC gap with opposite sign to each other. Grey points represent the position of the node. (a) Isotropic s -wave SC gap on a 3D isotropic FS typically observed in the BCS superconductors. (b) Axial p -wave SC gap with point nodes on the 3D isotropic FS. (c) Polar p -wave SC gap with a line node on an 3D isotropic FS. (d) Isotropic 2D $s_{\pm}$ -wave gap structure with opposite sign of gaps. (e) $s_{\pm}$ -wave gap with accidental nodes. (f) d -wave gap typically observed in the cuprate high- T_c superconductors. Grey arrows in (d)-(f) represent the nesting vectors.

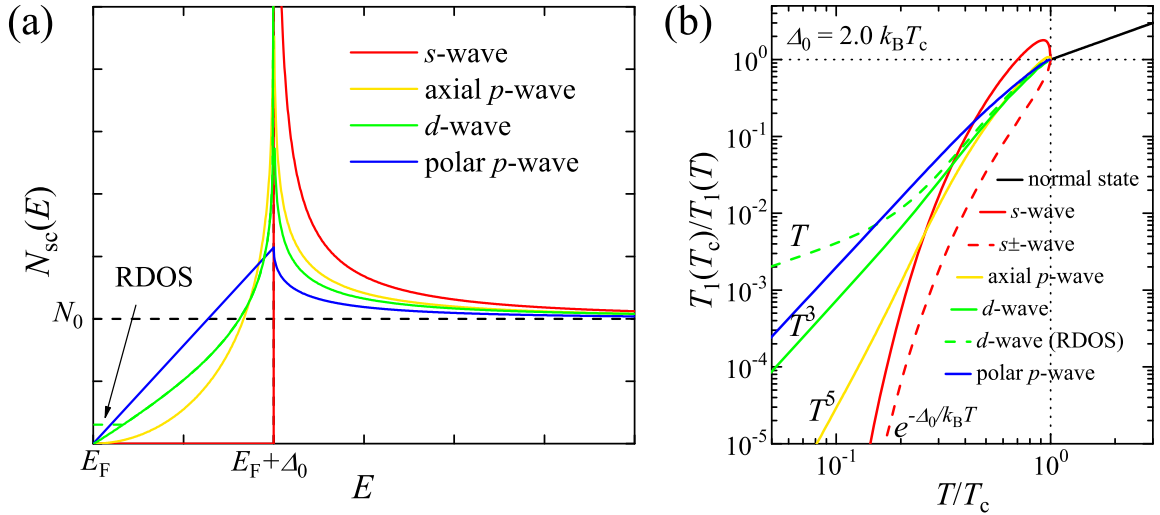


Figure 2.5: (a) Energy dependence of the quasiparticle density of states in SC state. A broken line indicates the residual density of states (RDOS) induced by disorder in the sample. (b) Temperature dependence of normalized $1/T_1$ in the SC state for each gap symmetry.

Chapter 3

Experimental

This Chapter will introduce elements needed for NMR experiments such as magnets, cryogenics, probes, and electronics specifying which setup would be used particularly for the measurements done in this work. An overview of the samples used for the measurements will be also given.

3.1 Measurement Equipment

3.1.1 Magnets and Cryogenics

During the course of this thesis, four NMR magnets have been used. One magnet (Oxford Instruments) can be fixed to any desired magnetic field value between 0 and 15 T by adjusting the current through its large SC coil. Magnetic field homogeneity is of the order of $\Delta H/H \sim 10^{-3}$. Another one (Cryomagnetics, Inc.) also has variable magnetic field system between 0 and 15 T. The homogeneity is $\Delta H/H \sim 10^{-5}$. Persistent mode where the SC circuit is closed keeping eddy current value constant and power supply is turned off can be available in these two magnets. In persistent mode, the current in the SC coil decays with ~ 1 ppm/h. The third one is the split-type magnet (Wang NMR Inc.) with variable magnetic field system between 0 and 8 T. We can investigate the field angle dependence of single crystals by rotating an NMR probe horizontally. Its field homogeneity is as high as $\Delta H/H \sim 10^{-5}$. These magnets are the systems of our group in Kyoto University. The last one (Cryomagnetics, Inc.) is the magnet of CNRS-LNCMI group in Grenoble, which is variable field system from 0 to 17 T. The homogeneity is $\Delta H/H \sim 10^{-5}$. Persistent mode is also available and the current decay is less than 1 ppm/h. These four magnets are summarized in Table 3.1. For all magnets, the variable temperature insert (VTI) is directly

Table 3.1: Characteristics of four SC magnets used in this study.

Magnet	Oxford Instruments	Cryomagnetics	Wang NMR	Cryomagnetics
Lab.	Kyoto	Kyoto	Kyoto	Grenoble
Figure	3.2(a)	3.2(b)	3.2(c)	3.2(d)
Available field	0 - 15 T	0 - 15 T	0 - 8 T	0 - 17 T
Field direction	longitudinal	longitudinal	transverse	longitudinal
Rotator (Fig. 3.1)	-	Horizontal	Horizontal	-
Homogeneity	$\sim 10^{-3}$	$\sim 10^{-5}$	$\sim 10^{-5}$	$\sim 10^{-5}$
Current decay in persistent mode	> 1 ppm/h	~ 1 ppm/h	-	≤ 1 ppm/h
Chapter	5, 6	5, 6	5, Appendix H	7

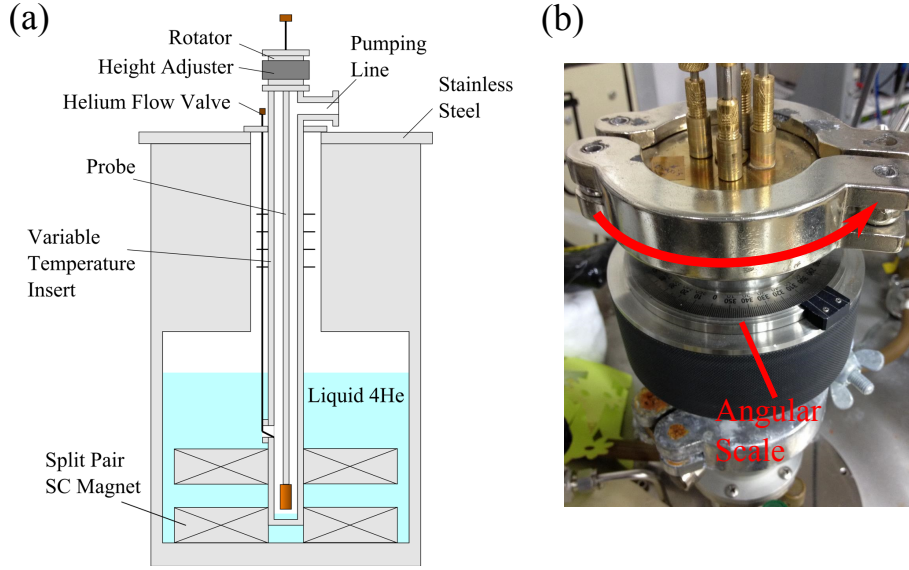


Figure 3.1: (a) Schematic description of the cryostat with a split transverse magnet (corresponding to Fig. 3.2(c)) and an inserted NMR probe. (b) A photograph of the probe rotator mounted on top of the cryostat. An NMR probe can be rotated horizontally with an accuracy of $\pm 0.5^\circ$.

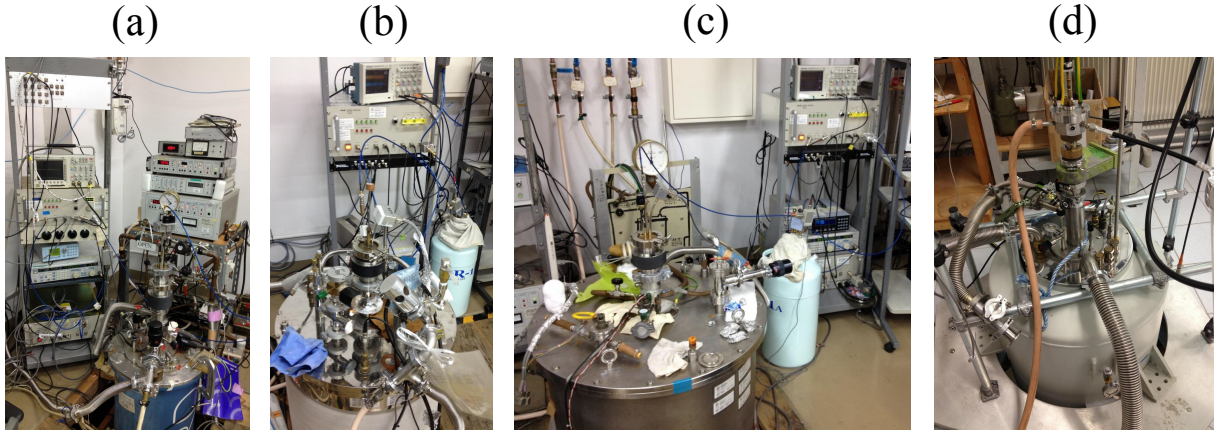


Figure 3.2: Photographs of the magnets for our NMR measurements. (a) 15 T SC magnet (Oxford Instruments) which produces a vertical field. (b) 15 T SC magnet with high homogeneity (Cryomagnetics). (c) Split-type 8 T magnet (Wang NMR) equipped with horizontal rotator. (d) 15 T SC magnet with high homogeneity in CNRS-LNCMI NMR group laboratory.

connected to the helium bath which cools the SC coil via a needle valve. The temperature of the sample space is controlled with an Oxford ITC 503 (503S for the system in Grenoble) temperature controller and by regulating the opening of the needle valve of the VTI and by pumping. For heating the sample space quickly to the target temperature, we attached copper cylinder covering the sample space to the probe head, around which Manganin wires are wound.

3.1.2 NMR Probes

A resonant circuit for NMR/NQR measurements has to fulfill two conditions: it must be tunable to the desired frequency in the MHz-range and it must have an impedance of 50Ω such that it couples optimally to the rest of the electronic measurement equipment. This ensures that

the power is optimally coupled into and out of the resonant circuit, which leads to optimal sensitivity and avoids reflecting power back to the amplifier. Various NMR probes were used for measurements according to the desired frequency and the required additional equipment such as the matching capacitor and the sample rotator. Each of these probes was equipped with one out of two different types of resonant circuits (see Fig. 3.4): one containing a variable cylindrical capacitor for the tuning and a mutual inductance coupling loop (Fig. 3.4(a)); and one containing two trimmer capacitors for tuning and impedance matching (Fig. 3.4(b)). The approach of the circuit A (Fig. 3.4(a)) is mutual inductive coupling. The circuit consists of the NMR coil L_1 , a one- or two-turn loop coil L_2 tightly wined around L_1 , an Ohmic resistance R , and the tuning capacitor C_T . This method requires no electrical connection to the main tuned circuit. The circuit B (Fig. 3.4(b)) consists of the coil L , resistance R , and the tuning capacitor C_T in series. Parallel to both is the matching capacitor C_M . The total serial impedance is

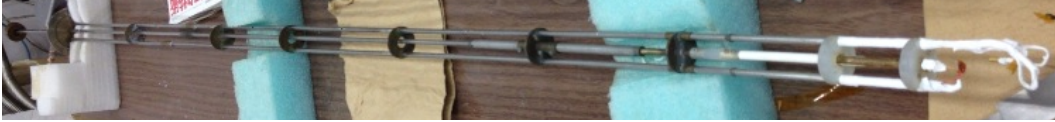
$$Z = i\omega L + \frac{1}{i\omega C_T} + R. \quad (3.1)$$

In order to achieve the resonance frequency $\omega = \omega_R$, $|Z|$ has to be minimal, i.e.

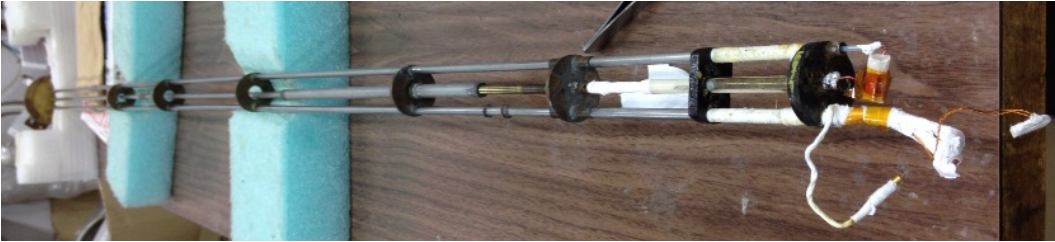
$$i\omega_R L + \frac{1}{i\omega_R C_T} = 0 \Rightarrow \omega_R = \frac{1}{\sqrt{LC_T}}. \quad (3.2)$$

Thus, the tuning to the measurement frequency is done by changing C_T (NMTM120CEK, Voltronics Corp.), while the impedance of 50Ω is reached by changing C_M (NMQM22GEK, Voltronics Corp.). A resonant circuit composed of two capacitors is advantageous because it covers a broad frequency range, due to their wide capacity range (2 to 120 pF in the case of the probes used in this study). For instance, the measurements on single crystalline $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ranged from 43 MHz (^{75}As) up to 104 MHz (^{31}P) at $\mu_0 H = 6$ T and from 107 MHz (^{75}As) up to 260 MHz (^{31}P) at $\mu_0 H = 15$ T without changing coil in each case.

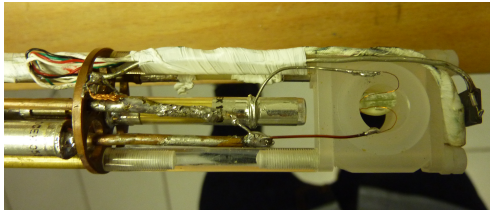
(a) Probe I



(b) Probe II



(c) Probe III



(d) Probe IV

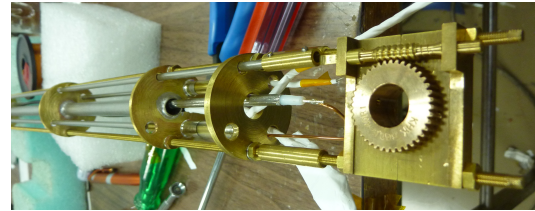


Figure 3.3: Photographs of (a) NMR probe I , (b) probe II, (c) probe III, (d) probe IV.

Four different NMR probes shown in Fig. 3.3 are used throughout the study of this thesis. Characteristics of each probe are summarized in Table 3.2.

Table 3.2: Characteristics of four different NMR probes used in this study.

Probe	Rotator	Circuit type	Thermometer	Chapter
I (User4)	-	A	CERNOX-1050-AA	5, 6
II (X45385)	-	A	CERNOX-1050-AA	5, 6
III (Grenoble)	one-axial rotator (PTFE)	B	CERNOX ($T < 200$ K), PT (platinum) ($T \geq 200$ K)	7
IV (X87709)	one-axial rotator (brass)	B	CERNOX-1050-AA	Appendix H

3.1.3 NMR Coils

All the NMR measurements in this study were performed by using solenoidal copper coils. The desired frequency and the size of the sample for each measurement strongly restrict the configuration of the coil. In principle, a solenoidal coil with the sample inside has the following characteristic inductance

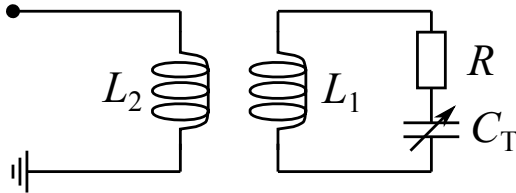
$$L = \frac{\mu N^2 S}{l} = \frac{\mu l S}{\phi_d^2} = \frac{\mu_0(1 + \xi_{\text{fill}}\chi)lS}{\phi_d^2}, \quad (3.3)$$

where ϕ_d represents the diameter of copper wire, N number of turns, S cross section area, $l = N\phi_d$ length, and $\mu = \mu_0(1 + \xi_{\text{fill}}\chi)$ magnetic permeability of the sample with susceptibility of the sample χ and the filling factor ξ_{fill} . Hence the resonance frequency of the LC circuit is

$$f = \frac{1}{2\pi\sqrt{LC}} = \frac{\phi_d}{2\pi\sqrt{\mu_0(1 + \xi_{\text{fill}}\chi)lSC}}. \quad (3.4)$$

The coil length l and area S should be adjusted to the sample length and sample area as close as possible because the filling factor directly relates to the strength of NMR signal. This defines the configuration (namely, l and S) of the coil. Thus, the desired frequency is obtained by adopting appropriate diameter of the copper wire ϕ_d . Since the excitation pulse field $\mathbf{H}_1$ is

(a) Circuit A



(b) Circuit B

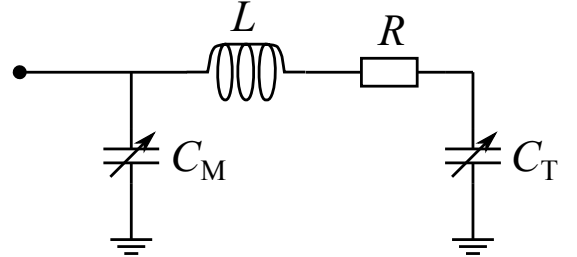


Figure 3.4: Schematic drawing of the resonance circuits. C_T , C_M , and R represent tuning, matching capacitors, and resistance, respectively. Both L and L_1 are inductors (NMR coils), while L_2 is a one- or two-turn loop for mutual inductance. (a) The circuit with a tuning capacitor and a one- or two-turn loop coil. (b) The circuit with tuning and matching capacitors.

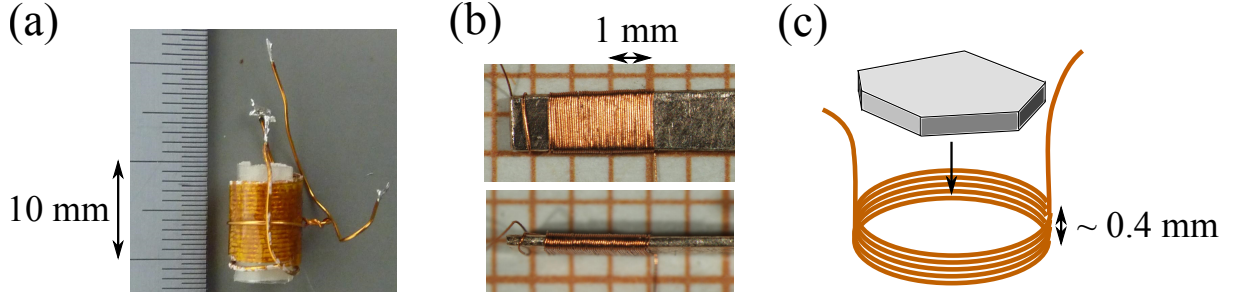


Figure 3.5: (a) A typical copper coil for NMR measurement of polycrystalline sample used in Chaps. 5 and 6. (b) An NMR coil with copper wire of $\phi_d = 50 \mu\text{m}$ for the NMR measurement of the single crystal used in Chap. 7. (c) A schematic drawing of a single crystal (upper light grey object) and an NMR coil with copper wire of $\phi_d = 50 \mu\text{m}$ for the measurement of single crystal used in Appendix H.

applied perpendicular to the cross section of the NMR coil, this direction should be perpendicular to the applied external magnetic field $\mathbf{H}$ to cause nuclei excitation. This means that we are allowed to measure the external field orientation dependence only in the plane perpendicular to $\mathbf{H}_1$. Because of the plate-like shape of the single crystal, a - c (or b - c) angle dependence can be measured with the coil shown in Fig. 3.5(b) and a - b (in-plane) angle dependence can be measured with the coil in Fig. 3.5(c).

3.1.4 Pressure Cell

In Chap. 6, NMR measurements on the pressurized sample with $x = 0.20$ were performed. To apply pressure, we used a CuBe-NiCrAl hybrid piston-cylinder-type pressure cell as shown in Fig. 3.6 [147]. The pressure cell can apply hydrostatic pressure up to $p \sim 2.5$ GPa. Daphne 7373 was used as the pressure transmitting medium.

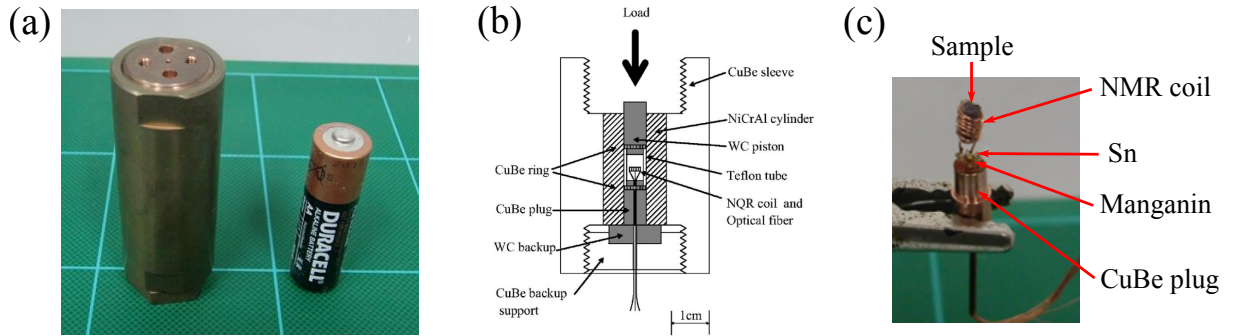


Figure 3.6: (a) A photograph of the pressure cell we used in Chap. 6. (b) A schematic drawing of cross-section view of the pressure cell [147]. (c) A photograph of the attached NMR coil inside the Teflon tube.

3.1.5 Electronics

Since high frequency pulses have to be generated and at the same time very weak echo signals from the sample have to be detected, the setup of the electronic measurement equipment is challenging. Figure 3.7 shows the main electronic elements of a typical NMR instrumental

setup. The receiver is a super-heterodyne design to realize a very wide-band operation, and has the symmetric layout for the transmitter (TX) and the receiver (RX). The transmitting pulse is modulated by quadrature amplitude modulation (QAM). The receiving signal is demodulated by phase sensitive detectors (PSD). Network analyzers were also used before each measurement to tune and match the resonant circuit to the desired frequency. Electronics used in each measurement system are listed in Table 3.3.

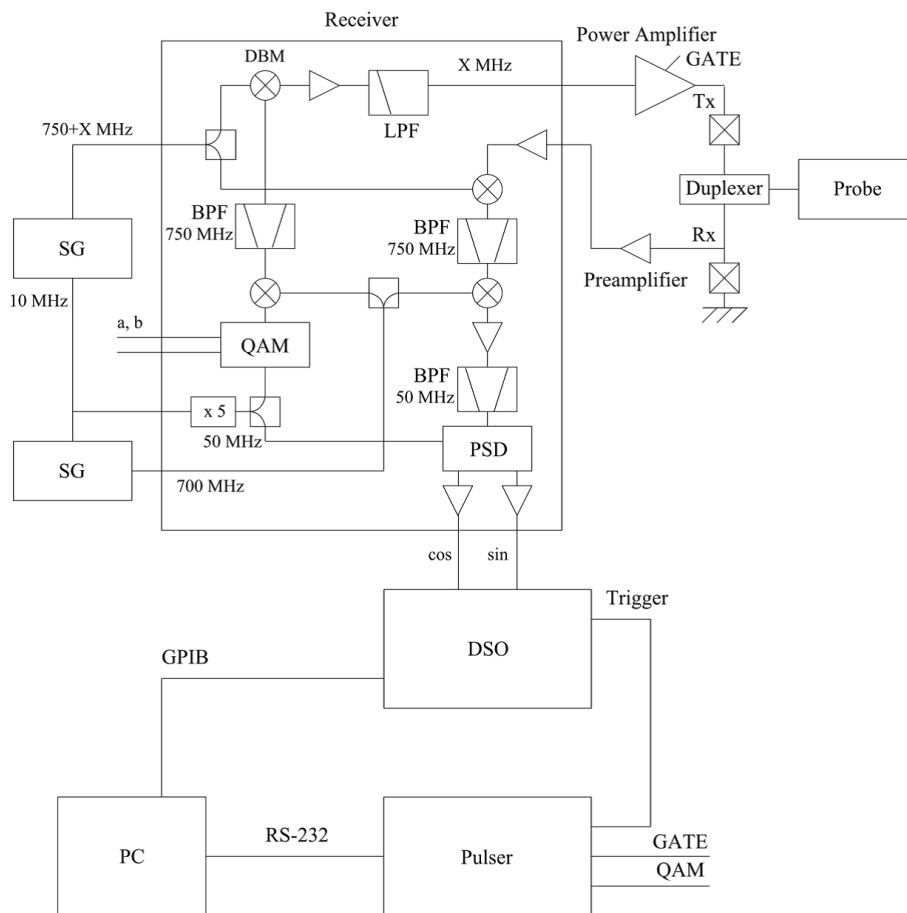


Figure 3.7: Schematic diagram of a typical NMR instrumental setup.

Table 3.3: Electronics used in each measurement system.

Lab. Magnet	Kyoto Oxford Instruments	Kyoto Cryomagnetics	Kyoto Wang NMR	Grenoble Cryomagnetics
Temperature controller	Oxford ITC 503	Oxford ITC 503	Oxford ITC 503	Oxford ITC 503S
Magnet power supply	Oxford IPS 120-10	Oxford IPS 120-10	Oxford IPS 120-10	Bouhnik SAS -
Amplifier	Thamway N146-5049A	Thamway N146-5559A	Thamway N146-5049A	Bruker BioSpin BLAX1000
Signal generator	Kenwood SG-7130	Kenwood SG-7130	Kenwood SG-7130	Hameg HM8134-3
Temperature controller	Cryocon 62	Cryocon 32B	Cryocon 32	Keithley 2000
DC power supply	Takasago TP035-2D	Takasago TP035-2	Takasago TP035-2	Alim Dec. -
Receiver	Thamway PROT-3202MR	Thamway N320-804AA	Thamway N320-804AA	Lab-made
Pulser	Lab-made (Dr K. Kitagawa)	NI CA-1000	NI CA-1000	Lab-made
Preamplifier	Thamway N141-305AA	Thamway N141-304AA	Lab-made(Kitagawa) LAN-4R3-NO.1	Miteq AU-1466
Oscilloscope	Tektronix TDS 3012	Tektronix TDS 2014B	Tektronix TDS 2004B	LeCroy WaveRunner 104Xi
Network Analyzer	Agilent Technologies E5061A	or	Hewlett Packard 8752C	Agilent 8172ET

3.2 NMR Measurement

All of our NMR experiments were performed with the spin-echo method using a super-heterodyne type spectrometer. The nuclear parameters; spin I , gyromagnetic ratio γ , natural abundance, magnetic moment $\mu(= \gamma\hbar I)$, and electric quadrupole moment Q are listed for the nuclei used in this study in Table 3.4 [140]. Our measurement system is connected to the computer via an USB-port and controlled by C/C++ program “KAME” which is developed by Kentaro Kitagawa.

Table 3.4: Physical constants of nuclei used in this study [140].

Nucleus	spin I [$\hbar$]	Gyromagnetic ratio γ [MHz/T]	Natural abundance [%]	Magnetic moment μ [μ_N]	Electric quadrupole moment Q [10^{24} cm ²]
³¹ P	1/2	17.235	100	+1.1306	0
⁶³ Cu	3/2	11.285	80	+2.2206	-0.211
⁷⁵ As	3/2	7.2919	100	+1.4349	+0.29

3.2.1 NMR Spectrum and Knight Shift Measurement

NMR spectra were obtained by integrating Fourier-transformed spin-echo intensity as a function of external field at a fixed frequency or as a function of frequency at a fixed magnetic field.

In Chapter 5 and 6, the Knight shift ^{31}K which is the measure of the local susceptibility at ³¹P nuclear site was determined from the peak frequency ^{31}f of each resonance spectrum at the fixed external field H_0 by comparing the resonance frequency $^{31}f_0(= ^{31}\gamma\mu_0 H_0/2\pi)$ of the reference material H₃PO₄ with $K = 0$ as follows:

$$^{31}K = \frac{^{31}f - ^{31}f_0}{^{31}f_0}. \quad (3.5)$$

The measurement of H₃PO₄ was performed immediately after the ^{31}f measurement to avoid any slight change of magnetic field due to the drift or decay of the current in SC magnets.

In Chapter 7 and Appendix H, ^{75}K and ^{31}K , for As and P nuclei, respectively, were determined from the peak frequency ^{75}f and ^{31}f of each spectrum by comparing the peak frequency ^{63}f of ⁶³Cu-NMR signal with well-known value of ^{63}K , which is from copper NMR coil itself, as follows:

$$^{31}K = \frac{^{31}f}{^{31}f_0} - 1 = \frac{^{31}f}{\frac{^{31}\gamma}{2\pi}\mu_0 H_0} - 1 = \frac{^{31}f}{\frac{^{31}\gamma}{2\pi} \left[\frac{^{63}f}{\frac{^{63}\gamma}{2\pi}(1+^{63}K)} \right]} = \frac{^{63}\gamma}{^{31}\gamma} \frac{^{31}f}{^{63}f} (1 + ^{63}K) - 1 \quad (3.6)$$

$$^{75}K = \frac{^{75}f - \frac{3\nu_z^2}{16} \frac{^{75}f_0}{^{75}\gamma}}{^{75}f_0} - 1 = \frac{^{63}\gamma}{^{75}\gamma} \frac{^{75}f}{^{63}f} (1 + ^{63}K) - 1 - \frac{3}{16} \left[\frac{^{63}\gamma}{^{75}\gamma} \frac{\nu_z}{^{63}f} (1 + ^{63}K) \right]^2, \quad (3.7)$$

where the third term of the last equation is the correction for the second-order quadrupole shift and ν_z is the quadrupole frequency along the principal axis (z -axis) of the EFG tensor. Note that Eq. (3.7) is the expression for $\mathbf{H}_0 \perp \mathbf{z}$. Here, the value of ^{63}K at each temperature is estimated by linear interpolation between $^{63}K(300 \text{ K}) = 0.002394$ and $^{63}K(4 \text{ K}) = 0.00238$ [140]:

$$^{63}K = 0.00238 + \frac{0.000014}{296} \times (T - 4). \quad (3.8)$$

Although ^{63}Cu has the spin of $I = 3/2$, the electric field gradient $^{63}V_{\alpha\alpha} = 0$ because the crystal structure of copper wire is face-centered cubic.

Since the coils used for the single-crystal measurements can be tuned from $f \approx ^{75}\gamma\mu_0 H/2\pi$ up to $f \approx ^{31}\gamma\mu_0 H/2\pi$ and $\frac{^{75}\gamma}{2\pi} < \frac{^{63}\gamma}{2\pi} < \frac{^{31}\gamma}{2\pi}$ ($7.2919 < 11.285 < 17.235$ MHz/T), all the signals from ^{75}As , ^{63}Cu , and ^{31}P nuclei can be detected *in-situ* with the identical coil.

3.2.2 Spin-Lattice Relaxation Rate Measurement

To measure the spin-lattice relaxation rate $1/T_1$, one has to change the spin population from their thermal equilibrium values, for example by applying rf field, and then watch the populations until the spin populations come back to equilibrium. In our experiments, we used the saturation recovery method to measure the spin-lattice relaxation rate $1/T_1$. In this method, the spin populations are driven to zero net nuclear magnetization by applying a number of $\pi/2$ pulses to the nuclear-spin system.

The time evolution of the nuclear moment after saturation, $M(t)$, can be described by a set of standard rate equations. The equations are readily solved under the specific initial conditions of an experiment. For ^{31}P nuclei with a spin $I = 1/2$, the equation describing the return to equilibrium is given by:

$$M(t) = M(\infty) \left[1 - A \exp\left(-\frac{t}{T_1}\right) \right], \quad (3.9)$$

where $M(\infty)$ is the nuclear magnetization in the thermal equilibrium and a constant A represents the initial saturation of the nuclear magnetization in the experimental conditions. The recovery curve of ^{75}As with $I = 3/2$ for $m = 1/2 \leftrightarrow -1/2$ is given by:

$$M(t) = M(\infty) \left\{ 1 - A \left[0.1 \exp\left(-\frac{t}{T_1}\right) + 0.9 \exp\left(-\frac{6t}{T_1}\right) \right] \right\}. \quad (3.10)$$

However, for ^{31}P -NMR measurement on some polycrystalline samples (mosaics of tiny pieces of single crystal) of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, the deviation of recovery curve from the theoretical curve described by Eq. (3.9) starts to appear on approaching T_c , indicating the distribution of T_1 in the sample. In this temperature region with distributed T_1 , a stretched exponential fit to the recovery curves is useful [148]: for ^{31}P -NMR,

$$M(t) = M(\infty) \left[1 - A \exp\left(-\frac{t}{T_1^*}\right)^\beta \right], \quad (3.11)$$

and for ^{75}As -NMR,

$$M(t) = M(\infty) \left\{ 1 - A \left[0.1 \exp\left(-\frac{t}{T_1^*}\right)^\beta + 0.9 \exp\left(-\frac{6t}{T_1^*}\right)^\beta \right] \right\}, \quad (3.12)$$

where the stretching exponent β is a measure of distribution in T_1 , which is in the range of $0 < \beta < 1$. In case $\beta > 1$ was obtained from the fitting, we fitted the recovery curves again with fixing $\beta = 1$, since $\beta > 1$ is physically meaningless. To avoid any arbitrariness, we used Eqs. (3.11) and (3.12) for fit to the recovery curves at first at all the measured temperature in this study. The detail of the stretched exponential function is discussed in Appendix A. Typical recovery curves $m(t) \equiv (M(\infty) - M(t))/M(\infty)$ of ^{31}P and ^{75}As for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is shown in Fig. 3.8. A single component of T_1 in the relaxation process was obtained across the measured temperature range in the single crystal of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $x = 0.04$ as shown in Figs. 3.8(a) and 3.8(b). Also for the polycrystalline samples of $x = 0.07, 0.14$, and 0.20 , the relaxation curves were fitted with the theoretical curves of a single T_1 component in the entire temperature range

(Figs. 3.8(c) and 3.8(d)). On the other hand, the relaxation curves of $x = 0.25$, 0.27 , and 0.33 showed deviation from the theoretical ones (Fig. 3.8(e) and 3.8(f)). A decrease of β from 1 starts below ~ 60 K for $x = 0.25$ and 0.27 and below ~ 40 for $x = 0.33$ as shown in Fig. 3.9. After taking minimum at $T_c \sim 30$ K, β starts to increase on cooling down to the lowest temperature. The deviation of T_1 is mainly attributed to the spatial inhomogeneity of the doping level x . Since T_N , to which $(T_1 T)^{-1}$ diverges, changes steeply in the region $0.25 \leq x \leq 0.33$ on the phase diagram, even slight distribution of x causes strong distribution of T_1 in the sample, resulting in the bending of relaxation curves and hence a reduction of β . As discussed in Chap. 6, for the region of $\beta < 0.85$, we measured T_1 at the tail of ^{31}P spectrum coming from AFM ordered region with lower x in the sample and extracted a single component of T_1 at AFM ordered state. For $x \geq 0.41$, where the divergence of $(T_1 T)^{-1}$ is weaker than in $0.25 \leq x \leq 0.33$, β shows almost no change against temperature (Fig. 3.8(g), (h) and Fig. 3.9 for $x = 0.41 - 0.64$) and $\beta \approx 1$.

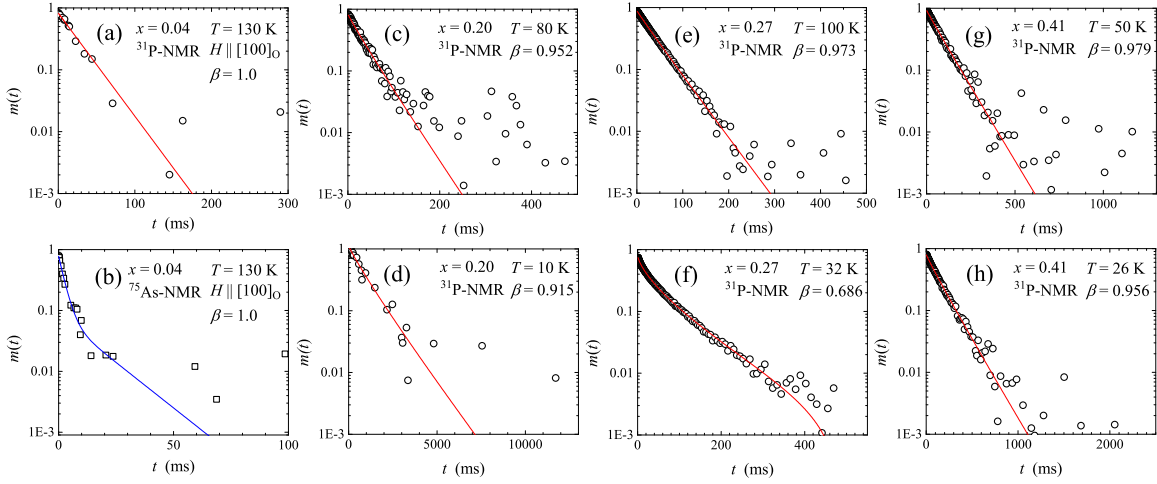


Figure 3.8: Typical recovery curves $m(t) \equiv (M(\infty) - M(t))/M(\infty)$ for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Experimental data of ^{31}P (open circle) and ^{75}As (open square) are fitted with theoretical curves described by Eqs. (3.11) (solid red line) and (3.12) (solid blue line), respectively.

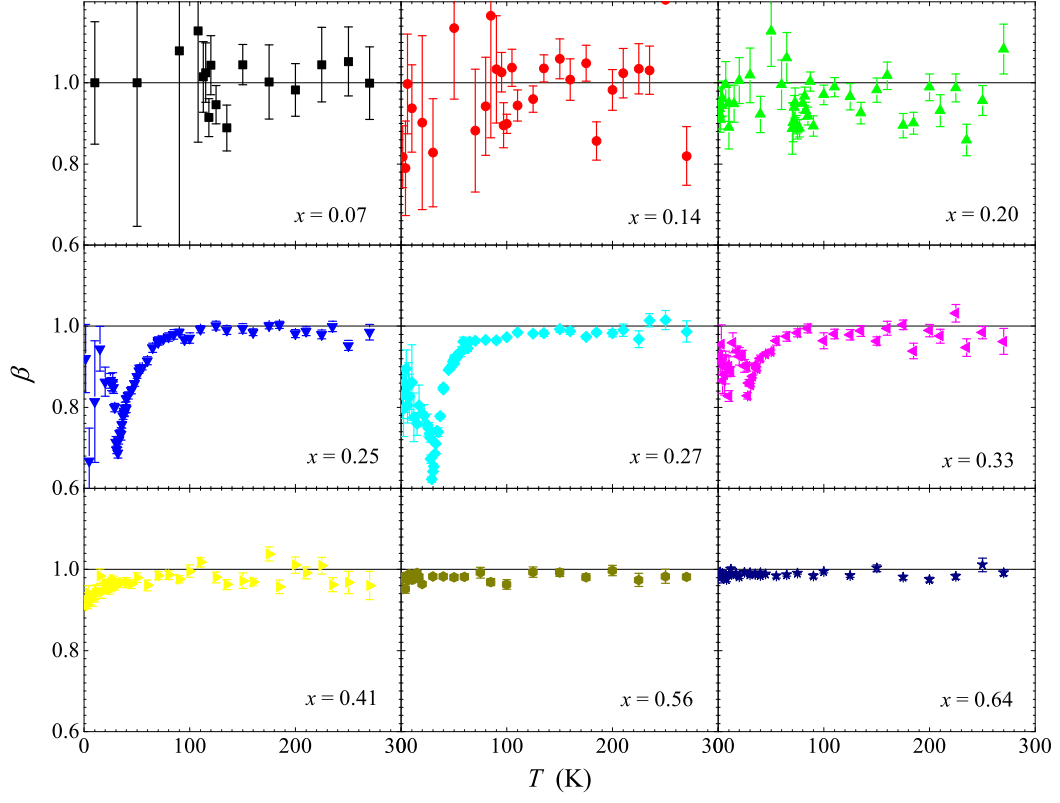


Figure 3.9: Temperature dependence of the stretching exponent β for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

3.3 Samples

3.3.1 Sample Preparation

All of the samples for NMR measurements in this work are provided by Shigeru Kasahara. Single crystals of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with typical dimensions of $100 \times 100 \times 50 \mu\text{m}^3$ were grown from stoichiometric mixtures of Ba (flakes), and FeAs, Fe, P, or FeP (powders) placed in an alumina crucible, sealed in an evacuated quartz tube [83]. It was heated up to $1150 - 1200^\circ\text{C}$, kept for 12 h, and then cooled slowly down to $\sim 800^\circ\text{C}$ at the rate of 1.5°C/h . x values were determined by an energy dispersive x-ray analyzer. The single crystals of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ are not so air-sensitive that any change of the physical properties due to exposure of the samples to air was not discernible through this study. However, to make sure, all the samples are kept with vacuum in the same desiccator.

For NMR measurements in Chap. 5 and 6 ($x = 0.07, 0.14, 0.20, 0.25, 0.27$, and 0.33) as well as all the previous NMR measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ($x = 0.33, 0.41, 0.56, 0.64$) [100; 146; 149; 150], we used a mosaic of single crystals for each P-concentration x . Each mosaic of single crystals was put into a straw of which bottom is capped with fixed Araldite. Varnish was poured into the straw in order to fix the alignment of the crystals randomly. The fixed single crystals were covered with gauze and fixed with glue. The procedure for sample preparation is schematically shown in Fig. 3.10(a). The actual appearance of a properly prepared sample can be seen in Fig. 3.10(b). Each of the samples was inserted into the NMR copper coil. The coil was attached to the probe head and the probe was inserted into the cryostat to perform NMR measurement.

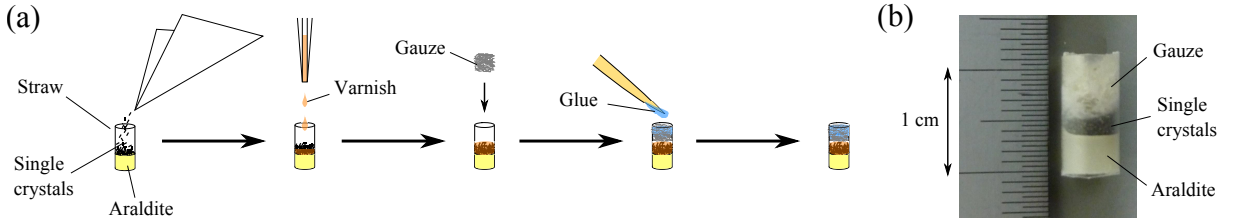


Figure 3.10: (a) Schematic drawing of the process for sample preparation. (b) A photograph of a prepared sample for NMR measurements.

3.3.2 Sample Characterization

The SC transition of the sample can be detected by recording the detuning of an NMR tank circuit as a function of temperature. The tuning frequency of the NMR circuit with inductance L and capacitance C is given by

$$f_{\text{tune}} = \frac{1}{2\pi\sqrt{LC}}. \quad (3.13)$$

If the inductance changes a small amount to $L + \delta L$, the new frequency can be written as

$$f_{\text{tune}} + \delta f_{\text{tune}} = \frac{1}{2\pi\sqrt{(L + \delta L)C}} = \frac{1}{2\pi\sqrt{LC}\sqrt{1 + \frac{\delta L}{L}}} \approx f_{\text{tune}} \left(1 - \frac{1}{2} \frac{\delta L}{L}\right), \quad (3.14)$$

where, for the last transformation, the expression was expanded for small values of δL to the first order. The self-inductance of a solenoidal NMR coil can be described as $L = \mu_0(1 + \xi_{\text{fill}}\chi)lS/\phi_d^2$ (see Eq. (3.3)). Then, Eq. (3.14) can be rewritten as

$$\delta f_{\text{tune}} \approx -\frac{1}{2} \frac{\delta L}{L} f_{\text{tune}} = -\frac{1}{2} \frac{\xi_{\text{fill}}\delta\chi}{1 + \xi_{\text{fill}}\chi} f_{\text{tune}} \propto -\delta\chi. \quad (3.15)$$

When doing NMR measurements we normally tune the tank circuit to the same frequency of rf pulse H_1 at the desired NMR resonant frequency f_0 . We use a network analyzer to monitor the tuning frequency f_{tune} as we vary temperature while maintaining constant C . When the sample undergoes an SC transition, χ would become negative because of Meissner effects. By tuning the circuit to a frequency of $f_{\text{tune}}(T_c)$ at a temperature slightly above T_c and observing $\delta f_{\text{tune}} \propto -\delta\chi$ (as shown above) with sweeping temperature down to ~ 1.5 K, we can determine the T_c 's of our samples with $x = 0.14, 0.20, 0.25, 0.27, 0.33$ using an identical NMR coil. SC transitions were detected for $x = 0.20, 0.25, 0.27, 0.33, 0.41, 0.56$, and 0.64 although the change in δf for $x = 0.20$ does not saturate even at the lowest temperature (1.5 K), suggesting a small volume fraction of SC region in the sample of $x = 0.20$ (Fig. 3.11(a)). Determined T_c 's are consistent with the resistivity measurement performed by S. Kasahara (Fig. 3.11(b)) [83].

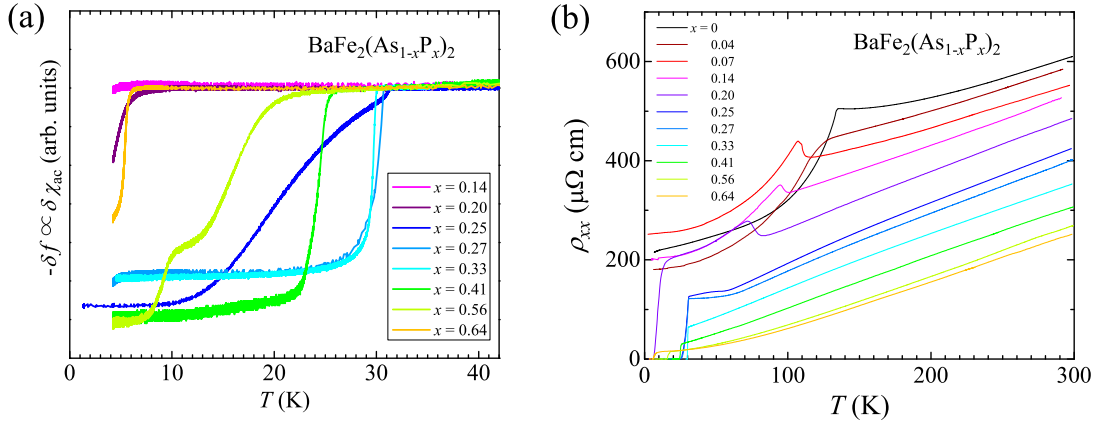


Figure 3.11: (a) The temperature dependence of Meissner signal measured with an NMR coil. Saturations of δf at low temperatures indicate full Meissner shieldings. (b) The temperature dependence of the resistivity for each P-concentration x [83]. The unpublished data for $x = 0.04, 0.14$ and 0.25 are also given by S. Kasahara.

Here, in Table 3.5, we summarize the sample weight, T_N^{NMR} determined by NMR measurements, $T_{c,\text{on}}^{\text{NMR}}$ determined by the onset temperature of detuning of an NMR coil, T_S^{Res} defined as the onset of upturn, T_N^{Res} defined as the peak, and $T_{c,0}^{\text{Res}}$ below which the zero-resistivity is achieved. Further details of the characterization are described in experimental sections in each chapter.

Table 3.5: Sample weight and T_N^{NMR} , $T_{c,\text{on}}^{\text{NMR}}$ determined by NMR measurements, T_S^{Res} , T_N^{Res} , and $T_{c,0}^{\text{Res}}$ determined by the resistivity measurement for each x . T_N^{NMR} for $x = 0$ is adopted from Ref. [36].

P-concentration x	Weight [mg]	T_N^{NMR} [K]	$T_{c,\text{on}}^{\text{NMR}}$ [K]	T_S^{Res} [K]	T_N^{Res} [K]	$T_{c,0}^{\text{Res}}$ [K]
0 (Ref. [36])	-	135	-	135	135	-
0.04 (single crystal)	-	121	-	121	121	-
0.07	45.3	113	-	115.0	108.0	-
0.14	97.7	95	5.0	101.0	94.0	-
0.20	139.4	73	9.1	83.7	71.8	5.3
0.20 ($p \sim 2$ GPa)	40.3	61	20.0	-	-	-
0.25	95.1	60	31.0	63.1	52.0	25.1
0.27	107.8	41	30.8	64.25	-	25.2
0.33	153.4	-	30.1	-	-	29.8
0.41	69.9	-	26.0	-	-	24.4
0.56	94.4	-	23.0	-	-	15.6
0.64	152.6	-	6.5	-	-	5.9

Chapter 4

Previous NMR Studies of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

4.1 NMR Study on BaFe_2As_2

It is quite important to understand the basic physical properties of BaFe_2As_2 as a parent compound of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system. Splendid ^{75}As -NMR measurements on a single crystal of BaFe_2As_2 have been already performed by Kitagawa *et al.* at the first stage [36]. In what follows, their outstanding NMR results are introduced.

4.1.1 Basic Properties

Figure 4.1(a) shows ^{75}As -NMR spectra at the fixed frequency of 48.41 MHz obtained by sweeping the magnetic field parallel and perpendicular to the c -axis at several different temperatures. The spectra at $T = 141$ K are representative of the paramagnetic (PM) phase, while the spectra at the other temperatures belong to the AFM ordered phase. As ^{75}As nuclei have spin $3/2$, the NMR frequencies are generally expressed by a perturbation series when the magnetic Zeeman interaction dominates over the quadrupole interaction, Eq. (2.31). Here, the crystal axes are defined with respect to the orthorhombic ($Fmmm$) unit cell. Note that the $mm2$ symmetry of the As sites in the orthorhombic phase guarantees that the crystalline a -, b -, and c -axes are the principal axes of EFG tensor. In the tetragonal phase, the NMR spectrum is independent of in-plane field orientation ϕ , since $\nu_a = \nu_b = -\nu_c/2$. As shown in Fig. 4.1(a), the NMR spectra at $T = 141$ K show a sharp central line ($m = 1/2$) with the full width at half maximum (FWHM) of 3.5 kHz and two broader satellite lines ($m = 3/2$ and $1/2$) with the FWHM of 100 kHz. The quadrupole frequency along the c -axis ν_c is determined from the separation between the two satellite lines for $H \perp c$ ($\theta = \pi/2$), which is half of the separation for $H \parallel c$ ($\theta = 0$) as expected. The value of ν_c is plotted against temperature in Fig. 4.1(b).

The Knight shift ^{75}K was determined from the resonance position of the central line after correcting for the demagnetization field and the second-order quadrupolar shift. The temperature dependence of ^{75}K is shown in the inset of Fig. 4.2(a) for $H \parallel c$ and for $H \perp c$ above 140 K. For both directions, ^{75}K decreases slightly with decreasing temperature. In general, the Knight shift consists of the T -dependent spin shift, and the T -independent chemical (orbital) shift: $K(T) = K_{\text{chem}} + K_{\text{spin}}(T)$. Likewise, the susceptibility is the sum of the contributions from core diamagnetism, orbital (van Vleck) paramagnetism, and spin paramagnetism: $\chi(T) = \chi_{\text{dia}} + \chi_{\text{orb}} + \chi_{\text{spin}}(T)$. The spin shift is linearly related to the spin susceptibility via the hyperfine coupling constant A_{spin} ,

$$K_{\text{spin}}(T) = \frac{A_{\text{spin}}\chi_{\text{spin}}(T)}{N_A\mu_B} \quad (4.1)$$

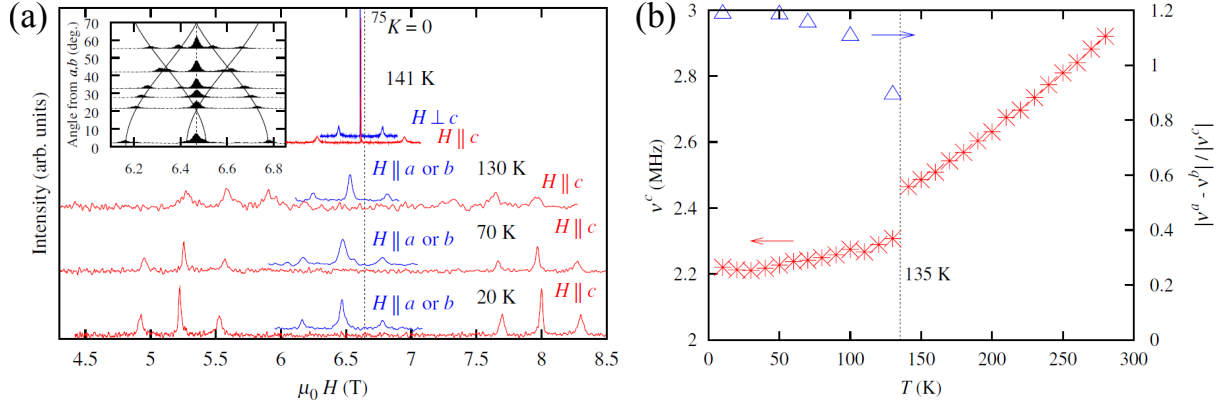


Figure 4.1: (a) The temperature evolution of field-swept ^{75}As -NMR spectra. In the PM state at 141 K, the spectrum consists of a sharp central line and two broader satellite lines. Below 135 K, the internal fields along the c -axis due to commensurate AFM order splits the NMR spectra for $H \parallel c$ (red lines) and shifts the spectra to lower fields for $H \parallel a$ - or b -axis (blue lines). The insert shows the angular variation of the NMR spectrum at 20 K for the field rotated in the ab -plane. The two sets of satellite lines originate from the twinned structural domains in the orthorhombic phase. The satellite positions are fitted to Eq. 2.31 with the quadrupole parameters; $\nu_c = 2.21$ MHz, $|\nu_a - \nu_b|/|\nu_c|$ (solid lines). (b) Nuclear quadrupole frequency along the c -axis, ν_c , and the asymmetry parameter $|\nu_a - \nu_b|/|\nu_c|$ are plotted as a function of temperature. The emergence of the asymmetric parameter below 135 K and a jump in ν_c indicate the first-order structural transition into orthorhombic phase. These figures are adopted from Ref. [36].

We have indeed observed linear relations between ^{75}K and the magnetic susceptibility as displayed in the main panel of Fig. 4.2(a). The slope of these plots gives the values of the spin hyperfine coupling constant as $^{75}A_{\text{spin}}^{ab} = 2.64 \pm 0.07$ T/ μ_B and $^{75}A_{\text{spin}}^c = 1.88 \pm 0.06$ T/ μ_B . However, the authors pointed out the possibility that the hyperfine coupling is temperature-dependent.

When the temperature is lowered below 135 K, the NMR spectrum develops a two-fold splitting for $H \parallel c$. This is the direct evidence for a two-sublattice AFM order. The AFM moments generate a spontaneous internal field with alternating sign $\pm\Delta$. The temperature dependence of Δ determined from the separation between the split center lines is shown in Fig. 4.2(b) by crosses. No splitting was observed when the field is applied along the a - or b -axis. Instead, the whole spectrum is shifted to lower fields as seen in Fig. 4.1(a). This indicates that the internal field is parallel to the c -axis. When $H \perp c$, the effective field H_{eff} is given by the magnitude of the vector sum of the mutually orthogonal external and internal fields, $H_{\text{eff}} = \sqrt{H^2 + \Delta^2}$, giving positively shifted unsplit resonance lines. In Fig. 4.2(b), Δ determined also from the shift of the central line for $H \parallel a$ or b is plotted by squares. The values of Δ for the two field orientations show good agreement, indicating that the magnitude and the direction of the AFM moment are independent of the field direction. The behavior in the vicinity of the phase transition was investigated by recording the peak intensity of the Fourier transformed spectrum at the resonance position of the PM phase with changing temperature as shown in the insert of Fig. 4.2(b). The magnetic transition was found to be very sharp with the transition width less than 1 K, indicating good homogeneity of the crystal. It also shows a clear hysteresis in temperature about 4 K wide, providing a conclusive evidence for the first-order transition. This is also inferred from the discontinuous development of the internal field as well as a discontinuous structural transition suggested by a pronounced change of symmetry of EFG. As shown in the

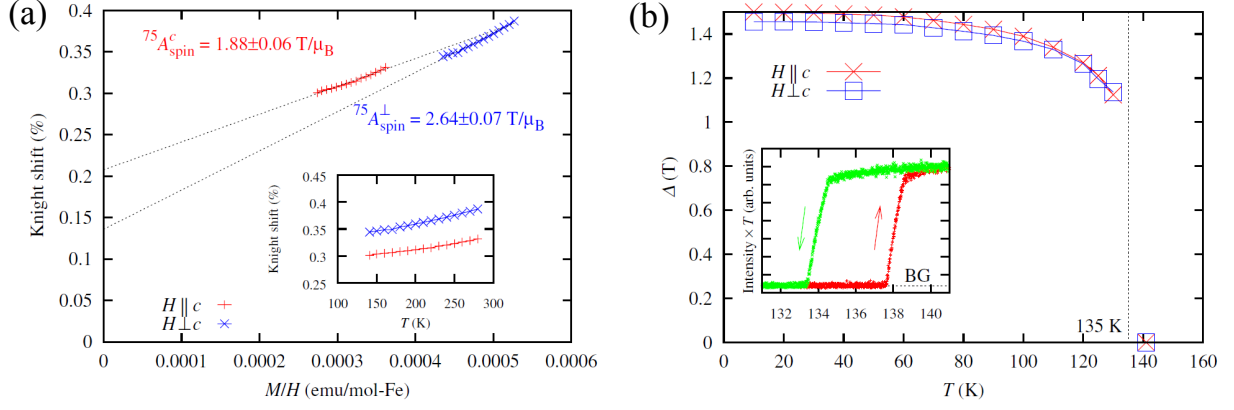


Figure 4.2: (a) Inset: the temperature dependence of the Knight shift ^{75}K for $H \parallel c$ and $H \perp c$. Main panel: ^{75}K is plotted against the bulk susceptibility χ measured by Wang *et al* [151]. The dotted lines represent the fits to a linear relation. (b) The temperature dependence of the internal field at the As nuclei associated with the AFM order. The inset shows the intensity of the central line at the resonance position of the PM phase for $H \perp c$. The abrupt change with hysteresis is the evidence for the first-order magnetic transition. These figures are adopted from Ref. [36].

inset of Fig. 4.1(a), the quadrupole splitting at 20 K varies with the field direction (ϕ) in the ab -plane, indicating that $\nu_a \neq \nu_b$. This is consistent with the orthorhombic symmetry. The angular variation of the NMR spectra displayed in the inset of Fig. 4.1(a) shows two branches of satellite lines, which are shifted by 90° . This comes from the twinned orthorhombic domains. The ϕ dependence of the satellite lines can be fit to Eq. (2.31). The extrema of the angular variation correspond to the field directions parallel to either a - or b -axis. The asymmetry parameter of EFG defined by $|\nu_a - \nu_b|/|\nu_c|$ is plotted in Fig. 4.1(b). The asymmetry parameter, which is zero in the tetragonal phase, is observed to develop abruptly below the transition temperature, and a jump in ν_c is also observed across the transition. These results establish the simultaneous structural and magnetic transition. The large value of asymmetry parameter, exceeding one in the low-temperature phase, implies that the principal axis for the largest EFG changes by 90° across the transition. This suggests that the band structure or the nature of the Fe-As bonds becomes highly anisotropic in the ab -plane.

The ^{75}As -NMR spectra gives the valuable information about the spin structure in the AFM ordered state. There are two major experimental constraints: (i) the internal field at the As sites is parallel to the c -axis; and (ii) the AFM state has a simple two-sublattice structure. A possible spin structure compatible with the NMR experiments is shown in Fig. 4.3(a), which generates a finite c -component of the internal field at the As sites. In this configuration, the AFM order is described by the wave vector (101) or (100), forming stripes with the AFM moments directed perpendicular to the stripe.

The spin-lattice relaxation rate divided by temperature $(T_1T)^{-1}$ is shown in Fig. 4.3(c). In the PM phase, $(T_1T)^{-1}$ shows anisotropic temperature dependence. Substantial enhancement is seen for $H \parallel a$ or b with decreasing temperature, while $(T_1T)^{-1}$ is nearly constant for $H \parallel c$. Across the first-order structural/magnetic transition, $(T_1T)^{-1}$ drops discontinuously by a factor of three. At low temperatures, $(T_1T)^{-1}$ approaches a constant value for both field orientation expected for a Fermi liquid. This is consistent with the metallic behavior of the resistivity. The low-temperature phase is characterized as an itinerant antiferromagnetic phase. Although the AFM order may be driven by FS nesting, these results demonstrate that the order

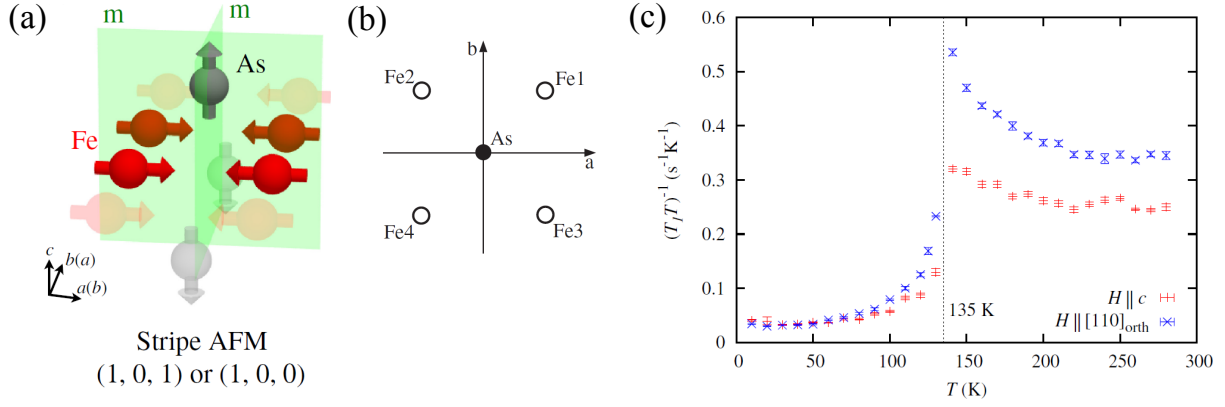


Figure 4.3: (a) An experimentally determined spin configuration in the AFM ordered state in BaFe_2As_2 . (b) A configuration of the As and Fe sites viewed from the top. (c) $(T_1T)^{-1}$ is plotted as a function of temperature for $H \parallel c$ and $H \parallel [110]_{\text{ortho}}$.

is commensurate and a sizable density of states at the Fermi level remains down to $T = 0$ K.

4.1.2 Geometrical Consideration of Hyperfine Coupling Tensor between As and Fe sites

Since the long range dipolar interaction gives only small contribution to the internal field, it is reasonable to assume that the dominant contribution to the hyperfine field at $Pn (= \text{As}, \text{P})$ sites results from the short range transferred hyperfine interaction between the Pn nucleus and ordered moments on the four nearest neighbor Fe sites [36]. Pn site is located at the apex of a four-sided pyramid formed by Fe atoms as shown in Fig. 4.3(b). The hyperfine fields at the Pn site can be written as the sum of contributions from each Fe sites:

$$\mathbf{H}_{\text{hf}}^{Pn} = \sum_{i=1}^4 \mathbf{B}_i \cdot \mathbf{S}_i, \quad (4.2)$$

where $\mathbf{S}_i$ is the Fe electron spin at the i -th Fe site and $\mathbf{B}_i$ is the hyperfine coupling tensor between the As nucleus and i -th Fe site. For the Fe1 site as an example, the tensor components of $\mathbf{B}_1$ are expressed as:

$$\mathbf{B}_1 = \begin{pmatrix} B_{aa} & B_{ab} & B_{ac} \\ B_{ba} & B_{bb} & B_{bc} \\ B_{ca} & B_{cb} & B_{cc} \end{pmatrix}. \quad (4.3)$$

The coupling tensor for other sites can be determined by symmetry consideration. Since the Fe2 site is related to the Fe1 site by mirror reflection with respect to the bc -plane, $\mathbf{B}_2$ is given as

$$\mathbf{B}_2 = \begin{pmatrix} B_{aa} & -B_{ab} & -B_{ac} \\ -B_{ba} & B_{bb} & B_{bc} \\ -B_{ca} & B_{cb} & B_{cc} \end{pmatrix}. \quad (4.4)$$

Likewise

$$\mathbf{B}_3 = \begin{pmatrix} B_{aa} & -B_{ab} & B_{ac} \\ -B_{ba} & B_{bb} & -B_{bc} \\ B_{ca} & -B_{cb} & B_{cc} \end{pmatrix}, \quad \mathbf{B}_4 = \begin{pmatrix} B_{aa} & B_{ab} & -B_{ac} \\ B_{ba} & B_{bb} & -B_{bc} \\ -B_{ca} & -B_{cb} & B_{cc} \end{pmatrix}. \quad (4.5)$$

In the PM phase, the Fe spin is uniform $\mathbf{S}_i = \mathbf{S}$, therefore,

$$\mathbf{H}_{\text{hf}}^{Pn} = \left(\sum_{i=1}^4 \mathbf{B}_i \right) \cdot \mathbf{S} = 4 \begin{pmatrix} B_{aa} & 0 & 0 \\ 0 & B_{bb} & 0 \\ 0 & 0 & B_{cc} \end{pmatrix} \cdot \mathbf{S}. \quad (4.6)$$

These diagonal components in the PM state can be determined from $K - \chi$ plot in Fig. 4.2(a) as $B_{aa} = B_{bb} = 0.66 \text{ T}/\mu_B$, $B_{cc} = 0.47 \text{ T}/\mu_B$.

On the other hand, when Fe spins have a stripe-type AFM correlation specified by the wave vector $\mathbf{Q} = [10l]_o$ shown in Fig. 4.3(a), $\mathbf{S}_1 = -\mathbf{S}_2 = \mathbf{S}_3 = -\mathbf{S}_4 = \mathbf{S}_{\text{stripe}}$ and thus $\mathbf{H}_{\text{hf}}^{Pn}$ can be described as:

$$\mathbf{H}_{\text{hf}}^{Pn} = \sum_{i=1}^4 \mathbf{B}_i \cdot \mathbf{S}_i = 4 \begin{pmatrix} 0 & 0 & B_{ac} \\ 0 & 0 & 0 \\ B_{ca} & 0 & 0 \end{pmatrix} \cdot \mathbf{S}_{\text{stripe}}. \quad (4.7)$$

B_{ac} is determined to be $0.43 \text{ T}/\mu_B$ with using the ordered moment $0.87 \mu_B$ reported from the neutron scattering measurement [55].

More in general, the $\mathbf{q}$ -dependence of hyperfine coupling tensor can be expressed with each components $A^{\alpha\beta}(\mathbf{q}) = \sum_i \exp(i\mathbf{q} \cdot \mathbf{r}_i) B_i^{\alpha\beta}$ ($\alpha, \beta = \{a, b, c\}$) as [152]:

$$\mathbf{A}_{\text{hf}}^{Pn}(\mathbf{q}) = 4 \begin{pmatrix} B_{aa}c_ac_b & -B_{ab}s_as_b & iB_{ac}s_ac_b \\ -B_{ba}s_as_b & B_{bb}c_ac_b & iB_{bc}c_as_b \\ iB_{ca}s_ac_b & iB_{cb}c_as_b & B_{cc}c_ac_b \end{pmatrix}, \quad (4.8)$$

where

$$c_a = \cos \frac{q_a a_o}{2}, \quad c_b = \cos \frac{q_b b_o}{2}, \quad (4.9)$$

$$s_a = \sin \frac{q_a a_o}{2}, \quad s_b = \sin \frac{q_b b_o}{2}. \quad (4.10)$$

4.2 NMR Studies on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

Now, let us move on to the introduction to our previous NMR studies on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [100; 146; 149; 150].

4.2.1 Spin Dynamics in the Normal State

Spin-fluctuation-mediated superconductivity associated with the suppression of the antiferromagnetism is one likely scenario [31] for unconventional superconductivity seen in iron pnictides, but the identification of the mechanism is far from settled [63; 79]. The difficulty in examining the SC mechanism could arise from complexity in the materials that can lead to ambiguous interpretations; e.g., non-universal SC gap functions and limited sample quality. It is thus essential to find a suitable model system to examine the mechanism of superconductivity. We consider that $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is an ideal system to investigate relationship between magnetism and superconductivity since isovalent P substitution is not expected to add carriers [83].

We have performed ^{31}P -NMR measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.2 \leq x \leq 0.64$ in order to investigate their normal-state spin dynamics. Samples of a mosaic of single crystals were prepared as described in Sec. 3.3. The dHvA experiments observed signals in single crystalline samples from the same batch as $x = 0.41, 0.56$, and 0.64 , indicating the excellent quality of our samples [90]. The high quality of our samples is also suggested by the sharp SC transitions [83]. ^{31}P -NMR spectra were obtained by sweeping frequency in a fixed magnetic field of 4.12 T. Each spectrum consists of a single line, ruling out microscopic inhomogeneity caused by P substitution. The Knight shift K was determined with respect to the ^{31}P -signal of the reference material H_3PO_4 . The ^{31}P nuclear spin-lattice relaxation rate $1/T_1$ was determined by fitting the time dependence of spin-echo intensity after saturation of nuclear magnetization to a theoretical $I = 1/2$ curve with a single component of T_1 .

K , which measures the effective field at the nucleus produced by electrons, is described as $K = K_{\text{spin}} + K_{\text{chem}}$; K_{spin} is the spin part of K and is related to the uniform spin susceptibility $\chi(\mathbf{q} = 0)$, which is proportional to the density of states (DOS) at the Fermi energy $N(E_F)$. K_{chem} is the chemical shift, which is unrelated to $\chi(\mathbf{q} = 0)$, and is estimated to be ~ 0.018 % as follows. Since no obvious AFM fluctuations were detected by NMR at high temperatures as seen in Fig. 4.4(b), it would be a good approximation to assume that $(T_1T)^{-1/2}$ is proportional to $N(E_F)$ at high temperatures, i.e. to assume that the usual Korringa relation holds at 270 K. Based on the plot of $(T_1T)^{-1/2}$ against K at 270 K for different x shown in the inset of Fig. 4.4(a), we can estimate K_{chem} as the intercept assuming that K_{chem} is x -independent. The obtained K_{chem} is 0.018 ± 0.019 %, indicating that K_{spin} accounts for 86 % of the observed Knight shift for $x = 0.33$. Note that this K_{chem} would be a reasonable value, since the chemical shift for ^{31}P in many diamagnetic insulators is of the order of some hundreds of ppm, which is comparable to this K_{chem} [140]. By assuming $K_{\text{spin}} \propto \chi(\mathbf{q} = 0) = 2\mu_B^2 N(E_F)$, the P-substitution dependence of K_{spin} at 270 K suggests that the change in $N(E_F)$ would be at most 10 % for $x \leq 0.64$, which is quantitatively consistent with the result of our band calculation discussed in Appendix D.

As shown in Fig. 4.4(a), K is almost temperature independent for $x \leq 0.56$, and that the absolute value of K in the normal state decreases only slightly upon P substitution. These data indicate that P substitution does not produce significant changes in $\chi(\mathbf{q} = 0)$ and $N(E_F)$. This is in stark contrast to carrier-doped iron-pnictide superconductors as discussed in Appendix D. Large changes in FSs via charge-carrier doping thus necessarily involve dramatic modification in the DOS and FS nesting resulting in changes in spin fluctuations. In addition to possible changes in T_c due to the modification of spin excitation spectrum [153], drastic changes in $N(E_F)$ can also affect severely T_c [154], and the suggested giant magnetoelastic coupling may lead to

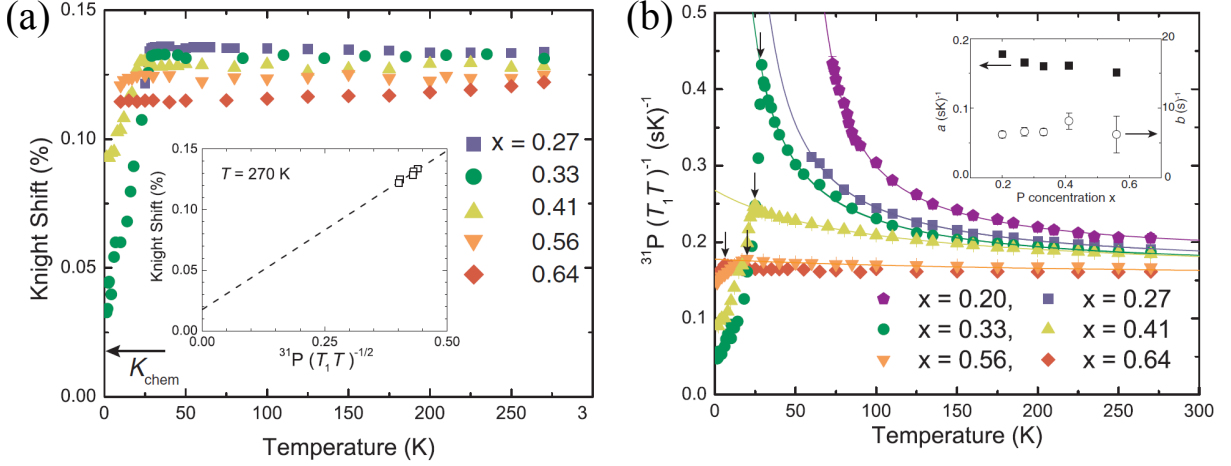


Figure 4.4: (a) P substitution evolution of ^{31}P Knight shift determined by the spectral peak in the field of 4.12 T. The arrow indicates the chemical shift K_{chem} . The abrupt decrease in K at low temperatures is due to the onset of superconductivity. Inset: $^{31}\text{P} K$ vs $^{31}\text{P} (T_1 T)^{-1/2}$ at 270 K for different P concentrations x . (b) The ^{31}P nuclear spin-lattice relaxation rate divided by temperature $(T_1 T)^{-1}$ for BaFe₂(As_{1-x}P_x)₂ at 4.12 T. Solid lines represent fits to $(T_1 T)^{-1} = a + b(T + \theta)^{-1}$. As AFM fluctuations are suppressed as inferred from the suppression of $(T_1 T)^{-1}$, T_c (denoted by arrows) also decreases. Inset: The fitting parameters a and b are plotted against P concentration x . The a and b weakly depend on x , but θ shows a strong x dependence. The small value of θ at $x = 0.33$ ($\theta \sim 0$) are insensitive to the fitting parameters of a and b . These figures are taken from Ref. [100].

further suppressions of T_c [155]. Therefore, the decrease in $N(E_F)$ as well as the suppression of spin fluctuations should be taken into account for the interpretation of possible changes in T_c for electron-doped Ba(Fe_{1-y}Co_y)₂As₂. In contrast, the nearly unperturbed K_{spin} by isovalent P-doping demonstrates that BaFe₂(As_{1-x}P_x)₂ is an ideal model system to test the relevance of spin fluctuations to superconductivity.

Significant low-energy AFM fluctuations are probed near the maximum T_c via $1/T_1$. The Korringa law $T_1 T K^2 = \text{const.}$ generally holds in a Fermi-liquid (FL) state, but is inapplicable to BFAP near the AFM phase since Curie-Weiss (CW) behavior is observed in $(T_1 T)^{-1}$. For $x = 0.33$, $(T_1 T)^{-1}$ increases significantly down to T_c whereas the Knight shift is constant. These $(T_1 T)^{-1}$ and K data demonstrate convincingly that AFM fluctuations with finite $\mathbf{q}$ continue to grow down to T_c at optimal doping.

The AFM spin fluctuations in BaFe₂(As_{1-x}P_x)₂ are enhanced significantly as the P concentration is reduced towards the maximum T_c ($x \simeq 0.33$), as evidenced by the rapid increase in $(T_1 T)^{-1}$ from conventional FL behavior at $x = 0.64$, where $(T_1 T)^{-1}$ and K are almost constant. The crossover from FL to CW behavior in $(T_1 T)^{-1}$ correlates perfectly with the change in the resistivity results [83]. As the system evolves from a FL ($x = 0.71$) towards the maximum T_c ($x = 0.33$) near the AFM phase, the temperature dependence of the resistivity changes from T^2 - to T -linear, one hallmark of non-FL behavior. The exponent of the temperature dependence of the resistivity is shown as a contour plot in Fig. 4.5. Specifically, the CW behavior of $(T_1 T)^{-1}$ and the T -linear resistivity at $x = 0.33$ can be explained by the existence of 2D AFM spin fluctuations in the theory of nearly AFM metals [156]. Indeed, the evolution of the AFM spin excitations measured by $(T_1 T)^{-1}$ upon P substitution can be fit consistently by the equation expected from the same theory [156], $(T_1 T)^{-1} = a + b(T + \theta)^{-1}$ (see solid lines in Fig. 4.4(b)). Such 2D AFM fluctuations were experimentally observed in the parent BaFe₂As₂

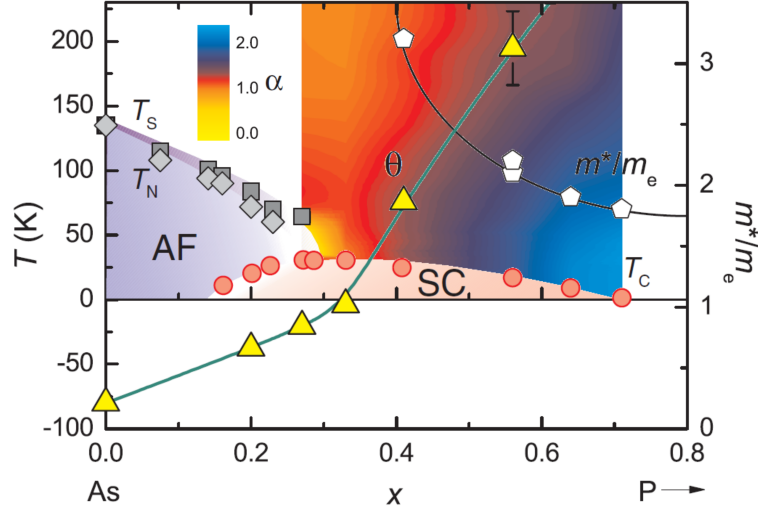


Figure 4.5: Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Colors represent the exponent of the temperature dependence of resistivity at zero magnetic field, $\alpha = d(\ln \Delta\rho_{ab})/d(\ln T)$ in Ref. [83], where $\Delta\rho_{ab} = \rho_{ab} - \rho_{ab}(T \rightarrow 0 \text{ K})$. The triangles represent θ obtained by fitting $(T_1T)^{-1}$ data to the equation, $(T_1T)^{-1} = a + b(T + \theta)^{-1}$. T -linear resistivity, suggesting quantum-critical behavior, is observed in proximity to a magnetic instability signaled by $\theta \sim 0$ at $x = 0.33$. These quantum-critical fluctuations are found to correlate with the enhancement of the effective mass as denoted by the pentagons [90]. These figures are taken from Ref. [100].

via neutron scattering experiments [157]. According to band calculations [103], substantial 2D AF fluctuations can be generated by the interband spin excitations between the multiple FSs predominantly derived from Fe d electrons.

Our central finding in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is that the 2D AFM fluctuations of a quantum-critical nature have a clear correlation with the enhancement of quasiparticle effective mass and T_c as summarized in Fig. 4.5. We found that the Weiss temperature θ obtained from the fitting increases with P substitution and becomes almost zero near $x = 0.33$ where the maximum T_c is achieved. $\theta = 0 \text{ K}$ implies that the dynamical susceptibility probed by the $(T_1T)^{-1}$ measurement diverges at absolute zero, or that the magnetic correlation length continues to increase down to $T = 0 \text{ K}$. Our result thus strongly suggests the presence of an AFM QCP near the maximum T_c in proximity to the AFM phase boundary. As the P concentration is varied towards optimal doping ($x \sim 0.33$) from $x = 0.64$ where the FL state is observed, the magnetic fluctuations become dramatically enhanced as θ decreases. Importantly, the quasiparticle mass and T_c increase as θ approaches 0 K. This strongly suggests that the AFM quantum-critical fluctuations lead to strong mass renormalization and unconventional superconductivity. Our systematic NMR measurements, which are compared with transport measurements, thus provide the first evidence that the quasiparticle mass enhancement is strongly coupled to the AFM quantum-critical fluctuations in iron-pnictide superconductors as previously observed in heavy fermion systems [158]. Furthermore, since $N(E_F)$ generally correlates with T_c in conventional BCS superconductors, the enhancement of T_c with approaching the QCP from the overdoped side cannot be accounted for by a nearly unperturbed $N(E_F)$, demonstrating clearly that superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is tuned predominantly by the AFM fluctuations. Therefore, we conclude that the 2D AFM quantum-critical fluctuations are likely to play a central role in the occurrence of unconventional superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

Previous NMR measurements also indicated that there is a strong connection between low-

energy spin fluctuations and superconductivity in 122 [146], 111 [159; 160], and 11 iron-based superconductors [161; 162; 163; 164]. These suggest that the relevance of spin fluctuations to the high- T_c superconductivity is universal despite the non-universal gap structure. The strong connection would be naturally understood if one considers the superconductivity observed near magnetic phase and the well-nested hole and electron FSs. By contrast, our group reported that the connection is relatively weaker in $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ [75; 165; 166]. Such a weak link may originate from much lower T_c of 26 K in $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ than that of $\text{RFeAs}(\text{O}_{1-x}\text{F}_x)$ ($R = \text{Ce, Pr, Sm, etc.}$). However, it remains unresolved whether spin fluctuations are also important for high- T_c superconductivity in the 1111 system with T_c exceeding 50 K, since magnetic rare-earth atoms R hinder quasiparticle excitations responsible for superconductivity [167]. Therefore, examinations of the connection between magnetic fluctuations and superconductivity of high- T_c 1111 iron pnictides would be crucial for establishing general view of iron-pnictide superconductivity.

4.2.2 Analysis of Normal-State Spin Dynamics Based on Spin-Fluctuation Theory

We analyze experimental results of the $(T_1T)^{-1}$ data of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ in more detail based on the self-consistent renormalization (SCR) theory of spin fluctuations, since this system is suggested to be close to an AFM QCP [100]. The SCR theory, developed by Moriya and co-workers, has been applied for weak ferromagnetism and antiferromagnetism of d -electron itinerant magnets, and succeeded in characterizing properties of spin fluctuations. As recent studies have shown the importance of both the itinerant and localized nature of the magnetism of iron pnictides [168; 169; 170; 171], it is important to show to what extent experimental results are understood within an itinerant and local-moment picture.

Outline of the Self-Consistent Renormalization Theory

The SCR theory gives quantitative relations between dynamical susceptibility and physical properties. In nearly and weakly AFM metals, dynamical susceptibility above T_N for a wave vector near the AFM ordering vector $\mathbf{Q}$ may generally be written as follows:

$$\chi(\mathbf{Q} + \mathbf{q}, \omega) = \frac{\chi(\mathbf{Q} + \mathbf{q})}{1 - i\omega/\Gamma_{\mathbf{Q}+\mathbf{q}}} = \chi(\mathbf{Q} + \mathbf{q}) \left(\frac{\Gamma_{\mathbf{Q}+\mathbf{q}}}{\omega^2 + \Gamma_{\mathbf{Q}+\mathbf{q}}^2} + i \frac{\omega \Gamma_{\mathbf{Q}+\mathbf{q}}}{\omega^2 + \Gamma_{\mathbf{Q}+\mathbf{q}}^2} \right), \quad (4.11)$$

with

$$\chi(\mathbf{Q} + \mathbf{q})^{-1} = \chi(\mathbf{Q})^{-1} + Aq^2, \quad \Gamma_{\mathbf{Q}+\mathbf{q}} = \Gamma(\kappa^2 + q^2), \quad \kappa^2 = \frac{1}{A\chi(\mathbf{Q})}, \quad (4.12)$$

where $\kappa^{-1} \equiv \xi_T$ is the temperature-dependent magnetic correlation length, and A and Γ are temperature-independent constants, which are the fundamental parameters of the theory. Using the above relations, the dynamical spin susceptibility $\chi''(\mathbf{Q}, \omega)$ is written as

$$\begin{aligned} \chi''(\mathbf{Q} + \mathbf{q}, \omega) &= \chi(\mathbf{Q} + \mathbf{q}) \frac{\omega \Gamma_{\mathbf{Q}+\mathbf{q}}}{\omega^2 + \Gamma_{\mathbf{Q}+\mathbf{q}}^2} = \frac{\chi(\mathbf{Q}) \kappa^2}{\kappa^2 + q^2} \frac{\omega \Gamma(\kappa^2 + q^2)}{\omega^2 + [\Gamma(\kappa^2 + q^2)]^2} = \frac{\Gamma}{A} \frac{\omega}{\omega^2 + [\Gamma(\kappa^2 + q^2)]^2} \\ &= \frac{\pi \frac{\Gamma q_B^2}{2\pi}}{\frac{A q_B^2}{2}} \frac{\omega}{\omega^2 + \left[2\pi \frac{\Gamma q_B^2}{2\pi} \left(\frac{\kappa^2}{q_B^2} + \frac{q^2}{q_B^2} \right) \right]^2} = \frac{\pi T_0}{T_A} \frac{\omega}{\omega^2 + \left\{ 2\pi T_0 \left[y + \left(\frac{q}{q_B} \right)^2 \right] \right\}^2}, \end{aligned} \quad (4.13)$$

where q_B is the cutoff wave vector and has a relation of $s_0 q_B^2 / 4\pi = 1$ with s_0 being the area per magnetic atom in the 2D plane. In this formula, important spin-fluctuation parameters are the

following two characteristic temperatures,

$$T_0 = \frac{\Gamma q_B^2}{2\pi}, \quad T_A = \frac{A q_B^2}{2}, \quad (4.14)$$

which characterize the width of the spin excitation spectrum in frequency ω - and momentum $\mathbf{q}$ -space, respectively. The dimensionless inverse susceptibility $y(T)$ at $\mathbf{Q} = \mathbf{Q}_{\text{AFM}}$ of AFM wave vectors is defined as

$$y(T) = \frac{\kappa^2}{q_B^2} = \frac{1}{A\chi(\mathbf{Q})q_B^2} = \frac{1}{2T_A\chi(\mathbf{Q})}. \quad (4.15)$$

Here y_0 is the zero temperature limit of y , and characterizes the proximity to the magnetic instability. $y_0 = 0$ indicates an AFM QCP, where $\chi(\mathbf{Q})$ diverges down to zero temperature.

The staggered susceptibility or y is determined self-consistently from the relation of the mean square local amplitude of the zero point and thermal spin fluctuations, and is calculated from

$$y = y_0 + \frac{y_1 t}{2} \left\{ \phi\left(\frac{y}{t}\right) - \phi\left(\frac{y}{t} + \frac{1}{t}\right) \right\}, \quad (4.16)$$

where $t = T/T_0$, y_1 is the parameter which governs the mode-mode coupling of AFM spin fluctuations, and $\phi(x)$ is given as

$$\phi(x) = -\left(x - \frac{1}{2}\right) \log x + x + \log \Gamma(x) - \log \sqrt{2\pi}. \quad (4.17)$$

Now we can calculate $1/T_1$ by using Eq. (4.13) and neglecting the $\mathbf{q}$ dependence of $A_{\mathbf{q}}$ as follows [156]:

$$\frac{1}{T_1} = \frac{\gamma_N^2 T}{N_A} \lim_{\omega_0 \rightarrow 0} \sum_{\mathbf{q}} \frac{|A_{\mathbf{q}}|^2 \chi''(\mathbf{q}, \omega_0)}{\omega_0} = \frac{2\gamma_N^2 A_{\text{hf}}^2 T}{N_A} \sum_{\mathbf{q}} \frac{\pi T_0}{T_A \left\{ 2\pi T_0 \left[y + \left(\frac{q}{q_B}\right)^2 \right] \right\}^2} = \frac{\gamma_N^2 A_{\text{hf}}^2}{2\pi T_A} \frac{1}{\bar{T}_1}, \quad (4.18)$$

$$\frac{1}{\bar{T}_1} = 2 \frac{T}{T_0} \int_0^1 dx \frac{x}{(y + x^2)^2} = t \left(\frac{1}{y} - \frac{1}{y+1} \right), \quad (4.19)$$

Thus, $1/T_1$ directly measures the temperature dependence of $\chi(\mathbf{Q}) = [2T_A y(T)]^{-1}$.

In the framework of the SCR theory, a predominant contribution to the resistivity arises from the spin fluctuations with AFM wave vectors around $\mathbf{Q}_{\text{AFM}}$. The electrical resistivity in a electron system scattered by those spin fluctuations is calculated based on the Boltzmann equation and is given by [156]:

$$R(T) = r \bar{R}(T), \quad (4.20)$$

$$\bar{R}(T) = t \left[\phi\left(\frac{y}{t}\right) - \phi\left(\frac{y+1}{t}\right) \right] + y \left[\log\left(\frac{y}{t}\right) - \psi\left(\frac{y}{t}\right) \right] - (y+1) \left[\log\left(\frac{y+1}{t}\right) - \psi\left(\frac{y+1}{t}\right) \right], \quad (4.21)$$

where r is an adjustable fitting constant which represents the coupling between the spin fluctuations and conduction electrons, and $\psi(x)$ is the digamma function.

Application of SCR Theory to Experimental Results

Equations (4.18) and (4.19) only give the contribution of spin fluctuations around the AFM wave vector $\mathbf{Q}_{\text{AFM}}$. Although the AFM contribution around $\mathbf{Q}_{\text{AFM}}$ is expected to be predominant for the relaxation rate in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, there is an additional contribution arising from spin

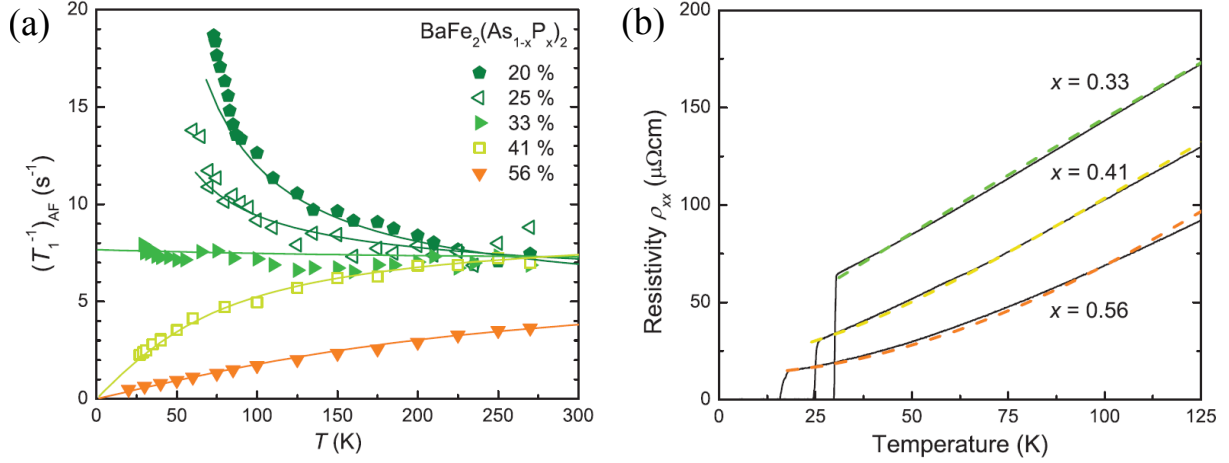


Figure 4.6: (a) The experimental and calculated relaxation rates arising from the $\mathbf{q} \sim \mathbf{Q}_{\text{AFM}}$ mode of spin fluctuations in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The data points represent the experimental data, while the solid lines indicate the calculated data using the SCR parameters listed in Table 4.1. (b) The experimental (Ref. [83]) and calculated electrical resistivity of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The solid lines represent the experimental data, while the dotted lines indicate the calculated data using the SCR parameters listed in Table 4.1. These figures are cited from Ref. [150].

fluctuations around $\mathbf{q} = 0$. The observed relaxation rate is thus decomposed into the following two components: $(T_1 T)^{-1} = (T_1 T)^{-1}_{\mathbf{q} \sim \mathbf{Q}_{\text{AFM}}} + (T_1 T)^{-1}_{\mathbf{q} \sim 0}$. Since the uniform susceptibility of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is almost temperature independent as shown in Fig. 4.4(a), the relaxation rate arising from the small- $\mathbf{q}$ fluctuations $(T_1 T)^{-1}_{\mathbf{q} \sim 0}$ is also expected to be temperature independent. In order to estimate $(T_1 T)^{-1}_{\mathbf{q} \sim 0}$, the observed $(T_1 T)^{-1}$ is fit by the CW-type equation $(T_1 T)^{-1} = a + b(T + \theta)^{-1}$. We relate the first constant term a with the $(T_1 T)^{-1}_{\mathbf{q} \sim 0}$ and estimated $(T_1 T)^{-1}_{\mathbf{q} \sim \mathbf{Q}_{\text{AFM}}}$ as shown in Fig. 4.6(a). The nearly constant $(T_1 T)^{-1}_{\mathbf{q} \sim \mathbf{Q}_{\text{AFM}}}$ of $x = 0.33$ suggests that y_0 is very close to zero at $x = 0.33$ [156]. For simulating the NMR data, we need to determine the SCR parameters y_0 , y_1 , T_0 , and T_A . These parameters can be estimated by the data of magnetic susceptibility and specific heat. In the framework of the SCR theory, we can relate the magnetic susceptibility to T_A using the following relation [172]:

$$T_A = \frac{0.75}{\chi} \quad (\text{in emu/mol}). \quad (4.22)$$

In order to determine T_A , we assume the magnetic susceptibility χ is proportional to K_{spin} . By using $\chi = 9.4 \times 10^{-4}$ emu/mol at 200 K and $\gamma = 27$ mJ/mol K² in BaFe_2As_2 [173; 174], we thus estimate the P concentration dependence of T_A . On the other hand, the characteristic spin-fluctuation energy T_0 can be estimated from specific heat experiment by using the following relation [172; 175]:

$$\gamma = \frac{6200}{T_0} (2x_c - \pi y_0^{-1/2}) \quad (\text{mJ/mol K}^2), \quad (4.23)$$

where x_c is the cutoff wave vector of which magnitude is the order of unity. Note that we used the first term for $y_0 < 0$ [172]. T_0 of $x = 0.33$ with $y_0 = 0$ can be estimated from reported specific heat experiments [108] by using Eq. (4.23). Assuming that the P concentration dependence of γ is identical to that of K_{spin} , which is the measure of the DOS at the Fermi energy, we can estimate γ for the other P concentrations and obtain the P concentration dependence of T_0 using Eq. (4.23). We here neglect the second term in Eq. (4.23) for simplicity.

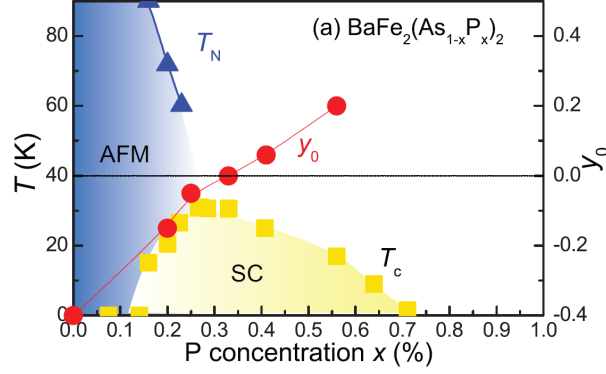


Figure 4.7: The phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with an SCR parameter y_0 .

By using the SCR parameters listed in Table 4.1, which are obtained from our simulation for NMR experimental results shown in Fig. 4.6(a), we calculated the temperature exponent of electrical resistivity. For 2D AFM fluctuations, a T -linear resistivity is expected near the QCP [176]. Away from the QCP, the temperature dependence of the resistivity crossovers to a FL-like T^2 as T decreases. The experimental data is actually consistent with the simulated temperature dependence as shown in Fig. 4.6(b).

According to the SCR theory, we can also estimate the in-plane spin correlation length $\xi(T)$ and the damping constant $\Gamma(T)$ from $(4\pi y)^{-1/2}$ and from $2\pi T_0 y$, respectively [177]. We calculated ξ/a and $\Gamma(T)$ at T_c for different P concentrations as shown in Table 4.1, which may be confirmed by future neutron scattering experiments. The y_0 increases with chemical substitution from a negative value in BaFe_2As_2 to nearly zero around an optimal concentration $x \approx 0.33$ as shown in Fig. 4.7(a). Since y_0 is a measure of the closeness to a QCP, this indicates that their optimal concentration corresponds to an AFM QCP and the closeness to the QCP is controllable by P substitution.

In order to understand a relationship between AFM spin fluctuations and superconductivity, we plot T_c against spin-fluctuation parameters T_0 and T_A of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ ¹ as well as those of unconventional superconductors in Fig. 4.8(a) and 4.8(b), respectively. Note that only optimal $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and nearly optimal $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ are plotted, since the (nearly) optimal samples are close to an AFM QCP [176; 180]. The linear scaling between the spin-fluctuation temperature T_0 and T_c in Ce-based heavy fermion (HF)

Table 4.1: The SCR parameters of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The in-plane spin correlation length ξ/a and damping constant Γ at T_c are also shown. Note that a is the in-plane lattice constant.

x	y_0	y_1	T_0 [K]	T_A [K]	$\xi(T_c)/a$	$\Gamma(T_c)$ [meV]
0	-0.4	8.0	460	800		
0.20	-0.15	15	760	1320		
0.25	-0.05	10	770	1340	3.0	3.7
0.33	0	8.0	780	1350	1.9	9.2
0.41	0.06	5.0	800	1390	1.1	27
0.56	0.2	6.0	850	1480	0.6	96

¹Following a similar procedure as in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, we analyzed the experimental data of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ taken from Refs. [153; 174; 178; 179].

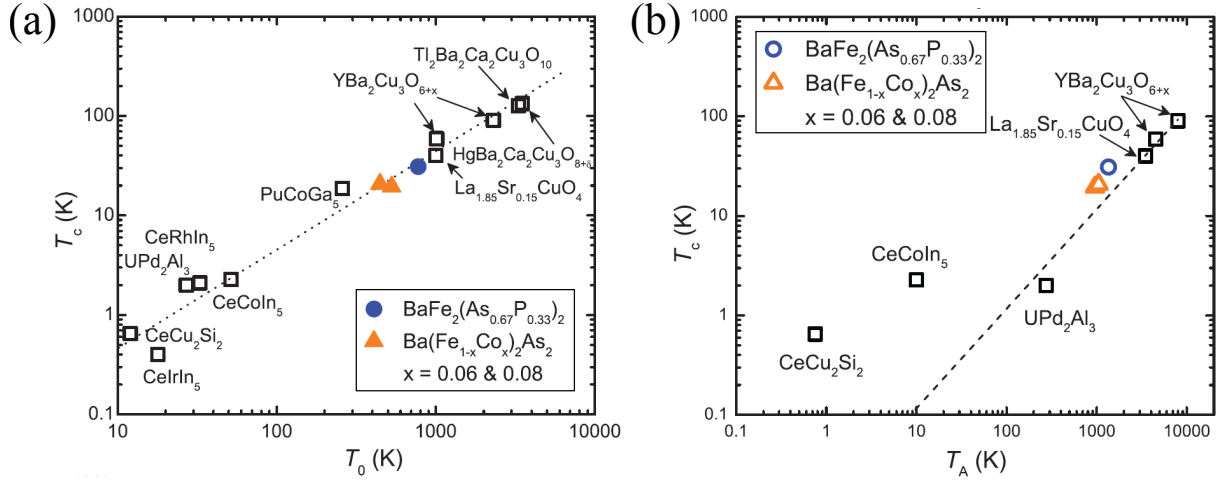


Figure 4.8: The SC transition temperature T_c vs the spin-fluctuation temperature (a) T_0 and (b) T_A for various superconductors. The data for T_c and T_0 were cited from Refs. [173; 175]. The dotted lines represent linear curve fittings. T_c is linear with T_0 , as suggested in Ref. [173], and the iron-pnictide superconductors lie on the same line. This might be the signature that unconventional superconductivity in iron-pnictides, heavy-fermions, and cuprates are mediated by AFM spin fluctuations.

superconductors and the cuprates was interpreted as an indication of spin-fluctuation mediated superconductivity in these unconventional superconductors and that a higher spin-fluctuation temperature can give rise to a pairing interaction and thus resulting in higher T_c [176; 180]. Interestingly, optimal $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ has a higher T_0 and T_c than $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, and these “122” iron-pnictide superconductors have intermediate values of T_0 and T_c among other unconventional superconductors. This suggests that the physics of “122” iron-pnictide superconductors may be more closely related to the physics of HF and cuprate superconductors than previously expected, and they may be classified into magnetically mediated superconductors. Moreover, only the optimal superconductivity lies on the curve. This suggests that quantum criticality is another important ingredient for an understanding of the linearity between spin-fluctuation temperature and T_c , as discussed in the HF superconductors such as CeMIn_5 [181; 182].

In addition, it is noteworthy that T_A is roughly scaled to T_c as shown in Fig. 4.8(b), and hence to T_0 . This implies that the spin-fluctuation spectra are renormalized with T_0 , where the renormalized $(T_1T)^{-1}$ of various unconventional superconductors approximately scales onto the same curve against T/T_c . Because T_c values in these superconductors are different by two orders of magnitude, the scaling of $(T_1T)^{-1}$ is surprising and suggests that spin fluctuation spectra are related to their unconventional superconductivity.

Possible Coupling between AFM Spin Fluctuations and Nematicity

Kasahara *et al.* reported from the torque magnetometry and precise x-ray measurements that the electronic fourfold symmetry is broken in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ below T^* that is much higher than T_S , and suggested the formation of an electronic nematic state below T^* [132]. We compare temperature and P concentration dependence of $(T_1T)^{-1}$ with the P concentration evolution of T^* in Fig. 4.9, where the values of $(T_1T)^{-1}$ are shown as a contour plot. It seems that $(T_1T)^{-1}$ starts to be enhanced approximately below T^* , particularly obvious in the low P concentration region. The enhancement below T^* can be understood by the fact that the development of

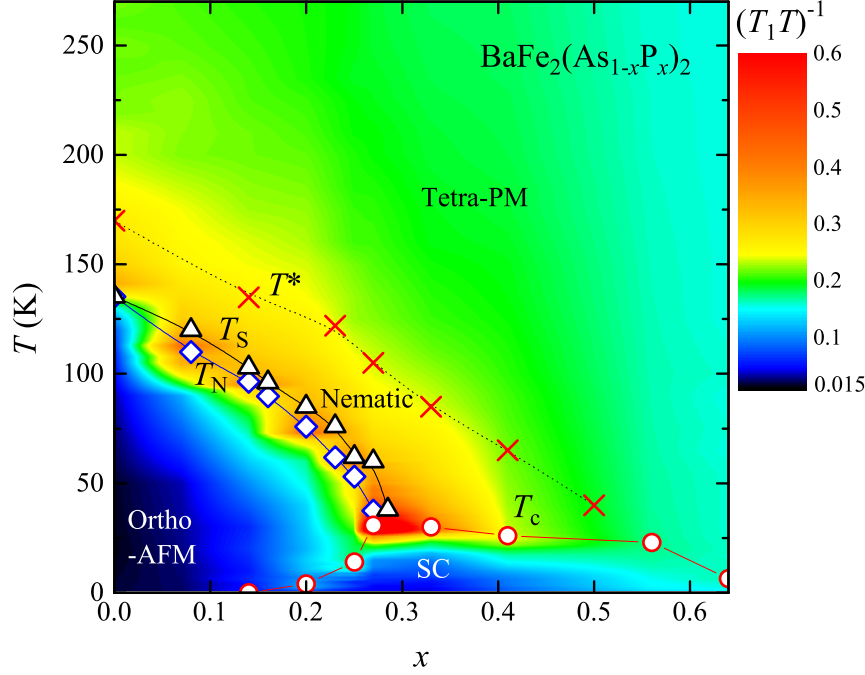


Figure 4.9: The nematic transition temperature T^* and $(T_1T)^{-1}$ are compared. The magnitude of $(T_1T)^{-1}$ is shown as a contour plot. $(T_1T)^{-1}$ seems to increase below T^* , particularly in the low P concentration, suggestive of a close relationship between T^* and AFM spin fluctuations.

the stripe AFM correlations should be determined by breaking the fourfold symmetry in the tetragonal phase, resulting in that the direction of the stripe correlations is fixed and that the correlation length is allowed to be extended more easily.

The iron-pnictide compounds are a unique system, where the spin and orbital degrees of freedom are strongly coupled with each other. Although we indicated here that the spin-fluctuation theory is successfully applicable to the 122 systems, the interplay between the spin fluctuation and the orbital degrees of freedom remains to be solved.

4.2.3 Superconducting State

The SC properties of optimally-doped $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ were investigated by ^{31}P -NMR measurements [146].

The inset in Fig. 4.10(a) shows ^{31}P -NMR spectra obtained by sweeping frequency at a fixed magnetic field of 4.12 T. The Knight shift K was determined with respect to a resonance line in H_3PO_4 ($K = 0$ in Fig. 4.10(a)). K is temperature independent ($K = 0.131 \pm 0.001$ %) in the normal state and decreases in the SC state. From the magnetic field dependence of K , we find that this decrease is dominated by the SC diamagnetic shift in the mixed state. The large SC diamagnetic shift prevents us from determining variations in the spin susceptibility in the SC state. The ^{31}P -NMR spectra show no evidence for AFM order at any temperature.

We observed a marked $^{31}(1/T_1)$ behavior, which is distinctly different from the other iron pnictides. Fig. 4.10(b) shows that $^{31}(1/T_1)$ decreases sharply just below T_c and there is no evidence for a coherence peak. We found $1/T_1 \propto T$ below ~ 4 K down to 100 mK, indicating the existence of a residual density of states (RDOS) at zero energy. Below about 10 K ($\sim 0.3T_c$), $1/T_1$ depends on the magnetic field (see Fig. 4.10(c)). By extrapolating to zero field, we still find $(T_1T)^{-1} = \text{const.}$ behavior below ~ 4 K, excluding the possibility that this behavior

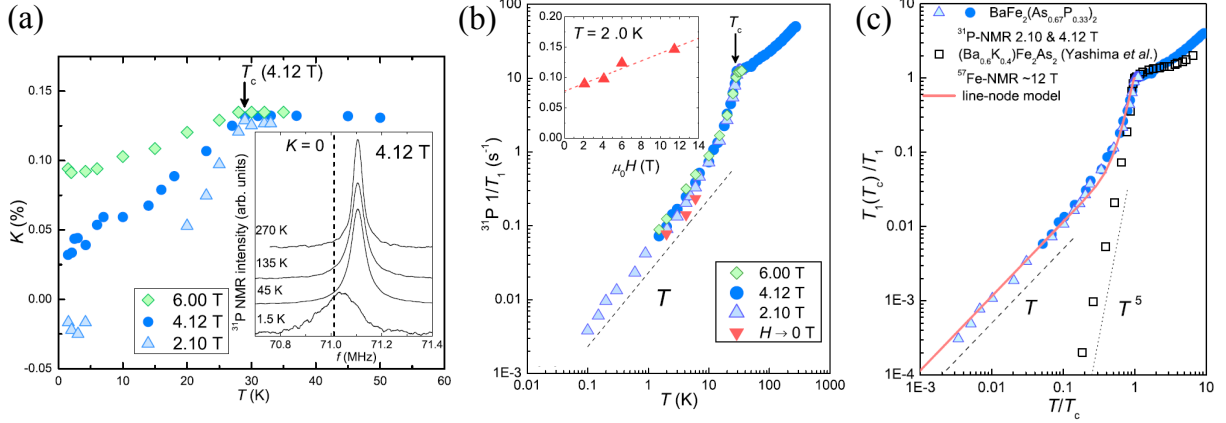


Figure 4.10: (a) ^{31}P Knight shift K for different magnetic fields. Inset shows ^{31}P -NMR spectra in 4.12 T. The spectra have been offset vertically. (b) ^{31}P $1/T_1$ under $\mu_0 H = 2.10, 4.12, 6.00$ T. Inset shows ^{31}P $1/T_1$ versus magnetic field at 2 K; a linear fit is used to extrapolate $1/T_1$ for $H \rightarrow 0$ T. (c) Normalized ^{31}P $1/T_1$ for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $(\text{Ba}_{0.6}\text{K}_{0.4})\text{Fe}_2\text{As}_2$ (Ref. [190]). The solid curve shows a calculation for a line-node gap function $\Delta(\phi) = \Delta_0 \sin 2\phi$ with $2\Delta_0 = 6k_B T_c$ and $N_{\text{res}}/N_0 = 0.34$.

originates in the applied fields. The existence of an RDOS in $H \rightarrow 0$ inferred from NMR is consistent with thermal-conductivity results on $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ that revealed a finite thermal conductivity divided by temperature κ_0/T at $T \rightarrow 0$ K under zero field [103]. There are two possible contributions to the field dependence of $1/T_1$ arising from quasiparticle excitations in the mixed state: localized quasiparticles inside vortex cores and delocalized quasiparticles originating from nodes in the SC gap. Since the applied fields are much smaller than $H_{c2} \approx 52$ T, localized quasiparticles inside vortex cores are unlikely to contribute to the relaxation at these fields ($H/H_{c2} \leq 0.22$). In fact, the thermal-conductivity measurements also show a sizable field dependence of $\kappa_0(H)/T$ at low fields, attaining nearly 70 % of the normal-state value even at $0.2H_{c2}$, indicative of the predominance of delocalized quasiparticles. These results suggest that the field dependence of $1/T_1$ is attributable to the contribution from delocalized quasiparticles originating from nodes in the gap, compatible with the existence of an RDOS in the SC state. The existence of an RDOS in the SC state of $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ differs strikingly from the other iron arsenides, including “1111” [64; 75; 142; 165; 183; 184; 185; 186] and “122” superconductors [187; 188; 189; 190], instead resembling the cuprates and heavy fermion superconductors, which have nodes in their SC gaps.

As shown in Fig. 4.10(c), $1/T_1$ of ^{57}Fe in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ near optimal doping exhibits a T^5 -like dependence well below T_c [190]. The fairly large exponent of ~ 5 in $1/T_1$ can be understood by a fully gapped state in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$, and was analyzed in terms of $s\pm$ -wave superconductivity with two gaps [190]. In the $s\pm$ models with unitary scatterings, in-gap states at zero energy can be induced without severely reducing T_c and can in principle account for the $1/T_1 \propto T$ behavior. However, the penetration depth $\Delta\lambda(T) \propto T$ at low temperatures observed in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ is incompatible with these models [191; 192], but is consistent with line nodes in the gap [103]. In a symmetry-imposed nodal superconductor such as described by a line-node model $\Delta = \Delta_0 \sin 2\phi$, $1/T_1 \propto T^3$ in the clean limit, but impurity scattering induced near gap nodes gives rise to an enhanced $1/T_1$ that is proportional to temperature at low temperatures [193]. P dopants in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ can provide a source for nonmagnetic scatterers, consistent with the existence of Fermi-level DOS. In fact, the $1/T_1$ data of $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ are well fit by the line-node model with $2\Delta_0/k_B T_c = 6$ and $N_{\text{res}}/N_0 = 0.34$, where N_{res}/N_0 is the

ratio of an RDOS in the SC state to that in the normal state (see Fig. 4.10(c)). Therefore, NMR, penetration-depth, and thermal conductivity results on $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ are consistent with the existence of line nodes in the SC gap. In the case of nodes imposed by symmetry, an RDOS at zero energy is a natural consequence of the impurity scattering that broadens the nodes. However, this is not clear for the case of “accidental” nodes not imposed by symmetry, as in the extended s -wave case because impurity scattering will lift the nodes and produce a more isotropic gap [194]. Our experimental findings impose significant constraints on candidate theoretical descriptions of iron pnictide superconductivity.

The strikingly different behavior of $1/T_1$ in the SC state between $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ is surprising because they have comparable T_c values and similar FSs. This implies that high- T_c superconductivities with and without nodes are nearly degenerate and that subtle differences can significantly modify the nature of superconductivity [32; 32; 194; 195; 196]. Changes in the pnictogen height may lead to nodal superconductivity, but its T_c should be much lower than that of fully gapped $s\pm$ states [32]. However, this is not the case in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$. One notable difference inferred from band structure calculations [83; 103] is that $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ is more 3D than $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$, suggesting that a 3D model is required. Reconciling their comparable T_c values and fundamentally different SC gap functions needs further theoretical and experimental works.

4.3 Summary of Previous Studies

A high-quality single crystal of BaFe_2As_2 have been investigated by ^{75}As -NMR by Kitagawa *et al* [36]. The spin structure in the AFM ordered phase is determined to be of stripe type from the NMR spectra. The substantial symmetry change of the EFG tensor at the As nuclei at the magneto-structural transition indicates drastic change of the charge distribution associated with the hybridization of Fe-3*d* and As-4*p* orbitals in spite of the apparently small orthorhombic crystal distortion. The EFG shows strong temperature dependence even within the tetragonal phase, indicating continuous change of the local charge distribution. $(T_1T)^{-1}$ shows distinct behavior for different field orientations. The enhancement of $(T_1T)^{-1}$ for $H \perp c$ with decreasing temperature implies development of stripe AFM fluctuations, which is anisotropic in spin space. Since the stripe AFM order appears by a first-order transition, persistence of such fluctuations in the PM phase is unexpected.

The ^{31}P -NMR measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with various P-doping levels reveal that 2D AFM spin fluctuations are notably enhanced with little change in static susceptibility on approaching the AFM ordered phase from the SC dome, and that magnetically ordered temperature θ deduced from $(T_1T)^{-1}$ vanishes at optimal doping. These results strongly indicate the presence of an AFM QCP, and suggest that the AFM spin fluctuations with the quantum critical character play a central role in the high- T_c superconductivity.

Moreover, we show that the temperature dependence of the nuclear spin-lattice relaxation rate and the electrical resistivity in the PM phase of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ can be understood quantitatively in the framework of the SCR theory. A consistent description of these physical properties of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ based on the SCR theory suggests that an itinerant picture is at work for the “122” iron-pnictide superconductors at the low-energy scale and AFM quantum criticality would be deeply related to the high- T_c superconductivity. We suggest that $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ shares the commonality with heavy-fermion superconductors which are also in the proximity of magnetic ground states.

The $1/T_1$ result in the SC state on $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ shows the existence of an RDOS at zero energy, which is consistent with the presence of nodes in the SC gap also inferred from a field dependence of $1/T_1$ and the experimental results of thermal conductivity and penetration-depth.

Chapter 5

Evolution of Antiferromagnetism toward Quantum Critical Point in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

In this chapter, we report ^{31}P -NMR measurements in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.07 \leq x \leq 0.33$ that bring direct evidence of the existence of an AFM QCP. The central result of this systematic investigation is that an AFM order parameter at the zero-temperature limit evaluated from above T_c successively decreases upon P substitution toward $x \sim 0.35$. This verifies the existence of an AFM QCP at $x \sim 0.35$ by the physical parameter tuning at zero-temperature. The present results together with the effective mass enhancement [90] and the temperature dependence of resistivity and $1/T_1T$ in the normal state [83; 100] establish $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ as one of the most accessible systems for unraveling the nature of quantum criticality and the relationship between quantum criticality and unconventional superconductivity.

5.1 Motivation

The relationship between magnetism and superconductivity is one of the central topics in condensed-matter physics, because unconventional superconductors have been discovered near a magnetic phase. One of the promising theories for unconventional superconductivity is the pairing induced by AFM spin fluctuations [156; 197]. In this scenario, T_c becomes highest when the system locates at around an AFM QCP where the AFM ordering occurs at $T = 0$ K, since the AFM fluctuations are strongest above the QCP. Since very clean single crystals are available in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system [83; 90], it is a suitable system to study intrinsic physics of iron pnictides. In our previous NMR results on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, the temperature dependence of the nuclear spin-lattice relaxation rate divided by temperature $1/T_1T$ in the normal state has suggested the existence of a QCP at $x \sim 0.35$ where T_c takes almost the maximum [100]. Observed anomalous T -linear resistivity at $x = 0.33$ [83] and an increase in the quasiparticle effective mass toward $x \sim 0.33$ [90] are also characteristic phenomena of the systems in proximity to a QCP [158; 198]. However, these experimental results are based on the normal state physical properties, which are relatively indirect to prove the existence of a QCP. To establish the presence of a QCP, experimental evidence of a second-order quantum phase transition of an order parameter as a function of tuning parameter at the zero-temperature limit is indispensable and could be more direct evidence.

5.2 ^{31}P -NMR Measurements of Underdoped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

We used mosaics of single crystals of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $x = 0.07, 0.14, 0.20, 0.25, 0.27$, and 0.33 . The details of these samples are described in Sec. 3.3. ^{31}P -NMR spectra are obtained at a fixed frequency of 71 MHz by sweeping magnetic field around 4.12 T.

Figure 5.1 shows the temperature evolution of ^{31}P -NMR spectra for $x = 0.07 - 0.27$. The single sharp spectra were observed above each T_N . No remarkable differences between the spectra of $T \geq T_S$ and $T_S \geq T \geq T_N$ were detected within our experimental resolution, where T_S was deduced from a concave kink in the T dependence of resistivity [83]. The Knight shift is almost unchanged with respect to temperature and x in the normal state [199]. In contrast, each of NMR spectra for $x = 0.07 - 0.27$ becomes broadened and its intensity decreases when the system sets in the AFM state below T_N . In the parent BaFe_2As_2 , Fe ordered moments lying in the ab plane with the stripe correlation induce internal magnetic field H_{int} along the c -axis at the As site due to the off-diagonal terms of the hyperfine coupling tensor [36]. In such a commensurate AFM ordered state with a homogeneous amplitude of internal field H_{int} at the P site, a powder pattern of $I = 1/2$ becomes nearly rectangular shape in case H_{int} is smaller enough than the applied magnetic field (see Appendix B for a mathematical proof). Such NMR spectra were actually observed in $x = 0.07$ and 0.14 at 1.5 K as well as the other iron pnictide $(\text{Ca}_4\text{Al}_2\text{O}_6)\text{Fe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.5 \leq x \leq 0.95$ [200]. However, the rectangular-shaped spectrum turns into a bell-shaped one at $x = 0.20$ and 0.25 , suggestive of a distribution of H_{int} [201]. In

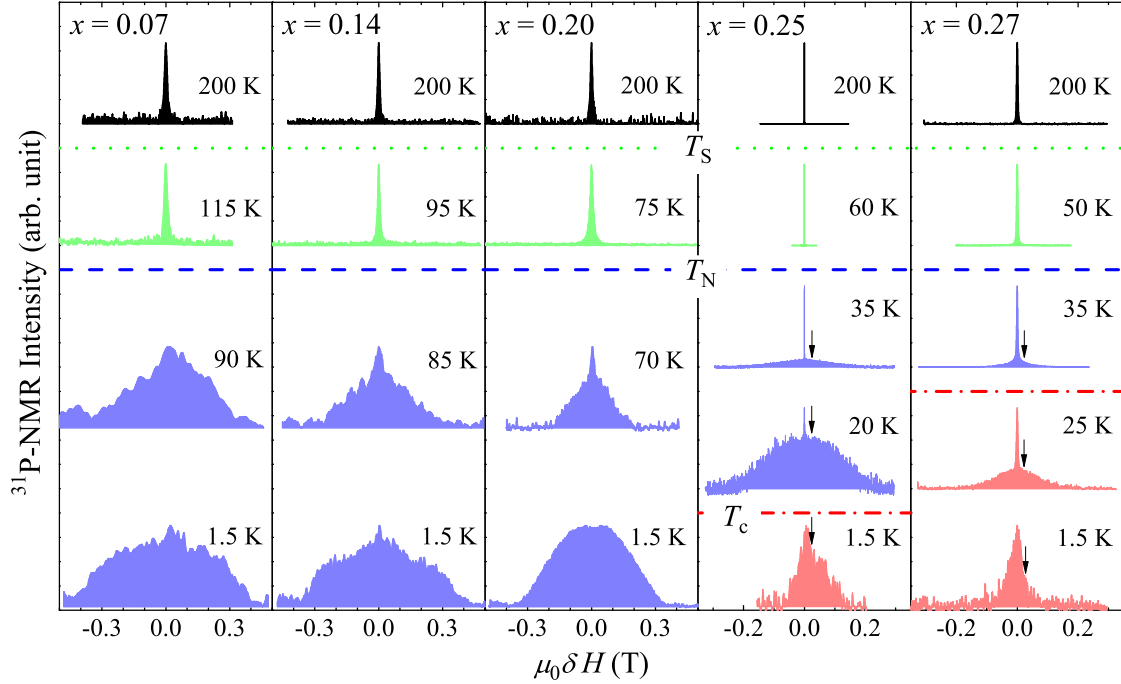


Figure 5.1: The temperature dependence of ^{31}P -NMR spectra for $x = 0.07 - 0.27$. The origin of the horizontal axis of each x is set to the temperature-independent peak field of the paramagnetic NMR spectra above T_c . The dotted, broken, and chain lines denote T_S , T_N , and T_c , respectively. The black arrows indicate the resonance field $\mu_0 H \sim 4.14$ T, where T_1 in magnetically ordered state is measured site-selectively.

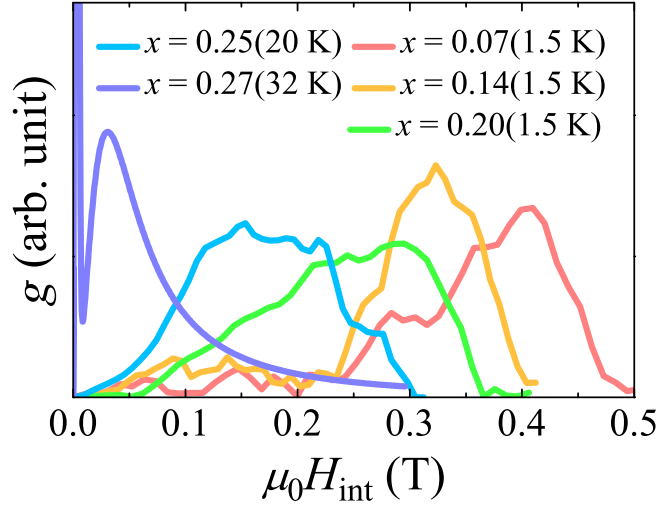


Figure 5.2: The distribution of magnetic volume fraction with H_{int} at the P site $g(H_{\text{int}})$ deduced from ^{31}P -NMR spectra of $x = 0.07, 0.14$, and 0.20 at 1.5 K, $x = 0.25$ at 20 K, and $x = 0.27$ at 32 K. $\mu_0 H_{\text{int}}$ -integral of each $g(H_{\text{int}})$ spectrum is normalized.

case of an incommensurate AFM order or stripe-type AFM order with distribution of ordered moments, H_{int} at the P site becomes inhomogeneous and the bell-shaped ^{31}P -NMR spectrum is observed, which is composed of a sum of the above commensurate AFM spectra with various internal fields (see Appendix C for detail). Therefore, the magnetic volume fraction g with H_{int} can be computed from an observed ^{31}P -NMR spectrum as follows:

$$g(H_{\text{int}}) \propto \left| \delta H \frac{d^{31}I(\delta H)}{d\delta H} \right| = \left| H_{\text{int}} \frac{d^{31}I(H_{\text{int}})}{dH_{\text{int}}} \right|, \quad (5.1)$$

where δH is a resonance field measured from the magnetic field of the temperature-independent paramagnetic ^{31}P -NMR spectra above T_N and $^{31}I(\delta H)$ is the ^{31}P -NMR intensity at δH . The positive (negative) δH corresponds to H_{int} ($-H_{\text{int}}$). Figure 5.2 shows $g(H_{\text{int}})$ obtained from the NMR spectra of $x = 0.07 - 0.27$ at low temperatures. In $x = 0.25$ and 0.27 , $g(H_{\text{int}})$ is obtained from the NMR spectra above T_c , since the averaged internal field decreases below the bulk T_c as discussed later. Figure 5.2 indicates that the average of internal field at the P site decreases, but its distribution seems to increase with increasing x . Such changes might be caused by the change of spin structure from a commensurate to an incommensurate type and/or disorder introduced by the P substitution.

Next, we estimate the average of the internal field at the P site $\langle H_{\text{int}} \rangle$ from each spectrum in the magnetically ordered state of Fig. 5.2 in order to discuss the development of an AFM order parameter. $\langle H_{\text{int}} \rangle$ is calculated as the first moment of each volume fraction spectrum $g(H_{\text{int}})$:

$$\langle H_{\text{int}} \rangle = \frac{\int_0^\infty H_{\text{int}} g(H_{\text{int}}) dH_{\text{int}}}{\int_0^\infty g(H_{\text{int}}) dH_{\text{int}}} = \frac{\int_0^\infty H_{\text{int}}^2 dI}{\int_0^\infty H_{\text{int}} dI}. \quad (5.2)$$

$\langle H_{\text{int}} \rangle$ abruptly increases below T_N and saturates at low temperatures for $x \leq 0.20$, as shown in Fig. 5.3(a). The temperature dependence of $\mu_0 \langle H_{\text{int}} \rangle$ for $x \leq 0.20$ can be fit to a conventional behavior of an order parameter $c(T_N - T)^\alpha$. Note that the data of $x = 0.25$ and 0.27 used for

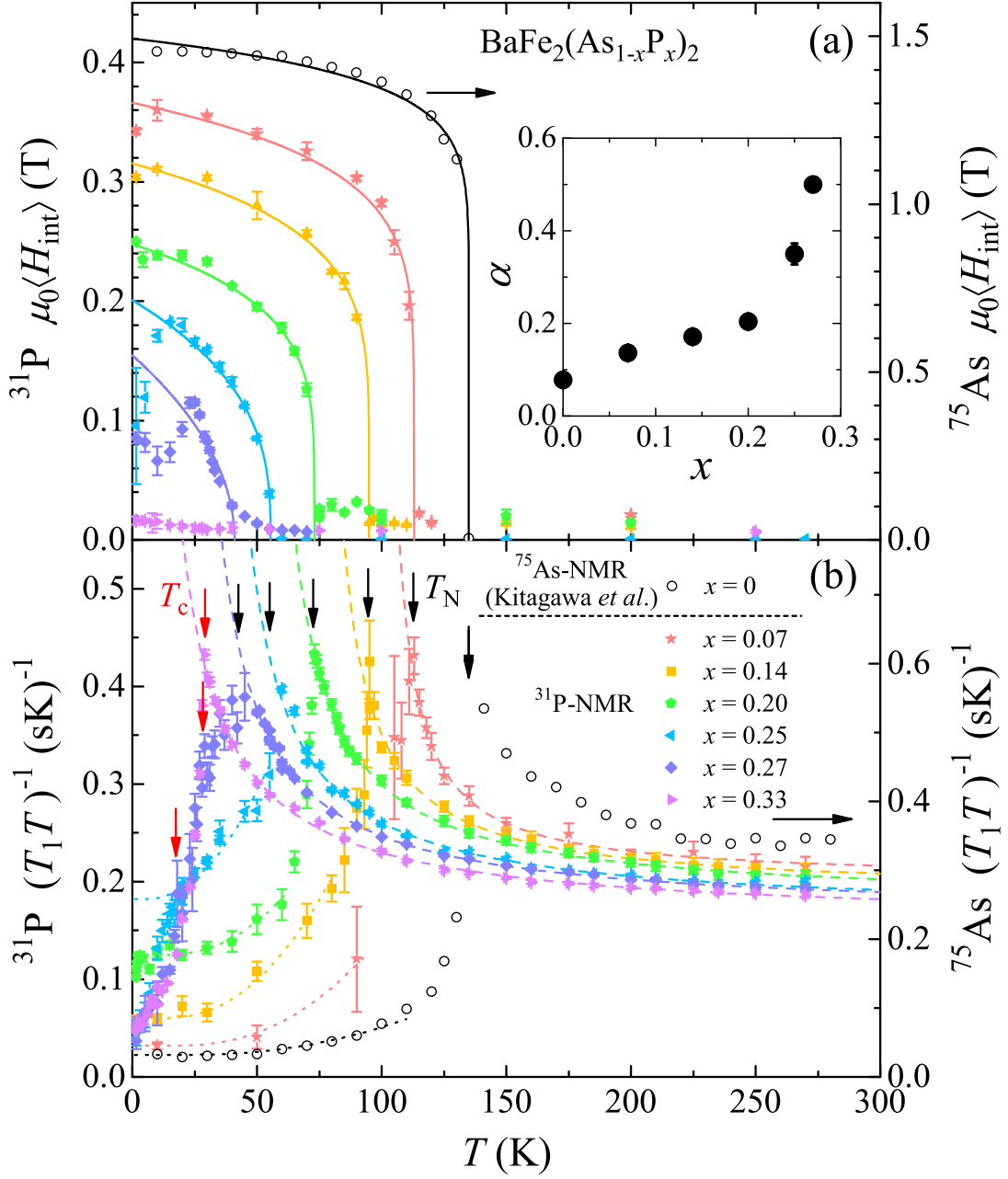


Figure 5.3: (a) The temperature dependence of the averaged internal magnetic field $\mu_0 \langle H_{\text{int}} \rangle$ at the P site. Internal magnetic field at the As site for $x = 0$ is plotted for comparison [36]. The solid line for each x is the fitting of the data below T_N to the phenomenological expression $c(T_N - T)^\alpha$. The inset shows x dependence of α . (b) The temperature dependence of ^{31}P $(T_1 T)^{-1}$ in $x = 0.07 - 0.27$ along with ^{75}As $(T_1 T)^{-1}$ in $x = 0$ [36]. The black and red arrows indicate T_N and T_c , respectively. The broken line for each x is the fitting of the plots to the expected equation for 2D AFM spin fluctuations: $(T_1 T)^{-1} = a + b/(T + \theta)$ [156]. For $x = 0.27$, the data above 65 K were used for the fitting. The dotted line for each x is the fitting of $(T_1 T)^{-1}$ below T_N to the phenomenological two-fluid model: $(T_1 T)^{-1} = C_{\text{inc}} + C_{\text{coh}} \Phi(k_B T / \Delta_S) / T$ (see text for detail) [152; 202]

Table 5.1: Critical exponent of the order parameter α in the different models [203].

Model	3D	2D
mean field Ising	$\frac{5}{16}$	$\frac{1}{8}$
Heisenberg	$\sim \frac{1}{3}$	No long range order

the fitting were restricted to ranges of $20 \text{ K} \leq T \leq 50 \text{ K}$ and $31 \text{ K} \leq T \leq 40 \text{ K}$, respectively, since the suppression of $\langle H_{\text{int}} \rangle$ was observed below T_c due to the competition between AFM and SC order parameters (see Sec. 6 for detail).

The experimentally determined critical exponent α is shown in the inset of Fig. 5.3. α depends on the dimensionality of the system, the symmetry of the order parameter, and the correlation length [203]. Theoretically expected values for α in each model are listed in Table 5.1. Since theories for critical phenomenon close to a phase transition point become more and more reliable with approaching the transition temperature, the critical exponent should be determined by fitting the experimental data of limited region close to the transition temperature. Unfortunately, the number and error bar of our data points are not good enough to determine α precisely. Thus, we used all the data points in AFM ordered state for fitting to roughly estimate α . For $x = 0$, experimental value $\alpha = 0.078$ is lower than 0.125 indicating the transition is almost first-order. This is consistent with the temperature hysteresis in the ^{75}As -NMR intensity observed in $x = 0$ (Fig. 5.4(a)). α increases up to ~ 0.5 with increasing x from 0 to 0.27, which suggests order of the phase transition changes from first- to second-order like. This is attributed to the separation of T_S and T_N , the evolution of dimensionality of FS from 2D to 3D and/or the decrease in magnetic correlation length. There is a possibility that the second-order character of magnetic phase transition is masked by the generally first-order structural phase transition due to its closeness. Wilson *et al.* discussed the critical exponent of AFM order parameter for various iron pnictides via elastic neutron scattering experiment in detail and concluded that the change of α is related to the separation of T_S and T_N [204]. In actual, $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ system shows simultaneous structural and magnetic transition ($T_S = T_N$) for $x = 0$, and they are gradually separated by the P substitution [83; 132].

To investigate the order of magnetic phase transition, we measured the temperature dependence of peak intensity of the ^{31}P -NMR spectrum for $x = 0.07, 0.14$, and 0.20 on cooling and warming (Fig. 5.4). A sharp decrease in the peak intensity due to magnetic broadening was observed at T_N for each x , whereas no appreciable hystereses exceeding an experimental error ($\Delta T \sim 0.5 \text{ K}$) were observed. These results are in contrast to the results of $x = 0$ [36] and indicate that the AFM transitions at T_N in $x = 0.07 - 0.20$ are almost the second-order transitions, consistent with the enhancement of α by P substitution.

The dynamics of magnetic properties can be probed by measuring the nuclear spin-lattice relaxation rate T_1^{-1} . The time dependence of spin-echo intensity $M(t)$ at the peak of NMR spectrum after saturation of nuclear magnetization can be fit to a theoretical curve of nuclear spin $I = 1/2$ with a single component of T_1 . However, for $x = 0.25$ and 0.27 , $M(t)$ at $T \lesssim 65 \text{ K}$ measured at the sharp peak deviates from the theoretical curves with a single T_1 component due to the inhomogeneity of samples originating from distribution of P concentration. Since the x dependence of T_N is quite steep at around $x \sim 0.26$, a slight distribution of P concentration may cause the phase separation around T_N , resulting in T_1 distribution at low T . Thus, T_1 for $x = 0.25$ and 0.27 in this report was measured site-selectively at the AFM region, which is 0.02 T higher than the sharp peak since the AFM region is dominant at low temperatures. The obtained relaxation curves in the AFM region were nicely fit with a single T_1 component down to the lowest temperature.

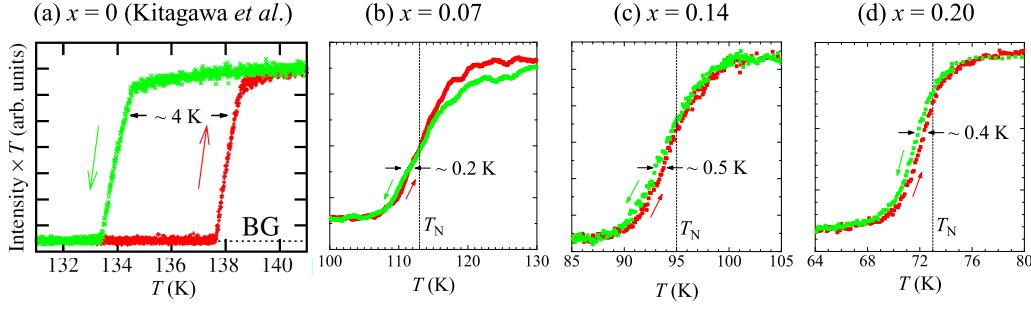


Figure 5.4: The temperature dependence of ^{31}P -NMR peak intensity multiplied by temperature for (a) $x = 0$ [36] (for comparison), (b) $x = 0.07$, (c) $x = 0.14$, and (d) $x = 0.20$. Red plots are obtained by T -warming sweep, while green plots are obtained by T -cooling sweep. The T -sweep rates are kept slower than 0.1 K/min for $0.07 \leq x \leq 0.20$.

The temperature dependence of $(T_1T)^{-1}$ is shown for each x in Fig. 5.3(b). Since $(T_1T)^{-1}$ is expressed by the wave-vector $\mathbf{q}$ -integral of the imaginary part of the dynamical susceptibility $\chi''(\mathbf{q}, \omega)$, the Curie-Weiss (CW) behavior of $(T_1T)^{-1}$ and the temperature-independent Knight shifts K related to $\chi(\mathbf{q} = 0)$ in the normal state indicate the development of low-energy AFM fluctuations [199]. On further cooling, the samples for $x = 0.07 - 0.27$ exhibit magnetic ordering, which is inferred from the peaks of $(T_1T)^{-1}$ at T_N due to critical slowing down of the stripe-type AFM spin fluctuations. In addition, $(T_1T)^{-1}$ in the $x = 0.25$ and 0.27 samples drops sharply at T_c due to the opening of SC gaps. CW behavior of $(T_1T)^{-1}$ is well fitted up to room temperatures by the equation anticipated for 2D AFM spin fluctuations, $(T_1T)^{-1} = a + b/(T + \theta)$, where the first term a is the intraband contribution proportional to the square of the density of states $N^2(E_F)$ and the second CW term is the contributions from the interband AFM spin fluctuations with a constant b and the characteristic temperature of AFM fluctuations θ [156]. The x dependence of the other parameters a and b are discussed more in detail in Appendix D.

As all five Fe $3d$ -bands cross the Fermi level, we investigate now how different parts of the FS evolve below T_N upon P substitution. $(T_1T)^{-1}$ data below T_N exhibit a strong temperature and x dependence (Fig. 5.3(b)). The observed suppression of $(T_1T)^{-1}$ below T_N is a consequence of the opening of the spin-density-wave (SDW) gap in the spin excitation spectrum. Nevertheless, $(T_1T)^{-1}$ does not approach zero at the lowest temperatures but it levels off at a finite value for each x , adopting a simple Korringa relation. This comes from the spin-lattice relaxation channel controlled by the gapless incoherent particle-hole excitations, which remains active down to the lowest temperatures. On the other hand, the temperature-dependent contribution to $(T_1T)^{-1}$ which vanishes at the lowest temperatures is from the gapped coherent spin wave excitations. Such two spin-lattice relaxation channels are proposed by Smerald *et al.* in their two-fluid description of magnetic excitations below T_N [152; 202] that gives

$$\frac{1}{T_1} = C_{\text{inc}}T + C_{\text{coh}}\Phi\left(\frac{k_B T}{\Delta_S}\right). \quad (5.3)$$

Here, Δ_S is an SDW gap in the spin excitation, $\Phi(x) = x^2\text{Li}_1(e^{-\frac{1}{x}}) + x^3\text{Li}_2(e^{-\frac{1}{x}})$ and $\text{Li}_n(z) = \sum_{k=0}^{\infty} z^k/k^n$ is the n -th polylogarithm of z . The first term, C_{inc} , describes the relaxation via the incoherent gapless particle-hole excitations, and is thus proportional to $N^2(E_F)$. The second term describes the relaxation via the coherent spin-wave excitations with dispersion

$\omega_{\mathbf{k}} = \sqrt{\Delta_S^2 + v_x^2 k_x^2 + v_y^2 k_y^2 + v_z^2 k_z^2}$ as found in neutron scattering experiments, where $\mathbf{v}$ is the spin-wave velocity. $(T_1 T)^{-1}$ below T_N are fitted to the above equation for $0.07 \leq x \leq 0.25$. The data in the limited temperature range $(T_c <) T < 0.8 * T_N$ are used for fitting after the fitting range adopted in Ref. [152; 202]. From the fitting, we can obtain three fitting parameters C_{inc} , C_{coh} , and Δ_S . A roughly linear decrease of the SDW gap value Δ_S against x is found (Fig. 5.3(b)), which is consistent with the linear decrease of T_N and $\langle H_{\text{int}} \rangle$. Results of the other two parameters are discussed in Appendix D

It should be noted that $\mu_0 \langle H_{\text{int}} \rangle$ at $T \rightarrow 0$ K is directly related to the AFM order parameter $\langle m \rangle$. We estimated $\langle m \rangle$ using the relation $\mu_0 \langle H_{\text{int}} \rangle = {}^{31}\text{A}_{\text{hf}} \langle m \rangle$, where ${}^{31}\text{A}_{\text{hf}}$ is the off-diagonal term of the hyperfine coupling tensor at the P site and is assumed to be independent of x . ${}^{31}\text{A}_{\text{hf}}$ is calculated to be $0.61 \text{ T}/\mu_B$ from the ordered moment of $x = 0.08$ ($0.60 \mu_B$) reported from the elastic neutron scattering measurements [205]. $\langle m \rangle$ at the ground state, deduced from extrapolating each fitting curve of $\mu_0 \langle H_{\text{int}} \rangle$ to $T \rightarrow 0$ K and the relationship between $\langle m \rangle$ and $\mu_0 \langle H_{\text{int}} \rangle$, is plotted against x in Fig. 5.5(b). $\langle m \rangle$ at $T \rightarrow 0$ K successively decreases from $x = 0.07$ to $x = 0.27$. In contrast to the pronounced increase in $\mu_0 \langle H_{\text{int}} \rangle$ below T_N for $x = 0.07 - 0.27$, only a slight increase due to SC diamagnetism is observed in $x = 0.33$, indicative of the absence of magnetic ordering.

In Fig. 5.5, we summarize our NMR data of the x dependence of θ , Δ_S , and $\langle m \rangle$ together with the $T - x$ phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. As shown in Fig. 5.5(b), $\langle m \rangle$ at $T \rightarrow 0$ K is systematically suppressed toward $x \sim 0.35$, suggestive of the existence of an AFM QCP at $x \sim 0.35$. Suppression of Δ_S toward $x \sim 0.35$ estimated from $(T_1 T)^{-1}$ in the AFM state could be supportive evidence of the QCP although error bars of the data points are large. These are also consistent with a sign-change of θ at $x \sim 0.35$, which indicates the existence of a QCP from the view of the normal-state spin dynamics [100]. All of these three parameters together with T_N changes linearly and vanish at $x \sim 0.35$, indicating that the phase transition as a function of P content x is second-order. Our NMR results clearly demonstrate that the AFM QCP is present at $x \sim 0.35$ and that P substitution for As acts as a tuning parameter for second-order quantum phase transition in BaFe_2As_2 . As pointed out previously [100], it is noteworthy that the maximum T_c is observed near the QCP, suggesting that the AFM quantum critical fluctuations play a vital role for the occurrence of unconventional superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The importance of AFM critical fluctuations for superconductivity appears to be a common feature of the “122” iron-pnictide superconductors, since a maximum T_c at around a doping level where T_N disappears was also reported in $\text{Ba}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2$ [153; 206].

It is noteworthy that the interplay between magnetism and superconductivity seems to be quite different between the “122” and “1111” superconductors. The importance of AFM fluctuations to superconductivity in “122” discussed above should be compared with a weak correlation between AFM spin fluctuation and superconductivity in “1111” [75; 166]. The phase diagrams of the “1111” iron-pnictide superconductors are essentially different from those of the “122” superconductors; T_S and T_N abruptly disappear as if structural and magnetic transitions are the first-order transition and superconductivity appears suddenly in $\text{LaFeAsO}_{1-x}\text{F}_x$ [207; 208]. Furthermore, superconductivity in $\text{CeFeAs}(\text{O}_{1-x}\text{F}_x)$ seems to appear after disappearance of magnetic ordering [209].

In addition, we point out that, in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, the quantum critical fluctuation extends up to room temperature in $x = 0.33$ as can be confirmed by the excellent fitting of the T_1 data up to 270 K with the theoretical curve of 2D AFM fluctuation and T -linear resistivity [146]. This is contrary to naive expectations for quantum phase transition realized at 0 K. Such robust quantum criticality up to high temperatures of the order of J/k_B , where J is the strength of the exchange interaction, is in fact suggested by theoretical study [210]. Since the exchange interaction of iron pnictides was estimated to be the order of 100 K [211], our finding of robust

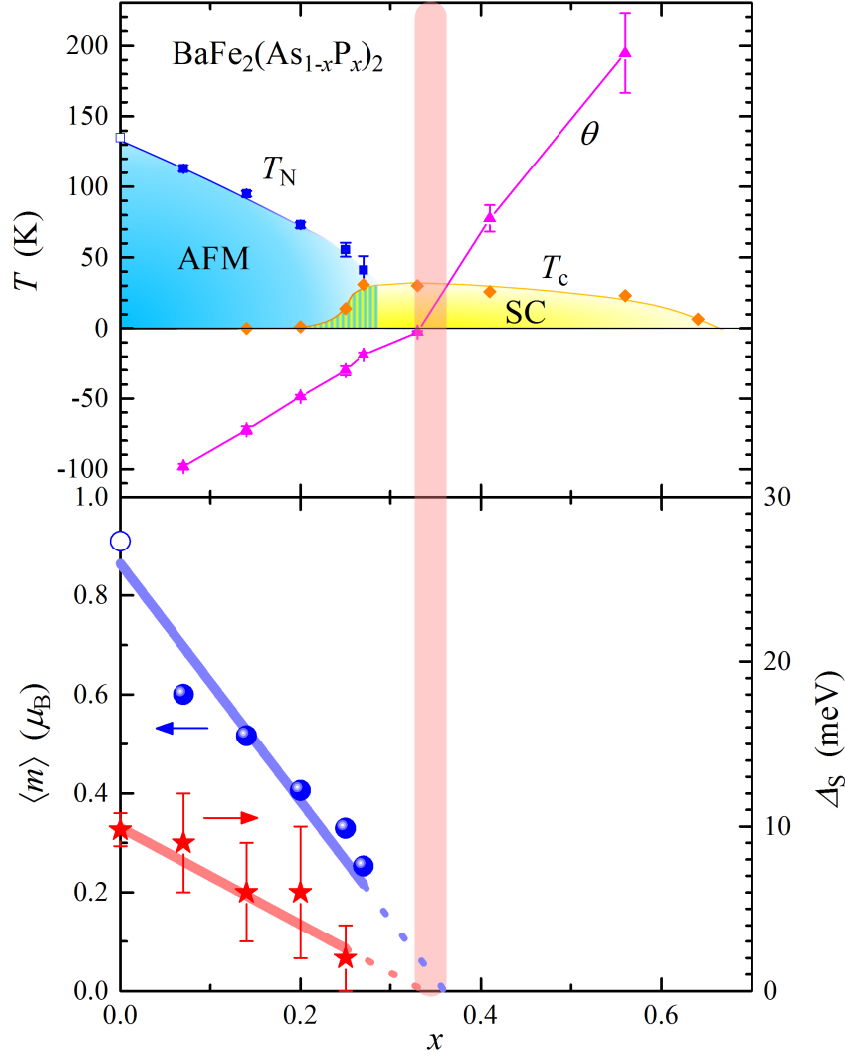


Figure 5.5: (Upper panel) $T - x$ phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ determined from our NMR measurements. T_N for $x = 0$ is taken from Ref. [36]. The triangles represent the characteristic temperatures of AFM fluctuations θ inferred from $(T_1T)^{-1}$ [100; 199]. (Lower panel) The x dependence of $\langle m \rangle$ at $T \rightarrow 0$ K obtained by extrapolating the fitting curve in Fig. 5.3(a) and using the equation $\langle m \rangle = \mu_0 \langle H_{\text{int}} \rangle / {}^{31}\text{A}_{\text{hf}}$, where ${}^{31}\text{A}_{\text{hf}} = 0.61 \text{ T}/\mu_B$ is deduced using $\langle m \rangle = 0.60 \mu_B$ for $x = 0.08$ [205]. The magnetic moment of $x = 0$, $0.91 \mu_B$, is taken from Ref. [157]. The gradual decrease in $\langle m \rangle$ (blue balls) at $T \rightarrow 0$ K from $x = 0$ to 0.27 can be extrapolated to $x \sim 0.35$. The broken line is a guide for the eyes. The evolution of the SDW gap Δ_S (red stars) with increasing x is also shown. The vertical broad red line at $x \sim 0.35$ indicates the expected position of the AFM QCP.

quantum criticality in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is not unexpected. The present material thus provides an accessible route to unraveling the nature of quantum criticality and emergent quantum order such as unconventional superconductivity.

Finally, we comment on the slight difference between the location of QCP inferred from

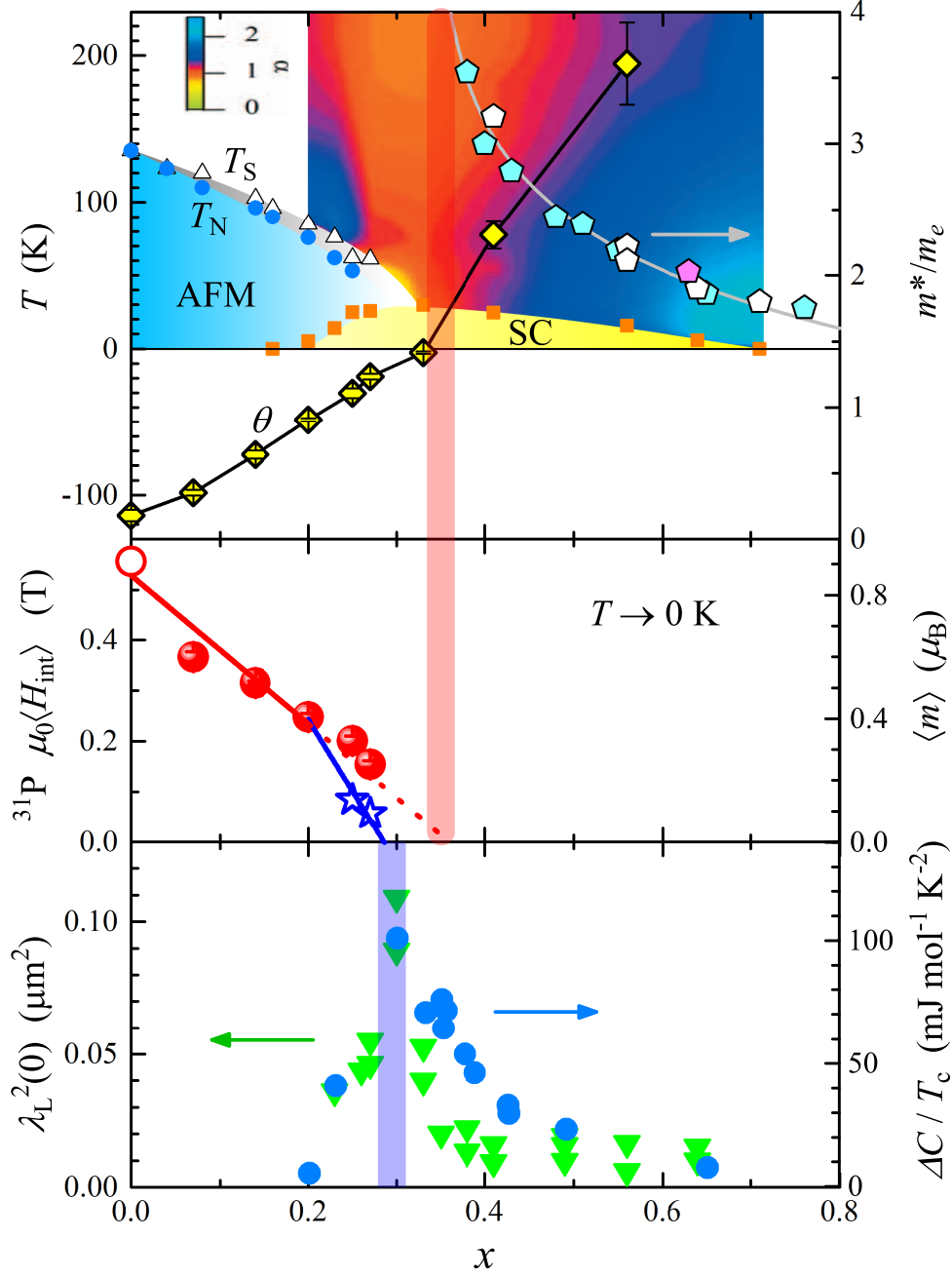


Figure 5.6: (Upper panel) Phase diagram of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with the characteristic temperatures of AFM fluctuations θ (NMR [100; 199]), effective mass enhancement factor m^*/m_e (dHvA [90]) in right-axis, and the exponent of the temperature dependence of resistivity $\alpha = d(\ln \Delta\rho_{ab})/d(\ln T)$ (resistivity [83]) in color scale. (Middle panel) x -evolution of $\langle m \rangle$ at $T \rightarrow 0$ K obtained by extrapolating the fitting curve for data $T_N > T > T_c$ (red balls) and $T_N > T_c > T$ (open blue stars). Lines are guides to the eyes. (Lower panel) The x dependence of effective mass enhancements m^*/m_e derived from dHvA measurements and $\Delta C/T_c$ related to effective mass derived from specific heat measurements. The vertical broad red (blue) line at $x \sim 0.35$ (~ 0.30) indicates the location of the AFM QCP expected from the normal-state and AFM properties (SC property).

NMR ($x \approx 0.35$) and from penetration depth and specific heat ($x \approx 0.30$) [48; 128; 129]. As shown in Fig. 5.6, The location of a QCP deduced from NMR measurement is inferred from the normal and AFM state. Both states are outside the SC dome. The location $x \approx 0.35$ is determined by extrapolating the change in physical parameters outside the SC phase. On the other hand, the location of a QCP at $x \approx 0.30$ deduced from the other techniques is based on the physical parameters in the SC phase or related to SC transition. The position of QCP is slightly shifted from higher $x \sim 0.35$ to the lower $x \sim 0.30$ due to the occurrence of superconductivity. Such a shift of x is actually discussed theoretically in Ref. [212; 213; 214] and is also expected intuitively when superconductivity and magnetism are competing. For $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, even the backbending of structural and magnetic transition lines is observed [215; 216]. In P-doped system, there is a moderate coupling between SC and AFM order parameter as shown in the next chapter in fact. Although which of the QCP, the original position at $x \approx 0.35$ or the shifted position affected by superconductivity $x \approx 0.30$, is important for the occurrence of high- T_c superconductivity is not clear, more and more evidence of the existence of QCP in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is reported.

5.3 Short Summary

In summary, static and dynamic magnetic properties in lightly P-substituted $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ($0.07 \leq x \leq 0.33$) were investigated by ^{31}P -NMR. The averaged magnetic ordered moment $\langle m \rangle$, the SDW gap value Δ_S , and the characteristic temperature of AFM spin fluctuations θ decrease successively toward $x \sim 0.35$ with increasing P concentration. These results verify the existence of an AFM QCP at $x \sim 0.35$, suggesting that AFM quantum critical spin fluctuations play a crucial role in superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

Chapter 6

Competitive Coexistence of Superconductivity and Magnetism in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

We discuss the coexisting state of magnetism and superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with $x = 0.25$ ($p = 0$ GPa) and 0.20 ($p \sim 2$ GPa) from microscopic point of view in this chapter. We found that SC transition occurs in a magnetic region with static ordered moments and that the moments are suppressed below T_c in the samples near the phase boundary of magnetism and superconductivity. Our results indicate that magnetism and superconductivity coexist microscopically in the real space but compete with each other on the same FSs. The competing coexistence state is qualitatively different from that observed in other unconventional superconductors and gives a strict constraint on the theoretical model for superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

6.1 Motivation

The study of the coexistence of magnetism and superconductivity, which is observed in the phase boundary, would give important information about the SC properties and mechanism. There are experimental reports not only from macroscopic and neutron scattering measurements [215; 217; 218] but from microscopic measurements [44; 219; 220; 221] of the coexistence and competition of magnetism and superconductivity in iron pnictides. However, we point out that diffraction measurements give magnetic moments averaged over a wide spatial region and cannot provide microscopic information about the coexistence. It remains an open question whether an SC phase transition below T_N occurs in a magnetic region of a sample or the SC transition is induced by the proximity effect of a nonmagnetic SC region and whether the same or the different electronic states contribute to magnetism and superconductivity. In the following sections, we report the occurrence of the SC transition in a magnetic region of AFM ordering, which is concluded from the investigation of internal magnetic field and nuclear spin-lattice relaxation rate $1/T_1$ by site-selective NMR measurements.

6.2 Experimental Details

We used mosaics of single crystals (~ 100 mg) for $\text{BaFe}_2(\text{As}_{0.80}\text{P}_{0.20})_2$ and $\text{BaFe}_2(\text{As}_{0.75}\text{P}_{0.25})_2$, both of which are located near the phase boundary of magnetic and SC phases in the phase diagram [83]. In order to drive the sample of $x = 0.20$ to have higher (lower) T_c (T_N), we applied pressure of $P \sim 2$ GPa using piston-cylinder-type cell and Daphne 7373 as a pressure

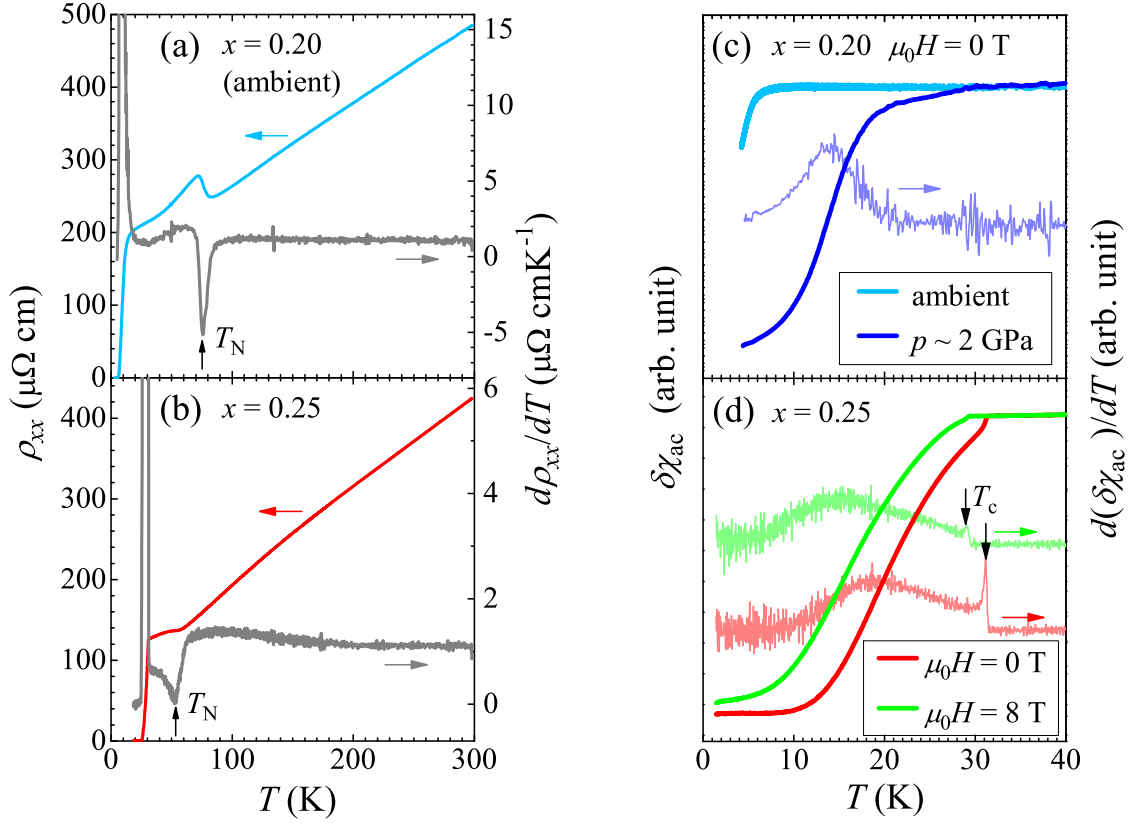


Figure 6.1: (a) and (b): $\rho_{xx}(T)$ and the temperature derivative of the $\rho_{xx}(T)$ for (a) $x = 0.20$ and (b) $x = 0.25$ at ambient pressure. T_N 's are determined by the minima of $d\rho_{xx}/dT$, as shown by black arrows. (c) and (d): Temperature dependence and the temperature derivative of the tuning frequency (c) for $x = 0.20$ at ambient pressure and $p \sim 2$ GPa, and (d) for $x = 0.25$ at ambient pressure.

transmitting medium. Figures 6.2(a) and 6.2(b) show the temperature dependence of the in-plane resistivity ρ_{xx} for $x = 0.20$ and 0.25 samples. The magnetic transition temperature derived from the temperature derivative of ρ_{xx} is in good agreement with the NMR results shown later. The ac susceptibility measurements indicate non-bulk superconductivity at ambient pressure but bulk superconductivity at $T_c^* \sim 13$ K at $p \sim 2$ GPa in the $x = 0.20$ sample (Fig. 6.2(c)). In the $x = 0.25$ sample, the gradual shift of the tuning frequency below $T_c^{\text{on}} \sim 30$ K and the SC transition suggested by a broad peak at around $T_c^* \sim 14$ K in the temperature derivative of the Meissner signal is observed (Fig. 6.2(d)). Note that the detuned frequency saturates at low temperatures, indicative of bulk superconductivity in these samples.

6.3 ^{31}P -NMR Measurements of Coexisting Regime of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

The NMR spectrum becomes broader and inhomogeneous below T_N . To detect a site-selective electronic state in the inhomogeneous state, we measured ^{31}P $(T_1 T)^{-1}$ across the resonance signal. We applied as small RF fields as possible for the site-selective $1/T_1$ measurements in order to obtain the recovery curve of nuclear magnetization with a single T_1 component.

Figure 6.3(a) shows the temperature variation of ^{31}P -NMR spectrum for $x = 0.25$ at a fixed

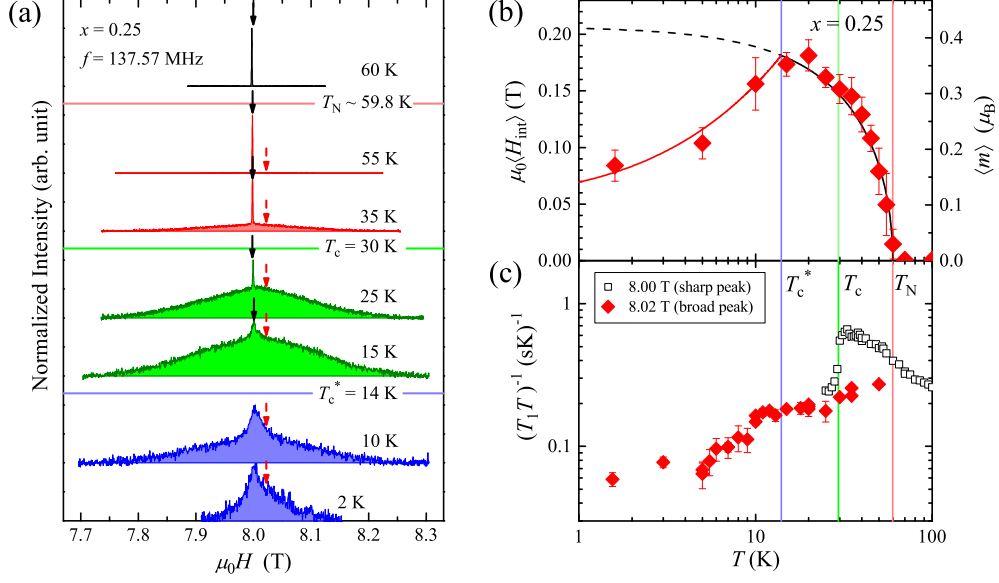


Figure 6.2: (a) Field-swept ^{31}P -NMR spectra in $\text{BaFe}_2(\text{As}_{0.75}\text{P}_{0.25})_2$. The solid black and dashed red arrows indicate the magnetic fields where $(T_1T)^{-1}$ is measured for the paramagnetic and AFM states, respectively. Each spectra is shifted vertically for clarity. (b) Temperature dependence of the averaged internal field $\langle H_{\text{int}} \rangle$ estimated from the observed NMR spectra. $\langle H_{\text{int}} \rangle$ increases below T_N but decreases at T_c^* . The black broken and solid lines represent the fitting of $(T_1T)^{-1}$ data ranging $T_N > T > T_c^*$ to the GL model in the case of homogeneous coexistence [216; 222] $((\mu_0 H_{\text{int}})^2 = A(T_N - T) + B(T - T_c^*))$ with $A = 7.17 \times 10^{-4} \text{ (T}^2/\text{K)}$, $T_N = 59.8 \text{ (K)}$, $B = 0 \text{ (T}^2/\text{K)}$. The red solid line represents the fitting of $(T_1T)^{-1}$ below T_c^* to the same model with the parameters $A = 7.17 \times 10^{-4} \text{ (T}^2/\text{K)}$, $T_N = 59.8 \text{ (K)}$, $B = 2.87 \times 10^{-3} \text{ (T}^2/\text{K)}$, and $T_c^* = 14 \text{ (K)}$. (c) Temperature dependence of $(T_1T)^{-1}$ measured site-selectively at the sharp paramagnetic NMR signal (open squares) and at the broad magnetic NMR signal (filled diamonds).

frequency of $f = 137.57 \text{ MHz}$ obtained by sweeping external field. A single sharp spectrum was observed above T_N , but no anomaly was detected in the NMR spectrum at the structural transition T_S determined by ρ_{xx} . Below T_N , a broad NMR spectrum with a Gaussian shape develops gradually overlapping with a sharp peak down to the lowest temperatures. We measured $(T_1T)^{-1}$ at the sharp and broad peaks shown by the solid black and dashed red arrows, respectively. Figure 6.3(c) shows the temperature dependence of $(T_1T)^{-1}$ at those peaks. $(T_1T)^{-1}$ measured at the sharp peak continues to increase down to T_c , indicative of the absence of a magnetic order, but $(T_1T)^{-1}$ at the broad peak shows a kink at T_N , indicative of the presence of a magnetic order. These results suggest that the sharp (broad) NMR peak arises from the region where P concentration is slightly higher (lower) than $x = 0.25$ in the sample. Thus, the two-peak structure around T_c^{on} is ascribed to the spatial inhomogeneity of the P concentration x , since the variation of T_N is very steep against x around $x \sim 0.25$.

The ^{31}P -NMR spectrum in the AFM state gives information about magnetic ordered moments, since the internal field H_{int} at the P site originates from the moments. The shape of

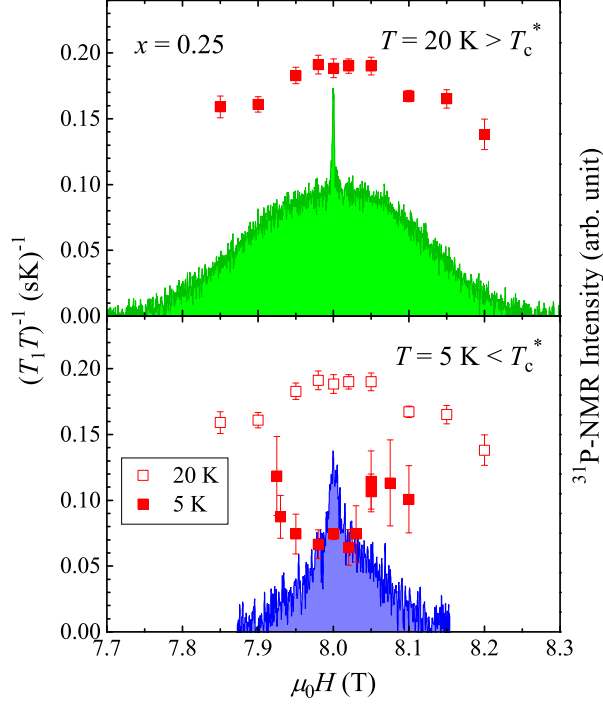


Figure 6.3: $(T_1T)^{-1}$ measured across the ^{31}P -NMR spectrum (Upper panel) at $T = 20\text{ K} (> T_c^*)$ and (Lower panel) at $T = 5\text{ K} (< T_c^*)$. $(T_1T)^{-1}$ over the entire spectrum at 5 K is smaller than that at 20 K, indicative of the occurrence of superconductivity over the entire region of the sample.

the spectrum reflects the field distribution at the P site; thus, the magnetic structure of Fe site can be inferred from the obtained spectrum. Since we used randomly oriented samples for the measurements and the nuclear spin of ^{31}P is $I = 1/2$, a rectangular NMR spectrum is expected when the moments are in a commensurate structure (see Appendix C). The broad Gaussian-shaped NMR spectrum indicates the large distribution of the internal field at the P site and suggests a change of spin structure from commensurate- to incommensurate-type and/or from ordered to disordered-type caused by P-dopant. The averaged internal field $\langle H_{\text{int}} \rangle$ at the P site is coupled to the ordered moment $\langle m \rangle$ with the hyperfine coupling constant $^{31}A_{\text{hf}} \sim 0.61\text{ T}/\mu_{\text{B}}$ as $\langle H_{\text{int}} \rangle = ^{31}A_{\text{hf}}\langle m \rangle$ (The hyperfine-coupling constant $^{31}A_{\text{hf}}$ at the P site is estimated from the ratio between $\langle H_{\text{int}} \rangle$ and $\langle m \rangle$ in underdoped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ samples. The $\langle m \rangle$ in $x = 0.08$ was estimated to be $0.60\ \mu_{\text{B}}$ by elastic neutron scattering measurements [205] and $\mu_0\langle H_{\text{int}} \rangle$ for $x = 0.07$ at the lowest temperature is 0.3662 T). $\langle H_{\text{int}} \rangle$ is evaluated from each broadened NMR spectrum below T_{N} as:

$$\langle H_{\text{int}} \rangle = \frac{\int_0^\infty H_{\text{int}}^2 dI}{\int_0^\infty H_{\text{int}} dI}, \quad (6.1)$$

where, experimentally, H_{int} is a resonance field measured from the peak field of the temperature-independent paramagnetic ^{31}P -NMR spectrum above T_{N} and I is the ^{31}P -NMR intensity. This is the same quantity derived as the internal magnetic field in Eq. (5.2).

Figure 6.3(b) shows the temperature variations of $\langle H_{\text{int}} \rangle$ in the left scale and estimated $\langle m \rangle$ using $^{31}A_{\text{hf}}$ in the right scale. $\langle H_{\text{int}} \rangle$ increases below T_{N} but decreases below $\sim 14\text{ K}$. $(T_1T)^{-1}$ measured at the broad magnetic signal decreases clearly below $T_c^* \sim 14\text{ K}$, as shown in Fig. 6.3(c), indicative of the occurrence of superconductivity in the magnetic region of the sample. Here, T_c^* is confirmed to be an SC transition temperature of magnetic ordered region in the

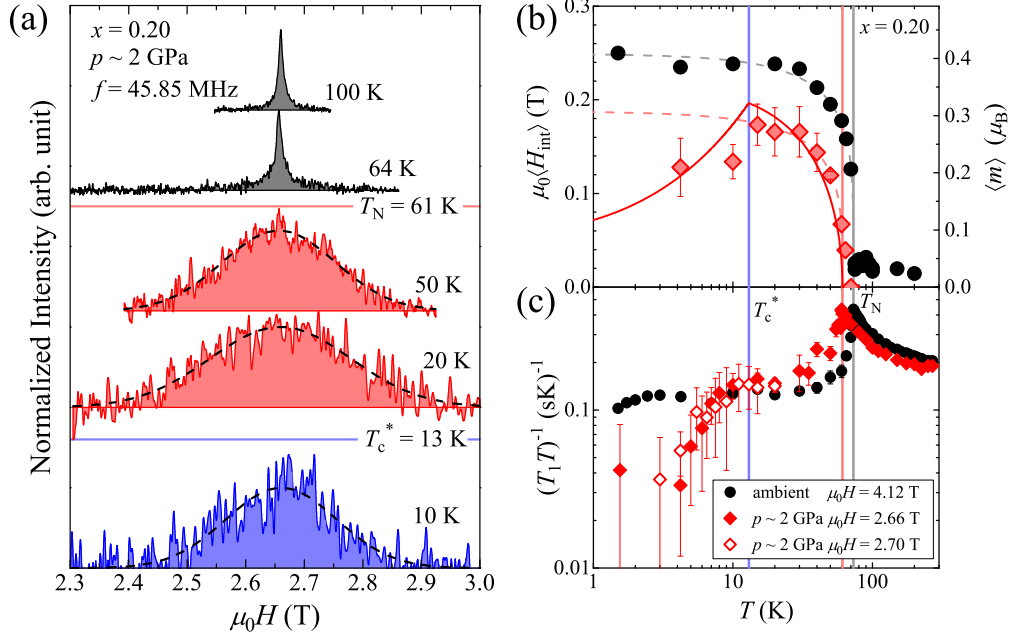


Figure 6.4: (a) Field-swept ^{31}P -NMR spectra in $\text{BaFe}_2(\text{As}_{0.80}\text{P}_{0.20})_2$ at $p \sim 2$ GPa. (b) Temperature dependence of the averaged internal field $\langle H_{\text{int}} \rangle$ estimated from the observed NMR signals at ambient pressure (black dots) and at $p \sim 2$ GPa (diamonds). $\langle H_{\text{int}} \rangle$ increases below T_N but decreases below T_c^* at $p \sim 2$ GPa. The broken lines indicate the fitting of the data ranging from T_c^* to T_N to the phenomenological formula of $c(T_N - T)^\alpha$ with $c = 0.10$ (0.067), $T_N = 73.0$ (61.0) K, and $\alpha = 0.20$ (0.25) for ambient pressure ($p \sim 2$ GPa). The red solid line represents the fitting of $(T_1 T)^{-1}$ below T_c^* to the GL model with the parameters $A = 8.04 \times 10^{-4}$ (T^2/K), $T_N = 61.0$ (K), $B = 3.59 \times 10^{-3}$ (T^2/K), and $T_c^* = 13$ (K). (c) Temperature dependence of $(T_1 T)^{-1}$ values measured in $\mu_0 H = 4.12$ T at ambient pressure, in $\mu_0 H = 2.7$ T and 2.66 T at $p \sim 2$ GPa.

sample. In addition, we measured $(T_1 T)^{-1}$ across the ^{31}P -NMR spectra at 20 K ($> T_c^*$) and 5 K ($< T_c^*$), as shown in Fig. 6.3, and confirmed that $(T_1 T)^{-1}$ in all regions of the spectrum at 5 K is smaller than that at 20 K. This indicates that superconductivity occurs over the entire region of the sample. The sharp decrease in $(T_1 T)^{-1}$ at T_c^* means that superconductivity is a phase transition in the magnetic region and excludes the possibility that superconductivity in the magnetic region is induced by the proximity effect of the SC region in the sample.

A similar nature of coexistence of magnetism and superconductivity was also observed in the $x = 0.20$ sample at a pressure of ~ 2 GPa. Figures 6.3(a) and 6.3(b) show the field-swept NMR spectra and the temperature dependence of the $\langle H_{\text{int}} \rangle$ at the P site and estimated $\langle m \rangle$, which are determined by the same procedure as that in the case of the $x = 0.25$ sample. For comparison, $\langle H_{\text{int}} \rangle$ at ambient pressure is also shown in Fig. 6.3(b). $\langle H_{\text{int}} \rangle$ increases below $T_N \sim 61$ K but decreases below $T_c^* \sim 13$ K at $p \sim 2$ GPa, as observed in the $x = 0.25$ sample. It should be noted that the paramagnetic signal was not observed at all in the sample, indicating that the entire region of the $x = 0.20$ sample at $p \sim 2$ GPa is in the magnetic state below T_N and then shows superconductivity below T_c^* . These results indicate the microscopic coexistence

of magnetism and superconductivity in real space, and the suppression of the magnetic order parameter below T_c^* both for the $x = 0.25$ sample at ambient pressure and for the $x = 0.20$ sample at $p \sim 2$ GPa.

Now, we compare the present results with experimental results in other iron pnictides and unconventional superconductors. It was revealed by muon spin rotation (μ SR) that strongly disordered but static magnetism coexists with superconductivity in the narrow range of $0.1 < x < 0.13$ on $\text{SmFeAsO}_{1-x}\text{F}_x$ with the “1111” structure [44]. However, neither the suppression of the ordered moments below T_c nor the SC transition in a magnetic region was observed in $\text{SmFeAsO}_{1-x}\text{F}_x$. At present, the suppression of the magnetism below T_c , which is observed in this study, have been reported in “122” and “111” type compounds: $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [216; 217; 223; 224; 225], in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [218; 221; 226], in $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ [227; 228; 229; 230; 231], in $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ [232], in $\text{Ba}(\text{Fe}_{1-x}\text{Rh}_x)_2\text{As}_2$ [233], in $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ [234], and $\text{Na}(\text{Fe}_{1-x}\text{Co}_x)\text{As}$ in [235; 236; 237]. The suppression of structural order parameter have been also reported [215; 238]. The competition between the magnetic and SC order parameters as well as the spatial coexistence are common features of the “122” compounds. It thus seems that the relationship between the magnetic and SC phases is different between the “1111” and “122” compounds. The spatial coexistence is also realized in heavy-fermion superconductors, whereas the nature of coexistence differs from that in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, i.e., magnetism and superconductivity occur at different parts of the FSs. For example, it was reported that the spatial coexistence is observed microscopically in $\text{CeCo}(\text{In}_{1-x}\text{Cd}_x)_5$ [239; 240] and CeRhIn_5 at a certain pressure [241; 242], where T_N is higher than T_c . In these compounds, the magnetically ordered moments develop below T_N ; however, they become constant below T_c without further change at low temperatures. This suggests that magnetism and superconductivity emerge from different parts of the FSs, thus a single $4f$ state could satisfy the coexistence of magnetism and superconductivity. The suppression of the ordered moments below T_c was not observed in the U-based superconductor UPd_2Al_3 or UNi_2Al_3 , where plural $5f$ electrons are subdivided into localized and itinerant electrons [243; 244; 245]. This is also the case in ferromagnetic superconductors, such as UGe_2 [246], URhGe [247], and UCoGe [248; 249]. In contrast, the suppression of the ordered moments below T_c can be well understood by the assumption that the same FSs contribute to both magnetic ordering and superconductivity with a competitive relationship [213; 222; 250]. In $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, cylindrical FSs, particularly hole FSs, are modified to be more 3D, and nesting between hole and electron FS becomes weaker with P substitution, resulting in the suppression of the AFM order. It is considered that the nesting vector becomes distributed and the AFM order (superconductivity) occurs at stronger (weaker) nesting vectors. In this regard, the competitive relationship between the two phases might have a common aspect with that in cuprate superconductors [251], whose AFM order is induced by the applied strong magnetic field that imposes the vortex lattice.

The competition between superconductivity and AFM ordering near the phase boundary can be described in terms of a Ginzburg-Landau (GL) theory of coupled order parameters [213; 222; 252; 253]. The homogeneous part of the free energy is given by

$$F_{\text{GL}}(\Delta, \mathbf{M}) = \int dr \left(\frac{a_s}{2} |\Delta|^2 + \frac{u_s}{4} |\Delta|^4 + \frac{\gamma}{2} |\Delta|^2 \mathbf{M}^2 + \frac{a_m}{2} \mathbf{M}^2 + \frac{u_m}{4} \mathbf{M}^4 \right), \quad (6.2)$$

where Δ and $\mathbf{M}$ denote the SC and AFM order parameters, respectively [222]. The leading term in the order-parameter competition is characterized by the coefficient γ , which determines the phase diagram and the character of two phase transitions; SC and AFM states coexist homogeneously with two second-order phase lines for $0 < \gamma < \sqrt{u_s u_m}$, but two phases compete and are separated by a first-order transition for $\gamma > \sqrt{u_s u_m}$. Our experimental results, indicating the homogeneous coexistence and presence of the AFM and SC transitions at different temperatures, suggest that the former ($0 < \gamma < \sqrt{u_s u_m}$) condition is realized in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. According

to the recent theoretical studies, an extended s -wave ($s_{\pm}$ -wave) state[213; 222], in which the SC gap changes sign between the hole and electron bands, satisfies the $0 < \gamma < \sqrt{u_s u_m}$ condition and can coexist with an incommensurate SDW state over a much wider range of parameters than a conventional s -wave state. In fact, the temperature dependence of $\langle m \rangle$ can be fit with the GL expression in the case of homogeneous coexistence[216; 222], as shown in Figs. 6.3(b) and 6.3(b) with red curves. In this sense, our results are consistent with the $s_{\pm}$ -wave state. However, we should note that the theory by Fernandes *et al.* does not include the effect from five Fe-bands with different character.

6.4 Short Summary

In conclusion, our NMR results on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ reveal the microscopic coexistence of AFM and SC states in real space, and the direct coupling between the two order parameters. The coexistence behavior can be consistently interpreted by the simplified $s_{\pm}$ model [222]. Our results strongly suggest that antiferromagnetism and superconductivity occur at the same FS and compete with each other.

Chapter 7

Emergence of Static Orbital Polarization in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ above Structural Transition

In this chapter, we report ^{75}As -NMR measurements in single crystalline $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$ for magnetic fields parallel to the orthorhombic $[110]_o$ and $[100]_o$ directions above the structural transition temperature $T_S \simeq 121$ K. A large difference in the line width between the two field directions reveals in-plane anisotropy of the electric field gradient, even in the tetragonal phase. This provides microscopic evidence of population imbalance between As- $4p_x$ and $4p_y$ orbitals, which reaches $|n_x - n_y| \sim 0.004$ electron at $T \rightarrow T_S$ and is a natural consequence of orbital ordering of Fe- $3d_{xz}$ and d_{yz} electrons. Surprisingly, this orbital polarization is found to be already static near room temperature, suggesting that it arises from the pinning of anisotropic orbital fluctuations by disorder. Furthermore, the appearance of nematicity in torque and photoemission measurements is found to coincide with an upturn in the line broadening below ~ 150 K, which reveals either a crossover in the magnitude/length of the orbital-nematic correlations, or a phase transition.

7.1 Motivation

The relationship between spin, orbital and lattice degrees of freedom is a central issue in iron pnictides since fluctuations in these channels are potentially at the origin of the high- T_c superconductivity. The problem is best illustrated by the presence of two interrelated structural and magnetic transitions, at temperatures T_S and T_N , respectively, which both disappear near the optimal T_c in most pnictides [100; 128; 153; 254]. Although the tetragonal-to-orthorhombic transition slightly precedes (or coincides with) the antiferromagnetic (AFM) transition, the latter is not necessarily a consequence of the former: whether the orthorhombic distortion is driven by magnetic or orbital fluctuations has been the subject of continuing debate ([255] and references therein). Furthermore, the tetragonal phase above T_S turns out to be unconventional: various electronic properties have been found to break the fourfold symmetry of the Fe-As planes [132; 133; 134; 135; 136; 138; 229; 256; 257; 258; 259; 260; 261; 262; 263; 264; 265; 266; 267; 268]. The relative role, as well as the microscopic origin, of the spin and orbital instabilities leading to such an “electronic nematic state” are also controversial [267; 269; 270; 271; 272; 273; 274; 275; 276; 277; 278; 279; 280]. Actually, because magnetic and orbital degrees of freedom are entangled and most likely cooperate [?], it is challenging to determine which one, if any, is leading. While both the magnetic and orbital scenarios find support in experiments [133; 136; 254; 255; 265; 281; 282; 283; 284; 285], the nematic state remains puzzling: can a

nematic phase transition be defined? Are the observed phenomena truly static or fluctuating? What is the role of disorder? How to deconvolute experimental results from the effect of uniaxial stress, frequently used to align the twin nematic domains?

Here, we report nuclear magnetic resonance (NMR) measurements above T_S in underdoped $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$. We demonstrate that orbital polarization of the As-4*p* orbitals, related to Fe-3*d* polarization (*i.e.* ordering), is present within electronic domains in the tetragonal phase, even without any applied uniaxial stress. We estimate the magnitude of this polarization and we show that it is static. We further reveal an unanticipated temperature dependence: while the onset of the nematic state, as inferred from torque and photoemission experiments [132; 138], is manifested by an upturn near 150 K in our linewidth data, static orbital polarization is found to be already present at much higher temperatures. This suggests that short-range orbital order is first nucleated around defects and that its evolution towards longer-range order is directly involved in the manifestation of nematicity at the macroscopic scale.

7.2 Experimental Details

The edges of the single crystalline $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$ were cut along $[110]_o$ (As-Fe direction), $[100]_o$ (As-As or Fe-Fe direction), and $[1\bar{1}0]_o$ (see Fig. 7.1(a)) and the resulting dimension of the crystal was $2.0 \times 1.4 \times 0.25 \text{ mm}^3$. The NMR coils, fitted into the crystal size as shown in Fig. 7.1(b), were prepared for the field directions of $[110]_o$, $[100]_o$, and $[1\bar{1}0]_o$, respectively. The coil with the crystal inside was attached to the uniaxial rotational system equipped on the probe head. The field direction was controlled to be parallel to the *ab*-plane within $\pm 1^\circ$. ^{75}As -NMR spectra were obtained by sweeping frequency in the fixed magnetic field of 15 T.

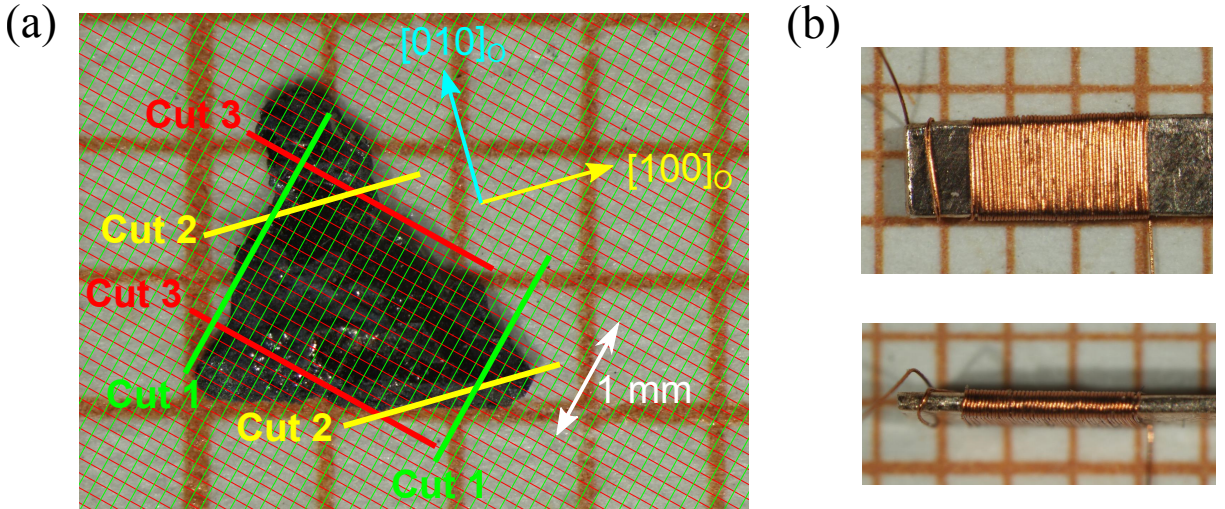


Figure 7.1: (a) A photograph of the (001) surface of the single crystal of $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$ with grid scales by $0.1 \text{ mm} \times 0.1 \text{ mm}$. The green (red) thin grid lines are along $[110]_o$ ($[1\bar{1}0]_o$) direction in FeAs-layer. The single crystal was cut three times along green thick lines (Cut1 along $[110]_o$), yellow thick lines (Cut2 along $[100]_o$), and red thick lines (Cut3 along $[1\bar{1}0]_o$) in turn. (b) Top and side views of the copper coil used for our NMR measurement of $H \parallel [110]_o$. The coil was made by winding copper wire $50 \mu\text{m}$ in diameter around the copper plate with the same dimension as the sample.

The in-plane resistivity measurement for the crystal taken from the same batch as the one for our NMR measurements was performed (Fig. 7.2(a)). A sharp upturn of the resistivity, often

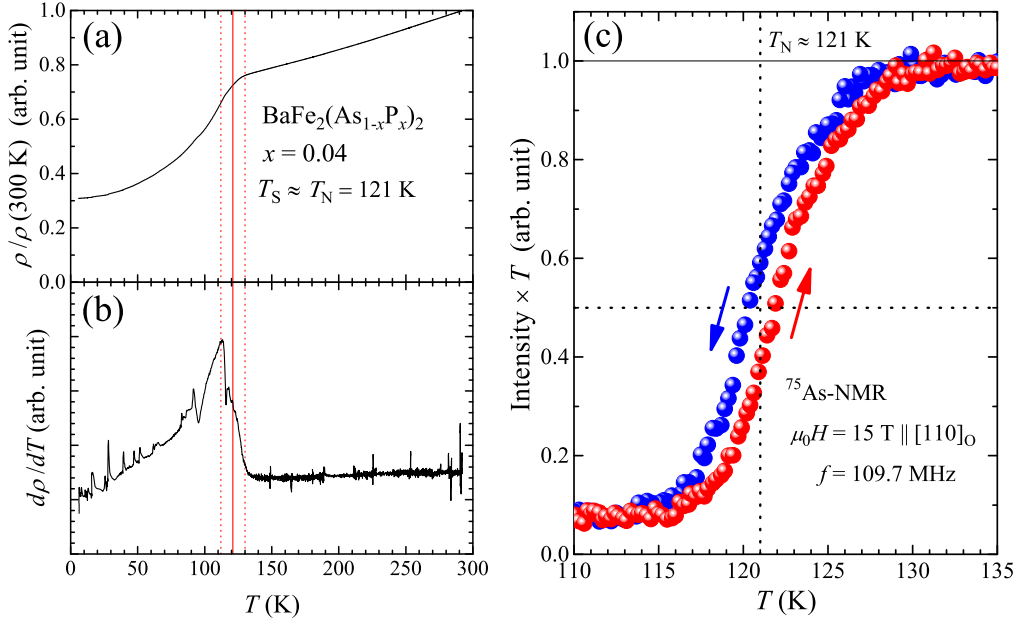


Figure 7.2: The temperature dependence of (a) resistivity and (b) temperature derivative of the resistivity for $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$. The dotted red line at higher (lower) temperature represents the temperature at which $d\rho/dT$ starts to change (shows a peak). The solid red line is the mid-point of the two dotted red lines and is defined as T_S . (c) ^{75}As -NMR intensity recorded on cooling (blue balls) and warming (red balls) at around the phase transition temperature, respectively for $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$. The horizontal dotted line indicates a half of the intensity in the paramagnetic state. The vertical dotted line of 121 K is the temperature averaged for cooling and warming at which a half of the intensity is lost, and it corresponds well to T_S determined by resistivity.

seen below T_S for the sample with well separated T_S and T_N , is not observed. This suggests the simultaneous structural and magnetic transition $T_S = T_N$ in the $x = 0.04$ sample as also reported for $x = 0 - 0.07$ [83; 85]. In this study, T_S is defined as the mid-point of the temperature at which the temperature derivative of resistivity starts to change and shows a peak and thus $T_S \approx T_N \approx 121\text{ K}$ (Fig. 7.2(b)). We also checked the magnetic phase transition by tracking ^{75}As -NMR peak intensity of the Fourier transformed spectrum at the resonance position for $\mu_0 H = 15\text{ T} \parallel [110]_O$ in the paramagnetic phase with changing temperature. For both cooling and warming process, the temperature sweep rate was kept slower than 0.1 K/min in order to minimize the difference between the actual temperature of the sample and the temperature at the thermometer tip. The intensity showed a reduction at $T_N \sim 121\text{ K}$ due to the broadening of the NMR signal from magnetic ordered sites (Fig. 7.2(c)), which corresponds to the result of resistivity. It also showed a hysteresis in temperature about 1.6 K wide. Although the hysteresis is narrower than that observed in $x = 0$ [36], the first-order-like character of the phase transition seems still present for $x = 0.04$.

7.3 In-Plane Field Orientation Dependence of ^{75}As -NMR Spectrum of $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$

^{75}As -NMR spectra are measured at 200 K in the field of 15 T along $[110]_o$, $[100]_o$ and $[1\bar{1}0]_o$. Since ^{75}As nuclei have a spin $I = 3/2$, the spectrum shows three lines corresponding to the transitions $I_z = m \leftrightarrow m - 1$ ($m = \pm 1/2, 3/2$) at the frequencies

$$\begin{aligned} {}^{75}f_{m \leftrightarrow m-1}(\theta, \phi) = & \frac{{}^{75}\gamma}{2\pi} \mu_0 H_{\text{ext}} (1 + {}^{75}K(\theta, \phi)) \\ & + \frac{\nu_c}{2} \left(m - \frac{1}{2} \right) (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi) \\ & + (2^{\text{nd}}\text{-order quadrupolar correction}), \end{aligned} \quad (7.1)$$

where (θ, ϕ) indicates polar and azimuthal angles of the applied field in the orthorhombic basis (a_o, b_o, c) , ${}^{75}\gamma/2\pi = 7.2919$ MHz/T is the ^{75}As gyromagnetic ratio, $\mu_0 H = 15$ T here, and ${}^{75}K(\theta, \phi)$ represents the Knight shift which is proportional to the magnetic susceptibility $\chi(q=0, \omega=0)$. The angular dependence of the quadrupole frequency ν_α is expressed as $\nu(\theta, \phi) =$

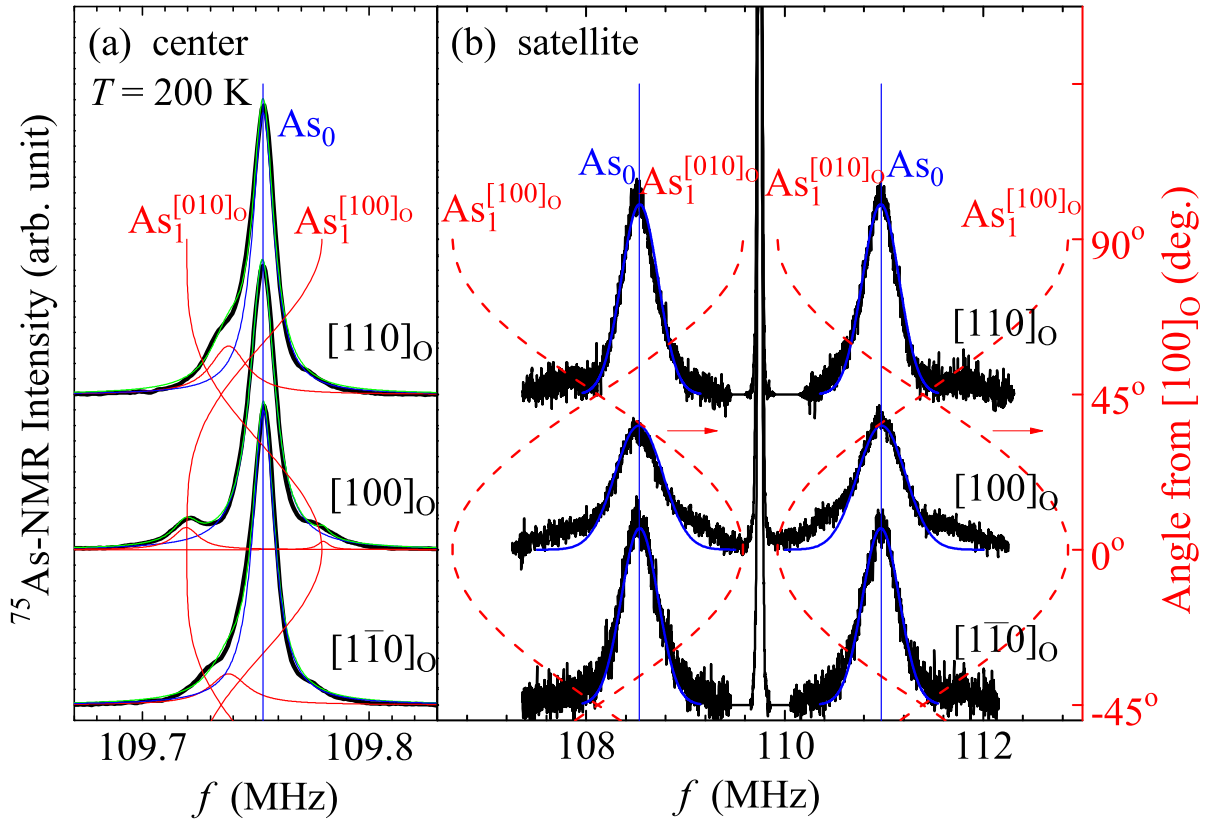


Figure 7.3: (a) An in-plane field direction dependence of ^{75}As -NMR spectrum at 200 K for center peak with Lorentzian fitting curves for As_0 and As_1 . Expected resonance positions tracking for As_0 and As_1 are represented by blue and red lines, respectively. (b) An in-plane field direction dependence of ^{75}As spectrum at 200 K for satellite peaks with Gaussian fitting curves for As_0 . Expected resonance positions tracking for As_0 and As_1 are shown as solid blue and broken red lines, respectively.

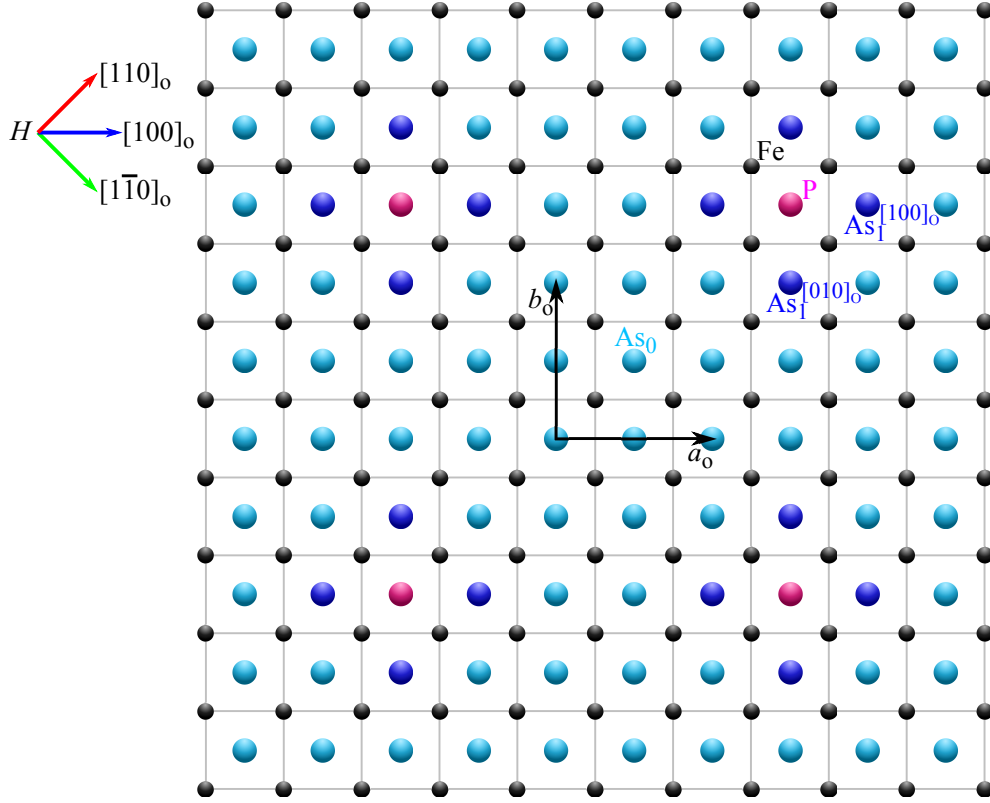


Figure 7.4: $FePn$ -layers of $BaFe_2(As_{0.96}P_{0.04})_2$ and applied field directions. Black and Pink points indicate Fe site and P dopants, respectively. As_0 sites where no P dopants exist in its nearest neighbor (NN) are shown by sky-blue points. $As_1^{[100]_o}$ and $As_1^{[010]_o}$ where a P dopant locates on the NN site in $[100]_o$ and $[010]_o$ are shown by blue points. Note that this image assumes the ideal allocation of P dopants for 4 % concentration that one P atom exists for every five As atoms in line.

$(\nu_c/2)(m - 1/2)(3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi)$. ν_α is proportional to the diagonal components of the electric field gradient (EFG) tensor $V_{\alpha\alpha} \equiv \partial^2 V / \partial r_\alpha^2$: $\nu_\alpha = eV_{\alpha\alpha}Q/2h$ ($\alpha = a, b, c$), where Q is the electric quadrupole moment. The EFG tensor of the so-called As_0 sites far from any P dopant (see Fig. 7.4) is diagonalized in the ortho-basis (a_o, b_o, c) [36]. The in-plane EFG anisotropy is defined as $\eta \equiv |V_{aa} - V_{bb}|/|V_{cc}| = |\nu_{a_o} - \nu_{b_o}|/|\nu_c|$ with $\nu_a + \nu_b + \nu_c = 0$. Therefore, $\eta = 0$ in a local tetragonal environment. The third term indicates the contribution from the second perturbation of electric quadrupolar effect [140]. Small additional peaks observed in the tail of the central line (Fig. 7.3(b)) are attributed to those As sites (hereafter called As_1) having one P dopant among their four nearest neighbor (NN). The As_1 resonance splits into two peaks for $H \parallel [100]_o$ because $As_1^{[100]_o}$ and $As_1^{[010]_o}$ sites (defined in Fig. 7.4) are inequivalent, while they are equivalent for $H \parallel [110]_o$ and $[1\bar{1}0]_o$. In $Ba(Fe_{1-x}Co_x)_2As_2$, NN to Co dopants produce similar peaks [153; 219; 220]. The angle dependence of the resonance frequency of the As_1 center peak is reproduced with the parameters $|\nu_z| = 5$ MHz, $\eta = 0.24$ and $\delta = 30^\circ$, where δ is the tilt angle of the principal axis (z -axis) of the EFG from the crystalline c -axis (Fig. 7.3(a)). The Knight shift of As_1 is assumed to be the same as that of As_0 . These parameters enable us to estimate the positions of the As_1 satellite peaks (Fig. 7.3(b)). Although it is difficult to distinguish the weak and broad satellites of As_1 from those of As_0 , semi-quantitative agreement with the data is obtained. It is clear from Fig. 7.3(b) that the central part of each satellite signal is essentially representative of the As_0 sites.

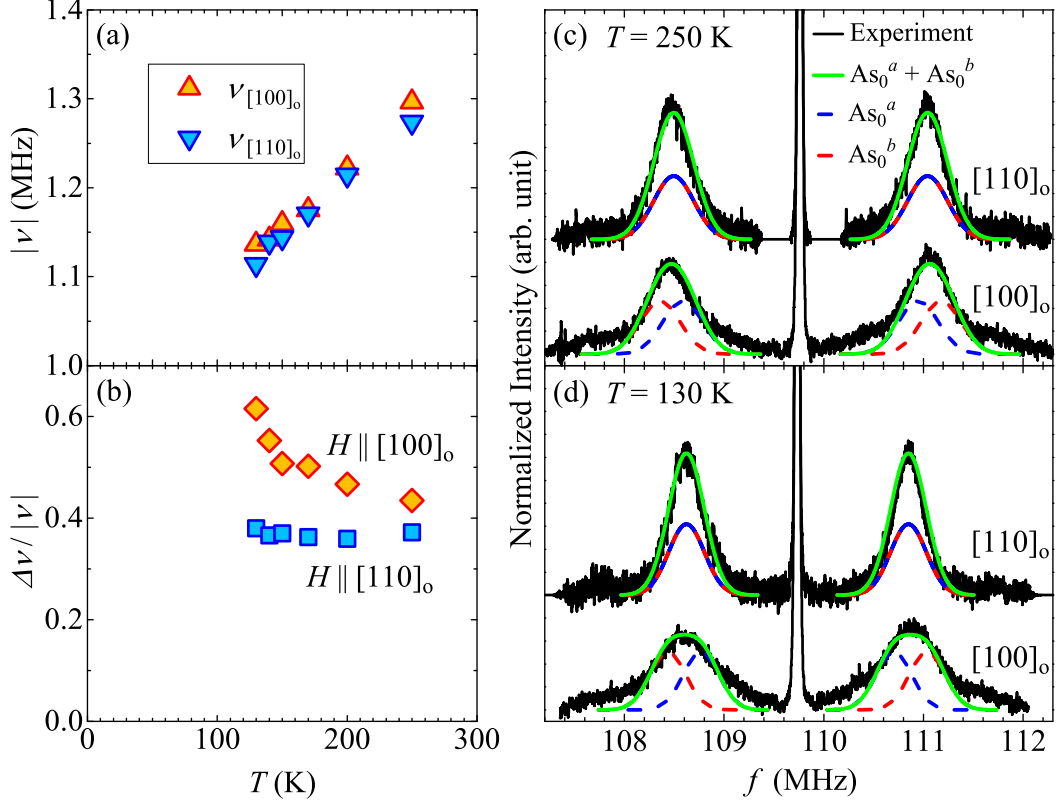


Figure 7.5: (a) T dependence of the quadrupole frequency $|\nu|$. (b) T dependence of the distribution $\Delta\nu/|\nu|$ where $\Delta\nu$ is the full-width at half-maximum of a satellite line. ^{75}As satellites at 250 K (c) and at 130 K (d) for $H \parallel [100]_o$ and $[110]_o$, respectively. Broken blue and red lines represent As_0^a and As_0^b sites, respectively, obtained from Gaussian fits to the lineshape (their sum is shown as a solid green line). The two sites are identical for $H \parallel [110]_o$, while they split for $H \parallel [100]_o$.

Below, we discuss the electronic state of the As_0 sites by analyzing two quantities: i) the absolute value of their quadrupole frequency $|\nu|$, directly determined from the half of the separation between the high and low frequency satellites $|\nu(\phi)| = |f_{\frac{3}{2} \leftrightarrow \frac{1}{2}} - f_{-\frac{1}{2} \leftrightarrow -\frac{3}{2}}|/2 = |\nu_c|(1 + \eta \cos 2\phi)/2$, ii) the distribution of quadrupole frequencies $\Delta\nu/|\nu|$, where $\Delta\nu$ is the full-width at half-maximum obtained by Gaussian fit of the As_0 satellite peak.

The central observation of our study is shown in Figs. 7.5(a) and 7.5(b): while the values of $|\nu|$ are almost identical for $H \parallel [110]_o$ and for $H \parallel [100]_o$, the values of $\Delta\nu/|\nu|$ for these two orientations are different and this difference increases on cooling. That the width for $H \parallel [100]_o$ is anomalously large and that it grows with decreasing T (instead of being constant as for $H \parallel [110]_o$) can naturally be explained by the existence of two types of As_0 sites, having identical EFG tensor components but a non-zero η and in-plane principal axes perpendicular to each other, that means, perpendicular domains in each of which the in-plane fourfold symmetry of the EFG is broken. Note that the central and satellite lines were found to have identical width for $H \parallel [110]_o$ and for $[1\bar{1}0]_o$ (Fig. 7.3(a,b)). In addition to ensuring the accuracy of the crystal alignment with respect to H , this result suggests that twin nematic domains within the sample prohibit direct detection of the planar anisotropy by comparing NMR spectra in perpendicular field orientations.

We thus performed new fits to the sharp part of the satellite peaks (*i.e.* excluding the tails

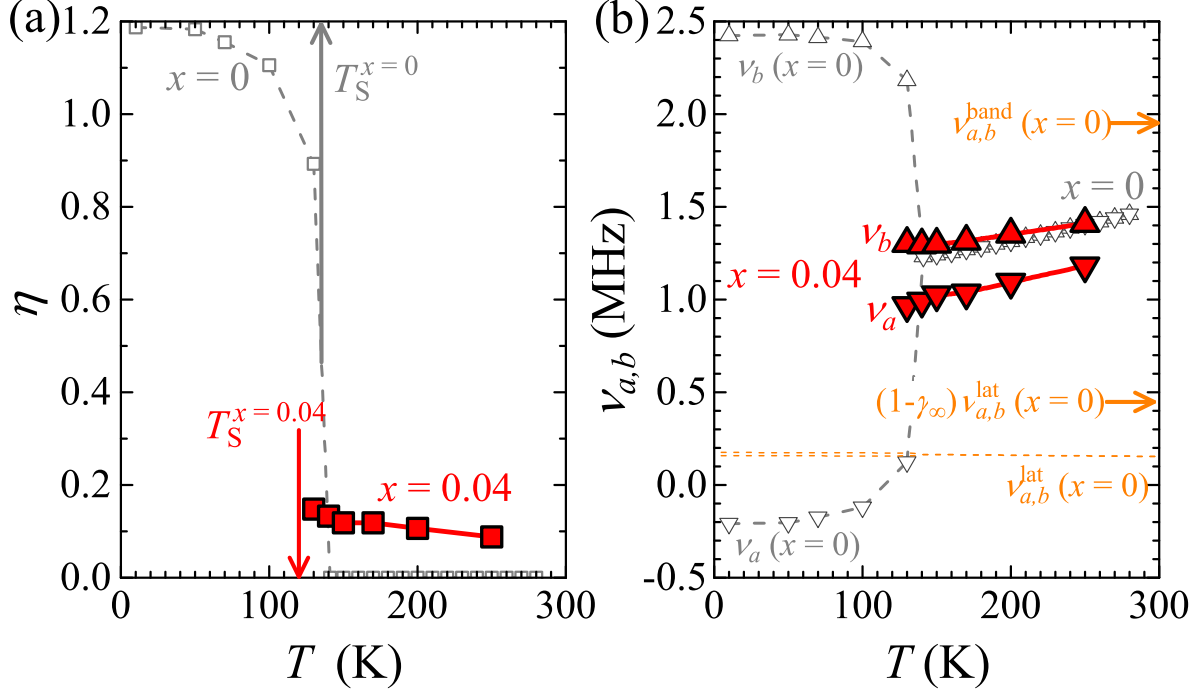


Figure 7.6: (a) T dependence of in-plane EFG anisotropy parameter η for $x = 0.04$ (this work) and $x = 0$ (from Ref. [36]). For $x = 0.04$, η is derived from the angular dependence of the satellite linewidth with respect to the field. For $x = 0$, however, it is deduced from the satellite splitting due to twinned orthorhombic domains [36]. If domains are present above T_S , this method does not allow detecting $\eta \neq 0$ locally. (b) T dependence of $\nu_{a,b}$ for $x = 0.04$ together with the $x = 0$ data from Ref. [36]. $\nu_{a,b}^{\text{band}}$ is the quadrupole frequency estimated from band-structure calculations. $\nu_{a,b}^{\text{lat}}$ is the value calculated using a point charge model and the lattice parameters from Refs. [218; 286]. $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ is derived from ν versus K^{spin} plot (see text).

due to As_1) for $H \parallel [100]_o$ with two Gaussian functions, each having a linewidth fixed to the value measured for $[110]_o$ (Figs. 7.5(c,d)). The corresponding two sites are named As_0^a and As_0^b and they are defined by their respective quadrupole frequencies $|\nu_a| < |\nu_b|$ for $H \parallel [100]_o$. It is important to realize that the frequency difference between the satellite peaks of As_0^a and As_0^b actually corresponds to $|\nu_a - \nu_b|$ for perpendicular domains in which a and b are rotated by 90° . Dividing this value by $|\nu_c| = |\nu_a + \nu_b| = 2|\nu_{[110]_o}|$, the EFG anisotropy parameter η can be estimated. As shown in Fig. 7.6(a), η is already non-zero at 250 K but it increases on cooling and shows an upturn below ~ 150 K.

In general, the EFG has two origins: $\nu_\alpha = \nu_\alpha^{\text{on}} + (1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$, where ν_α^{on} is the contribution from the on-site charge density and ν_α^{lat} is the contribution from the surrounding charged ions in the lattice, multiplied by the anti-shielding factor $(1 - \gamma_\infty)$ [287]. Therefore, in-plane anisotropy ($\eta \neq 0$) can occur because the lattice symmetry is locally orthorhombic (while still globally tetragonal) and/or because of nematic order, *i.e.* electronic states locally break fourfold symmetry.

In order to obtain information on the on-site wave function, let us now examine the relative weight of these two contributions. First, we performed band-structure calculations for $x = 0$ within the local-density-approximation (LDA) for nonspin-polarized BaFe_2As_2 , using the WIEN2K package in the APW + local orbital basis [89] and using lattice parameters from Ref. [286]. Since the obtained $\nu_{a,b}^{\text{band}} = +1.95$ MHz at 300 K is consistent with the experimental

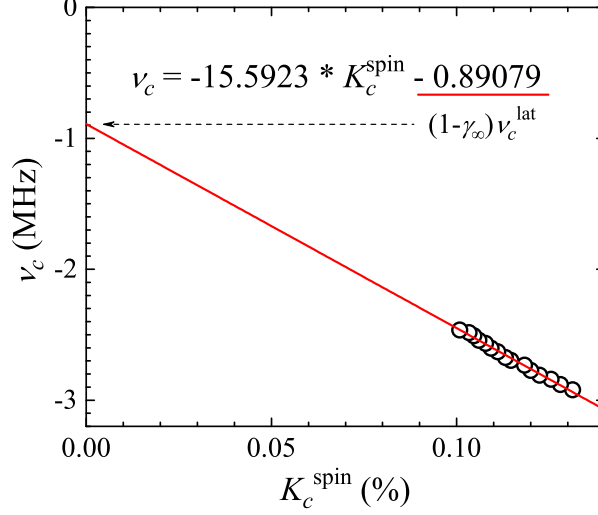


Figure 7.7: K_c^{spin} - ν_c plot for $x = 0$ as an implicit parameter of temperature. The values of K_c and ν_c are adopted from Ref. [36] and K_c^{spin} is estimated by $K_c^{\text{spin}} = K_c - K_c^{\text{chem}}$, where $K_c^{\text{chem}} = 0.2\%$. The linear relationship between K_c^{spin} and ν_c is extrapolated by a straight red line to the ν_c -intercept of -0.89 MHz. The intercept corresponds to the almost temperature-independent lattice contribution $(1 - \gamma_\infty)\nu_c^{\text{lat}}$. $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ in the main text is deduced by using Laplace's equation $\nu_{a,b}^{\text{lat}} = -\frac{\nu_c^{\text{lat}}}{2}$ as follows: $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}} = (1 - \gamma_\infty)\nu_c^{\text{lat}} \times (-\frac{1}{2}) = -0.89 \times (-\frac{1}{2}) \approx 0.45$ MHz.

value $|\nu_{a,b}| = 1.5$ MHz [36], the sign of $\nu_{a,b}$ is chosen to be positive in Fig. 7.6(b) for both $x = 0$ and 0.04 in the tetragonal phase.

Based on theoretical [288] and experimental [289] grounds, the on-site contribution ν^{on} is expected to scale with the spin part of the Knight shift K^{spin} as a function of temperature. By extrapolating to $K^{\text{spin}} \rightarrow 0$ the actually linear relationship between ν and K^{spin} (with T as an implicit parameter) for the parent compound $x = 0$ (Fig. 7.7), we estimate the T independent lattice contribution $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}} = 0.45$ MHz. This contribution thus accounts for less than half of the total $\nu_{a,b}$ in both $x = 0$ and 0.04 . As a cross-check, we deduce $(1 - \gamma_\infty) \simeq 2.7$ after calculating $\nu_{a,b}^{\text{lat}}$ by a point charge model (Fig. 7.6(b)). A value of $|1 - \gamma_\infty| < 10$ agrees with expectations based on the fact that BaFe_2As_2 is a metal [140; 290]. We do not expect the 4% P doping to significantly affect the value of $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ and we expect it to be essentially T -independent. Indeed, the thermal variation of the lattice parameters over the whole T range across the structural transition [218; 286] produces an almost negligible change in $\nu_{a,b}^{\text{lat}}$ (Fig. 7.6(b)). So, for the lattice contribution to reproduce the experimental change of $\nu_{a,b}$ between 250 and 130 K, an unrealistic value $(1 - \gamma_\infty) = -26$ would have to be used.

ν_α^{on} is then deduced by subtracting $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$ from the experimental values of ν_α for $x = 0$ and 0.04 . Defining $i = (x, y, z)$ with $4p_x$ and $4p_y$ orbitals of As directed toward As NN, ν_α^{on} can be expressed in terms of the occupation number n_i for each As- $4p_i$ orbital as follows [291; 292]:

$$\begin{aligned} \nu_a^{\text{on}} &= \nu_0 \left(n_x - \frac{n_y + n_z}{2} \right) \\ \nu_b^{\text{on}} &= \nu_0 \left(n_y - \frac{n_z + n_x}{2} \right) \\ \nu_c^{\text{on}} &= \nu_0 \left(n_z - \frac{n_x + n_y}{2} \right), \end{aligned} \quad (7.2)$$

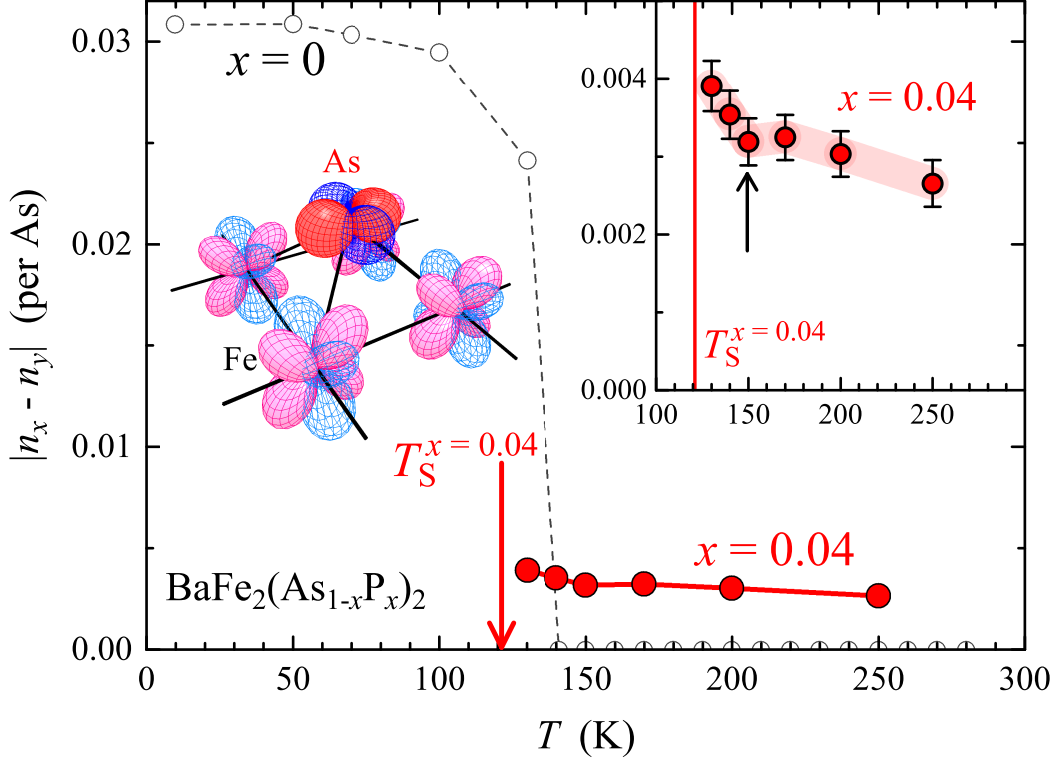


Figure 7.8: T dependence of the orbital polarization $|n_x - n_y|$ for $x = 0$ and 0.04 estimated by ν_α^{on} and Eq. (7.3). The right inset shows $x = 0.04$ data in an expanded scale. The black arrow shows a crossover in the T dependence, coinciding with observations of a nematic state in bulk measurements [132]. The left inset is a schematic description of Fe-3d and As-4p orbital orderings.

where $\nu_0 = \frac{3}{20} \frac{e^2 Q}{h} \frac{1}{4\pi\epsilon_0} \frac{4}{5} \langle r^{-3} \rangle_{4p} = 56.90$ MHz with $\langle r^{-3} \rangle_{4p} = 6.958$ a.u. The orbital polarization corresponding to an occupation difference between As-4 p_x and 4 p_y is then:

$$|n_x - n_y| = \frac{2}{3\nu_0} |\nu_a^{\text{on}} - \nu_b^{\text{on}}|. \quad (7.3)$$

Note that in doing so, we attribute all of the T -dependent broadening for $H \parallel [100]_o$ to the splitting, thus to the magnitude of the orbital polarization $|n_x - n_y|$. However, part of the broadening must be accounted for by the T dependence of the correlation length. Taking this effect into account is clearly beyond the scope of this paper. Hence, the values of $|n_x - n_y|$ reported in Fig. 7.8 should be considered as lower bounds.

$|n_x - n_y|$ for $x = 0.04$ is much smaller than in the orthorhombic phase of $x = 0$, but it clearly increases with decreasing T , especially below ~ 150 K. This characteristic temperature of ~ 150 K matches the temperature at which twofold symmetry appears in magnetic torque, lattice parameters and Fe-3d orbital polarization [132; 138]. While quantitative evaluation of the polarization of the Fe-3d orbitals has been reported in a few experiments for the AFM ordered state [136; 293; 294], no such measurement has been reported for the As-4p orbitals above T_S , to the best of our knowledge. Furthermore, the low timescale of NMR (set by the inverse linewidth of ~ 0.5 MHz) implies that the observed orbital ordering is static. The imbalance between 4 p_x and 4 p_y occupations most likely results from ordering within the Fe-3d orbitals, that is, the degeneracy of Fe-3 d_{zx} and 3 d_{yz} orbitals is lifted. Indeed, LDA calculations found that a reduction of the Fe-3 d_{yz} partial density of states (PDOS) is accompanied by a decrease in the

As-4 p_y PDOS in the AFM ordered state for $x = 0$ [295]. This suggests that orbital ordering above T_S for BaFe₂(As_{0.96}P_{0.04})₂ produces $n_x < n_y$ for the As-4 p orbitals. This in-plane orbital anisotropy must participate in lifting the degeneracy of stripe spin correlations between [100]_o and [010]_o directions, but our results do not exclude that spin-nematic fluctuations contribute as well and that they are possibly leading. A similar relationship between the lattice symmetry breaking and the enhancement of spin fluctuations has been observed in LaFeAsO [208; 296]. In any event, our point here is that static orbital ordering is present and it must thus be taken into account as an important ingredient of the physics of FeAs planes.

An important and unanticipated aspect of our data is that η at the As₀ sites, albeit small, is non-zero even at the highest measured temperature of 250 K, that is, well above the claimed nematic transition at $T^* \sim 150$ K [132]. We suspect that orbital ordering would be entirely fluctuating at high temperatures in the absence of disorder but it is made static due to pinning by defects (most likely P dopants here). Such phenomenon is analogous to the pinning of charge-density-wave fluctuations above the phase transition in NbSe₂ [297; 298] and high- T_c cuprates [299; 300] or to the pinning of AFM fluctuations around impurities in high- T_c cuprates and low-dimensional antiferromagnets [301; 302; 303]. In iron-based superconductors, there is actually theoretical [304; 305] and especially experimental evidence from scanning tunneling microscopy [261; 306; 307; 308] and transport measurements [102] that defects play a role in the nematic response.

Intrinsic spin and/or orbital nematic correlations are not produced by defects but they can be revealed by them. We expect this to be particularly true in the absence of any aligning field, *i.e.* in the unstressed tetragonal phase. In a simplified picture, static, but short-range correlated, orbital order is nucleated around P sites. Its magnitude, proportional to the amplitude of the intrinsic nematic susceptibility of the pure system, and its spatial extent, set by the nematic correlation length of the pure system, both grow on cooling. Here, given the mean P-P distance as small as five lattice spacings for 4% doping, short-range orbital order may concern essentially all of the As sites and not only the P nearest neighbors, over a wide temperature range.

Finally, another new and important aspect of our results is the observation of an upturn in the line broadening below ~ 150 K (Figs. 7.5(b) and 7.8). This reveals that coinciding anomalies reported in magnetic torque and photoemission measurements correspond either to a crossover in the magnitude and/or the length of the orbital-nematic correlations or to a true nematic phase transition [132; 138].

7.4 Short Summary

To summarize, our NMR work provides evidence for unequal population of the As 4 p_x and 4 p_y orbitals, itself due to Fe-3 d orbital ordering in the (unstressed) tetragonal phase of BaFe₂(As_{0.96}P_{0.04})₂. The data reveal that these orbital-nematic correlations are involved in the appearance of a nematic state detected below ~ 150 K by other probes [132; 138]. Furthermore, the magnitude of the orbital polarization, its static nature and its persistence at temperatures well above 150 K place strong constraints on microscopic models of nematic order in this class of superconductors.

Chapter 8

Conclusion

Systematic ^{31}P - and ^{75}As -NMR measurements on the iron pnictides $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for a wide P concentration range $0.04 \leq x \leq 0.64$ have been performed. The measurements revealed unconventional and intriguing properties of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. In this chapter, we summarize our NMR experimental results.

Antiferromagnetic state

One of the promising theories for unconventional superconductivity is the pairing induced by AFM spin fluctuations. In this scenario, the SC dome is predicted to appear around an AFM QCP. Hence, to find evidence of a QCP gives strong constraint on the theories for the superconductivity in the system. To establish the presence of a QCP, experimental evidence of a second-order quantum phase transition of an order parameter at zero-temperature limit is required. This could be more direct evidence than the anomalous behaviors at finite temperatures presumably originating from the QCP. Chapter 5 reported such direct evidence of the existence of an AFM QCP by ^{31}P -NMR studies on lightly P-substituted $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $0.07 \leq x \leq 0.33$. Static and dynamic magnetic properties of each sample were investigated via ^{31}P -NMR spectrum and T_1 measurements, respectively. The averaged magnetic ordered moment $\langle m \rangle$ (as an order parameter) at the zero-temperature limit shows a continuous decrease toward $x \sim 0.35$ with increasing P concentration x , verifying that a second-order quantum phase transition occurs at $x \sim 0.35$. The SDW gap Δ_S estimated from the reduction of $(T_1T)^{-1}$ below T_N and the characteristic temperature of AFM spin fluctuations θ estimated from the enhancement of $(T_1T)^{-1}$ in the normal state also decrease toward $x \sim 0.35$ with increasing x . All these results indicate the existence of an AFM QCP at $x \sim 0.35$, suggesting that AFM quantum critical spin fluctuations play a crucial role for the pairing mechanism in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

Coexisting state of superconductivity and antiferromagnetism

The coexisting state of magnetism and superconductivity is one of the most intriguing subject for study since the mechanism of unconventional superconductivity is expected to be highly related to magnetism. The researchers often take an interest in how they coexist: the mixing state of two different orderings is either macroscopic, i.e. inhomogeneous / phase-separated coexistence or microscopic, i.e. homogeneous coexistence in the real space. However, the probe which can distinguish these states are limited. NMR is a powerful technique to clarify them because we can measure static and dynamic properties of the electronic state at the specific nuclei selectively and investigate whether the SC transition occurs at magnetically ordered site or not. Chapter 6 reported ^{31}P -NMR measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ for $x = 0.25$ at

ambient pressure and $x = 0.20$ at hydrostatic pressure of $p \sim 2$ GPa. We observed ^{31}P $(T_1T)^{-1}$ measured at the magnetically ordered site shows SC transition in both $x = 0.25$ and $x = 0.20$ ($p \sim 2$ GPa) samples. This is the direct evidence of spatial coexistence of superconductivity and magnetism in microscopic scale. Moreover, ^{31}P -NMR spectrum became narrow below T_c , indicative of the suppression of internal magnetic field due to competition between SC and AFM order parameters. Our results strongly suggest that antiferromagnetism and superconductivity occur at the same Fermi surfaces but compete with each other.

Orbital nematic state

In the research field of iron pnictides, the importance of orbital degrees of freedom has been recognized as well as the spin and lattice degrees of freedom since fluctuations related to these degrees of freedom are believed to be at the origin of their high- T_c superconductivity. Recently, the electronic nematic state has been observed above T_S by various experiments in which the electronic state spontaneously breaks the four-fold lattice symmetry thus making various physical properties two-fold symmetric in the plane. Although the relationship between nematicity and orbital ordering has been debated, few microscopic and quantitative experimental information has been reported so far. NMR can potentially detect the local anisotropy since it gives microscopic information by using a specific nuclear site as a local probe. In Chapter 7, we reported in-plane field orientation dependence of ^{75}As -NMR of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ single crystal for $x = 0.04$ above T_S . A large difference in the linewidth between $H \parallel [100]_o$ and $H \parallel [110]_o$ reveals in-plane anisotropy of the electric field gradient, even in the tetragonal phase. This provides microscopic evidence of population imbalance between As- $4p_x$ and $4p_y$ orbitals, which reaches $|n_x - n_y| \sim 0.004$ electron at $T \rightarrow T_S$ and is a natural consequence of orbital ordering of Fe- $3d_{xz}$ and d_{yz} electrons. Surprisingly, this orbital polarization is found to be already static near room temperature, suggesting that it arises from the pinning of anisotropic orbital fluctuations by disorder. Furthermore, the appearance of nematicity in torque and photoemission measurements is found to coincide with an upturn in the line broadening below ~ 150 K, which reveals either a crossover in the magnitude/length of the orbital-nematic correlations, or a phase transition. These results impose strong constraints on microscopic models of the nematic state.

Finally, we conclude that, from our NMR measurement outside of SC dome various exotic state are observed. Dynamic spin fluctuations associated with an AFM QCP seem to support superconductivity, while static AFM order competes with superconductivity. As- $4p$ orbital polarization in the nematic state which can potentially enhance the spin fluctuation by lifting degeneracy of $(\pi, 0)$ and $(0, \pi)$ nesting vectors indicates the importance of hybridization of Fe and As orbitals and the strongly coupled spin, orbital, and lattice degrees of freedom in the iron pnictides. These observations will promote theoretical understanding of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and impose important constraints on the pairing mechanism of the iron-based superconductor.

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Appendices

A Distribution of T_1 : Stretched Exponential Function Analysis

The stretched exponential function can be written as a sum of pure exponential decays, with a particular probability distribution P of $1/T_1$ values for a given value of β . In such a probability distribution, one must normalize $1/T_1$ to the characteristic relaxation rate $1/T_1^*$ appearing in Eqs. (3.11) and (3.12). Hence for such systems one can write the stretched exponential function in Eq. (3.11) as

$$\exp \left\{ - \left(\frac{t}{T_1^*} \right)^\beta \right\} = \int_0^\infty P(s, \beta) \exp \left\{ -s \frac{t}{T_1^*} \right\}, \quad (\text{A.1})$$

where

$$s \equiv \frac{1/T_1}{1/T_1^*}. \quad (\text{A.2})$$

Since $P(s, \beta)$ is a probability density, one has $\int_0^\infty P(s, \beta) ds = 1$. For $\beta = 1$, the stretched exponential function Eq. (3.11) is a pure exponential with relaxation rate $1/T_1 = 1/T_1^*$ and hence the probability density $P(s, 1)$ is a Dirac δ function at $s = 1$. For general β , $P(s, \beta)$ is given by:

$$P(s, \beta) = \frac{1}{\pi} \int_0^\infty \exp \left[-u^\beta \cos \left(\frac{\pi\beta}{2} \right) \right] \cos \left[su - u^\beta \sin \left(\frac{\pi\beta}{2} \right) \right] du. \quad (\text{A.3})$$

The evolution of $P(s, \beta)$ versus s at fixed β is shown in Fig. A.1(a). From the figure, $\beta < 1$ causes the Dirac δ -function-shaped $P(s, 1)$ to broaden. $P(s)$ becomes asymmetric, and the peak moves towards slower rates. Thus, the physical interpretation of $1/T_1^*$ should not be taken as the average of $1/T_1$. The average value of $1/T_1$ can be generally estimated as follows [309]:

$$\frac{1}{T_1^{\text{ave}}} = \frac{\beta}{\Gamma\left(\frac{1}{\beta}\right)} \frac{1}{T_1^*}. \quad (\text{A.4})$$

The β evolution of the ratio T_1^{ave}/T_1^* is shown in Fig. A.1(b). As for the physical interpretation of β , it can be considered to be related to the logarithmic FWHM of $P(s)$ as shown in Fig. A.1(c).

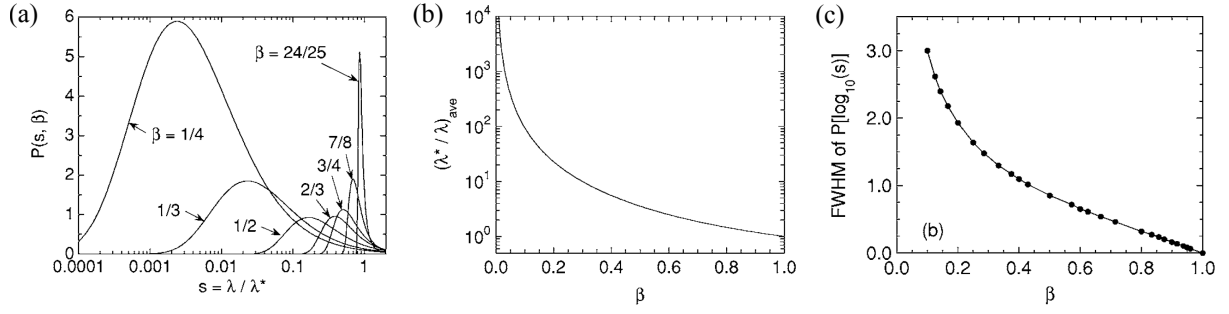


Figure A.1: (a) Semi-log plots of the probability density $P(s, \beta)$ for the relaxation versus normalized relaxation $s = (1/T_1)/(1/T_1^*)$ for several rational values of β . (b) Semi-log plot of the average T_1^{ave}/T_1^* versus the stretching exponent β according to Eq. (A.4). (c) FWHM versus β of $P(\log_{10}(s))$ on a logarithmic s scale.

B ^{31}P -NMR Spectrum for a Commensurate Antiferromagnetic Ordered State of Polycrystalline Sample

In this section, I develop the expression for ^{31}P -NMR ($I = 1/2$) spectral shape in the stripe-type commensurate AFM ordered state of polycrystalline sample. Such spectrum is actually observed in P-underdoped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Here, all of the tiny crystals in polycrystalline sample is considered to be fixed with varnish to avoid preferential alignment of the crystal in the applied magnetic field.

First, we assume that an external magnetic field is applied along z -axis: $\mathbf{H} = (0, 0, H)$. Internal magnetic field is defined as $\mathbf{H}_{\text{int}} = (H_{\text{int}} \sin \theta, 0, H_{\text{int}} \cos \theta)$, where we may assume without loss of generality that x -axis is the tilting direction of $\mathbf{H}_{\text{int}}$ with respect to $\mathbf{H}$ (Fig. B.2). Then, the Zeeman Hamiltonian becomes

$$\mathcal{H}_z = -\gamma \hbar \mathbf{I} \cdot \mathbf{H} \quad (\text{B.5})$$

$$= -\gamma \hbar [I_x H_{\text{int}} \sin \theta + I_z (H + H_{\text{int}} \cos \theta)] \quad (\text{B.6})$$

$$= -\gamma \hbar \left[\frac{1}{2} (I_+ + I_-) H_{\text{int}} \sin \theta + I_z (H + H_{\text{int}} \cos \theta) \right]. \quad (\text{B.7})$$

To obtain the eigen value E of this Hamiltonian, the eigen value $x = -E/\gamma \hbar$ of the expression inside the square bracket $[]$ in the above equation is calculated as follows:

$$[x + (H + H_{\text{int}} \cos \theta)] [x - (H + H_{\text{int}} \cos \theta)] - H_{\text{int}}^2 \sin^2 \theta = 0 \quad (\text{B.8})$$

$$x^2 - (H + H_{\text{int}} \cos \theta)^2 - H_{\text{int}}^2 \sin^2 \theta = 0 \quad (\text{B.9})$$

$$x^2 - (H^2 + 2HH_{\text{int}} \cos \theta + H_{\text{int}}^2 \cos^2 \theta + H_{\text{int}}^2 \sin^2 \theta) = 0 \quad (\text{B.10})$$

$$x^2 - (H^2 + 2HH_{\text{int}} \cos \theta + H_{\text{int}}^2) = 0 \quad (\text{B.11})$$

$$x = \pm \sqrt{H^2 + 2HH_{\text{int}} \cos \theta + H_{\text{int}}^2}. \quad (\text{B.12})$$

Thus, the eigen value of the Zeeman Hamiltonian and the resonance angular frequency ω can

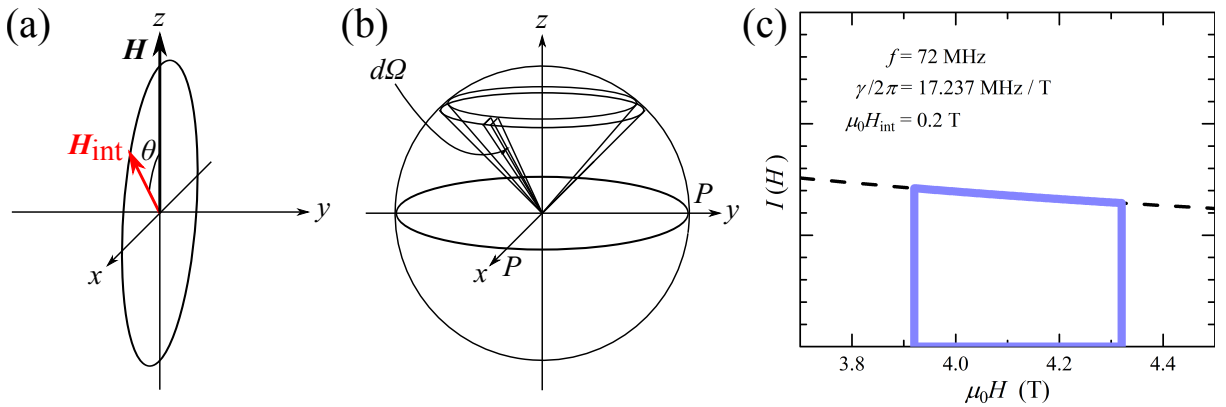


Figure B.2: (a) Positional relationship between the applied external field $\mathbf{H}$ and internal field $\mathbf{H}_{\text{int}}$. The angle between these two field vectors is defined as θ . (b) Schematic image of solid angle integral of the constant number density P . (c) Calculated ^{31}P -NMR spectrum at $f = 72 \text{ MHz}$ with $\mu_0 H_{\text{int}} = 0.2 \text{ T}$. The broken line indicates the calculated result of Eq. (B.28).

be derived as

$$E = \hbar\omega = \gamma\hbar\sqrt{H^2 + 2HH_{\text{int}}\cos\theta + H_{\text{int}}^2} \quad (\text{B.13})$$

$$\omega = \gamma\sqrt{H^2 + 2HH_{\text{int}}\cos\theta + H_{\text{int}}^2} \quad (\text{B.14})$$

since $\omega > 0$. Considering $-1 \leq \cos\theta \leq 1$, the range of ω is obtained:

$$-1 \leq \frac{\left(\frac{\omega}{\gamma}\right)^2 - (H^2 + H_{\text{int}}^2)}{2HH_{\text{int}}} \leq 1 \quad (\text{B.15})$$

$$\gamma|H - H_{\text{int}}| \leq \omega \leq \gamma|H + H_{\text{int}}|. \quad (\text{B.16})$$

In order to reproduce the spectral shape, we derive the number density of P nuclei as a function of angular frequency $g(\omega)$ as a next step. Since the total number of P nuclei should conserve, the following equation holds:

$$\int_{\gamma|H-H_{\text{int}}|}^{\gamma|H+H_{\text{int}}|} g(\omega)d\omega = \int_{\Omega} P(\theta, \phi)d\Omega = \int_0^{2\pi} \int_0^{\pi} P \sin\theta d\theta d\phi = -2\pi P \int_{\gamma|H-H_{\text{int}}|}^{\gamma|H+H_{\text{int}}|} \sin\theta \frac{d\theta}{d\omega} d\omega, \quad (\text{B.17})$$

where Ω is solid angle and $P(\theta, \phi)$ represents the number density of P nuclei sensing the internal magnetic field along (θ, ϕ) -direction as shown in Fig. B.2(b). As no preferential alignment of crystals is considered in the present situation, $P(\theta, \phi) = P$, i.e., constant. Taking θ -derivative of Eq. (B.14),

$$\frac{d\omega}{d\theta} = -\gamma(H^2 + 2HH_{\text{int}}\cos\theta + H_{\text{int}}^2)^{-\frac{1}{2}} HH_{\text{int}} \sin\theta. \quad (\text{B.18})$$

By substituting the inverse of Eq. (B.18) into Eq. (B.17), we obtain

$$g(\omega) = -2\pi P \sin\theta \frac{\sqrt{H^2 + 2HH_{\text{int}}\cos\theta + H_{\text{int}}^2}}{-\gamma HH_{\text{int}} \sin\theta} \quad (\text{B.19})$$

$$= \frac{2\pi P}{\gamma HH_{\text{int}}} \sqrt{H^2 + 2HH_{\text{int}}\cos\theta + H_{\text{int}}^2} \quad (\text{B.20})$$

$$= \frac{2\pi P\omega}{\gamma^2 HH_{\text{int}}}. \quad (\text{B.21})$$

$g(\omega)$ corresponds to the ^{31}P -NMR spectral shape obtained by frequency-sweep. In our experiment of Chapter 5, we obtained spectra by sweeping external field. Therefore, we need to deduce

H dependence of g as follows:

$$g(H) = g(\omega) \frac{d\omega}{dH} \quad (\text{B.22})$$

$$= \frac{2\pi P \omega}{\gamma^2 H H_{\text{int}}} \frac{\gamma}{2} (H^2 + 2H H_{\text{int}} \cos \theta + H_{\text{int}}^2)^{-\frac{1}{2}} (2H + 2H_{\text{int}} \cos \theta) \quad (\text{B.23})$$

$$= \frac{2\pi P (H + H_{\text{int}} \cos \theta)}{H H_{\text{int}}} \frac{\omega}{\gamma \sqrt{H^2 + 2H H_{\text{int}} \cos \theta + H_{\text{int}}^2}} \quad (\text{B.24})$$

$$= 2\pi P \frac{H + H_{\text{int}} \cos \theta}{H H_{\text{int}}} \quad (\text{B.25})$$

$$= 2\pi P \frac{H + \frac{\left(\frac{\omega}{\gamma}\right)^2 - (H^2 + H_{\text{int}}^2)}{2H}}{H H_{\text{int}}} \quad (\text{B.26})$$

$$= 2\pi P \frac{H^2 + \left(\frac{\omega}{\gamma}\right)^2 - H_{\text{int}}^2}{2H^2 H_{\text{int}}} \quad (\text{B.27})$$

$$= \frac{\pi P}{H_{\text{int}}} \left\{ 1 + \frac{1}{H^2} \left[\left(\frac{\omega}{\gamma} \right)^2 - H_{\text{int}}^2 \right] \right\}. \quad (\text{B.28})$$

The resulting spectral shape is displayed in Fig. B.2(c). When $H_{\text{int}}/H \ll 1$, the shape becomes more like rectangular. The spectrum spans from $H - H_{\text{int}}$ to $H + H_{\text{int}}$.

C Probability Distribution of Internal Magnetic Field Deduced from ^{31}P -NMR Spectrum in Magnetically Ordered State of Polycrystalline Sample

The probability distribution of the magnitude of internal field $g(H_{\text{int}})$ can be calculated by using the experimentally obtained spectral shape of polycrystalline sample $I(H_{\text{int}})$ as a function of $H_{\text{int}} = H - H_{\text{peak}}$, where H_{peak} is the center peak frequency of the spectrum. In the track of the previous Section B, we assume that an internal magnetic field H_{int} without any distribution of magnitude makes rectangular spectral shape whose constant intensity is $2\pi P/H_{\text{int}}$ (see Fig. C.3(a) and (b)). This assumption is valid when $H_{\text{int}} \ll H$. As shown in Fig. C.3(c), we approximate the experimental spectral shape with the summation of multiple rectangular-shaped spectra with H_{int}^i . We take $H_{\text{int}}^0, H_{\text{int}}^1, \dots, H_{\text{int}}^i, \dots$ toward 0 at regular intervals ΔH_{int} . Then, the equation

$$I(H_{\text{int}}^i) - I(H_{\text{int}}^{i-1}) = \frac{2\pi P}{H_{\text{int}}^{i-1}} g(H_{\text{int}}^{i-1}), \quad (\text{C.29})$$

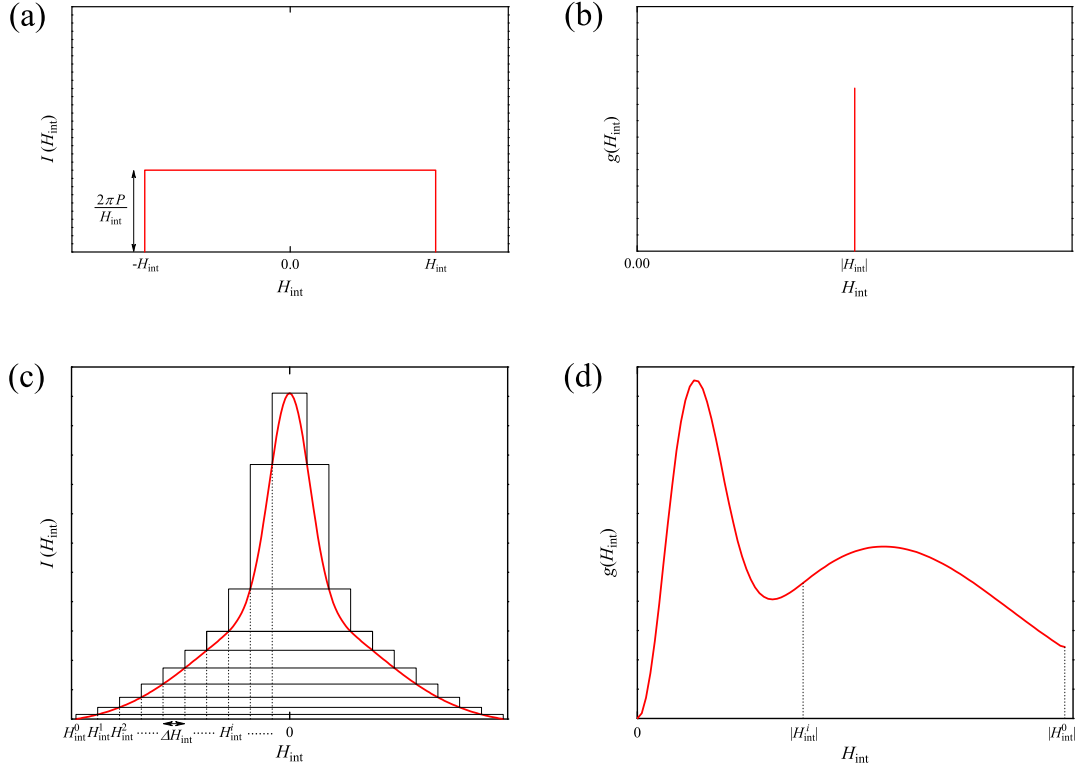


Figure C.3: (a) Approximated NMR spectrum for $I = 1/2$ in rectangular shape in commensurate AFM ordered state. (b) The probability distribution of H_{int} expected from lineshape of (a) deduced from Eq. (B.28). (c) NMR spectrum for $I = 1/2$ in magnetically ordered state with distributed amplitude of H_{int} as an example. (d) The probability distribution of H_{int} expected from lineshape of (c) deduced from Eq. (B.28).

holds for any i . Here, the integral of $g(H_{\text{int}})$ is assumed to be normalized. Then, the probability for H_{int}^i can be calculated as

$$g(H_{\text{int}}^i) = \frac{H_{\text{int}}^i}{2\pi P} [I(H_{\text{int}}^{i+1}) - I(H_{\text{int}}^i)] \quad (\text{C.30})$$

$$\propto H_{\text{int}}^i [I(H_{\text{int}}^{i+1}) - I(H_{\text{int}}^i)] \quad (\text{C.31})$$

$$\propto H_{\text{int}}^i \frac{I(H_{\text{int}}^{i+1}) - I(H_{\text{int}}^i)}{\Delta H_{\text{int}}} \quad (\text{C.32})$$

$$\propto H_{\text{int}}^i \frac{I(H_{\text{int}}^{i+1}) - I(H_{\text{int}}^i)}{H_{\text{int}}^{i+1} - H_{\text{int}}^i}. \quad (\text{C.33})$$

By taking $\Delta H_{\text{int}} (= H_{\text{int}}^{i+1} - H_{\text{int}}^i) \rightarrow 0$, we obtain

$$g(H_{\text{int}}) \propto H_{\text{int}} \frac{dI(H_{\text{int}})}{dH_{\text{int}}}. \quad (\text{C.34})$$

The spectrum shown in Fig. C.3(d) is the probability distribution of H_{int} derived from the NMR spectrum in Fig. C.3(c) using Eq. (C.34). Note that $g(H_{\text{int}})$ close to $H_{\text{int}} \rightarrow 0$ is not much reliable because smearing effect often seen in the experimentally obtained spectrum due to statistical distribution of observables underestimate the probability close to $H_{\text{int}} \rightarrow 0$.

D Phosphorus-Concentration Dependence of the Density of States in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

In case of conventional phonon-mediated superconductivity, T_c is closely related to the quasiparticle density of states $N(E_F)$ in the form of $T_c = 1.14\omega_D e^{-2/gN(E_F)}$, where ω_D is the characteristic frequency of collective excitations involved in pairing interaction and g is the appropriate dimensional coupling constant. Since there is a possibility that the changes in T_c by chemical substitution and/or physical pressure is attributed to the changes in $N(E_F)$, it should be examined with a proper system to discuss the nature of dominant pairing interaction.

$\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is one of the ideal system to study this problem because P substitution introduces chemical pressure without doping charge carriers in contrast with hole-doping $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ and electron-doping $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$. Our investigation clarified that $N(E_F)$ remains almost unchanged by P substitution, while the characteristic temperature of AFM spin fluctuation θ deduced from the normal-state $(T_1T)^{-1}$ largely changes with a sign change across an anticipated QCP at $x \sim 0.35$. These suggest that the change in AFM correlations related to the quantum critical character is more important than the change in $N(E_F)$ for T_c variation in the P-substituted system.

The resonance frequencies of ^{31}P -NMR spectra consisting of a single line for $0.07 \leq x \leq 0.64$ are temperature-independent in the normal state as already partly seen in our previous publication [100]. The temperature variation of K is shown in Fig. D.4(a). K in the normal state slightly decrease with increasing P-concentration x . In general, K is considered to be composed of the temperature-dependent spin shift K_{spin} and the temperature-independent chemical shift K_{chem} : $K(T) = K_{\text{spin}}(T) + K_{\text{chem}}$. K_{spin} is proportional to $^{31}A_{\text{hf}}^{\text{dia}}N(E_F)V$, where $^{31}A_{\text{hf}}^{\text{dia}}$ is the average of diagonal components of the hyperfine coupling tensor between P and Fe sites and V is the unit cell volume, while K_{chem} is unrelated to $N(E_F)$. Since no obvious AFM fluctuations were detected via $(T_1T)^{-1}$ at high temperatures as seen in Fig. D.4(b), it would be a good approximation to consider that $(T_1T)^{-1}$ is proportional to $|A_{\text{hf}}^{\text{off}}|^2N^2(E_F)V^2$ at high

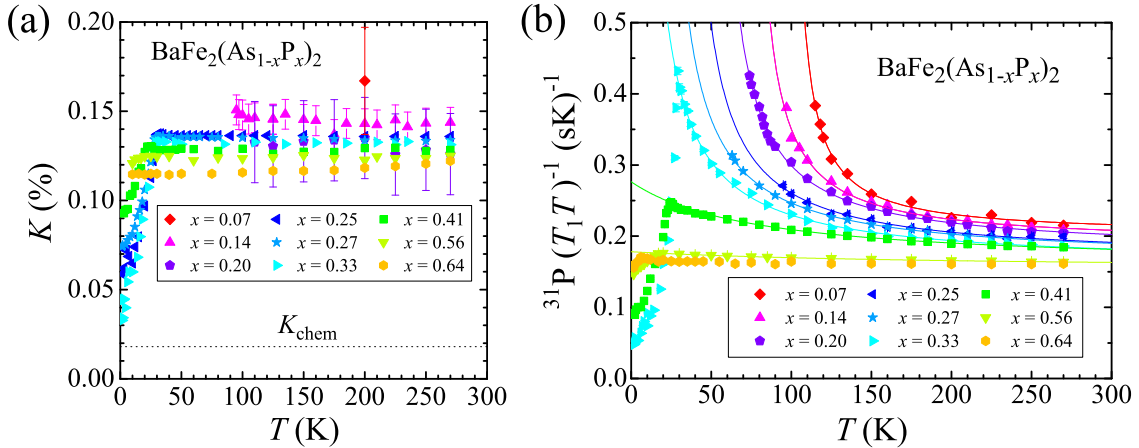


Figure D.4: (a) The temperature dependence of K for $0.07 \leq x \leq 0.64$ in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The black arrow denotes the value of $K_{\text{chem}} = 0.018 \pm 0.019$ % determined by $(T_1T)^{-1/2} - K$ plot (Fig. D.5). (b) The temperature dependence of $(T_1T)^{-1}$ for $0.07 \leq x \leq 0.64$ in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The solid lines are the fitting curves to $(T_1T)^{-1} = a + b/(T + \theta)$. The inset shows x dependence of the fitting parameters a and θ , and the dotted line corresponds to 0 K in the right axis.

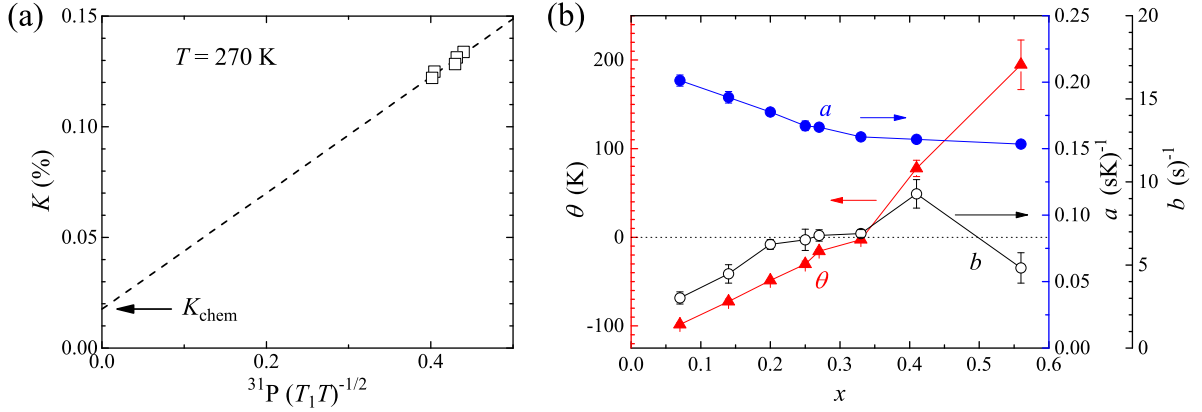


Figure D.5: (a) K vs $(T_1T)^{-1/2}$ plot at 270 K as an implicit function of x . (b) The x dependence of the CW fitting parameters a , b and θ . The dotted line indicates 0 K in the left axis.

temperatures, i.e., to assume that the usual Korringa relation holds, where $A_{\text{hf}}^{\text{off}}$ is the off-diagonal component of the hyperfine coupling tensor between P and Fe sites. Based on the plot of $(T_1T)^{-1/2}$ against K at 270 K as an implicit parameter of x shown in Fig. D.5(a), we estimated $K_{\text{chem}} = 0.018 \pm 0.019$ % from the intercept on the assumption of x independent K_{chem} [100]. This value would be reasonable since K_{chem} for ^{31}P in many diamagnetic insulators is of the order of some hundreds of ppm [140]. Subtracting the obtained K_{chem} from K , we deduced K_{spin} at 200 K for each x and plotted them in Fig. D.6(a). Assuming that the hyperfine coupling tensor $\mathbf{A}_{\text{hf}}$ is independent of P concentration, x evolution of $N(E_F)$ can be followed by plotting K_{spin}/V as a function of x . The x dependence of K_{spin}/V suggests that the change in $N(E_F)$ is at most 7 % for superconducting region from $x = 0.20$ to 0.64. This result is quantitatively consistent with the change in $N(E_F)$ deduced from $(T_1T)^{-1/2}/V$ and our band calculation. The band calculations by local-density-approximation (LDA) were performed for nonspin-polarized BaFe_2As_2 and BaFe_2P_2 , using the WIEN2K package in the Augmented plane wave (APW) + local orbital basis [100]. Here, for the LDA calculations and calculation of $V = a^2c$, we used linearly-interpolated structural parameters $(a, c, z) = [a_0(1-x) + a_1x, c_0(1-x) + c_1x, z_0(1-x) + z_1x]$, where $a_{0(1)}$, $c_{0(1)}$, and $z_{0(1)}$ are the experimental values for the crystallographic parameters of BaFe_2As_2 (BaFe_2P_2) [83; 88; 286]. The calculated $N(E_F)$ is plotted as a solid line in Fig. D.6(a), which agrees quite well with the experimental results.

Low energy spin fluctuations are probed by measuring $(T_1T)^{-1}$. AFM spin fluctuations are enhanced significantly with decreasing x from $x = 0.64$ where $(T_1T)^{-1}$ is almost constant. The measured $(T_1T)^{-1}$ can be well fitted by the equation expected from the SCR theory under the existence of 2D AFM spin fluctuations [156]: $(T_1T)^{-1} = a + b(T + \theta)^{-1}$, which is shown as solid lines in Fig. D.4(b). The first term is the contribution originating from intraband scattering and is proportional to $(N(E_F)V)^2$, the second term is the contribution of interband AFM spin fluctuation. x dependence of a , b and θ are demonstrated in Fig. D.5(b). With increasing x , the parameter a decreases slightly whereas θ increases significantly with a sign change around $x \sim 0.33$ where an AFM QCP is anticipated. Since the parameter b is a product of multiple physical parameters defined in the SCR theory, the origin of this behavior is too complex to discuss and thus we skip. All the fitting parameters for $x = 0.07 - 0.56$ are listed in Table D.1.

We found the three different doping evolution of $N(E_F)$ by plotting $(T_1T)^{-1/2}/V$ at high temperatures for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ [310; 311], and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [153;

Table D.1: Curie-Weiss fitting parameters a , b , and θ for $(T_1 T)^{-1}$ in the normal state. The fitting equation is expressed as: $(T_1 T)^{-1} = a + b/(T + \theta)$.

x	a (sK) $^{-1}$	b (s $^{-1}$)	θ (K)
0.07	0.201	3.02	-98.4
0.14	0.189	4.46	-72.4
0.20	0.178	6.24	-48.7
0.25	0.167	6.51	-30.3
0.27	0.166	6.78	-15.8
0.33	0.159	6.89	-2.64
0.41	0.157	9.28	77.7
0.56	0.153	4.82	194.6

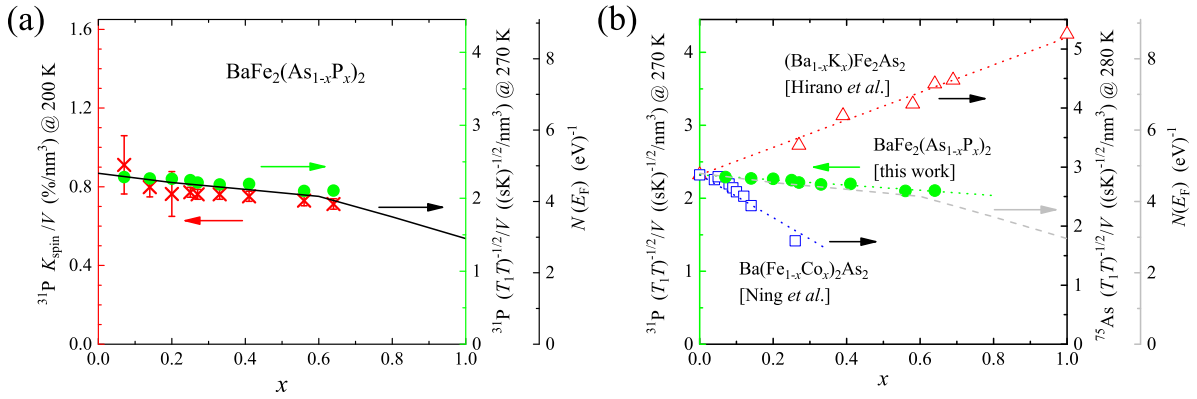


Figure D.6: (a) x dependence of $^{31}\text{P } K_{\text{spin}}/V$ at 200 K, $^{31}\text{P } (T_1 T)^{-1/2}/V$ at 270 K and $N(E_F)$ derived from the band calculation of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. (b) x dependence of $^{31}\text{P } (T_1 T)^{-1/2}/V$ at 270 K and $N(E_F)$ from band calculation of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $^{75}\text{As } (T_1 T)^{-1/2}/V$ at 280 K of $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ [310; 311] and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [153; 312]. The dotted lines are guides to the eye. The vertical axes of ^{31}P and $^{75}\text{As } (T_1 T)^{-1/2}/V$ are adjusted to unify the value of $N(E_F)$ of BaFe_2As_2 in the outer right axis.

[312] with a scale of $N(E_F)$ in the outer right axis for comparison. The K- and Co-substitution induce significant changes in $N(E_F)$, while the P-substitution has little effects on $N(E_F)$. Note that the change in $N(E_F)$ from the value of BaFe_2As_2 for superconducting dome region is $\sim +60\%$ for $0.2 \leq x \leq 1$ in $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ and $\sim -16\%$ for $0.04 \leq x \leq 0.14$ in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, whereas the change in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ is only $\sim -7\%$. Since $N(E_F)$ changes linearly with all the three chemical substitution, the increasing/decreasing rates of $N(E_F)$ can be calculated to be $\sim +0.039 \text{ eV}^{-1}/x$ (% K), $\sim -0.007 \text{ eV}^{-1}/x$ (% P), and $\sim -0.061 \text{ eV}^{-1}/x$ (% Co) for K, P, Co-doped system, respectively. The significantly low change rate of $N(E_F)$ in P-doped system indicates that there is almost no shift in the Fermi level by P substitution as expected from the isovalency of P and As ions, i.e., indicates no charge-doping. On the other hand, relatively high change rates with positive (negative) sign in K(Co)-doped system can be understood by lowering (lifting) of the Fermi level in the band structure of BaFe_2As_2 within the rigid band model [313]. In spite of the remarkable difference in doping evolution of $N(E_F)$ among K-, P-, and Co-doped systems, the phase diagrams for these three systems are similar. The dome shaped changes of T_c as a function of x are not understandable only by the change of $N(E_F)$.

These results suggest that the change of $N(E_F)$ is not a primary role for superconductivity in the “122” compounds. Rather, the AFM fluctuations with the quantum critical character are more important for superconductivity. Our experiments clarified that T_c in the “122” system is not mainly determined by the $N(E_F)$ change but by the AFM spin fluctuations.

E Two-Fluid Model Fitting for $(T_1T)^{-1}$ in Magnetically Ordered State of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

As proposed by Smerald *et al.*, the temperature dependence of $(T_1T)^{-1}$ in the AFM ordered state of iron pnictides is reproduced by assuming the two-fluid model: one is from spin-lattice relaxation channel by the gapless particle-hole excitations and the other is from the channel by the gapped spin-wave excitations [202]. $(T_1T)^{-1}$ in the AFM ordered state for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ can be also reproduced by this model, using the expression of

$$\frac{1}{T_1} = C_{\text{inc}}T + C_{\text{coh}}\Phi\left(\frac{k_{\text{B}}T}{\Delta_{\text{S}}}\right), \quad (\text{E.35})$$

where the constant C_{inc} describes the relaxation via the gapless particle-hole excitations, the constant C_{coh} represents the relaxation via the gapped spin-wave excitations, Δ_{S} is a spin gap, $\Phi(x) = x^2\text{Li}_1(e^{-\frac{1}{x}}) + x^3\text{Li}_2(e^{-\frac{1}{x}})$ and $\text{Li}_n(z) = \sum_{k=0}^{\infty} z^k/k^n$ is the n -th polylogarithm of z .

The x dependence of the two-fluid fitting parameters for $(T_1T)^{-1}$ below T_{N} in BFAP is summarized in Table E.2.

According to Ref. [202],

$$C_{\text{inc}} = \frac{1}{4}\pi\hbar\gamma^2|A_{\text{hf}}|^2g_{\text{L}}^2V^2N^2(E_{\text{F}})k_{\text{B}} \propto |A_{\text{hf}}|^2V^2N^2(E_{\text{F}}) \quad (\text{E.36})$$

$$C_{\text{coh}} = \frac{|A_{\text{hf}}|^2m_0^2\hbar V^2\gamma^2\Delta_{\text{S}}^3}{8\pi^3\chi_{\perp}^2\bar{v}_{\text{S}}^6} \propto \frac{|A_{\text{hf}}|^2m_0^2V^2\Delta_{\text{S}}^3}{\chi_{\perp}^3\bar{v}_{\text{S}}^6}, \quad (\text{E.37})$$

where g_{L} is the Landé g -factor, $\bar{v} = (v_x v_y v_z)^{1/3}$ the geometric mean spin wave velocities, the zero-temperature bare moment m_0 , transverse susceptibility $\chi_{\perp}$. We can discuss the P-doping evolution of these parameters. In the Chapter 5, we have already discussed the continuous suppression of Δ_{S} toward the anticipated AFM QCP. Here, since C_{coh} includes too many individual variables to discuss x dependence, we focus on x dependence of C_{inc} . $C_{\text{inc}}^{-1/2}/V$ is proportional to the residual density of states RDOS in the AFM ordered phase on the assumption of the constant $|A_{\text{hf}}|$ against x . The experimentally obtained x -dependence of DOS for each state spanning from $x = 0$ to 1 is exhibited together with the band calculation result of $N(E_{\text{F}})$ in Fig. E.7. RDOS in the AFM ordered state increases as x increases. This behavior is considered to be related to the suppression of the magnitude of Δ_{S} and the ordered moment m . The suppression of the antiferromagnetism results in expanding the area of residual FSs after the magnetic transition, and thus, $N(E_{\text{F}})$ in the AFM state increases. However, $(T_1T)^{-1/2}/V$ value in the AFM state just above T_{c} shows diverging enhancement with increasing x and even exceeds the

Table E.2: Two-fluid fitting parameters C_{inc} , C_{coh} , and Δ_{S} for $(T_1T)^{-1}$ in the AFM ordered state. The fitting equation is expressed as: $(T_1T)^{-1} = C_{\text{inc}} + C_{\text{coh}}\Phi(k_{\text{B}}T/\Delta_{\text{S}})/T$.

x	$C_{\text{inc}} (\text{sK})^{-1}$	$C_{\text{coh}} (\text{s}^{-1})$	$\Delta_{\text{S}} (\text{meV})$
0	0.032	7.5	9.8
0.07	0.032	15	9 ± 3
0.14	0.06	8	6 ± 3
0.20	0.125	7	6 ± 4
0.25	0.182	0.45	2 ± 2

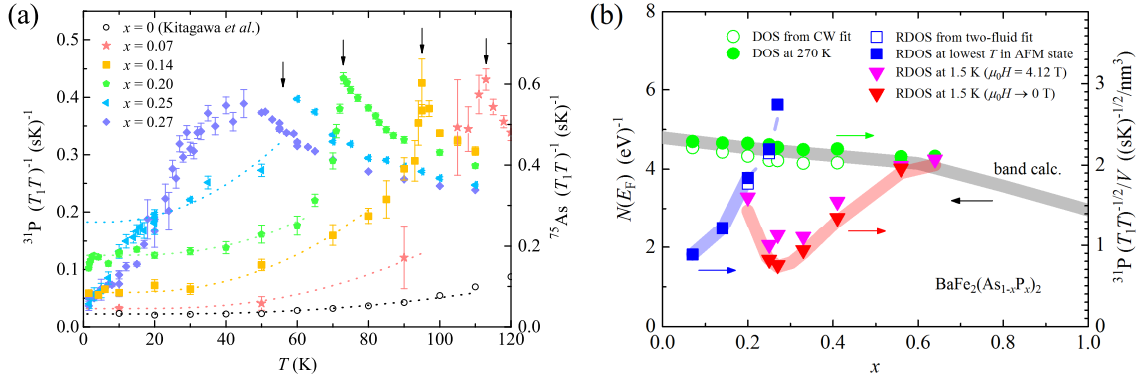


Figure E.7: (a) Two-fluid fitting curves to $(T_1T)^{-1}$ below T_N shown by dotted lines. The black arrow indicates T_N for each x . (b) The experimentally determined x dependence of $N(E_F)$ in PM, AFM, and SC states for $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The grey band is $N(E_F)$ deduced from the band structure calculation (see Sec. D).

normal state density of states shown by green plots at $x = 0.27$. Possible reason for this is that $(T_1T)^{-1}$ detects finite spin fluctuations originating from the largely-remaining residual FS. From the RDOS in the SC state shown by red plots, we can infer that the superconductivity with the highest T_c and the largest SC gap occurs at $x \sim 0.3$ as shown by Hashimoto *et al.* [128] because RDOS takes minimum at $x = 0.27$. This is consistent with the discussion about the difference between the location of QCP inferred from inside and outside SC dome, held in the previous section (Sec. D)

F Point Charge Simulation of Electric Field Gradient

Calculations of the electric field gradient contributed from the charge of lattice ions, i.e. ν_α^{lat} , were done in Sec. 7.3 using the point charge model. In this section, we briefly explain the process and results of simulation. The basic concept behind this model is to approximate each ion in a crystal lattice by its ionic charge, centered at a point of radius zero.

In general, the EFG is a difficult quantity to compute, since it must be derived by differentiating the potential

$$V(\mathbf{r}_0) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{r} d\mathbf{r}', \quad (\text{F.38})$$

where the integral is taken over a volume swept out by $\mathbf{r}'$, and the vector $\mathbf{r} = \mathbf{r}' - \mathbf{r}_0$. Since our simulations assume a point charge distribution, Eq. (F.38) can be simplified to

$$V(\mathbf{r}_0) = \frac{1}{4\pi\epsilon_0} \sum_k \frac{q_k}{r'_k}, \quad (\text{F.39})$$

by substituting in the charge distribution of k point charges $\rho(\mathbf{r}) = \sum_k q_k \delta^3(\mathbf{r} - \mathbf{r}_k)$. This equation for $V(\mathbf{r}_0)$ can be differentiated as:

$$V_{ij}(\mathbf{r}_0) = \frac{\partial^2}{\partial x_i \partial x_j} \left(\frac{1}{4\pi\epsilon_0} \sum_k \frac{q_k}{r'_k} \right) = \frac{1}{4\pi\epsilon_0} \sum_k q_k \left(\frac{\partial^2}{\partial x_i \partial x_j} \frac{1}{r'_k} \right) = \frac{1}{4\pi\epsilon_0} \sum_k V_{ij}^{(k)}, \quad (\text{F.40})$$

where

$$V_{ij}^{(k)} = q_k \left(\frac{3x'_i x'_j - \delta_{ij} r_k'^2}{r_k'^5} \right) \quad (\text{F.41})$$

is the contribution of each charge towards the (i, j) -th component of the EFG tensor. To calculate the EFG, one need only specify the partial EFG due to each point charge, and sum each contribution. In the case of an infinite number of charges to consider, an approximation to the EFG can be made over a finite number of n unit cells:

$$\tilde{V}_{ij} = \frac{1}{4\pi\epsilon_0} \sum_{n_a} \sum_{n_b} \sum_{n_c} \sum_{\text{unitcell}} V_{ij}^{(k)}, \quad (\text{F.42})$$

where n_a , n_b , and n_c are the number of unit cells from the center basing unit cell where the As site of interest locates along a_o -, b_o -, and c_o -axes, respectively. The forth sum indicates the summation of contribution of atoms inside the unit cell (Fig. F.8(a)). Now we can calculate ν_i for As nucleus ($I = 3/2$) as follows:

$$\nu_i^{\text{lat}} = \frac{3eQ}{2hI(2I-1)} \tilde{V}_{ii} = \frac{eQ}{2h} \tilde{V}_{ii}. \quad (\text{F.43})$$

We checked that the calculation result rapidly converges by n_α^{-3} dependence and for $n \geq 10$ it shows almost no change (~ 0.00001 %/unit cell). We adopted sufficiently large values $(n_a, n_b, n_c) = (50, 50, 20)$ for the calculation of EFG to obtain reliable results. This corresponds to set the range for calculation to be $101 \times 101 \times 41$ unit cells with the approximate dimension of $550 \times 550 \times 530 \text{ \AA}^3$.

The lattice parameters used for the calculation are summarized in Fig. F.8(b)-(d). These parameters are taken from Refs. [218; 286]. The resultant temperature dependence of ν is shown in Fig. F.8 for each component. The absolute value itself and the temperature dependence are quite small compared to the experimentally obtained ones $\nu_\alpha(T)$ in Sec. 7.3. Hence we assumed that ν_α^{lat} is temperature-independent constant for further analyses in Sec. 7.3. We can also confirm that η^{lat} is too small to explain the experimental $\eta \sim 1.2$ [36], indicating that most of the large value of η is ascribed to the on-site contribution from polarized As-4p orbitals.

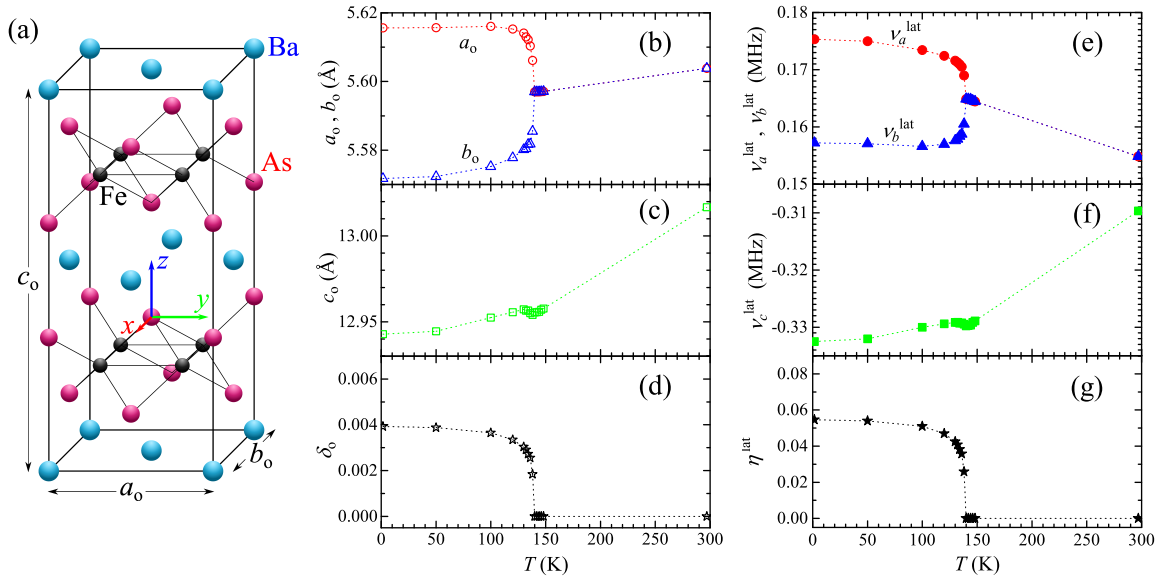


Figure F.8: (a) Coordinates of atoms in the unit cell of BaFe₂As₂ for the point charge model calculation. (b)-(d) Temperature dependence of lattice parameters, a_0 , b_0 , c_0 , and orthorhombicity $\delta_0 = (a_0 - b_0)/(a_0 + b_0)$. The data are taken from Ref. [218; 286]. (e)-(g) Temperature dependence of calculated EFG parameters of lattice contribution, ν_a^{lat} , ν_b^{lat} , ν_c^{lat} , and anisotropy parameter of EFG $\eta^{\text{lat}} = (\nu_a^{\text{lat}} - \nu_b^{\text{lat}})/(\nu_c^{\text{lat}})$.

G Comparative Study of On- and Off-Site Contributions to Electric Field Gradient in “122” family

The charge distribution and resultant EFG around a nucleus has two sources: the one from the charges on the lattice ions other than the subject ion and the other from the electrons in orbitals of unfilled shells on the subject ion. Therefore, electric quadrupole parameter ν related to EFG can be described by two terms as

$$\nu_\alpha = (1 - R)\nu_\alpha^{\text{on}} + (1 - \gamma_\infty)\nu_\alpha^{\text{lat}}, \quad (\text{G.44})$$

where R and γ_∞ are Sternheimer shielding and anti-shielding factors, respectively. The first term is the contribution from the on-site orbitals and the second term is from lattice charges. $(1 - R)$ and $(1 - \gamma_\infty)$ arise from the electronic charge distribution surrounding the nucleus distorting in response to a non-homogeneous EFG [287; 314]. The net effect of this is to either shield or enhance the quadrupole moment of an ion as shown in Fig. G.9. In solids there is an additional effect which may be quite large, particularly in ionic compounds, where an electron from one atom may be essentially transferred to another. The resulting change of charge on the atom causes a redistribution of all the other electrons of the atom, including the inner core electrons. Small redistributions of inner core electrons (with large $1/r^2$) can produce large changes in the EFG, thus changing the measured quadrupole interaction by a corresponding amount. In the case of metals, the charge transfer is more subtle than in ionic materials and hence charge redistribution effects near the nuclei are reduced. A comparison for a typical nucleus in an ionic environment with the same nucleus in a metallic environment, shows the measured quadrupole coupling constant in the metal to be some two orders of magnitude smaller than in the ionic salt.

The shielding factor R is generally of the order of ~ 0.1 and thus we neglect it in this study for simplicity, while $(1 - \gamma_\infty)$ is of the order of 10 to 100 in some ionic salts [315]. Then, Eq. (G.44) is rewritten as

$$\nu_\alpha = \nu_\alpha^{\text{on}} + (1 - \gamma_\infty)\nu_\alpha^{\text{lat}}. \quad (\text{G.45})$$

From NMR experiments, one can only obtain the absolute value of ν_α . In order to discuss the origin of EFG in detail, we need to determine the sign of each ν_α and to separate the two contributions ν_α^{on} and ν_α^{lat} .

First, to determine the sign of ν_c , experimentally obtained $|\nu_c|$ for three “122”-type parent compounds BaFe_2As_2 , SrFe_2As_2 , and CaFe_2As_2 near the room temperature taken from Refs.

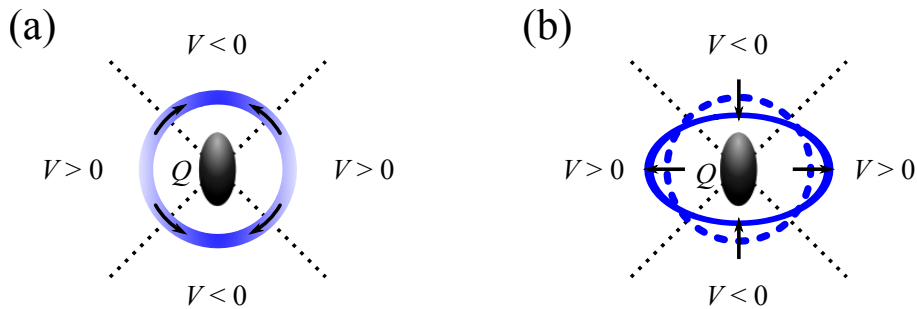


Figure G.9: A center black ellipsoid represents an electric quadrupole moment. (a) A redistribution of inner core electrons occurs in response to the presence of the electric quadrupole moment, partially cancelling Q . This results in shielding effect. (b) Closed shell radius is pulled out in response to the EFG, slightly enhancing the effective electric quadrupole moment. This results in anti-shielding effect.

Table G.3: Comparison of experimentally obtained $|\nu_c|$ and the band calculation results of ν_c^{band} . RT in the table is an abbreviation of “Room Temperature”.

	$ \nu_c $ (MHz)	ν_c^{band} (MHz)
BaFe ₂ As ₂	2.92 (at 280 K [36])	-3.90 (at RT)
SrFe ₂ As ₂	2.03 (at 300 K [316])	-0.25 (at RT)
CaFe ₂ As ₂	11.9 (at 270 K [317])	9.98 (at RT)

[36; 316; 317] are compared with our band calculation results of ν_c^{band} as listed in Table G.3. Note that the band calculation includes both orbital and lattice contributions as well as shielding and anti-shielding effects. If we take ν_c for BaFe₂As₂ as negative, the experimental values and material dependence become consistent with the calculation. Moreover, the temperature dependence of ν_c for BaFe₂As₂ becomes similar to the other two systems as naturally expected from the similarity of temperature dependence of the various physical properties among these three systems. Hence, we assume hereafter that the experimental ν_c for $x = 0$ and $x = 0.04$ in BaFe₂(As_{1-x}P_x)₂ are negative ($\nu_c < 0$) and, correspondingly, $\nu_{a,b}$ are positive ($\nu_{a,b} > 0$).

Next, we attempt to estimate the contribution to EFG from on-site orbitals ν_c^{on} in the experimental ν_c . ν_c for all the systems exhibit the large temperature dependence and first-order-like jump at T_S despite the small temperature change in lattice constants from room temperature to T_S and the jump at T_S , both of which are less than 1 %. There are two possibilities for this large temperature dependence: one is the case that the the dominant contribution to EFG is ν_α^{on} and the temperature dependence is ascribed to the change in ν_α^{on} , and the other is the case that the temperature dependence of ν_α^{lat} is magnified by the large anti-shielding factor $(1 - \gamma_\infty)$. We show the three different analyses (A), (B) and (C) in what follows.

For the first analysis (A), we consider that the temperature dependence of ν_α comes only from ν_α^{on} but there is a constant contribution from $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$ assuming the temperature-independency as we performed in Sec. 7.3. Figure G.10 shows the temperature dependence of ν_c , the band calculation results ν_c^{band} at 300 K, and temperature-independent constant $(1 - \gamma_\infty)\nu_c^{\text{lat}}$ evaluated from the $\nu - K_{\text{spin}}$ plot, which is discussed later, for BaFe₂As₂, SrFe₂As₂, and CaFe₂As₂. The data of ν_α for SrFe₂As₂ and CaFe₂As₂ are taken from Refs. [316; 317], respectively. As for CaFe₂As₂, K_{spin} is deduced from $K_c - \chi_c$ plot using the magnetic susceptibility in Ref. [318]. For simplicity, $\nu_{a,b}$, $\nu_{a,b}^{\text{band}}$, $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ are not shown. We can confirm that the band calculation results are systematically consistent with the experimentally obtained ν_α if we consider the negative sign of ν_c for BaFe₂As₂. As shortly introduced in Sec. 7.3, Majumder *et al.* reported recently that the temperature dependence of ν_α scales with that of K_α in some pnictides like BaFe₂As₂, LiFeAs, PrCoAsO and in the other itinerant magnets MnSi, NaCo₂O₄, and so on [289]. To explain the linearity of ν_α and K_α in MnSi, a theory based on SCR approach was already developed [288]. A contribution to ν_α^{on} in terms of quadrupolar charge susceptibility, which can be influenced by spin-fluctuations through the mode-mode coupling between charge and spin density fluctuations, was calculated and for which a linear relation between ν^{on} and K^{spin} was found. Therefore, one can easily evaluate the magnitude of $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$ by extrapolating the linear portion of ν_α versus K^{spin} plot (as an implicit function of T) to $K_\alpha^{\text{spin}} = 0$. From these plots, we obtained $(1 - \gamma_\infty)$ of +2.71185, -11.34411, -24.41588 for BaFe₂As₂, SrFe₂As₂, and CaFe₂As₂ respectively and show them in Fig. G.10(a) by broken lines. From the Eq. 7.2 with fixed parameter of the total occupation number $N = 1.5$, the temperature dependence of n_α as in Fig. G.10(b) can be deduced. For all of the systems, clear splitting between n_a and n_b of the similar order ~ 0.4 below T_S can be seen, although we cannot determine which is which. Another characteristic result is that the difference between $n_{a,b}$ and n_c becomes larger in order

of Ba-, Sr-, and CaFe_2As_2 keeping the relation $n_{a,b} < n_c$.

For the second analysis (B), we try to reproduce the temperature dependence of ν_α above T_S only by $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$, and regard ν_α^{on} as a temperature-independent contribution at least above T_S . By using simulated ν_α^{lat} as described in the previous Appendix section, one can reproduce the temperature dependence of ν_α not only for above T_S but also for below T_S with a magnifying parameter $(1 - \gamma_\infty) = -26, -26, -30$ for Ba-, Sr-, Ca-122 systems, respectively as shown in G.11(a)-(f). However, the jump of ν_α at the structural transition can not be explained only by the lattice contribution, indicating substantial change in the balance of the occupation number of each As-4p orbital. Figures G.11(g) and G.11(h) shows the temperature dependence of $\nu_\alpha^{\text{on}} = \nu_\alpha - (1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$. ν_α^{on} 's do not show any remarkable temperature dependence in each state as expected except for the moment when the sample shows the phase transition at T_S since the temperature dependence is totally ascribed to $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$. From the Eq. 7.2, we can deduce the temperature dependence of n_α as in Fig. G.12(a). The temperature dependence of n_α seems somewhat material-independent, and clear splitting of n_a and n_b is confirmed again for all systems. The order of splitting is comparable to the previous result of analysis (A). However, the difference between $n_{a,b}$ and n_c is quite large and material-independent.

In general metals with the small charge transfer, Sternheimer anti-shielding effect can be regarded as small enough [140]. Therefore, as the third analysis (C), we consider $(1 - \gamma_\infty)\nu_\alpha^{\text{lat}}$ to be negligible. This is the direct opposite case to the previous case of analysis (B). In this

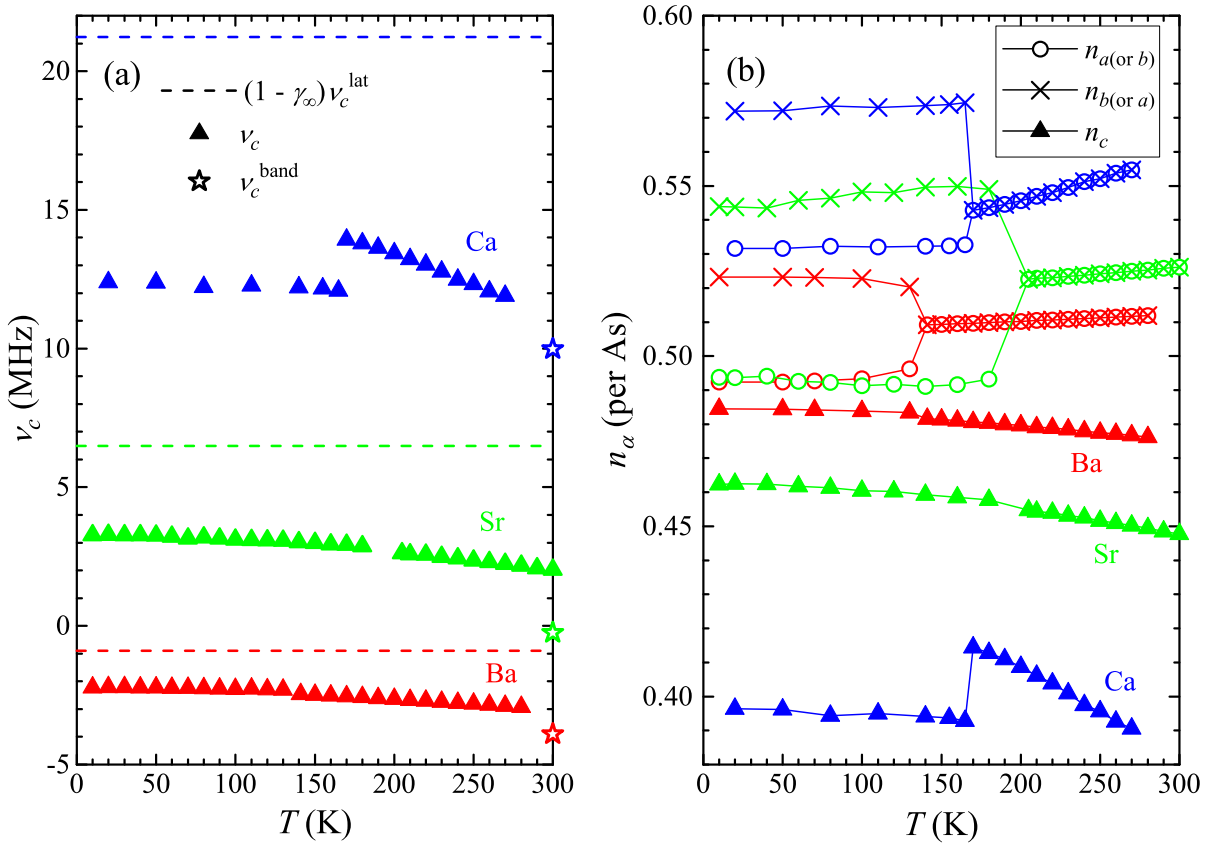


Figure G.10: The results of analysis (A): (a) The temperature dependence of experimental ν_c adopted from Refs. [36; 316; 317], the band calculation results ν_c^{band} at 300 K, and temperature-independent constant $(1 - \gamma_\infty)\nu_c^{\text{lat}}$ evaluated from the $\nu_c - K_c^{\text{spin}}$ plot for BaFe_2As_2 , SrFe_2As_2 , and CaFe_2As_2 . (b) The temperature dependence of the occupation number for each As-4p orbitals.

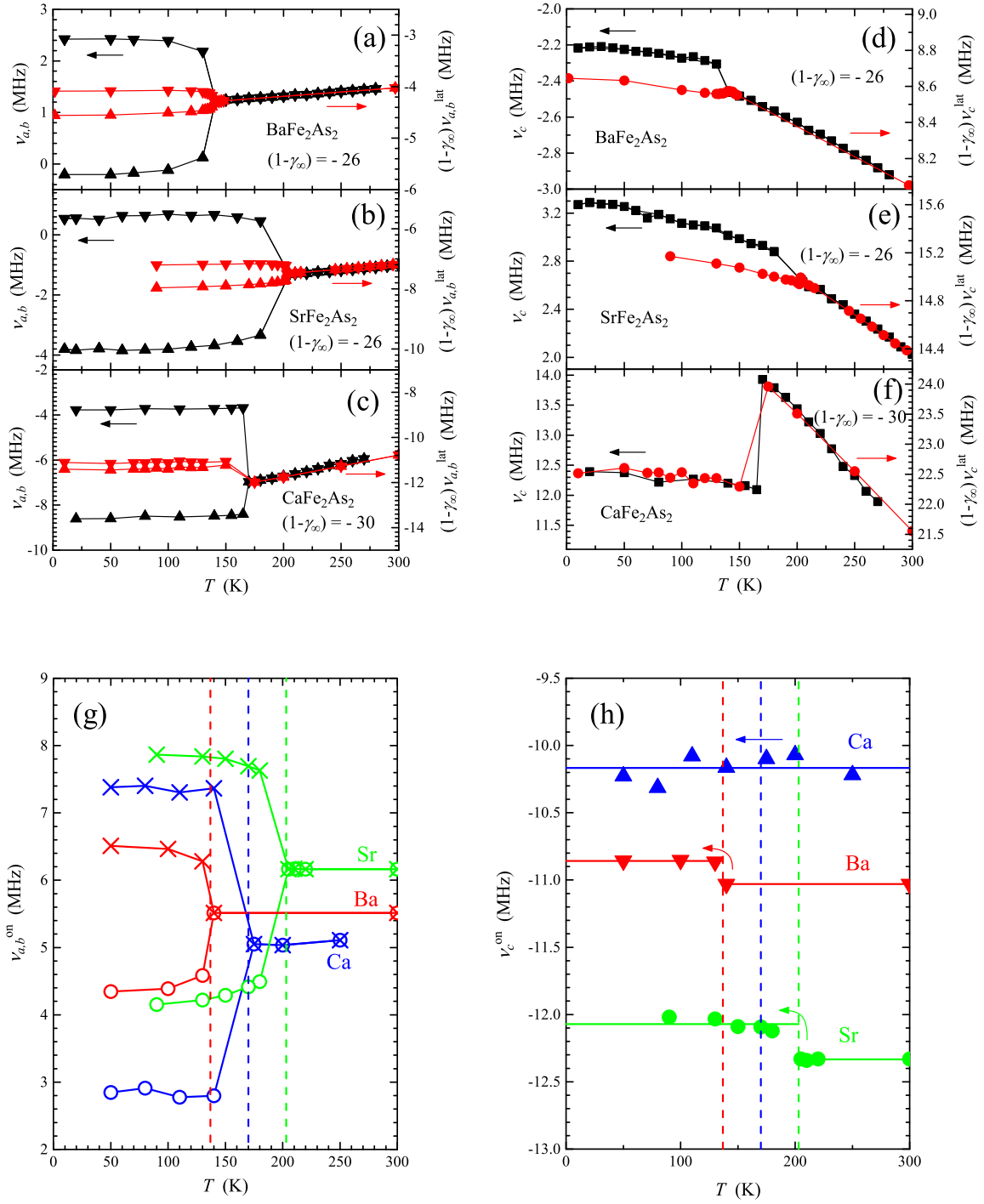


Figure G.11: The results of analysis (B): Comparison of the temperature dependence of the experimental (a)-(c) $\nu_{a,b}$ adopted from Refs. [36; 316; 317] with $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ and (d)-(f) ν_c with $(1 - \gamma_\infty)\nu_c^{\text{lat}}$ for BaFe₂As₂, SrFe₂As₂, and CaFe₂As₂, respectively. (g) The temperature dependence of $\nu_{a,b}^{\text{on}}$ evaluated by subtracting $(1 - \gamma_\infty)\nu_{a,b}^{\text{lat}}$ from ν_a . (h) The temperature dependence of ν_c^{on} evaluated by subtracting $(1 - \gamma_\infty)\nu_c^{\text{lat}}$ from ν_a .

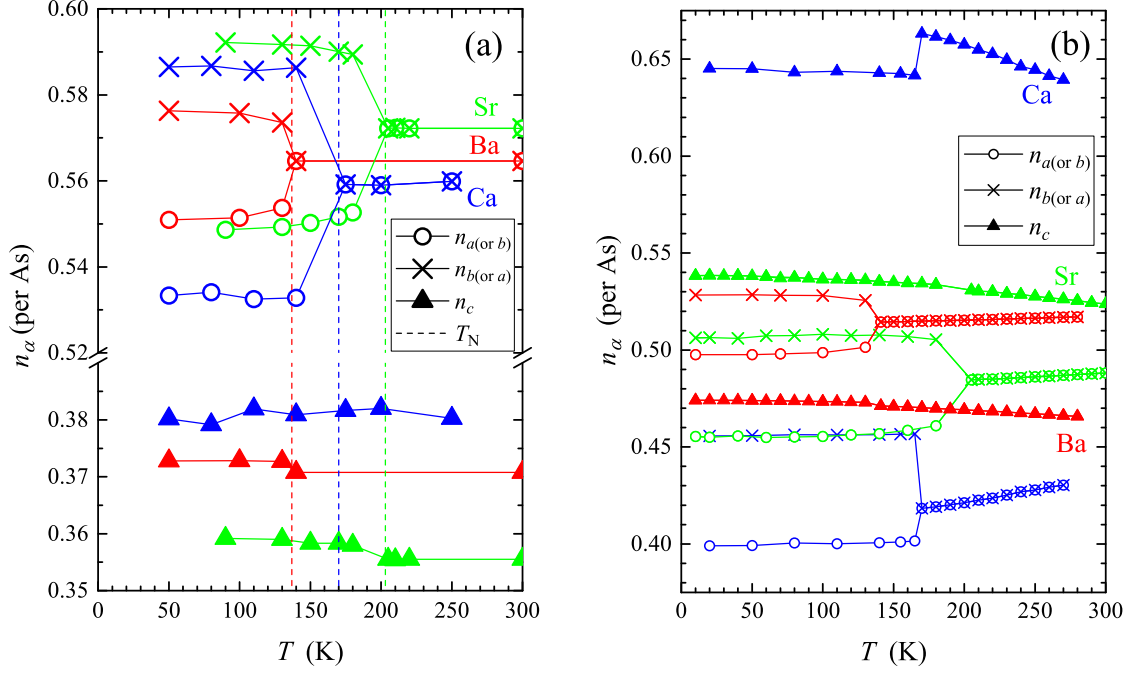


Figure G.12: The results of analyses (B) and (C): The temperature dependence of n_α obtained (a) from the analysis (B) and (b) from the analysis (C) for BaFe_2As_2 , SrFe_2As_2 , and CaFe_2As_2 .

case, n_α can be directly calculated from $\nu_\alpha = \nu_\alpha^{\text{on}}$ as shown in Fig. G.12(b). The resultant n_α shows somewhat larger material dependence than the results of the analyses (A) and (B). The order of the split width of n_a and n_b below T_S is almost the same as the result of (A) and (B). However, there are large increase in n_c from Ba- to Sr- and CaFe_2As_2 and the relation $n_{a,b} > n_c$ turns into $n_{a,b} < n_c$ for Sr- and CaFe_2As_2 .

From these three different analyses, the magnitude of the difference between n_a and n_b can be considered to be common and it does not depend on the analyses. This indicates that the orbital polarization of p_x and p_y at As site is undoubtedly realized below T_S .

H In-Plane Anisotropy above Structural Transition in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ Revealed by ^{75}As - and ^{31}P -NMR

In this section, we present the results of the in-plane field angle dependence and temperature dependence of ^{75}As - and ^{31}P -NMR spectra above the structural transition temperature $T_S \sim 121$ K for a single crystalline $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$. An in-plane anisotropy of the centerline widths for ^{75}As spectrum increases gradually with cooling, indicative of the development of an in-plane anisotropy of electric field gradient (EFG) due to the population imbalance between $\text{As-}4p_x$ and $4p_y$ orbitals. Similar but more subtle in-plane anisotropy was found in ^{31}P -NMR spectra. In addition, we observed the pronounced frequency dependence of the spin-lattice relaxation rate $1/T_1$ in ^{75}As -NMR spectrum above T_S . This indicates that the spin fluctuations are highly in-plane anisotropic even above the structural transition as well as $\text{As-}4p_x/p_y$ orbital polarization. We point out that these in-plane anisotropies above T_S implies the strong interrelation between orbital polarization and spin fluctuations.

H.1 Motivation

Recently, the so-called “electronic nematic state”, in which the electronic state spontaneously breaks the four-fold lattice symmetry and shows the in-plane anisotropic physical properties, has been observed above T_S by resistivity [133], optical conductivity [135; 260], ARPES [136; 138], x-ray linear dichroism [262] and torque magnetometry [132] in BaFe_2As_2 family. The questions that what kind of degree of freedom is broken in the nematic state and whether their properties are static or dynamic are under dispute. Although the relationship between the nematic state and the orbital order or spin nematic state has been frequently debated, few microscopic and quantitative experimental information have been reported so far. However, the local in-plane anisotropy originating from the nematic state would be smeared out if bulk-sensitive measurements are performed since the nematic state forms the twinned domain structure. In contrast, an NMR measurement can potentially detect the local in-plane anisotropy since it gives microscopic information around a nucleus by using a specific nuclear site as a local probe. Here, we show experimental results of an NMR study of the underdoped single crystalline $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$.

H.2 Experimental Details

We used the same single crystalline $\text{BaFe}_2(\text{As}_{0.96}\text{P}_{0.04})_2$ as the one used in Chap. 7. The flat NMR coil shown in Fig. 3.5 is adopted for the purpose of measuring in-plane field angle dependence of NMR spectrum and spin dynamics. The coil was mounted on the one-axis goniometer equipped on the probe IV (see Table 3.2). The probe was inserted into the cryostat with split-type magnet (Wang NMR, see Table 3.1). This allows us to align the external magnetic field to any desired direction with respect to the crystal by combining vertical rotation of the goniometer and horizontal rotation of the probe (Fig. H.13). The field direction was thus accurately controlled to be parallel to the ab -plane within $\pm 1^\circ$. A methodology of precise alignment of the external field parallel to FeAs plane is introduced in the next Appendix I. ^{75}As and ^{31}P -NMR spectra corresponding to the transition $m = 1/2 \leftrightarrow -1/2$ were obtained by fast-Fourier-transform of spin-echo signals in the fixed magnetic field $\mu_0 H = 6$ T.

H.3 In-Plane Field Angle Dependence of ^{75}As - and ^{31}P -NMR Spectrum

^{75}As -NMR spectrum shows three resonance lines: one sharp central peak corresponding to the transition $m = 1/2 \leftrightarrow -1/2$ and two broad satellite peaks corresponding to the transition $\pm 3/2 \leftrightarrow \pm 1/2$ as we saw in Chapter 7. In this study, we concentrate on the sharp central line because of its higher intensity than that of satellites. When the external field is applied

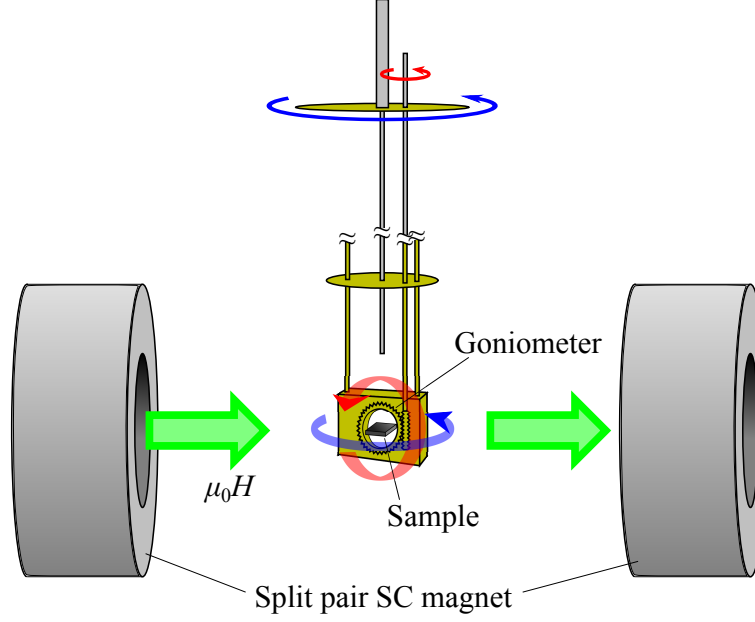


Figure H.13: An outline sketch of two-axes rotation. Horizontal rotation (blue arrows) in the transverse field generated by a split-type magnet is made by manual rotation of the probe and vertical rotation (red arrows) is made by one axis goniometer equipped on the NMR probe IV.

perpendicular to the c -axis, i.e. $\theta = 90^\circ$, where θ denotes the polar angle of the field with respect to the crystal c -axis, and assuming that the principal axes of the EFG and Knight shift tensors corresponds to the orthorhombic basis (a_o, b_o, c_o) , the in-plane field angle ϕ -dependent resonance frequency of ^{75}As nuclei can be expressed using Eq. (2.31) in the following form:

$$\begin{aligned}
 {}^{75}f(\phi) = & f_0 \left(1 + \frac{{}^{75}K_a + {}^{75}K_b}{2} + \frac{{}^{75}K_a - {}^{75}K_b}{2} \cos 2\phi \right) \\
 & + \frac{\nu_c^2}{f_0(1 + {}^{75}K_{\text{iso}})} \left[\frac{3}{16} - \frac{\eta}{8} \cos 2\phi - \frac{\eta^2}{48} (8 - 9 \cos^2 2\phi) \right] \\
 \simeq & f_0 \left(1 + \frac{{}^{75}K_a + {}^{75}K_b}{2} + \frac{3\nu_c^2}{16f_0} \right) + \left(f_0 \frac{{}^{75}K_a - {}^{75}K_b}{2} - \frac{\eta\nu_c^2}{8f_0} \right) \cos 2\phi.
 \end{aligned} \tag{H.46}$$

Here, since the contribution of K_{iso} and η^2 is small enough at least for above T_S , these terms are neglected for simplicity. On the other hand, ϕ -dependent resonance frequency of ^{31}P nuclei can be expressed using Eq. (2.29) as follows:

$${}^{31}f(\phi) = f_0 \left(1 + \frac{{}^{31}K_a + {}^{31}K_b}{2} + \frac{{}^{31}K_a - {}^{31}K_b}{2} \cos 2\phi \right). \tag{H.47}$$

FWHMs of ^{75}As -NMR spectrum measured at 200 K shows oscillatory behavior as a function of ϕ (Fig. H.14). As seen in Eqs. (H.46) and (H.47), oscillating term may arise from the in-plane anisotropy in Knight shift and/or EFG for As case. In case there are twinned domains having in-plane symmetry axes that are rotated by 90° relative to one another, corresponding to $\eta \neq 0$ and/or ${}^{75}K_a \neq {}^{75}K_b$, ϕ dependence of FWHM should exhibit sharp minima such as the one observed in the hidden ordered phase in URu_2Si_2 [319]. We fitted the oscillatory behavior of FWHM with the linear combination of twofold and fourfold oscillations: $A|\cos 2(\phi - \phi_0)| + B \cos 4(\phi - \phi_0) + C$, based on the model of Ref. [319]. Here, A and B is the amplitude of

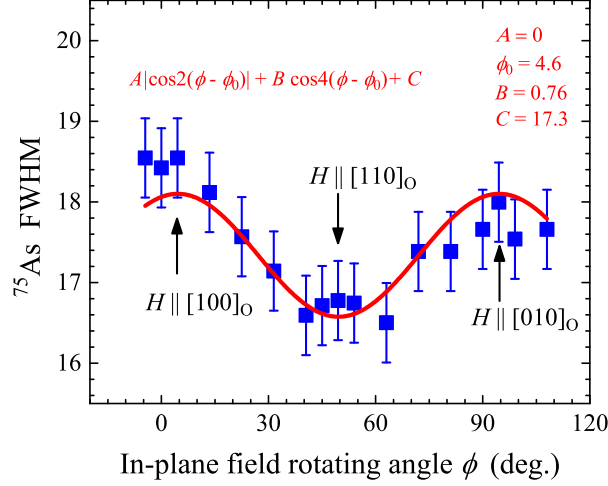


Figure H.14: In-plane field angle dependence of FWHM of ^{75}As (upper panel) and ^{31}P (lower panel) NMR spectra. Red curves are fittings of the equation shown in each figure to the data. Obtained fitting parameters are also shown in each case.

twofold and fourfold oscillating term, respectively, C is the constant, ϕ indicates relative angle of in-plane field rotation, and ϕ_0 represents the angle corresponds to $H \parallel [100]_o$. Sharp minima were not clearly observed but only fourfold oscillating term was detected from the fitting to the above equation. This fourfold oscillating term is possibly due to the combination of hyperfine coupling having dipolar anisotropy with crystalline disorder and/or P-dopant as is the case for URu_2Si_2 [319]. With considering the NMR results of Chap. 7, we regard the direction which shows broad minima as $H \parallel [110]_o$. In-plane field directions parallel to $[100]_o$ and $[110]_o$ are thus determined.

Temperature dependence of ^{75}As -NMR spectrum for $H \parallel [100]_o$ and $H \parallel [110]_o$ is shown in Fig. H.15(a) and (b). While the peak frequency shows the same temperature dependence for both field orientations, spectral shape as well as intensity and linewidth exhibit difference. To see the temperature evolution of the spectral shape, we show the normalized NMR spectra as a function of the relative frequency measured from the peak frequency δf_{peak} (Fig. H.15(c) and (d)). Each spectrum has the small additional peaks in the tail of the main peak. As discussed in Chap. 7, the small peaks in Fig. H.15(c) are the contribution from the As_1 sites having one P dopant among their four nearest neighbors: $\text{As}_1^{[010]_o}$ and $\text{As}_1^{[100]_o}$. In Fig. H.15(d), there is another small peak which was not discussed in Chap. 7. This peak is the contribution from the As_1 sites having one P dopant in their next nearest neighbors: $\text{As}_1^{[110]_o}$ and $\text{As}_1^{[\bar{1}\bar{1}0]_o}$. Although the peak frequency of As_0 has a relatively large temperature dependence, the ^{75}As -NMR spectral shape and the distance between $\text{As}_1^{[100]_o}$ and As_0 ($\text{As}_1^{[110]_o}$ and As_0) for $H \parallel [100]_o$ (for $H \parallel [110]_o$) show almost no qualitative changes, indicating that these small peaks have their origin in As_1 sites in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and are not the contribution from impurities.

Figure H.16(a) represents temperature dependence of Knight shift of ^{75}As , ^{75}K derived from Eq. (3.7) using the value of ν_c determined by the previous experiment in Chap. 7. The values and temperature dependence of ^{75}K for $H \parallel [100]_o$ and $H \parallel [110]_o$ are almost identical. On the other hand, the temperature dependence of FWHM of center line $\Delta^{75}f_{\text{center}}$ for these two field directions are undoubtedly different. The difference increases weakly on cooling from the room temperature and shows an upturn below ~ 160 K. This behavior is in qualitative agreement with the temperature dependence of the difference in $\Delta\nu/|\nu|$ (Fig. 7.5), indicating a significant contribution of in-plane anisotropy in EFG ($\eta \neq 0$) to the center linewidth. However, as seen

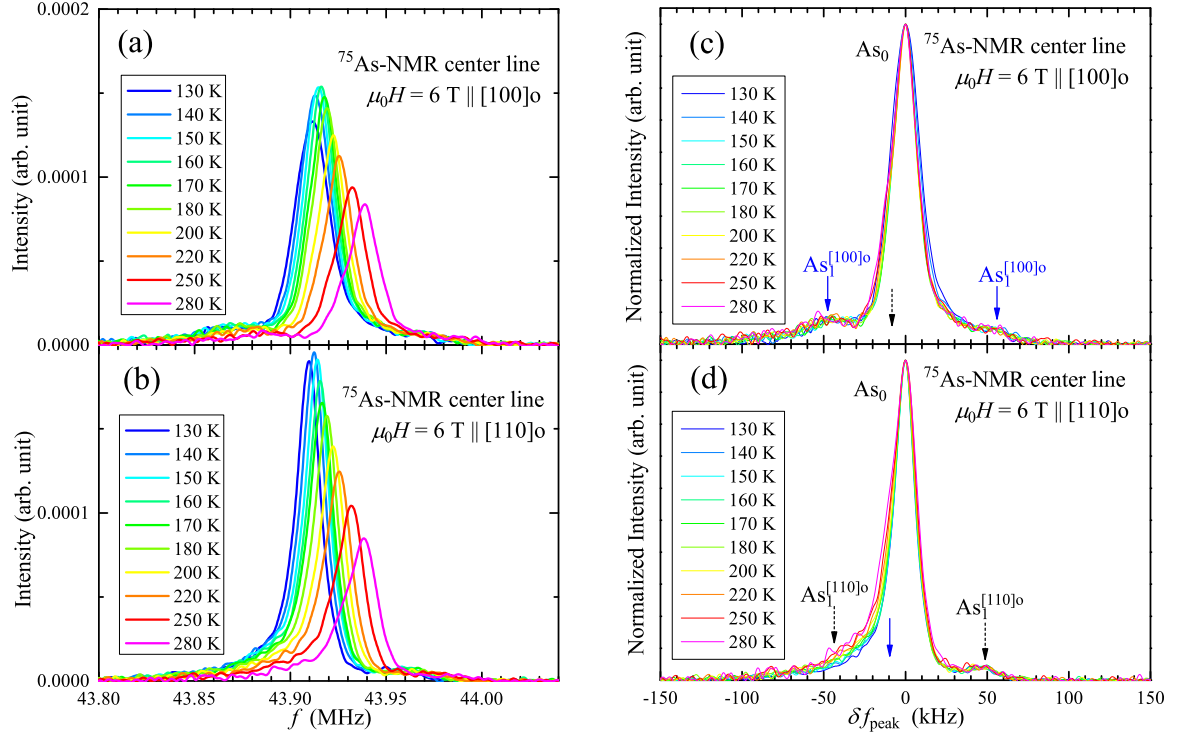


Figure H.15: Temperature evolution of ^{75}As -NMR center line spectrum above T_S for (a) $H \parallel [100]_o$ and (b) $H \parallel [110]_o$. Normalized ^{75}As -NMR center line spectrum as a function of the frequency measured from the peak frequency δf_{peak} for (c) $H \parallel [100]_o$ and (d) $H \parallel [110]_o$. The solid blue (broken black) arrows represent the approximately expected resonance positions of $\text{As}_1^{[100]_o}$ ($\text{As}_1^{[110]_o}$). Since we cannot distinguish $\text{As}_1^{[100]_o}$ and $\text{As}_1^{[010]_o}$ or $\text{As}_1^{[110]_o}$ and $\text{As}_1^{[1\bar{1}0]_o}$, we express both peaks as $\text{As}_1^{[100]_o}$ and $\text{As}_1^{[110]_o}$ for $H \parallel [100]_o$ and $H \parallel [110]_o$, respectively.

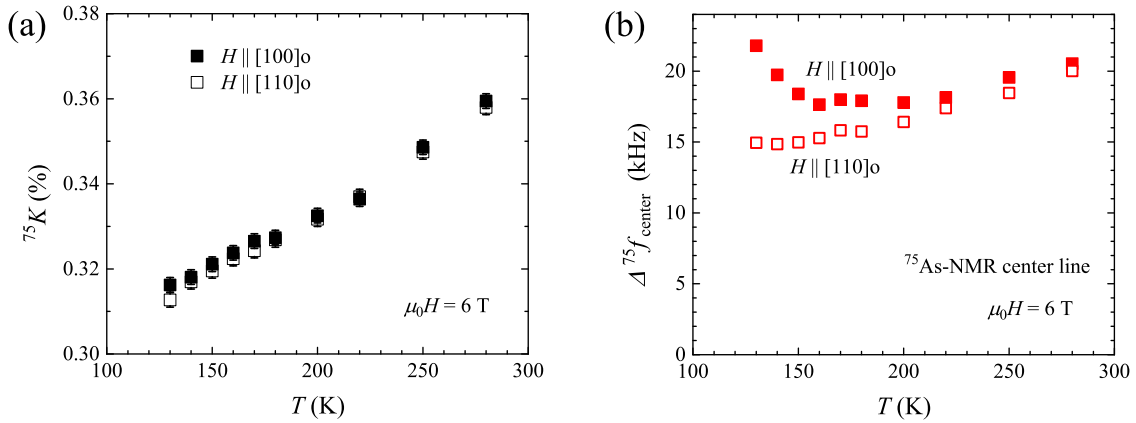


Figure H.16: Temperature dependence of (a) Knight shift and (b) FWHM of ^{75}As center line spectrum for $H \parallel [100]_o$ and $H \parallel [110]_o$.

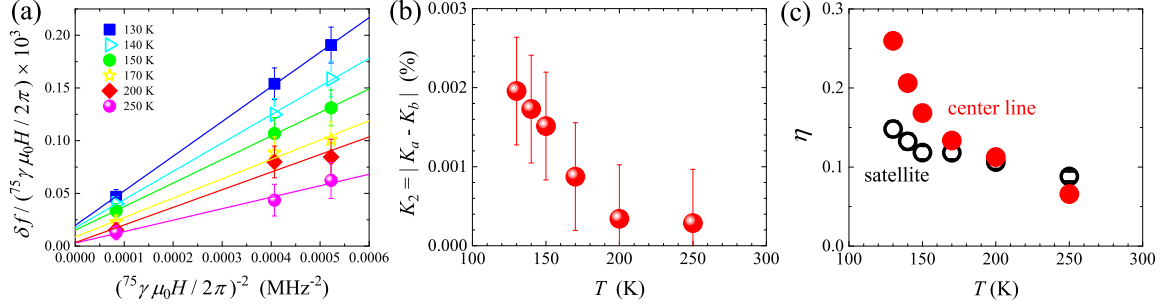


Figure H.17: (a) The plot for separating the contributions to the central linewidth of ${}^{75}\text{As}$ from the in-plane anisotropy in Knight shift and in EFG. Note that the intercept of the line of 250 K is set to 0, since if we fit the data of $\mu_0 H = 6$ T and 15 T with a line, the intercept becomes the negative value but the sign change of K_2 is unlikely. (b) Temperature dependence of in-plane anisotropy in Knight shift $K_2 = |{}^{75}K_a - {}^{75}K_b|$ estimated from the intercept of the plot in the figure (a). (c) Temperature dependence of in-plane EFG anisotropy η estimated from the slope of the lines in the figure (a) together with η estimated from satellite lines in Chap. 7.

in Eq. (H.46), the difference between the two field directions is contributed both from η and in-plane anisotropy in Knight shift ${}^{75}K_2 \equiv |{}^{75}K_a - {}^{75}K_b|$. There are two ways to estimate η and ${}^{75}K_2$ separately: one is to measure the field dependence of the line width since these two contributions have different field dependence [320] and the other is to measure the in-plane anisotropy using ${}^{31}\text{P}$ nuclei because ${}^{31}\text{P}$ is sensitive only to magnetism and does not detect the EFG.

First, we check by the first method. Assuming that each of the domains with twofold symmetry occupy a half of the crystal, we performed the fits to the sharp part of the center line for $H \parallel [100]_o$ with two Lorentzian functions, each having a linewidth fixed to the value measured for $[110]_o$, likewise the fitting used in Chap. 7. Difference of frequency between these two domains is defined as δf . As shown in Eq. H.46, δf contains two contributions from in-plane anisotropy in Knight shift, K_2 , and in EFG, η . δf can be described as follows:

$$\frac{\delta f}{f_0} = \frac{{}^{75}f(0^\circ) - {}^{75}f(90^\circ)}{f_0} = ({}^{75}K_a - {}^{75}K_b) - \frac{\eta\nu_c^2}{4f_0^2}, \quad (\text{H.48})$$

where $f_0 \equiv {}^{75}\gamma\mu_0 H / 2\pi$. From Eq. (H.48), the linear relationship between $\delta f/f_0$ and f_0^{-2} is expected. If this relation is satisfied, the intercepts of the lines connecting the estimated values for $\mu_0 H = 6$ T and $\mu_0 H = 15$ T shown in Fig. H.17(a) give the value of K_2 . In addition, the value of η can be calculated from the slope of the lines. The derived K_2 and η are exhibited in Figs. H.17(b) and (c), respectively. Figure H.17(b) indicates there is a finite K_2 already above T_S and T_N . This suggests that not only the orbital degree of freedom but also the spin degree of freedom becomes in-plane anisotropic microscopically above T_S , which is consistent with the results of torque magnetometry measurement [132]. Although the qualitative behavior of K_2 might be reliable, we cannot conclude whether the appearance of K_2 is the transition or the crossover. Furthermore, the value of K_2 is strongly affected the value for $\mu_0 H = 15$ T, and thus we cannot discuss from which temperature K_2 appears. In-plane EFG anisotropy η estimated from the slope is plotted in Fig. H.17(c) with the one estimated from satellite lines in Chap. 7. Although the value of η in the lower temperatures differs between the two different estimation, qualitatively similar behavior can be seen. Both of them shows an upturn below 150-160 K, indicating the close relationship between As-4p orbital polarization and Fe-3d orbital ordering reported from ARPES experiments.

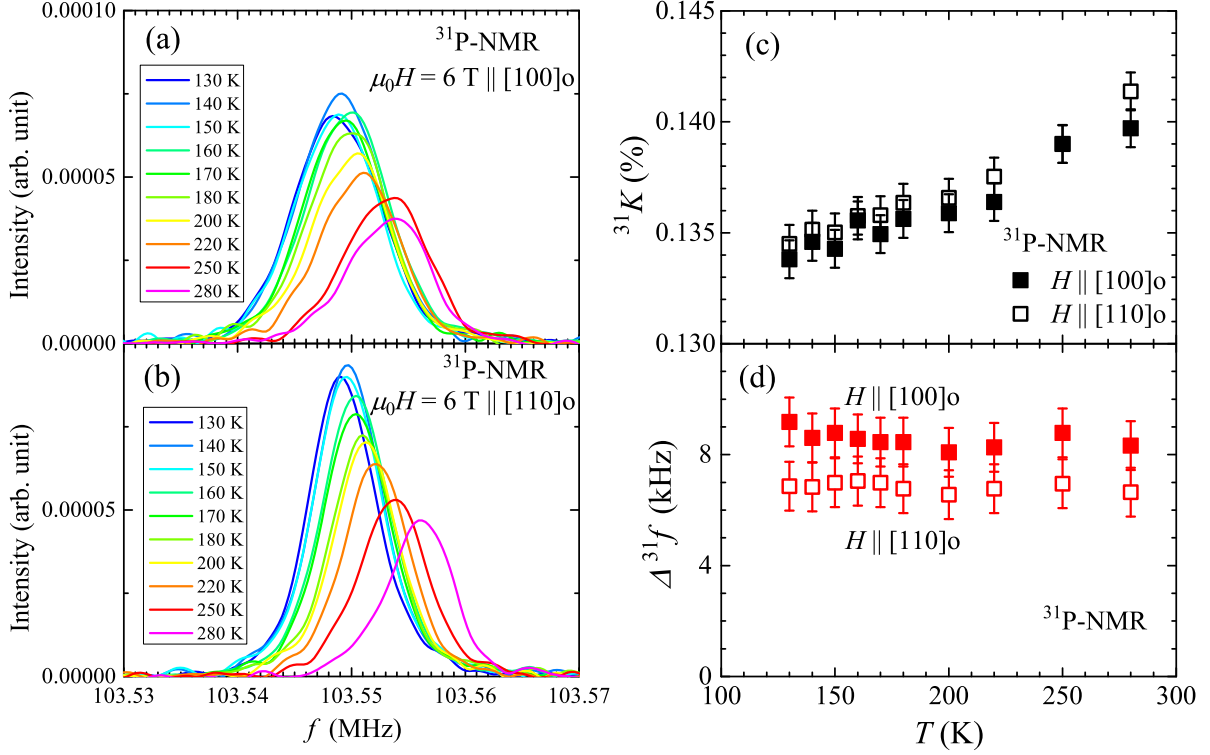


Figure H.18: Temperature evolution of ^{31}P -NMR spectrum above T_S for (a) $H \parallel [100]_o$ and (b) $H \parallel [110]_o$. Temperature dependence of (c) Knight shift and (d) FWHM of ^{31}P spectrum for $H \parallel [100]_o$ and $H \parallel [110]_o$.

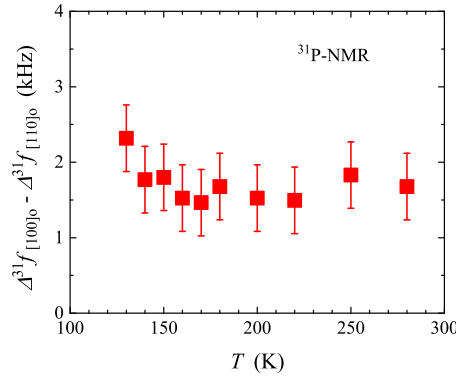


Figure H.19: Temperature dependence of the difference in FWHM of ^{31}P -NMR spectrum above T_S for $H \parallel [100]_o$ and $H \parallel [110]_o$.

Next, we show the in-plane anisotropy in ^{31}P -NMR spectrum. Figures H.18(a) and (b) show temperature evolution of ^{31}P -NMR spectra taken for $H \parallel [100]_o$ and $H \parallel [110]_o$, respectively. Unlike the center line of ^{75}As -NMR spectra in Fig. H.15, no additional peaks are found in ^{31}P -NMR spectra. Knight shifts of ^{31}P , ^{31}K derived from Eq. (3.6) for the two field directions exhibit almost identical temperature dependence as observed in ^{75}K . However, the temperature change is significantly smaller than that of ^{75}K , implying the smallness of the hyperfine coupling constant of P compared to As. On the other hand, the temperature dependence of FWHM of center line $\Delta^{75}f_{\text{center}}$ for these two field directions are different at any temperatures.

The origin of this anisotropy is unclear but we might have to consider the contribution from the fourfold oscillation term observed in the in-plane field angle dependence of the FWHM of center line for ^{75}As (Fig. H.14). The anisotropy in FWHM is plotted against temperature as shown in Fig. ???. There is an only slight enhancement below ~ 150 K, which might be corresponding to the appearance of $^{75}K_2$. However, possibly due to its smallness of the hyperfine coupling constant of P nuclei, it is difficult to conclude the existence of in-plane anisotropy in ^{31}K .

H.4 Short Summary

To summarize, the linewidth of centerline of ^{75}As -NMR spectrum is broadened for the field along $[100]_o$, while it remains narrow in the field along $[110]_o$. From its field dependence, the in-plane anisotropy in Knight shift, K_2 , and in EFG, η , are estimated independently. K_2 is developed on cooling, providing the microscopic evidence of the appearance of twofold symmetry in susceptibility. This result is consistent with the torque magnetometry experiments [132]. Temperature dependence of η estimated from the field dependence of center line is qualitatively consistent with the one estimated from satellite broadenings in Chap. 7. It is clarified from microscopic point of view that the nematicity appears in both spin and orbital degrees of freedom even above T_S in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$.

I Methodology for Controlling External Field Direction with Respect to Sample

If one need to measure the in-plane (parallel to ab -plane) field angle dependence precisely, the knowledge of the relation between the in-plane field angle and the angle which can be controlled by the goniometer or the rotator, which always satisfy $H \perp c$ will be useful.

Here, we define all the angles and coordinates as shown in Fig. I.20. The red axes (x, y, z) indicates the coordinate based on the NMR probe and the goniometer. y -axis is defined as the longitudinal direction of the probe and z -axis is the rotational axis of the goniometer. We define θ as the angle of external field with respect to x -axis. Next, we define arbitrary crystal orientation with c -axis tilted by the angle α from z -axis. The angle β denotes the azimuthal angle of c -axis in the (x, y, z) -coordinate, corresponding to the rotation angle controlled by the goniometer. a -axis is fixed along the line of intersection of ab -plane and xy -plane. The angle ϕ represents the angle of external field with respect to a -axis, corresponding to the in-plane field angle.

Note that the horizontal rotation of the probe directly controls θ in xz -plane without changing any other angles. The vertical rotation by the goniometer is directly related to β . This rotation does not change α but changes θ and ϕ . The goal of this section is to obtain the relation between β , θ , and ϕ .

First, we assume the arbitrary point m on the ab circle (black line). Let us express the

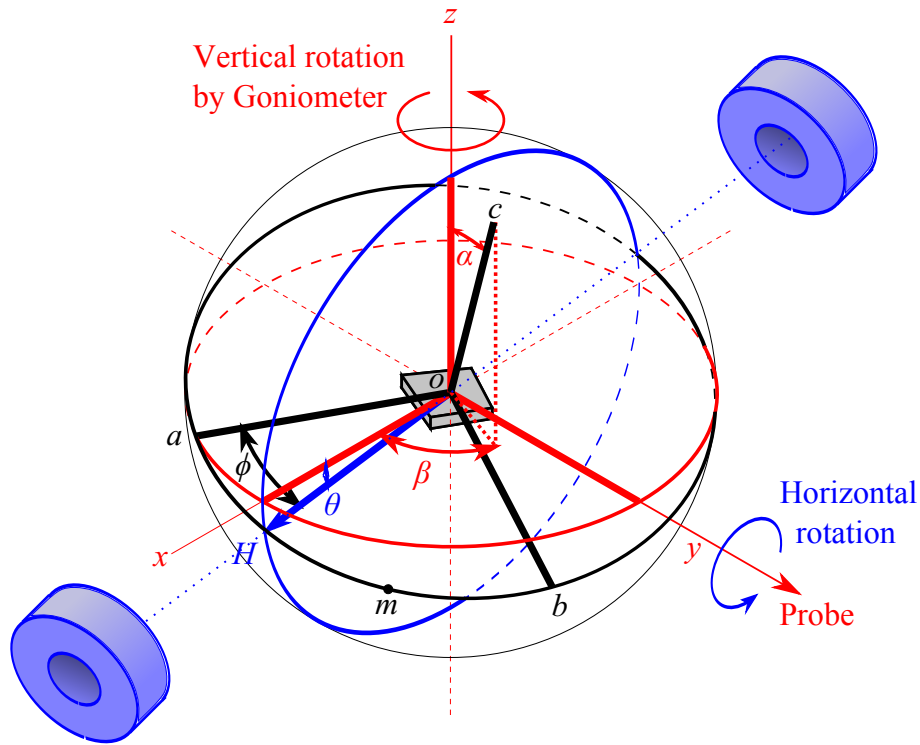


Figure I.20: Definition of the angles and coordinates in the two-axes rotation system. The red axes (x, y, z) denotes the coordinate based on the NMR probe and the goniometer. y -axis corresponds to the longitudinal direction of the probe and z -axis corresponds to the rotational axis of the goniometer. The black axes (a, b, c) denotes the crystal coordinate. The angles (α, β) are polar and azimuthal angles of c -axis in the (x, y, z) -coordinate, respectively. The angles (θ, ϕ) are the field direction with respect to x - and a -axes, respectively.

location of the point m in the (x, y, z) -coordinate. A normal unit vector to the ab -plane (parallel to c -axis) is described as:

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} \sin \alpha \cos \beta \\ \sin \alpha \sin \beta \\ \cos \alpha \end{pmatrix}. \quad (\text{I.49})$$

Defining an angle $\phi_m \equiv \angle aom$, $c_\alpha \equiv \cos \alpha$ and $s_\alpha \equiv \sin \alpha$, the coordinate of the point m can be expressed as the point rotated around c -axis by ϕ_m from the point $a = (\cos(\beta - 90^\circ), \sin(\beta - 90^\circ), 0)$:

$$\begin{aligned} \begin{pmatrix} x_m \\ y_m \\ z_m \end{pmatrix} &= \begin{pmatrix} n_x^2(1 - c_{\phi_m}) + c_{\phi_m} & n_x n_y(1 - c_{\phi_m}) - n_z s_{\phi_m} & n_z n_x(1 - c_{\phi_m}) + n_y s_{\phi_m} \\ n_x n_y(1 - c_{\phi_m}) + n_z s_{\phi_m} & n_y^2(1 - c_{\phi_m}) + c_{\phi_m} & n_y n_z(1 - c_{\phi_m}) - n_x s_{\phi_m} \\ n_z n_x(1 - c_{\phi_m}) - n_y s_{\phi_m} & n_y n_z(1 - c_{\phi_m}) + n_x s_{\phi_m} & n_z^2(1 - c_{\phi_m}) + c_{\phi_m} \end{pmatrix} \begin{pmatrix} c_{\beta-90^\circ} \\ s_{\beta-90^\circ} \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} s_\alpha^2 c_\beta^2(1 - c_{\phi_m}) + c_{\phi_m} & s_\alpha^2 s_\beta c_\beta(1 - c_{\phi_m}) - c_\alpha s_{\phi_m} & s_\alpha c_\alpha c_\beta(1 - c_{\phi_m}) + s_\alpha s_\beta s_{\phi_m} \\ s_\alpha^2 s_\beta c_\beta(1 - c_{\phi_m}) + c_\alpha s_{\phi_m} & s_\alpha^2 s_\beta^2(1 - c_{\phi_m}) + c_{\phi_m} & s_\alpha c_\alpha s_\beta(1 - c_{\phi_m}) - s_\alpha c_\beta s_{\phi_m} \\ s_\alpha c_\alpha c_\beta(1 - c_{\phi_m}) - s_\alpha s_\beta s_{\phi_m} & s_\alpha c_\alpha s_\beta(1 - c_{\phi_m}) + s_\alpha c_\beta s_{\phi_m} & c_\alpha^2(1 - c_{\phi_m}) + c_{\phi_m} \end{pmatrix} \begin{pmatrix} s_\beta \\ -c_\beta \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} [s_\alpha^2 c_\beta^2(1 - c_{\phi_m}) + c_{\phi_m}]s_\beta + [s_\alpha^2 s_\beta c_\beta(1 - c_{\phi_m}) - c_\alpha s_{\phi_m}](-c_\beta) \\ [s_\alpha^2 s_\beta c_\beta(1 - c_{\phi_m}) + c_\alpha s_{\phi_m}]s_\beta + [s_\alpha^2 s_\beta^2(1 - c_{\phi_m}) + c_{\phi_m}](-c_\beta) \\ [s_\alpha c_\alpha c_\beta(1 - c_{\phi_m}) - s_\alpha s_\beta s_{\phi_m}]s_\beta + [s_\alpha c_\alpha s_\beta(1 - c_{\phi_m}) + s_\alpha c_\beta s_{\phi_m}](-c_\beta) \end{pmatrix} \\ &= \begin{pmatrix} s_\beta c_{\phi_m} + c_\alpha c_\beta s_{\phi_m} \\ c_\alpha s_\beta s_{\phi_m} - c_\beta c_{\phi_m} \\ -s_\alpha s_{\phi_m} \end{pmatrix}. \quad (\text{I.50}) \end{aligned}$$

If $y_m = 0$, the line mo is parallel to the desired field direction and $\phi_m = \phi$. Then one can relate ϕ to α and β :

$$y_m = 0 \Leftrightarrow c_\alpha s_\beta s_\phi - c_\beta c_\phi = 0 \Leftrightarrow c_\alpha s_\beta s_\phi = c_\beta c_\phi \Rightarrow \tan \phi = \frac{c_\beta}{c_\alpha s_\beta}. \quad (\text{I.51})$$

Furthermore,

$$\cos \phi = \frac{c_\alpha s_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}}, \quad \sin \phi = \frac{c_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}}. \quad (\text{I.52})$$

Now, the coordinate of the point H at the intersection of the line of the external field and the ab circle can be described as:

$$\begin{pmatrix} x_H \\ y_H \\ z_H \end{pmatrix} = \begin{pmatrix} s_\beta \frac{c_\alpha s_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}} + c_\alpha c_\beta \frac{c_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}} \\ 0 \\ -s_\alpha \frac{c_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}} \end{pmatrix} = \begin{pmatrix} \frac{c_\alpha}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}} \\ 0 \\ \frac{-s_\alpha c_\beta}{\sqrt{c_\alpha^2 s_\beta^2 + c_\beta^2}} \end{pmatrix}. \quad (\text{I.53})$$

Finally, one relates θ to α and β :

$$\theta = \arctan \left(\frac{z_H}{x_H} \right) = \arctan \left(\frac{-s_\alpha c_\beta}{c_\alpha} \right), \quad (\text{or } \tan \theta = -\tan \alpha \cos \beta). \quad (\text{I.54})$$

Next, we consider the actual correspondence relation between the goniometer and the horizontal rotator in the experiments. First, we define B and Θ as the offset values of the goniometer and rotator, respectively. The relation between β and θ which keeps the applied field parallel

to ab plane can be obtained by three sets of experimentally obtained β and θ : (β_1, θ_1) , (β_2, θ_2) , (β_3, θ_3) , in which the fields are indeed aligned into the ab plane. For simplicity, let us consider the case of (β_1, θ_1) , $(\beta_1 + 90^\circ, \theta_2)$, $(\beta_1 + 180^\circ, \theta_3)$. By assigning these values to Eq. I.54, we obtain three sets of equations with three unknowns, α , B , Θ as follows:

$$\tan(\theta_1 - \Theta) = -\tan \alpha \cos(\beta_1 - B) \quad (\text{I.55})$$

$$\tan(\theta_2 - \Theta) = -\tan \alpha \cos(\beta_1 + 90^\circ - B) = \tan \alpha \sin(\beta_1 - B) \quad (\text{I.56})$$

$$\tan(\theta_3 - \Theta) = -\tan \alpha \cos(\beta_1 + 180^\circ - B) = \tan \alpha \cos(\beta_1 - B). \quad (\text{I.57})$$

This system of equations can be solved as follows:

$$\Theta = \frac{\theta_1 + \theta_3}{2} \quad (\text{I.58})$$

$$B = \beta_1 + \arctan \left[\frac{\tan \left(\theta_2 - \frac{\theta_1 + \theta_3}{2} \right)}{\tan \left(\theta_1 - \frac{\theta_1 + \theta_3}{2} \right)} \right] \quad (\text{I.59})$$

$$\alpha = \arctan \left[\sqrt{\tan^2 \left(\theta_1 - \frac{\theta_1 + \theta_3}{2} \right) + \tan^2 \left(\theta_2 - \frac{\theta_1 + \theta_3}{2} \right)} \right]. \quad (\text{I.60})$$

By substituting the above formulas into the equation

$$\tan(\theta - \Theta) = -\tan \alpha \cos(\beta - B), \quad (\text{I.61})$$

we obtain the desired relation between θ and β .

As an example, we show our experimental results in Fig. I.21. Our goniometer has 1,000 scales per a quarter-rotation (90°). We chose the goniometer scales as $\beta_1 = 400$, $\beta_2 = 1400$, and $\beta_3 = 2400$. For each β , proper value of θ to align the field parallel to the plane was found by recording relative change of the resonance frequency as a function of θ as shown in Fig. I.21(a)-(c). We derived each peak value of θ , i.e. θ_1 , θ_2 , and θ_3 , by fitting the data to Gaussian curves. The obtained three sets of (β, θ) are: $(\beta_1, \theta_1) = (400, 309.0)$, $(\beta_2, \theta_2) = (1400, 308.7)$, $(\beta_3, \theta_3) = (2400, 328.3)$. These allow us to derive the three unknowns, the offset of rotator Θ , the offset of goniometer B , and the tilt angle α as follows:

$$\Theta = 318.65^\circ, \quad B = 909.936 (= 81.89^\circ), \quad \alpha = 13.73^\circ. \quad (\text{I.62})$$

By using Eq. I.54 and the above values we can deduce the relation between θ and β , which keeps the applied field always in-plane, shown by red curves in Fig. I.21(d). To check the accuracy of this curve, we take another set of (β, θ) (Fig. I.21(e)). The obtained point $(\beta_4, \theta_4) = (543, 307.4)$ is actually on the curve as shown in Fig. I.21(d) by a blue square. This ensures the accuracy of this method for adjusting magnetic field direction into the plane.

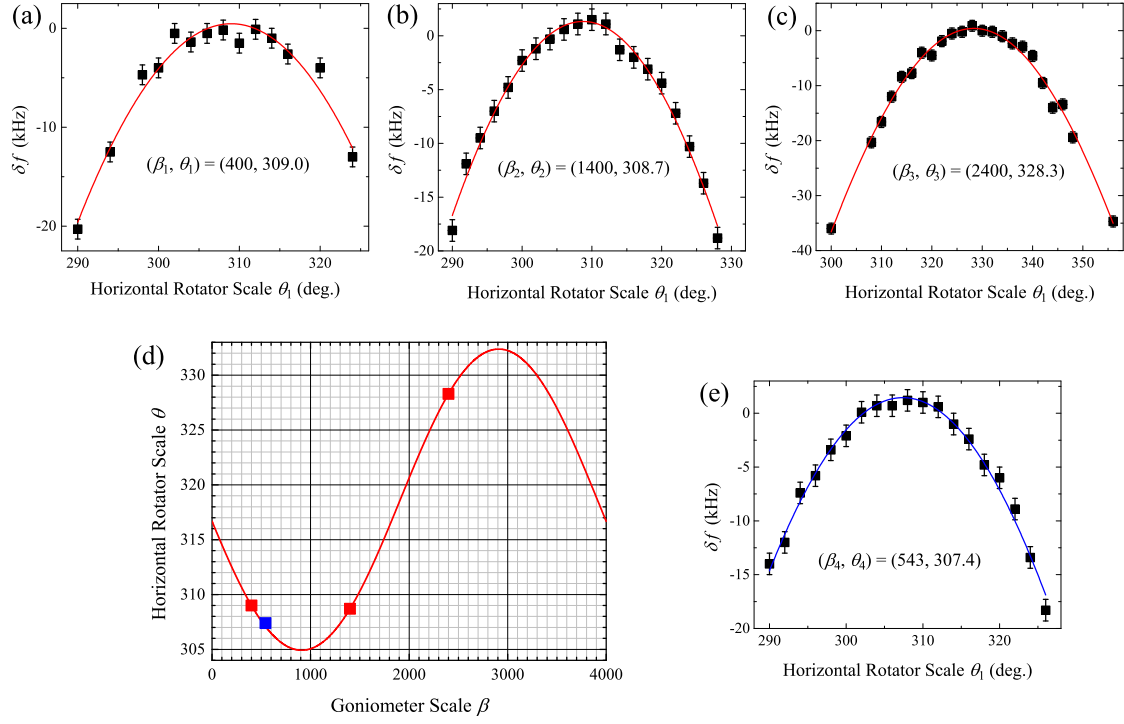


Figure I.21: (a)-(c),(e) Control of the field direction into the plane by adjusting θ for each fixed β values. (d) The red curve indicates the relation between θ and β which keeps the field always in-plane. The red squares represents (β_1, θ_1) , (β_2, θ_2) , (β_3, θ_3) obtained by the measurements of Figs. (a), (b), and (c), respectively. The blue points denotes (β_4, θ_4) obtained by the measurement of Fig. (e) performed in order to confirm the accuracy of the red curve determined from the measurements of Figs. (a)-(c).

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List of Publications

Preprints

1. **T. Iye**, M.-H. Julien, H. Mayaffre, M. Horvatić, C. Berthier, K. Ishida, H. Ikeda, S. Kasahara, T. Shibauchi, and Y. Matsuda,
“*How orbital-nematic order develops in the tetragonal phase of $BaFe_2(As_{1-x}P_x)_2$* ”,
Submitted to Physical Review Letters.

Journal Articles

1. S. Kitagawa, **T. Iye**, Y. Nakai, K. Ishida, C. Wang, G.-H. Cao and Z.-A. Xu,
“*Relationship between Superconductivity and Antiferromagnetism in $LaFe(As_{1-x}P_x)O$ Revealed by ^{31}P -NMR*”,
Accepted for publication in Journal of the Physical Society of Japan.
2. Y. Nakai, **T. Iye**, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, H. Ikeda, and T. Terashima,
“*Normal-state spin dynamics in the iron-pnictide superconductors $BaFe_2(As_{1-x}P_x)_2$ and $Ba(Fe_{1-x}Co_x)_2As_2$ probed with NMR measurements*”,
Physical Review B **87**, 174507 (2013).
3. **T. Iye**, Y. Nakai, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, and T. Terashima,
“*Gradual suppression of antiferromagnetism in $BaFe_2(As_{1-x}P_x)_2$: Zero-temperature evidence for a quantum critical point*”,
Physical Review B **85**, 184505 (2012).
4. Y. Nakai, S. Kitagawa, **T. Iye**, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono,
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5. **T. Iye**, Y. Nakai, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, and T. Terashima,
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7. **T. Iye**, T. Nagatochi, R. Ikeda, and A. Matsuda,
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Journal of the Physical Society of Japan **79**, 114711 (2010).
8. Y. Nakai, **T. Iye**, S. Kitagawa, K. Ishida, H. Ikeda, S. Kasahara, H. Shishido, T. Shibauchi,
Y. Matsuda, and T. Terashima,
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9. S. Kitagawa, Y. Nakai, **T. Iye**, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono,
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10. Y. Nakai, **T. Iye**, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, and T.
Terashima,
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Review

1. K. Ishida, Y. Nakai, S. Kitagawa, and **T. Iye**,
“*NMR studies on iron-pnictide superconductors: $LaFeAs(O_{1-x}F_x)$ and $BaFe_2(As_{1-x}P_x)_2$* ”,
Comptes Rendus Physique **12**, 515 (2011).

Conference Proceedings

1. **T. Iye**, Y. Nakai, S. Kitagawa, K. Ishida, H. Ikeda, S. Kasahara, T. Shibauchi, Y. Mat-
suda, and T. Terashima,
“*P-concentration dependence of the quasiparticle density of states in $BaFe_2(As_{1-x}P_x)_2$* ”,
International Conference on Strongly Correlated Electron Systems (SCES 2011),
August 29-September 3, 2011, Cambridge, UK:
Journal of Physics: Conference Series **391**, 012127 (2012).
2. S. Kitagawa, Y. Nakai, **T. Iye**, K. Ishida, Y. F. Guo, Y. G. Shi, K. Yamaura, and E.
Takayama-Muromachi,
“*Nuclear spin-lattice relaxation rate in the superconducting state on $La(Fe_{1-x}Zn_x)AsO_{0.85}$
studied by ^{75}As -NMR*”,
International Conference on Strongly Correlated Electron Systems (SCES 2011),
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3. C. Nakashima, **T. Iye**, and A. Matsuda,
“*Periodic DOS modulation in underdoped $Bi2223$* ”,
24th International Symposium on Superconductivity (ISS 2011),
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4. **T. Iye**, T. Nagatochi, and A. Matsuda,
“*Dimensional crossover in underdoped $Bi_{2.2}Sr_{1.8}Ca_2Cu_3O_{10+\delta}$* ”,
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5. Y. Nakai, T. Iye, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, and T. Terashima,
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