

Anomalous spin fluctuations deep in the
superconducting state of S-substituted
FeSe revealed by ^{77}Se NMR

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Abstract

The study of the iron-based superconductor FeSe has resulted in various intriguing topics. Especially, the isovalent compound, $\text{FeSe}_{1-x}\text{S}_x$, has provided an opportunity of detangling the effect of nematicity and/or magnetism on superconductivity (SC), due to its unique phase diagram. With the shallow Fermi surfaces of $\text{FeSe}_{1-x}\text{S}_x$, one can control these properties by parameters such as pressure or external field.

In particular, S-substitution levels larger than the quantum critical point (QCP) has garnered much attention due to the finite density of states (DOS) remaining at low temperatures. This unusual residual of DOS has been observed by experimental methods, such as scanning-tunneling-spectroscopy and specific heat measurements. Recently, a topologically protected ultranodal state, referred to as Bogoliubov Fermi surfaces (BFSs), has been proposed to explain this unusual phenomenon. The theoretical model demonstrated that BFSs can manifest under the conditions of spin-orbit coupling, multi-band systems, and superconductivity with time-reversal symmetry breaking (TRSB). Calculations specific to $\text{FeSe}_{1-x}\text{S}_x$ are known in agreement with the experimental results. Further theoretical investigation has pointed out that BFSs possibly has a C_2 symmetry, despite that it is in the tetragonal phase, which is consistent with the result of angle-resolved photoemission spectroscopy (ARPES).

Here we report the observation of spin fluctuations originating from BFSs in the superconducting state via ^{77}Se -nuclear magnetic resonance (NMR) measurements on $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) to 100 mK. In a heavily S-substituted FeSe, we found an anomalous enhancement of low-energy spin fluctuations deep in the SC state, which cannot be explained by impurity effect. The low-energy spin fluctuations are enhanced with decreasing temperature, supporting strong Bogoliubov quasiparticle interactions associated with BFSs. Further investigation on the pressure effect of this peculiar behavior has also been conducted. The results demonstrated that the anomalous enhancement is suppressed but persists under pressure, implying that quasiparticle interactions become weak by applying pressure. Furthermore, spin fluctuations in the normal state exhibit different temperature dependence from those deep in the SC state, suggesting that the nesting properties of normal electrons differ from those of Bogoliubov quasiparticles. These findings are consistent with the theoretical model of BFSs with C_2 symmetry and strengthen evidence for Bogoliubov quasiparticle interactions, providing insights into the unconventional pairing state of this system.

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Chapter 1

Introduction

In this chapter, a brief review of the main compound focused in this study, iron-based superconductor (SC) $\text{FeSe}_{1-x}\text{S}_x$, will be presented. The pure compound FeSe is unique among iron-based superconductors, because it exhibits superconductivity without magnetism at ambient pressure, and has a unique P - T phase diagram where the nematic order in a low- P regime and the magnetic order in a high- P regime are separated, despite that the two orders usually overlap in most Fe-based superconductors. As a result, FeSe-based superconductors give a platform to explore the effect of nematicity on superconductivity. Moreover, a novel phenomenon, namely finite residual density of states (DOS) is induced with S substitution. The residual DOS has been observed by several experimental techniques. I will briefly summarize these unusual phenomena in both experimental and theoretical viewpoints in this chapter.

1.1 Properties of $\text{FeSe}_{1-x}\text{S}_x$

FeSe, along with its isovalent compound $\text{FeSe}_{1-x}\text{S}_x$, has become one of the exciting topics in the research of exotic superconducting states. The superconductivity of FeSe was first discovered in 2008 by Wu group [1]. The bulk of FeSe exhibits the superconducting (SC) transition temperature (T_c) of 9 K, and T_c can be dramatically enhanced under different conditions. For instance, T_c reaches 37 K under hydrostatic pressure for bulk FeSe [2], whereas monolayer FeSe thin films grown on SrTiO_3 have T_c above 65 K [3]. FeSe possesses a simple crystal structure, as shown in Fig. 1.1, with layers of tetragonal Fe/Se lattices weakly coupled by van der Waals interaction. When decreasing temperature, FeSe undergoes a structural transition at $T_s \approx 90$ K from tetragonal structure to orthorhombic structure [4], which is known as the electron nematic transition, as shown in Fig. 1.2. Unlike most of the iron-based

superconductors, FeSe does not undergo a magnetic order, although it has a high T_s . The separation of nematicity and magnetism gives a good opportunity to study the effect of nematicity on superconductivity. Moreover, the nematicity is tunable by chemical substitution and/or hydrostatic pressure P [5,6]. I will introduce the effect of S-substitution and pressure on FeSe in the following.

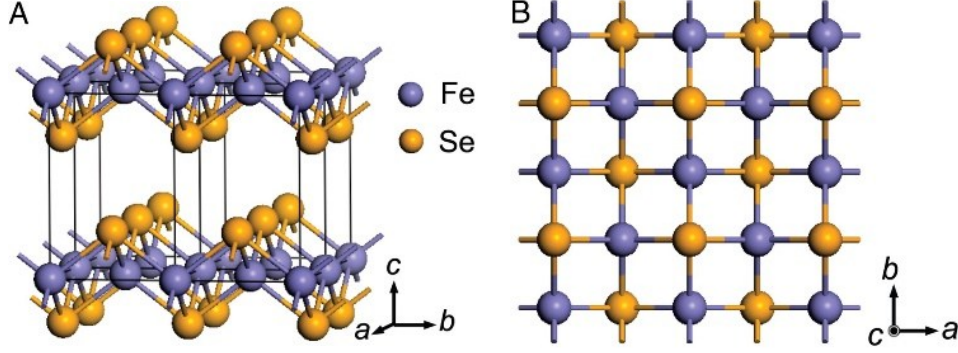


Fig. 1.1 Crystal structure of FeSe in the normal state. [1]

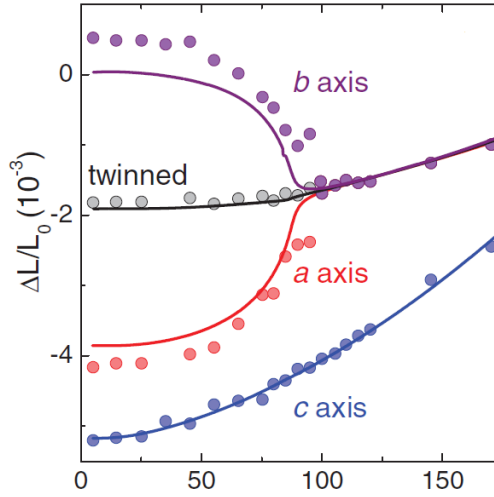


Fig. 1.2 Relative length changes along the three crystal directions. The shrinkage of the unit length for the a axis and the expansion for the b axis in the nematic phase are shown by red and purple points, respectively. [1]

1.1.1 Sulfur substitution

Pure FeSe possesses T_s of around 90 K [4]. However, with substituting Se with S, $\text{FeSe}_{1-x}\text{S}_x$ exhibits a decrease of T_s , and the nematic phase completely disappears at a substitution level of $x \approx 0.17$ [7,8], as shown in Fig. 1.3(a). This substitution level is known as the nematic quantum

critical point (QCP), $x_c \approx 0.17$. Inside the nematic phase, the crystal structure of $\text{FeSe}_{1-x}\text{S}_x$ is orthorhombic and the x dependence of T_c shows a broad peak (~ 10 K) at around $x \approx 0.08$. With increasing S substitution, T_c goes from ~ 8 K inside the nematic phase, to ~ 4 K crossing x_c . Furthermore, the nematic susceptibility also exhibits a Curie-Weiss temperature dependence [7], and the Curie-Weiss temperature T_θ goes to zero at x_c . This indicates that the nematic susceptibility diverges at x_c towards $T = 0$, as shown in Fig.1.3(b). In Fig. 1.3(c), T_c s are precisely measured at heavily S-substituted regime [9], showing intuitively that T_c s below and above QCP differ a lot. In addition, the P - T phase diagram of $\text{FeSe}_{1-x}\text{S}_x$ exhibits a large magnetic dome in a high P regime [6], which will be discussed in the next section. These experimental results have provided evidence of the presence of the nematic QCP.

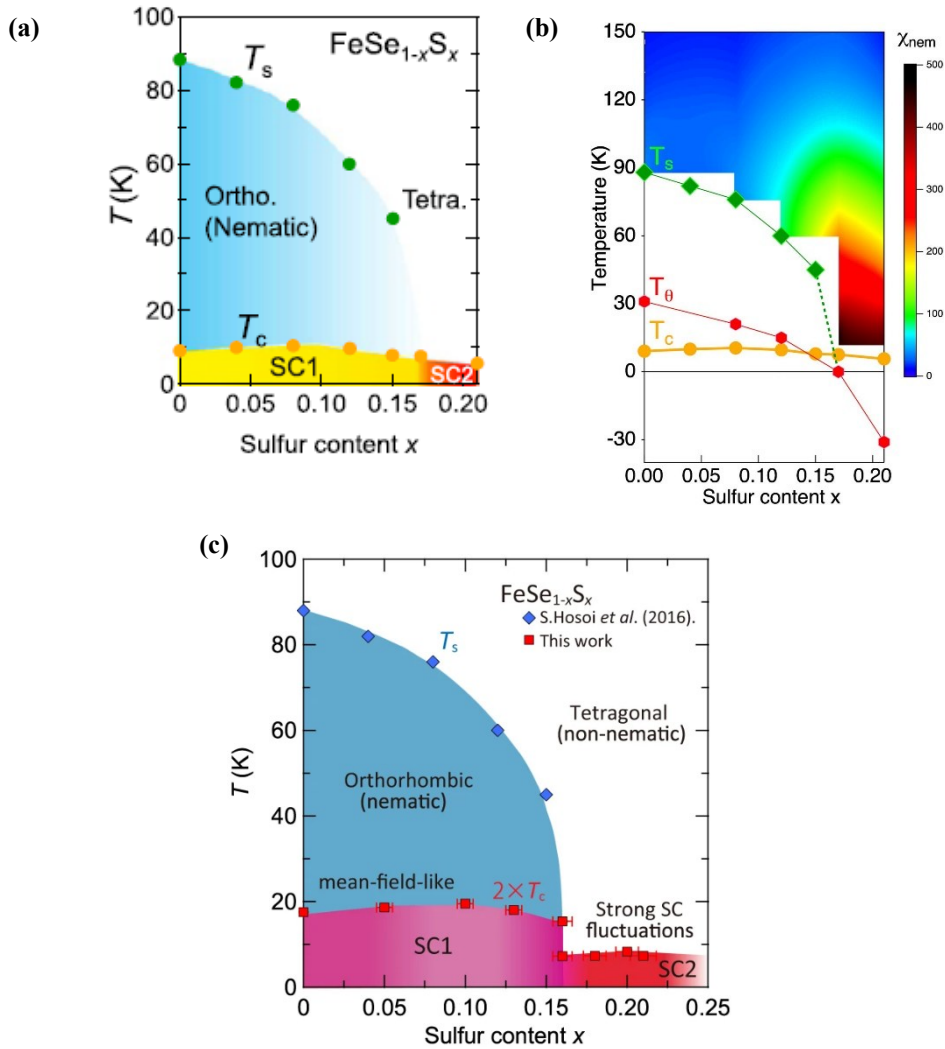


Fig. 1.3 Phase diagrams of $\text{FeSe}_{1-x}\text{S}_x$ determined by different experimental techniques. [7–9]

The parent compound FeSe is a compensated semimetal, which possesses the same number of electrons and holes. This leads FeSe-based superconductors to an intrinsically multiband system. The Fermi surface of FeSe mainly consists of d_{xy} , d_{yz} , and d_{xz} orbitals, as the conducting electrons originate from 3d orbitals of Fe [10]. These orbitals form well separated hole pockets and electron pockets: hole pockets are located at Γ point, the center of Brillouin zone, while the electron pockets are located at X, Y points, the corners of Brillouin zone. The Fermi surfaces of FeSe_{1-x}S_x are extremely shallow and smaller than those for other iron-based superconductors. Furthermore, they are much smaller than those predicted in density functional theory (DFT) calculations [10–12], as shown in Fig. 1.4. These facts allow nematicity, magnetism, and superconductivity to be controlled by parameters such as pressure or external field to an experimentally attainable extent.

For pure FeSe, angle-resolved photoemission spectroscopy (ARPES) experiments have reported that two hole pockets are present at room temperature in the tetragonal phase, as shown in Fig. 1.4(b). However, in the nematic phase, one hole pocket is shifted below Fermi level and only one hole pocket has been observed at Γ point [13]. The presence of nematic order breaks the fourfold rotational symmetry. Therefore, the hole pocket in the nematic phase is elliptically shaped, with the main contribution from d_{yz} band along the long axis and d_{xz} band along the short axis, whereas the d_{xy} band lies below the Fermi level.

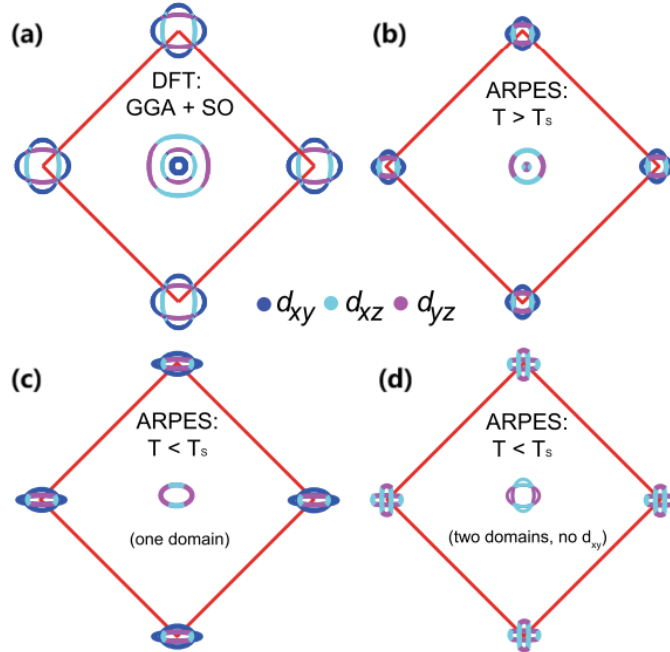


Fig. 1.4 (a) Band-structure calculation of the Fermi surface in the high-temperature tetragonal phase. (b) Schematic high-temperature Fermi surface of FeSe in the tetragonal phase. (c) Low-temperature Fermi surface in the nematic phase with the effect of one domain and (d) two domains. [11]

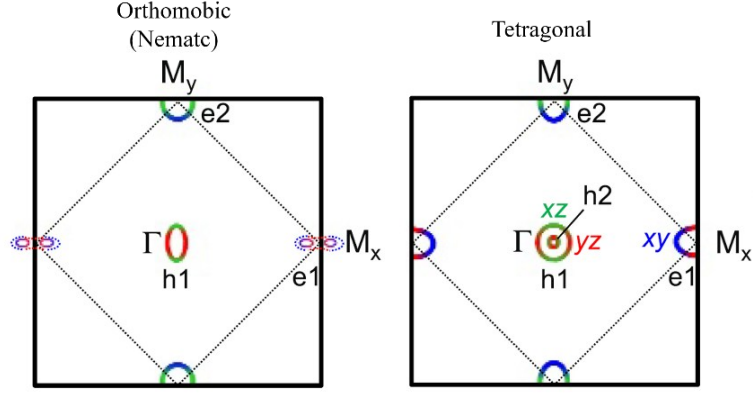


Fig. 1.5 Schematic illustrations of the Fermi surface of Fe(Se,S) in the nematic and the tetragonal phases. [8]

Sulfur substitution in $\text{FeSe}_{1-x}\text{S}_x$ acts as an isovalent chemical pressure that compresses the lattice and broadens the electronic bandwidth. As substitution level increases, the hole bands shift upward and the area of hole pockets expands monotonically, leading to the suppression of electronic correlations and the gradual weakening of nematic distortion [14]. The inner hole band, which resides below the Fermi level in FeSe, progressively moves upward with S substitution and eventually crosses E_F near $x \approx 0.11$ [15,16]. Beyond the nematic end point $x > x_c$, the Fermi surface becomes almost circular and isotropic, which is consistent with the restoration of four-fold symmetry in tetragonal phase, as shown in Fig. 1.5 and 1.6. For both nematic and tetragonal phase, the d_{xy} band gradually shifts upward but remains below E_F , and its contribution to the Fermi surface remains negligible.

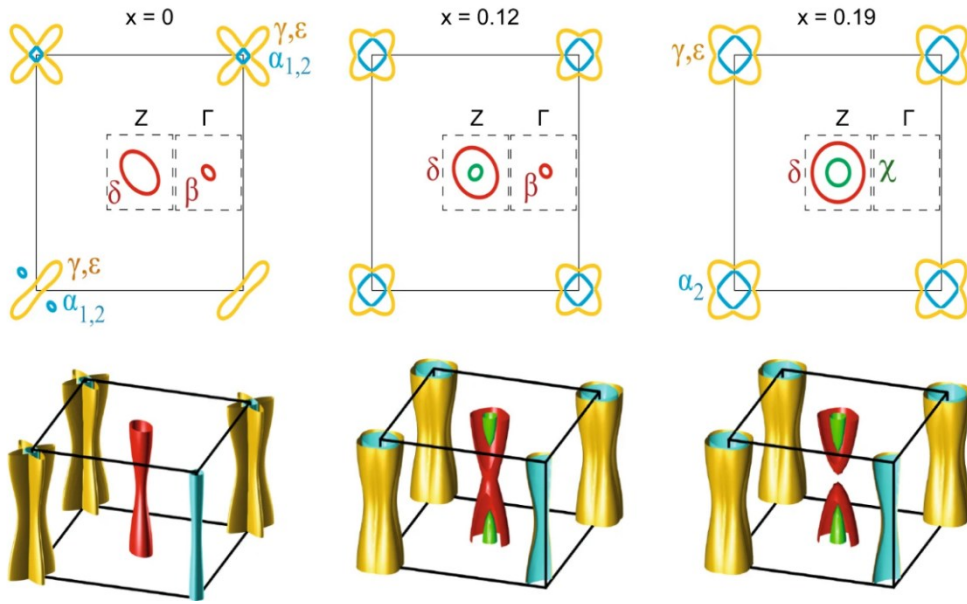


Fig. 1.6 Evolution of the Fermi surface of $\text{FeSe}_{1-x}\text{S}_x$ derived from Shubnikov-de Haas oscillation experiments. [14]

On the other hand, the composition and evolution by S substitution of electron pockets are not as clear as hole pockets [14,17]. This is due to the previously mentioned signature of shallow Fermi surfaces of $\text{FeSe}_{1-x}\text{S}_x$. High resolution ARPES measurements are required for the extremely shallow Fermi surfaces but they are only available for a limited range of momentum around the Γ point. Nano-ARPES experiments have indicated a single electron pocket at X point [18]. As for the electron pocket at Y point, some experiments gave evidence of the presence, while other experiments support the absence [17]. Moreover, ARPES measurements have suggested that the electron pocket at X point is bowtie shaped, while quantum oscillation measurements have suggested a nontrivial Berry phase [14]. For simplicity, an elliptical shape is assumed in this study with the contribution from d_{yz} band along the long axis and from d_{xy} band along the short axis.

1.1.2 Pressure effect on $\text{FeSe}_{1-x}\text{S}_x$

As Sulfur substitution in $\text{FeSe}_{1-x}\text{S}_x$ acts as an isovalent chemical pressure, mechanical pressure P also plays an important role in tuning the nematic and magnetic orders of $\text{FeSe}_{1-x}\text{S}_x$. Fig. 1.7 shows a series of P - T phase diagrams for several substitution levels, where T_s and T_m are determined by resistivity measurements, and T_c are determined by both zero resistivity and magnetic susceptibility measurements [6]. For pure FeSe, the nematic phase is completely suppressed at around 2 GPa, similar to the effect of S substitution. In contrast to S substitution, an antiferromagnetic (AFM) order starts to emerge before the disappearance of the nematic phase. The appearance of AFM order also accompanies an increase in T_c , from 9 K at ambient pressure to 38 K at above 6 GPa.

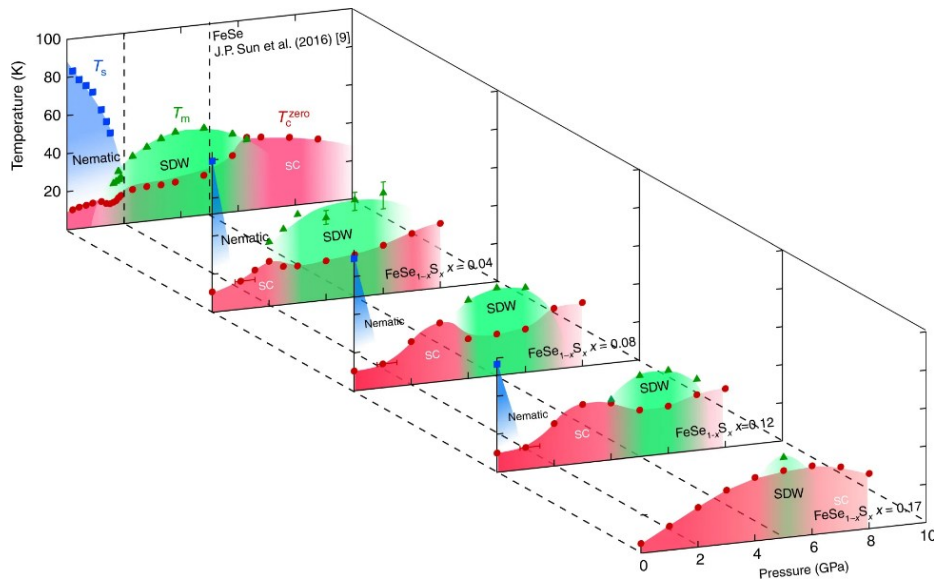


Fig. 1.7 P - T - x phase diagram of $\text{FeSe}_{1-x}\text{S}_x$ determined from anomalies in resistivity measurements. [6]

With sulfur substitution, the nematic phase shrinks to lower pressure side while the AFM dome shifts to higher pressure side. The pressure range of AFM order also shrinks with the increase in S substitution and disappears at $x \approx 0.17$. As a result, a tetragonal phase with a higher T_c s appears between the nematic and AFM phases. It is intuitive from the P - T - x phase diagram that magnetism at the higher-pressure side suppresses superconductivity, which offers a good opportunity for the study of how nematicity and magnetic order affect superconductivity.

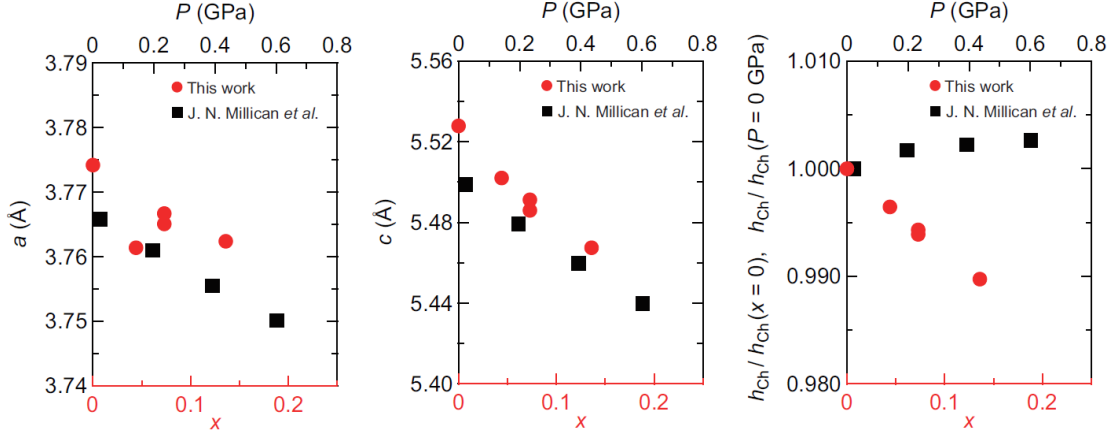


Fig. 1.8 Comparison between mechanical pressure and isovalent substitution effects on the structural parameters of $\text{FeSe}_{1-x}\text{S}_x$. [6]

The mechanical and chemical pressure both play an important role in the properties of $\text{FeSe}_{1-x}\text{S}_x$. Fig. 1.8 shows how mechanical pressure and isovalent substitution affect the structural parameters [6]. Both of the two factors have similar effect on the lattice structure, that is, the lattice constant a and c are both suppressed by pressure and S substitution. Quantitatively speaking, it is suggested that 10% of S substitution corresponds to ~ 0.3 GPa of pressure. On the other hand, however, the chalcogen height h_{Ch} from the iron plane is enhanced by pressure while being suppressed by S substitution.

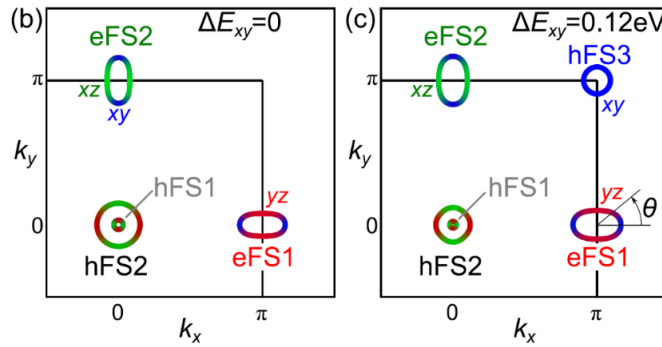


Fig. 1.9 Schematic of the pressure induced Lifshitz transition. [19]

According to theoretical investigation, an extra hole pocket is predicted to emerge under pressure at M point, $\mathbf{k} = (\pi, \pi)$, the corner of Brillouin zone of FeSe [19], as shown in Fig. 1.9. This Lifshitz transition also causes changes in the nesting properties of Fermi surfaces since d_{xy} orbital is enlarged, while those on the d_{xz} and d_{yz} orbitals are reduced gently.

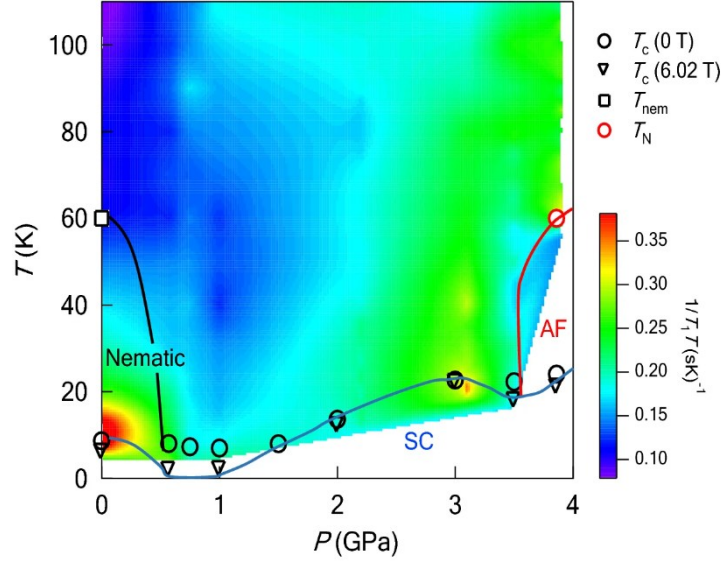


Fig. 1.10 P - T phase diagram of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.12$) with correspondence to color plot of spin fluctuation intensities. [20]

Recently, the pressure-induced Lifshitz transition has been reported from a nuclear magnetic resonance (NMR) experiment in $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.12$) [20]. The P - T phase diagram derived from the NMR measurements shows an AFM order above 3.9 GPa, and a change of spin fluctuations corresponding to the Lifshitz transition has been observed at around 1 GPa as shown in Fig. 1.10. The Lifshitz transition has also been observed from the P dependence of the Knight shift [20]. Spin fluctuations are suppressed in the pressure regime between nematic and AFM order, and a high T_c dome also emerges in this regime, indicating that this behavior is crucial for understanding the mechanism of superconductivity.

Altogether, the two parameters, substitution level x and pressure P , are very efficient and important tools to discover and understand the $\text{FeSe}_{1-x}\text{S}_x$ system. This study also utilizes these two parameters to gain a better comprehension of $\text{FeSe}_{1-x}\text{S}_x$ from the experimental perspective.

1.1.3 The superconducting gap structure

The superconducting (SC) gap structure $\Delta(\mathbf{k})$ provides crucial information for determining the pairing symmetry and underlying interactions. For FeSe, the SC gap exhibits a highly anisotropic feature, which is closely related to its unique electronic properties. In bulk FeSe, the superconducting gap is generally considered to be nodeless but strongly anisotropic on the Fermi surfaces. An ARPES experiment has revealed that the gap magnitude varies significantly along the hole pockets [21], as shown in Fig. 1.11. As the Fermi surface at hole pocket shows an ellipsoidal shape, the gap around Γ point also possesses a two-fold symmetry. Moreover, $\Delta(\mathbf{k})$ reaches almost zero (gap minima) at 90 and 270 degree, which suggests possible nodes near this direction [21,22], as shown in Fig. 1.11 and 1.12.

The superconducting order parameter is often described as an anisotropic s -wave or $s_{\pm}$ -wave type, where the gap on different Fermi pockets may have opposite signs but no symmetry-protected nodes [17].

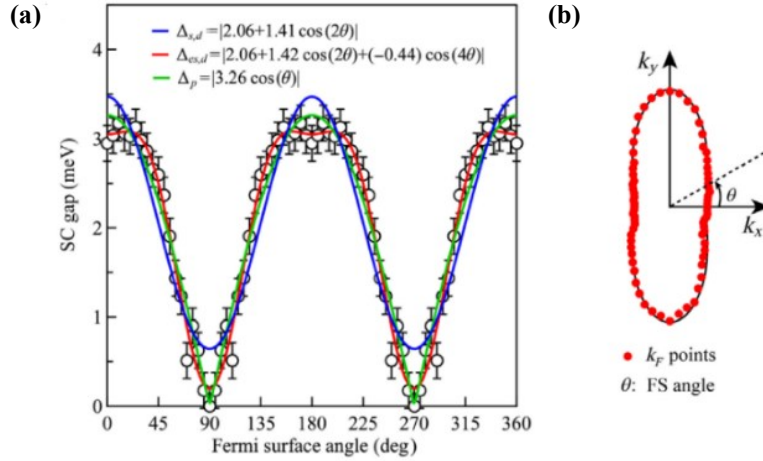


Fig. 1.11 Momentum dependence of the superconducting gap on the hole pocket of FeSe determined by ARPES measurement at 1.6 K. (a) Momentum dependence of the superconducting gap, with averaging over the four quadrants. The measured gap (empty circles) is fitted by several gap forms. (b) Location of the Fermi momentum defined by the Fermi surface angle θ . [21]

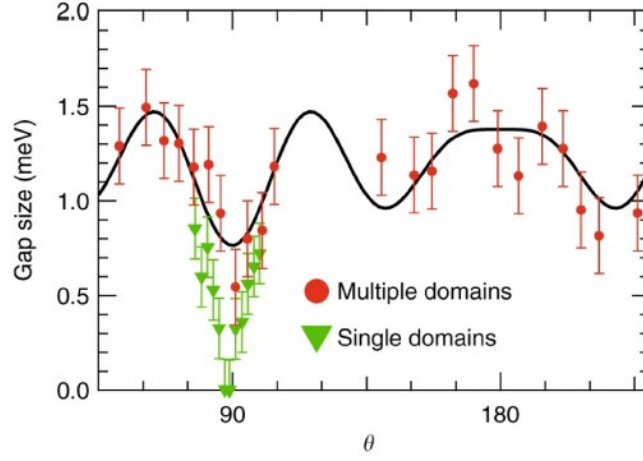


Fig. 1.12 Momentum dependence of the gap along the hole Fermi surface ellipsoid in single-domain (green triangles) and multiple-domain (red circles) samples. [22]

The anisotropy of the gap becomes weaker with increasing S content, suggesting that nematicity plays a key role in shaping the gap anisotropy. At higher pressure levels where magnetic order appears, changes in the pairing interaction may also modify the gap symmetry.

1.2 Unusual behavior in the superconducting state of heavily doped $\text{FeSe}_{1-x}\text{S}_x$

One of the recent focuses among topics of $\text{FeSe}_{1-x}\text{S}_x$ is the unusual behavior of density of states (DOS) remaining remarkably for $x > x_c$ at low temperature. In this section, some experimental evidence and theoretical predictions will be introduced for this topic.

1.2.1 Residual DOS at low temperature

In a conventional fully-gapped superconductor, the DOS at the Fermi level vanishes as the temperature approaches zero, because all quasiparticles are paired into the superconducting condensate. However, in many real materials, a finite residual DOS remains even at the lowest temperatures, as observed through quantities such as the specific heat, thermal conductivity.

As discussed in Sect. 1.1, significant changes occur in superconducting properties at the nematic critical concentration which implies that the nematicity, or rotational symmetry breaking, strongly affects superconductivity. The superconducting gap structure is changed abruptly at the nematic QCP [8], which is evidenced by studies of the specific heat C , as shown in Fig. 1.13. Clear residual of DOS is observed for heavily doped sample ($x = 0.20$) outside the QCP, as C/T maintains a finite value even when temperature approached zero. The T dependence of thermal conductivity also shows large residual DOS at low temperature. Although impurity may also cause such phenomenon, the nearly 100% Meissner signal and the sharp jump in specific heat guarantee the high quality of the samples. This reassures that the cause of such large residual DOS is indeed caused by intrinsic factors.

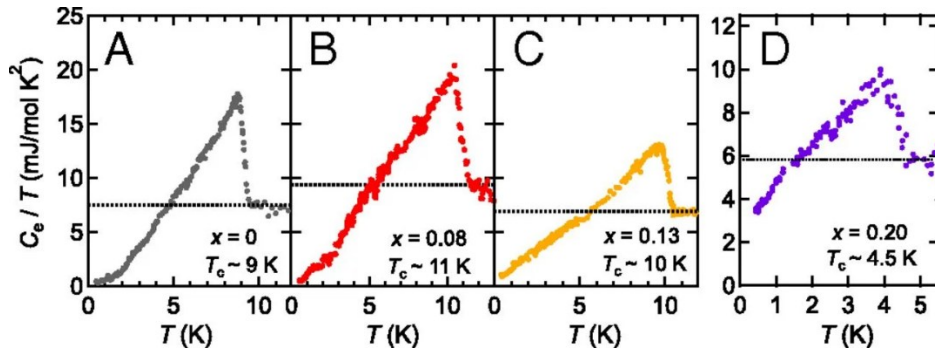


Fig. 1.13 T dependence of the electronic component of the specific heat divided by temperature, C_e/T , in $\text{FeSe}_{1-x}\text{S}_x$ for $x = 0, 0.08, 0.13$, and 0.20 . [8]

This remarkable change in superconducting gap has also been suggested by systematic scanning tunneling spectroscopy (STS) studies [18]. Within the nematic phase, tunneling conductance remains unchanged even with increasing S-substitution level x , but after crossing the nematic QCP ($x > x_c$), the spectrum of superconducting gap changes drastically, as shown in Fig. 1.14. Below x_c , clear quasiparticle peaks appear around ± 2.5 meV, accompanied by a very small zero-bias conductance. In contrast, when x exceeds x_c , the quasiparticle peaks become broadened and the superconducting gap shrinks to below ~ 1.5 meV. In the meantime, the zero-bias conductance becomes markedly enhanced compared with that of $x < x_c$ samples. This pronounced increase in zero-bias conductance is consistent with thermodynamic measurements, where the specific heat data shows a large residual DOS only for $x > x_c$.

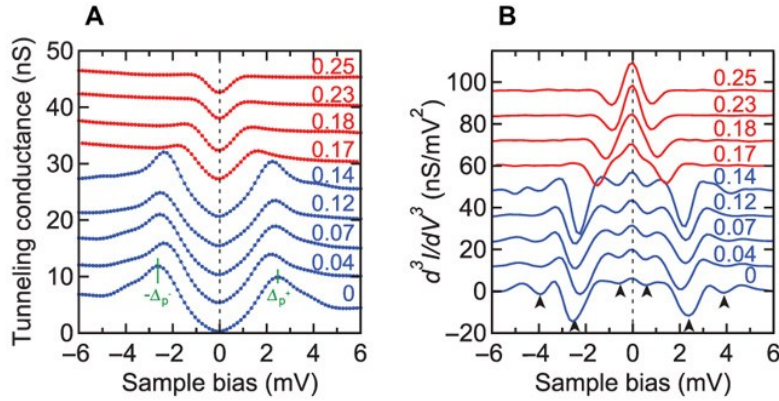


Fig. 1.14 Averaged tunneling conductance spectra of $\text{FeSe}_{1-x}\text{S}_x$ for $0 < x < 0.25$. Each curve is shifted vertically for clarity. Blue (red) curves are representing the orthorhombic (tetragonal) phase. [18]

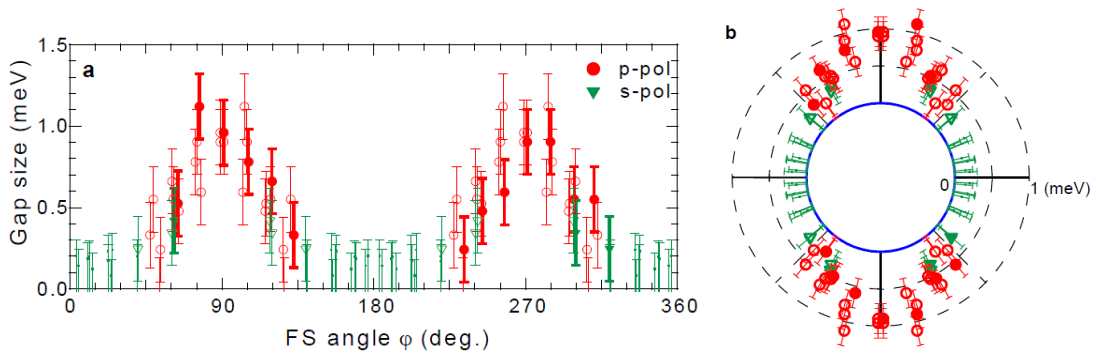


Fig. 1.15 Superconducting gap anisotropy of the hole FS. (a) SC gap size plotted by solid symbols as a function of φ . The open symbols are symmetrized by assuming the two-fold and mirror symmetries. (b) SC gaps shown in (a) are plotted in polar coordinates. The distance from the central circle corresponds to the gap size. [23]

A recent ARPES experiment pointed out this unusual behavior more directly [23]. Although for $\text{FeSe}_{1-x}\text{S}_x$ ($x < x_c$), the Fermi surface is naturally anisotropic due to the nematic crystal structure, Fermi surfaces in the tetragonal phase is inherently considered to be of four-fold (C_4) symmetry. However, in this ARPES result, unexpected extended nodal planes of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.22$) are found around $\varphi = 0^\circ$ and 180° , where φ represents the FS-angle, as shown in Fig. 1.15. This gives clear evidence of the two-fold (C_2) symmetry of the Fermi surface, despite the crystal shows a C_4 symmetry.

These findings all strongly evidence that the superconducting state in the tetragonal phase is different from that of the nematic phase. The non-negligible DOS residual and the trivial behavior of C_2 symmetry Fermi surface cannot be explained by traditional s -wave or $s_{\pm}$ -wave, leading to new investigation of the electronic nature of heavily S-substituted FeSe. A recent theoretical prediction of the existence of Bogoliubov Fermi surfaces in $\text{FeSe}_{1-x}\text{S}_x$ ($x > x_c$) is highly promising to explain above-mentioned phenomena, which will be further introduced in the following section.

1.2.2 Bogoliubov Fermi surfaces

As mentioned in Sect. 1.1.3, the pairing symmetry of $\text{FeSe}_{1-x}\text{S}_x$ is generally considered as an anisotropic $s_{\pm}$ -wave. In this framework, repulsive inter-band interactions between hole and electron pockets lead to a superconducting gap that changes sign across the Fermi surface. Such a paradigm can successfully explain many iron-pnictide superconductors. However, for $\text{FeSe}_{1-x}\text{S}_x$, the situation becomes more complicated. Due to the small Fermi surfaces of hole and electron pockets, the conventional $s_{\pm}$ scenario appears insufficient to describe all experimental observations, particularly those related to residual of low-energy excitations and anomalous thermodynamic behavior, as described in Sect. 1.2.1.

An inspiring theoretical proposal that may account for these anomalous superconducting states in $\text{FeSe}_{1-x}\text{S}_x$ ($x > x_c$) has been recently made by C. Setty, *et al* [24,25]. They have suggested the existence of extended zero-energy excitations forming continuous contours in momentum space, known as Bogoliubov Fermi surfaces (BFSs). The superconducting state thus becomes an ultra-nodal SC state. This ultra-nodal state holds extended line nodes in the two-dimensional momentum space instead of usual point nodes.

Theoretically, BFSs arise in multiband systems when specific symmetry conditions are satisfied. The Bogoliubov-de Gennes Hamiltonian of such a system can be characterized by a Pfaffian topological invariant, whose sign determines whether the spectrum is fully gapped or possesses zero-energy surfaces. When the Pfaffian changes sign at some momentum points, topologically protected BFSs emerge.

Multiband superconductors with dominant spin singlet, intraband pairing of spin- $\frac{1}{2}$ electrons can undergo a transition to a state with Bogoliubov Fermi surfaces if spin-orbit coupling, interband pairing and time-reversal symmetry breaking (TRSB) are also present [26]. Experimental evidence supporting TRSB behavior has been reported by μ SR measurements [27]. The symmetry-breaking effects may be further reinforced by spin-orbit coupling, which can naturally generate complex phase relationships between the superconducting components in multi-orbital systems.

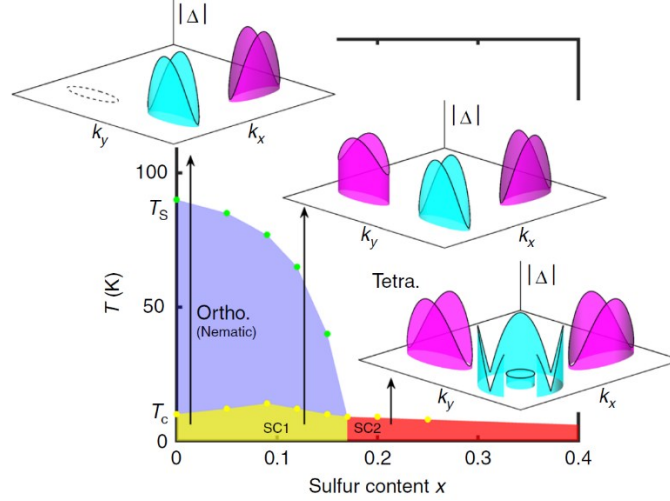


Fig. 1.16 Schematic plot of the phase diagram and intra-pocket order parameters used on the electron and hole bands in different phases across the transition. [24]

Figure 1.16 shows a simplified three-pocket model (Γ , X, Y) in two dimensions with correspondence to the x - T phase diagram. This model captures the essential electronic structure of the $\text{FeSe}_{1-x}\text{S}_x$ system that helps explain the strange thermal behavior that appears for substitution levels beyond the nematic transition. The band dispersions are quadratic, centered around Γ and X/Y points. Blue and purple colors indicate opposite signs of the order parameter on hole and electron pockets, as in the conventional $s_{\pm}$ state. This figure thus summarizes the assumed evolution of the gap anisotropy and symmetry that leads to the emergence of the ultranodal state with BFSs.

When the usual intraband pairing weakens and interband interactions become dominant, the superconducting state changes from a fully gapped state to an ultranodal state with BFSs, where quasiparticles can exist even at zero energy. Fig. 1.17 shows the topological evolution from a fully gapped superconducting state to an ultranodal state with BFSs. Panels (a-d) show how the quasiparticle spectrum evolves as the ratio of intraband isotropic gap component to anisotropic components decreases. This evolution corresponds to the increase of S-substitution. When the isotropic gaps are large (a), the system is fully gapped. As these components are reduced (b-d), the Pfaffian sign changes, indicating the emergence of BFSs. These BFSs first appear as small

C_2 symmetric nodes and is expected to expand to a C_4 symmetry shape as nematicity disappears, indicating an increasing region of gapless excitations. Fig. 1.17(e, f) relates this evolution to experimental results. The specific heat goes to a finite value at low T due to residual DOS, and the tunneling conductance shows a finite zero-bias value accompanied by suppressed coherence peaks. Together, these features demonstrate that the BFSs arises when the interband and TRSB pairing components overcome the isotropic intraband pairing, leading to a topological superconducting phase with coexisting of superconducting order and metallic-like low-energy excitations.

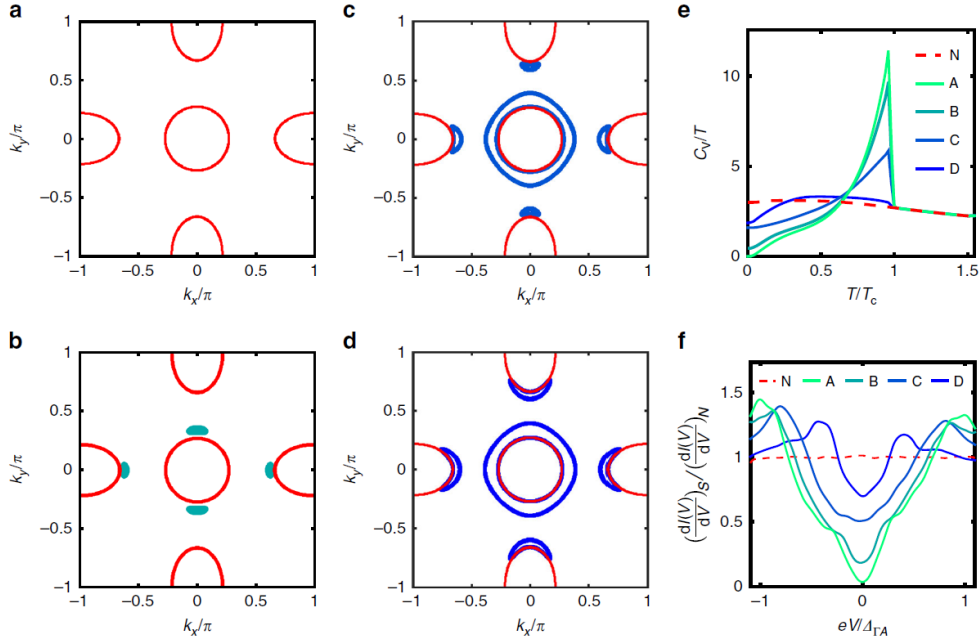


Fig. 1.17 Transition from normal state into the ultranodal state. (a)-(d) Normal state Fermi surface (red contour) and Bogoliubov Fermi surface in superconducting state (blue/green patches) for different values of the isotropic gap parameters on each pocket. (e) Temperature dependence of the specific heat and (f) tunneling conductance dI/dV calculated theoretically and normalized to normal state value. [24]

Further theoretical study has been proposed by Y. Cao, *et al.* which studies how the coupling strength of the various orders may affect the pairing symmetry [28]. The ultranodal state can be realized under a very strict parameter range. In addition to the two-hole bands, electron bands at X and Y points are also relative to the correlation. The Hamiltonian of this four band model is

$$\begin{aligned}
H = & \sum_{\substack{\mathbf{k}, \sigma \\ i=\{1,2,3,4\}}} \epsilon_{i\mathbf{k}} c_{i\mathbf{k}\sigma}^\dagger c_{i\mathbf{k}\sigma} + H_m + H_T \\
& + \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ i,j=\{1,2,3,4\}, i \leq j}} \Gamma_{ij}(\mathbf{k}, \mathbf{k}') c_{i\mathbf{k}\uparrow}^\dagger c_{i-\mathbf{k}\downarrow}^\dagger + c_{j-\mathbf{k}'\downarrow} c_{j\mathbf{k}'\uparrow}
\end{aligned} \tag{1.1}$$

where H_m is the term that describes the magnetic interaction of electrons in two hole pockets, H_T is the pairing interaction between interband triplets, and the last term describes the interaction of the repulsive $s_\pm$ pairing.

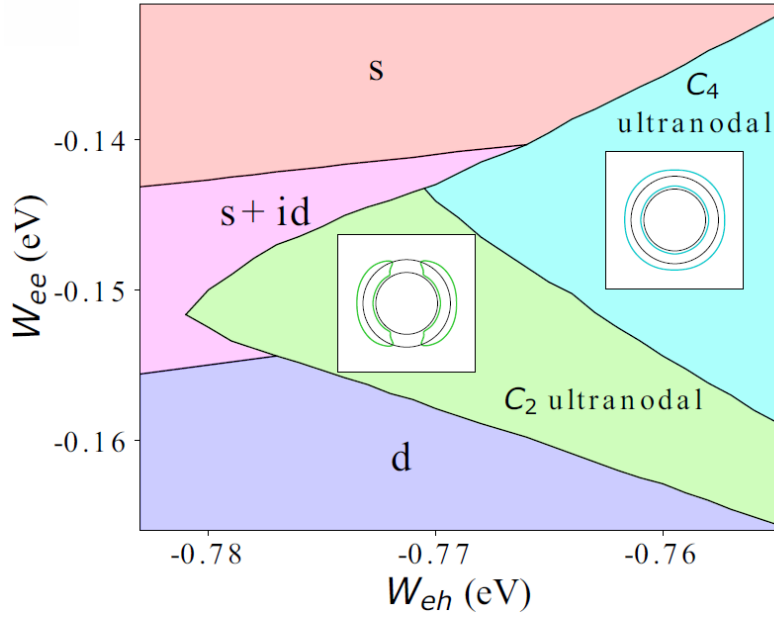


Fig. 1.18 Phase diagram near zero temperature derived from calculation for the four band model Hamiltonian. [28]

Figure 1.18 demonstrates the emergence of BFSs within the four-band model relevant to tetragonal $\text{FeSe}_{1-x}\text{S}_x$. As shown in Fig. 1.18, depending on the relative strength of the electron-hole and electron-electron pairing interactions (W_{eh} and W_{ee}), the system hosts several superconducting phases, including conventional s - and d -wave states, a mixed $s+id$ state, and two distinct ultranodal phases with either preserved C_4 or spontaneously broken C_2 symmetry. The insets demonstrate the typical shapes of the BFS in these ultranodal states. While the C_4 ultranodal phase maintains zero-energy contours around the hole pockets, the C_2 ultranodal phase develops anisotropic BFSs elongated along one axis, indicating spontaneous rotational-symmetry breaking. Calculations show that the lowest quasiparticle excitation energy becomes zero over a wide angular range in the C_2 ultranodal state, confirming the existence of continuous zero-energy areas instead of spontaneous nodes. This C_2 ultranodal state is also consistent with

the ARPES experiment.

Noted that this model is based on the assumption of the presence of ferromagnetic interaction in the tetragonal phase, for the purpose of stabilizing the nonunitary triplet pairing and thus the BFSs. However, no evidence has shown that $\text{FeSe}_{1-x}\text{S}_x (x > x_c)$ has a ferromagnetic property at ambient pressure.

Recently, T. Nagashima, *et al.* investigated how nonmagnetic disorder affects the superconductivity and the stability of BFSs in the tetragonal $\text{FeSe}_{1-x}\text{S}_x (x = 0.25)$ [29]. Impurity was induced by electron irradiation, and the results revealed that increasing impurities cause a nonmonotonic change in the low-temperature penetration depth, indicating a transition from a nodal to a nodeless and finally gapless state. Their study suggested that the BFSs can be lifted by disorder.

Chapter 2

Purpose

The purpose of this study is to investigate the low-temperature electronic properties of the $\text{FeSe}_{1-x}\text{S}_x$ system across a wide range of sulfur substitution and pressure levels, more specifically, to investigate the unusual residual of density of states (DOS) in tetragonal $\text{FeSe}_{1-x}\text{S}_x$ near absolute zero Kelvin. Understanding of this novel phenomenon from a microscopic point of view is highly essential for revealing the underlying pairing mechanism and for exploring the unconventional superconductivity.

In this work, we mainly focus on spin fluctuations deep in the SC state and their evolution under S substitution and/or P application. Nuclear magnetic resonance (NMR) measurements were performed down to 100 mK using a dilution refrigerator with several pressure levels, allowing us to probe the quasiparticle behavior in both the superconducting and normal states. NMR experiments at such low temperature provide microscopic insights that are inaccessible through other bulk measurements, enabling the observation of subtle changes in the spin susceptibility and antiferromagnetic fluctuations.

By systematically studying $\text{FeSe}_{1-x}\text{S}_x$ under these extreme conditions, we aim to investigate whether this exotic superconducting state, theoretically predicted as Bogoliubov Fermi surfaces, can emerge under certain circumstances. The results of this research are expected to contribute to a deeper understanding of the pairing symmetry and SC mechanism of FeSe-based superconductors.

This thesis is composed as follows. In the previous Chapter 1, a brief review of the focus compound $\text{FeSe}_{1-x}\text{S}_x$ was introduced, in which the unusual behaviors of residual DOS in heavily S-substituted samples are also included. In Chapter 3, the main experimental technique, NMR, is introduced, including basic NMR concepts in solid state physics and its application on $\text{FeSe}_{1-x}\text{S}_x$ specifically. In Chapter 4, other experimental conditions, such as the principle of dilution refrigerator, the pressure cell, and NMR setup, are introduced. Chapter 5 describes the experimental results with brief analyzing. The main result of this study will be discussed in detail in Chapter 6. Finally, Chapter 7 summarizes this work.

Chapter 3

Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is a phenomenon that comes from the energy level splitting of atomic nuclear spins in an external magnetic field, followed by resonant transitions in response to radio frequency fields of appropriate frequencies. It is not only a fundamental physical phenomenon of nuclear spin systems, but also an important experimental tool for probing the internal electronic properties.

In this section, the basic concept and methods of measuring of NMR will be introduced [30–32].

3.1 Nuclear Resonance

A nucleus consists of protons and neutrons, whose spin angular momentum and orbital angular momentum are combined to the nucleus's own spin angular momentum $\hbar I$, in which $I = 1/2, 1, 3/2, \dots$, $\hbar = h/2\pi$, h being the Planck constant. For a system with non-zero nuclear spin, the nucleus carries a magnetic moment μ associated with the spin angular momentum,

$$\mu = g_N \mu_N I \quad (3.1)$$

$$= \gamma \hbar I \quad (3.2)$$

in which g_N , μ_N , γ are the g-factor of the nucleus, nuclear magneton, gyromagnetic ratio respectively. This magnetic moment means that the nucleus can interact with the external magnetic field, causing the nuclear energy levels to split. When a uniform static magnetic field

$\mathbf{H}_0$ is applied externally, the nuclear magnetic moments tend to align parallel or antiparallel to the direction of the magnetic field. Quantum mechanics results indicate that these orientations are not continuous but rather discretized into a series of energy levels known as the Zeeman splitting. The Zeeman interaction with a magnetic field of $\mathbf{H}_0$ is

$$\mathcal{H}_0 = -\boldsymbol{\mu} \cdot \mathbf{H}_0 \quad (3.3)$$

$$= -\gamma \hbar \mathbf{I} \cdot \mathbf{H}_0 \quad (3.4)$$

Assume $\mathbf{H}_0$ is along z-axis, the eigenvalue of energy is,

$$E_m = -\gamma \hbar H_0 m \quad (3.5)$$

where m is the eigen value of I_z , the z compound of $\mathbf{I}$. When the system reaches thermal equilibrium at T , magnetization M becomes

$$\begin{aligned} M(T, H) &= \frac{N_0 \gamma \hbar \sum_{m=-I}^I m e^{\frac{\gamma \hbar H_0 m}{k_B T}}}{\sum_{m=-I}^I m e^{\frac{\gamma \hbar H_0 m}{k_B T}}} \\ &= N_0 \gamma \hbar I B_I(Ix) \end{aligned} \quad (3.6)$$

N_0 is the number of spins per unit volume, $x \equiv \gamma \hbar H_0 / k_B T$, k_B is the Boltzmann constant. $B_I(y)$ is the Brillouin function that

$$B_I(y) = \frac{2I+1}{2I} \coth\left(\frac{2I+1}{2I} y\right) - \frac{1}{2I} \coth\left(\frac{y}{2I}\right) \quad (3.7)$$

Usually, $x \ll 1$ with magnetic field applied, and the nuclear magnetic susceptibility follows the Curie–Weiss law,

$$\chi_0(T) = \frac{M}{H} = \frac{N_0 \gamma^2 \hbar^2}{3k_B T} I(I+1) \quad (3.8)$$

Although nuclear magnetic susceptibility is much smaller than that of electronic systems, the slight nuclear spin polarization induced by an external magnetic field produces a measurable magnetization that gives rise to the NMR signal.

However, a static magnetic field alone cannot directly produce measurable resonance phenomena. To induce spin transitions between these energy levels, a radio frequency field must be applied perpendicular to the static magnetic field. In addition to H_0 , adding an

oscillating magnetic field $H_1 \cos \omega t$ ($H_1 \ll H_0$), the perturbation to the Hamiltonian becomes

$$\mathcal{H}_1 = -\gamma \hbar H_1 I_x \cos \omega t \quad (3.9)$$

When $\omega \simeq \omega_0 \simeq \gamma H_0$, transition occurs between level of m and $m \pm 1$, and its probability is given by

$$\begin{aligned} W_{m \pm 1, m} &= \frac{2\pi \gamma^2 \hbar^2 H_1^2}{\hbar} \frac{1}{4} \langle m \pm 1 | I_{\pm} | m \rangle^2 \rho(E) \\ &= \frac{\pi \omega_1^2}{2} \{I(I+1) - m(m \pm 1)\} g(\omega) \end{aligned} \quad (3.10)$$

with $\omega_1 \equiv \gamma H_1$. $\rho(E)$, $g(\omega)$ are the density of states corresponding to level spread, and are normalized as

$$\int_0^\infty \rho(E) dE = \int_0^\infty g(\omega) d\omega = 1 \quad (3.11)$$

In fact, the existence of transition probabilities implies that spins continuously exchange energy with their surroundings. When an applied radio frequency field causes the nuclear spins to deviate from their equilibrium distribution, these energy exchanges gradually restore the system to thermal equilibrium. Macroscopically, this recovery process manifests as a time-dependent regression of the magnetization intensity, with its characteristic time defined as the spin-lattice relaxation time T_1 . Therefore, starting from the transition probability of a single spin, it is natural to understand T_1 as the population-scale relaxation time, reflecting the efficiency of energy exchange between the nuclear spins and the environment and a crucial physical quantity for studying the dynamics of electronic systems.

3.2 Free induction decay (FID) and spin echo (SE)

Magnetic resonance can be observed by applying a radio frequency magnetic field with a pulse width of t_p ($\omega_1 t_p = \pi/2$). After application of the $\pi/2$ pulse, the spin rotates 90° from the z -axis into the xy -plane and then clockwise in the xy -plane. Due to the rotational motion of the magnetic moment, an induced oscillating field is generated in the coil for applying the

radio frequency magnetic field according to Faraday's law. By amplifying this oscillating field, resonance can be observed as a change in the amplitude of the magnetic moment over time. The time revolution of the induced electromotive force is $V(t) \propto \mu\omega_0 \cdot \exp(-t/T_2^*)$, and the free induction decay (FID) after $\pi/2$ pulse decreases exponentially.

In the case of solid-state NMR, the distribution width $1/T_2^*$ of the local magnetic field becomes large due to various magnetic interactions, making it difficult to observe FID. However, (a) after applying a $\pi/2$ pulse, (b) $t = \tau$ seconds later, and (c) adding a pulse with a pulse width of $2t_p$, the signal recovers after (d) $t = 2\tau$, as shown in Fig. 3.1. This signal is called Spin Echo (SE) and was discovered by Hahn. Fig. 3-1 summarizes the generation principle of SE. In solid-state NMR, magnetic resonance measurements are mainly performed by observing this SE.

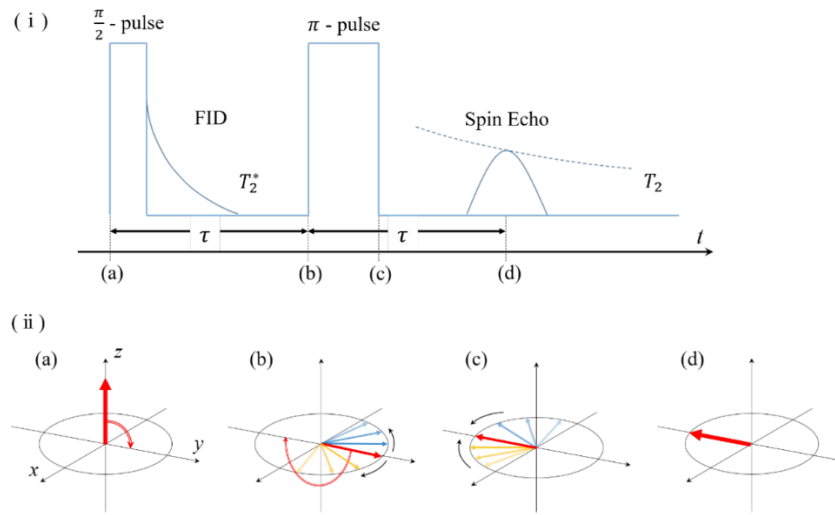


Fig. 3.1 Summary of the generation principle of SE.

3.3 Knight-shift

When a magnetic field H_0 is applied, the resonance frequency of a material will be shifted like

$$\begin{aligned}
 \omega &= \omega_0 + \Delta\omega \\
 &= \omega_0(1 + K) \\
 &= \gamma H_0(1 + K)
 \end{aligned} \tag{3.12}$$

from the original position ω_0 , where γ is the gyromagnetic ratio of a certain nucleus, and K is called the Knight-shift.

This shift of resonance frequency is caused by hyperfine interaction, a magnetic interaction

between nuclear spins and the magnetic moments of surrounding dipoles. These electrons in the background introduce a local magnetic field ΔH , which in turn affects the energy levels and resonance frequency of the atom nucleus. As a result, by studying the shift of nuclei's resonance frequency, the state of electrons can be explored.

For a system of $3d$ electrons, Knight shift is composed of mainly two parts, the spin part K_s and the orbital part K_{orb} .

$$K = K_s + K_{orb} \quad (3.13)$$

The spin contribution K_s comes from Fermi contact interaction, which causes polarization of spins of conducting electrons. K_s is proportional to spin susceptibility of the material and the density of states (DOS) at Fermi level $N(E_F)$. The orbital contribution K_{orb} , on the other hand, comes from the orbital movement of electrons in magnetic field, and thus is generally independent to temperature. In FeSe, due to the complex orbital structure, K_{orb} usually takes up a large part of K . To determine the orbital part of K , a K - χ plot is often employed. The K - χ plot represents the relationship between K and the bulk magnetic susceptibility χ . By plotting K against χ with temperature as an implicit parameter, one can separate the spin and orbital contributions to the Knight shift, as shown in Fig. 3.2. The linear part of the plot indicates a proportionality between K and χ , from which the hyperfine coupling constant can be determined.

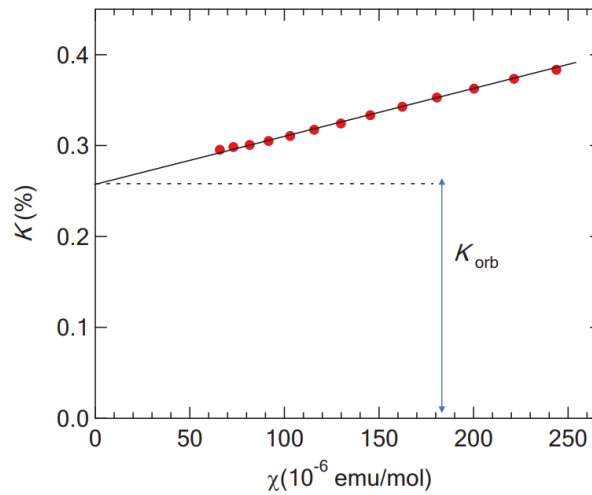


Fig. 3.2 ^{77}K - χ plot for 12% S-substituted FeSe. [20]

When conducting experiments, the external field H_0 can be precisely determined by using the Knight shift of Cu, which is a constant value with respect to temperature. The absorption spectrum can be obtained by Fourier transforming the SE, and the frequency shift can be measured from the peak frequency.

3.4 Nuclear Spin–Lattice Relaxation Rate

Systems with degrees of freedom other than nuclear spin, such as ions and electrons, are called lattice systems. When nuclear spins are excited by an oscillating magnetic field, they return to the original thermal equilibrium state after a finite time T_1 due to energy exchange with the lattice system. This T_1 is called the nuclear spin–lattice relaxation time.

The nuclear spin–lattice relaxation rate $1/T_1$ divided by temperature, $1/T_1T$, gives a measure of spin magnetic fluctuations. While K_s gives static information, $1/T_1T$ gives dynamic information of electronic systems as Eq. 3.14

$$\frac{1}{T_1T} \propto \sum_{\mathbf{q}} \frac{\text{Im}\chi(\mathbf{q}, \omega)}{\omega} \quad (3.14)$$

where ω and $\chi(\mathbf{q}, \omega)$ represent the NMR frequency and the dynamical spin susceptibility, respectively. For non-magnetic metals, the interaction among conducting electrons is very weak. Under this condition, $1/T_1T$ can be expressed as proportional to the square of $N(E_F)$, and as a result, we can derive the relation between T_1 and K_s as

$$\frac{1}{T_1TK_s} = \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_n}{\gamma_e} \right)^2 K(\alpha) \quad (3.15)$$

Eq. 3.15 is called the Korringa relation, where k_B and $\hbar$ are the Boltzman and Planck constants, respectively, $\gamma_{n(e)}$ is the gyromagnetic ratio of $^{77}\text{Se}(\text{electron})$, and $K(\alpha)$ is a function of the Stoner enhancement factor α . The Stoner factor is expressed as $\alpha = I\chi(0)$ where I represents the interaction coupling. $K(\alpha)$ provides a measure of electron correlation. In unconventional superconductors, it is said that magnetic fluctuations are involved in the emergence of superconductivity. Thus, the information obtained by T_1 is crucial to understand the behavior of an electron system. For free electrons, $\alpha = 0$ and $K(\alpha) = 1$. For ferromagnetic metals, $K(\alpha) < 1$, whereas for antiferromagnetic metals, $K(\alpha) > 1$.

When measuring the relaxation rate, saturation recovery method with a comb pulse is used. The SE intensity $M_z(t)$ is observed after t seconds from the state immediately after the nuclear magnetization is tilted in the xy plane ($M_z = 0$) by comb pulse, and T_1 is obtained from the relaxation curve.

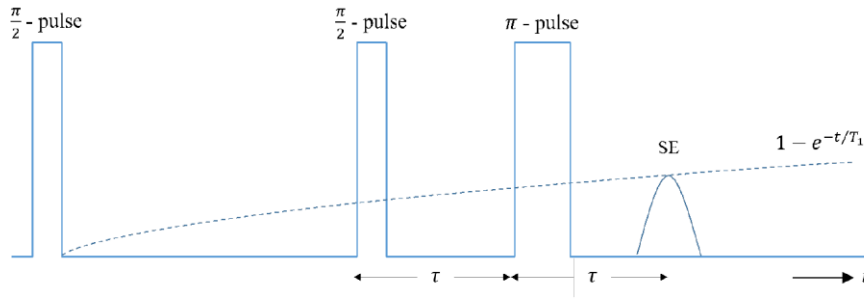


Fig. 3.3 Conceptual diagram of saturation recovery method.

Fig. 3.3 is a conceptual diagram of the saturation recovery method. In this study, NMR measurements were performed at the ^{77}Se nucleus side ($I = 1/2$, $\gamma/2\pi = 8.118 \text{ MHz/T}$). The relaxation curve at $I = 1/2$ is

$$R(t) = 1 - \frac{M_z(t)}{M_0} = e^{-\frac{t}{T_1}} \quad (3.16)$$

Eq. 3.16 was used to fit the experimental data. Fig 3.4 shows a set of actual data measured at 0.8K, ambient pressure, with the sample of $x = 0.18$.

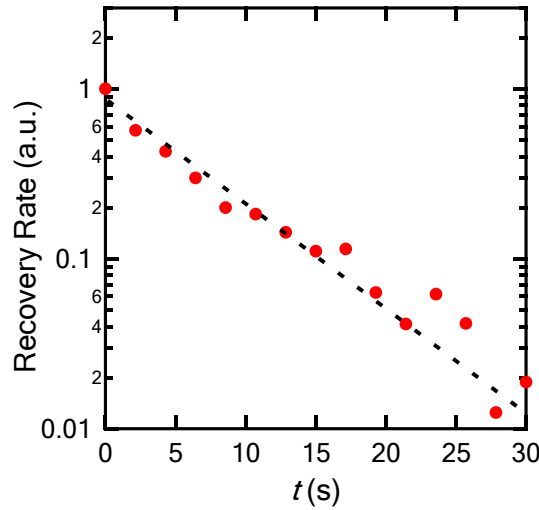


Fig. 3.4 Actual recovery rate calculate data.

3.5 FeSe_{1-x}S_x from the viewpoint of NMR

In superconductors, NMR plays a crucial role in revealing the microscopic nature of the superconducting state that cannot be accessed by other bulk measurements. The temperature dependence of the Knight shift K below the superconducting transition is a powerful tool to distinguish between spin-singlet and spin-triplet pairing. Meanwhile, the nuclear spin-lattice relaxation rate T_1 provides insight into the low-energy excitations. At low temperatures, it detects sensitively the presence of residual DOS. ^{77}Se -NMR measurements have been extensively used to probe the low-energy electronic states of FeSe_{1-x}S_x across S substitution and pressure levels [20,33–36].

The Knight shift, which reflects the uniform spin susceptibility, shows a gradual decrease upon cooling for all S substitution levels. In pure FeSe, a clear splitting of the Knight-shift line appears below the structural transition temperature T_s . With increasing S substitution, this splitting becomes progressively smaller and eventually vanishes around $x_c \approx 0.17$, where the tetragonal symmetry is restored. This behavior demonstrates that sulfur substitution effectively suppresses the nematic order.

The spin-lattice relaxation rate divided by temperature, $1/T_1T$, provides complementary information on dynamical magnetic susceptibility. For $x < x_c$, $1/T_1T$ also increases with decreasing T showing a Curie-Wiess-like behavior [33,36]. As S substitution level increases, the overall magnitude of $1/T_1T$ slightly decreases, reflecting a weakening of spin fluctuations. This gives strong evidence of the connection between AFM fluctuations and nematicity.

However, for x larger than QCP, enhancement of $1/T_1T$ when cooling towards T_c becomes more subtle, indicating that AFM fluctuations is strongly suppressed in the tetragonal phase.

Under applied pressure, NMR spectra reveal additional evolution of the low-energy magnetic dynamics. According to a recent NMR study, when applied pressure, the nematic phase is suppressed around 0.5 GPa and a Fermi-liquid region emerges before long-range AFM order appears at higher pressure [36]. For $x = 0.12$, pressure first suppresses the nematic order and then enhances AFM fluctuations, as evidenced by a pronounced increase in $1/T_1T$ toward lower temperatures [20]. The P - T phase diagram derived from NMR thus shows two superconducting domes: the first associated with the nematic phase, and the second correlated with strong AFM fluctuations under higher pressure. The Knight-shift data under pressure also show a gradual reduction of the spin susceptibility, consistent with Fermi-surface reconstruction observed in transport measurements. Overall, ^{77}Se -NMR experiments serve as a strong tool to explore the pressure effect on FeSe_{1-x}S_x.

Chapter 4

Experimental Conditions

In this chapter, I will introduce the basic concept of the experimental methods, as well as the details of how the experiments are conducted. The principles of the dilution refrigerator used for achieving low temperatures and the pressure cell setup for applying hydrostatic pressure are introduced.

4.1 Dilution Refrigerator (DR)

The low temperature part of this study is conducted with the help of dilution refrigerator (DR), which is located at Uwatoko lab, ISSP.

4.1.1 Principle

Dilution refrigerators are the only systems capable of providing continuous cooling below 300 mK, reaching temperatures below 10 mK without moving parts at low-temperature stages. The cooling procedure relies on the heat of mixing between the two helium isotopes, ^3He and ^4He . It also requires a starting temperature of about liquid helium (4.2 K) or lower to start the cycle.

The cooling cycle is possible due to special properties of $^3\text{He}/^4\text{He}$ mixtures at low temperatures. With saturated vapor pressure, ^4He becomes superfluid below 2.17 K, resulting in completely different properties of the two isotopes below this transition temperature. Diluting ^4He with ^3He results in a decreasing superfluid transition temperature, as shown in Fig. 4.1. At temperatures below 0.8 K, depending on concentration, the $^3\text{He}/^4\text{He}$ mixture separates into two

phases: a ^3He rich phase (concentrated phase) and a ^3He poor phase (dilute phase). Near absolute zero temperature, the concentrated phase becomes pure ^3He , and the dilute phase contains ^3He of about 6.4%. Since ^3He has higher enthalpy in the dilute phase, moving ^3He atoms from concentrated to the dilute phase across the phase boundary requires energy from the surroundings, namely the mixing chamber. As a result, cooling occurs.

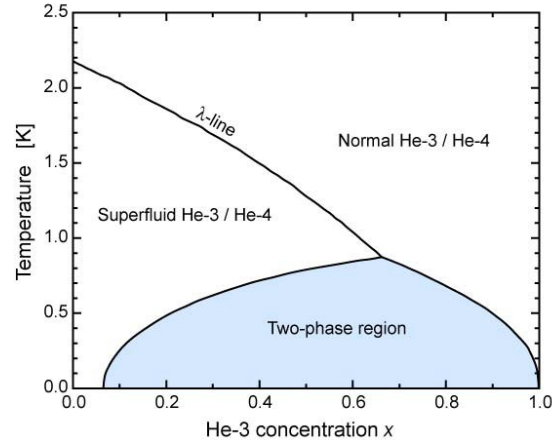


Fig. 4.1 Phase diagram of $^3\text{He}/^4\text{He}$. [37]

4.1.2 The Dilution System

The layout of the dilution system equipped at Uwatoko Laboratory in ISSP is displayed in Fig. 4.2 and 4.3. In this setup, a Pulse Tube (PT) cooler provides sufficiently low temperatures to initiate the DR cycle. The 50 K and quasi-4 K radiation shields are thermally connected to the first and second stages of the PT, respectively. The incoming ^3He gas is gradually pre-cooled below 4.2 K through a series of heat exchangers: first, a cold trap at 50 K flange removes any contamination of circulation from the circulating gas by freezing, while also serving as a heat exchanger. The gas is then further cooled and thermalized in the regenerator tube and at the PT's second stage.

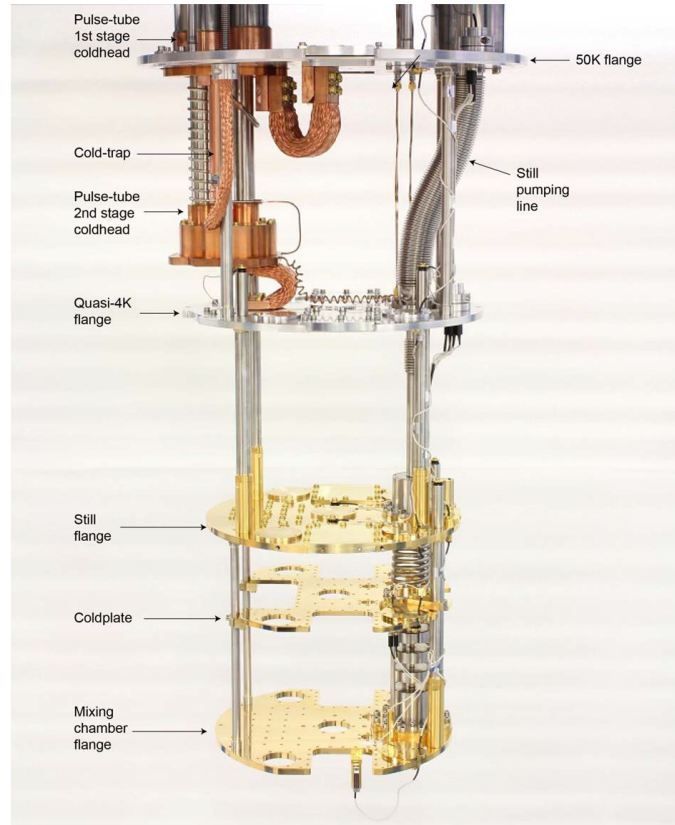


Fig. 4.2 Cryostat insert layout. [37]

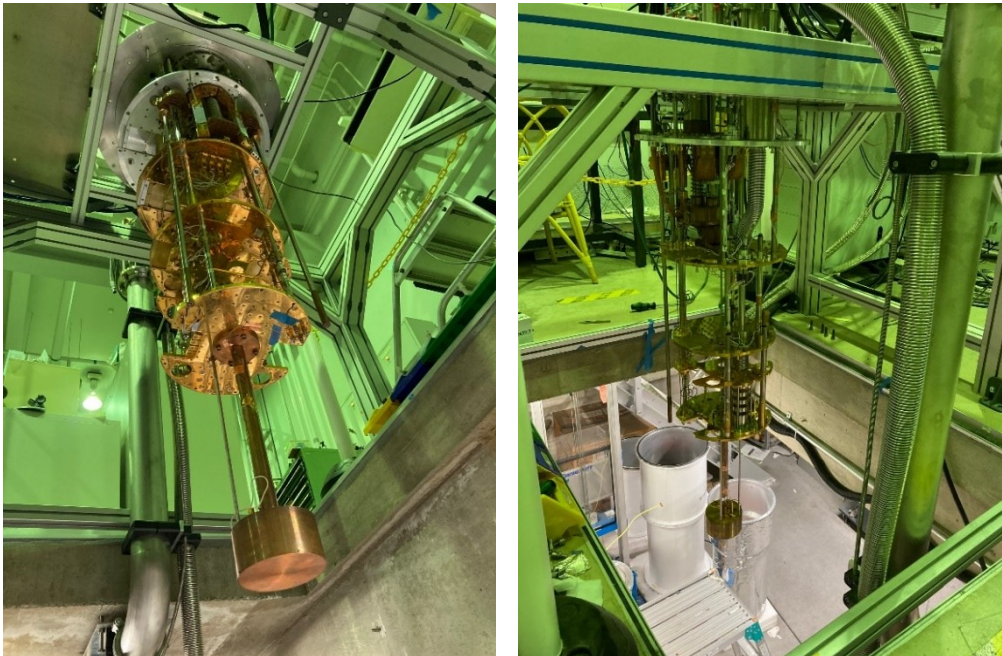


Fig. 4.3 The DR with a sample holder attached to the bottom (Uwatoko Laboratory).

Fig. 4.4 shows the principal parts of the DR, including the quasi-4 K flange, still, heat exchangers, mixing chamber, and heat switches. The heat switches (HS) enable pre-cooling of the refrigerator from room temperature to the initial operating temperature (~ 4.2 K). Switches are installed between the quasi-4 K flange and the still (HS-STILL), as well as between the still and the mixing chamber (HS-MC). After pre-cooling, these switches must be disconnected thermally from the PT to allow the DR to function properly. Each HS contains helium gas that allows heat to transfer between two copper heat-exchange plates. The upper part of each switch is connected to an active carbon pump. When the pump is cooled below 10 K, it adsorbs all the helium gas inside the switch, breaking the thermal link effectively. The switch then becomes thermally insulated. To reopen the connection, small heaters are used to warm up the carbon pump, releasing the absorbed gas.

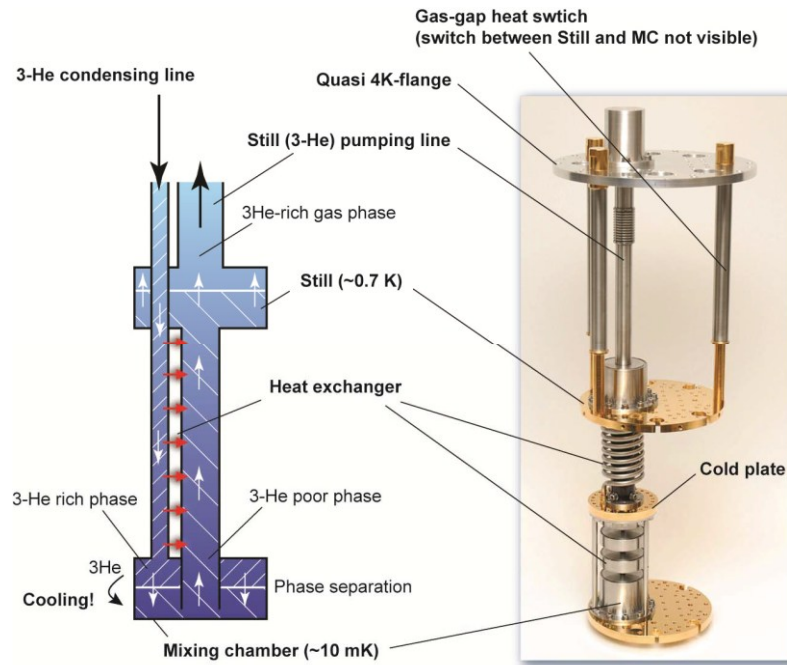


Fig. 4.4 Dilution refrigerator principal parts. [37]

Once the DR is pre-cooled below 4.2 K, the $^3\text{He}/^4\text{He}$ mixture needs to be condensed into the circuit. A compressor raises the pressure of the mixture to approximately 2 bar, and the incoming gas is successively cooled by heat exchangers in the condensation line. When the mixture passes through the main flow impedance, which is located inside the upper part of the still, it will be partially condensed. After all mixture is condensed, there will be enough liquid to fill the mixing chamber, heat exchangers and part of the still. The cooling process of DR begins when the still is pumped. The helium pumped away from the still is returned into the system through the condensing line. Pumping will result in the evaporative cooling and the temperature is lowered below 0.8 K. At this stage, phase separation occurs: the denser ^4He -rich (dilute) phase accumulates at the bottom of the mixing chamber due to gravity, while the ^3He -

rich (concentrated) phase remains above. Eventually the dilute and concentrated phase will settle.

At this stage, the helium pumped away from the dilute phase of the still is almost pure ^3He due to its much higher vapor pressure compared with ^4He . This ^3He gas is condensed and pre-cooled again via a counter-flow heat exchanger before returning to the mixing chamber. As it crosses the phase boundary between the concentrated and dilute phases, cooling happens because of the enthalpy difference. An osmotic pressure drives the diluted ^3He from the mixing chamber back toward the still, completing the circulation loop. As a result, the DR's cooling power mainly depends on the flow rate of ^3He atoms crossing the boundary. To obtain a high enough flow rate, heat is applied to the still to raise the temperature, thus raising its vapor pressure, enhancing the circulation rate and the cooling power. Overall, the DR system's performance strongly depends on the efficiency of the counter-flow heat exchangers and the pumping system.

4.2 Pressure

4.2.1 Piston-Cylinder Pressure Cell

To perform NMR measurements at high pressure, NiCrAl–CuBe hybrid piston-cylinder pressure cells are applied to pressurize the sample[38]. Fig. 4.5 shows the cross section of the pressure cell. The piston-cylinder type cell has a large sample space with a relatively small cell size. Moreover, by wrapping the NiCrAl cylinder with a CuBe support cylinder, high durability can be preserved, and good hydrostatic pressure can be maintained even under high pressure. While a conventional CuBe piston-cylinder cell can be stably used at a maximum of 2.4 GPa, the NiCrAl–CuBe hybrid method is capable of applying pressure up to 3.7 GPa when a clamp is used. As a result, it is possible to perform stable experiments at high pressures for microscopic measurements.

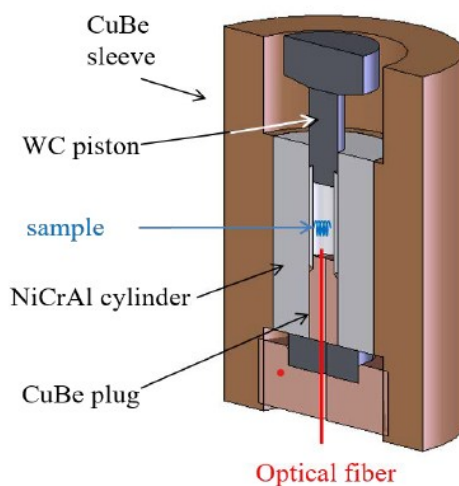


Fig. 4.5 Structure of a cylinder pressure cell.

4.2.2 Determination of the Pressure

The pressure was determined by the ruby fluorescence method [38]. An optical fiber with ruby powder attached to the tip was fixed to the plug, and light was introduced through the fiber. Ruby is an aluminum oxide (Al_2O_3) in which the Al sites are replaced by about 0.1% Cr. The red color is due to light absorption by the energy level of Cr^{3+} , and when excited by a laser or

other device, it emits strong fluorescence called the R line. It is known that the wavelength of this R line shifts to the longer wavelength side as the pressure increases and satisfies the following relationship in Eq. 4.1.

$$P \text{ (GPa)} = 2.74 \times \Delta\lambda \text{ (nm)} \quad (4.1)$$

The pressure inside the capsule is determined by this equation.

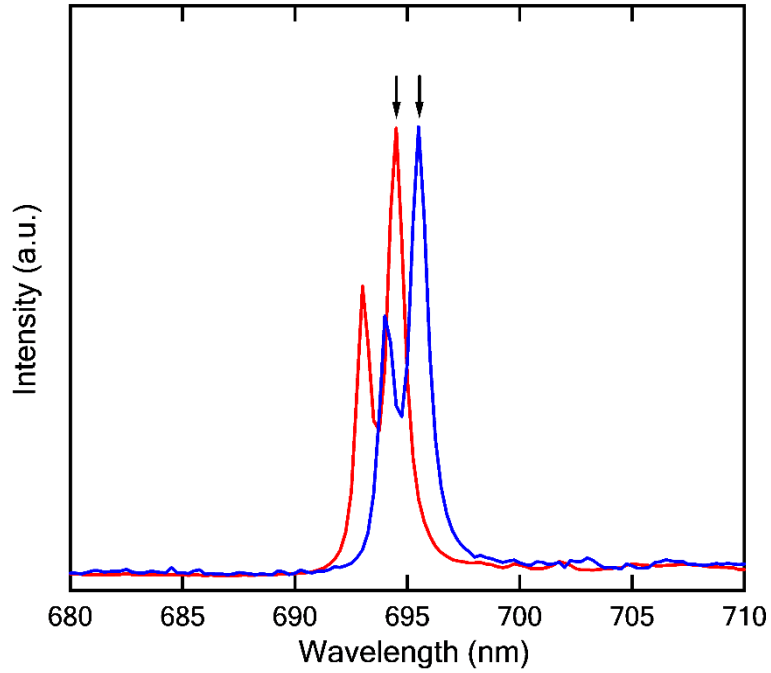


Fig. 4.6 Wavelength spectra of ambient pressure(red) and 3.0 GPa(blue).

Fig. 4.6 shows the spectra of R line wavelength at ambient pressure and high pressure, with peak positions at 694.47 nm and 695.50 nm, respectively. From Eq. 4.1, the pressure level of blue line is approximately 2.82 GPa.

4.3 Experimental Setup

4.3.1 Sample

Samples are provided by T. Shibauchi's group in Dept. of Adv. Mater. Sci., Univ. of Tokyo using the chemical vapor transport technique [7]. This technique makes it possible to grow high quality single crystals of $\text{FeSe}_{1-x}\text{S}_x$. The quality of these samples was confirmed by resistivity [6], ARPES, and quantum oscillation experiments [14]. Clear T_c has also been observed by resonant frequency change and drop of $1/T_1T$ value due to superconducting gap opening.

4.3.2 NMR Set-up

The basic illustration of NMR devices is shown in Fig. 4.7. First, a signal generator generates a sin wave as a seed signal, which is then processed into a rectangular pulse signal by a pulse generator. Next, the signal amplified through the main amp is input to the LC circuit at the bottom of the probe, generating an oscillating magnetic field inside the coil. By applying an oscillating magnetic field with a frequency corresponding to the Zeeman splitting to the sample, the nuclear spins are excited and undergo precession as described above. This precession generates an induced electromotive force in the coil corresponding to FID and SE, and FID and SE can be observed by extracting the envelope of the appropriate frequency band from the generated signal by Phase Sensitive Detection (PSD). The obtained analog signal is digitized by an A/D converter and input to a PC to obtain voltage vs. time series data.

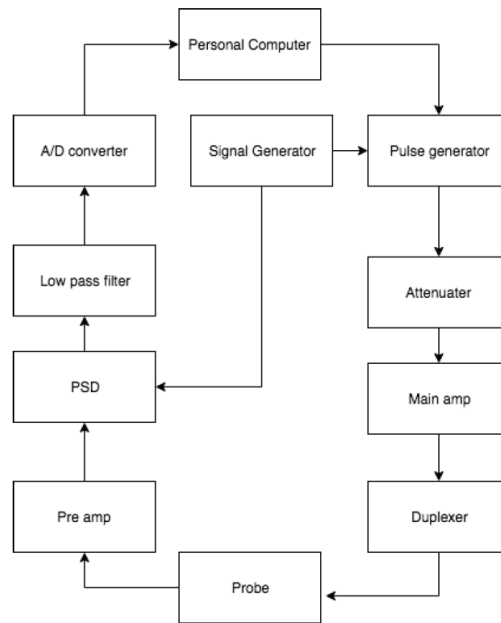


Fig. 4.7 Basic illustration of NMR devices.

Fig. 4.8 shows that a tank circuit is attached to the end of the probe under the mixing chamber flange of DR (see in Fig. 4.3).

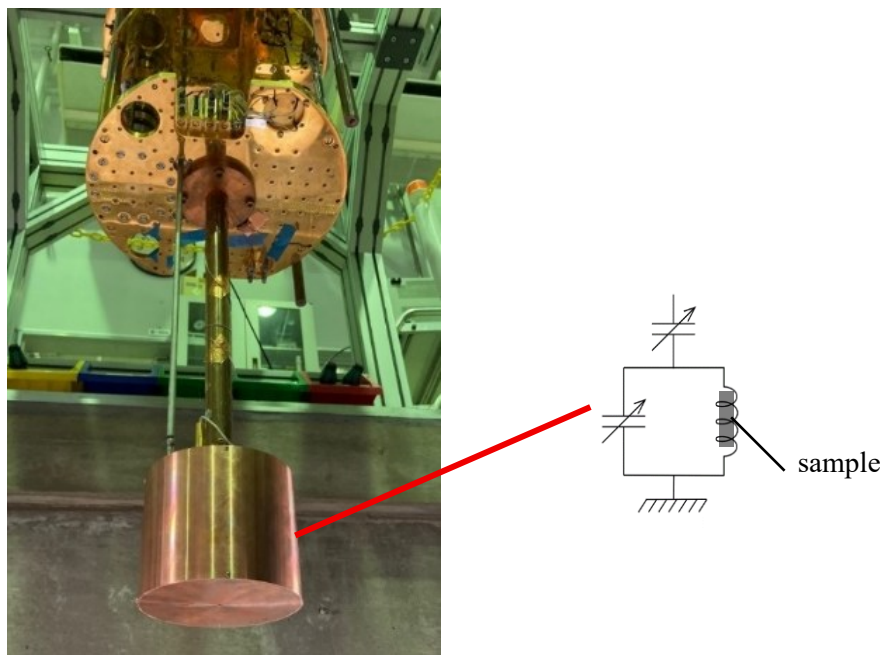


Fig. 4.8 Image of the tank circuit.

4.3.3 Determining T_c Using Network Analyzer

T_c was determined by measuring the temperature change of the resonant frequency of the LC parallel resonant circuit (tank circuit) for NMR using a network analyzer. The principle is as follows: assume the inductance of the NMR coil is L , and the capacitance of the variable capacitor in the circuit is C , the resonant frequency f of the LC circuit is

$$f = \frac{1}{2\pi\sqrt{LC}} \quad (4.2)$$

The inductance L with sample in the coil is obtained by using the magnetic susceptibility of the sample and the original inductance L_0 ,

$$L = L_0(1 + 4\pi\chi) \quad (4.3)$$

When the sample becomes superconductive, $\chi \sim -1/4$ due to the Meissner effect, and the resonance frequency f increases divergently below T_c . By measuring this change, T_c can be determined.

Chapter 5

Results

In this chapter, the experimental results obtained from the present NMR study are presented. The measurements were performed over several S-substitution levels and pressures in order to investigate both low temperature and pressure effects on the properties of $\text{FeSe}_{1-x}\text{S}_x$. We performed AC susceptibility, the Knight shift, and T_1 measurements. These results provide crucial insights into the superconducting and normal-state characteristics of $\text{FeSe}_{1-x}\text{S}_x$, which will be discussed in detail in the following chapter.

5.1 Superconducting Temperature T_c

First, T_c of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10, 0.18$) was determined using a network analyzer.

Figure 5.1 shows the temperature dependence of the resonance frequency of the tank circuit for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.18$) at the magnetic field of 0 T and for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10, 0.18$) at 6.02 T, respectively.

Figure 5.2 shows the temperature dependence of the resonance frequency of the tank circuit $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) at ambient pressure, 1.0 GPa, and 2.0 GPa at the magnetic field of 0 T and 6.02 T, where NMR measurements were performed.

The magnetic field was applied parallel to the FeSe plane ($\mathbf{B} // \text{ab}$) similarly to the T_1 measurements.

The frequency increases gradually with decreasing temperature due to a gradual decrease in L during the cooling process, and changes drastically at T_c owing to the Meissner effect. T_c is determined as the intersection point of two T -linear lines shown as dashed lines.

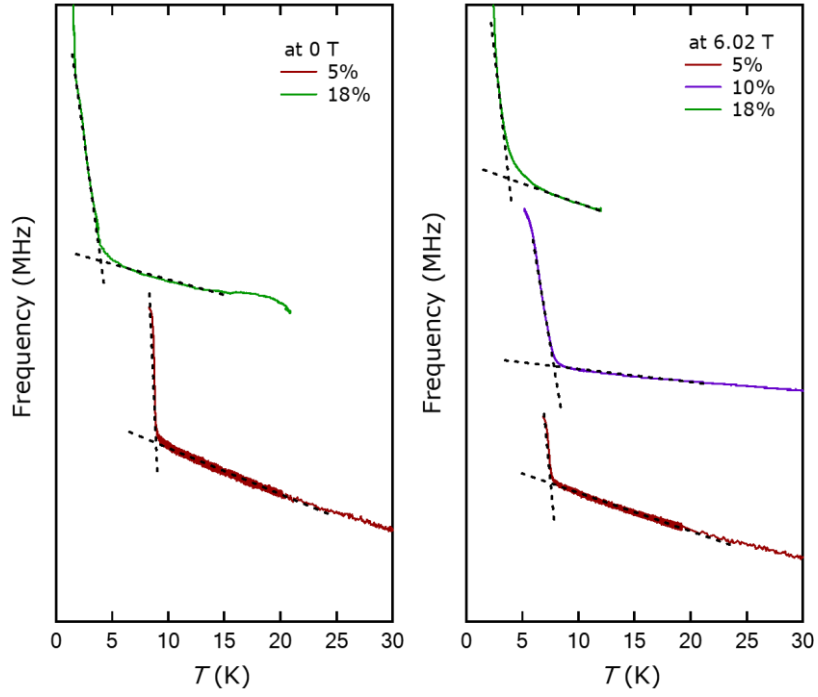


Fig. 5.1 AC susceptibility measurements for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10, 0.18$) using the tank circuit attached on the top of an NMR probe. T_c is determined from the crosspoints of dashes lines. Left and right panels represent the measurements at zero field and 6.02 T, respectively.

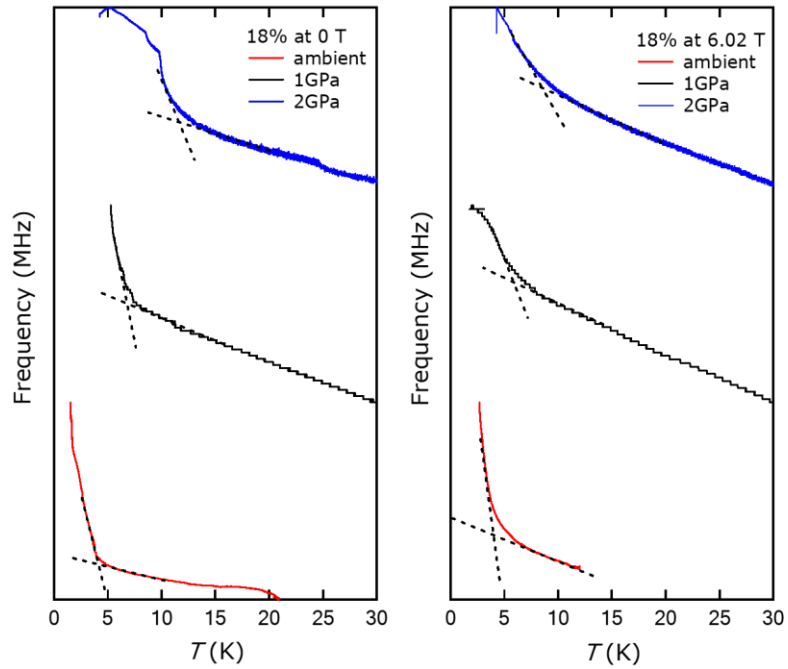


Fig. 5.2 AC susceptibility measurements for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) using the tank circuit attached on the top of an NMR probe. Left and right panels represent the measurements at zero field and 6.02 T, respectively.

Table 5.1 shows T_c at zero field and 6.02 T of $x = 0.05, 0.10, 0.18$ samples at ambient pressure.

x	T_c (K) at 0 T	T_c (K) at 6.02 T
0.05	8.8	7.6
0.10	8.7	7.8
0.18	4.0	2.8

Table 5.1 T_c of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10$, and 0.18) at zero magnetic field and 6.02 T.

Table 5.2 shows T_c at zero field and 6.02 T of each pressure level. While T_c is enhanced significantly by applying pressure, it is slightly suppressed by applying magnetic field.

P (GPa)	T_c (K) at 0 T	T_c (K) at 6.02 T
ambient	4.0	2.8
1.0	6.7	6.1
2.0	12.4	9.5

Table 5.2 T_c of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) at different pressure levels at zero magnetic field and 6.02 T.

For measurements at ambient pressure, $x = 0.05$ and 0.10 shows similar value both with or without magnetic field, while $x = 0.18$ has a rather low T_c . This is consistent with other experimental techniques, such as resistivity and specific heat, showing that T_c of samples in the tetragonal phase is suppressed compared to that of the nematic phase. On the other hand, pressure application gives rise to T_c significantly, reaching 12.4 K at 2.0 GPa for $x = 0.18$ sample with zero magnetic field.

5.2 NMR Spectra

The ^{77}Se -NMR spectra are shown in Fig. 4.3 and 4.4. The spectra are obtained by fast Fourier transform (FFT) of the spin-echo signal for each doping level. The spectra are shown as percentage of shifts for better visualization.

Figure 5.3 shows ^{77}Se -NMR spectra at various temperatures for $x = 0.05, 0.12$ [20], and 0.18 at ambient pressure [39]. The FFT results for $x = 0.05$ split into two peaks corresponding to the nematic order appears below T_s , while the broadening of the linewidth is observed at low temperatures for $x = 0.12$, which can be treated as two peaks overlapping. Meanwhile, no such

double-peak behavior is present for $x = 0.18$ sample, proving that nematicity disappears above x_c .

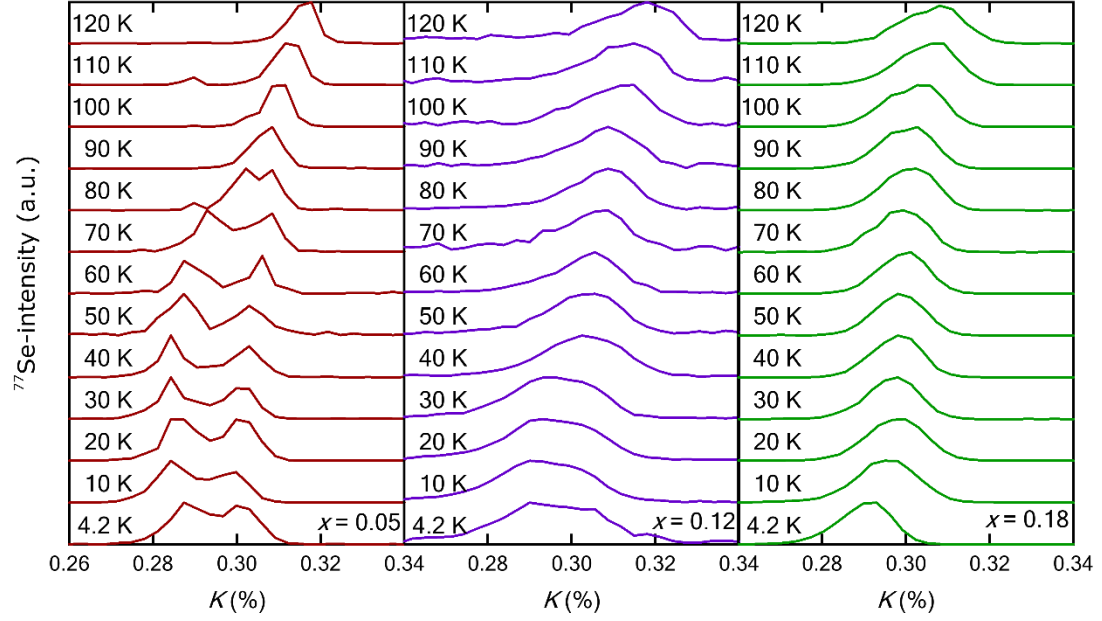


Fig. 5.3 NMR spectra for ^{77}Se at various temperature for $x = 0.05, 0.12$ [20], and 0.18.

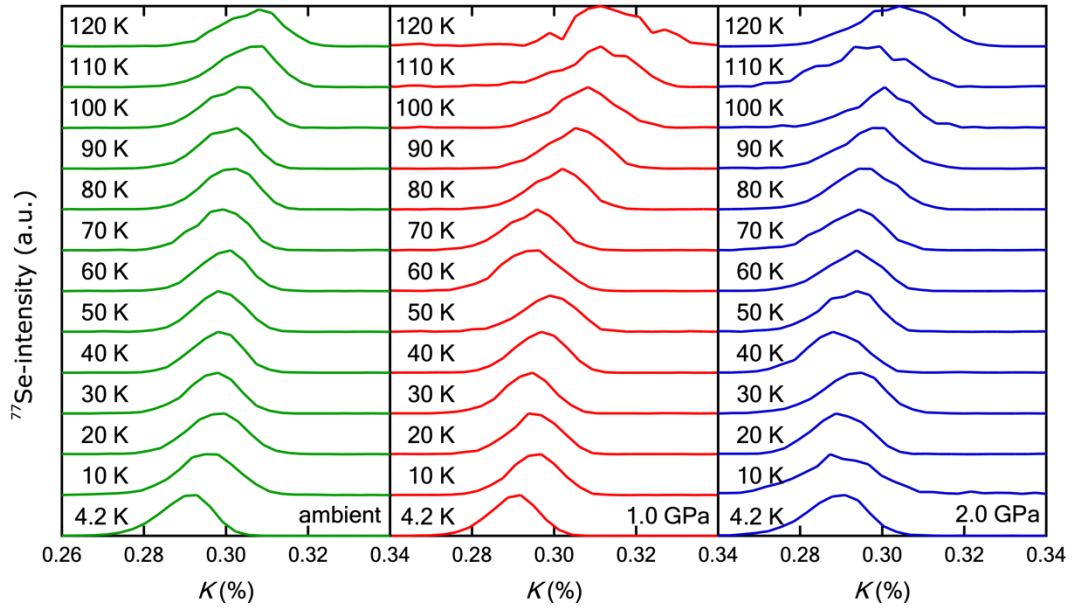


Fig. 5.4 NMR spectra for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) at ambient pressure, 1.0 GPa, and 2.0 GPa, resulting from the FFT of the spin-echo signal.

The ^{77}Se -NMR spectra for $x = 0.18$ at ambient pressure, 1.0 GPa and 2.0 GPa are shown in Fig. 5.4 [40]. Clear shifts of the peak position are also observed for all P with increasing the temperature. For all three pressure levels, double-peak structure corresponding to the nematic order was not observed throughout the measured temperature range, which is consistent with the results obtained by other techniques. The double-peak structure has been detected at the substitution level below x_c at ambient pressure.

5.3 Knight-shift

The Knight-shift (K) was obtained from the peak frequencies of the NMR spectra fitted with Gaussian functions.

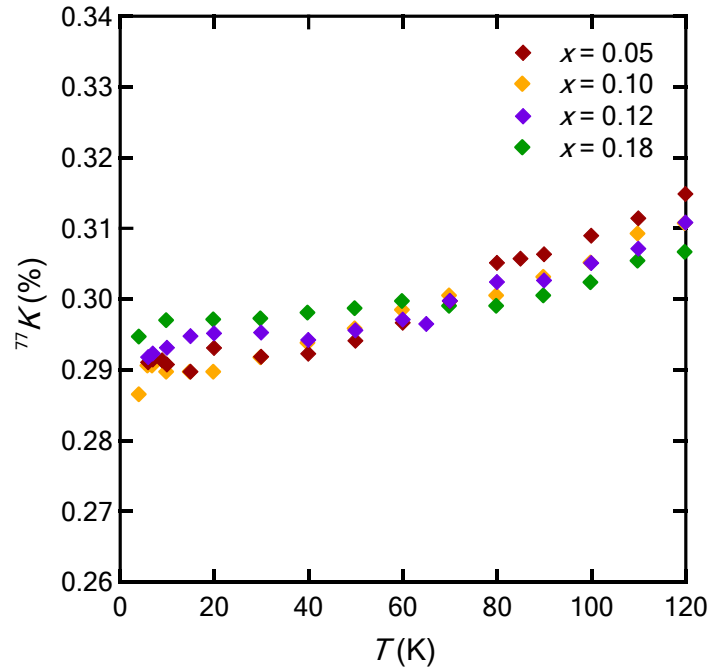


Fig. 5.5 Knight-shift of $x = 0.05, 0.10, 0.12$ [20] and 0.18 at ambient pressure.

Figure 5.5 shows the Knight-shift of $x = 0.05, 0.10, 0.12$ [20] and 0.18 at ambient pressure [39]. For all four substitution levels, Knight-shift decreases with decreasing temperature. As S-substitution level increases, the temperature dependence of the Knight shift becomes weaker.

Figure 5.6 shows Knight-shift for $x = 0.05$ and 0.12 [20] with the analyzed double peak position. The nematic transition for both substitution levels are clearly seen from the splitting of K below nematic transition temperature T_s . The splitting happens at below ~ 80 K for $x = 0.05$ while for $x = 0.12$, the splitting (or broadening) starts from ~ 60 K. This is consistent with the suppression of nematic order by S substitution.

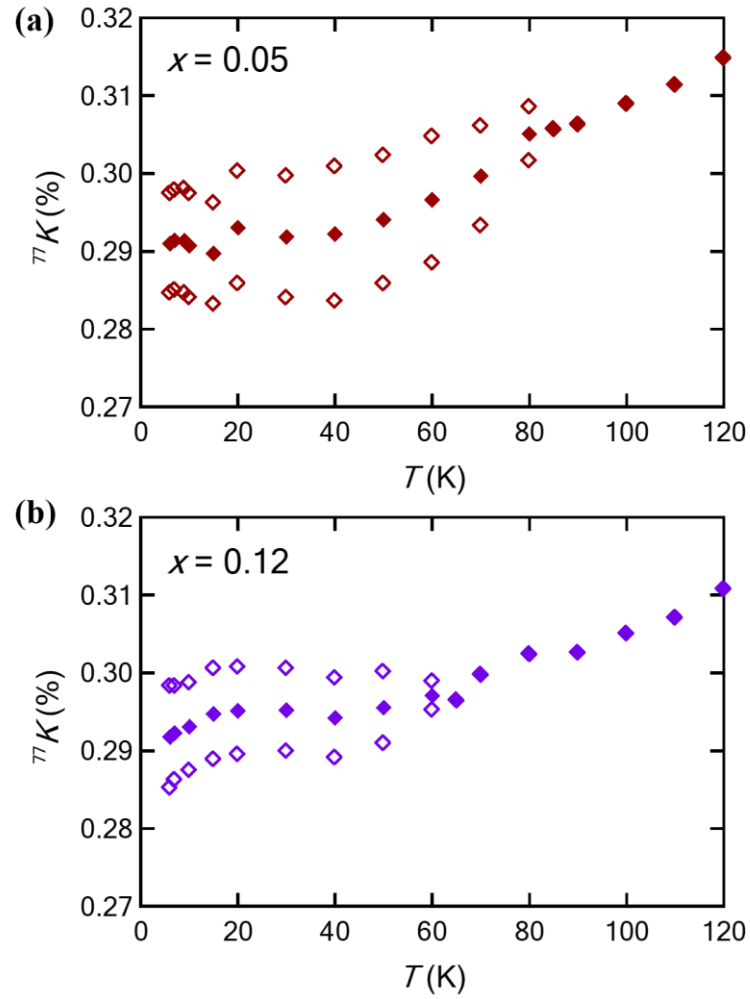


Fig. 5.6 Knight-shift of (a) $x = 0.05$ and (b) $x = 0.12$ [20], at ambient pressure. Hollow points represent the shift corresponding to the double peak, and solid points are their average.

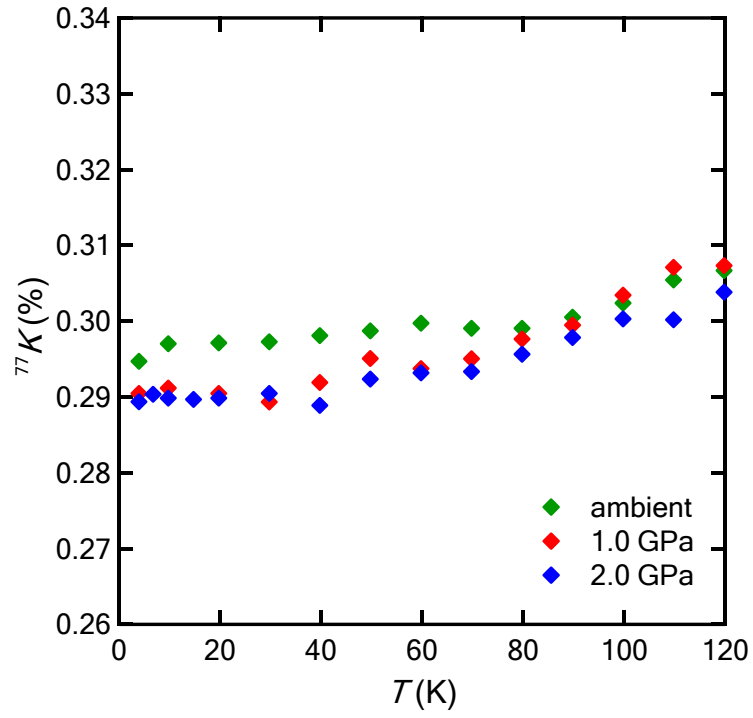


Fig. 5.7 Knight shift obtained from NMR spectra in Fig. 5.4.

Figure 5.7 shows the Knight-shift of $x = 0.18$ at different pressure levels [40]. In all three pressure levels, K decreases gently with decreasing temperature and becomes a constant at lower temperature regions. Additionally, K also decreases slightly with increasing pressure.

5.4 Relaxation Rate $1/T_1$

Figure 5.8 shows the temperature (T) dependence of relaxation rate ($1/T_1$) divided by T , $1/T_1T$, obtained from ^{77}Se -NMR experiments at ambient pressure using single crystals of $\text{FeSe}_{1-x}\text{S}_x$ [39]. The magnetic field was applied parallel to the FeSe plane. $1/T_1T$ provides a measure of low-energy spin fluctuations. Strong enhancement of spin fluctuations is observed for $x < x_c$, but barely observable for $x > x_c$. Figure 5.9 shows a color plot of Fig. 5.8. Straightforwardly, spin fluctuations develop inside the nematic phase and are strongly suppressed in the tetragonal phase.

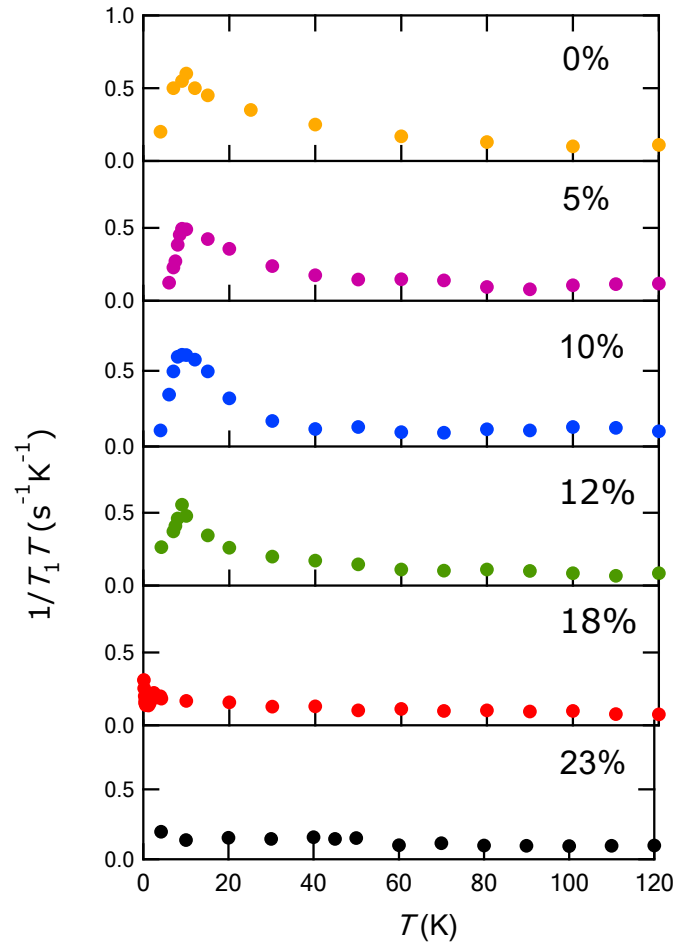


Fig. 5.8 Temperature (T) dependence of $1/T_1T$, relaxation rate ($1/T_1$) divided by T , of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0, 0.05, 0.10, 0.12$ [20], 0.18, 0.23).

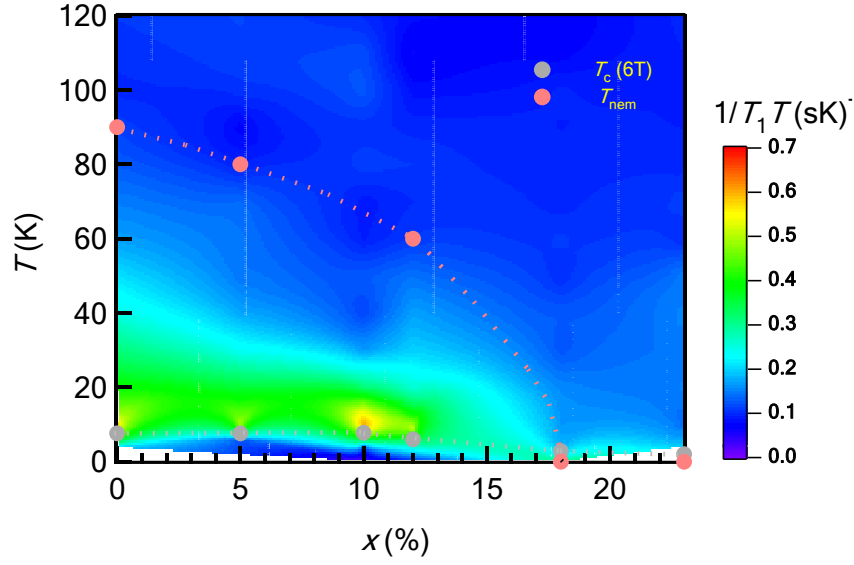


Fig. 5.9 Color plot of $1/T_1T$ shown in Fig. 5.8.

Figure 5.10 shows comparison of $1/T_1T$ of $x = 0.05$, 0.12 [20] and 0.18 [40]. The upturn of $1/T_1T$ towards T_c from higher temperatures was observed for both $x = 0.05$ and 0.12 , while the upturn vanished above 1 GPa and became almost constant for $x = 0.12$. This is consistent with the fact that nematic order vanishes above 1 GPa for $x = 0.12$.

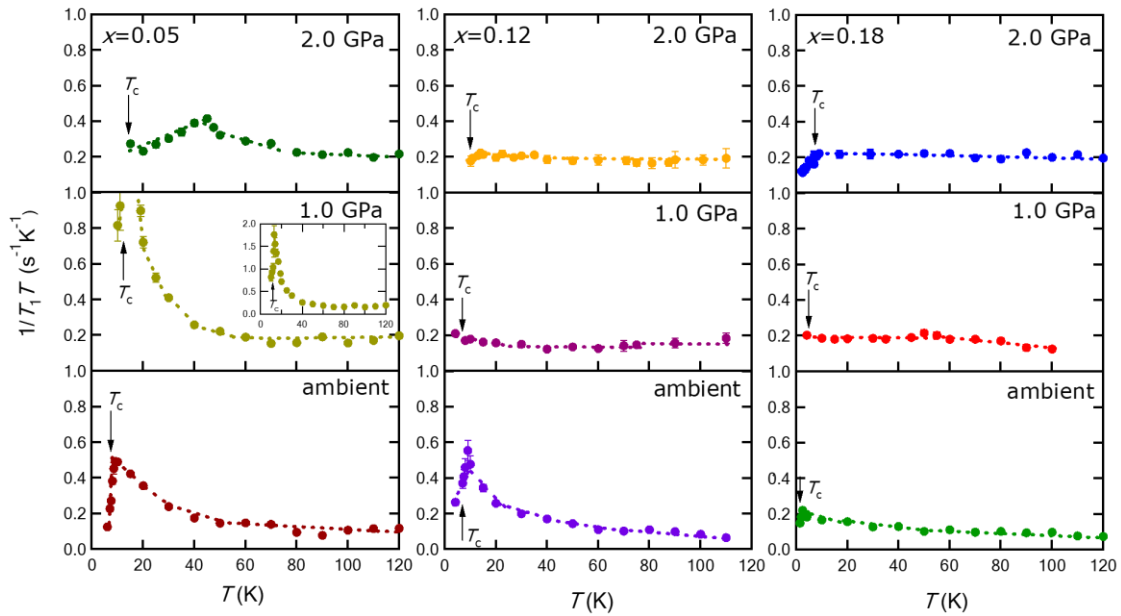


Fig. 5.10 An overview of $1/T_1T$ for three different substitution levels, $x = 0.05$, 0.12 [20], 0.18 , crossing the nematic QCP. The data of the inset is the same with those of the main panel but displayed in different scale.

Figure 5.11 shows the low temperature $1/T_1T$ results of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10, 0.18$) down to 100 mK [39]. For substitution levels below x_c , $x = 0.05$ and 0.10 , $1/T_1T$ decreases just below T_c and becomes constant toward low temperature. Even though the two substitution levels are both in the nematic phase and have similar T_c , the constant value at low temperature differs of one order. This will be discussed in Chapter 6. On the other hand, for $x = 0.18$, above x_c in the tetragonal phase, a slight decrease is observed just below T_c , but $1/T_1T$ upturns further with decreasing temperature. The T dependence of $1/T_1T$ below T_c is anomalous if originated from an intrinsic origin, since $1/T_1T$ should go to zero towards zero temperature due to the opening of the SC gap. The unusual behavior will also be discussed in Chapter 6.

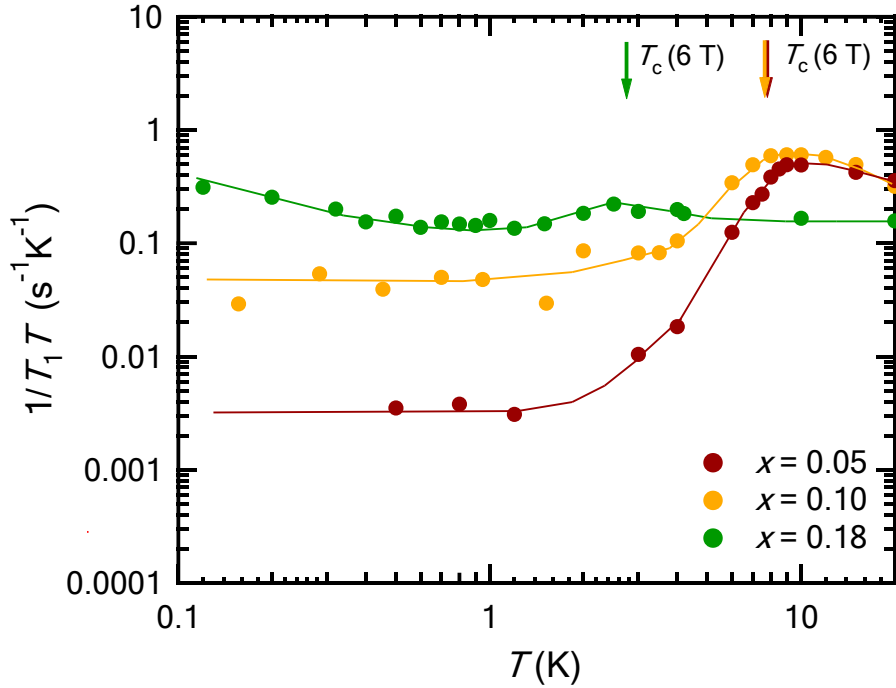


Fig. 5.11 $1/T_1T$ of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.05, 0.10, 0.18$) obtained at low temperature deep in the super conducting state.

Figure 5.12 shows $1/T_1T$ at several pressure levels on a single crystal of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$) measured at low temperatures deep in the SC state [40]. Drop of $1/T_1T$ due to gap opening just below T_c is observed under pressure. The increase of $1/T_1T$ towards low temperature still remains up to 2.0 GPa, despite that it becomes weaker under pressure.

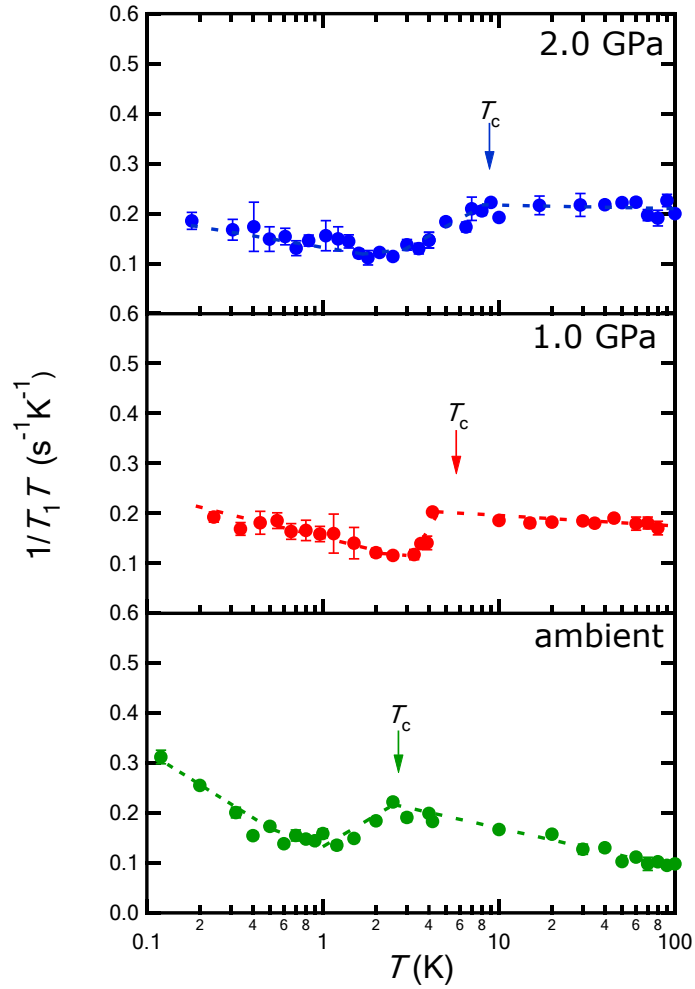


Fig. 5.12 Temperature T dependence of $1/T_1T$, obtained from ^{77}Se -NMR experiments at several pressure levels on a single crystal of $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.18$).

Chapter 6

Discussion

One of the main results of this study is summarized in Fig. 5.11. In this chapter, I will discuss the possible origins of this phenomenon, and the pressure effect of this behavior.

6.1 Unusual behavior of $\text{FeSe}_{1-x}\text{S}_x$ at ambient pressure

For both $x < x_c$ and $x > x_c$, unusual behavior of low temperature $1/T_1T$ was observed. For samples in the nematic phase ($x = 0.05, 0.10$), $1/T_1T$ shows a constant behavior at low temperature, while the sample in the tetragonal phase ($x = 0.18$) exhibits an increase when temperature is approaching zero. These two phenomena will be discussed separately in the following.

6.1.1 Possible Causes of $1/T_1T = \text{constant}$

First, I will discuss the behavior of $1/T_1T = \text{const.}$ at the substitution level of $x = 0.05$ and 0.10 . There are several possible origins:

- (1) impurity effect
- (2) Volovik effect
- (3) coexistence of normal and superconducting states

(1) Impurity effect

The impurity effect on $1/T_1T$ has been studied theoretically in the early stage of $s_{\pm}$ -wave scenario[41]. The evolution of the DOS and $1/T_1T$ for several impurity doping levels, Γ/Δ , are shown in Fig. 6.1. Γ/Δ gives a measure of the doping level, and $\Gamma=0$ means zero doping. For a small impurity doping, the quasiparticle DOS is V-shaped as a function of energy, and the T dependence of $1/T_1T$ shows a T^2 dependence at temperatures below T_c . For a fairly large impurity doping, the quasiparticle DOS has a finite value at zero energy, and $1/T_1T$ exhibits a T -independent behavior followed by a T^2 dependence with decreasing temperature. The residual DOS appears for the heavily doped regime ($\Gamma/\Delta = 0.08$).

The present experimental value of $1/T_1T$ at low T differs almost one order of magnitude between $x = 0.05$ and 0.10 . According to the theory, the impurity doping level should be very much different between these two S-substitution levels, and thus T_c should be remarkably different. However, T_c is almost the same between $x = 0.05$ and 0.10 . Furthermore, the upturn of $1/T_1T$ for $x = 0.18$ cannot be explained by the impurity effect. Therefore, this effect is excluded.

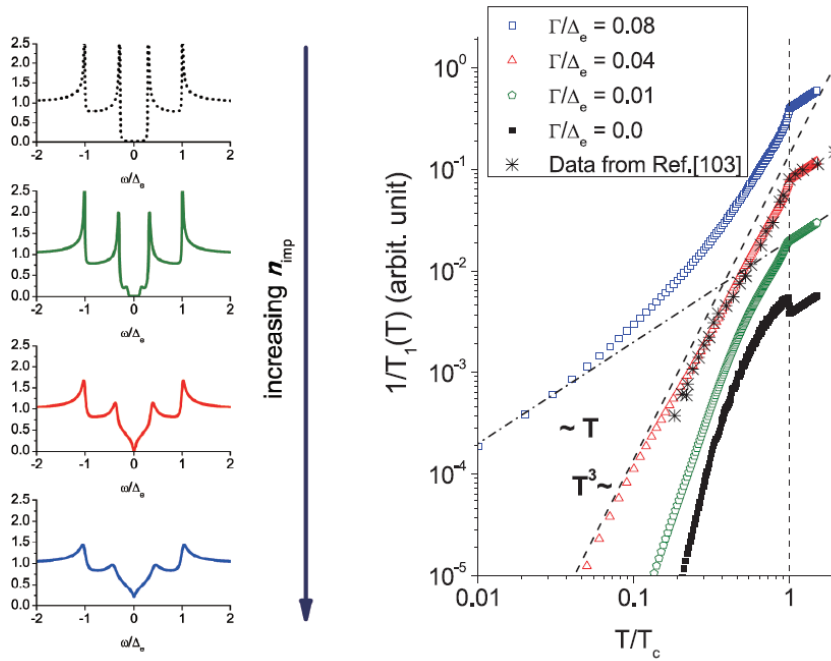


Fig. 6.1 Calculated $1/T_1T$ for different impurity concentrations. [41]

(2) Volovik effect

The Volovik effect can also induce an in-gap state similarly to the impurity effect[42]. The DOS can be induced by applying magnetic field owing to the Doppler shift of quasiparticle energy. Fig. 6.2 shows how an in-gap state develops depending on the location from a vortex

core. The field dependence of $1/T_1T$ has been theoretically investigated for $s_{\pm}$ - and d -wave cases. This effect should result in almost the same $1/T_1T$ values between $x = 0.05$ and 0.10 , as in Fig. 6.3, because the strength of the applied field is the same, so the SC gap or T_c is almost the same between them. Therefore, this effect is excluded as well as the impurity effect.

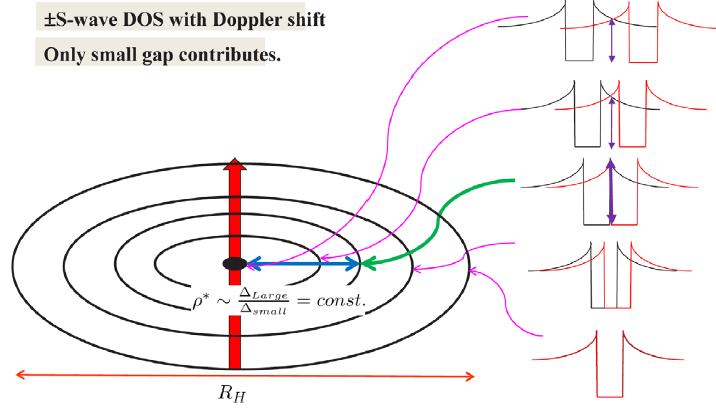


Fig. 6.2 Illustration of the local DOS of the small gap band of the $s_{\pm}$ -wave superconductor. Within the finite range, the small-gap develops zero energy excitations. [41]

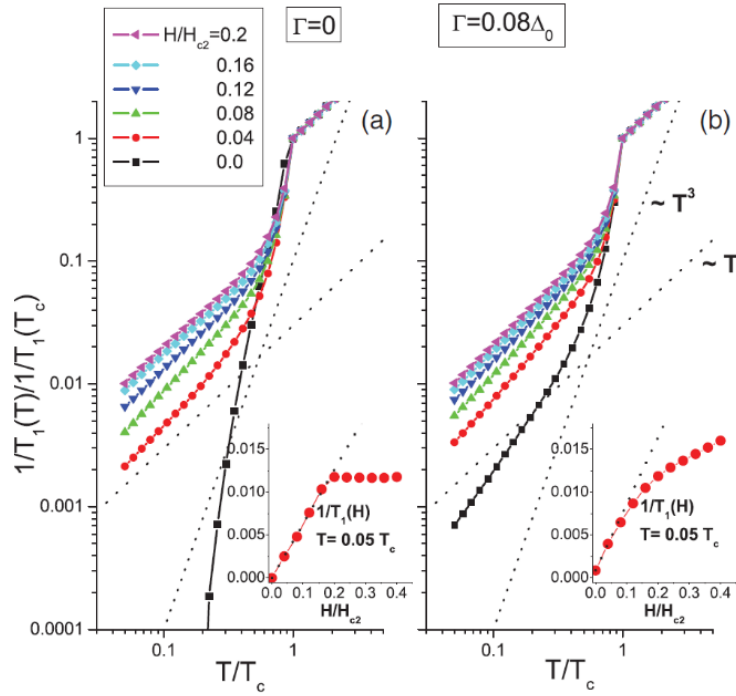


Fig. 6.3 Normalized spin-lattice relaxation rates $[1/T_1(T)]/[1/T_1(T_c)]$ of the $s_{\pm}$ -wave SC state for various magnetic fields. (a) The results without impurities ($\Gamma = 0$). (b) The results with the impurity concentration ($\Gamma = 0.08\Delta_L$) of the unitary scatterer. [42]

(3) Coexistence between normal and superconducting states

Another possibility is the coexistence of SC and normal states. The coexistence in real space would imply that SC and normal metallic domains coexist. However, such a case can be excluded by the rather homogeneous spectra observed in the STS measurements. Instead of the coexistence in real space, the coexistence in momentum space would be promising. The behavior of the normal state below T_c can be explained for the Fermi surfaces with nodal points or BFSs proposed theoretically as previously mentioned. In the view of the STS and specific heat results, the nodal points and BFSs discussed in Sect. 1.2 would play important roles for $x < x_c$ and $x > x_c$, respectively.

The existence of the nodal points was demonstrated from the ARPES measurements on pure FeSe as discussed in Sect. 1.1.3. The points nodes were observed for pure FeSe. From the specific heat measurements, the DOS seems to expand gradually crossing x_c . This behavior is consistent with our results: the residual DOS expected from $1/T_1T$ is approximately three times different between $x = 0.05$ and 0.10 if we assume the Korringa relation ($[1/T_1T]K_s^2 = \text{const.}$ where K_s is the spin part of the Knight shift) in the superconducting state. In this assumption, $1/T_1T = \text{const.}$ originates from the scattering between a nucleus and Bogoliubov quasiparticles, namely $1/T_1T \propto N(\epsilon)^2$ where $N(\epsilon)$ represents the density of states of Bogoliubov quasiparticles.

6.1.2 Enhancement of Spin Fluctuations at Low T

The estimation of the quasiparticle DOS for $x = 0.05$ and 0.10 is not applicable for $x = 0.18$, because the Korringa relationship breaks. Interestingly, the T dependence of $1/T_1T$ below T_c is similar to that above T_c , as shown in Fig. 6.4, implying that $\chi(\mathbf{q})$ does not significantly change across T_c . Therefore, the upturn of $1/T_1T$ might be attributed to the enhancement of $\chi(\mathbf{q})$ due to the nesting between BFSs on electron and hole pockets, similarly to the nesting in the normal state. However, this scenario seems disadvantageous to explain $1/T_1T$ under pressure because the T dependence is different between below and above T_c . Furthermore, the wide nodal region has not been experimentally observed on the electron pockets.

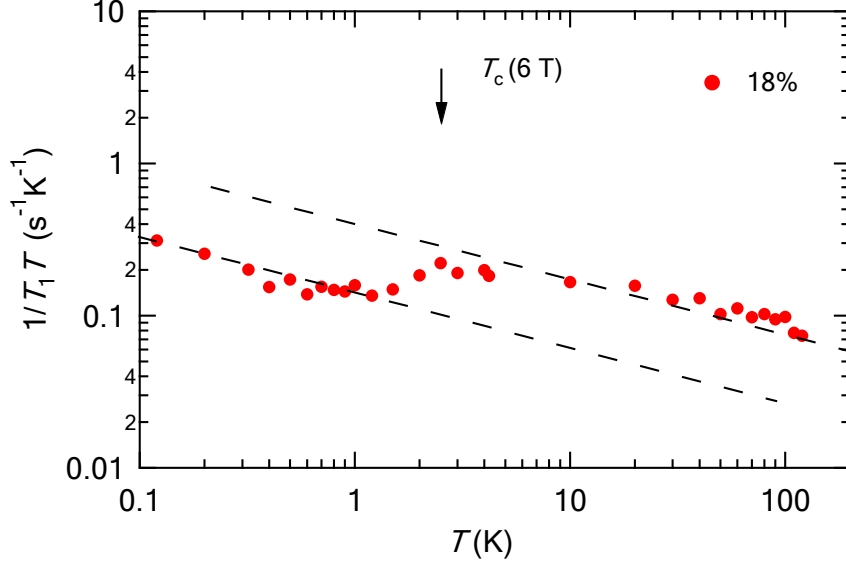


Fig. 6.4 Illustration of $1/T_1 T$ of both above and below T_c , which shows the same tendency.

Here an interesting theory of topologically protected nodal Fermi surface, Bogoliubov Fermi surfaces (BFSs) has been brought to attention. As mentioned in Sect. 1.2, BFSs represents an ultranodal SC state, where the spontaneous point nodes on superconducting gap are extended and form continuous Fermi surfaces. BFSs are acquirable under the condition of a multiband system, spin-orbital coupling and time-reversal symmetry breaking (TRSB).

Contrary to the scenario above, the recent theoretical investigation by Yifu Cao, *et al* pointed out that the upturn below T_c is explainable by assuming two hole pockets and BFSs with C_2 symmetry at Γ point[43]. The Hamiltonian of this model with intraband spin-singlet pairing and interband spin-triplet coupling is shown as below:

$$H = \sum_{\mathbf{k}, \sigma, i} \epsilon_{i\mathbf{k}\sigma} c_{i\mathbf{k}\sigma}^\dagger c_{i\mathbf{k}\sigma} - \sum_{\mathbf{k}, i} \Delta_i(\mathbf{k}) (c_{i\mathbf{k}\uparrow}^\dagger c_{i-\mathbf{k}\downarrow}^\dagger + c_{i-\mathbf{k}\downarrow} c_{i\mathbf{k}\uparrow}) - \sum_{\mathbf{k}, \sigma} \Delta_{\sigma\sigma}(\mathbf{k}) (c_{1\mathbf{k}\sigma}^\dagger c_{2-\mathbf{k}\sigma}^\dagger + c_{2-\mathbf{k}\sigma} c_{1\mathbf{k}\sigma}) \quad (6.1)$$

where $i = 1, 2$ indexes the band. The first term is the kinetic energy of two bands in a tight binding model. The second term represents intraband spin-singlet pairing and the third term represents the interband spin-triplet coupling. In this Hamiltonian, the interband triplet pairing is assumed to be nonunitary, i.e. $\Delta_{\uparrow\uparrow}(\mathbf{k})$ is nonzero while $\Delta_{\downarrow\downarrow}(\mathbf{k}) = 0$. This is because previous studies have shown that unitary pairing is insufficient to produce a Bogoliubov Fermi surface, while nonunitary interband pairing naturally expands the zero-energy excitation spectrum from a point node or line nodes to a two-dimensional contour, thus explaining the large residual of zero-energy excitations observed in experiments.

Figures 6.5(a) and (b) show the DOS and BFSs in the SC state, respectively. The wave number $\mathbf{q} = (0.4\pi, 0)$ corresponding to a span between two BFSs segments contributes to an enhancement of $\chi(\mathbf{q})$ under the strong Hubbard-type interaction U . The BFSs segments colored in green have the character of significant interband spin-triplet particle-hole mixing and moderate intraband spin-singlet particle-hole mixing. $1/T_1T$ was calculated under the random phase approximation (RPA) for two cases where $\mathbf{B}$ is applied parallel ($//$) and perpendicular ($\perp$) to the quantization axis (z -axis) of the spin-triplet as shown in Fig. 6.5(c) and (d), respectively. In Fig. 6.5(c) and (d), the red points represent our experimental data of $x = 0.18$ shown in Fig. 4. 11. In both cases, the upturn of $1/T_1T$ is reproduced. However, the case for $\mathbf{B} \perp z$ causes a significant upturn at low temperatures and seems to reproduce the experimental results better than that for $\mathbf{B} // z$.

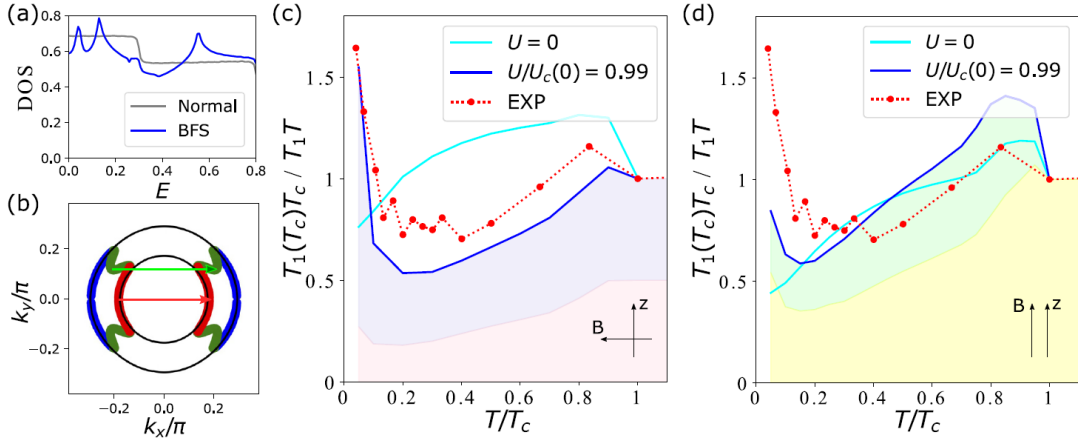


Fig. 6.5 (a) Theoretical calculation of zero temperature density of states for the Hamiltonian in Eq. 6.1. (b) Normal state (black) and Bogoliubov (colored) Fermi surfaces. (c) $1/T_1T$ calculation below T_c where the applied magnetic field is perpendicular to z direction. (d) $1/T_1T$ calculation below T_c where the applied magnetic field is parallel to z direction.[43]

In Fig. 6.5(a), the difference of DOS between BFSs and normal is very small, approximately 14% of that in normal state. With the assumption that K_s is estimated to be 0.03%, the decrease of Knight-shift is expected to be around a value of 0.004%. This leads to the assumption that the change of K induced by BFSs is not large enough to be distinguished from experimental errors. Thus, a theoretical investigation is needed to separate K_s from K_{orb} . Furthermore, K_{orb} may change below and above T_s in the lightly S-substituted regime, which renders the estimation of K_s much more challenging.

6.2 Pressure effect on the low temperature enhancement of spin fluctuations

It is obvious that spin fluctuations enhancement at low temperature is suppressed under pressure from Fig. 4.12. A clear decrease just below T_c is due to gap opening, which makes the enhancement unambiguous in the SC state. Fig. 6.6 shows a direct comparison between low temperature data at ambient pressure and 2.0 GPa. By increasing pressure, not only the upturn towards low T has weakened, $1/T_1T$ value in the normal state has also become flat at 2.0 GPa instead of increasing towards T_c at ambient pressure.

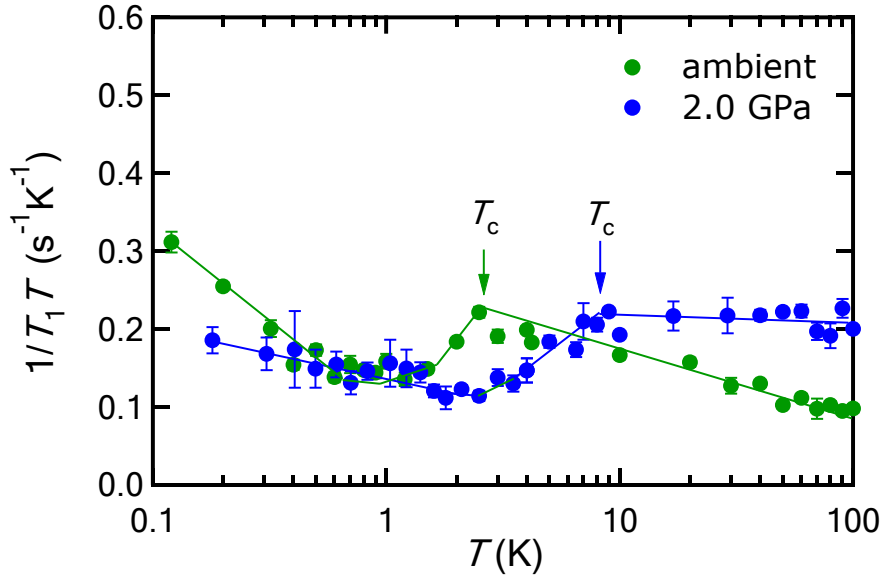


Fig. 6.6 Comparison of two pressure levels of $1/T_1T$ values at low temperature.

In a word, both $1/T_1T$ in normal state and superconducting state has a tendency of increasing by lowering temperature, while this tendency is suppressed by pressure. This behavior is not limited to $x = 0.18$ samples. For $x = 0.12$, flattened $1/T_1T$ tendency was also observed for several pressure levels. Another NMR study of $x = 0.20$ also gives evidence of this behavior, which was suggested to be originated from Fermi liquid.

For a wide range of substitution, pressure-induced Lifshitz transition on Fermi surfaces has been discussed for both theoretical point of view and in experiments. Such transition can lead to the suppression of spin fluctuations, which will be discussed in the following sections.

6.2.1 Pressure Effect on $1/T_1T$ in the Normal State

The suppression of $1/T_1T$ under pressure is not specific to $x=0.18$. For $x=0.12$, $1/T_1T$ also exhibits a similar tendency at several pressures. Another NMR study of $x=0.20$ also showed $1/T_1T = \text{const.}$ under pressure up to 2.0 GPa, and they attributed $1/T_1T = \text{const.}$ to Fermi-liquid behavior [36].

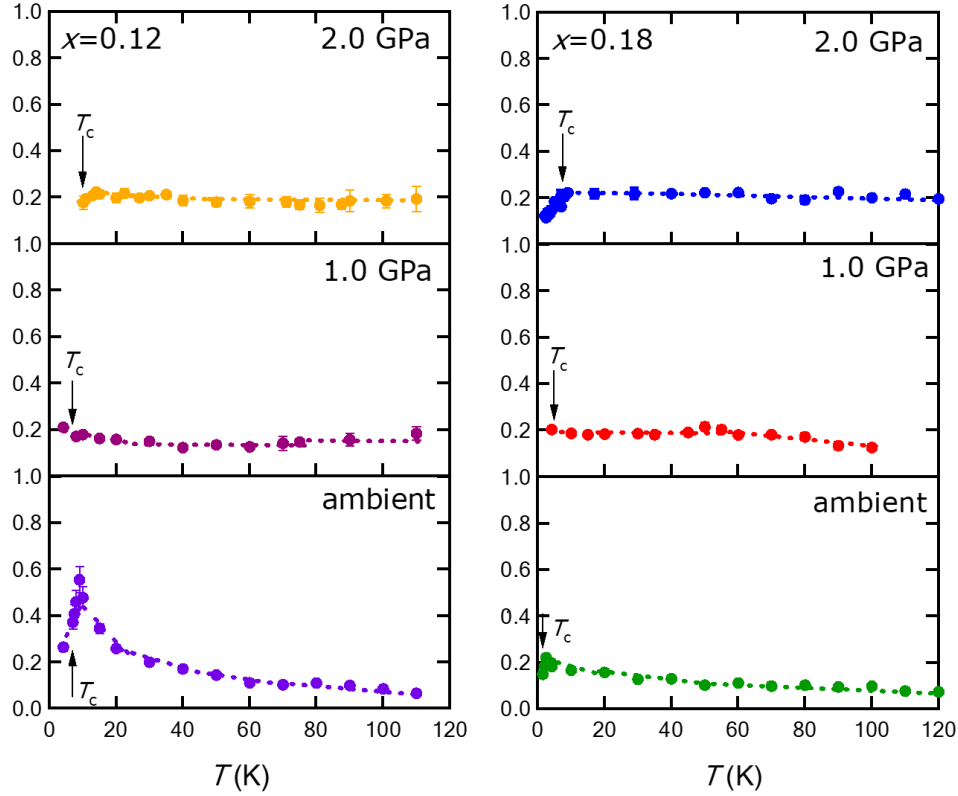


Fig. 6.7 Layout of $1/T_1T$ results for $\text{FeSe}_{1-x}\text{S}_x$ ($x = 0.12, 0.18$) at different pressure levels.

Recently, a pressure-induced Lifshitz transition has been discussed from both theoretical and experimental viewpoints. Such a pressure-induced transition could change spin fluctuations.

According to the theoretical investigation, reconstruction of the Fermi surfaces or predominant $\mathbf{q}$, namely Lifshitz transition, occurs at around 2 GPa due to the emergence of d_{xy} hole pocket at $\mathbf{k} \sim (\pi, \pi)$ as shown in Figs. 6.8(a) and (b), which could cause the $\mathbf{q} = (0, \pi)$ nesting between electron and hole pockets at a high pressure regime, as expected in the P - T phase diagram of $\text{Fe}(\text{Se}, \text{S})$. At the crossover region where the dominant $\mathbf{q}$ reconstructs and the nesting changes, spin fluctuations become tentatively T -independent before forming a new nesting condition.

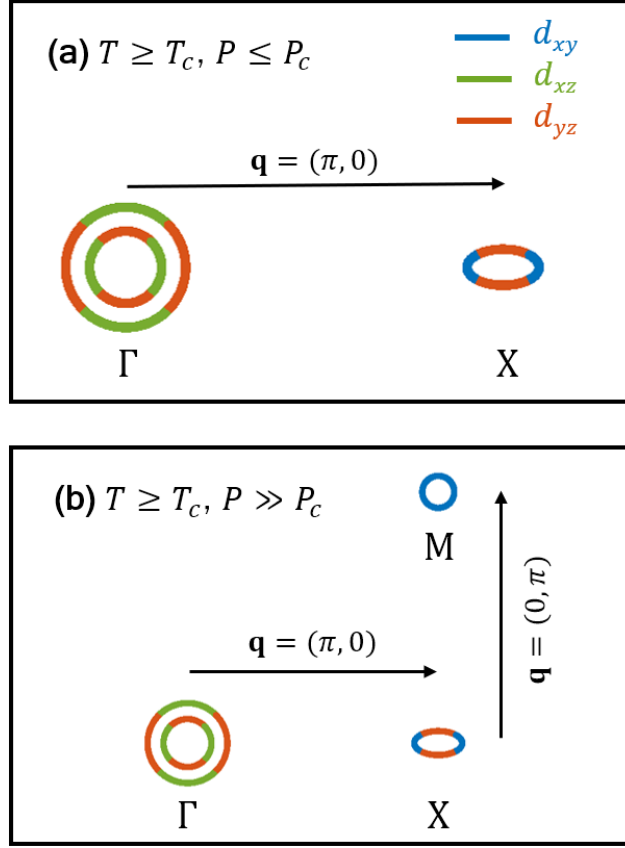


Fig. 6.8 (a)Original Fermi surfaces (OFSs) in the normal state at ambient pressure. (b)OFSs in the normal state under pressure with another hole pocket emerging at point M, $\mathbf{k} = (\pi, \pi)$.

The suppression of the upturn under pressure implies that the interaction between electrons becomes weak under pressure. The interaction at 2.0 GPa can be estimated given that $1/T_1T$ is almost T -independent and obeys the Korringa relation:

$$\frac{1}{T_1T} = \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_n}{\gamma_e} \right)^2 K_{\text{spin}}^2 K(\alpha). \quad (5.2)$$

The interaction U is included in α as $\alpha = U\chi_0$ where χ_0 is the uniform susceptibility of free electrons. $K(\alpha)$ provides a measure of electron correlation:

$$K(\alpha) = \frac{(1 - \alpha)^2}{\left\langle \left(1 - \frac{\alpha\chi_0(\mathbf{q})}{\chi_0} \right)^2 \right\rangle_{\text{FS}}}, \quad (5.3)$$

where $\left\langle \left(1 - \frac{\alpha\chi_0(\mathbf{q})}{\chi_0} \right)^2 \right\rangle_{\text{FS}}$ represents the average over $\mathbf{q}$ connecting two points on the Fermi surfaces, and $\chi_0(\mathbf{q})$ is the $\mathbf{q}$ -dependent susceptibility without the interaction. For ferromagnetic

metals, $K(\alpha) < 1$, whereas for antiferromagnetic metals, $K(\alpha) > 1$. For free electrons, $K(\alpha) = 1$ and $\alpha = 0$. For pure FeSe, $K_{\text{orb}} \simeq 0.23\%$ and $K_s = 0.06\%$ were estimated from the K - χ plot, while $K_{\text{orb}}/K_s \simeq 5$ estimated from RPA calculations leads to $K_{\text{orb}} \simeq 0.25\%$ and $K_s = 0.05\%$. For $x = 0.12$, $K_{\text{orb}} \simeq 0.26\%$ and $K_s = 0.03\%$ were estimated from the K - χ plot. These results imply that K is almost insensitive to S-substitution levels and is estimated to be approximately 0.3% for x up to ~ 0.29 . As for pressure dependence, K decreases only 0.01% by applying pressure of 2.0 GPa. The decrease is approximately the same for $x = 0.12$, implying that K is also almost insensitive to pressure. We estimate $K(\alpha) \simeq 15$ from $1/T_1 T \simeq 0.21$ assuming $K_s = 0.03\%$ at 2.0 GPa for $x = 0.18$. The results suggest that AFM fluctuations still remain even at 2.0 GPa, although AFM fluctuations or the upturn toward T_c is strongly suppressed with increasing pressure.

6.2.2 Pressure Effect on BFSs

Similarly to the normal state, we suggested that $1/T_1 T$ deep in the SC state would be explained by the nesting scenario, because the upturn below T_c resembles the upturn above T_c . However, this scenario seems disadvantageous because $1/T_1 T$ exhibits different T dependence between below and above T_c as mentioned in the previous section.

Contrary to the scenario above, the recent theoretical investigation pointed out that the upturn below T_c is explainable only by BFSs appearing at hole pockets as shown in Fig. 6.9(b). The wave number $\mathbf{q} \sim (0.4\pi, 0)$ corresponding to a span between two BFSs segments contributes to an enhancement of $\chi(\mathbf{q})$ under the strong Hubbard-type interaction, U .

The upturn of $1/T_1 T$ originates from the nesting between BFSs segments and the interaction. However, it is difficult to estimate which is effective from the experiments. According to the theoretical calculation of $1/T_1 T$, the upturn is absent for $U = 0$, and therefore the interaction is theoretically responsible for the upturn. As shown in Fig. 6.6, the upturn of $1/T_1 T$ below T_c is suppressed under pressure, implying that U becomes weak but nonzero under pressure. The result seems reasonable considering $K(\alpha) \simeq 15$ at 2.0 GPa in the normal state because $K(\alpha) \simeq 1$ should be expected for $U = 0$. The theoretical model would also explain why the T dependence of $1/T_1 T$ is different across T_c : this is clearly seen from the data at 2.0 GPa where $1/T_1 T = \text{const.}$ above T_c whereas $1/T_1 T$ exhibits an upturn below T_c . This change would be because the nesting properties change across T_c . The predominant $\mathbf{q}$ would change from $\mathbf{q} = (\pi, 0)$ above T_c to $\mathbf{q} \sim (0.4\pi, 0)$ below T_c , and $\chi_0(\mathbf{q})$ in the SC state would be different from that determined by the nesting between normal electrons. As a concluding remark, the Coulomb interaction is responsible to the upturn of $1/T_1 T$ for both normal and SC states. The Coulomb interaction seems to become weak temporarily around 1 to 2 GPa where the Lifschitz transition is expected to occur. The nesting properties would be different between below and above T_c considering

the T dependence of $1/T_1T$ at 2.0 GPa.

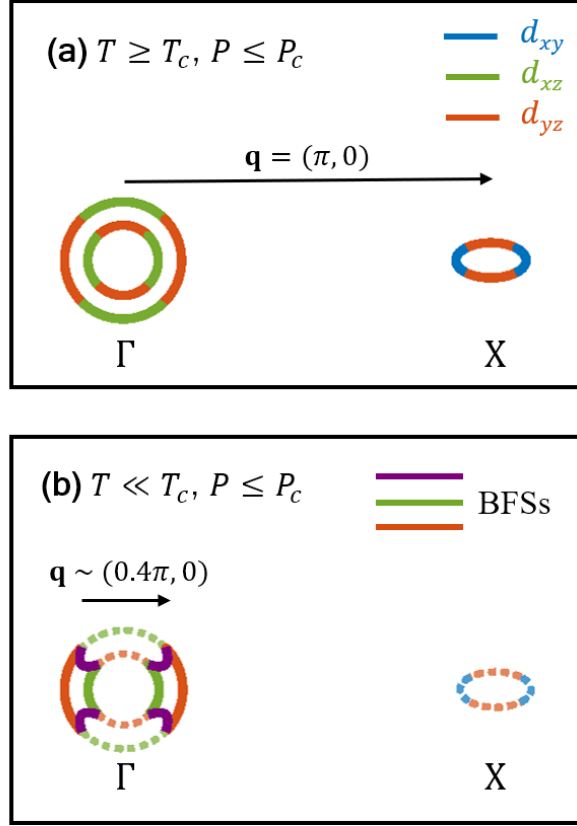


Fig. 6.9 (a)Original Fermi surfaces (OFSs) in the normal state at ambient pressure. (b)Bogoliubov Fermi surfaces (BFSs) in the SC state. OFSs in the normal metallic state are shown by dashed curves in (b) for comparison. BFSs in the superconducting state are plotted by solid curves. The segments colored in red and green represent BFSs with the character of small intraband spin-singlet particle-hole mixing, and the segments colored in purple represent BFSs with the character of significant interband spin-triplet particle-hole mixing.

Chapter 7

Conclusion

7.1 Summary

In this study, we have performed ^{77}Se -NMR measurements down to 100 mK on S-substituted FeSe, $\text{FeSe}_{1-x}\text{S}_x$, systematically across the nematic quantum critical point ($x_c \sim 0.17$), to reveal the nature of the unusual residual DOS in the tetragonal phase. For $x = 0.18$, a remarkable upturn of $1/T_1T$ was observed deep in the superconducting state. This anomalous behavior cannot be explained by impurity or Volovik effects but is consistent with the recent theoretical model of BFSs with C2 symmetry. The upturn of $1/T_1T$ is well reproduced as the enhancement of $\chi(\mathbf{q})$ at $\mathbf{q} \approx (0.4\pi, 0)$, a span between two BFSs segments with the character of significant interband spin-triplet particle-hole mixing. The results give evidence of not only the presence of BFS quasiparticle interactions but also the presence of BFSs itself.

Upon applying hydrostatic pressure up to 2.0 GPa, the upturn of $1/T_1T$ was suppressed while remaining a clear tendency of the upturn, suggesting that the quasiparticle interactions weaken but do not vanish under pressure. However, such a slight upturn disappears above T_c , and $1/T_1T$ becomes almost constant at 2.0 GPa. This change would be attributed to the fact that the nesting properties change across T_c , namely, the predominant $\mathbf{q}$ of $\chi(\mathbf{q})$ would change from $\mathbf{q} \sim (0.4\pi, 0)$ below T_c to $\mathbf{q} = (\pi, 0)$ above T_c .

Lastly, the unusual behavior discovered deep in the SC state in the present experiment highlights the unconventional nature of superconductivity of $\text{FeSe}_{1-x}\text{S}_x$, and provides important clues for its pairing symmetry. Altogether, the combination of low-temperature and high-pressure NMR studies would advance understanding of the mechanism of superconductivity of FeSe-based superconductors.

7.2 Future outlooks

Although our work has provided evidence for the presence of BFSs. Further investigations from both experimental and theoretical perspectives are crucial for exploring the nature of the exotic ultranodal state. As far as NMR measurements, more precise measurements of the Knight shift could give insight into an accurate estimation of the residual DOS.

On the theoretical side, a more quantitative framework incorporating both spin-orbit coupling and multiband effects would be needed to reproduce the evolution of the low- T behavior of $1/T_1T$ in the nematic phase. Such investigations will not only deepen understanding of FeSe systems but also shed light on the superconductivity of broader multiband systems.

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