

学位論文

**Quasiparticle excitations in FeSe in the
vicinity of BCS-BEC crossover studied by
thermal transport measurements**

平成 29 年 1 月博士 (理学) 申請
京都大学大学院理学研究科 物理学・宇宙物理学専攻

綿重 達哉

Abstract

The iron-based superconductor FeSe with the superconducting transition temperature $T_c \sim 8-9$ K has stirred great interest because it exhibits several unique properties, which had been covered until recently due to the difficulty in growing the clean single crystals. Here we report some of the interesting electronic and superconducting properties of FeSe revealed by using high-quality single crystals grown by the chemical vapor transport method.

BCS-BEC crossover in FeSe (Section 6)

The physics of the crossover between the weak-coupling Bardeen-Cooper-Schrieffer (BCS) and strong-coupling Bose-Einstein-condensate (BEC) limits gives a unified framework of quantum bound (superfluid) states of interacting fermions. In the region of this crossover, the size of the interacting pairs, which is represented by the coherence length ξ , becomes comparable to the average distance between particles, which is close to the inverse Fermi momentum $1/k_F$, i. e., $k_F\xi \sim 1$, and a new exotic state of matter has been expected to emerge. The BCS-BEC crossover has hitherto been realized experimentally in ultracold atomic gases. On the other hand, in solids, almost all superconductors are in the BCS regime, where the superconducting gap energy Δ is usually several orders of magnitude smaller than the Fermi energy ε_F , $\Delta/\varepsilon_F \sim 1/k_F\xi \ll 1$, and it has thus been extremely difficult to access the crossover regime.

Our quasiparticle interference (QPI), Seebeck, and penetration depth measurements revealed that FeSe has extremely small Fermi energies, $\varepsilon_F^h \approx 10$ meV for the hole band and $\varepsilon_F^e \approx 3$ meV for the electron bands. We found that FeSe is a multigap superconductor with two distinct superconducting gaps of $\Delta \sim 2.5$ and 3.5 meV by scanning

tunneling spectroscopy (STS) measurements. The comparable energy scale of ε_F and Δ indicates that superconductivity in FeSe is deep in the BCS-BEC crossover region. Moreover, we discover the emergence of an unexpected superconducting phase (*B*-phase) in strong magnetic fields, demonstrating that the Zeeman splitting comparable to the Fermi energy leads to a strong modification of the properties of fermionic systems in such a regime.

Quasiparticle excitations in FeSe in the BCS-BEC crossover region (Section 7)

FeSe has two unique features that may provide new insights into fundamental aspects of the physics of the BCS-BEC crossover. The first feature is the electronic structure: FeSe is a compensated semimetal with equal numbers of electron and hole carriers, and hence it is essentially a multiband superconductor. This renders the crossover physics in FeSe distinguishable from that in ultracold atomic gases. However, although the superconducting gap structure has been reported to be very anisotropic, the detailed gap structure in each band is still unclear. The second feature concerns the fate of the superfluid when the spin populations are strongly imbalanced. Although highly spin-imbalanced Fermi systems have been realized in ultracold atomic gases, the nature of the spin-imbalanced superfluid is still largely unexplored experimentally due to the difficulty in cooling the systems to sufficiently low temperature. In sec. 6, we report a high-field superconducting phase (*B*-phase) of FeSe induced by the extremely large spin imbalance, but very little is known about its nature.

To shed light on the above issues, detailed knowledge of the quasiparticle excitations in the superconducting state is crucial. Here we measured the thermal conductivity κ_{xx} and the thermal Hall conductivity κ_{xy} up to $\mu_0 H = 20$ T. Both quantities are sensitive probes of the delocalized low-energy quasiparticle excitations.

Our results reveal that a highly anisotropic small superconducting gap opens in the electron Fermi-surface pocket, whereas a more isotropic and larger gap forms in the

hole pocket. We also find that the quasiparticle scattering rate is strongly modified upon entering the B -phase. We discuss that this field-induced phase is likely to present a highly anomalous inhomogeneous superconducting state that has not been addressed before, rather than a conventional Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state.

Time-reversal symmetry breaking superconducting state around twin boundaries in FeSe (Section 5)

Junctions and interfaces consisting of unconventional superconductors provide an excellent experimental playground to study exotic phenomena related to the phase of the order parameter. Not only does the complex structure of unconventional order parameters have an impact on the Josephson effects, but it also may profoundly alter the quasiparticle excitation spectrum near a junction. Recent progress in scanning tunneling microscopy (STM) and spectroscopy (STS) technologies opens up a way to directly visualize the spatial variation of the electronic states near the superconducting heterostructures. However, STM or STS studies on superconducting junctions made of unconventional superconductors are still demanding because it is often challenging to obtain well-defined junctions of them.

To solve the problem, we performed STM/STS measurements on the nodal superconductor FeSe and visualize the spatial evolution of the local density of state (LDOS) near twin boundaries (TBs). We found that the critical current density across the TB is comparable to that of the bulk, indicating that TBs in FeSe are ideal junctions to investigate the Josephson effects on unconventional superconductors.

The $\pi/2$ rotation of the crystallographic orientation across the TB twists the structure of the unconventional order parameter, which may, in principle, bring about a zero-energy LDOS peak at the TB. The LDOS at the TB observed in our study, in contrast, does not exhibit any signature of a zero-energy peak, and an apparent gap amplitude remains finite all the way across the TB. The low-energy quasiparticle excitations associated with the gap nodes are affected by the TB over a distance more than

an order of magnitude larger than the coherence length ξ_{ab} . The modification of the low-energy states is even more prominent in the region between two neighboring TBs separated by a distance $\approx 7\xi_{ab}$. In this region, the spectral weight near the Fermi level ($\approx \pm 0.2$ meV) due to the nodal quasiparticle spectrum is almost completely removed. These behaviors suggest that the TB induces a fully gapped state, invoking a possible twist of the order parameter structure, which breaks time-reversal symmetry.

The thesis is structured as follows. In Section 1, we will give a brief account of BCS-BEC crossover. In Section 2, we will introduce the purpose of this study. In Section 3, we will describe the detailed procedures of sample growth and experimental setups for STM/STS measurements in RIKEN and thermal transport measurements in HLD-EMFL in Dresden. In Section 4, we will review the properties of the iron-based superconductor FeSe. In Section 5, we will show the results of STM/STS measurements around TBs in FeSe and discuss the possible time-reversal-symmetry-broken superconducting state. In Section 6, we will show our results of QPI, Seebeck, and penetration depth measurements, and combining the recent SdH and ARPES measurements, we will suggest that the superconductivity in FeSe is deep in the BCS-BEC crossover region. We will also discuss a possible field-induced superconducting phase (B -phase) in FeSe with a brief introduction of FFLO state. In Section 7, we will discuss the detailed superconducting gap structure and the properties of the B -phase based on the results of the κ_{xx} and κ_{xy} measurements. Finally, we will summarize and conclude the present studies in Section 8.

Contents

1	Introduction	10
1.1	Superconductivity	10
1.2	BCS-BEC crossover	12
2	Purpose of this study	15
3	Experimental	18
3.1	Sample growth	18
3.2	Scanning tunneling microscopy and spectroscopy	20
3.3	Thermal and electrical transport	23
3.3.1	Thermal and electrical transport	23
3.3.2	Misalignment effect	26
3.3.3	Setups of thermal transport measurements	27
4	Properties of FeSe	29
4.1	Crystal structure	29
4.2	Properties of FeSe single crystals grown by self-flux method	31
4.3	Clean FeSe single crystals grown by the vapor transport method	33
4.4	Phase diagram of S-doped FeSe system	37
4.5	Superconducting gap structure in FeSe	40
4.6	Pressure effect	42
4.7	Mono-layer FeSe thin film	43
5	Time-reversal symmetry breaking superconducting state around twin boundaries in FeSe	46
5.1	Introduction	46

5.2	Twin boundary in FeSe	47
5.3	LDOS across the TBs	48
5.4	Possible TRSB SC state around TB	53
5.5	Summary	57
6	BCS-BEC crossover in FeSe	58
6.1	Extremely small Fermi energy in clean FeSe single crystal	59
6.1.1	Quasiparticle interference (QPI)	59
6.1.2	SdH measurements	61
6.1.3	Orbital ordering in FeSe	65
6.2	BCS-BEC crossover in FeSe	67
6.3	Field-induced SC phase (B -phase)	70
6.4	Possible FFLO state in B -phase	74
6.4.1	FFLO state	74
6.4.2	Pair-breaking effects	75
6.4.3	Requirements for FFLO state	77
6.5	Summary	81
7	Quasiparticle excitations in FeSe in the BCS-BEC crossover region studied by thermal transport measurements	82
7.1	Results	83
7.2	Superconducting gap structure	85
7.2.1	Doppler shift	85
7.2.2	Field dependence of thermal conductivity	87
7.2.3	Superconducting gap structure of FeSe	88
7.3	Field-induced superconducting phase (B -phase)	90
7.3.1	Phase diagram	90
7.3.2	Field dependence of thermal Hall angle	92
7.4	Possible FFLO state in FeSe	95
7.4.1	The lowest Landau level solutions in BCS and FFLO state	95
7.4.2	FFLO state with higher Landau levels	98

7.4.3	Possible FFLO state with higher Landau levels in FeSe	99
7.5	Summary	100
8	Conclusion	101

1 Introduction

1.1 Superconductivity

Superconductivity is one of the most drastic phenomena in condensed matter physics.

In 1911, Kamerlingh Onnes first discovered superconductivity in elemental mercury with $T_c = 4.2$ K. Since the discovery, the mechanism of superconductivity had been a long-standing issue. However, in 1957, John Bardeen, Leon Neil Cooper and John Robert Schrieffer developed a theory (the BCS theory) to explain the microscopic mechanism of superconductivity, where two electrons form a pair (Cooper pair) mediated by lattice vibrations (phonon) and the pairs condense into a ground state [1]. In the BCS superconductors, the attractive interaction between electrons driven by phonons is weak, therefore, the transition temperatures were expected to be at most 30-40 K. However, the very recent high-pressure experiments revealed that the sulfur hydride system H_2S transforms to a metal under very high pressure and exhibits superconductivity with the extremely high- T_c , 203.5 K at 155 GPa [2]. It has been theoretically suggested that the BCS theory can account for the high- T_c superconductivity in the hydride system [3].

One of the most important developments in condensed matter physics for the last several decades is the discovery of the high-temperature superconductivity. In 1986, Johannes Georg Bednorz and Karl Alexander Müller reported superconductivity below 30 K in the Ba – La – Cu – O system, where superconductivity occurs in CuO_2 plane [4]. This discovery has triggered enormous amount of research for the cuprate superconductors with high transition temperatures. Among them, the highest temperatures of superconducting transition have ever been reported are 133 K at ambient pressure [5] and 165 K under high pressure [6] in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$. In the cuprate system, the superconducting transition temperatures are far above the one which is expected in the framework of the BCS theory and this indicates that another pairing

mechanism should be considered.

Another class of high- T_c superconductors is the iron-pnictide (Fe-*Pn*) or iron chalcogenide (Fe-*Ch*) system. In 2006, the research group of Hideo Hosono discovered superconductivity below 4 K in LaFePO [7], and in February 2008, they succeeded in increasing the transition temperature up to 26 K by replacing P with As [8]. Soon after the discovery, in the bulk system, the transition temperature reached 56 K by substituting other lanthanoid elements for La [9]. In 2012, the Chinese groups have reported that FeSe mono-layer thin films on SrTiO₃ substrates exhibit superconducting transition at 65 K [10–12]. Moreover, the in-situ four-point probe electrical transport measurements on the thin film suggests that T_c is dramatically enhanced up to 110 K [13].

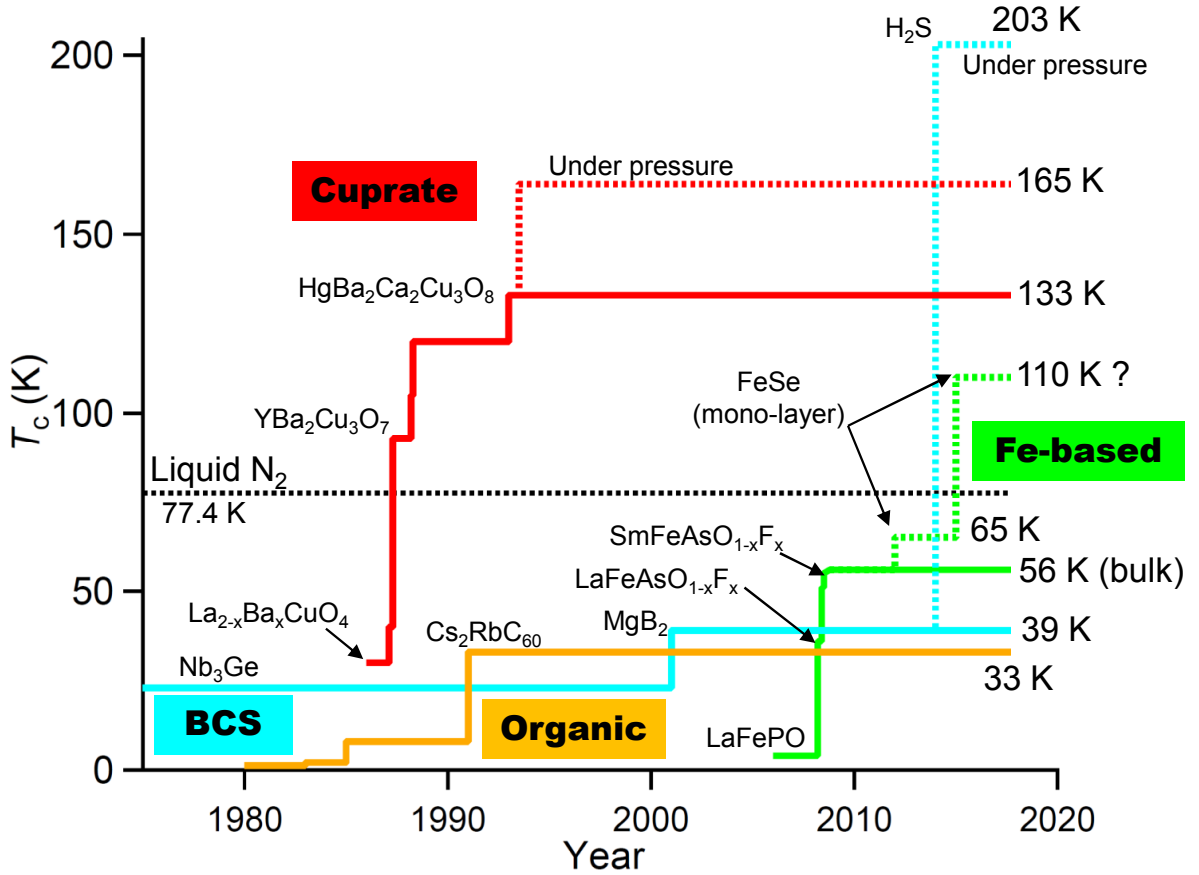


Figure 1.1: Superconducting transition temperature T_c vs time.

1.2 BCS-BEC crossover

Since the proposal of the BCS theory by Bardeen, Cooper and Schrieffer, there have been a number of theoretical works which suggest that the transition into the superconducting state can be considered as a sort of Bose-Einstein condensation (BEC), i.e., these two paradigms, BCS and BEC, are not distinct and can be understood from a unified standpoint [14–20].

Fig. 1.2(a) is a schematic phase diagram of the BCS-BEC crossover as a function of temperature T/ε_F and dimensionless coupling constant $1/k_F a$, where a is the scattering length [18–20]. The BCS limit $1/k_F a \rightarrow -\infty$ corresponds to weak attractive interaction, which is not able to form a two-body bound state in a vacuum, but nevertheless leads to a collective Cooper instability in the presence of a Fermi surface. In the weak-coupling BCS state, the Cooper pairs with the coherence length $\xi_{\text{pair}} \sim k_F^{-1} \exp(+\pi/2k_F |a|) \gg k_F^{-1}$ overlap each other, as schematically depicted in Fig. 1.2(b). Here k_F^{-1} denotes the mean interparticle space. In the opposite limit $1/k_F a \rightarrow +\infty$, the strong attractive interaction gives rise to tightly bound diatomic molecules with $\xi_{\text{pair}} \ll k_F^{-1}$ which exhibit BEC, as shown in Fig. 1.2(d). With increasing pairing interactions, the system is continuously shifted from BCS to BEC. At the unitary limit with $1/k_F a = 0$, right in the middle of BCS-BEC crossover region, the pair size is on the order of the mean interparticle space, $\xi_{\text{pair}} \approx k_F^{-1}$ (Fig. 1.2(c)). Hence, the interaction between Cooper pairs is significantly enhanced, and unique quantum condensed states are expected in the crossover region [21, 22]. The ratio of the condensation temperature T_c and Fermi energy ε_F is $k_B T_c / \varepsilon_F \simeq 0.2$, which is the highest value among fermionic superfluid systems. This means that the condensation energy Δ becomes comparable to ε_F in the crossover region. One of the other remarkable features of BCS-BEC crossover is the pseudogap above T_c . In the pseudogap phase, the incoherent pairs of electrons (preformed pairs) are formed below T^* and give rise to a strong suppression of the low-energy density of states.

BCS-BEC crossover has been experimentally realized in ultra-cold atoms, in which

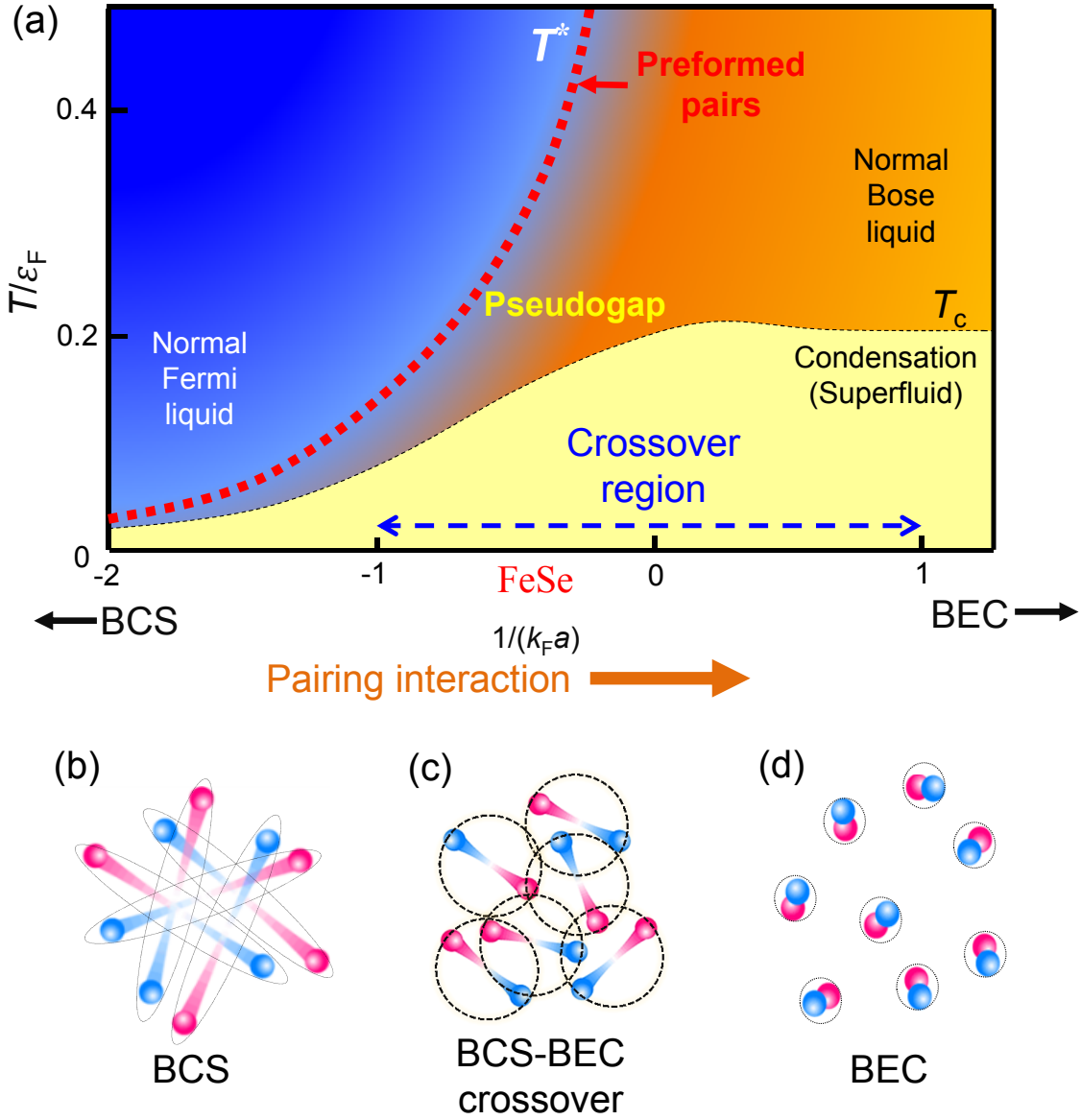


Figure 1.2: (a) Schematic phase diagram of BCS-BEC crossover [18–20]. $1/k_F a \rightarrow -\infty$ ($1/k_F a \rightarrow +\infty$) corresponds to BCS (BEC) limit. $1/k_F a = 0$ corresponds to the unitary limit, right in the middle of the BCS-BEC crossover region. Black dot line is the T_c -line where the condensation occurs. Red dashed line is the T^* -line where preformed pairs appear. In the temperature region between the T_c and T^* , pseudogap is formed. The following experimental results indicate that FeSe is located in the crossover region. (b)-(d) Schematic images of pairings in the BCS, BCS-BEC crossover, and BEC regions, respectively. In the crossover region, the pair size is on the order of the mean inter-particle space, $\xi_{\text{pair}} \approx k_F^{-1}$.

the pairing interactions are controlled by Feshbach resonance [23–29]. On the other hand, in solids, almost all superconductors are in the BCS regime, where the superconducting gap energy Δ is usually several orders of magnitude smaller than the Fermi energy, $\Delta/\varepsilon_F \sim 1/k_F\xi \sim 10^{-5} - 10^{-4} \ll 1$. In the underdoped high- T_c cuprates, the pseudogap phase appears above T_c [30] and there are some theoretical predictions which suggest that it comes from the BCS-BEC crossover physics [31, 32], however, the origin is still controversial. Moreover, even in the cuprates, which have relatively larger superconducting-gaps than ones of conventional superconductors, the ratio of the condensation energy Δ and Fermi energy E_F is still very small: $\Delta/\varepsilon_F \sim 10^{-3} - 10^{-2}$, indicating the deviation from the crossover regime. Hence, in superconducting electronic systems, the BCS-BEC crossover has been extremely difficult to be achieved.

However, the iron-based superconductor FeSe with transition temperature $T_c \sim 8-9$ K has recently stirred great interest, because it has been experimentally revealed that it is a strong candidate for a superconductor located in the BCS-BEC crossover region. In the following sections, we will discuss the detailed electronic structures of FeSe.

2 Purpose of this study

Time-reversal symmetry breaking superconducting state around twin boundaries in FeSe (Section 5)

Junctions and interfaces consisting of unconventional superconductors provide an excellent experimental playground to study exotic phenomena related to the phase of the order parameter. Not only does the complex structure of unconventional order parameters have an impact on the Josephson effects, but it also may profoundly alter the quasiparticle excitation spectrum near a junction. Recent progress in scanning tunneling microscopy (STM) and spectroscopy (STS) technologies opens up a way to directly visualize the spatial variation of the electronic states near the superconducting heterostructures. However, STM or STS studies on superconducting junctions made of unconventional superconductors are still demanding because it is often challenging to obtain well-defined junctions of them.

To solve the problem, we performed STM/STS measurements on the nodal superconductor FeSe and visualize the spatial evolution of the local density of state (LDOS) near twin boundaries (TBs).

BCS-BEC crossover in FeSe (Section 6)

The physics of the crossover between the weak-coupling Bardeen-Cooper-Schrieffer (BCS) and strong-coupling Bose-Einstein-condensate (BEC) limits gives a unified framework of quantum bound (superfluid) states of interacting fermions. In the region of this crossover, the size of the interacting pairs, which is represented by the coherence length ξ , becomes comparable to the average distance between particles, which is close to the

inverse Fermi momentum $1/k_F$, i. e., $k_F\xi \sim 1$, and a new exotic state of matter has been expected to emerge. The BCS-BEC crossover has hitherto been realized experimentally in ultracold atomic gases. On the other hand, in solids, almost all superconductors are in the BCS regime, where the superconducting gap energy Δ is usually several orders of magnitude smaller than the Fermi energy ε_F , $\Delta/\varepsilon_F \sim 1/k_F\xi \ll 1$, and it has thus been extremely difficult to access the crossover regime.

To investigate the electronic properties of FeSe, we performed scanning tunneling microscopy/spectroscopy (STM/STS), quasiparticle interference measurements, and some other bulk measurements. In the section, we will discuss whether the superconductivity in FeSe is in the crossover regime. Moreover, performing thermal conductivity measurements, we explored the high-field superconducting state with a large spin imbalance in FeSe.

Quasiparticle excitations in FeSe in the BCS-BEC crossover region (Section 7)

FeSe has two unique features that may provide new insights into fundamental aspects of the physics of the BCS-BEC crossover. The first feature is the electronic structure: FeSe is a compensated semimetal with equal numbers of electron and hole carriers, and hence it is essentially a multiband superconductor. This renders the crossover physics in FeSe distinguishable from that in ultracold atomic gases. However, although the superconducting gap structure has been reported to be very anisotropic, the detailed gap structure in each band is still unclear. The second feature concerns the fate of the superfluid when the spin populations are strongly imbalanced. Although highly spin-imbalanced Fermi systems have been realized in ultracold atomic gases, the nature of the spin-imbalanced superfluid is still largely unexplored experimentally due to the difficulty in cooling the systems to sufficiently low temperature. In sec. 6, we report a high-field superconducting phase (*B*-phase) of FeSe induced by the extremely large spin imbalance, but very little is known about its nature.

To shed light on the above issues, detailed knowledge of the quasiparticle excitations in the superconducting state is crucial. Here we measured the thermal conductivity κ_{xx} and the thermal Hall conductivity κ_{xy} up to $\mu_0 H = 20$ T. Both quantities are sensitive probes of the delocalized low-energy quasiparticle excitations.

3 Experimental

3.1 Sample growth

Since the electronic features of FeSe are very sensitive to impurities and defects, clean FeSe single crystals are very crucial for investigating the itinerant electronic structures. Recently, the Karlsruhe Institute of Technology (KIT) group in Germany have succeeded in growing FeSe single crystals of unprecedented quality using a KCl/AlCl₃ chemical vapor transport technique [33]. In Kyoto University, we fabricated high-quality FeSe single crystals with the chemical vapor transport method for the thermal transport measurements. The following is the procedures of the sample growth.

A mixture of Fe and Se powders was sealed in an evacuated SiO₂ ampoule together with KCl and AlCl₃ powders (Fig. 3.1(c)). To prevent contamination of the starting materials, such as oxidization and water contamination, all the sealing procedures were done in the Ar-filled glove box (Fig. 3.1(b)) with a very low O₂ concentration (<1 ppm) and under a high vacuum (< 10⁻⁴ Pa). High-purity Fe (99.998 %) and Se (99.99 %) powders with a total mass of 3.0 g were mixed in an atomic ratio 1:1:1. We found that the amount of Fe defects can be reduced by mixing some extra Fe powder; as a result, the *RRR* of the electrical resistivity is strikingly enhanced. Additionally, we mixed KCl (99.99 %) and AlCl₃ (99.99 %) powders with the ratio 3:7 and the total amount was 7.0 g. One end of the ampoule was heated to 390 °C near the center of the tube furnace, while the other end was kept at ~160 °C at the edge of the furnace. The temperature of the low-*T* end was monitored by a thermocouple thermometer (Fig. 3.1(a)). We tilted the furnace to keep the liquidized mixture at the high-*T* edge. In this vapor transport technique, KCl/AlCl₃ vapor containing FeSe is generated from the liquidized mixture at the high-*T* end and condensed at the low-*T* end, as schematically illustrated in Fig. 3.1(d). After 2-4 weeks, single crystals of FeSe with tetragonal morphology were extracted at the low-*T* end. The typical size of the obtained single crystal was $\sim 2 \times 2 \times 0.05 \text{ mm}^3$ (Fig. 3.1(e)).

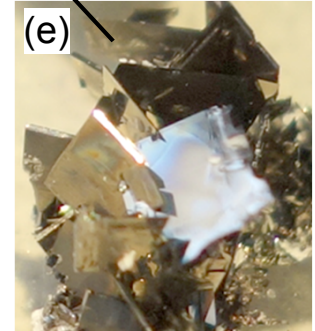
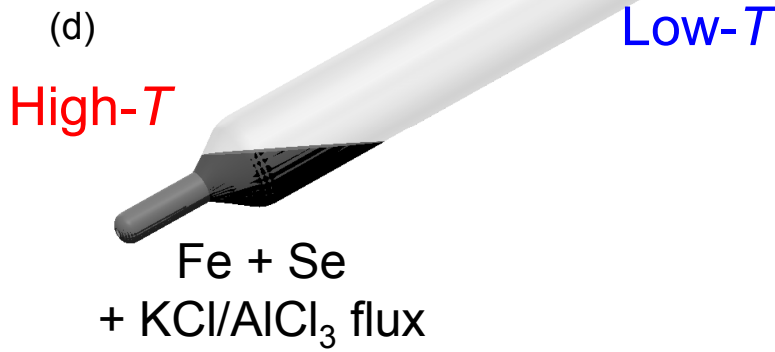
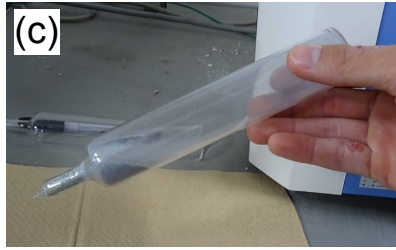


Figure 3.1: (a),(b) Tube furnace and glove box used for the sample growth in Kyoto University, respectively. The glove box is filled with Ar-gas. The O_2 concentration is kept below 1 ppm by the circulation and purification systems. (c) Quartz ampoule with the mixture of Fe and Se powders and KCl/AlCl₃ flux. (d) Schematic image of the vapor transport technique. (e) Obtained FeSe single crystals. The typical size is $\sim 2 \times 2 \times 0.05 \text{ mm}^3$.

3.2 Scanning tunneling microscopy and spectroscopy

Here we briefly introduce the principle of scanning tunneling microscopy (STM) and spectroscopy (STS). STM is an instrument for imaging surfaces with the atomic resolution [34]. And STS is used to provide information about the density of states (DOS) in a sample as a function of their energy. The STM/STS are based on the concept of quantum tunneling. When a conducting tip, made of such as W and Pt/Ir, is brought very near to the surface and a bias voltage V is applied between the two, tunneling current flows through the vacuum between them. The resulting tunneling current at low temperature ($k_B T \ll eV$) is denoted as

$$I_t(\mathbf{r}, z, V) \propto \int_0^{eV} LDOS_{\text{sample}}(\mathbf{r}, E) T(\mathbf{r}, z, eV, E) dE \quad (3.1)$$

Here, the energy level $E = 0$ represents the chemical potential level, z is the distance between the tip and the examined sample, and $LDOS_{\text{sample}}(\mathbf{r}, E)$ is the local density of states (LDOS) of the sample. And the tunneling probability T is

$$T(\mathbf{r}, z, eV, E) \propto \exp(-2\kappa(\mathbf{r}, eV, E)z) \quad (3.2)$$

$$\kappa(\mathbf{r}, eV, E) = \frac{\sqrt{2m(\phi(\mathbf{r}) - E + eV/2)}}{\hbar}. \quad (3.3)$$

Since, in general, the work function $\phi(\mathbf{r}) \ll eV, E$, we eventually obtain the tunneling current

$$I_t(\mathbf{r}, z, V) \propto \exp(-2\kappa(\mathbf{r})z) \int_0^{eV} LDOS_{\text{sample}}(\mathbf{r}, E) dE \quad (3.4)$$

$$\kappa(\mathbf{r}) = \frac{\sqrt{2m\phi(\mathbf{r})}}{\hbar}. \quad (3.5)$$

In Fig. 3.2, the schematic views of scanning tunneling microscopy (STM) and spectroscopy (STS) appear. When the tip is moved across in the xy -plane of the sample with keeping tunneling current I_t constant, the surface height maps $z(\mathbf{r})$ (STM topographic images) are obtained. The typical value of the damping coefficient κ in Eq. 3.5 is $\sim 1 \text{ \AA}^{-1}$, the STM images have very high spatial resolution, $1 \text{ \AA}$ for the horizontal direction and $0.1 \text{ \AA}$ for the vertical direction with respect to the observed surfaces. On the other hand, in the STS mode, we change the bias voltage V with keeping the tip position fixed ($z = \text{const.}$). Then the tunneling current is denoted as

$$I_t(\mathbf{r}, V) \propto \int_0^{eV} LDOS_{\text{sample}}(\mathbf{r}, E) dE. \quad (3.6)$$

Differentiating both sides with respect to V , we obtain the tunneling conductance dI/dV

$$\frac{dI_t}{dV}(\mathbf{r}, V) \propto LDOS_{\text{sample}}(\mathbf{r}, E). \quad (3.7)$$

Hence, in the STS mode, we can investigate the modulation of $LDOS_{\text{sample}}$ with atomic resolution.

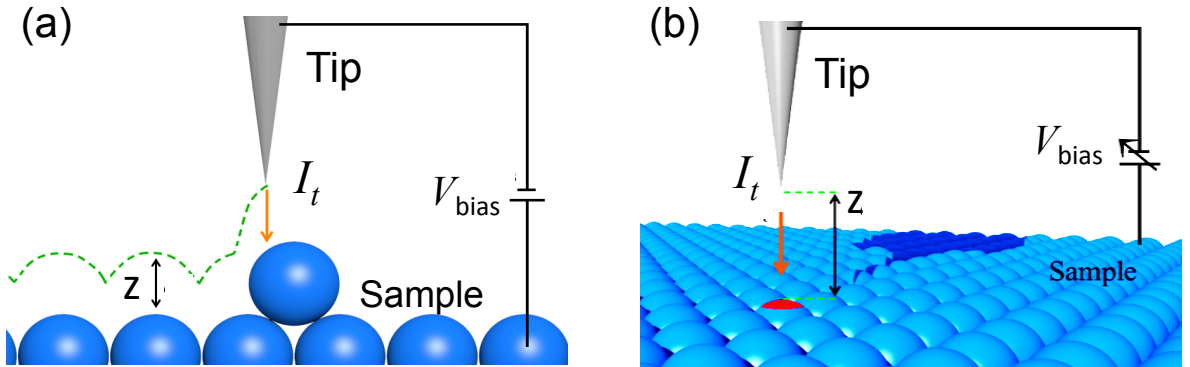


Figure 3.2: (a), (b) Schematic views of STM and STS, respectively.

We performed the STM/STS measurements in the RIKEN CEMS. The used system is presented in the picture in Fig. 3.3. We used electropolished tungsten wires for the STM tips. To avoid pollution of the observed surfaces, the FeSe single crystals were cleaved under ultrahigh vacuum ($< 10^{-8}$ Pa) on the cleave stage cooled to liquid nitrogen temperature. Then we immediately load the sample into the observation space. We cooled the sample temperature down to 0.4 K with a ^3He sorption system and applied magnetic fields up to 12 T.

Our STM/STS measurement results appear in section 5 and 6.

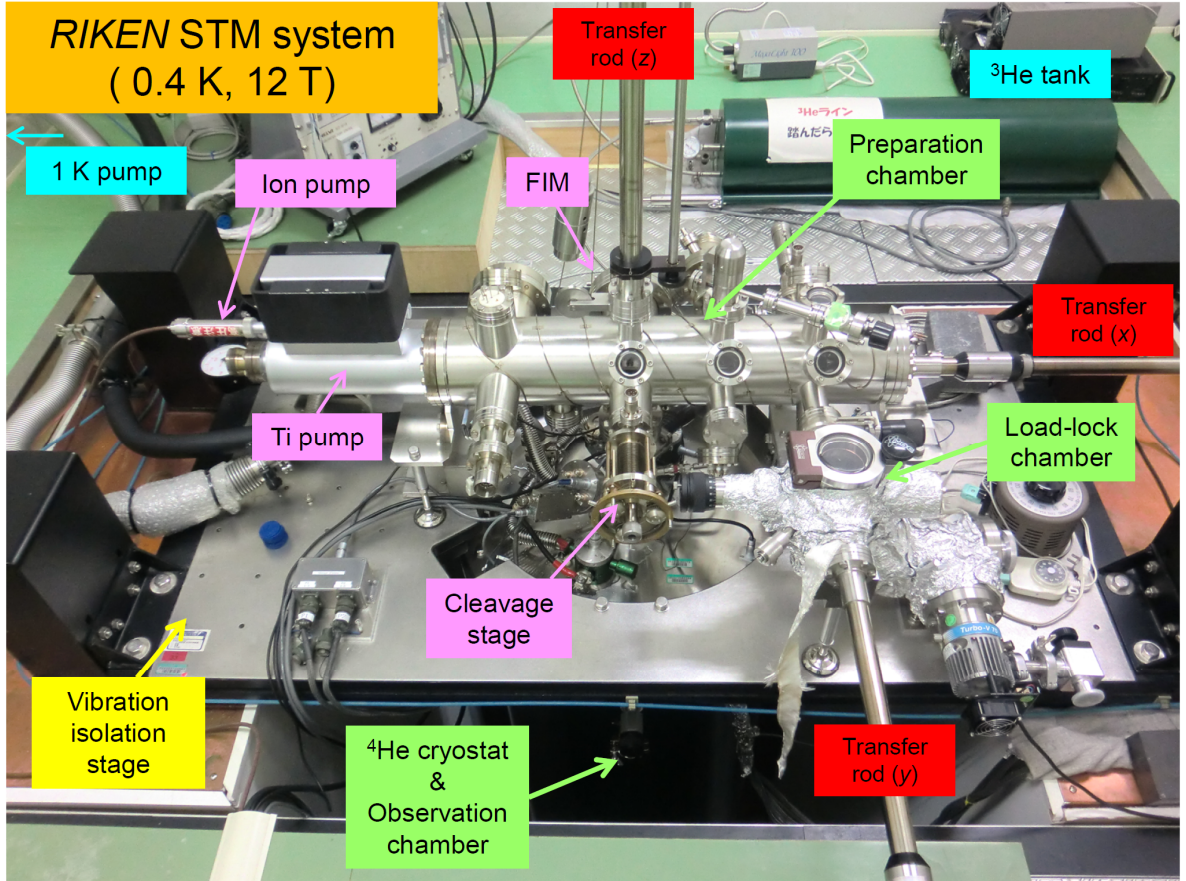


Figure 3.3: A picture of the used STM/STS system in RIKEN CEMS.

3.3 Thermal and electrical transport

3.3.1 Thermal and electrical transport

Thermal transport κ_{xx} , κ_{xy} measurements were performed by a standard steady-state method. The experimental configurations with a FeSe single crystal are displayed in Fig. 3.4(c) and illustrated schematically in Fig. 3.4(d).

In the steady-state, thermal conductivity κ is defined as

$$\mathbf{q} = -\bar{\kappa}\nabla T, \quad (3.8)$$

where $\bar{\kappa}$ is the thermal conductivity tensor, $\mathbf{q}$ is the thermal current density (or thermal energy flux density), and ∇T is the thermal gradient. Now, we assume that the magnetic fields are applied parallel to the $z(c)$ -axis and heat flows in the $xy(ab)$ -plane, as displayed in Fig. 3.4(d). When the magnetic field is not applied or the transversal component of thermal conductivity κ_{xy} is absent, Eq. 3.8 is reduced to a one-dimensional form, and the thermal conductivity $\kappa = \kappa_{xx}$ is given by

$$q = -\kappa\nabla T. \quad (3.9)$$

Here $\nabla T = dT/dx$ is the thermal gradient along the longitudinal direction to the heat flow. As a result, we obtain

$$\kappa = \frac{Q}{\Delta T} \frac{l}{wt}, \quad (3.10)$$

where Q is the applied heat power, $\Delta T = T_{\text{high}} - T_{\text{low}}$ is the temperature difference between two contacts, and l , w , and t are the distances between the contacts, width, and thickness of the sample, respectively.

When the magnetic field $\mathbf{H} \parallel c$ is applied and the transversal component of thermal

conductivity κ_{xy} appears, Eq. 3.8 can be written as

$$\begin{pmatrix} q_x \\ q_y \end{pmatrix} = - \begin{pmatrix} \kappa_{xx} & \kappa_{xy} \\ \kappa_{yx} & \kappa_{yy} \end{pmatrix} \begin{pmatrix} \nabla_x T \\ \nabla_y T \end{pmatrix}, \quad (3.11)$$

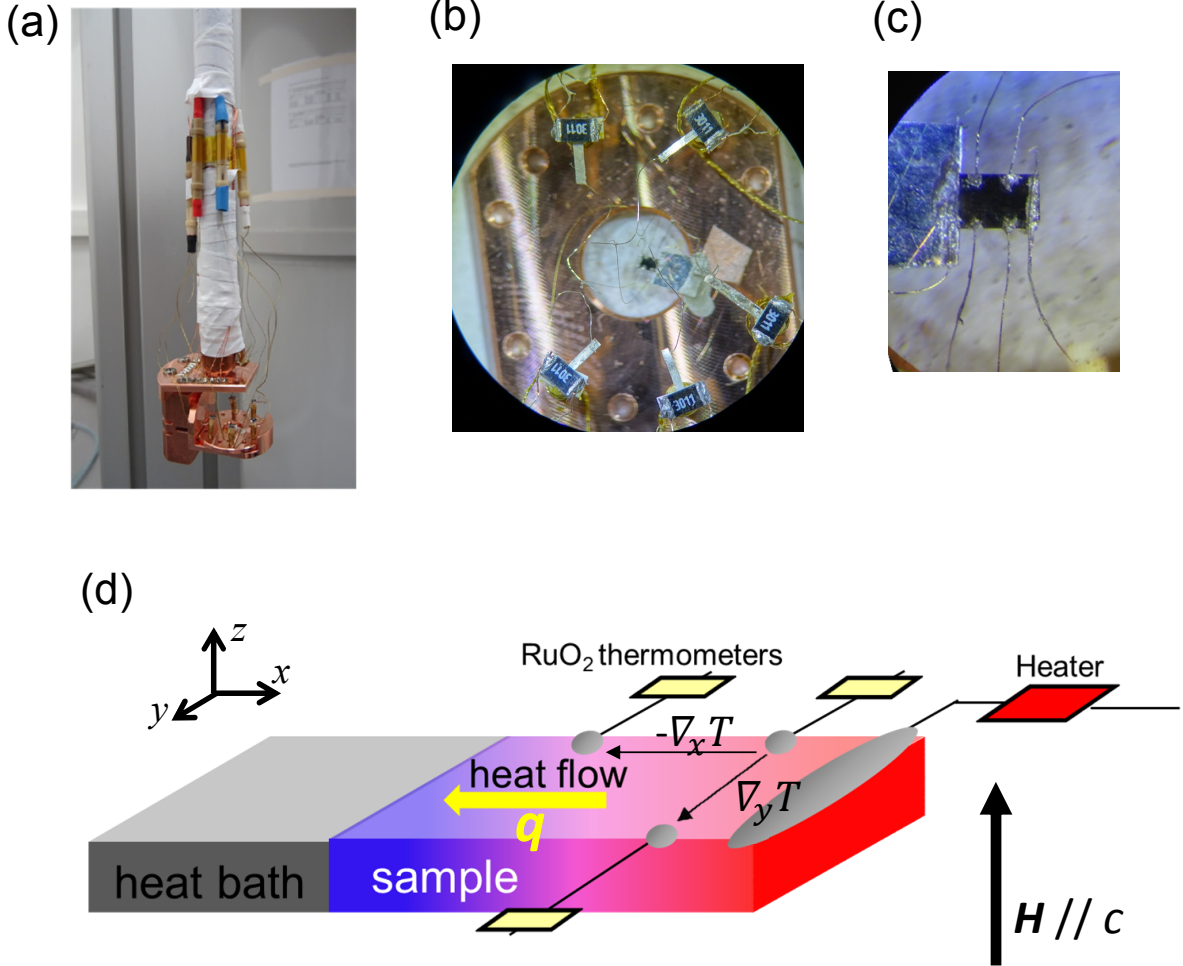


Figure 3.4: (a) Bottom of the ^3He cryostat. The measurement cell is located at the lowest part. (b) Measurement cell for thermal and electrical transport measurements. There are five RuO₂ bare chips, one is for the heater and four are for the thermometers. Three thermometers are sufficient for the κ_{xx} and κ_{xy} measurements, hence, one of the thermometers is a backup. (c) Measured FeSe single crystal with the contacts. To reduce contact resistance, we attached gold wires by indium soldering. (d) Schematic illustration of the setup for the thermal transport measurements. When $\mathbf{H} \parallel c$ is applied, the transversal component of thermal conductivity κ_{xy} appears. Here, $\nabla_x T$ and $\nabla_y T$ denote the longitudinal and transversal thermal gradient, respectively, and $\mathbf{q}(\parallel x)$ is the heat flow.

where $\kappa_{yx} = -\kappa_{xy}$, $\kappa_{xx} = \kappa_{yy}$, and q_x , q_y are the longitudinal and transverse thermal current densities, respectively. In the steady state, $q_y = 0$, and hence,

$$q = -\kappa_{xx}\nabla_x T - \kappa_{xy}\nabla_y T, \quad (3.12)$$

$$0 = \kappa_{xy}\nabla_x T - \kappa_{xx}\nabla_y T, \quad (3.13)$$

where ∇_x and ∇_y are the thermal gradients along the heat current and the ones generated along the transverse direction, respectively. Finally, we obtain

$$\kappa_{xx} = \frac{W_{xx}}{W_{xx}^2 + W_{xy}^2}, \quad (3.14)$$

$$\kappa_{xy} = \frac{W_{xy}}{W_{xx}^2 + W_{xy}^2}, \quad (3.15)$$

where the longitudinal thermal resistivity W_{xx} and thermal Hall resistivity W_{xy} are given by

$$W_{xx} = -\frac{\nabla_x T}{q} = -\frac{\Delta_x T}{Q} \frac{wt}{l}, \quad (3.16)$$

$$W_{xy} = -\frac{\nabla_y T}{q} = -\frac{\Delta_y T}{Q}. \quad (3.17)$$

Here $\Delta_x T$ and $\Delta_y T$ are the longitudinal and transverse components of the temperature differences, respectively, and we assume that the distance between the pair of transverse contacts is the sample width w , therefore, the transverse thermal gradient can be denoted as $\nabla_y T = \Delta_y T/w$.

We also performed the electrical longitudinal resistivity ρ_{xx} and Hall resistivity ρ_{xy} measurements in the same setups used for the κ -measurements. In the normal state, the thermal conductivity tensors $\bar{\kappa}$ are directly related to the electrical conductivity tensors $\bar{\sigma}$ through the Wiedemann-Franz law, i.e.,

$$\bar{\kappa} = L_0 T \bar{\sigma}, \quad (3.18)$$

where $L_0 = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ is the Lorentz number. In a tetragonal phase

with the transverse condition,

$$\kappa_{xx}^{\text{qp}} = L_0 T \sigma_{xx}, \quad (3.19)$$

$$\kappa_{xy} = L_0 T \sigma_{xy}, \quad (3.20)$$

where the electrical conductivities σ_{xx}, σ_{xy} are given by

$$\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2} \quad (3.21)$$

$$\sigma_{xy} = \frac{\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2}. \quad (3.22)$$

Here, the quasiparticle contribution of the thermal conductivity κ_{xx}^{qp} is obtained by subtracting the phonon contribution κ_{xx}^{ph} from κ_{xx} . In general, the thermal Hall conductivity κ_{xy} is purely electronic in origin.

The thermal Hall angle, Θ_H is defined as

$$\tan \Theta_H \equiv \frac{\kappa_{xy}}{\kappa_{xx}^{\text{qp}}}. \quad (3.23)$$

3.3.2 Misalignment effect

In a real setup for the transport measurements, there may be some misalignment of the contacts. Hence, the thermal gradient $\nabla T(H)$ for the thermal transport measurements and the electrical voltage for the resistivity measurements $V(H)$ between two contacts may contain both the longitudinal and transverse components. Inverting the applied magnetic field direction, we can avoid the misalignment effect and extract the exact longitudinal and transverse gradients, like

$$\nabla_x T(H) = [\nabla T(H) + \nabla T(-H)]/2, \quad (3.24)$$

$$\nabla_y T(H) = [\nabla T(H) - \nabla T(-H)]/2, \quad (3.25)$$

$$V_L(H) = [V(H) + V(-H)]/2, \quad (3.26)$$

$$V_H(H) = [V(H) - V(-H)]/2. \quad (3.27)$$

Here, V_L and V_H are the exact longitudinal and transverse components of the electrical voltage, respectively. Then, we obtain the field dependence of the thermal and electrical resistivity tensors,

$$W_{xx}(H) = -\frac{\nabla_x T(H)}{q}, \quad (3.28)$$

$$W_{xy}(H) = -\frac{\nabla_y T(H)}{q}, \quad (3.29)$$

$$\rho_{xx}(H) = \frac{V_L(H)}{J} \frac{wt}{l}, \quad (3.30)$$

$$\rho_{xy}(H) = \frac{V_H(H)t}{J}. \quad (3.31)$$

Here J is the electrical current.

3.3.3 Setups of thermal transport measurements

The thermal conductivity and thermal Hall conductivity were measured by the standard six-wire steady-state method with a one-heater and four-thermometer technique. One of the thermometers is for backup. The actual setup is presented in Figs. 3.4(b) and (c). Low contact resistance is required because a large contact (thermal) resistance may mask the sample response. In this study, we adopted indium-soldering with an ultrasonic iron for making contacts to reduce the contact resistance. Actually, attaching the normal silver pastes on FeSe may cause a large contact resistance of more than several k Ω s because the surface of the FeSe may be oxidized. Using the ultrasonic iron, we can remove the oxidized layers without using any chemical flux which may cause damage to the sample surface. Eventually, we obtained a contact resistance less than 100 m Ω , which is sufficient for the thermal and electrical transport measurements in this study.

The sample was thermally anchored to a Cu heat sink through the attached silver foil. To read the temperatures at each contact, the RuO₂ thermometers were thermally connected through the gold wires and silver foils attached in the back. The four RuO₂ thermometers and the resistive heater are thermally isolated from the heat sink, using Manganin wires with low thermal conductivity as their electrical leads, and they are

glued using a GE varnish on top of wooden sticks.

The thermal and electrical transport measurements were performed down to ~ 250 mK using a ^3He cryostat, and we applied a static magnetic field up to 20 T along the c -axis of the FeSe single crystal at the HLD-EMFL high magnetic field laboratory in Dresden in Germany.

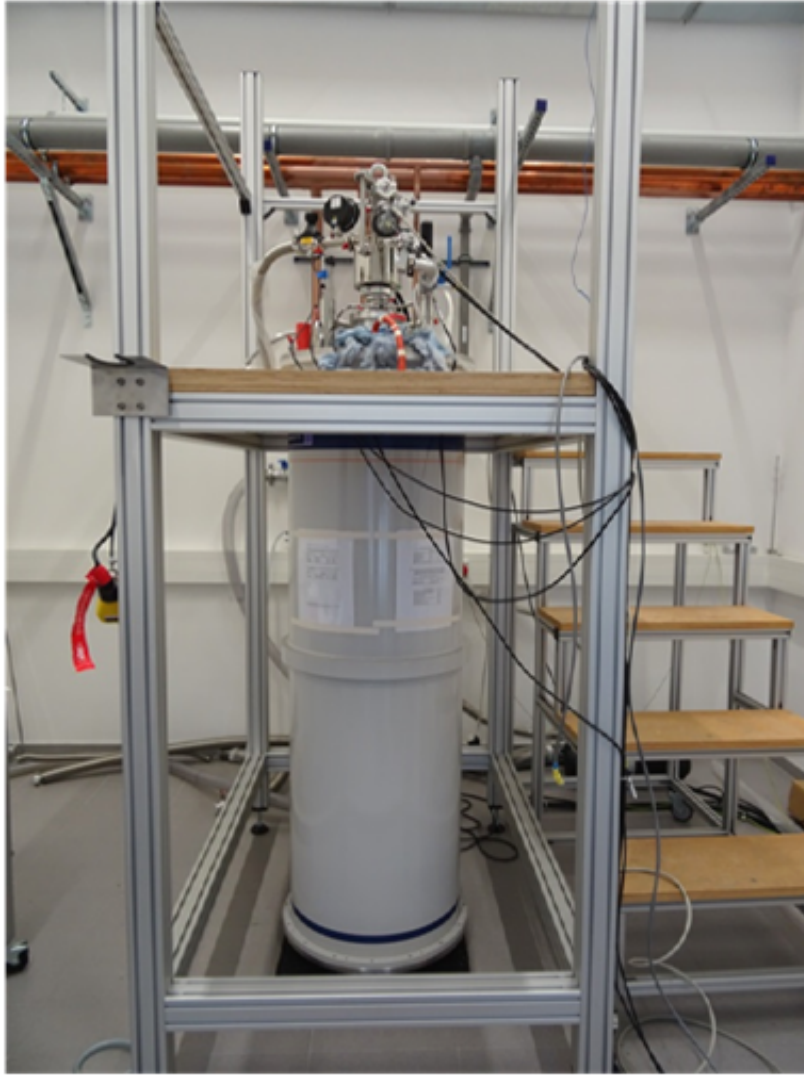


Figure 3.5: Dewar at the HLD-EMFL in Dresden in Germany. A 20-22 T magnet is inserted. In this picture magnetic field is applied along the vertical direction, and we applied the static magnetic field along the c -axis in this study.

4 Properties of FeSe

4.1 Crystal structure

Among iron-based superconductors, FeSe has the simplest crystal structure, with PbO-type structure as shown in Fig. 4.1 [35]. FeSe contains only two kinds of elements, Fe and Se, which form the electronically conducting iron-chalcogenide (Fe-*Ch*) layers stacked along *c*-axis. At room temperature, the crystal structure is tetragonal, with the space group $P4/nmm$ as shown in Fig. 4.1(b). In the tetragonal phase, the lattice constants are $a = 3.774 \text{ \AA}$ and $c = 5.524 \text{ \AA}$, respectively. With decreasing temperature, the transition from tetragonal to orthorhombic crystal structure occurs, and the in-plane lattice parameter splits into a and b ($a > b$) at the temperature $T_s \sim 90 \text{ K}$ (Fig. 4.2). In the orthorhombic phase, the lattice distortion $\delta = (a - b)/(a + b)$ is $\sim 0.3\%$ [36].

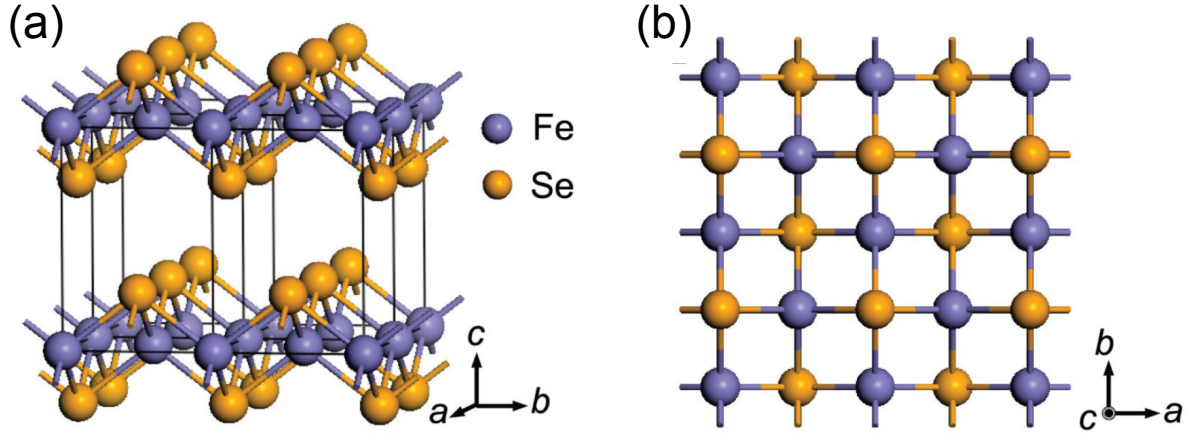


Figure 4.1: (a),(b) Schematic crystal structure of FeSe. The conducting Fe-Se layers are stacked along the *c*-axis. At room temperature, the crystal structure is tetragonal [35].

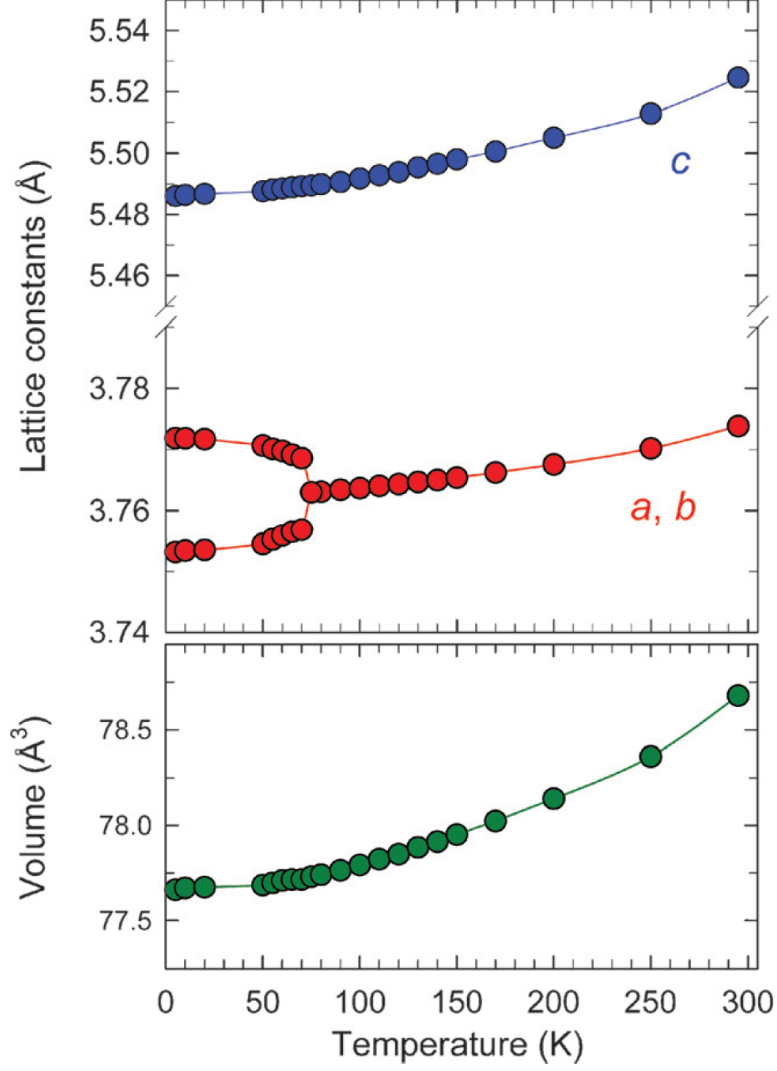


Figure 4.2: Temperature dependence of the lattice constants (top) and the unit cell volume (bottom) in $\text{FeSe}_{0.92}$, confirmed by synchrotron X-ray diffraction measurements [36]. The lattice parameters of the a - and b -axes show the deviation due to the structural transition from tetragonal to orthorhombic structure.

4.2 Properties of FeSe single crystals grown by self-flux method

Fig. 4.3 shows the temperature dependence of the electrical resistivity ρ and the H - T phase diagram obtained from the resistivity curves at each magnetic fields in a FeSe_{0.88} single crystal fabricated by the self-flux method [35]. In the low temperature region, the zero resistivity due to the superconducting transition occurs at $T_c^0 \sim 8$ K. In contrast to most superconductors, T_c is suppressed linearly with respect to the magnetic field H down to 0 K [35, 37]. The linear extrapolation of the H_{c2} -curve gives rise to

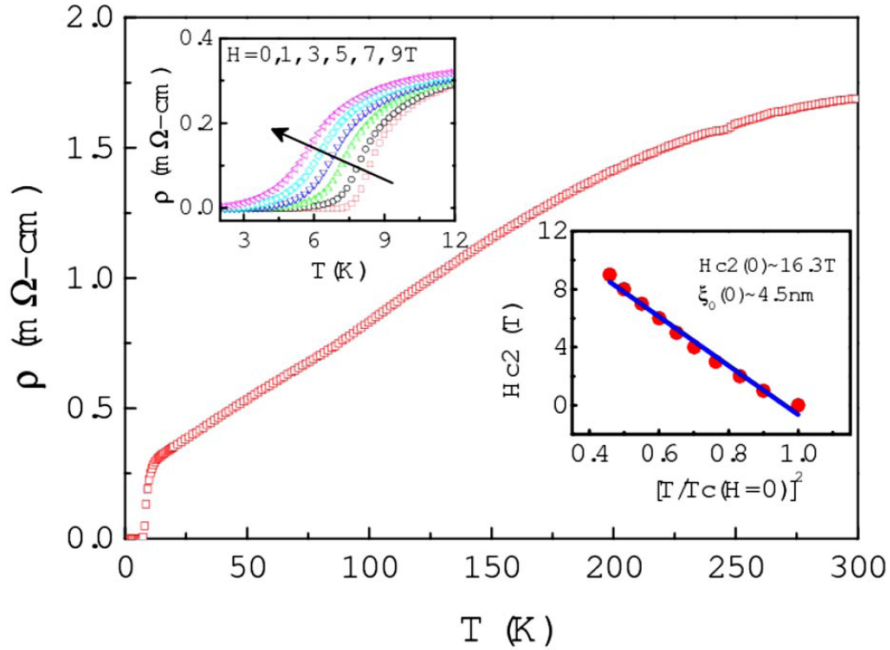


Figure 4.3: Temperature dependence of the electrical resistivity ρ of a FeSe_{0.88} single crystal fabricated by the self-flux method [35]. The left inset is ρ vs. T in the low temperature region under a magnetic field $\mathbf{H} \parallel c$. The right inset is the H - T phase diagram. In the high temperature region around $T_s \sim 90$ K, where the structural transition occurs, an anomalous downturn appears in the resistivity. At $H = 0$ T, the zero resistivity due to the superconducting transition occurs at $T_c^0 \sim 8$ K. T_c is suppressed linearly with respect to the magnetic field H and the linear extrapolation of the H_{c2} -curve gives rise to $H_{c2}(T = 0 \text{ K}) \sim 16.3$ T. The residual resistivity ratio (RRR) is ~ 6 . In the normal state, the positive but small magnetoresistance appears under the magnetic field.

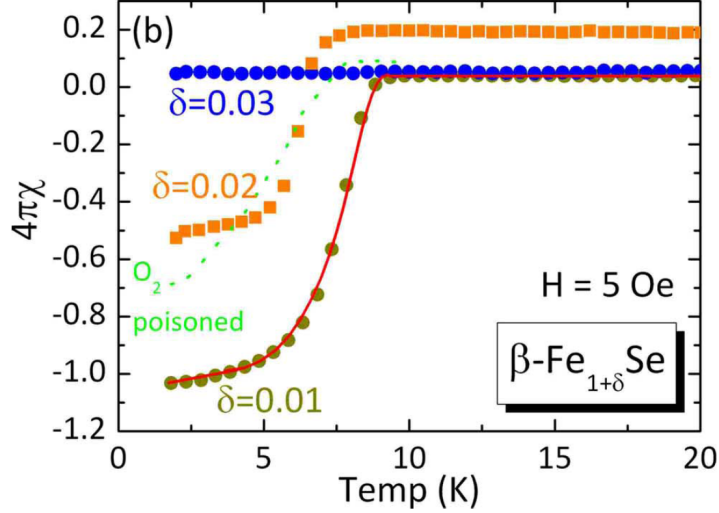


Figure 4.4: Temperature dependence of the magnetic susceptibility χ in $\text{Fe}_{1+\delta}\text{Se}$, where δ denotes the concentration of excess Fe atoms. At $\delta = 0.03$, the diamagnetism due to the superconducting transition is not observed down to 2 K, while the Meissner effect is observed with the onset temperature $T_c^{\text{onset}} \sim 8.5$ K. This indicates that the superconductivity is dramatically suppressed by excess Fe atoms [39], i.e., the electronic properties of FeSe are very sensitive to impurities and defects.

$H_{c2}(T = 0 \text{ K}) \sim 16.3$ T in this sample. The residual resistivity ratio (RRR) is ~ 6 . In the normal state, the resistivity slightly goes up with increasing magnetic field, indicating a positive but small magnetoresistance with $\Delta\rho/\rho \sim 10\%$ at 9 T, where $\Delta\rho = \rho(H) - \rho(0)$.

In the high temperature region, around 90 K, an anomalous kink appears in the resistivity. This comes from the structural transition from the tetragonal to the orthorhombic phase. As will be discussed later, the electronic nematic transition triggered by the d_{xz}/d_{yz} orbital ordering at the same temperature [38] and the electronic structures along the a - and b -axes become nonequivalent. Unlike the other iron-based superconductors, such as 1111 and 122 systems, no antiferromagnetic order has been reported down to $T = 0$ K at ambient pressure, i.e., peculiar electronic properties associated with the nematicity appear below T_s .

However, 1:1 stoichiometric and clean single crystals which are sufficient for investigating the itinerant properties of FeSe are difficult to obtain with the above self-flux

method because of the large amount of impurities or defects, such as contaminated excess Fe atoms. In fact, it has been reported that the superconductivity is rapidly suppressed as the concentration of excess Fe atoms δ increases, and no superconducting transition is shown at $\delta = 0.03$ down to 2 K, as shown in Fig. 4.4 [39]. This means that the electronic properties of FeSe are very sensitive to impurities and defects.

4.3 Clean FeSe single crystals grown by the vapor transport method

Recently, using a vapor transport technique with KCl and AlCl₃ flux, the KIT group in Germany has succeeded in growing ultraclean and stoichiometric FeSe single crystals with an extremely low impurity level [33]. The detailed procedures of the sample growth are presented in Ref. 33 and in the following section in Section 6.

According to Ref. 33, X-ray powder diffraction confirms the tetragonal structure with lattice constants $a = 3.7707(12)$ Å and $c = 5.521(3)$ Å, which are the almost same values reported in the single crystals grown by the self-flux method. The stoichiometric composition of Fe and Se within the error (Fe:Se = 0.995(4):1) is confirmed by structural refinement with a four-circle diffractometer.

Previously, we reported the physical properties of these samples in Ref. 37. Fig. 4.5(a) is ρ vs. T in all temperature regions. A clear kink anomaly at $T_s \approx 87$ K appears due to the structural transition. Below T_s , the resistivity goes down linearly with respect to T . As a result of linear extrapolation of the resistivity down to 0 K, we obtained the residual resistivity $\rho_0 \sim 1.7 \mu\Omega\text{cm}$, which gives rise to $RRR \sim 240$. The small value of ρ_0 and large value of RRR indicate an ultraclean single crystal. In the low temperature region, the superconductivity appears and the resistivity goes to zero at $T_c^0 \sim 9.40$ K, which is slightly higher than the one in single crystals grown by the self-flux method. In Fig. 4.5(b), the magnetic susceptibility measured under zero-field cooling conditions shows a superconducting transition with the width (10–90%) of $\delta T_c \sim 0.3$ K, which is much sharper than one in samples grown by the self-flux method, as shown in Fig. 4.4 [39].

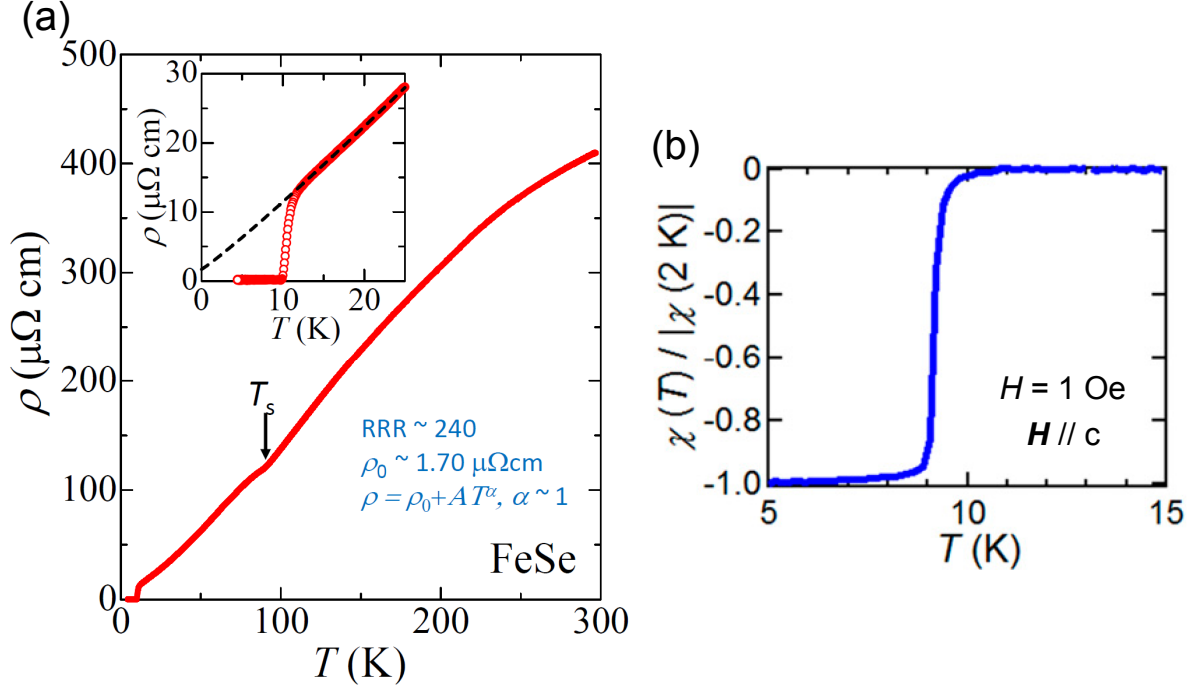


Figure 4.5: (a) Temperature dependence of the resistivity of the FeSe single crystals grown by the KCl/AlCl₃ vapor transport technique. The inset is ρ vs. T in the low temperature region. (b) Low-temperature magnetic susceptibility of the FeSe single crystal grown by the vapor transport method. The measurements were performed under zero-field cooling conditions. The superconducting transition temperature defined as the midpoint is $T_c^x \approx 9.25$ K, which is very close to T_c^0 determined by the resistivity measurement. The width (10-90%) of the transition is $\Delta T_c \sim 0.3$ K, which is much sharper than the one in samples grown by self-flux method, as shown in Fig. 4.4 [39], indicating the high homogeneity of the measured sample in Ref. [37].

Fig. 4.6(a) shows the ρ - T curves in the low temperature region under magnetic fields up to 12 T, and Fig. 4.6(b) is the field dependence of normalized magnetoresistance $\Delta\rho/\rho = (\rho(H) - \rho)/\rho$ in the normal state. In contrast to the self-flux samples, the resistivity in the normal state is dramatically enhanced with the increasing applied field, indicating a huge magnetoresistance. $\Delta\rho/\rho = (\rho(H) - \rho)/\rho$ exhibits an H^α ($\alpha \sim 2$) dependence without saturation, which demonstrates the nearly perfect compensation, i.e., an equal density of electrons and holes, $n_h = n_e$ [37, 40]. In a compensated metal, the magnetoresistance is given by

$$\Delta\rho/\rho = (\omega_c^e \tau_e)(\omega_c^h \tau_h), \quad (4.1)$$

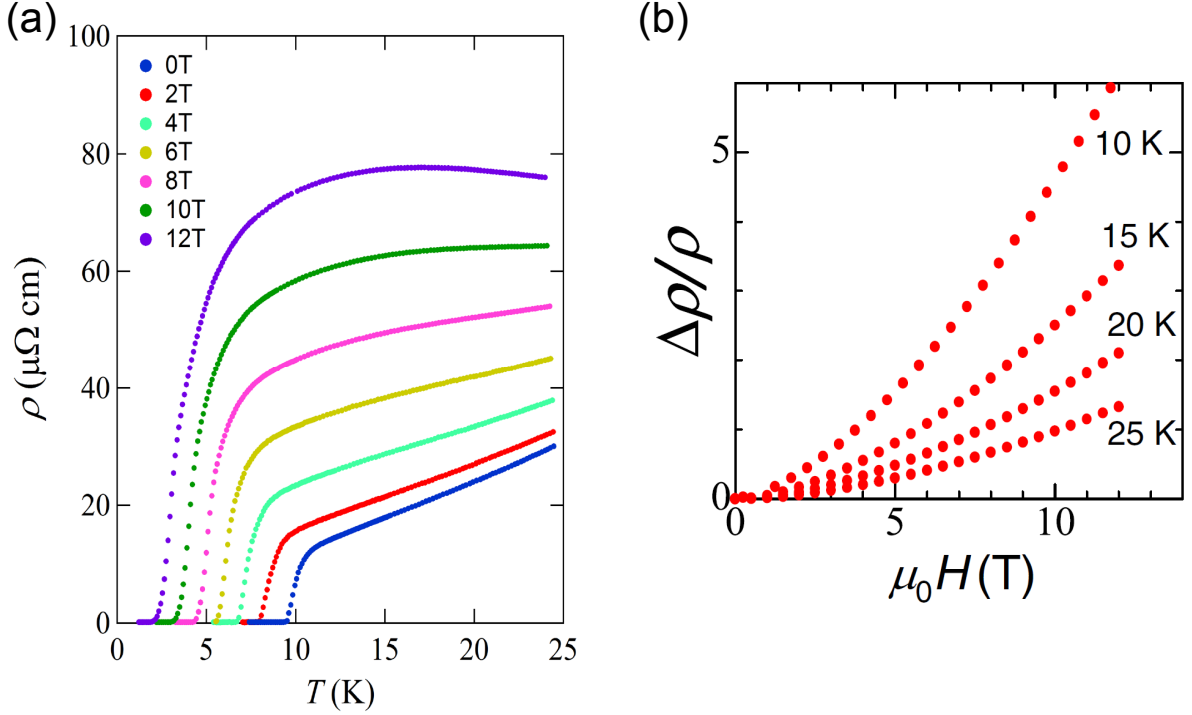


Figure 4.6: (a) ρ - T curves in the low temperature region under magnetic fields up to 12 T. From bottom to top, the applied magnetic fields are $\mu_0 H = 0, 2, 4, 6, 8, 10$, and 12 T. (b) Field dependence of the normalized magnetoresistance $\Delta\rho/\rho = (\rho(H) - \rho)/\rho$ in the normal state. $\Delta\rho/\rho$ exhibits an H^α ($\alpha \sim 2$) dependence without saturation, which indicates that the sample is a compensated metal with an equal density of electrons and holes, $n_h = n_e$. [37].

where $\omega = eB/m$ is the cyclotron frequency for carriers with mass m and scattering time τ [41]. The suffixes e and h denote “electron” and “hole,” respectively. At $T = 10$ K, we estimate $(\omega_c^e \tau_e)(\omega_c^h \tau_h) \approx 5$ at 10 T, indicating the high mobility of the charge carriers $\mu = e\tau/m$.

The extremely small level of impurities and defects are also confirmed by scanning tunneling microscope (STM) topography with atomic spatial resolution [37]. Fig. 4.7(a) is a $5 \times 5 \text{ nm}^2$ and Fig. 4.7(b) is a $45 \times 45 \text{ nm}^2$ topographic image taken at $T \sim 0.4$ K in the orthorhombic phase, respectively. Since the orthorhombic distortion is too small to be resolved by STM, the observed topmost Se atoms of the Fe-Se layers form a square lattice with the obtained in-plane lattice constant $\sim 3.7 \text{ \AA}$, which shows good agreement with other reports [33, 36]. The white bright spots scattered across the

topographic image in Fig. 4.7(b) are impurities or defects, whose concentration is less than 1/5000 Fe atoms.

Since the breakthrough in sample growth, large amounts of research has been done on clean FeSe single crystals and have reported that it exhibits several unique properties.

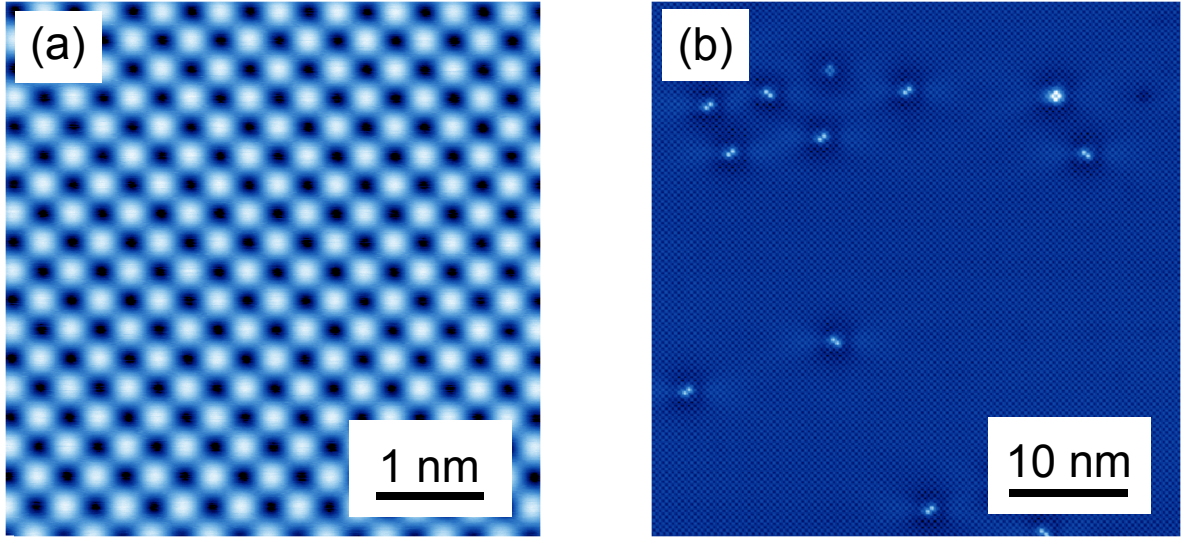


Figure 4.7: (a) $5 \times 5 \text{ nm}^2$ topographic image taken at $T \sim 0.4 \text{ K}$ in the orthorhombic phase. Set-point conditions are sample bias voltage $V_s = +95 \text{ mV}$ and tunneling current $I_t = 100 \text{ pA}$. Since the orthorhombic distortion is too small to be resolved by STM, the observed topmost Se atoms of the Fe-Se layers form a square lattice. The obtained lattice constant is $a \approx b \sim 3.7 \text{ \AA}$. (b) $45 \times 45 \text{ nm}^2$ topographic image taken at $T \sim 0.4 \text{ K}$. Set-point conditions are sample bias voltage $V_s = +50 \text{ mV}$ and tunneling current $I_t = 100 \text{ pA}$. White bright spots are impurities or defects, whose concentration is less than 1/5000 Fe atoms. [37].

4.4 Phase diagram of S-doped FeSe system

In this section, we will discuss substitution effect on FeSe and show the phase diagram of S-doped FeSe system.

First, for comparison, we display phase diagrams of F-doped LaFeAsO [42] and P-doped BaFe₂As₂ systems in Fig. 4.8 [43]. In the La-1111 system, replacing O atoms for F atoms, the electron-carriers are doped. In the undoped and underdoped regions with the F-substitution below 4.5 %, superconductivity does not appear. Instead, in the non-superconducting region, the structural transition from tetragonal (space group P4/nmm) to monoclinic (space group P112/n) [44] and antiferromagnetic ordering have been reported [44, 45]. Above 4.5 %, the structural and antiferromagnetic transitions disappear and the superconducting phase appears. In the Ba-122 system, the parent compound BaFe₂As₂ shows antiferromagnetic order with the structural transition from tetragonal to orthorhombic structure at the temperature $T_N, T_s = 135$ K, while the superconductivity does not appear in the low temperature region. With increasing electron doping (Co substitution for Fe atoms) [46], hole doping (K substitution for Ba atoms) [47], or isovalent substitution (P replacement for As atoms) [48], T_s and T_N are suppressed and the dome-shaped superconducting phase appears. In these systems,

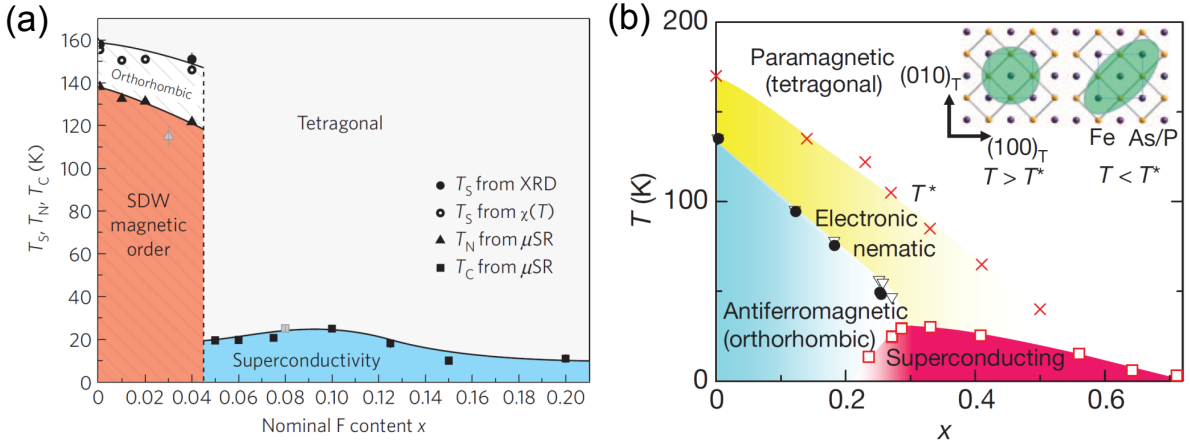


Figure 4.8: Phase diagram of (a) F-doped La-1111 system [42] and (b) P-doped Ba-122 systems [43]. The superconducting phases are located near the SDW phases. In the 122 systems, the electronic nematic phase transition has been reported above T_s [43, 49, 50].

electronic nematic phase transitions above T_N and T_s have been reported, as shown in the phase diagram of the $\text{BaFe}_2(\text{As}, \text{P})_2$ system (Fig. 4.8(b)) [43, 49, 50]. In the nematic phase, the symmetry of the electronic structure spontaneously breaks the rotational symmetry of the crystal structure. In these systems, the superconducting phases are located in the vicinity of the SDW phase.

However, the substituted FeSe system is strikingly different from typical iron-based superconductors in some points as shown in the phase diagram of S-doped FeSe system (Fig. 4.9(c)) [51]. Firstly, the parent compound FeSe shows a superconductivity with $T_c \approx 8 - 9$ K, unlike the non-superconducting parent compounds LaFeAsO and BaFe_2As_2 . With increasing the sulfur concentration x , T_c slightly goes up to ≈ 10.5 K around the optimal doping level $x \sim 0.08$, and after that, starts to decline. Secondly, no antiferromagnetic order has been reported down to $T = 0$ K at ambient pressure, while the structural transition from the tetragonal to the orthorhombic phase and the nematic transition at around 90 K occur, as discussed in the previous section. The nematic transition temperature T_s monotonically decreases with increasing the S-doping level, and completely vanishes at around $x \sim 0.17$. It has been reported that the nematic susceptibility is divergently enhanced at the point $x \sim 0.17$, as shown in Fig. 4.9(c). This result indicates that a nematic quantum critical point (QCP) is located at $x \sim 0.17$, where the nematic fluctuation are diverging toward $T \rightarrow 0$ K. In 122 systems, the nematic phases have been also reported, however, they are located in the vicinity of the SDW phase and the SDW QCP [52]. Since the magnetic order is absent unlike most of iron-based superconductors, FeSe is a unique platform to investigate the relationship between the superconductivity and the non-magnetic nematic QCP.

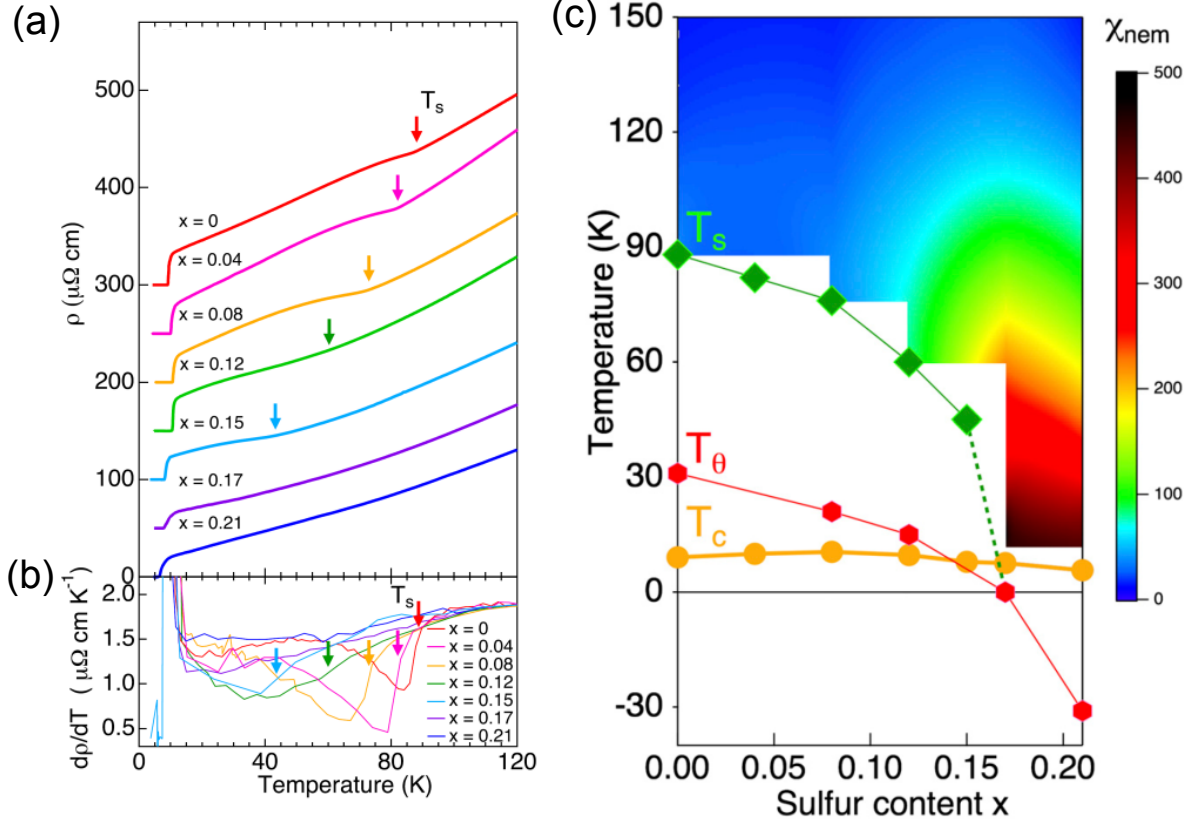


Figure 4.9: (a),(b) Temperature dependence of resistivity ρ and the differential $d\rho/dT$ in FeSe_{1-x}S_x single crystals with different x , respectively. The arrows indicate the nematic (structural) transition temperature T_s estimated from the inflection point. (c) Phase diagram of FeSe_{1-x}S_x obtained from the resistivity and nematic susceptibility data. Temperature dependence of the nematic transition (T_s , green diamonds) and the superconducting transition temperature (T_c , orange circles) determined by the zero resistivity criteria. The magnitude of the nematic susceptibility χ_{nem} in the tetragonal phase is superimposed in the phase diagram by a color contour. The nematic transition temperature T_s monotonically decreases with increasing the S-doping level, and completely vanishes at around $x \sim 0.17$, where χ_{nem} is strongly enhanced. This result indicates that a nematic QCP is located at $x \sim 0.17$ [51].

4.5 Superconducting gap structure in FeSe

Scanning tunneling spectroscopy (STS) is a powerful probe to investigate the detailed superconducting-gap structure, since the taken tunneling conductance dI/dV is proportional to the local density of states (LDOS).

Figure 4.10(a) shows the tunneling conductance spectrum in the superconducting state [37]. Distinct peaks and shoulder structures in the spectra indicate the presence of (at least) two superconducting gaps ($\Delta_1 \approx \pm 2.5$ meV and $\Delta_2 \approx \pm 3.5$ meV), reflecting the multigap nature. The ratios $2\Delta/k_B T_c$ are 6.4 for Δ_1 and 9.0 for Δ_2 , much larger than the value in the BCS limit, indicating strong pairing interactions. This result is consistent with the specific heat measurements in which large specific heat jumps are observed at T_c [53–55].

The V-shaped spectrum at low bias voltages indicates the presence of line nodes, which is consistent with previous STS observations in the ultraclean thin film with an impurity level of less than 1/70,000 Fe atoms [56]. Recently, our thermal conductivity measurements on the ultra clean single crystals have also reported a finite residual thermal conductivity κ_0/T at $T \rightarrow 0$, which comes from low-energy quasiparticle excitation near the line nodes [37] (Fig. 4.10(b)).

However, there are several reports which suggest nodeless structure, probed by muon-spin-rotation [57], specific heat [53, 55], thermal conductivity [58, 59], and STS measurements [55, 60]. These results indicate that the line nodes are easily lifted by small amounts of impurities, i.e., are not symmetry-protected. Moreover, we have also reported that twin boundaries (TBs), the interfaces between two neighboring crystallographic domains, lift the superconducting-gap nodes even in the ultraclean samples due to the time-reversal symmetry breaking (TRSB) effect, as will be discussed in the following section [61].

To be summarize, ultraclean FeSe is a multi-gapped extended *s*-wave superconductor with accidental line nodes; however, they are easily lifted by impurities or twin boundaries.

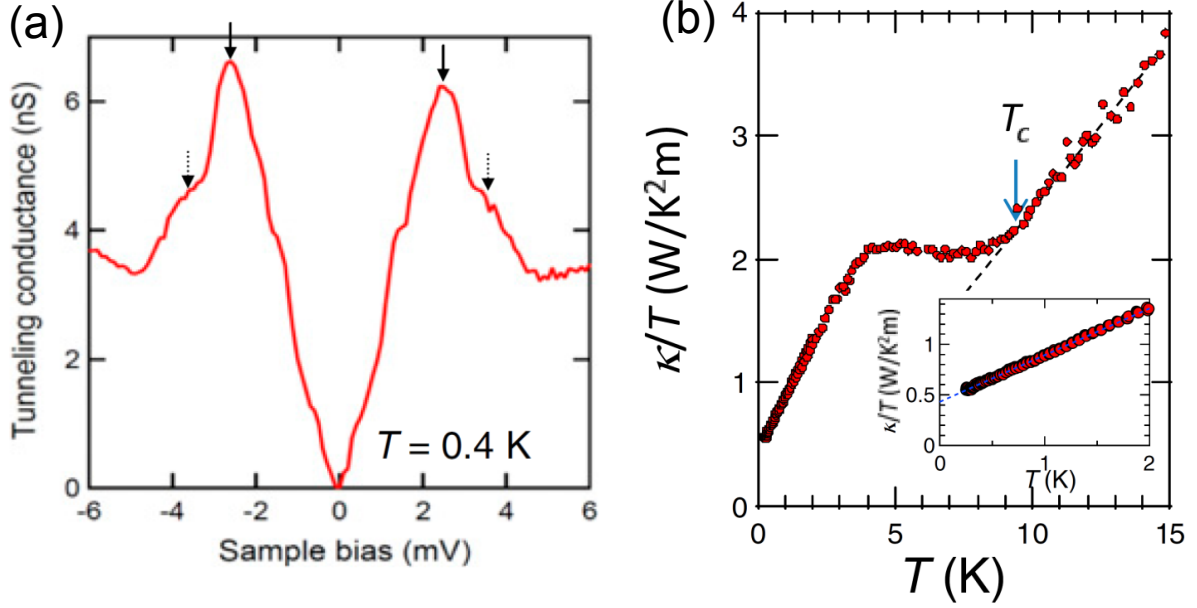


Figure 4.10: (a) STS spectrum at $T \sim 0.4$ K. The peaks at $\Delta_1 \approx \pm 2.5$ meV (arrows) and shoulder structures at $\Delta_2 \approx \pm 3.5$ meV (dashed arrows) indicate multiple superconducting gaps [37]. (b) Temperature dependence of the in-plane thermal conductivity divided by temperature, κ/T . Arrow marked T_c indicates the superconducting transition temperature determined by zero resistivity in Fig.4.5(a). The inset is κ/T at low- T , with the fit to $\kappa/T = \kappa_0/T + \beta T$ (blue dashed line). The extrapolation to $T = 0$ leads to a finite residual thermal conductivity κ_0/T , indicating the presence of nodes [37].

4.6 Pressure effect

Pressure effects on FeSe have attracted significant interest, because it shows a complex phase diagram with respect to pressure and T_c is dramatically enhanced under pressure, unlike other iron-based superconductors [62–68].

Fig. 4.11(a),(b) show the temperature dependence of resistivity under pressure and Fig. 4.11(c) is the T - P phase diagram in FeSe obtained from the results in Fig. 4.11(a) and (b) [68]. At ambient pressure, the structural and nematic transition occurs at $T_s \sim 90$ K and the resistivity goes to zero due to the superconducting transition at $T_c \approx 9$ K. The nematic phase is suppressed by the applied pressure and completely disappears at around ~ 2 GPa. What is interesting is that another kink anomaly appears in the resistivity in the normal state above 1.63 GPa, indicating the pressure-induced magnetic order at T_m , while at ambient pressure no magnetic transition has been observed down to 0 K. The magnetic order has been corroborated by the recent quantum oscillation measurements under pressure; the Fermi surface reconstruction due to the antiferromagnetic transition has been observed [69, 70]. The spin density wave

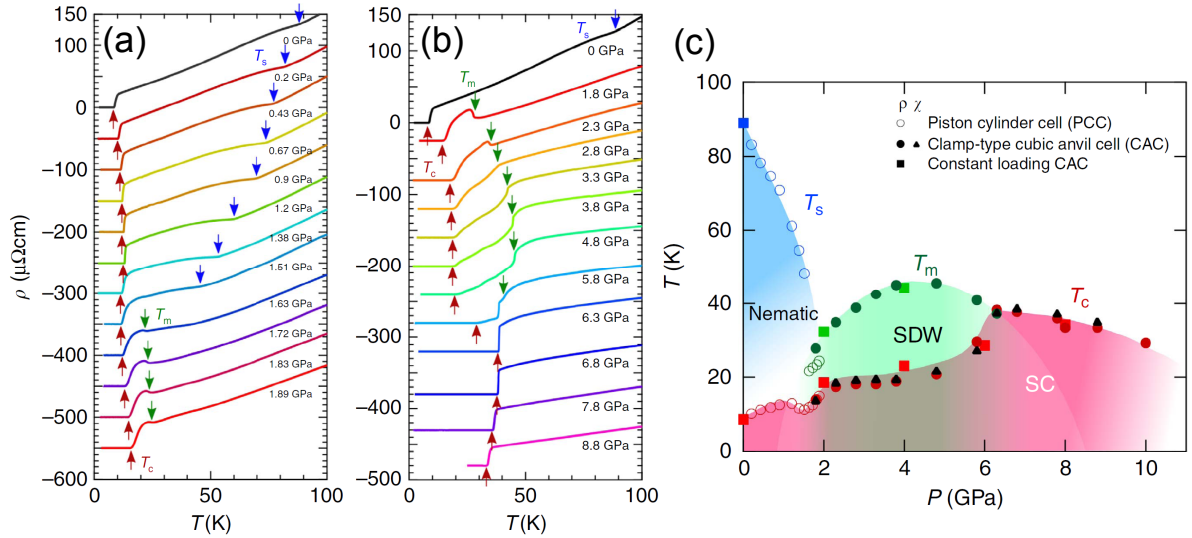


Figure 4.11: (a),(b) Temperature dependence of the resistivity in clean FeSe single crystals under high pressure. The structural and nematic (T_s), antiferromagnetic (T_m), and superconducting transition temperatures (T_c) are marked by the blue, green, and red arrows, respectively. (c) Temperature-pressure phase diagram of bulk FeSe. [68].

(SDW) phase exhibits a dome-shaped pressure dependence with the maximum $T_m \approx 45$ K at 4.8 GPa. The pressure dependence of T_c shows nearly step-like enhancements at ~ 2 GPa ($\sim 10 \rightarrow 20$ K) and ~ 6 GPa ($\sim 20 \rightarrow 38.5$ K), which are close to the two ends of the dome-shaped SDW phase. This result indicates that the superconductivity in FeSe is intimately correlated with the magnetism. The highest superconducting transition temperature is $T_c = 38.5$ K at 5.8 GPa, more than four times larger than the value at ambient pressure.

The measurements were conducted on clean single crystals grown by the vapor transport method. Similar behavior also appears in the self-flux samples and powder samples [62, 65, 66].

4.7 Mono-layer FeSe thin film

Among the bulk systems of iron-based superconductors, the reported highest superconducting transition temperature is $T_c \sim 55$ K in $\text{SmFeAsO}_{0.9}\text{F}_{0.1}$ [9]. On the other hand, recent experiments have revealed that the T_c values can be well above 60 K in single-layer FeSe on SrTiO_3 substrate [10–12].

Fig. 4.12(a) is the symmetrized energy distribution curves (EDCs) for the electron-like Fermi surface near the M point at different temperatures in the single-layer FeSe, taken by angle-resolved photoemission spectroscopy (ARPES) measurements. In the low- T spectra, pairs of superconducting coherence peaks appear, and the suppression of density of states due to the superconductivity is observed around the Fermi energy. Remarkably, this behavior still remains at 65 K, indicating extremely high- T_c in the mono-layer FeSe thin film. The size of the superconducting gap can be estimated from the ARPES spectra. Fig. 4.12(b) is the temperature dependence of the energy gap size. The finite gap exists up to $T_c \approx 65$ K, and the extrapolation of the $\Delta(T)$ curve to $T \rightarrow 0$ gives rise to $\Delta(0) \sim 19$ meV, which is more than five times larger than the one in the bulk [12].

Scanning tunneling spectroscopic (STS) measurements have also confirmed the extremely large energy gap of the one-layer FeSe. The STS spectrum taken at $T = 4.2$ K

is shown in Fig. 4.12(c) [71]. The pair of coherence peaks implies that the anomalously large superconducting gap $\Delta \approx \pm 15$ meV is opening. STS spectra in the superconducting state provide important information about the gap structure. The taken spectrum has a completely flat region with the zero conductance around the Fermi energy, indicating a fully-gapped plane *s*-wave superconductor.

The diamagnetic response under a magnetic field, i.e., the Meissner effect, can strongly corroborate the superconductivity. Fig. 4.12(d) is the temperature dependence of the Meissner signal of the single-layer FeSe, taken by the mutual inductance measurements, and a clear Meissner effect is observed below $T_c = 65$ K [72].

The ARPES measurements have revealed that the single-layer FeSe is strikingly different from the bulk FeSe in terms of the Fermi surface structure. Fig. 4.12(e) is the Fermi surface of the monolayer FeSe sample. The hole cylinder at the Γ point is absent, and the Fermi surface consists of only the electron-like cylinder around the M point in the single-layer FeSe [10], while in bulk FeSe single crystals, one hole pocket at the Γ -point and one (or two) electron pocket(s) exist, as will be discussed in the later sections. The strong deviations in the Fermi surface structures originate from the electron-like carrier doping from the SrTiO_3 substrate, which is crucial for the emergence of high- T_c superconductivity in the FeSe thin films. In fact, it has been reported that with low carrier concentrations the one-layer FeSe film is insulating, however, with increasing carrier density, the insulating gap shrinks and closes, and instead the superconducting gap appears, as shown in Fig. 4.12(f) [73].

The carrier doping effect has also been investigated in a K-doped three monolayer FeSe system [74]. Electron-like carriers are doped by depositing K-atoms on the bare three monolayer FeSe, which does not exhibit superconductivity, and they have succeeded in inducing high- T_c superconductivity, with the maximum transition temperature $T_c^{\text{max}} \sim 50$ K. In addition, similar T_c enhancement has been reported in FeSe film with an electric double-layer structure [75].

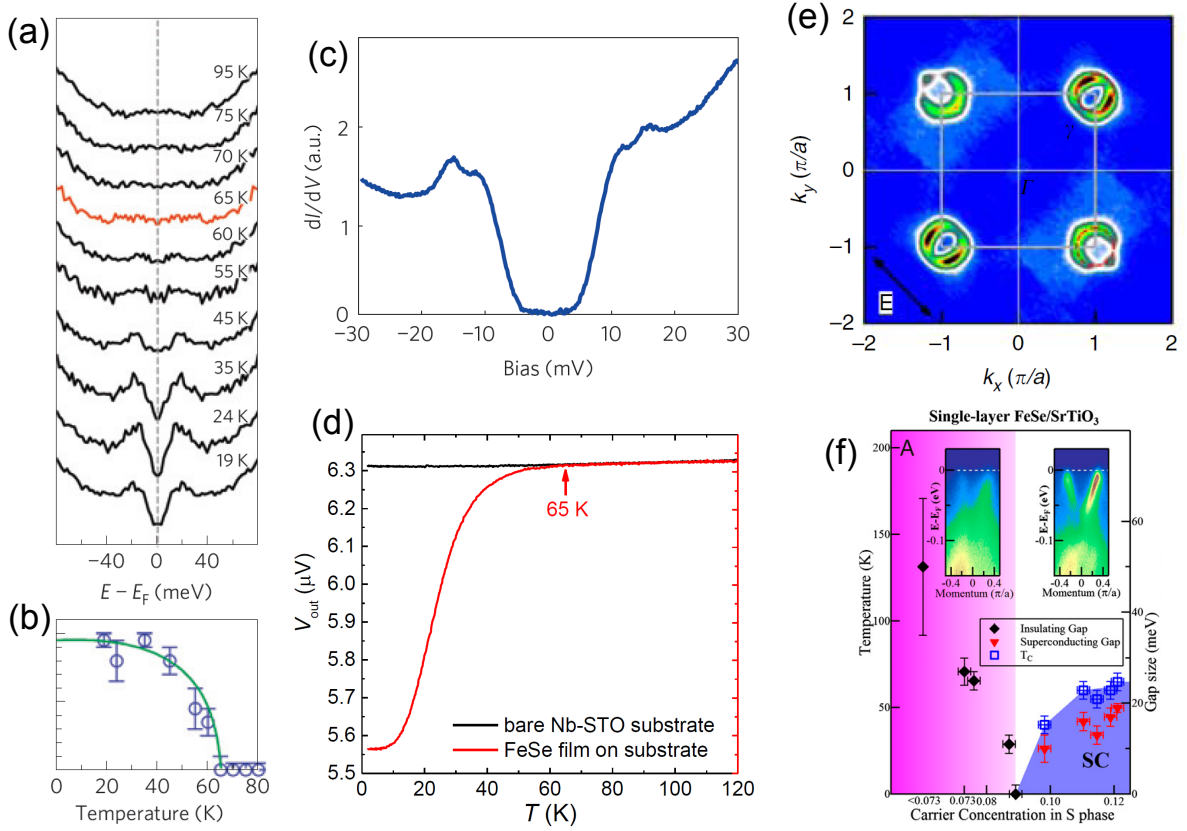


Figure 4.12: (a) Symmetrized EDCs for the electron-like Fermi surface near the M point at different temperatures in the single-layer FeSe, taken by ARPES. Up to $T_c \approx 65$ K, the suppression of density of states due to the superconductivity is observed around the Fermi energy. (b) Temperature dependence of the energy gap size estimated from the ARPES spectra in (a) [12]. (c) STS spectrum of the mono-layer FeSe at $T = 4.2$ K. The anomalously large superconducting gap $\Delta \approx \pm 15$ meV is observed. The completely flat region at the bottom of the spectrum indicates a fully-gapped plane s -wave superconductor [71]. (d) Temperature dependence of the Meissner signal of the single-layer FeSe taken by the mutual inductance measurements (red line) [72]. The black line represents the background which comes from the Nb-doped SrTiO₃ substrate. (e) Fermi surface structure of the single-layer FeSe superconductor revealed by the ARPES measurement. In stark contrast to the bulk FeSe, the hole cylinder at the Γ point is absent and the Fermi surface consists of only the electron-like cylinder around the M point in the single-layer FeSe [10]. (f) Phase diagram of the single-layer FeSe as a function of the carrier concentration x . There is a crossover from insulator to superconductor at $x_c \approx 0.089$. Increasing the carrier concentration above x_c , the superconducting gap and the transition temperature T_c are significantly enhanced [73].

5 Time-reversal symmetry breaking superconducting state around twin boundaries in FeSe

Although we introduced several prominent properties of FeSe in sec. 4, there are still more remarkable electronic and superconducting features in FeSe. The first one is the time-reversal symmetry broken (TRSB) superconducting state around twin boundaries (TBs), and the second one is the comparable scale of the Fermi and the condensation energies, indicating BCS-BEC crossover. As for the second feature, we will discuss it later in sec. 6. In this section, we report the possible TRSB superconducting state near the TB interfaces, revealed by our scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements [61] (**Main work No.2**).

5.1 Introduction

When two superconductors are in close proximity, they are influenced by each other via the tunneling of Cooper pairs. The Cooper pair tunneling results in the flow of a superconducting Josephson current which has been studied for decades and is used in various superconducting quantum devices [76]. The Josephson current is governed by the phase difference of the order parameters of the two superconductors. Therefore, Josephson junctions consisting of unconventional superconductors, where the superconducting order parameter changes its sign depending on the momentum direction, serve as a unique platform where novel phase-related phenomena, e.g., spontaneous formation of half-flux quanta in a trijunction of cuprate superconductors [77], take place. Compared to the well-investigated Josephson currents, the spatial and energy dependence of the superconducting order parameter and quasiparticle states around these junctions

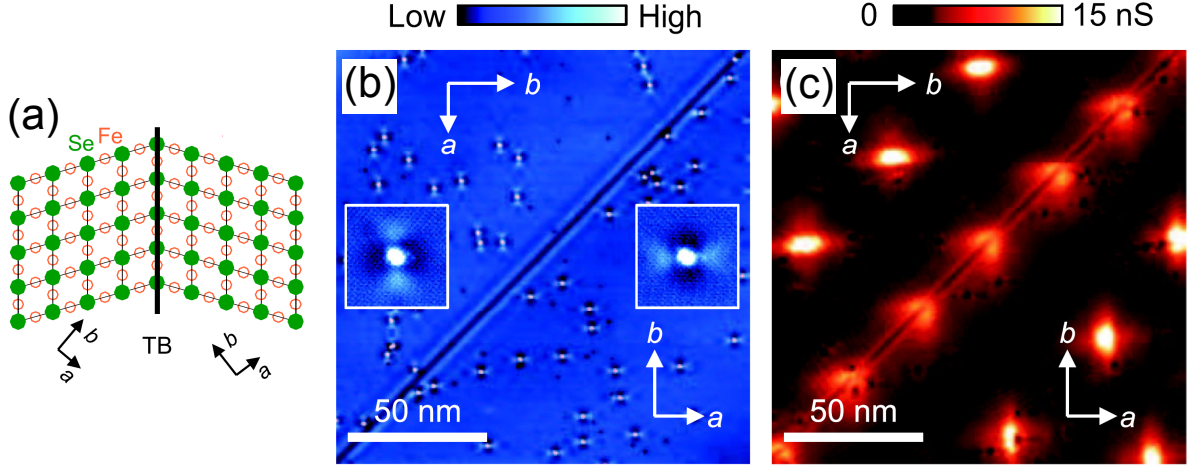


Figure 5.1: (a) Schematic top view of the atomic arrangement near the TB of FeSe (not in scale). Green filled circles and orange open circles denote the topmost Se and Fe atoms, respectively. Se atoms beneath the Fe layer are not shown. (b) A constant-current STM image ($150 \times 150 \text{ nm}^2$) of the cleaved (001) surface of FeSe at 1.5 K showing the TB running from bottom left to top right. Crystallographic axes parallel to the Fe-Fe direction are shown by white arrows ($b > a$). The two insets show a magnified image of the defect ($8.8 \times 8.8 \text{ nm}^2$) in the upper-left and lower-right domain. Note that the pattern is rotated by $\pi/2$ between the two domains. (c) Zero-bias conductance image $g(\mathbf{r}, E = 0)$ at 1.5 K showing vortices. A magnetic field of 1 T is applied along the c axis. The field of view for (b) and (c) is the same [61].

remain to be understood.

STM and STS are powerful probes to visualize the spatial evolution of the electronic states in superconductors. However, STM or STS studies on superconducting junctions made of unconventional superconductors are still demanding. One of the reasons is that it is often challenging to artificially fabricate well-defined junctions of unconventional superconductors. In this study, we found that TBs act as atomically well-defined junctions in FeSe and investigated the superconducting properties around TBs.

5.2 Twin boundary in FeSe

The TB is a crystallographic plane in a crystal shared by two neighboring domains with one being the mirror image of the other. The TBs are often formed by a tetragonal-to-orthorhombic structural phase transition, which reduces the fourfold (C_4) symmetry

at high temperatures to twofold (C_2) symmetry at low temperatures. In such a case, the orthorhombic crystal may contain the TBs parallel to the (110) plane. In FeSe, The tetragonal-to-orthorhombic structural phase transition occurs at $T_s \approx 90$ K and the TBs are spontaneously formed in the orthorhombic phase, as illustrated in Fig. 5.1(a).

Fig. 5.1(b) depicts an STM image of the cleaved surface of a FeSe single crystal at temperature $T = 1.5$ K. There is a shallow groove running along the $[110]$ direction of the Fe lattice, across which the unidirectional feature around the point defect is rotated by $\pi/2$, indicating that the groove represents the TB. We also observe that the elongated vortex cores, which are imaged by the conductance map at the Fermi level ($g(\mathbf{r}, E = 0) \equiv dI/dV(\mathbf{r}, E = 0)$) in a magnetic field, are rotated by $\pi/2$ across the TB (Fig. 5.1(c)). What is intriguing is that the vortices trapped at the TB are not elongated along the TB, demonstrating that the critical current density across the TB is comparable to that of the bulk. This result strongly indicates that in FeSe ideal junctions are formed by TBs.

5.3 LDOS across the TBs

We examine the evolution of the local density of states (LDOS) across the TB by taking a series of $g(\mathbf{r}, E)$ along the line depicted in Fig. 5.2(a). Here and in the following, we are interested only in the evolution of $g(\mathbf{r}, E)$ along the x -axis running perpendicular to the TB, leaving the y -coordinate constant, hence, $g(x, E)$. Fig. 5.2(b) shows an intensity plot of $g(\mathbf{r}, E)$. Individual spectra taken at representative points are depicted in Fig. 5.2(c). At the position far away from the TB (I), $g(\mathbf{r}, E)$ exhibits nodal multigapped superconducting structure with gap sizes $\Delta_1 \approx \pm 2.5$ meV and $\Delta_2 \approx \pm 3.5$ meV, which is consistent with the results in Fig. 4.10(a) [37]. Even right at the TB (III), the residual LDOS at $E = 0$ is negligibly small, indicating that the TB hardly gives rise to a pair-breaking effect. In the vicinity of the TB, the coherence peak and the shoulder associated with the superconducting gap diminish, and instead, sharp particle-hole symmetric peaks appear at $E \approx \pm 1.5$ meV. It is important to note that the spatial evolution of the spectrum does not accompany the smooth change in

the coherence-peak energy; instead, the 1.5 meV peak coexists with the 2.5 meV peak in the crossover region (II). This means that the 1.5 meV peak is not caused by the suppression of the superconducting gap due to the TB, but represents the bound state generated by the TB. The 1.5 meV peak is observed over about 5 nm from the TB, which is close to the “averaged” in-plane coherence length $\xi_{ab} \approx 4.5$ nm obtained from the upper critical field $H_{c2}(\parallel c) \approx 17$ T [37].

Another interesting observation is that low-energy quasiparticle excitations are suppressed over very long distances from the TB. High-resolution $g(\mathbf{r}, E)$ spectra at the positions of (I), (II), and (III) are plotted in Fig. 5.2(d). While the overall V-shaped behavior is maintained, the exact shape near the bottom of the gap depends on the position. In order to examine this behavior, we fit an empirical power law $g(\mathbf{r}, E) \propto |E|^\alpha$ to the low-energy ($|E| < 0.5$ meV) spectra and plot the exponent α as a function of the distance from the TB at $x = 0$ (Fig. 5.2(e)). Except when close to the TB ($|x| \lesssim \xi_{ab}$), where the 1.5-meV peaks dominate, α increases gradually with decreasing x by about ≈ 40 %. This implies the suppression of the low-energy quasiparticle excitations, most probably due to the opening of a small gap induced by the TB. The salient feature is that α continues to change even at $|x| > 10\xi_{ab}$ (≈ 50 nm), indicating an unexpectedly long-distance influence of the TB.

The long-distance TB effect on the LDOS can be seen in a more dramatic way in two junctions in series formed by two TBs. As shown in Fig. 5.3(a), we find an area where two TBs are running parallel to each other. The distance between the TBs is 34 nm, which is about 7 times larger than ξ_{ab} . Fig. 5.3(b) shows the spatial evolution of $g(\mathbf{r}, E)$ across the double TBs. Individual spectra at the representative points are plotted in Fig. 5.3(c). The overall spectral features, the 2.5 meV peak, the 3.5 meV shoulder, and the 1.5 meV peak observed near a single TB are all reproduced (positions (I), (II), and (III)). However, the low-energy spectrum taken inside the central domain (position (IV)) shows a striking anomaly that is absent in the case of a single TB. Fig. 5.3(d) depicts $g(\mathbf{r}, E)$ spectra at low energies. It is clear that, in between the double TBs, there is a finite energy range where $g(\mathbf{r}, E)$ is almost completely zero. The noticeable difference of the gap structure between inside and outside the central domain

is clearly seen in Fig. 5.3(e), which shows the exponent α plotted as a function of the distance from one of the TBs; α is strongly enhanced in the central domain and peaks at the middle of the domain. The large power $\alpha \approx 4$, which is about 3 times larger than the values at large x , is essentially indistinguishable from an exponential energy dependence. This apparent large power again corroborates the finite gap opening in the excitation spectrum of the quasiparticle.

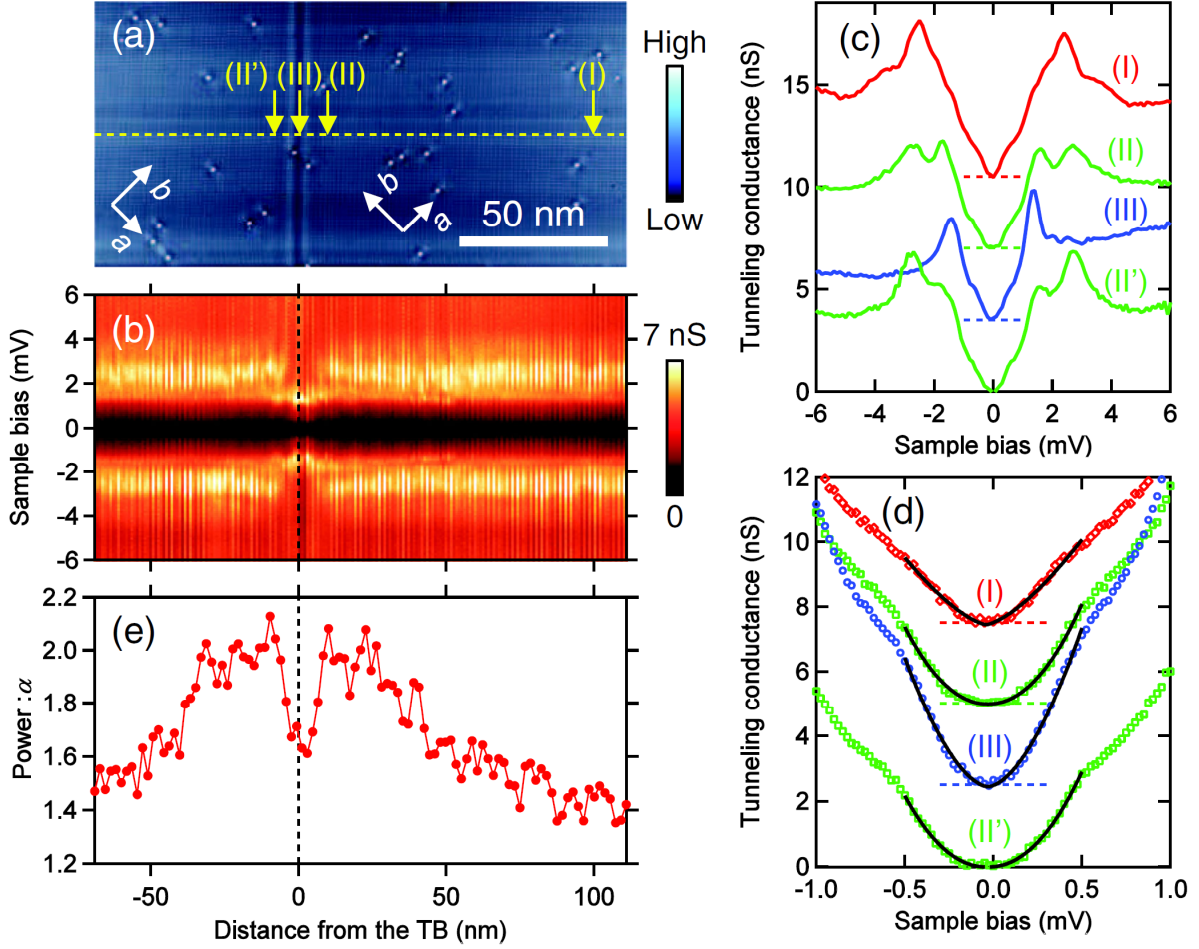


Figure 5.2: (a) Constant-current STM image ($180 \times 90 \text{ nm}^2$) at 1.5 K near a TB. (b) Intensity plot of $g(\mathbf{r}, E = 0)$ along the yellow broken line in (a). Spectroscopic measurements are done at the lowest temperature $T = 0.4 \text{ K}$. (c) Tunneling spectra at the representative points indicated in (a). Positions (II) and (II') are symmetric about the TB. (d) High-resolution tunneling spectra at low E taken at the same positions as for (c). Open symbols and solid lines denote experimental data and fitted results, respectively. Apparent kinks are observed at $\approx \pm 0.5 \text{ mV}$ regardless of the position. The origin of these features is unclear. The fitting is made below this energy scale. Spectra shown in (c) and (d) are shifted vertically for clarity. (e) The exponent α ($g(\mathbf{r}, E) \propto |E|^\alpha$) determined from the fit to the experimental data in the range of $|E| \leq 0.5 \text{ meV}$ plotted as a function of the distance from the TB. The vertical black dashed lines in (b) and (e) denote the position of the TB [61].

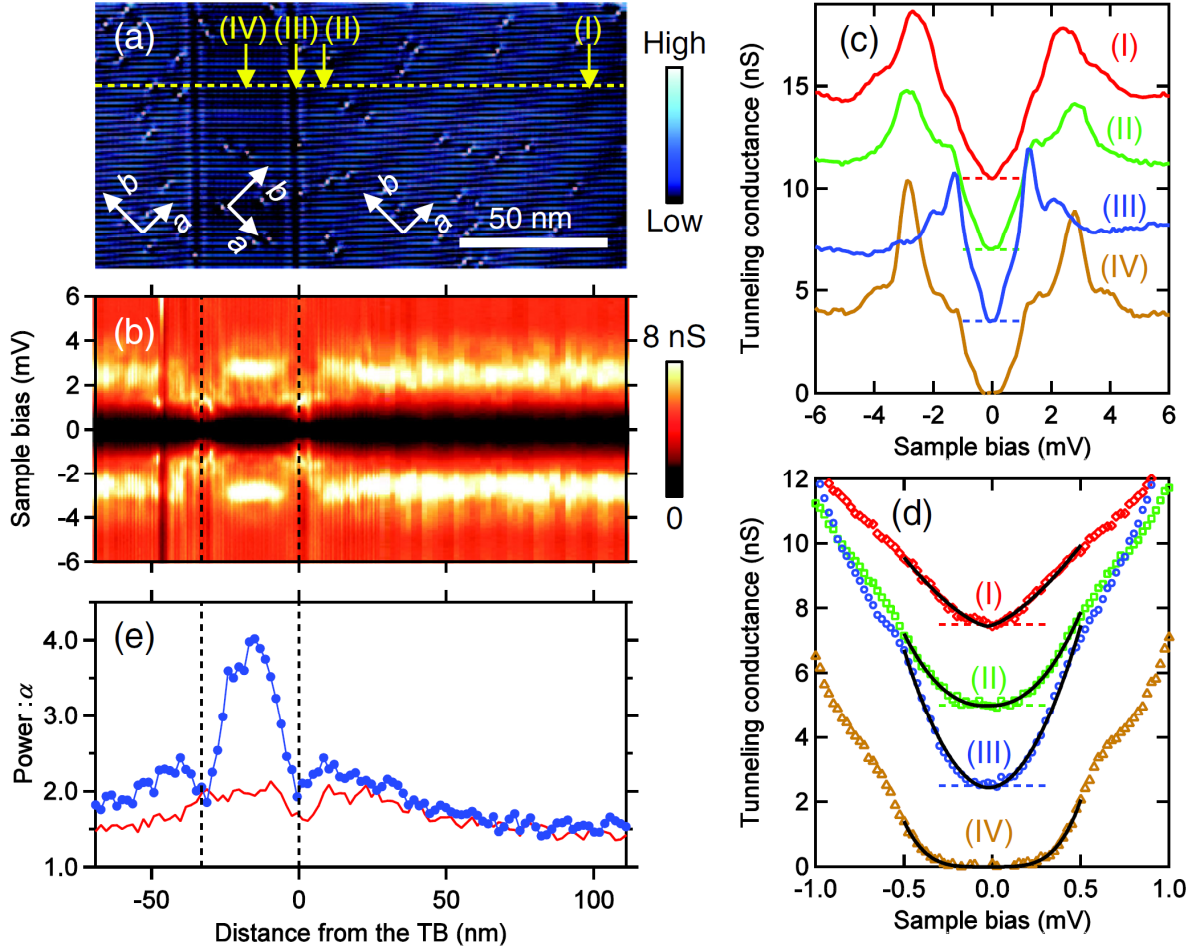


Figure 5.3: (a) A constant-current STM image ($180 \times 90 \text{ nm}^2$) at 1.5 K around double TBs. (b) Intensity plot of $g(\mathbf{r}, E = 0)$ along the yellow broken line in (a). Spectroscopic measurements are done at the lowest temperature $T = 0.4 \text{ K}$. (c) Tunneling spectra at the representative points (I)-(IV) indicated in (a). (d) High-resolution tunneling spectra at low E taken at the same positions as for (c). Open symbols and solid lines denote experimental data and fitted results, respectively. Spectra shown in (c) and (d) are shifted vertically for clarity. At the position (IV), there is a finite region where the conductance is almost completely zero, indicating that the line nodes are completely lifted between the double TBs. (e) The exponent α ($g(\mathbf{r}, E) \propto |E|^\alpha$) determined from the fit to the experimental data in the range of $|E| \leq 0.5 \text{ meV}$ plotted as a function of the distance from the TB. The red solid line denotes the data of the single TB, for reference [61].

5.4 Possible TRSB SC state around TB

The above observations, the TB-induced bound states at finite energies and the suppression of the low-energy quasiparticle excitations over a length scale much longer than ξ_{ab} , suggest a novel role of the TB in an unconventional superconductor. In order to understand the origin of these anomalies, it is important to examine the structure of the gap node in momentum space.

The existence of the line nodes along the c axis, which is consistent with the strong in-plane anisotropy observed in the superconducting state, such as an elongated vortex core in Fig. 5.1(c), is confirmed by the taken STS spectra. The Fermi surface of FeSe consists of one hole and one (or two) electron pockets (see sec. 6), and the superconducting gap opens on each surface. Now we assume that the line nodes appear on the electron cylinder and the gap on the hole cylinder is fully opened. Although it is still controversial which cylinder has the line nodes, the following discussion applies not only for this particular case but also for other cases. In this case, there are two possible phase structures for the symmetry of the superconducting gap across a TB, as schematically illustrated in Fig. 5.4, where the global phase of the superconducting gap is either fixed to the crystallographic axis (Fig. 5.4(a)) or flipped across the TB (Fig. 5.4(b)).

The assumed gap structure can be separated into the 4-fold symmetric nodal gap component $\Delta_{4\phi}$ and the isotropic fully-gapped component Δ_{iso} , as shown in Fig. 5.4. We note that the sign of either $\Delta_{4\phi}$ or Δ_{iso} is reversed between the two domains in Figs. 5.4(a) or 5.4(b), respectively. This means that the amplitude of at least one of the gaps vanishes at the TB, giving rise to the zero-energy quasiparticle state that should appear as a zero-energy peak in $g(\mathbf{r}, E)$.

The observed bound state peak at ± 1.5 meV apparently contradicts this conjecture and suggests instead that the TB induces an additional gap component that shifts the position of a zero-energy peak to a finite energy. We point out that, as long as the induced gap is real, the sum of the bulk gap and the TB-induced gap reverses its sign at a finite distance from the TB and still gives rise to a zero-energy peak. However, as shown in Fig. 5.2(b), we do not observe a zero-energy peak in $g(\mathbf{r}, E)$ over more

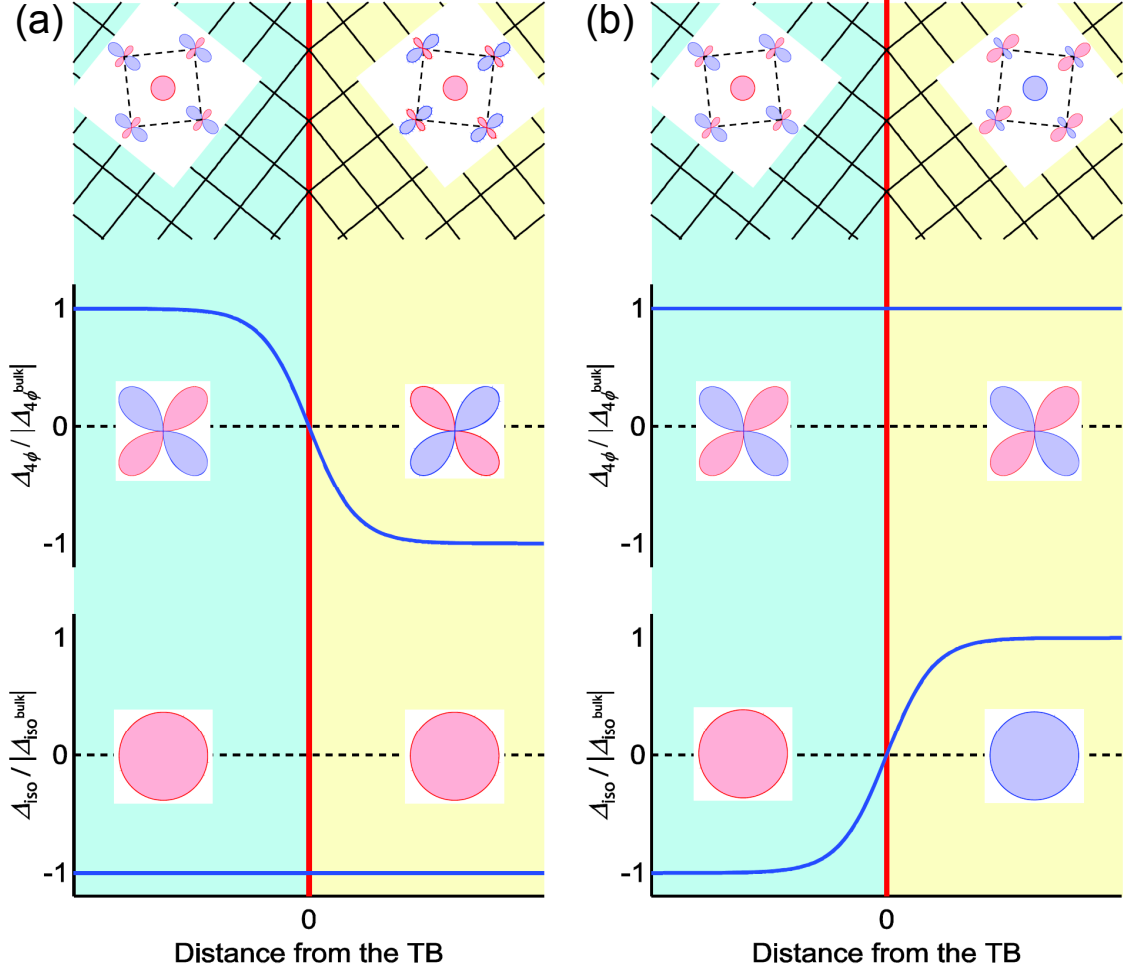


Figure 5.4: Schematic illustration of the phases of the superconducting gaps across the TB shown by the red line. Top panel represents the iron lattice near the TB together with the momentum-space phase structure of the superconducting gaps opening at multiple Fermi cylinders, a hole cylinder at the center, and electron cylinders at the corner of the Brillouin zone (black broken square). Crossing a TB, the electronic structures are rotated by $\pi/2$. Different colors (red and blue) denote different signs of the phase. We assume that the gap node exists on the electron cylinder and the sign reversal is between the main lobe of the gap on the electron cylinder and the gap on the hole cylinders, but the argument given in the text applies not only for this particular case but also for other cases. There are two possibilities: the phase structure is either fixed to the lattice (a) or flipped across the TB (b). In the former case, the nodal component $\Delta_{4\phi}$ should change its sign across the TB, whereas the sign of the isotropic component Δ_{iso} (either due to the fully gapped Fermi cylinder or associated with the C_2 symmetry of the nodal gap) should be reversed in the latter case. [61].

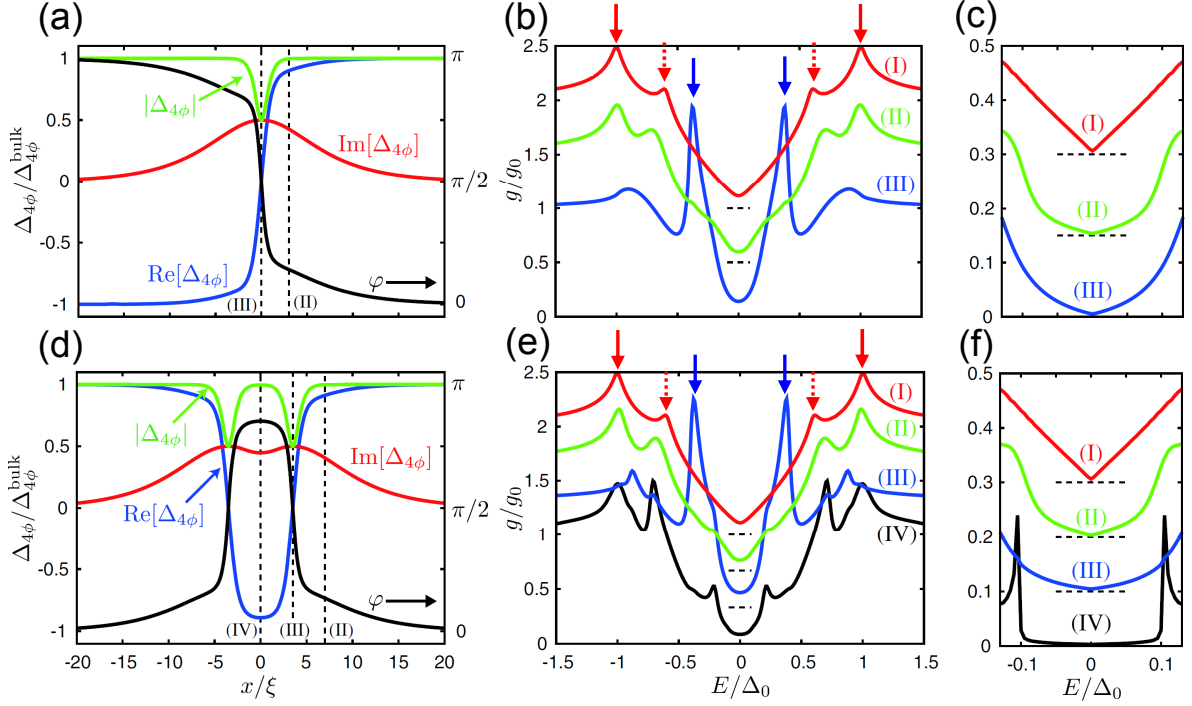


Figure 5.5: (a) Model order parameter $\Delta_{4\phi}$ with a TB located at $x = 0$. To take account into the TRSB effect around the TB, we introduced the imaginary component $\text{Im}[\Delta_{4\phi}]$. (b),(c) Calculated LDOS spectra in the bulk (I), at $x = 3\xi$ (II), and on the TB (III). The red solid and dashed arrows denote the bulk superconducting gap energies $|\Delta| = \Delta_{4\phi}^{\text{bulk}} \pm \Delta_{\text{iso}}$, respectively. In the vicinity of the TB, the bound states with finite energies $E \approx \pm 0.4\Delta_0$ appear (blue arrows). (d) A model order parameter $\Delta_{4\phi}$ with a TB located at $x = \pm 3.5\xi$. (e),(f) Calculated LDOS spectra in the bulk (I), at $x = 7\xi$ (II), on the TB (III), and at the middle point between the double TBs (IV). The low-energy excitations are strongly suppressed in the region separated by the double TBs [61].

than 100 nm from the TB. Thus, we speculate that the induced gap has an imaginary component, which means that time-reversal symmetry is locally broken near the TB. In such a case, bound state peaks are located at finite energies $E = \pm \Delta \cos(\delta\phi/2)$ because the phase shift $\delta\phi$ on the TB is reduced from π [78, 79]. Here, Δ is the amplitude of the superconducting gap. The possibility of the TB-induced time-reversal-symmetry-broken state has been argued for *d*-wave $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a small *s*-wave component [80], and the splitting of the zero-energy peak has been argued theoretically as well [81–83]. However, experimental observations are still lacking.

Taking into account the C_2 symmetry, the nodal gap, and the broken time-reversal

symmetry near the TBs, we performed a theoretical calculation with a minimal model. Fig. 5.5 is the results of the calculation. The details of the procedures appear in Ref. 61 and 80. As shown in Fig. 5.5(a), when the imaginary gap component $\text{Im}[\Delta_{4\phi}]$ is induced around the single TB, the gap amplitude $|\Delta_{4\phi}|$ remains finite even just on the TB, although the real component $\text{Re}[\Delta_{4\phi}]$ crosses zero. Therefore, no zero-energy bound state appears in the calculated spectra in Fig. 5.5(b) and (c). Alternatively, the spectrum at the TB exhibits a sharp peak structure at $E \approx \pm 0.4\Delta_0$, which corresponds to the bound states whose energies are shifted from $E = 0$ due to the time-reversal symmetry breaking in $\Delta_{4\phi}$. In Fig. 5.5(c), we show the LDOS at lower energy scales. The clear V-shaped LDOS in the bulk (I) changes to the U-shaped LDOS upon approaching the TB. The low-energy LDOS is finite in the vicinity of the TB, (II) and (III), because low-energy quasiparticles with momenta along the nodal directions of the bulk gap can linger over long distances and reach the TB, even though the local gap does not vanish near the TB where $\text{Im}[\Delta_{4\phi}] \neq 0$. We also revealed that when the time-reversal symmetry is broken, the order parameter around the TB changes with another length scale $\tilde{\xi}$, which is much longer than the coherence length ξ [61, 80]. These features are in good agreement with the experimental data of the single TB shown in Fig. 5.2. We also calculated the LDOS for double TBs in Fig. 5.5(d)-(f). They are separated by the interval distance $d = 7\xi$, as they were in the experimental data. We note that a clear energy gap extending over $|E| \lesssim 0.1\Delta_0$ appears in the calculated spectrum between the double TBs (position (IV)), which is consistent with the strong suppression of the LDOS between TBs observed in our STM and STS measurements in Fig. 5.3. The origin may be in a sort of interference effect, i.e. the bulk low-energy quasiparticles cannot penetrate into the region between the double TBs.

5.5 Summary

We report on the visualization of the atomic scale variation of the quasiparticle states of the nodal superconductor FeSe near TBs that enforce a sign inversion of the superconducting gap. In contrast to the expectation that the sign inversion generates a zero-energy quasiparticle bound state near the TB, the TB-induced quasiparticle states are not at zero but at finite energies $E \approx \pm 1.5 \text{ meV}$. Moreover, the low-energy excitation spectrum is affected by the TB over an extremely long distance, which is a few tens of times larger than ξ_{ab} . An even more dramatic change in the low-energy spectrum is detected in the region between double TBs separated by a distance $\approx \xi_{ab}$, where the quasiparticle weight near the Fermi energy is almost completely removed in the energy range $|E| \leq 0.2 \text{ meV}$. These observations are qualitatively reproduced by a phenomenological model that assumes that the TB induces locally a superconducting state that breaks time-reversal symmetry.

6 BCS-BEC crossover in FeSe

Since the proposal of the BCS theory by Bardeen, Cooper and Schrieffer, there have been a number of theoretical works which suggest that the transition in the superconducting state can be considered as a sort of Bose-Einstein condensation (BEC), i.e., these two paradigms, BCS and BEC, are not distinct and can be understood from a unified standpoint [14–20]. In the BCS-BEC crossover region, the pairing size is on the order of the mean interparticle space, $\xi_{\text{pair}} \approx k_F^{-1}$, and unique quantum condensed states have been theoretically predicted due to the strong interaction between Cooper pairs. The BCS-BEC crossover has hitherto been realized experimentally in ultracold atomic gases. On the other hand, in solids, almost all superconductors are in the BCS regime, where the superconducting gap energy Δ is usually several orders of magnitude smaller than the Fermi energy ε_F : $\Delta/\varepsilon_F \sim 1/k_F\xi \ll 1$, and it has thus been extremely difficult to access the crossover regime.

In this section, we will report the extremely small Fermi energies ε_F of the iron-based superconductor FeSe revealed by our QPI, Seebeck, and penetration depth measurements. Combining the SdH and ARPES results with our data, we will discuss the detailed electronic structure of FeSe. We found that the superconducting gap sizes Δ are comparable to ε_F , indicating that FeSe is located in the BCS-BEC crossover region. Moreover, our thermal-conductivity measurements give evidence of a distinct phase line below the upper critical field (B -phase), where the Zeeman energy becomes comparable to ε_F and Δ [37].

This section includes the data of my main works (**Main work No.3**).

6.1 Extremely small Fermi energy in clean FeSe single crystal

6.1.1 Quasiparticle interference (QPI)

We can determine the electron and hole Fermi energies directly by measuring the electronic dispersion curves in momentum space, yielding the Fermi energies $\varepsilon_F^e = E_F - E_{EB}$ ($\varepsilon_F^h = E_{HT} - E_F$) for the electron (hole) band. Here E_{HT} (E_{EB}) is the energy of the bottom (top) of the electron (hole) band and E_F is the electrochemical potential. For this assignment, we exploited spectroscopic-imaging scanning tunneling microscopy to observe the quasiparticle interference (QPI) patterns associated with electron waves scattered off by defects.

Interference between the incident and reflected waves around impurities or defects

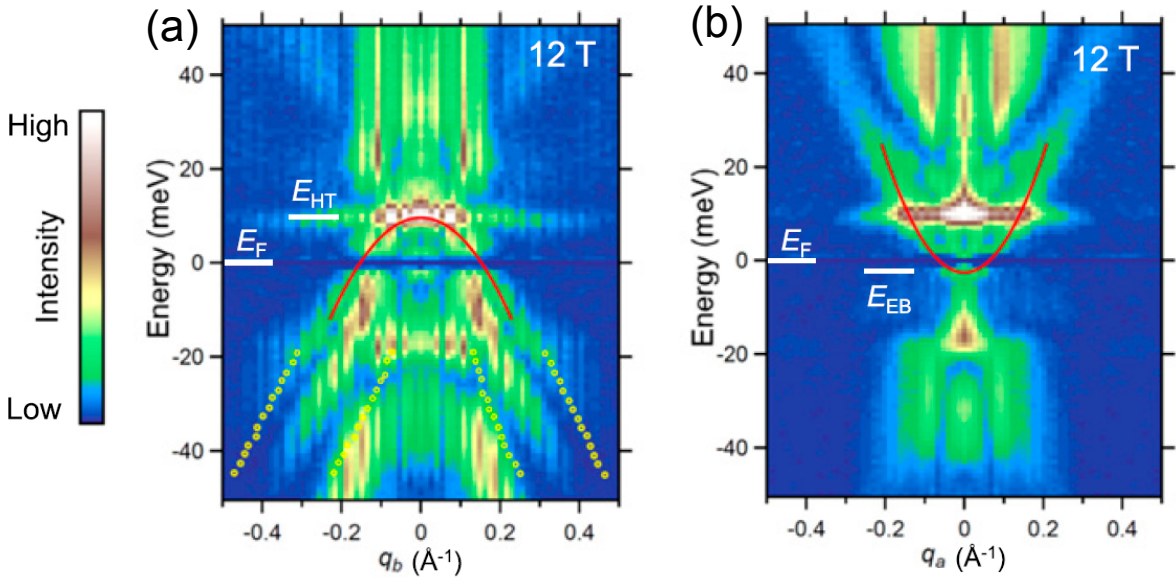


Figure 6.1: (a),(b) QPI dispersions at 12 T obtained by taking linecuts from the energy-dependent Fourier-transformed normalized conductance images in Fig. 6.2 along q_b and q_a ($a < b$), respectively. Peak positions of the representative branches are fitted with a parabolic function to obtain the Fermi energies and effective masses (solid lines). The top (bottom) of the hole (electron) band E_{HT} (E_{EB}) is indicated by a white bars. Expected intraband scattering vectors detected by ARPES [84] are plotted in (a) by yellow circles.

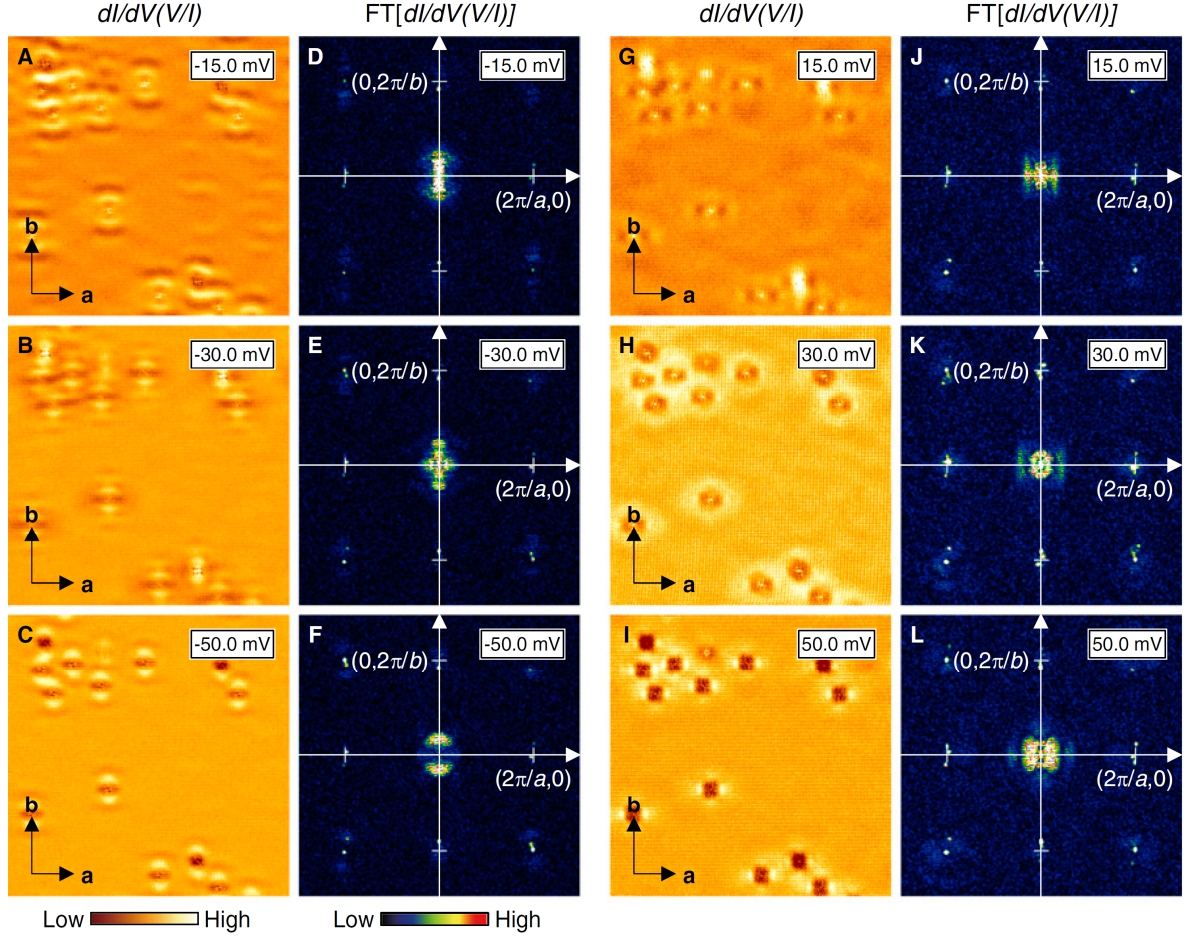


Figure 6.2: Energy-dependent QPI patterns at $T = 1.5$ K and $\mu_0 H = 12$ T. Scan area is $45 \text{ nm} \times 45 \text{ nm}$. (A-C) Normalized conductance, $dI/dV(V/I)$, images of the occupied states at $V = -15$ mV (A), -30 mV (B), -50 mV (C). (D-F) Fourier transform of the images shown in AC. (G-I) Normalized conductance images of the empty states at $V = +15$ mV (G), $+30$ mV (H), $+50$ mV (I). (J-L) Fourier transform of the images shown in G-I.

results in the formation of standing waves and the spatial modulation of the density of states, which can be directly imaged in the STM topographic maps or the differential conductance maps obtained by spectroscopic imaging STM [85,86]. By taking the Fourier transform of these images, we can obtain interference patterns in the reciprocal space (q -space), which include important information about the electronic structures, such as band dispersions and Bogoliubov quasiparticle information in the superconducting state [87–90].

Previously, we have reported the QPI effect and determined the band dispersion in

FeSe. Fig. 6.2 shows the normalized conductance ($dI/dV(V/I)$) map and the Fourier transform of it. By taking the Fourier transform of the $dI/dV(V/I)$ images, characteristic wave vectors of electrons at different energies reflecting the band dispersion can be determined. The observed QPI patterns of FeSe at 1.5 K consist of hole- and electron-like branches that disperse along the crystallographic b and $a(< b)$ directions, respectively. These branches in q -space can be ascribed to the hole and electron sheets in k -space illustrated in Fig. 6.4(c). The QPI signals exhibit a strong in-plane anisotropy caused by the orbital ordering in the nematic phase [38], as discussed in sec 4.1.3. Such an anisotropy is consistent with the largely elongated vortex core structure [56].

As shown in Fig. 6.1(a) and (b), full dispersion curves of hole- and electron-like branches are clearly identified by taking linecuts from the series of Fourier-transformed conductance images in Fig. 6.2. To primarily suppress superconductivity, we applied a magnetic field $\mu_0 H = 12$ T parallel to the c -axis. Here, the top of the hole branches (bottom of the electron branch) corresponds to the Fermi energy of the hole (electron) pocket and then we obtain the extremely small Fermi energies, $\varepsilon_F^h \sim 10$ meV for the hole band and $\varepsilon_F^e \sim 2 - 3$ meV for the electron band, respectively. When we assume a parabolic dispersion $E^e(k) = \frac{\hbar^2 k^2}{2m^*} - \varepsilon_F^e = \frac{\hbar^2 q^2}{8m^*} - \varepsilon_F^e$ ($E^h(k) = \varepsilon_F^h - \frac{\hbar^2 k^2}{2m^*} = \varepsilon_F^h - \frac{\hbar^2 q^2}{8m^*}$) for the electron (hole) band, we obtain the effective masses $2.5m_e$ ($3.5m_e$).

6.1.2 SdH measurements

The high quality of FeSe single crystals grown with the vapor transport method allows quantum oscillations to be observed. Several Shubnikov-de Haas (SdH) measurements on the ultra-clean FeSe single crystals have been performed in dc fields [91] and in pulsed fields [40, 92].

Fig. 6.3(a) shows the field dependence of the resistance of FeSe up to 35 T at $T = 40$ mK. The magnetic field is applied parallel to the c -axis. Above $H_{c2} \sim 16$ T in the normal state, an SdH oscillation with finite amplitude appears in the resistance. Fourier transforms of the oscillation vs. $F \cos \theta$, where θ is the field direction measured from the crystallographic c -axis, are shown in Fig. 6.3(b). Four fundamental branches α , β , γ , and δ (the 2α and 2β frequencies are the second harmonics) with small frequencies

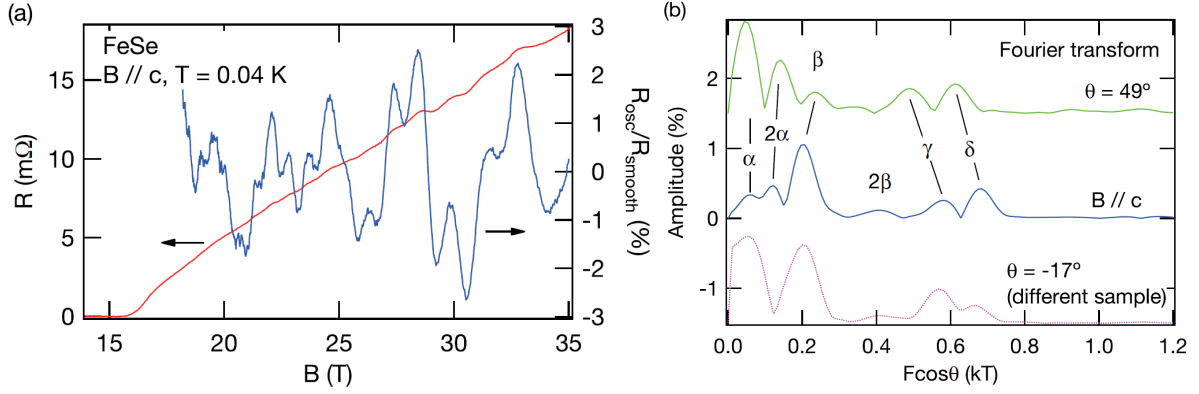


Figure 6.3: (a) Resistance R (left axis) and normalized quantum oscillation signal $R_{\text{osc}}/R_{\text{background}}$ (right axis) as a function of B , taken at $T = 0.04$ K. (b) Fourier transforms of SdH oscillations in inverse-field $1/B$ vs. $F \cos \theta$. Four fundamental SdH branches, α - δ , appear. 2α and 2β correspond to the second harmonics of α and β , respectively [91].

F , well below 1 kT, are observed. This result indicates the small cross-sectional areas of the corresponding Fermi surfaces A which cover only 0.2-2.3% of the 1st Brillouin zone, as shown in Table 6.1. The effective masses m^* , estimated from the temperature dependence of the oscillation amplitudes, are $1.9 - 7.2m_e$. When we assume circular orbits, the Fermi energy E_F and cross-sectional areas of the Fermi surface A are given by

$$E_F = \frac{\hbar^2 k_F^2}{2m^*} \quad (6.1)$$

$$A = \pi k_F^2 = \frac{2\pi e F}{\hbar}, \quad (6.2)$$

where k_F is the Fermi momentum. We note that the obtained Fermi energies, $E_F = 3.6 - 18$ meV, are extremely small compared with conventional metals with $E_F \sim 10^3 - 10^4$ meV.

In Ref. 37, we have also confirmed the extremely small Fermi energies in FeSe by other bulk probes, such as the penetration depth and Seebeck coefficient.

Now, we switch to the Fermi surface structure. Fig. 6.4(a) and (b) are the band structure and Fermi surfaces in the orthorhombic phase predicted by first-principles calculations, respectively. According to the calculations, all of the 3d-orbits cross the

Fermi energy and the Fermi surface consists of two electron cylinders at the M point of the BZ zone and three hole cylinders at the Γ point, similar to most iron-based superconductors [93–95].

According to Ref. 91, the angular dependence of the SdH frequencies has revealed that the α and β frequencies are from the minimal cross-sections, while γ and δ are from the maximal ones. This result suggests that only one electron Fermi surface around the M point and one hole Fermi surface around the Γ point exist. Moreover, according to recent SdH measurements in pulsed fields up to 90 T [40, 92], it has been suggested that a nontrivial Berry phase exists, implying one additional Dirac-like tiny electron pocket with high carrier mobilities around the M point. As a result, the experimentally determined Fermi surface of FeSe strongly deviates from the predictions of the calculations, as shown in Fig. 6.4(c).

Table 6.1: From left to right, SdH frequencies, effective masses, orbit areas A , Fermi momenta, and effective Fermi energies of each branch ($\alpha - \delta$) in FeSe, experimentally determined by the SdH measurements [91]. m_e is the free electron mass.

Branch	F (kT)	m^*/m_e	A (%BZ)	k_F ($\text{\AA}^{-1}$)	E_F (meV)
α	0.06	1.9(2)	0.20	0.043	3.6
β	0.20	4.3(1)	0.69	0.078	5.4
γ	0.57	7.2(2)	2.0	0.13	9.1
δ	0.68	4.2(2)	2.3	0.14	18

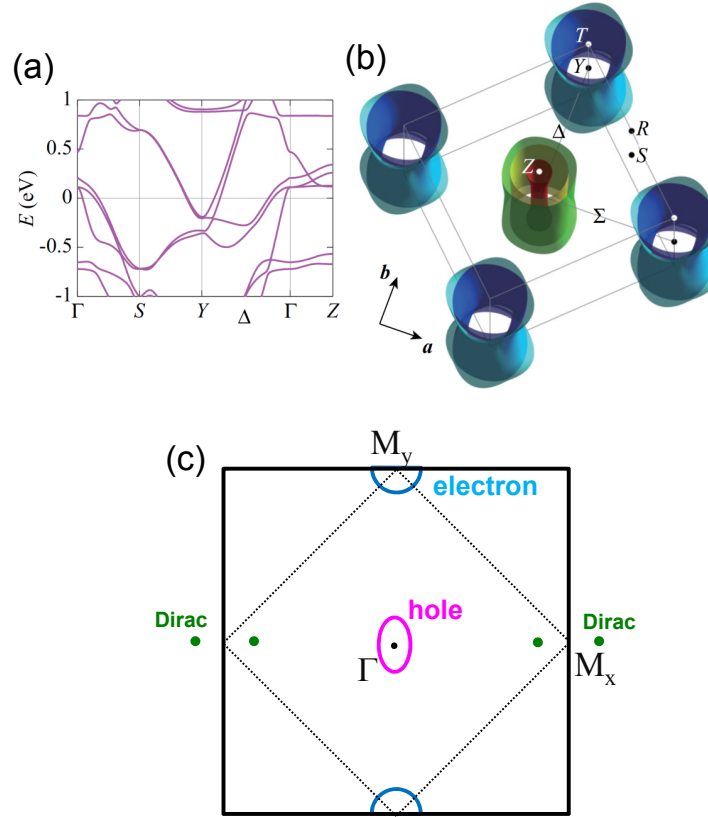


Figure 6.4: (a),(b) Band structure and Fermi surfaces in the orthorhombic phase predicted by first-principles calculations, respectively. All five $3d$ -orbitals cross the Fermi energy and the Fermi surface consists of two electron cylinders at the M (Y) point of the BZ zone and three hole cylinders at the Γ point [91]. (c) Experimentally determined Fermi surface by the SdH measurements in Ref. [91] (dc field) and Ref. 40 and 92 (pulsed field). The Fermi surface of FeSe consists of one hole cylinder at the Γ point and one electron cylinder with one tiny Dirac-like electron pockets at the M point.

6.1.3 Orbital ordering in FeSe

In the previous sections, we discussed the extremely small Fermi energies and the Fermi surfaces which show a strong deviation from the first-principles predictions. Moreover, the band dispersions obtained by QPI (Fig. 6.1) and the vortices imaged by SI-SIM (see Fig. 5.1(c) and Ref. 56) exhibit the large in-plane anisotropy. Below T_s , the crystal structure is orthorhombic, however, the distortion is at most 0.3% (Fig. 6.5(b)) [38]. Hence, it may be natural to consider that the anomalously large in-plane anisotropy in the electronic system originates from the electronic nematicity rather than the small crystal orthorhombicity. In the electronic nematic state, the electronic system spontaneously breaks the rotational symmetry. In fact, the emergence of nematic fluctuations above T_s has been experimentally reported, such as by Young's modulus [96], Raman spectroscopy [97] and elastoresistance measurements [51, 98]. These measurements have revealed that the nematic susceptibility $\chi_{\text{nem}}(T)$ exhibits a Curie-Weiss-like temperature dependence and diverges toward T_s .

Recent ARPES measurements suggest that the electronic nematic order is driven at T_s by the energy splitting between the d_{yz} and d_{xz} orbitals, the so-called orbital ordering [38, 99–101]. The EDCs at the M point taken by the ARPES are represented in Fig. 6.5(a). The degenerate d_{yz} and d_{xz} orbitals start to split into two at $T_s \approx 90$ K, and the bottom of the d_{yz} band, which corresponds to the Fermi energy of the electron pocket ε_F^e , is approaching the Fermi level E_F with lowering temperature. The estimated ε_F^e value at 20 K is extremely small, $\varepsilon_F^e \approx 5$ meV, which is consistent with the SdH and QPI results.

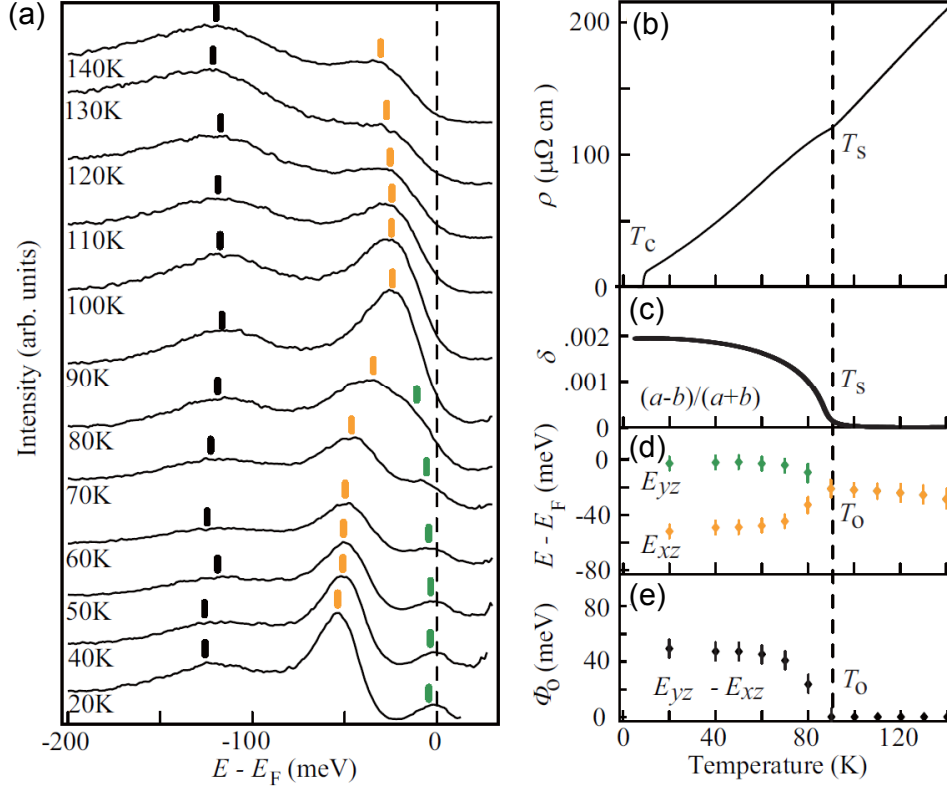


Figure 6.5: (a) The EDCs at the M point taken by ARPES. (b)-(e) Temperature dependence of the resistivity ρ , orthorhombic distortion $\delta = (a - b)/(a + b)$, energies of the d_{yz} and d_{xz} band bottoms, E_{yz} and E_{xz} , and the split energy $\Phi_0 = E_{yz} - E_{xz}$, respectively [38].

6.2 BCS-BEC crossover in FeSe

As discussed in the previous sections, the Fermi surface of FeSe consists of one hole pocket and one electron pocket (or additional two Dirac-like electron pockets) with their extremely small Fermi energies $\varepsilon_F \sim 3 - 18$ meV. Since the superconducting gap size obtained from the STS measurements is $\Delta \sim 3$ meV (Fig. 4.10(a)), the ratio Δ/ε_F becomes unity, whereas Δ/ε_F is on the order of $10^{-3} - 10^{-4}$ in most superconductors. This anomalous feature clearly appears in the QPI dispersions at 0 T, as shown in Fig. 6.6. The electron and hole band dispersions are observed in the same way as in QPI dispersions at 12 T. In addition, a pair of sharp intensity peaks ($\pm\Delta$), which corresponds to the coherence peaks of the superconducting gap in Fig. 4.10(a), appears at $E \approx 3$ meV. This result indicates that the superconducting gaps are of the same order as the Fermi energy of each band, $\Delta/\varepsilon_F^e \sim 0.3$ for the hole band (Fig. 6.6(a)) and $\Delta/\varepsilon_F^e \sim 1$ for the electron band (Fig. 6.6(b)), implying that FeSe is located in the

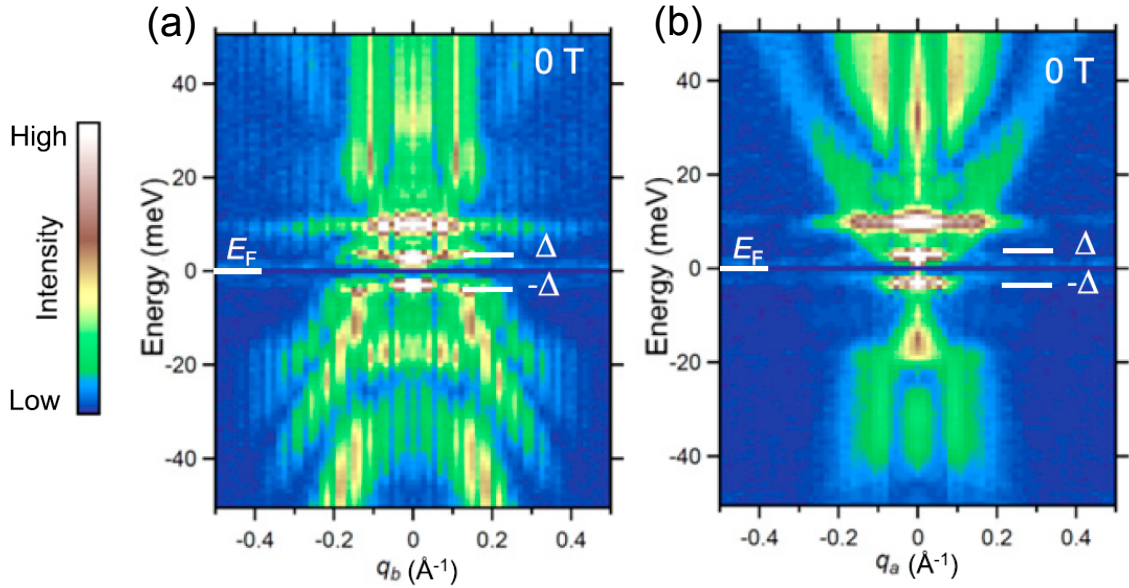


Figure 6.6: (a),(b) QPI dispersions at $H = 0$. The hole (electron) band dispersions appear along the a -axis (b -axis) as well at 12 T. A pair of sharp intensity peaks ($\pm\Delta$) appears at $E \approx \pm 3$ meV due to the opening of the superconducting gap. Superconducting gaps, defined by the positions of the coherence peaks (white bars), are comparable to the Fermi energies.

BCS-BEC crossover regime. Additional strong support for the crossover is provided by the extremely small $k_F\xi \sim 1 - 4$ due to the small Fermi momenta k_F [37, 91]. Here, k_F of the electron (hole) sheet obtained from Fig. 6.6(b) (Fig. 6.6(a)) is roughly 0.3 (0.75) nm^{-1} , and ξ determined from the upper critical field (17 T) is roughly 5 nm.

Moreover, in the bulk FeSe, giant superconducting fluctuations above T_c have been observed [102]. Fig. 6.7(a) is the temperature dependence of the non- H -linear diamagnetic contribution to the magnetization $|\chi_{\text{nl}}^{\text{dia}}|$ above T_c , obtained by magnetic torque measurements. $|\chi_{\text{nl}}^{\text{dia}}|$ in the magnetic fields starts to develop at $T^* \sim 20 \text{ K}$ ($> T_c$), while it is absent above T^* . In stark contrast to conventional superconductors, a large $|\chi_{\text{nl}}^{\text{dia}}|$, by far exceeding the standard Gaussian-type (AslamasovLarkin, AL) fluctuation susceptibility $|\chi_{\text{AL}}|$, is observed below T^* [103–105]. This result provides thermodynamic evidence of giant superconducting fluctuations in the normal state of FeSe. It is theoretically expected that, in the presence of preformed pairs associated with the BCS-BEC crossover, superconducting phase fluctuations arising from the mode coupling of fluctuations are significantly enhanced and produce a highly nonlinear diamagnetic response [31]. The anomalies at T^* have also been revealed by some other probes. The NMR relaxation rate $1/(T_1T)$ at low magnetic fields shows a noticeable deviation from the Curie-Weiss law below T^* , as shown in Fig. 6.7(b). Peak structures at T^* are observed in transport measurements; electrical Hall coefficient R_H (Fig. 6.7(c)), Seebeck coefficient S (Fig. 6.7(d)), and Nernst coefficient ν (Fig. 6.7(e)). These results strongly indicate the presence of the pseudogap phase associated with the BCS-BEC crossover in the temperature region between T_c and T^* as shown in the H - T phase diagram in Fig. 6.7(f).

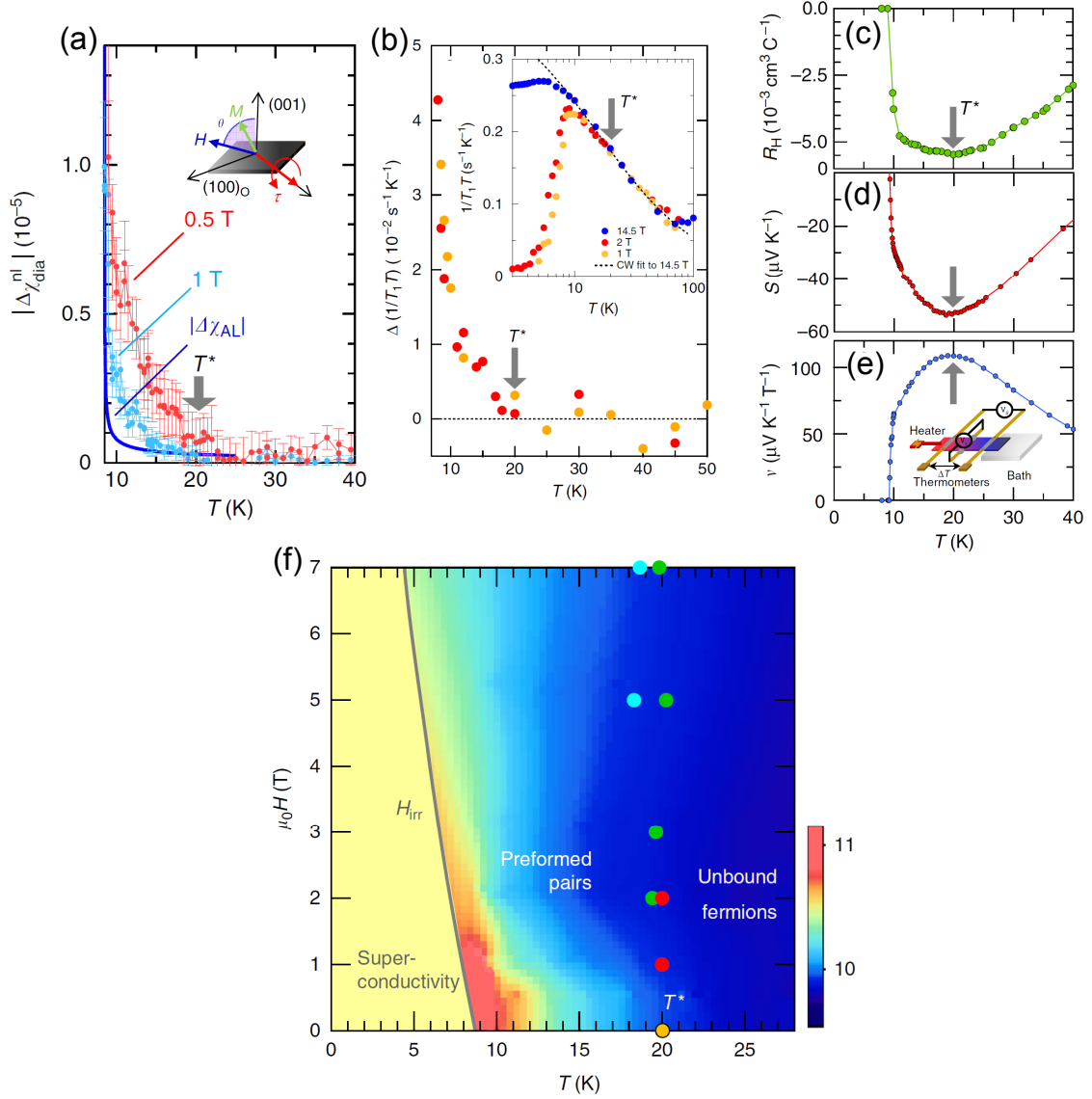


Figure 6.7: (a) Temperature dependence of the non-linear diamagnetic response $|\chi_{\text{nl}}^{\text{dia}}|$ at 0.5 and 1 T. The blue line represents the estimated $|\chi_{\text{AL}}|$ in the standard Gaussian fluctuation theory. (b) Temperature dependence of the NMR relaxation rate divided by temperature $1/T_1T$. The dashed line in the inset panel is the Curie-Weiss fitting of $1/T_1T$ at 14.5 T. The temperature dependence of the difference between the fitting and the low-field data, $\Delta(1/T_1T)$ vs. T , is presented in the main panel. (c)-(e) Temperature dependence of the electrical Hall coefficient R_H , Seebeck coefficient S , and Nernst coefficient ν , respectively. R_H and S show minimum structures and ν exhibits a peak structure at T^* . (f) Obtained H - T phase diagram of FeSe. The plotted circles denote the temperatures T^* at different magnetic fields determined by the above experiments. The incoherent electron pairs start to form at T^* and the pseudogap phase exists in the temperature range between T_c and T^* [102].

6.3 Field-induced SC phase (*B*-phase)

In superconductors, Zeeman splitting induces the spin imbalance in an applied magnetic field. The magnitude of the spin imbalance $P = (N_{\uparrow} - N_{\downarrow})/(N_{\uparrow} + N_{\downarrow})$, where $N_{\uparrow}$ and $N_{\downarrow}$ are the numbers of up and down spins, respectively, is roughly estimated as $P \approx \mu_B H / \varepsilon_F$. In stark contrast to most superconductors with very small $P \sim 10^{-3}$ - 10^{-2} even near the upper critical field H_{c2} , the highly spin-polarized superconducting state is induced due to the Zeeman splitting in the BCS-BEC crossover region, because the Zeeman energy $\mu_0 H$ becomes comparable to $\Delta(0)$ and ε_F , i.e., $\varepsilon_F \sim \Delta(0) \sim \mu_B H$. Comparable Fermi and Zeeman energies may lead to an unprecedented superconducting state of highly spin-polarized electrons, such as spin-triplet pairing, an admixture of even- and odd-frequency pairing [106], and a FuldeFerrellLarkinOvchinnikov (FFLO)-like state [107] (we will discuss this later). In fact, we have recently performed thermal conductivity measurements on FeSe and reported a possible new high-field superconducting phase, which is induced by the extremely large spin imbalance $P \sim 0.1$ in the crossover region [37].

Fig. 6.8(a) is the field-dependence of the thermal conductivity κ/T at temperatures well below T_c . κ/T shows a steep decrease at low fields and then becomes nearly H -independent in a wide range of magnetic fields. The origins of this behavior are still unclear; however, similar behavior has been reported for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [108] and CeCoIn_5 [109]. It has been suggested that the initial decrease of κ/T in the ultraclean sample is caused by the suppression of the extremely long mean free path l due to vortex scattering, since the quasiparticle contribution κ_{qp} and the phonon contribution κ_{ph} of thermal conductivity can be denoted as

$$\kappa_{\text{qp}} \propto N_{\text{del}}(0)v_F l_{\text{qp}}, \quad (6.3)$$

$$\kappa_{\text{ph}} \propto N_{\text{ph}}(0)c_v l_{\text{ph}}, \quad (6.4)$$

where $N_{\text{del}}(0)$ ($N_{\text{ph}}(0)$) is the density of states of the delocalized quasiparticles (phonons) at the Fermi energy, v_F is the Fermi velocity, c_v is the speed of sound, and l_{qp} (l_{ph})

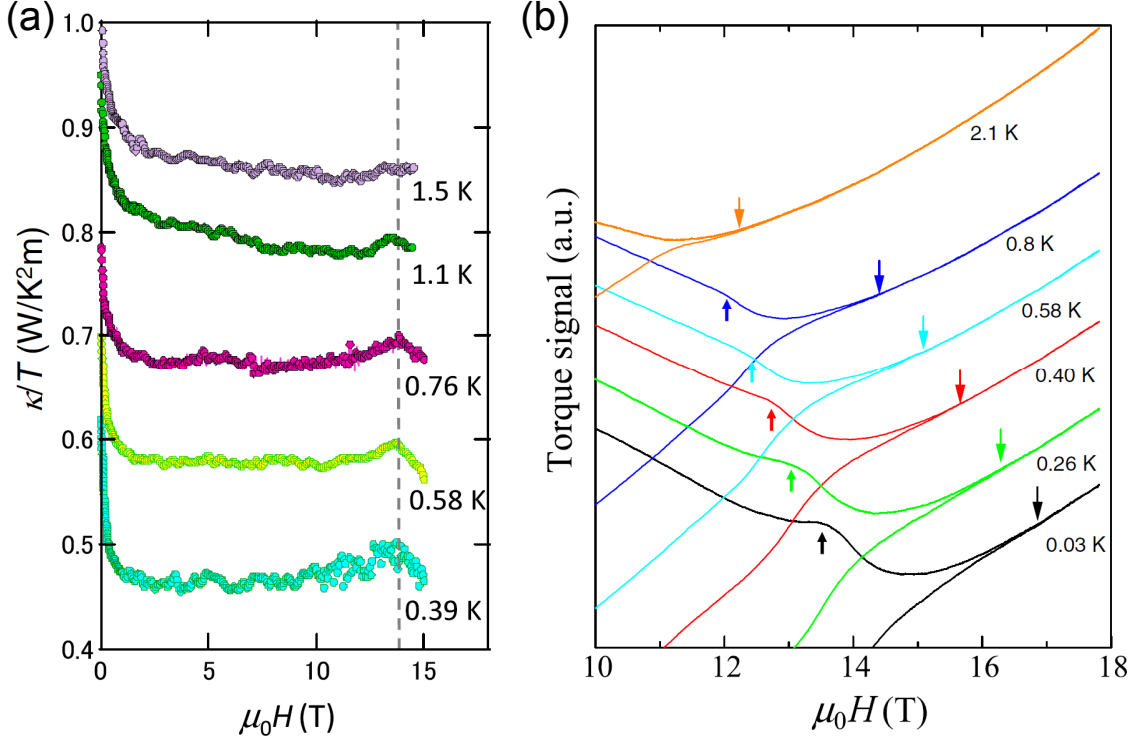


Figure 6.8: (a) Magnetic-field dependence of κ/T at low temperatures ($\mathbf{H} \parallel c$). κ/T shows a steep decrease at low fields and then becomes nearly H -independent in the wide range of magnetic field. At H^* , κ/T shows a cusp-like peak, suggestive of a nearly temperature-independent transition (dashed line). At 1.5 K, the cusp disappears and a weak structure (within the accuracy of the measurement) is observed at lower field. (b) Field dependence of the magnetic torque at low temperatures. Downward arrows mark the positions of the irreversibility field H_{irr} where the torque hysteresis loop has closed. In contrast to H^* in κ/T , H_{irr} is seen to be strongly temperature-dependent. Upward arrows correspond to the peak fields where the order-disorder transitions of the flux-line lattice occur. [37].

is the quasiparticle (phonon) mean free path. In addition, the nearly H -independent κ may reflect a compensation between the enhancement of the quasiparticle density of states $N_{\text{del}}(0)$ due to the Doppler shift in superconductors with nodes or anisotropic gaps and the concomitant reduction in l due to increased scattering from vortices [110].

At high fields, $\kappa(H)/T$ exhibits a cusp-like feature at a field $H^* \approx 13.5$ T that is practically independent of T . The height of the cusp-like peak decreases with increasing T , and at 1.5 K the anomaly disappears. Because the thermal conductivity has no fluctuation corrections [111], the cusp of $\kappa(H)/T$ usually corresponds to the mean-field

phase transition. We note that at H^* the field dependence of magnetic torque shows no discernible anomaly, as shown in Fig. 6.8(b), indicating the $\kappa(H)/T$ anomaly at H^* is not caused by a Lifshitz transition nor, for that matter, by a spin-density-wave type of magnetic order.

Fig. 6.9 displays the H - T phase diagram of FeSe for $\mathbf{H} \parallel c$. The irreversibility field H_{irr} is defined by the point where the torque hysteresis loop in Fig. 6.8(b) has closed. We note that H_{irr} determined by the magnetic torque coincides well with the H_{irr} defined by the zero resistivity in Fig. 4.6(a). The irreversibility fields H_{irr} at low temperatures extend to fields well above H^* , indicating that H^* is located inside the superconducting state.

As discussed above, in the high-field superconducting phase above H^* (B -phase in Fig. 6.9), the three characteristic energy scales are comparable, $\varepsilon_F \sim \Delta(0) \sim \mu_B H$. Hence, it is suggested that the B -phase is induced by the strong spin imbalance in the BCS-BEC crossover regime, $P \sim 0.1$, which is several orders of magnitude larger than in conventional superconductors.

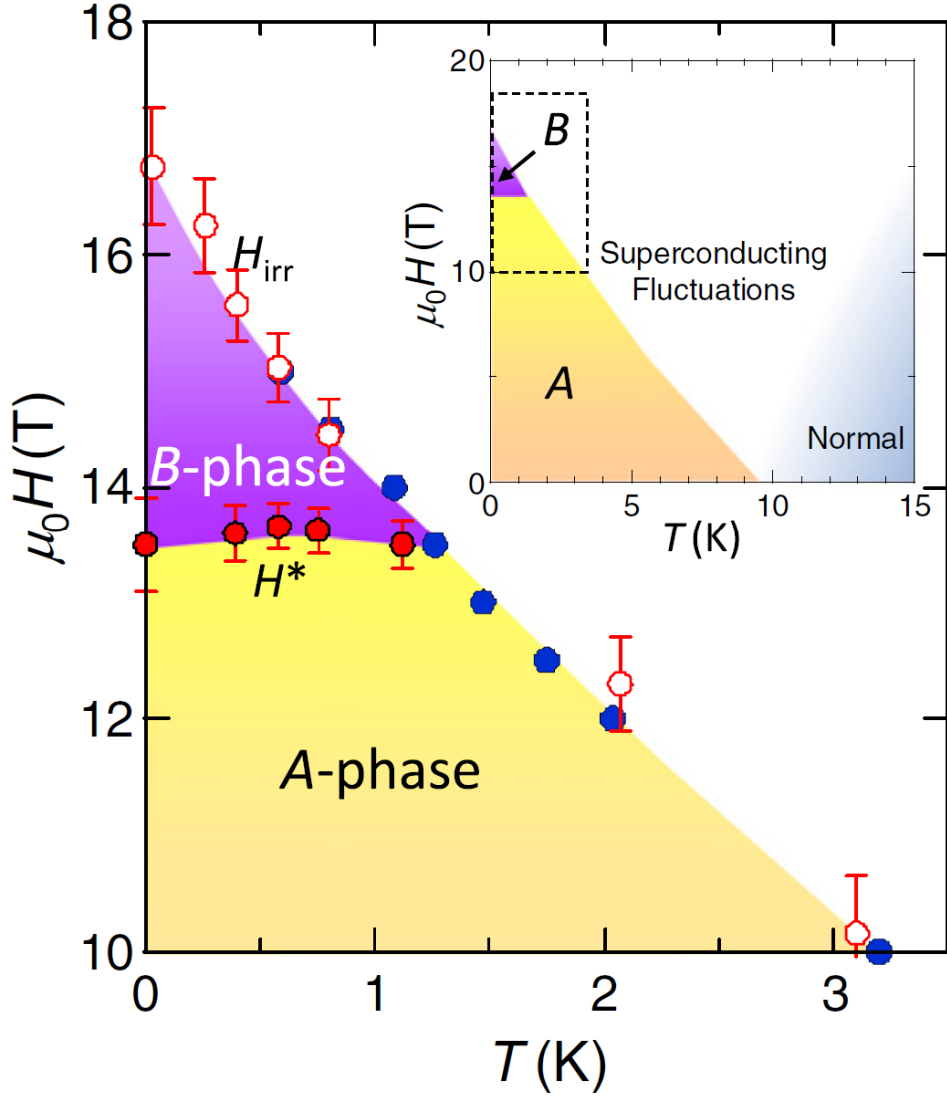


Figure 6.9: H - T phase diagram of FeSe for $\mathbf{H} \parallel c$ in low- T and high- H region. Solid blue and open red circles represent H_{irr} determined by zero resistivity and the onset of the hysteresis loops of the magnetic torque, respectively. The mean-field upper critical field is above H_{irr} . Solid red circles represent H^* determined by the cusp of $\kappa(H)/T$ shown in Fig. 6.8(a), separating a high-field superconducting phase (B -phase) from the low-field phase (A -phase). (Inset) Overall H - T phase diagram. [37].

6.4 Possible FFLO state in B -phase

6.4.1 FFLO state

As discussed in the previous section, we found that FeSe is located in the BCS-BEC crossover region and the new exotic superconducting phase (B -phase) induced by the extremely large spin imbalance $P \approx \mu_B H / \varepsilon_F \approx 0.1$ in high-field region. One of the candidates of the B -phase may be a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase [112, 113]. In this section, we introduce the FFLO state.

A novel superconductivity that belongs to a class of unconventional superconducting state was predicted by Fulde and Ferrell [112] and Larkin and Ovchinnikov [113] (FFLO) in 1964. In the FFLO state, the superconducting order parameter changes sign in real space. The FFLO state originates from the paramagnetism of conduction electrons. In the FFLO state, Cooper pair formation occurs between the Zeeman splitted parts of the Fermi surface and a new pairing state $(\mathbf{k} \uparrow, -\mathbf{k} + \mathbf{q} \downarrow)$ with finite $\mathbf{q}$ is realized

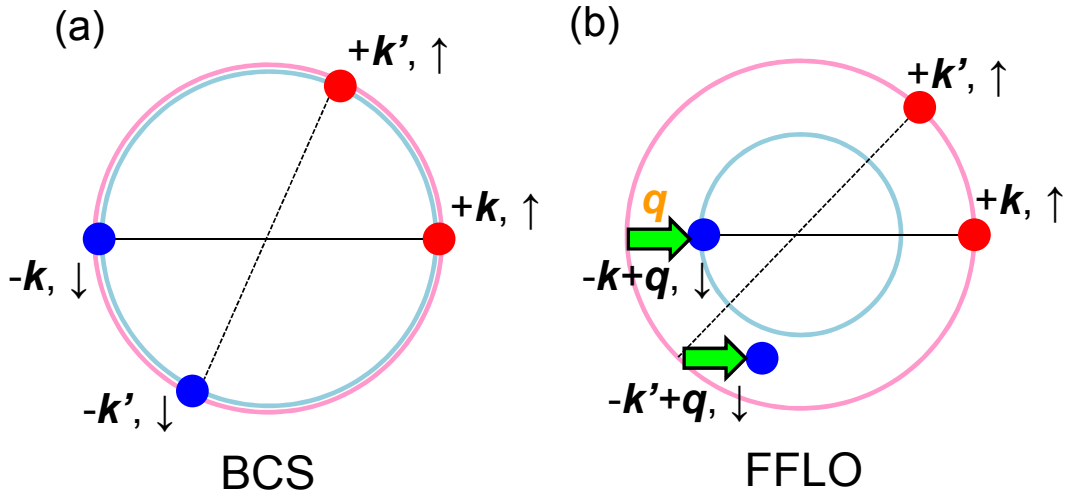


Figure 6.10: (a),(b) Schematic images of the BCS and FFLO pairing states, respectively. Here, $\uparrow$ and $\downarrow$ denote up and down spins, respectively. The red (blue) circle is the Fermi surface of the up (down) spin. In the BCS state, the formation of Cooper pairs occurs at $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$, i.e., the center-of-mass momenta are zero. In the FFLO state, the $(\mathbf{k} \uparrow, -\mathbf{k} + \mathbf{q} \downarrow)$ pairing state with finite center-of-mass momenta $\mathbf{q}/2$ is realized and the order parameters $\Delta(\mathbf{r})$ exhibit spatial oscillations. The electron with $-\mathbf{k}' + \mathbf{q} \downarrow$ is not on the inner Fermi surface.

(Fig. 6.10(b)); the Cooper pairs have finite center-of-mass momenta, which gives rise to the spatial symmetry breaking of the superconducting order parameter $\Delta(\mathbf{r})$. This strongly deviates from the $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$ pairing in the traditional BCS pairing state (Fig. 6.10(a)), where the center-of-mass momenta are zero and $\Delta(\mathbf{r})$ is spatially uniform.

In the FFLO state, there are mainly two ways in which the order parameters exhibit spatial oscillations. One is the FF state, originally proposed by Flude and Ferrell [112], where the order parameter is denoted as

$$\Delta(\mathbf{r}) = \Delta_0 e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (6.5)$$

In this order parameter, the amplitude is homogeneous; however, the phase changes in the real space, that is, time-reversal symmetry is spontaneously broken.

The other is the LO state, originally proposed by Larkin and Ovchinnikov [113]. In the gap equation, the two solutions $\Delta_0 e^{i\mathbf{q} \cdot \mathbf{r}}$ and $\Delta_0 e^{-i\mathbf{q} \cdot \mathbf{r}}$ represent degenerate superconducting states at a transition for a given $\mathbf{q}$. In the LO state, the degeneracy is lifted by forming the combination of $\Delta_0 e^{i\mathbf{q} \cdot \mathbf{r}}$ and $\Delta_0 e^{-i\mathbf{q} \cdot \mathbf{r}}$, and the order parameter is denoted as

$$\Delta(\mathbf{r}) = \Delta_0 (e^{i\mathbf{q} \cdot \mathbf{r}} + e^{-i\mathbf{q} \cdot \mathbf{r}}) = 2\Delta_0 \cos(\mathbf{q} \cdot \mathbf{r}). \quad (6.6)$$

In contrast to the FF state, the gap amplitude shows spatial oscillations along the $\mathbf{q}$ -vector, i.e., the translational symmetry is broken.

According to the theoretical calculations, the free energy of the LO state is lower than of the FF state in the whole temperature range where the inhomogeneous superconducting state appears, and thus the LO state is much more stable than the FF state [113]. Therefore, the FFLO state generally indicates the LO state.

6.4.2 Pair-breaking effects

Generally, in type-II superconductors, a magnetic field destroys the superconductivity in two distinct ways: orbital and paramagnetic pair breaking effects.

The orbital effect leads to the emergence of an Abrikosov vortex state, forming a regular array of vortex lines parallel to the applied magnetic field. The superconducting condensation energy is reduced by the kinetic energy of the superconducting current around the vortex. With increasing magnetic field, vortex cores start to overlap, and then the orbital limiting upper critical field H_{c2}^{orb} is given as

$$H_{c2}^{\text{orb}} = \frac{\phi_0}{2\pi\xi^2}, \quad (6.7)$$

where $\phi_0 = h/2e \cong 2.07 \times 10^{-15}$ Wb is the flux quantum and ξ is the coherence length.

The paramagnetic pair-breaking effect originates from the Zeeman splitting of single electron energy levels. In the superconducting state, spin-singlet Cooper pairs consist of spin-up and spin-down electrons. When the magnetic field is applied, one of the spins is flipped due to the Zeeman effect (Pauli paramagnetism), and the spin-singlet Cooper pairs are collapsed. This destruction of Cooper pairs occurs when the Pauli paramagnetic energy $E_P = (1/2)\chi_n H^2$ and the condensation energy $E_C = (1/2)N(0)\Delta^2$ are the same. Here $\chi_n = (1/2)(g\mu_B)^2 N(0)$ is the spin susceptibility in the normal state, where g is the g -factor of an electron ($g = 2$ for a free electron), μ_B is the Bohr magneton and $N(0)$ is the density of states at the Fermi level. Then we obtain the Pauli-limiting upper critical field H_{c2}^P

$$H_{c2}^P = \frac{\sqrt{2}\Delta}{g\mu_B}. \quad (6.8)$$

In general, the upper critical field H_{c2} is determined by both the orbital and Pauli pair-breaking effects. The Maki parameter α_M :

$$\alpha_M = \frac{\sqrt{2}H_{c2}^{\text{orb}}}{H_{c2}^P}, \quad (6.9)$$

which is the ratio of the orbital and Pauli limiting upper critical field and describes which pair-breaking effect is relatively dominant. In the BCS theory, the coherence length is $\xi = \hbar v_F / \pi \Delta$ at $T = 0$ K and finally the Maki parameter α_M can be estimated

with the formula

$$\alpha_M \approx 2 \left(\frac{m^*}{m_e} \right) \frac{\Delta}{\varepsilon_F}. \quad (6.10)$$

One of the requirements for the formation of the FFLO state is superconductivity with a large Maki parameter α_M , such that the upper critical field can easily approach the Pauli paramagnetic limit. In most superconductors, α_M is negligibly small, and the orbital pair-breaking effect is much more dominant in the suppression of the superconductivity because α_M is on the order of $\Delta/\varepsilon_F \sim 10^{-5} - 10^{-4}$. However, in some superconducting materials α_M can be even larger than unity. In the following section, we will introduce the candidate compounds for the FFLO state.

6.4.3 Requirements for FFLO state

As discussed in the previous section, the FFLO state requires superconductivity with a strong Pauli effect. There are some other requirements for the FFLO state besides a large Maki parameter.

One is a very clean sample with $\xi \ll l$, where l is the quasiparticle mean free path. In contrast to the BCS state of s -wave pairing, it has been theoretically predicted that the FFLO state is unstable against nonmagnetic impurities since the pair amplitude is suppressed due to impurity scattering in real space [114–116].

Second is an anisotropic Fermi surface and gap function. The large part of the pairing between spin-up and spin-down Fermi surfaces by the $\mathbf{q}$ -vector gives rise to stabilization of the FFLO state. Hence, the topology of the Fermi surface and the order parameter is crucial. For a three-dimensional system with a spherical Fermi surface, the spin-up and spin-down Fermi surfaces touch only at a point by a shift of the $\mathbf{q}$ -vector. On the other hand, for a two-dimensional system with a cylindrical Fermi surface, the two Fermi surfaces can touch on a line by a single $\mathbf{q}$ -vector. Therefore, low dimensionality favors the FFLO state [117]. Even in a three-dimensional system, if the Fermi surface is anisotropic and has some flat regions, the FFLO state is expected to be stabilized when the magnetic field $\mathbf{H}$ is oriented in an optimal direction of the

$\mathbf{q}$ -vector.

In most superconductors, the above requirements for the formation of the FFLO state are extremely hard to fulfil. This is why the FFLO state has not been experimentally observed until recently, whereas the theoretical prediction has been proposed more than five decades ago. Recently, the possibility of the FFLO state in heavy fermion and organic superconductors has been reported, because of their potentially large Maki parameters, very long quasiparticle mean free paths, and unconventional pairing mechanisms.

In heavy fermion compounds, the effective masses m^* become several orders of magnitude larger than the mass of a free electron m_e . The heavy electron masses give rise to low Fermi velocities, hence, H_{c2}^{orb} is significantly enhanced. As a result, a large Maki parameter is obtained and the Pauli pair-breaking effect is relatively dominant in some of the heavy fermion compounds.

In fact, the high-field superconducting phases, possible FFLO states, appear in the H - T phase diagram of heavy fermion superconductors CeRu₂ [118, 119] and UPd₂Al₃ [118, 120]. Fig. 6.11 shows the H - T phase diagram of UPd₂Al₃ for $\mathbf{H} \perp [001]$ and $\mathbf{H} \perp [110]$ determined by specific heat and thermal expansion measurements [120].

Since the heavy fermion superconductor CeCoIn₅ with the transition temperature $T_c \sim 2.3$ K and extremely large effective mass $m^* \sim 100 - 1000m_e$ was discovered in 2001 [121], it has received enormous attention because it has been revealed that CeCoIn₅ is a strong candidate for exhibiting the FFLO state. The system has the large Maki parameters, $\alpha_M \approx 5.0$ for $\mathbf{H} \parallel c$ and $\alpha_M \approx 4.6$ for $\mathbf{H} \parallel ab$, respectively [122]. Thus, the specific heat under the high magnetic field $\mathbf{H} \parallel c$ shows an anomalously sharp peak, indicating a first-order like superconducting transition due to the strong Pauli paramagnetic effect, as shown in Fig. 6.12(a) [123, 124]. Several experiments, such as the penetration depth [125], the transverse ultra-sound velocity [126], the NMR Knight shift [127, 128], show some anomalies in the low- T and high- H regime of the superconducting phase. Figs. 6.12(b) and (c) are the H - T phase diagrams of CeCoIn₅ for $\mathbf{H} \parallel c$ and $\mathbf{H} \parallel ab$ determined by these experimental results and a possible FFLO state appears in the superconducting state [107].

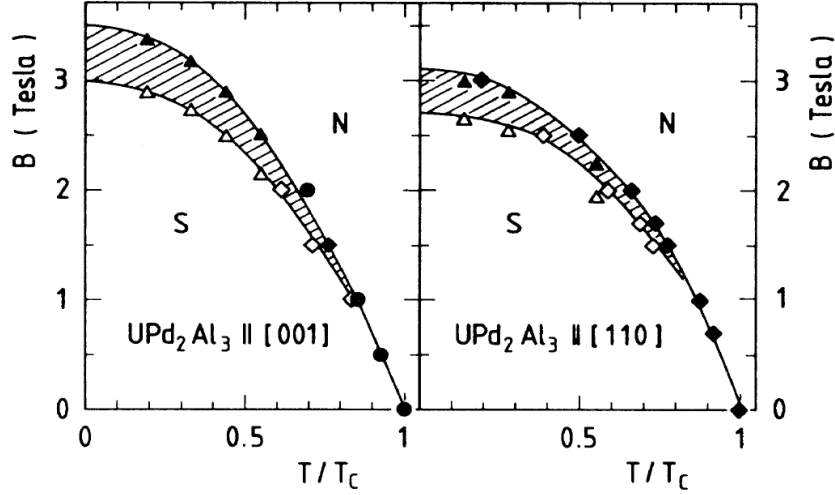


Figure 6.11: H - T phase diagram of UPd_2Al_3 for $\mathbf{H} \perp [001]$ (left panel) and $\mathbf{H} \perp [110]$ (right panel) determined by specific heat and thermal expansion measurements. The hatched high-field superconducting phase between the lines of the first- and second-order phase transitions indicates the existence of a nonuniform superconducting state [120].

The layered organic superconductors are also strong candidates for FFLO states. In these systems, the conducting and insulating block layers are stacked alternatively and thus the electronic properties become two dimensional [129, 130]. When the magnetic field is applied parallel to the conducting layers, the vortices can hardly penetrate into the layers and then H_{c2}^{orb} is remarkably increased [131]. In fact, possible high-field FFLO phases above the Pauli limit H_{c2}^P have been reported in materials such as $\kappa-(\text{BEDT} - \text{TTF})_2\text{Cu}(\text{NCS})_2$ [132, 133], $\lambda-(\text{BETS})_2\text{FeCl}_4$ [134] and $\lambda-(\text{BETS})_2\text{GaCl}_4$ [135].

In the BCS-BEC crossover region, where $\Delta \sim \varepsilon_F$, the Maki parameter α_M becomes several orders of magnitude larger than one in the BCS-limit. Indeed, it has been theoretically predicted that the LO phase becomes stable in a large part of the phase diagram of a spin-imbalanced Fermi gas [136–140].

Here, the superconductor FeSe is located in the BCS-BEC crossover regime and we obtain $\alpha_M \approx 2.5$ for the hole pocket and $\alpha_M \approx 5$ for the electron pocket when we apply the magnetic field $\mathbf{H} \parallel c$ [37]. Therefore, the observed high-field new phase (B -phase) may correspond to the FFLO state.

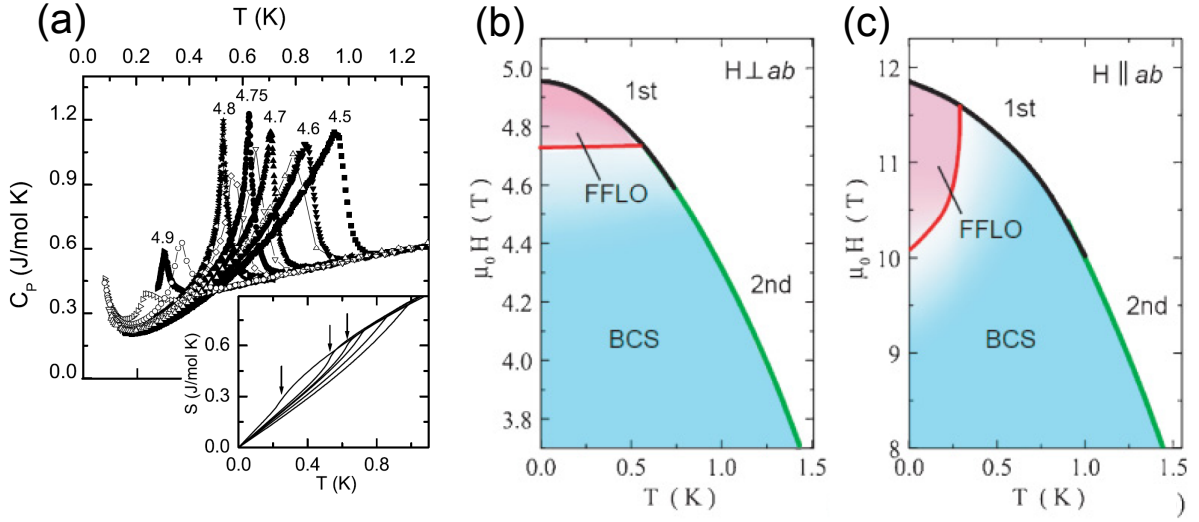


Figure 6.12: (a) Temperature dependence of the specific heat C_P in CeCoIn_5 at the magnetic field 4.5 – 4.9 T parallel to the c -axis [123]. The specific heat under the magnetic field shows an anomalously sharp peak, indicating the first-order-like superconducting transition due to the strong Pauli paramagnetic effect. (b),(c) The experimentally determined H - T phase diagrams of CeCoIn_5 for the magnetic fields $\mathbf{H} \parallel c$ and $\mathbf{H} \parallel ab$, respectively. In both magnetic field directions, the possible FFLO state appears in the low- T and high- H region of the superconducting phase [107, 125–128].

6.5 Summary

In this section, we discussed the detailed electronic structure of FeSe. Recent SdH measurements suggest that the Fermi surface of FeSe consists of one hole pocket at Γ point and one or two electron pockets, whose Fermi energies are several order of magnitude smaller than conventional metals. Our quasiparticle interference (QPI), Seebeck, and penetration depth measurements also revealed that FeSe has extremely small Fermi energies, $\varepsilon_F^h \approx 10$ meV for the hole band and $\varepsilon_F^e \approx 3$ meV for the electron bands. The uncovered electronic structure of FeSe is strikingly different from one predicted by the first-principle calculations due to the d_{xz}/d_{yz} orbital ordering. We found that FeSe is a multigap superconductor with two distinct superconducting gaps of $\Delta \sim 2.5$ and 3.5 meV by scanning tunneling spectroscopy (STS) measurements. The comparable energy scale of ε_F and Δ indicates that superconductivity in FeSe is deep in the BCS-BEC crossover region.

When we apply a magnetic field in the system located in the crossover region, the Zeeman energy $\mu_B H$ becomes comparable to ε_F and Δ near the upper critical field, and a large spin imbalance $P \approx \mu_B H / \varepsilon_F$ is mediated. Conducting thermal conductivity measurement on FeSe, we found that an unexpected superconducting phase (B -phase) induced by the extremely large spin imbalance $P \sim 0.1$ appears in high-field region. FeSe has large maki parameters, $\alpha_M \approx 2.5$ for the hole pocket and $\alpha_M \approx 5$ for the electron pocket, hence, one of the candidates of the B -phase may be a FFLO phase.

7 Quasiparticle excitations in FeSe in the BCS-BEC crossover region studied by thermal transport measurements

FeSe has two unique features that may provide new insights into fundamental aspects of the physics of the BCS-BEC crossover. The first feature is the electronic structure: FeSe is a compensated semimetal with equal numbers of electron and hole carriers, and hence it is essentially a multiband superconductor. This renders the crossover physics in FeSe distinguishable from that in ultracold atomic gases. However, although the superconducting gap structure has been reported to be very anisotropic, the detailed gap structure in each band is still unclear. The second feature concerns the fate of the superfluid when the spin populations are strongly imbalanced. Although highly spin-imbalanced Fermi systems have been realized in ultracold atomic gases, the nature of the spin-imbalanced superfluid is still largely unexplored experimentally due to the difficulty in cooling the systems to sufficiently low temperature. In sec. 6, we report a high-field superconducting phase (*B*-phase) of FeSe induced by the extremely large spin imbalance, but very little is known about its nature.

To shed light on the above issues, detailed knowledge of the quasiparticle excitations in the superconducting state is crucial. Here we measured the thermal conductivity κ_{xx} and the thermal Hall conductivity κ_{xy} up to $\mu_0 H = 20$ T. Both quantities are sensitive probes of the delocalized low-energy quasiparticle excitations.

7.1 Results

Fig. 7.1(a) and its inset show the T and H dependences of the in-plane resistivity ρ_{xx} , respectively. The temperature at which ρ_{xx} goes to zero is ≈ 8.0 K in the present sample. The resistivity at the superconducting onset $\rho_{xx}(T_c^+) \approx 24 \mu\Omega\text{cm}$ is roughly two times larger than that reported in Ref. 37, and the magnitude of the magnetoresistance $\Delta\rho_{xx}(H)/\rho_{xx}(0)$ is roughly halved. Fig. 7.1(b) depicts the H dependence of κ_{xx}/T and κ_{xy}/B (with $B = \mu_0 H$) at $T = 0.59$ K. As mentioned before, κ_{xy} , which is the nondiagonal element of the thermal-conductivity tensor in a perpendicular field, is generally purely electronic and the direct consequence of a transverse quasiparticle current, while κ_{xx} includes both electronic and phonon contributions. The ratio of κ_{xy}/T and electrical Hall conductivity, $\sigma_{xy} = \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2)$, is $(\kappa_{xy}/T)/\sigma_{xy} \approx 1.05L_0$ at $\mu_0 H = 20$ T, where $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)$ is the Lorenz number, indicating that the Wiedemann-Franz law holds within experimental error. At low fields, κ_{xx}/T increases with convex curvature, compatible with the $\sqrt{H}$ dependence expected for a nodal gap (see below), and becomes nearly independent of H between ~ 4 and 10 T. Above 2 T, κ_{xy}/B decreases in magnitude and then changes sign from negative to positive around $\mu_0 H_s \approx 12$ T. Above H_s , both κ_{xx}/T and κ_{xy}/B increase steeply and decrease after exhibiting a narrow plateau-like ridge at around 15 T. These broad maxima will be discussed later. In the normal state, above 17 T, both κ_{xx}/T and κ_{xy}/B decreases as the applied magnetic field increases because of the positive magnetoresistance.

In the following sections, we will discuss the detailed superconducting gap structure of FeSe and the properties of high-field superconducting phase (B -phase).

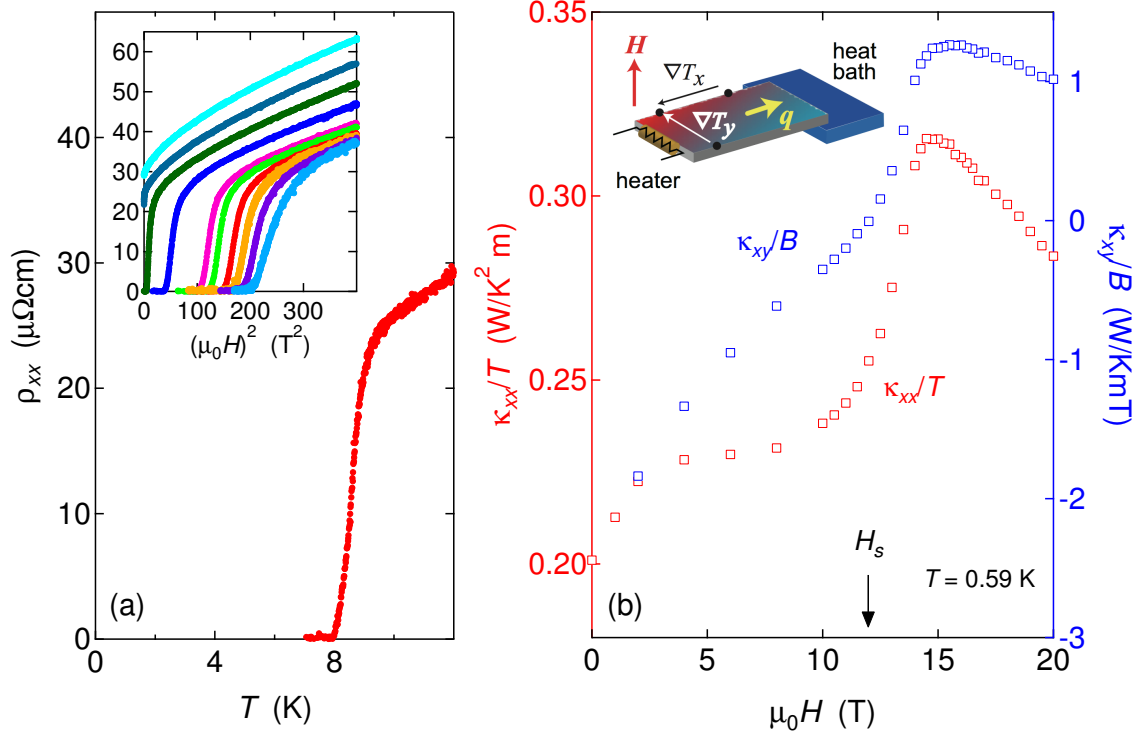


Figure 7.1: (a) Temperature dependence of the in-plane resistivity $\rho_{xx}(T)$ in zero field. The inset shows the field dependence of $\rho_{xx}(H)$ for $\mathbf{H} \parallel c$. From bottom to top, $T = 0.31, 0.61, 1.0, 1.4, 2.1, 2.6, 4.7, 6.6, 9.1$, and 12 K. (b) Field dependence of κ_{xx}/T (red squares, left axis) and κ_{xy}/B (blue squares, right axis) at 0.59 K. The initial increase of κ_{xx}/T with convex curvature at low fields has been reported in FeSe with similar residual resistivity and magnetoresistance [59]. The low-field behaviour of κ_{xx}/T in the present sample differs from that reported in FeSe with much smaller residual resistivity, in which κ_{xx}/T decreases rapidly with H [37]. This may be because in very clean FeSe, the extremely long quasiparticle mean free path is reduced by the vortex scattering, as observed in CeCoIn₅ [109]. The ratio of κ_{xy}/T and electrical Hall conductivity, $\sigma_{xy} = \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2)$ (where ρ_{xy} is the electrical Hall resistivity), is $(\kappa_{xy}/T)/\sigma_{xy} \approx 1.05L_0$ at $\mu_0H = 20$ T, where $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)$ is the Lorenz number, indicating that the Wiedemann-Franz law holds within experimental error. The inset shows a schematic of the measurement setup for the thermal-conductivity tensor.

7.2 Superconducting gap structure

7.2.1 Doppler shift

The magnetic field $\mathbf{H}$ can be useful as a tool for examining the difference in the superconducting properties between superconductors with anisotropic or nodal gap, such as d -wave or extended s -wave, and with isotropic gap, such as plane s -wave [141].

When a magnetic field is applied in type-II superconductors, it enters the superconductor as a vortex with a unit of quantum flux $\Phi_0 = \hbar/2e$. At low fields with $H \ll H_{c2}$ where the vortices are far apart, these vortices create a potential well for low-energy quasiparticles, leading to the formation of a bound state similar to a quantum mechanical picture of a particle in a cylindrical potential well of radius ξ . The bound state has a minimum discrete energy level spacing $\hbar\omega_0 \sim \Delta_0^2/\varepsilon_F$, where Δ_0 is the magnitude of superconducting gap. The energy broadening is given by $\hbar/\tau$. Since $\hbar\omega_0$ is usually 1-10 mK, and hence $\hbar\omega_0 \sim \hbar/\tau$ or $\hbar\omega_0 \ll k_B T$, the spectra of these bound states can be considered as a continuum, similar to the normal state. In an s -wave superconductor with a fully gapped structure, almost all quasiparticle states are localized in the vortex cores. Hence, the density of states in a single vortex at the Fermi energy can be estimated to be $\simeq N(0)\xi^2$, where $N(0)$ is the density of states at the Fermi energy. Eventually, total density of states of the localized state is given as $\simeq N(0)\xi^2 n_v \propto H$, where $n_v = H/H_{c2}$ denotes the number of vortices.

When the superconducting gap is highly anisotropic or has nodes, the density of states is dominated by contributions from the extended quasiparticle states outside the vortex cores (delocalized quasiparticles) rather than the bound states located inside the vortex cores (localized quasiparticles) [142]. In contrast to fully-gapped s -wave superconductors, quasiparticles are easily delocalized from the vortices due to the presence of nodes, and they extend over the entire crystal. The main effect on such delocalized quasiparticles with momentum $\mathbf{p}$ is the Doppler shift of the quasiparticle energy from a supercurrent flow $\mathbf{v}_s$ circulating around the vortices (Fig. 7.2(a)), which is given as

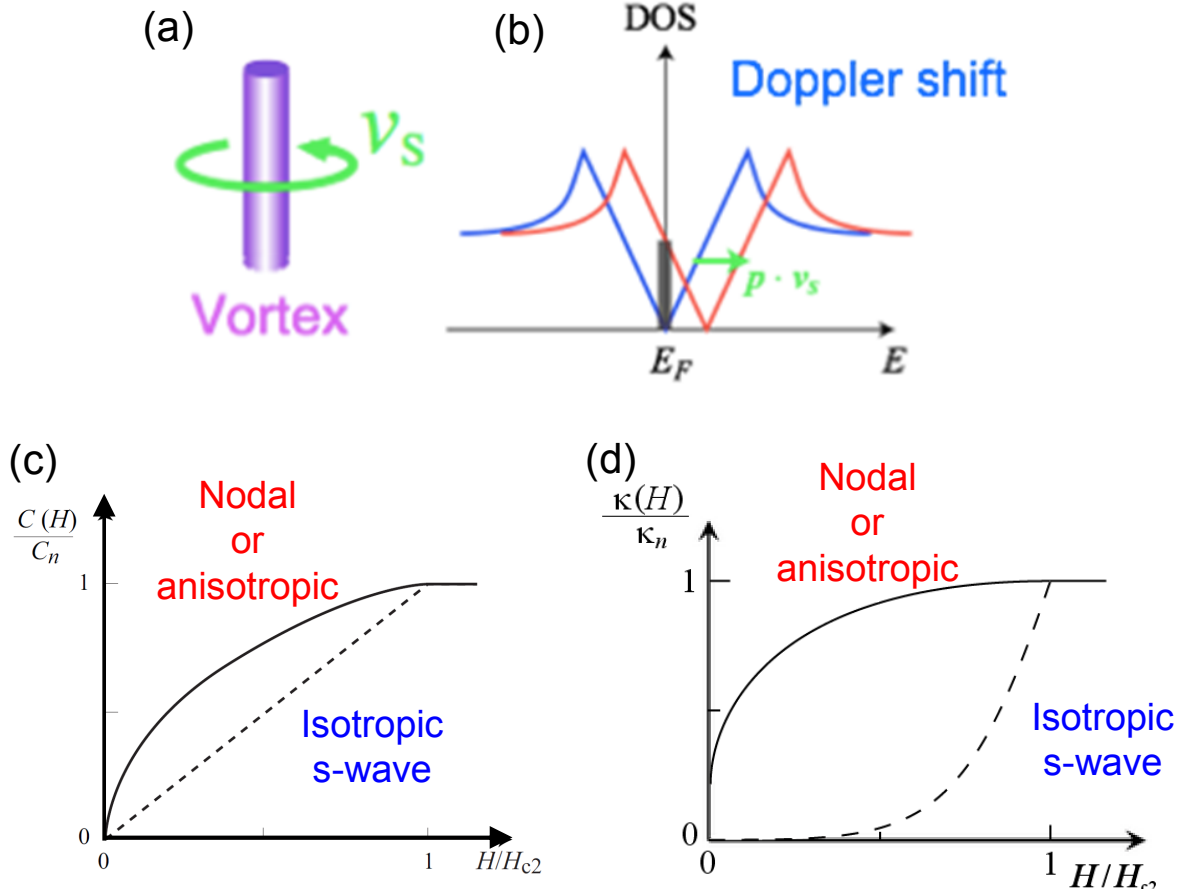


Figure 7.2: (a) Schematic image of a supercurrent flow $\mathbf{v}_s$ circulating around the vortices. (b) Schematic image of Doppler shift in a nodal superconductor with line nodes. Here, the energy is measured from the Fermi energy. The red and blue lines represent the quasiparticle spectrum in the presence and absence of a magnetic field, respectively. In the magnetic field, the finite residual density of states $N(0)$ appears at zero energy due to the Doppler shift. (c),(d) Field dependence of the specific heat and thermal conductivity, respectively. Solid lines are for nodal or anisotropic superconductors and dashed lines are for isotropic s -wave superconductors [141].

$$E(\mathbf{p}) \rightarrow E(\mathbf{p}) + \mathbf{v}_s \cdot \mathbf{p}. \quad (7.1)$$

In order to estimate the characteristic energy scale of the Doppler shift, we assume a single vortex case. In this case, we can approximate the velocity field as $\mathbf{v}_s = \hbar \hat{\phi}$, where r is the distance from the center of the vortex and $\hat{\phi}$ is a unit vector along the

circulating current. This expression is valid outside the vortex core and up to a cut-off of order $\min\{R, \lambda\}$, where $R = a\sqrt{\Phi_0/\pi H}$ is the intervortex distance, a is a geometric constant of order unity, and λ is the London penetration depth. Doppler shifted energy averaged over the vortex lattice, E_H , can be estimated by integrating over a vortex lattice unit cell and it is given by

$$E_H = \langle |\mathbf{v}_s \cdot \mathbf{p}| \rangle = \int_{|\mathbf{r}| < R} \frac{d^2\mathbf{r}}{\pi R^2} |\mathbf{v}_s \cdot \mathbf{p}| \simeq \frac{1}{R} v_F \Phi_0 \simeq \frac{4}{a\pi} \hbar v_F \sqrt{\frac{H}{\Phi_0}}, \quad (7.2)$$

Fig. 7.2(b) illustrates the quasiparticle spectrum in a nodal superconductor with line nodes in the superconducting gap function. In the case of highly anisotropic superconducting gap whose gap minimum is very small, the following discussion for the line nodes is almost applicable. In a superconductor with line nodes, where the density of states $N(E)$ has a linear energy dependence at low energy with $E \ll \Delta_0$, the finite residual density of states for delocalized quasiparticles $N(0)$ is induced by the Doppler shift, and it is roughly estimated to be $N(0) \propto E_H \propto \sqrt{H}$. Therefore, $\sqrt{H}$ -dependence is expected for the thermodynamic and transport properties such as specific heat and thermal conductivity.

In an s -wave superconductor with a fully gapped structure, the Doppler shift does not affect the physical properties since E_H is always smaller than the gap amplitude Δ_0 .

7.2.2 Field dependence of thermal conductivity

In a nodal superconductor, the Doppler shifted density of states governs the heat transport as for thermodynamic quantities at low temperatures and low fields with $T/T_c \ll H/H_{c2}$. Figs. 7.2(c) and (d) illustrate the field dependence of the specific heat and thermal conductivity for nodal or anisotropic and isotropic s -wave superconductors, respectively. We first discuss the field dependence of the specific heat. In the superconducting state, the specific heat measures all quasiparticle states. Therefore, in s -wave superconductors, the localized quasiparticle states bound in the vortex cores can

contribute to the specific heat, which exhibits H -linear dependence. In nodal superconductors, the specific heat contains contributions from both localized and delocalized quasiparticles, and shows $\sqrt{H}$ -dependence because of the dominance of the contribution from the delocalized quasiparticle state, as discussed in the previous section.

On the other hand, the localized quasiparticles cannot contribute to the heat transport, in contrast to the specific heat. Therefore, the thermal conductivity can probe the response purely originating from the delocalized quasiparticles, which directly reflects the Doppler shifted density of states. As a result, in s -wave superconductors, such as Nb [143], the thermal conductivity is almost zero and it exhibits an exponential behavior at low fields. At high fields near H_{c2} , the tunneling of quasiparticles between vortices becomes possible due to the overlapping of vortices and hence the thermal conductivity exhibits steep increase toward the normal state value. The $\sqrt{H}$ -dependence is also expected for the thermal conductivity in a nodal superconductor. A steep initial increase and $\sqrt{H}$ -like dependence in thermal conductivity has been observed in cuprates, such as Tl-2201 [144].

7.2.3 Superconducting gap structure of FeSe

As shown in Fig. 7.1(b), the initial increase of κ_{xx}/T with a convex curvature at low fields is a signature of superconductivity with line nodes, where the Doppler shift of the quasiparticle spectrum in the presence of supercurrents around vortices gives rise to a $\sqrt{H}$ increase in the population of delocalized quasiparticles [141]. The superconducting gap structure of FeSe is subject of extense discussion. A clear signature of the line nodes in the superconducting gap has been reported for very clean single crystals [37] or thin films [56] probed by scanning tunneling spectroscopy, thermal conductivity and magnetic penetration depth. In less clean crystals, however, a superconducting state with finite energy gap has been reported [58] (Sec. 4.5). Moreover, even in very clean crystals, twin boundaries lift the nodes and induce a fully-gapped state due to the time-reversal symmetry breaking effect [61] (Sec. 5). These results indicate that the line nodes are not symmetry protected and can be easily lifted by impurity and boundary scattering. The observed low-field convex curvature of κ_{xx}/T in Fig. 7.1(b) indicates the presence

of line nodes or large superconducting gap anisotropy. Similar field dependence has been reported in FeSe with similar residual resistivity and magnetoresistance [59]. We note that this low-field behavior of κ_{xx}/T differs from that reported in FeSe with much smaller residual resistivity, in which κ_{xx}/T decreases rapidly with magnetic field [37], possibly because in very clean FeSe, the extremely long quasiparticle mean free path is reduced by vortex scattering at low fields [109].

The nearly step-like behavior in the field dependence of κ_{xx}/T upon approaching 15 T is attributed to the multiband nature of superconductivity in FeSe [145–147]. A substantial portion of quasiparticles, which can be easily excited over the smaller gap, is already present at fields well below H_s , and therefore, κ_{xx}/T at high fields above ~ 4 T is governed by the larger gap. Note that a nearly H -independent behavior at low fields and a subsequent steep increase of κ_{xx}/T with a concave curvature is observed in fully gapped superconductors, where quasiparticles are localized in the vortex core and thus are unable to transport heat until these vortices overlap each other [141].

Although multigap superconductivity and a very anisotropic or nodal gap structure in FeSe have been suggested by several experiments, the detailed gap structure of electron and hole pocket has remained unclear. The combined results of the field dependence of κ_{xx} and the sign of κ_{xy} provide important information on this issue. The sign change of κ_{xy} at H_s evidences that the quasiparticles responsible for the thermal conduction are electron-like at low fields and hole-like at high fields. Therefore, the large gap anisotropy found at low fields should correspond to the electron pocket, whereas the concave increase above H_s and saturation of κ_{xx}/T below H_s indicate that the superconducting gap of the hole pocket is more isotropic and that its amplitude is larger than that of the electron pocket.

7.3 Field-induced superconducting phase (B -phase)

7.3.1 Phase diagram

Next we will focus on the high-field region and discuss the properties of B -phase. Figs. 7.3 (a) and (b) depict H dependences of κ_{xx}/T and κ_{xy}/B , respectively, at $T = 0.59$ K, while Figs. 7.3 (c) and (d) show the results at $T = 0.95$ K. Two distinct anomalies (kinks) can be identified in both κ_{xx}/T and κ_{xy}/B . We first point out

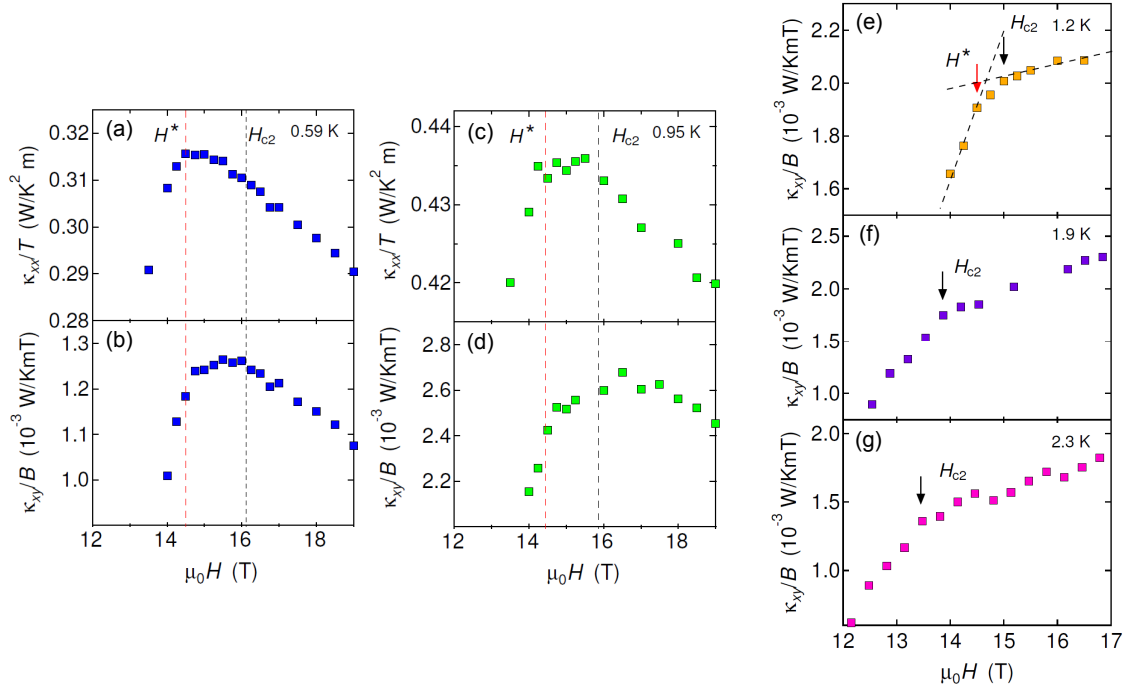


Figure 7.3: Field dependences of (a) $\kappa_{xx}(H)/T$, and (b) κ_{xy}/B at $T = 0.59$ K. (c) and (d) are the results at $T = 0.95$ K. (e), (f) and (g) show κ_{xy}/B at $T = 1.2$, 1.9 , and 2.3 K, respectively. The dashed red and black lines represent magnetic fields, which correspond to H^* and H_{c2} where the kink anomalies appear, respectively. The dashed lines in (e) represent the linear extrapolations below H^* and above H_{c2} . Our detailed measurements of the thermal transport coefficients, κ_{xx} and κ_{xy} , with small steps in the field scans allow us to observe two distinct anomalies at H^* and H_{c2} , which have been missed in a previous study [59]. The observed kink in $\kappa_{xx}(H)/T$ at H^* is distinct from the previously reported observations in very clean FeSe [37], where κ_{xx}/T exhibits a tiny peak at H^* . This may be caused by the very large magnetoresistance in the cleaner sample, which leads to the rapid decrease of κ_{xx}/T at low H and above H_{c2} , smearing out the rapid increase just below H^* and features at H_{c2} .

that the field marked by the dashed black line corresponds to the upper critical field H_{c2} because of the following reasons. First, above this field, κ_{xx}/T decreases rapidly with H , which is consistent with the large positive magnetoresistance in the normal state [148] [inset of Fig. 7.1(a)]. In addition, the fact that κ_{xx}/T is nearly independent of H below this field definitely indicates that the system at lower fields is not in the normal state. Second, the thermal conductivity has no fluctuation correction, in contrast to the resistivity, magnetic susceptibility, and specific heat, which all are subject to fluctuations, and, hence, often exhibits a kink anomaly at the mean-field upper critical field [149, 150]. Third, as will be shown later, this field is close to the superconducting onset field determined by the use of resistivity data. The fact that the admittedly weak kinks at H^* and H_{c2}^κ occur at the same fields for the different measurements at temperatures 0.59 and 0.95 K lends strong confidence to the identification of H^* and H_{c2} .

Figs. 7.3 (e), (f), and (g) show the H dependence of κ_{xy}/B at higher temperatures. At $T = 1.2$ K, no clear kink anomalies can be resolved, but κ_{xy}/B deviates from the linear lines extrapolated from the lower and higher field regimes, as shown in Fig. 7.3 (e). At $T = 1.9$ and 2.3 K, only one kink anomaly is observed, which is attributed to H_{c2} because, as will be shown later, these fields are close to the onset of superconductivity.

Fig. 7.5 displays the H - T phase diagram. The magnitudes of H^* and H_{c2}^κ in the present crystal are slightly larger than those reported in ref. [37]. We note that the superconducting onset field (black open circles) is close to H_{c2}^κ determined by the thermal transport coefficients, (black closed circles) supporting that the higher-field anomaly shown by the dashed black line in Figs. 7.3(a)-(g) is indeed due to the upper critical field H_{c2} . In contrast to H_{c2}^κ , H^* is nearly temperature independent and disappears when it meets the H_{c2}^κ line. We stress that this fact is an important additional feature establishing the H - T phase diagram, which was not seen in our previous work [37]. We further note that the B -phase above H^* is not related to magnetic ordering, because of the following reasons. First, magnetic-torque measurements show no anomaly at H^* [37]. Second, the size of the hole pocket determined by magnetic quantum oscillations above 20 T coincides with that determined from angle-resolved photoemission in

zero field, suggesting the absence of band folding [40]. Third, the H^* line is observable only in the superconducting regime.

7.3.2 Field dependence of thermal Hall angle

It has been reported that ρ_{xy} is positive and increases linearly with H and that the magnetoresistance increases with H as $\Delta\rho_{xx}(H)/\rho_{xx}(0) \propto H^2$ at $\mu_0 H \gtrsim 18$ T [40]. Since FeSe is a compensated metal, with the same number of hole and electron charge carriers and only a single hole pocket, these H dependences indicate that the transport properties in the high-field region are governed by that hole band [41, 148]. In this situation, the scattering time τ_{qp} of the quasiparticles is proportional to the thermal Hall angle, $\tan \Theta_H/B \propto \tau_{qp}$. Here the thermal Hall angle is defined by $\tan \Theta_H/B \equiv \kappa_{xy}/(\kappa_{xx}^{qp}B)$, where the quasiparticle contribution of thermal conductivity κ_{xx}^{qp} can be

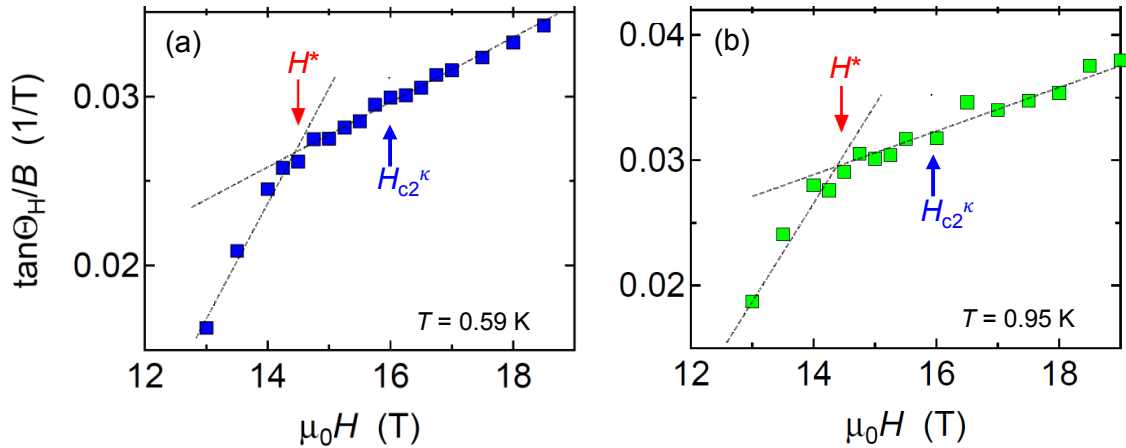


Figure 7.4: Field dependences of $\tan \Theta_H/B \equiv \kappa_{xy}/(\kappa_{xx}^{qp}B)$ at (a) $T = 0.59$ K and (b) $T = 0.95$ K near the upper critical field. κ_{xx}^{qp} is obtained by subtracting κ_{xx}^{ph} from κ_{xx} , where κ_{xx}^{ph} is estimated by using the Wiedemann-Franz law in the normal state at 20 T, $\kappa_{xx}^{ph}/T = \kappa_{xx}(20 \text{ T})/T - L_0\sigma_{xx}(20 \text{ T})$, and is assumed to be field independent. The red and black arrows represent magnetic fields, which correspond to H^* and H_{c2}^κ , respectively. In $\tan \Theta_H/B$, a clear kink anomaly appears at H^* , while no discernible anomaly is observed at H_{c2}^κ . The dashed lines represent the linear extrapolations below and above H^* , respectively. In a single band case, $\tan \Theta_H/B$ is proportional to quasiparticle scattering time τ_{qp} . The kink anomaly in $\tan \Theta_H/B$ at H^* strongly suggests that the quasiparticle scattering mechanism changes on entering the B -phase in the superconducting state.

estimated by using the Wiedemann-Franz law in the normal state at 20 T, $\kappa_{xx}^{\text{ph}}/T = \kappa_{xx}(20 \text{ T})/T - L_0\sigma_{xx}(20 \text{ T})$, and is assumed to be field independent. The clear kink at H^* in $\tan \Theta_H/B$ [Figs. 7.4(a) and (b)] indicates that the quasiparticle scattering mechanism changes when crossing the H^* line, suggesting a modification of the superconducting gap structure. At H_{c2}^κ , $\tan \Theta_H/B$ shows no discernible anomaly, while κ_{xx}/T shows a clear kink as shown in Figs. 7.3(a) and (c). Since κ_{xx} is proportional to the product of τ_{qp} and the quasiparticle density n_{qp} , $\kappa_{xx} \propto n_{\text{qp}}\tau_{\text{qp}}$, these results show that τ_{qp} barely changes while n_{qp} is reduced below H_{c2} . Thus, the observed anomalies in the thermal transport coefficients strongly suggest the emergence of a new high-field superconducting phase (B -phase) which is distinctly different from the A -phase at lower fields.

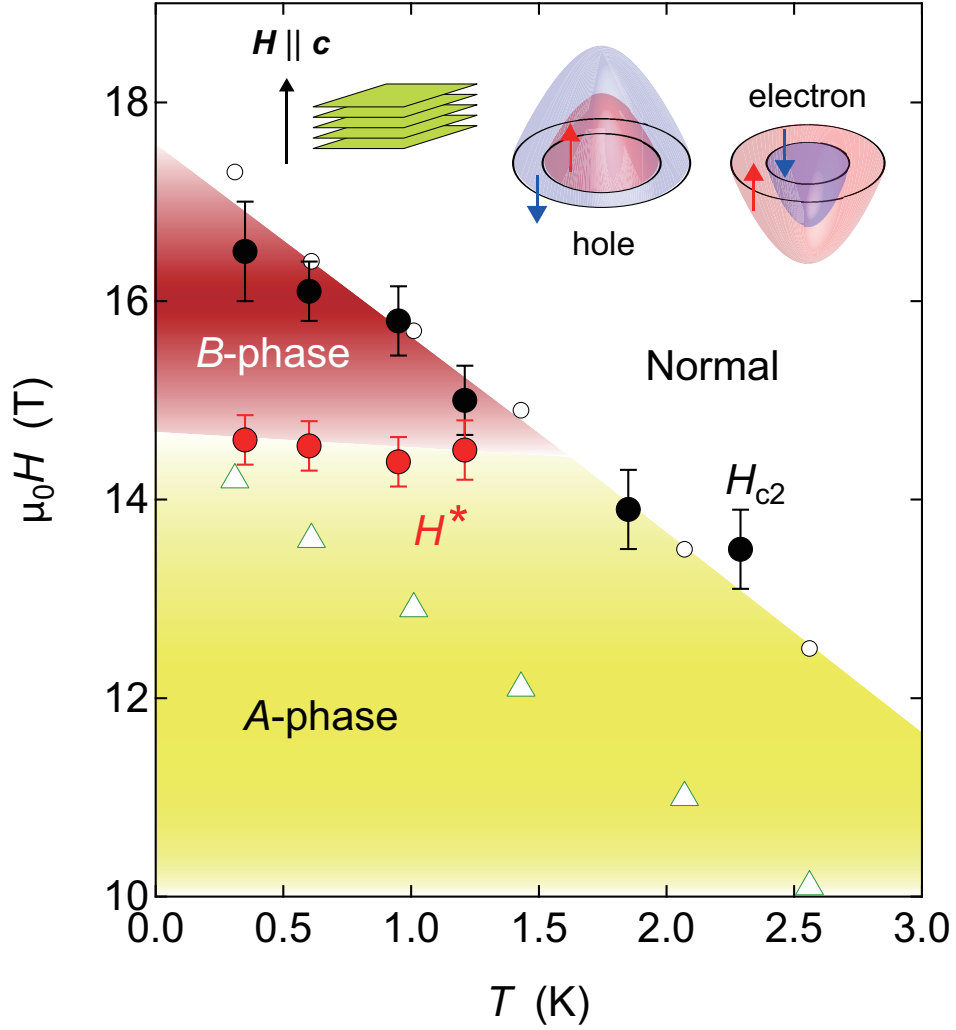


Figure 7.5: Field-temperature (H - T) phase diagram of FeSe in perpendicular field determined by the thermal-transport measurements. Black filled circles represent the upper critical field H_{c2}^κ and filled red circles represent H^* that separates A - and B -phases. The black open circles represent superconducting onset field at which the resistivity becomes 90% of the value extrapolated from the normal-state value under magnetic field, and the green open triangles represent the irreversibility fields determined by zero resistivity [inset of Fig. 7.1(a)]. The inset illustrates the electronic structure of hole and electron pockets at fields around H^* . Both Fermi surfaces are highly spin imbalanced.

7.4 Possible FFLO state in FeSe

Next we discuss the field-induced superconducting B -phase. We stress that this phase represents a highly unusual superconducting state because both electron and hole pockets are largely spin-imbalanced with $P \approx \mu_B H^* / \varepsilon_F \approx 0.1$, as illustrated in the inset of Fig. 7.5.

The nearly temperature-independent behavior of H^* suggests that this anomaly is not an artifact of a single broad peak of the H_{c2} anomaly, because in that case the two anomalies at H^* and H_{c2} should follow parallel lines.

One of the candidates for the B -phase may be a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase [112, 113], where the Cooper-pair formation occurs between Zeeman-split parts of the Fermi surface and a new pairing state $(\mathbf{k} \uparrow, -\mathbf{k} + \mathbf{q} \downarrow)$ with finite $\mathbf{q}$ is realized, as mentioned in sec. 6.4.

7.4.1 The lowest Landau level solutions in BCS and FFLO state

In real type-II superconductors, the orbital effect invariably exists due to the induced vortices. The $\mathbf{q}$ -vector, which causes the spatial oscillations of the order parameter, is determined by the cyclotron motion of the Cooper pairs around the vortices in the plane perpendicular to the magnetic field $\mathbf{H}$ [151].

Now we consider the three-dimensional isotropic case. The solutions of the order parameter are obtained by the eigen equation

$$\Pi^2 \psi_n^{(k)} = \epsilon_n \psi_n^{(k)}, \quad (7.3)$$

where

$$\Pi = -i\hbar\nabla - \frac{2e}{c}\mathbf{A}, \quad (7.4)$$

with the vector potential $\mathbf{A} = (0, Hx, 0)$ for a magnetic field along the z -axis $\mathbf{H} =$

$(0, 0, H)$. Here, the eigenfunctions of the operator $\mathbf{\Pi}^2$ can be written as

$$\mathbf{\Pi}^2 = \frac{2\hbar^2}{\xi_H^2} \left(\eta^\dagger \eta + \frac{1}{2} \right) - \hbar^2 \frac{\partial^2}{\partial z^2}, \quad (7.5)$$

where $\eta^\dagger$ and η are the boson creation and annihilation operators defined by

$$\eta = \frac{\xi_H}{\sqrt{2}\hbar} (\Pi_x - i\Pi_y), \quad (7.6)$$

$$\eta^\dagger = \frac{\xi_H}{\sqrt{2}\hbar} (\Pi_x + i\Pi_y), \quad (7.7)$$

respectively. Here, $\xi_H = \sqrt{\phi_0/2\pi H}$ is the interval between vortices. Eigenfunctions with respect to the degree of freedom perpendicular to $\mathbf{H}$ are described by the Abrikosov functions with Landau level index n ,

$$\psi_n^{(k)}(\boldsymbol{\rho}) = (-1)^n e^{ik_y} H_n \left[\sqrt{2} \frac{x - x_k}{\xi_H} \right], \quad (7.8)$$

for any real number k and $x_k = k\xi_H$, where H_n is the Hermite polynomial and $\boldsymbol{\rho} = (x, y)$. The eigenfunction for the lowest Landau level ($n = 0$) is given by

$$\psi_0^{(k)}(\boldsymbol{\rho}) = e^{ik_y} \exp \left[\frac{(x - x_k)^2}{2\xi_H^2} \right]. \quad (7.9)$$

In the BCS state, the eigenvalues ϵ_n are

$$\epsilon_n = \frac{2\hbar^2}{\xi_H^2} \left(n + \frac{1}{2} \right). \quad (7.10)$$

In general, the order parameter in the BCS state is described by the lowest Landau level solution

$$\Delta(\mathbf{r}) \propto \psi_0^{(k)}(\boldsymbol{\rho}) \quad (7.11)$$

which gives the highest upper critical field.

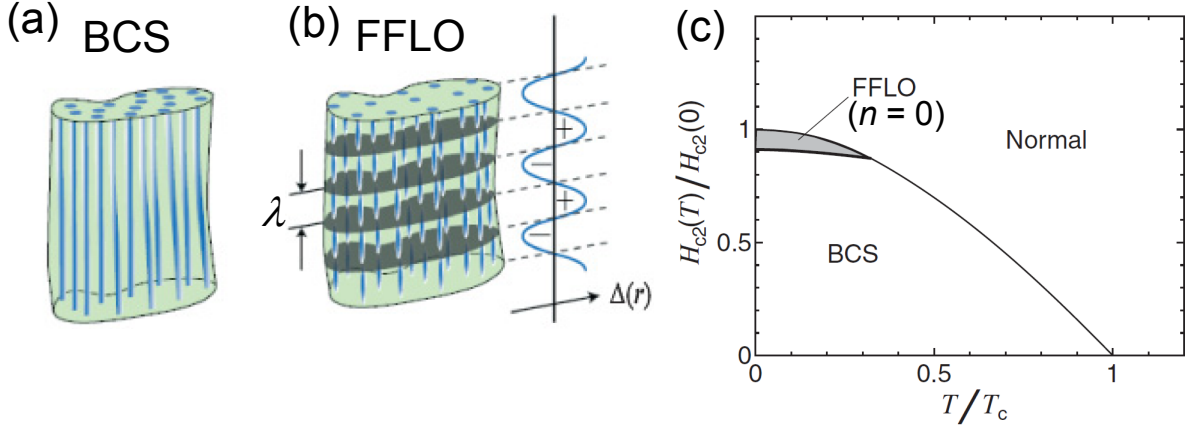


Figure 7.6: (a) Schematic image of the flux line lattice, with the magnetic field $\mathbf{H} = (0, 0, H)$, in the BCS state. (b) Flux line lattice in the FFLO state with the lowest Landau level solution. The amplitude of the order parameter for the LO state oscillates along the $\mathbf{q}$ -vector parallel to $\mathbf{H}$ and the two-dimensional nodal planes with the interplanar distance $\lambda = 2\pi/q$ are formed perpendicular to $\mathbf{H}$ [107]. (c) Theoretically proposed H - T phase diagram in the presence of the orbital effect [151]. The FFLO state with $n = 0$ is present above the BCS state. The transitions from the normal state to the FFLO and BCS states are of second order (solid line), while the transition from the FFLO state to the BCS state is of first order (thick solid line).

In the FFLO state, the eigenvalues ϵ_n can be obtained as

$$\epsilon_n = \frac{2\hbar^2}{\xi_H^2} \left(n + \frac{1}{2} \right) + \hbar^2 q^2, \quad (7.12)$$

where the second term is the kinetic energy of the Cooper pairs along $\mathbf{H}$ [107, 151]. The increased kinetic energy in Eq. 7.12 is compensated by the reduction of the Pauli paramagnetic energy. Now, we assume that the lowest Landau level ($n = 0$) gives the highest upper critical field also in the FFLO state. Then, the order parameter $\Delta(\mathbf{r})$ can be written as

$$\Delta(\mathbf{r}) \propto \exp(iqz)\psi_0^{(k)}(\boldsymbol{\rho}) \quad (\text{FFstate}) \quad (7.13)$$

$$\Delta(\mathbf{r}) \propto \cos(qz)\psi_0^{(k)}(\boldsymbol{\rho}) \quad (\text{LOstate}). \quad (7.14)$$

The order parameter for the LO state in Eq. 7.14 exhibits a spatial modulation along the $\mathbf{q}$ -vector parallel to $\mathbf{H}$ and the two-dimensional nodal planes with the interplanar dis-

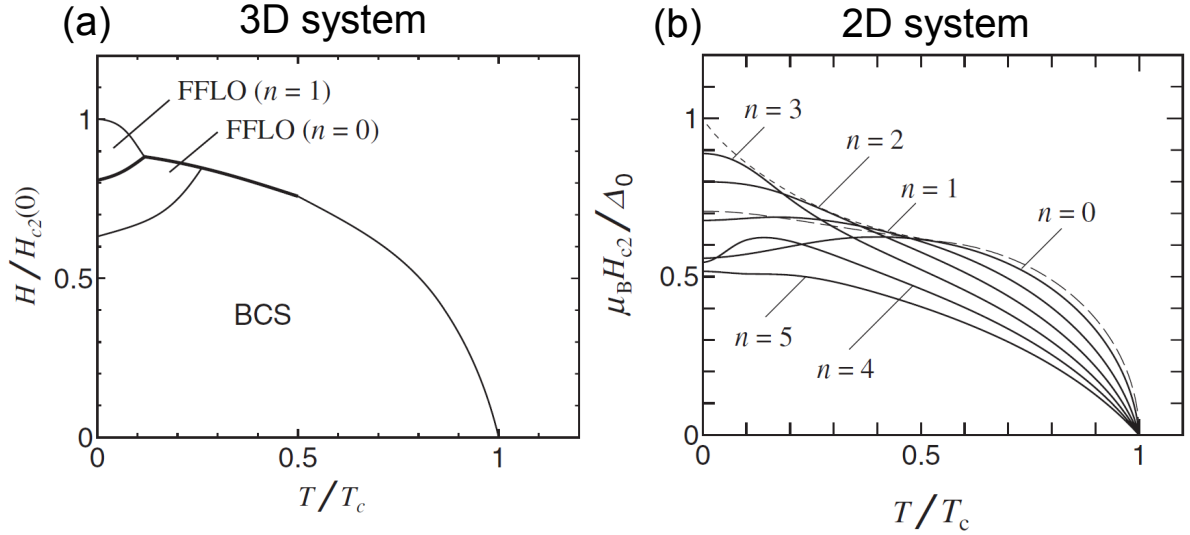


Figure 7.7: (a) H - T phase diagram for a three-dimensional system with the Maki parameter $\alpha_M = 1$ [116]. n is the Landau level index. FFLO states with the Landau levels $n = 0$ and $n = 1$ coexist. The thick and thin solid lines denote the first- and second-order transition lines, respectively. (b) Upper critical field curves with various Landau levels in a two-dimensional system with the magnetic field slightly tilted from the plane of the superconductor [153]. Since the physical critical field is the maximum one at each temperature, the FFLO states with the higher Landau levels $n \geq 1$ are realized in some temperature ranges.

tance $\lambda = 2\pi/q$ are formed perpendicular to $\mathbf{H}$, as shown in Fig. 7.6(b) [107]. Fig. 7.6(c) is the H - T phase diagram in the presence of the orbital effect, with $n = 0$ [151].

7.4.2 FFLO state with higher Landau levels

When the Pauli pairing effect is further increased in the system, it has been predicted that FFLO states with higher Landau levels appear in the H - T phase diagram [116, 152, 153]. This is because the Pauli paramagnetic energy is reduced as the number of nodal planes is increased, which means that the number of polarized quasiparticles is increased in the vicinity of the nodes. The theoretical calculations indicate that the FFLO state with the higher Landau level ($n > 1$) provides the higher upper critical field in some region of the H - T phase diagram.

Fig. 7.7(a) shows the schematic H - T phase diagram for a three-dimensional system with the Maki parameter $\alpha_M = 1$ [116]. In the even lower temperature and higher field

region, the FFLO state coexists with the Abrikosov state with the Landau level $n = 1$, which gives the highest upper critical field. In this phase, nodal planes are formed periodically, parallel to the vortex lattice.

An FFLO state with the higher Landau levels is also predicted in a two-dimensional system with the magnetic field slightly tilted from the plane of the superconductor [153]. Fig. 7.7(b) is the H_{c2} curves with various Landau levels in the two-dimensional system. In some low temperature regions, the calculated upper critical fields with the higher Landau levels become larger than one with $n = 0$.

7.4.3 Possible FFLO state with higher Landau levels in FeSe

As we mentioned before, one of the candidates for the B -phase may be a FFLO phase [112, 113]. The FFLO state has been reported in layered heavy-fermion and organic superconductors for magnetic fields parallel to the two-dimensional plane [107, 132]. However, based on our results and the previous discussion in sec. 7.4.1 and 7.4.2, we want to point out that the B -phase is unlikely to be a conventional FFLO phase. In fact, the B -phase coexists with the vortex-liquid state where the resistivity is finite. This is different from heavy-fermion and organic systems, where possible FFLO phases occur within the vortex-lattice state. Moreover, the FFLO state is stabilized when a large part of the spin-up Fermi surface is connected to the spin-down surface by a single $\mathbf{q}$ vector. For the lowest Landau level solution, the superconducting order parameter changes spatially as $\Delta(\mathbf{r}) \propto \cos(\mathbf{q} \cdot \mathbf{r})$ where $\mathbf{q} \parallel \mathbf{H}$, as discussed in sec. 7.4.1.

However, since the Fermi surface of layered FeSe is cylindrical, the spin-up Fermi surface cannot be connected to a large part of the spin-down Fermi surface by a single $\mathbf{q}$ -vector for $\mathbf{H} \parallel c$. This analysis leads us to consider that the B -phase may be an FFLO phase involving higher Landau levels, where the $\mathbf{q}$ -vector lies in the two-dimensional plane. Moreover, what makes FeSe distinctly different from ultracold atomic gases is that FeSe is a multiband system, where the interplay between the formation of bound pairs and superconductivity may lead to rich physics [154].

Thus, the field-induced B -phase appears to be a previously unidentified kind of inhomogeneous superconducting state with an unprecedented large spin imbalance, which

apparently is associated with the BCS-BEC crossover in a multiband system.

7.5 Summary

In summary, we measured the thermal longitudinal and thermal Hall conductivity in FeSe in the BCS-BEC crossover regime. The field dependences of thermal transport coefficients imply that the quasiparticle structure is strongly band-dependent; a highly anisotropic small superconducting gap forms at the electron Fermi-surface pocket whereas a more isotropic and larger gap forms at the hole pocket. The analysis of the thermal Hall angle provides evidence for the emergence of a highly anomalous inhomogeneous superconducting state, which is likely to be caused by the extremely high spin polarization. The strongly band-dependent quasiparticle structure and the emergent highly spin-polarized phase may be important and unique features of the BCS-BEC crossover in the multiband superconducting system.

8 Conclusion

BCS-BEC crossover in FeSe (Section 6 and 7)

To investigate the itinerant electronic structure of FeSe, we performed quasiparticle interference (QPI), Seebeck, and penetration depth measurements on high-quality FeSe single crystals grown by the KCl/AlCl₃ vapor transport technique. We revealed that FeSe has extremely small Fermi energies, $\varepsilon_F^h \approx 10$ meV for the hole band and $\varepsilon_F^e \approx 3$ meV for the electron bands. We found that FeSe is a multigap superconductor with two distinct superconducting gaps of $\Delta \approx 2.5$ and 3.5 meV by scanning tunneling spectroscopy (STS) measurements. The comparable energy scale of ε_F and Δ indicates that superconductivity in FeSe is deep in the BCS-BEC crossover region. The field dependence of thermal conductivity κ_{xx} and thermal Hall conductivity κ_{xy} imply that the quasiparticle structure is strongly band-dependent; a highly anisotropic small superconducting gap forms at the electron Fermi-surface pocket whereas a more isotropic and larger gap forms at the hole pocket.

Moreover, κ_{xx} and κ_{xy} exhibits a distinct kink anomaly at H^* in the high-field region of the superconducting phase, where the Zeeman splitting $\mu_B H$ is comparable to the Fermi energy ε_F and the superconducting gap Δ . This result indicates the emergence of a new superconducting phase (B -phase) mediated by the extremely large spin polarization $P \sim 0.1$. We also found that the quasiparticle scattering rate is strongly modified on entering the B -phase at H^* , hence, it is strongly suggested that the superconducting gap structure of the B -phase is distinctly different from that of the low-field superconducting phase (A -phase). This field-induced phase is likely to present a highly anomalous inhomogeneous superconducting state that has not been addressed before, rather than a conventional FFLO state.

The strongly band-dependent quasiparticle structure and the emergent highly spin-polarized phase may be important and unique features of the BCSBEC crossover in the

multiband superconducting system.

Time-reversal symmetry breaking superconducting state around twin boundaries in FeSe (Section 5)

We performed STM/STS measurements on the nodal superconductor FeSe and visualize the spatial evolution of the local density of state near twin boundaries, which are ideal junctions to investigate the Josephson effects on unconventional superconductors.

In contrast to the expectation that the sign inversion generates a zero-energy quasiparticle bound state near the TB, the LDOS at the TB observed in our study does not exhibit any signature of a zero-energy peak, and an apparent gap amplitude remains finite all the way across the TB. The low-energy quasiparticle excitations associated with the gap nodes are affected by the TB over a distance more than an order of magnitude larger than the coherence length ξ_{ab} . The modification of the low-energy states is even more prominent in the region between two neighboring TBs separated by a distance $\approx 7\xi_{ab}$; the spectral weight near the Fermi level ($\approx \pm 0.2$ meV) due to the nodal quasiparticle spectrum is almost completely removed. These behaviors suggest that the TB induces a fully gapped state, invoking a possible twist of the order parameter structure, which breaks time-reversal symmetry. Our minimal model calculations which include the time-reversal symmetry breaking effect around TBs reproduce our experimental results qualitatively.

These results suggest several important directions for future studies. Although several models that predict time-reversal-symmetry-broken superconducting state have been proposed, the microscopic mechanisms and the relevance to the TB in FeSe should be clarified by future theoretical studies. It is also interesting to go beyond the quasi-classical approximation because FeSe is a unique superconductor whose Fermi energy is of the same order as the superconducting gap, placing this system in the BCS-BEC crossover regime. Experiments that directly probe the time-reversal symmetry breaking, such as muon-spin rotation and local magnetometry, are highly desirable and would give us further insights into the unconventional superconducting junctions. We antici-

pate that the TBs in FeSe will stimulate further research on the role of the phase of the superconducting order parameter near the interface, which has been difficult to access experimentally.

References

- [1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, “Theory of Superconductivity,” *Phys. Rev.* **108**, 1175 (1957).
- [2] A. P. Drozdov, M. I. Erements, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, “Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system,” *Nature* **525**, 73 (2015).
- [3] J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, “The properties of hydrogen and helium under extreme conditions,” *Rev. Mod. Phys.* **84**, 1607 (2012).
- [4] J. G. Bednorz, K. A. Mueller, “Possible high- T_c superconductivity in the Ba-La-Cu-O system,” *Z. Phys. B* **64**, 189 (1986).
- [5] A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, “Superconductivity above 130 K in the Hg-Ba-Ca-Cu-O system,” *Nature* **363**, 56 (1986).
- [6] M. Monteverde, C. Acha, M. Nunez-Regueiro, D. A. Pavlov, K. A. Lokshin, S. N. Putilin and E. V. Antipov, “High-pressure effects in fluorinated $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$,” *Europhys. Lett.* **72**, 458 (2005).
- [7] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya and H. Hosono, “Iron-based layered superconductor: LaFePO ,” *J. Am. Chem. Soc.* **128**, 10012-10013 (2006).
- [8] Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, “Iron-based layered superconductor $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ ($x = 0.05 - 0.12$) with $T_c = 26$ K,” *J. Am. Chem. Soc.* **130**, 3296-3297 (2008).

- [9] Z. -A. Ren, W. Lu, J. Yang, W. Yi, X. -L. Shen, Z. -C. Li, G. -C. Che, X. -L. Dong, L. -L. Sun, F. Zhou, Z. -X. Zhao, “Superconductivity at 55 K in Iron-Based F-Doped Layered Quaternary Compound $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,” *Chin. Phys. Lett.* **25**, 2215-2216 (2008).
- [10] D. Liu, W. Zhang, D. Mou, J. He, Y.-B. Ou, Q.-Y. Wang, Z. Li, L. Wang, L. Zhao, S. He, Y. Peng, X. Liu, C. Chen, L. Yu, G. Liu, X. Dong, J. Zhang, C. Chen, Z. Xu, J. Hu, X. Chen, X. Ma, Q. Xue, and X.J. Zhou, “Electronic origin of high-temperature superconductivity in single-layer FeSe superconductor,” *Nat. Commun.* **3**, 931 (2012).
- [11] Q.-Y. Wang, Z. Li, W.-H. Zhang, Z.-C. Zhang, J.-S. Zhang, W. Li, H. Ding, Y.-B. Ou, P. Deng, K. Chang, J. Wen, C.-L. Song, K. He, J.-F. Jia, S.-H. Ji, Y. Wang, L. Wang, X. Chen, X. Ma, and Q.-K. Xue, “Interface-induced high-temperature superconductivity in single unit-cell FeSe films on SrTiO_3 ,” *Chin. Phys. Lett.* **29**, 037402 (2012).
- [12] S. He, J. He, W. Zhang, L. Zhao, D. Liu, X. Liu, D. Mou, Y.-B. Ou, Q.-Y. Wang, Z. Li, L. Wang, Y. Peng, Y. Liu, C. Chen, L. Yu, G. Liu, X. Dong, J. Zhang, C. Chen, Z. Xu, X. Chen, X. Ma, Q. Xue and X. J. Zhou, “Phase diagram and electronic indication of high-temperature superconductivity at 65 K in single-layer FeSe films,” *Nat. Mater.* **12**, 605 (2013).
- [13] J.-F. Ge, Z.-L. Liu, C. Liu, C.-L. Gao, D. Qian, Q.-K. Xue, Y. Liu, and J.-F. Jia, “Superconductivity above 100 K in single-layer FeSe films on doped SrTiO_3 ,” *Nat. mater.* **14**, 285 (2015).
- [14] M. R. Schafroth, S.T. Butler, and J.M. Blatt., “Possible pairing without superconductivity at low carrier concentrations in bulk and thin-film superconducting semiconductors,” *Helv. Phys. Acta.* **30**, 93 (1957).

- [15] D. M. Eagles, “Possible pairing without superconductivity at low carrier concentrations in bulk and thin-film superconducting semiconductors,” *Phys. Rev.* **186**, 456 (1969).
- [16] A. J. Leggett, “Modern trends in the theory of condensed matter,” edited by A. Pekalski, and R. Przystawa, (Springer-Verlag, Berlin, 1980).
- [17] P. Nozières, and S. Schmitt-Rink, “Bose condensation in an attractive fermion gas: From weak to strong coupling superconductivity,” *J. Low. Temp. Phys.* **59**, 195-211 (1985).
- [18] C. A. R. Sá de Melo, M. Randeria, and J. R. Engelbrecht, “Crossover from BCS to Bose superconductivity: Transition temperature and time-dependent Ginzburg-Landau theory,” *Phys. Rev. Lett.* **71**, 3202 (1993).
- [19] C. A. R. Sá de Melo, “When fermions become bosons: Pairing in ultracold gases,” *Phys. Today* **61**, 10, 45-51 (2008).
- [20] M. Randeria, and E. Taylor, “Crossover from Bardeen-Cooper-Schrieffer to Bose-Einstein condensation and the unitary Fermi gas,” *Annu. Rev. Condens. Matter. Phys.* **5**, 209-232 (2014).
- [21] M. Randeria, N. Trivedi, A. Moreo, and R. T. Scalettar, “Pairing and spin gap in the normal state of short coherence length superconductors,” *Phys. Rev. Lett.* **69**, 2001 (1992).
- [22] N. Trivedi, and M. Randeria, “Deviations from fermi liquid behavior above T_c in two dimensional short coherence length superconductors,” *Phys. Rev. Lett.* **75**, 312 (1995).
- [23] C. A. Regal, M. Greiner, and D. S. Jin, “Observation of resonance condensation of fermionic atom pairs,” *Phys. Rev. Lett.* **92**, 040403 (2004).

- [24] M.W. Zwierlein, C.A. Stan, C.H. Schunck, S.M.F. Raupach, A.J. Kerman, and W. Ketterle, “Condensation of pairs of fermionic atoms near a Feshbach resonance,” *Phys. Rev. Lett.* **92**, 120403 (2004).
- [25] J. Kinast, S.L. Hemmer, M.E. Gehm, A. Turlapov, and J. E. Thomas, “Evidence for superfluidity in a resonantly interacting Fermi gas,” *Phys. Rev. Lett.* **92**, 150403 (2004).
- [26] T. Bourdel, L. Khaykovich, J. Cubizolles, J. Zhang, F. Chevy, M. Teichmann, L. Tarruell, S.J.J.M.F. Kokkelmans, and C. Salomon, “Experimental study of the BEC-BCS crossover region in lithium-6,” *Phys. Rev. Lett.* **93**, 050401 (2004).
- [27] C. Chin, M. Bartenstein, A. Altmeyer, S. Riedl, S. Jochim, J. Hecker-Denschlag, and R. Grimm, “Observation of the pairing gap in a strongly interacting Fermi gas,” *Science* **305**, 1128 (2004).
- [28] G. B. Partridge, K. E. Strecker, R. I. Kamar, M. W. Jack, and R. G. Hulet, “Molecular probe of pairing in the BEC-BCS crossover,” *Phys. Rev. Lett.* **95**, 020404 (2005).
- [29] M. W. Zwierlein, J. R. Abo-Shaeer, A. Schirotzek, C. H. Schunck, and W. Ketterle, “Vortices and superfluidity in a strongly interacting Fermi gas,” *Nature* **435**, 1047 (2005). Wang2001,Emery1994,Keimer2015
- [30] G. B. Partridge, K. E. Strecker, R. I. Kamar, M. W. Jack, and R. G. Hulet, “Onset of the vortexlike Nernst signal above T_c in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Ba}_2\text{Sr}_{2-y}\text{La}_y\text{CuO}_6$,” *Phys. Rev. B* **64**, 224519 (2001).
- [31] V. J. Emery, and S. A. Kivelson, “Importance of phase fluctuations in superconductors with small superfluid density,” *Nature* **374**, 434 (1994).
- [32] B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, and J. Zaanen, “From quantum matter to high-temperature superconductivity in copper oxides,” *Nature* **518**, 179 (2015).

- [33] A. E. Böhmer, F. Hardy, F. Eilers, D. Ernst, P. Adelman, P. Schweiss, T. Wolf, and C. Meingast, “Lack of coupling between superconductivity and orthorhombic distortion in stoichiometric single-crystalline FeSe ,” *Phys. Rev. B* **87**, 180505(R) (2013).
- [34] G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel, “Surface Studies by Scanning Tunneling Microscopy ,” *Phys. Rev. Lett.* **49**, 57 (1982).
- [35] F.-C. Hsu, J.-Y. Luo, K.-W. Yeh, T.-K. Chen, T.-W. Huang, P. M. Wu, Y.-C. Lee, Y.-L. Huang, Y.-Y. Chu, D.-C. Yan, and M.-K. Wu, “Superconductivity in the PbO-type structure α -FeSe,” *Proc. Natl. Acad. Sci. USA* **105**, 14262-14264 (2008).
- [36] S. Margadonna, Y. Takabayashi, M. T. McDonald, K. Kasperkiewicz, Y. Mizuguchi, Y. Takano, A. N. Fitch, E. Suard, and K. Prassides, “Crystal structure of the new FeSe_{1-x} superconductor,” *Chem. Commun.* 2008, 5607 (2008).
- [37] S. Kasahara, T. Watashige, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. von Löhneysen, T. Shibauchi, and Y. Matsuda, “Field-induced superconducting phase of FeSe in the BCS-BEC cross-over ,” *Proc. Nat. Acad. Sci. USA* **111**, 16309-16313 (2014).
- [38] T. Shimojima, Y. Suzuki, T. Sonobe, A. Nakamura, M. Sakano, J. Omachi, K. Yoshioka, M. Kuwata-Gonokami, K. Ono, H. Kumigashira, A. E. Böhmer, F. Hardy, T. Wolf, C. Meingast, H. v. Löhneysen, H. Ikeda, and K. Ishizaka, “Lifting of xz/yz orbital degeneracy at the structural transition in detwinned FeSe ,” *Phys. Rev. B* **90**, 121111(R) (2014).
- [39] T. M. McQueen, A. J. Williams, P. W. Stephens, J. Tao, Y. Zhu, V. Ksenofontov, F. Casper, C. Felser, and R. J. Cava, “Tetragonal-to-orthorhombic structural phase transition at 90 K in the superconductor Fe_{1.01}Se,” *Phys. Rev. Lett.* **103**, 057002 (2009).

- [40] M. D. Watson, T. Yamashita, S. Kasahara, W. Knafo, M. Nardone, J. Béard, F. Hardy, A. McCollam, A. Narayanan, S. F. Blake, T. Wolf, A. A. Haghighirad, C. Meingast, A. J. Schofield, H. v. Löhneysen, Y. Matsuda, A. I. Coldea, and T. Shibauchi, “Dichotomy between the hole and electron behaviour in the multiband FeSe probed by ultra high magnetic fields ,” *Phys. Rev. Lett.* **115**, 027006 (2015).
- [41] A. B. Pippard, “Magnetoresistance in Metals ,” Cambridge Univ Press, Cambridge, UK (1989).
- [42] H. Luetkens, H. H. Klauss, M. Kraken, F. J. Litterst, T. Dellmann, R. Klingeler, C. Hess, R. Khasanov, A. Amato, C. Baines, M. Kosmala, O. J. Schumann, M. Braden, J. Hamann-Borrero, N. Leps, A. Kondrat, G. Behr, J. Werner and B. Buchner, “The electronic phase diagram of the $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ superconductor,” *Nat. Matter.* **8**, 305-309 (2009).
- [43] S. Kasahara, H. J. Shi, K. Hashimoto, S. Tonegawa, Y. Mizukami, T. Shibauchi, K. Sugimoto, T. Fukuda, T. Terashima, Andriy H. Nevidomskyy, and Y. Matsuda, “Electronic nematicity above the structural and superconducting transition in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$,” *Nature* **486**, 382 (2012).
- [44] N. Qureshi, Y. Drees, J. Werner, S. Wurmehl, C. Hess, R. Klingeler, B. Büchner, M. T. Fernández-Díaz, and M. Braden, “Crystal and magnetic structure of the oxypnictide superconductor $\text{LaFeAsO}_{1-x}\text{F}_x$: A neutron-diffraction study,” *Phys. Rev. B* **82**, 184512 (2010).
- [45] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang and P. Dai, “Magnetic order close to superconductivity in the iron-based layered $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ systems,” *Nature (London)* **453**, 899-902 (2008).
- [46] J.-H. Chu, J. G. Analytis, C. Kucharczyk, and I. R. Fisher, “Determination of the phase diagram of the electron-doped superconductor $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$,” *Phys. Rev. B* **79**, 014506 (2009).

- [47] M. Rotter, M. Tagel, and D. Johrendt, “Superconductivity at 38 K in the iron arsenide $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$,” *Phys. Rev. Lett.* **101**, 107006 (2008).
- [48] S. Kasahara, T. Shibauchi, K. Hashimoto, K. Ikada, S. Tonegawa, R. Okazaki, H. Shishido, H. Ikeda, H. Takeya, K. Hirata, T. Terashima, and Y. Matsuda, “Evolution from non-Fermi- to Fermi-liquid transport via isovalent doping in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$,” *Phys. Rev. B* **78**, 220510(R) (2008).
- [49] T.-M. Chuang, M. P. Allan, Jinho Lee, Yang Xie, Ni Ni, S. L. Bud’ko, G. S. Boebinger, P. C. Caneld, and J. C. Davis, “Nematic Electronic Structure in the “Parent ” State of the Iron-Based Superconductor $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$,” *Science* **327**, 181 (2010).
- [50] J.-H. Chu, J. G. Analytis, K. D. Greve, P. L. McMahon, Z. Islam, Y. Yamamoto, and I. R. Fisher, “In-Plane Resistivity Anisotropy in an Underdoped Iron Arsenide Superconductor,” *Science* **329**, 824 (2010).
- [51] S. Hosoi, K. Matsuura, K. Ishida, H. Wang, Y. Mizukami, T. Watashige, S. Kasahara, Y. Matsuda, and T. Shibauchi, “Nematic quantum critical point without magnetism in $\text{FeSe}_{1-x}\text{S}_x$ superconductors,” *Proc. Natl. Acad. Sci. USA* **113**, 8139-8143 (2016).
- [52] K. Hashimoto, K. Cho, T. Shibauchi, S. Kasahara, Y. Mizukami, R. Katsumata, Y. Tsuruhara, T. Terashima, H. Ikeda, M. A. Tanatar, H. Kitano, N. Salovich, R. W. Giannetta, P. Walmsley, A. Carrington, R. Prozorov, and Y. Matsuda, “A sharp peak of the zero-temperature penetration depth at optimal composition in the iron-based superconductor $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$,” *Science* **336**, 1554 (2012).
- [53] J.-Y. Lin, Y. S. Hsieh, D. A. Chareev, A. N. Vasiliev, Y. Parsons, and H. D. Yang, “Coexistence of isotropic and extended s-wave order parameters in FeSe as revealed by low-temperature specific heat ,” *Phys. Rev. B* **84**, 220507(R) (2011).

- [54] L. Wang, F. Hardy, T. Wolf, P. Adelman, R. Fromknecht, P. Schweiss, and C. Meingast, “Superconductivity-enhanced Nematicity and $s + d$ Gap Symmetry in $\text{FeSe}_{1-x}\text{S}_x$,” arXiv:1607.01288 (2016).
- [55] L. Jiao, C.-L. Huang, S. Rößler, C. Koz, U. K. Rößler, U. Schwarz, and S. Wirth, “Direct evidence for multi-gap nodeless superconductivity in FeSe ,” arXiv:1605.01908 (2016).
- [56] C.-L. Song, Y.-L. Wang, P. Cheng, Y.-P. Jiang, W. Li, T. Zhang, Z. Li, K. He, L. Wang, J.-F. Jia, H.-H. Hung, C. Wu, X. Ma, X. Chen and Q.-K. Xue, “Direct Observation of Nodes and Twofold Symmetry in FeSe Superconductor,” *Science* **332**, 1410 (2011).
- [57] R. Khasanov, K. Conder, E. Pomjakushina, A. Amato, C. Baines, Z. Bukowski, J. Karpinski, S. Katrych, H.-H. Klauss, H. Luetkens, A. Shengelaya, and N. D. Zhigadlo, “Evidence of nodeless superconductivity in $\text{FeSe}_{0.85}$ from a muon-spin-rotation study of the in-plane magnetic penetration depth,” *Phys. Rev. B* **78**, 220510(R) (2008).
- [58] J.K. Dong, T.Y. Guan, S.Y. Zhou, X. Qiu, L. Ding, C. Zhang, U. Patel, Z.L. Xiao, and S.Y. Li, “Multigap nodeless superconductivity in FeSe_x : Evidence from quasiparticle heat transport,” *Phys. Rev. B* **80**, 024518 (2009).
- [59] P. Bourgeois-Hope, S. Chi, D. A. Bonn, R. Liang, W. N. Hardy, T. Wolf, C. Meingast, N. Doiron-Leyraud, and L. Taillefer, “Thermal conductivity of the iron-based superconductor FeSe : Nodeless gap with strong two-band character,” *Phys. Rev. Lett.* **117**, 097003 (2016).
- [60] P. O. Sprau, A. Kostin, A. Kreisel, A. E. Böhmer, V. Taufour, P. C. Canfield, S. Mukherjee, P. J. Hirschfeld, B. M. Andersen, J. C. S. Davis, “Discovery of Orbital-Selective Cooper Pairing in FeSe ,” arXiv:1611.02134 (2016).
- [61] T. Watashige, Y. Tsutsumi, T. Hanaguri, Y. Kohsaka, S. Kasahara, A. Furusaki, M. Sigrist, C. Meingast, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda,

- “Evidence for time-reversal symmetry breaking of the superconducting state near twin-boundary interfaces in FeSe revealed by scanning tunneling spectroscopy,” *Phys. Rev. X* **5**, 031022 (2015).
- [62] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, “Superconductivity at 27 K in tetragonal FeSe under high pressure,” *Appl. Phys. Lett.* **93**, 152505 (2008).
- [63] S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Erements, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann and C. Felser, “Electronic and magnetic phase diagram of β -Fe_{1.01}Se with superconductivity at 36.7 K under pressure,” *Nat. Mater.* **8**, 630 (2009).
- [64] S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, and K. Prassides, “Pressure evolution of the low-temperature crystal structure and bonding of the superconductor FeSe ($T_c = 37$ K),” *Phys. Rev. B* **80**, 064506 (2009).
- [65] T. Imai, K. Ahilan, F. L. Ning, T. M. McQueen, and R. J. Cava, “Why does undoped FeSe become a high- T_c superconductor under pressure?,” *Phys. Rev. Lett.* **102**, 177005 (2009).
- [66] K. Miyoshi, K. Morishita, E. Mutou, M. Kondo, O. Seida, K. Fujiwara, J. Takeuchi, and S. Nishigori, “Anomalous Pressure Dependence of the Superconducting Transition Temperature in FeSe_{1-x} Studied by DC Magnetic Measurements,” *J. Phys. Soc. Jpn.* **78**, 093703 (2009).
- [67] K. Miyoshi, K. Morishita, E. Mutou, M. Kondo, O. Seida, K. Fujiwara, J. Takeuchi, and S. Nishigori, “Enhanced Superconductivity on the Tetragonal Lattice in FeSe under Hydrostatic Pressure,” *J. Phys. Soc. Jpn.* **83**, 013702 (2014).
- [68] J. P. Sun, K. Matsuura, G. Z. Ye, Y. Mizukami, M. Shimozawa, K. Matsubayashi, M. Yamashita, T. Watashige, S. Kasahara, Y. Matsuda, J.-Q. Yan, B. C. Sales, Y. Uwatoko, J.-G. Cheng, and T. Shibauchi, “Dome-shaped magnetic order competing

- with high-temperature superconductivity at high pressures in FeSe,” Nat. Commun. **7**, 12146 (2016).
- [69] T. Terashima, N. Kikugawa, A. Kiswandhi, D. Graf, E.-S. Choi, J. S. Brooks, S. Kasahara, T. Watashige, Y. Matsuda, T. Shibauchi, T. Wolf, A. E. Böhrer, F. Hardy, C. Meingast, H. v. Löhneysen, and S. Uji, “Fermi surface reconstruction in FeSe under high pressure,” Phys. Rev. B **93**, 094505 (2016).
- [70] T. Terashima, N. Kikugawa, S. Kasahara, T. Watashige, Y. Matsuda, T. Shibauchi, and S. Uji, “Magnetotransport study of the pressure-induced antiferromagnetic phase in FeSe,” Phys. Rev. B **93**, 180503(R) (2016).
- [71] Q. Fan, W. H. Zhang, X. Liu, Y. J. Yan, M. Q. Ren, R. Peng, H. C. Xu, B. P. Xie, J. P. Hu, T. Zhang, and D. L. Feng, “Plain *s*-wave superconductivity in single-layer FeSe on SrTiO₃ probed by scanning tunnelling microscopy,” Nat. Phys. **11**, 946 (2015).
- [72] Z. Zhang, Y. Wang, Q. Song, C. Liu, R. Peng, K. A. Moler, D. Feng, and Y. Wang, “Onset of the Meissner effect at 65 K in FeSe thin film grown on Nb doped SrTiO₃ substrate,” Sci. Bull. **60**, 1301 (2015).
- [73] J. He, X. Liu, W. Zhang, L. Zhao, D. Liu, S. He, D. Mou, F. Li, C. Tang Z. Li, L. Wang, Y. Peng, Y. Liu, C. Chen, L. Yu, G. Liu, X. Dong, J. Zhang, C. Chen, Z. Xu, X. Chen, X. Ma, Q. Xue, and X. J. Zhou, “Electronic evidence of an insulator-superconductor crossover in single-layer FeSe/SrTiO₃ films,” Proc. Nat. Acad. Sci. USA **111**, 18501 (2014).
- [74] Y. Miyata, K. Nakayama, K. Sugawara, T. Sato, and T. Takahashi, “High-temperature superconductivity in potassium-coated multilayer FeSe thin films,” Nat. Mater. **14**, 775 (2015).
- [75] J. Shiogai, Y. Ito, T. Mitsuhashi, T. Nojima, and A. Tsukazaki, “Electric-field-induced superconductivity in electrochemically etched ultrathin FeSe films on SrTiO₃ and MgO,” Nat. Phys. **12**, 42 (2016).

- [76] T. V. Duzer, and C. W. Turner, “Principles of Superconductive Devices and Circuits,” 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1998).
- [77] C. C. Tsuei and J. R. Kirtley, “Pairing Symmetry in Cuprate Superconductors,” *Rev. Mod. Phys.* **72**, 969 (2000).
- [78] D. Rainer, H. Burkhardt, M. Fogelström, and J. A. Sauls, “Andreev Bound States, Surfaces and Subdominant Pairing in High T_c Superconductors,” *J. Phys. Chem. Solids* **59**, 2040 (1998).
- [79] A. Furusaki, “Josephson Current Carried by Andreev Levels in Superconducting Quantum Point Contacts,” *Superlattices Microstruct.* **25**, 809 (1999).
- [80] M. Sigrist, K. Kuboki, P. A. Lee, A. J. Millis, and T. M. Rice, “Influence of Twin Boundaries on Josephson Junctions between High-Temperature and Conventional Superconductors,” *Phys. Rev. B* **53**, 2835 (1996).
- [81] M. E. Zhitomirsky and M. B. Walker, “Electronic States on a Twin Boundary of a d -Wave Superconductor,” *Phys. Rev. Lett.* **79**, 1734 (1997).
- [82] D. L. Feder, A. Beardsall, A. J. Berlinsky, and C. Kallin, “Twin Boundaries in d -Wave Superconductors,” *Phys. Rev. B* **56**, R5751 (1997).
- [83] W. Belzig, C. Bruder, and M. Sigrist, “Quasiclassical Theory of Twin Boundaries in High- T_c Superconductors,” *Phys. Rev. Lett.* **80**, 4285 (1998).
- [84] J. Maletz, V. B. Zabolotnyy, D. V. Evtushinsky, S. Thirupathaiah, A. U. B. Wolter, L. Harnagea, A. N. Yaresko, A. N. Vasiliev, D. A. Chareev, A. E. Böhmer, F. Hardy, T. Wolf, C. Meingast, E. D. L. Rienks, B. Büchner, and S. V. Borisenko, “Unusual band renormalization in the simplest iron-based superconductor FeSe_{1-x} ,” *Phys. Rev. B* **89**, 220506(R) (2014).
- [85] Y. Hasegawa and Ph. Avouris, “Direct Observation of Standing Wave Formation at Surface Steps Using Scanning Tunneling Spectroscopy,” *Phys. Rev. Lett.* **71**, 1071 (1993).

- [86] M. F. Crommie, C. P. Lutz and D. M. Eigler, “Imaging standing waves in a two-dimensional electron gas,” *Nature* **363**, 524 (1993).
- [87] Y. Kohsaka, C. Taylor, K. Fujita, A. Schmidt, C. Lupien, T. Hanaguri, M. Azuma, M. Takano, H. Eisaki, H. Takagi, S. Uchida, and J. C. Davis, “An Intrinsic Bond-Centered Electronic Glass with Unidirectional Domains in Underdoped Cuprates,” *Science* **315**, 1380 (2007).
- [88] T. Hanaguri, Y. Kohsaka, M. Ono, M. Maltseva, P. Coleman, I. Yamada, M. Azuma, M. Takano, K. Ohishi, and H. Takagi, “Coherence factors in a high- T_c cuprate probed by quasi-particle scattering off vortices,” *Science* **323**, 923 (2009).
- [89] M. P. Allan, F. Massee, D. K. Morr, J. Van Dyke, A. W. Rost, A. P. Mackenzie, C. Petrovic, and J. C. Davis, “Imaging Cooper pairing of heavy fermions in CeCoIn_5 ,” *Nature Phys.* **9**, 468 (2013).
- [90] T. Hanaguri, S. Niitaka, K. Kuroki and H. Takagi, “Unconventional s-Wave Superconductivity in $\text{Fe}(\text{Se},\text{Te})$,” *Science* **328**, 474 (2010).
- [91] T. Terashima, N. Kikugawa, A. Kiswandhi, E. -S. Choi, J. S. Brooks, S. Kasahara, T. Watashige, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. v. Löhneysen, M. Suzuki, R. Arita, and S. Uji, “Anomalous Fermi surface in FeSe seen by Shubnikov-de Haas oscillation measurements ,” *Phys. Rev. B* **90**, 144517 (2014).
- [92] S. Kasahara, T. Yamashita, *et al.*, preprint.
- [93] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, “Unconventional Pairing Originating from the Disconnected Fermi Surfaces of Superconducting $\text{LaFeAsO}_{1-x}\text{F}_x$,” *Phys. Rev. Lett.* **101**, 087004 (2008).
- [94] D. J. Singh and M. -H. Du, “Density Functional Study of $\text{LaFeAsO}_{1-x}\text{F}_x$: A Low Carrier Density Superconductor Near Itinerant Magnetism ,” *Phys. Rev. Lett.* **100**, 237003 (2008).

- [95] H. Ding, P. Richard, K. Nakayama, K. Sugawara, T. Arakane, Y. Sekiba, A. Takayama, S. Souma, T. Sato, T. Takahashi, Z. Wang, X. Dai, Z. Fang, G. F. Chen, J. L. Luo and N. L. Wang, “Observation of Fermi-surface-dependent nodeless superconducting gaps in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$,” *Europhys. Lett.* **83**, 47001 (2008).
- [96] A. E. Böhmer, T. Arai, F. Hardy, T. Hattori, T. Iye, T. Wolf, H. v. Löhneysen, K. Ishida, and C. Meingast, “Origin of the tetragonal-to-orthorhombic phase transition in FeSe: A combined thermodynamic and NMR study of nematicity,” *Phys. Rev. Lett.* **114**, 027001 (2015).
- [97] P. Massat, D. Farina, I. Paul, S. Karlsson, P. Strobel, P. Toulemonde, M.-A. Measson, M. Cazayous, A. Sacuto, S. Kasahara, T. Shibauchi, Y. Matsuda, and Y. Gallais, “Charge Induced Nematicity in FeSe,” *Proc. Natl. Acad. Sci. USA* **111**, 9177-9181 (2014).
- [98] M. A. Tanatar, A. E. Böhmer, E. I. Timmons, M. Schütt, G. Drachuck, V. Taufour, K. Kothapalli, A. Kreyssig, S. L. Bud’ko, P. C. Canfield, R. M. Fernandes, and R. Prozorov, “Origin of the Resistivity Anisotropy in the Nematic Phase of FeSe,” *Phys. Rev. Lett.* **117**, 127001 (2016).
- [99] M. D. Watson, T. K. Kim, A. A. Haghighirad, N. R. Davies, A. McCollam, A. Narayanan, S. F. Blake, Y. L. Chen, S. Ghannadzadeh, A. J. Schofield, M. Hoesch, C. Meingast, T. Wolf, and A. I. Coldea, “Emergence of the nematic electronic state in FeSe,” *Phys. Rev. B* **91**, 155106 (2015).
- [100] K. Nakayama, Y. Miyata, G. N. Phan, T. Sato, Y. Tanabe, T. Urata, K. Tanigaki, and T. Takahashi, “Reconstruction of Band Structure Induced by Electronic Nematicity in an FeSe Superconductor,” *Phys. Rev. Lett.* **113**, 237001 (2013).
- [101] Y. Suzuki, T. Shimojima, T. Sonobe, A. Nakamura, M. Sakano, H. Tsuji, J. Omachi, K. Yoshioka, M. K. Gonokami, T. Watashige, R. Kobayashi, S. Kasahara, T. Shibauchi, Y. Matsuda, Y. Yamakawa, “Momentum-dependent sign inversion of orbital order in superconducting FeSe,” *Phys. Rev. B* **92**, 205117 (2015).

- [102] S. Kasahara, T. Yamashita, A. Shi, R. Kobayashi, Y. Shimoyama, T. Watashige, K. Ishida, T. Terashima, T. Wolf, F. Hardy, C. Meingast, H. v. Lohneysen, A. Levchenko, T. Shibauchi, and Y. Matsuda, “Giant superconducting fluctuations in the compensated semimetal FeSe at the BCS-BEC crossover,” *Nat. Commun.* **7**, 12843 (2016).
- [103] S. Ullah, and A. T. Dorsey, “Effect of fluctuations on the transport properties of type-II superconductors in a magnetic field,” *Phys. Rev. B* **44**, 262 (1991).
- [104] I. Ussishkin, S. L. Sondhi, and D. A. Huse, “Gaussian Superconducting fluctuations, thermal transport, and the Nernst effect,” *Phys. Rev. Lett.* **89**, 287001 (2002).
- [105] F. Soto, H. Berger, L. Cabo, C. Carballeira, J. Mosqueira, D. Pavuna, and F. Vidal, “In-plane and transverse superconducting fluctuation diamagnetism in the presence of charge-density waves in 2H-NbSe₂ single crystals,” *Phys. Rev. B* **75**, 094509 (2007).
- [106] Y. Yanase, “FFLO superconductivity near the antiferromagnetic quantum critical point.,” *J. Phys. Soc. Jpn.* **77**, 063705 (2008).
- [107] Yuji Matsuda and Hiroshi Shimahara, “FuldeFerrellLarkinOvchinnikov State in Heavy Fermion Superconductors ,” *J. Phys. Soc. Jpn.* **76**, 051005 (2007).
- [108] K. Krishana, N. P. Ong, Q. Li, G. D. Gu, and N. Koshizuka, “Plateaus Observed in the Field Profile of Thermal Conductivity in the Superconductor Bi₂Sr₂CaCu₂O₈,” *Science* **277**, 83 (1997).
- [109] Y. Kasahara, Y. Nakajima, K. Izawa, Y. Matsuda, K. Behnia, H. Shishido, R. Settai, and Y. Onuki, “Anomalous quasiparticle transport in the superconducting state of CeCoIn₅,” *Phys. Rev. B* **72**, 214515 (2005).
- [110] M. Franz, “Mixed-State Quasiparticle Transport in High- T_c Cuprates,” *Phys. Rev. B* **82**, 1760 (1999).

- [111] S. Vishveshwara, and M. P. A. Fisher, “Critical dynamics of thermal conductivity at the normal-superconducting transition,” *Phys. Rev. B* **64**, 134507 (2001).
- [112] Peter Fulde and Richard A. Ferrkl, “Superconductivity in a Strong Spin-Exchange Field,” *Phys. Rev.* **135**, A550 (1964).
- [113] A. I. Larkin and Yu. N. Ovchinnikov, *Zh. Eksp. Teor. Fiz.* **47**, 1136 (1964).
- [114] S. Takada, “Superconductivity in a Molecular Field. II - Stability of Flude-Ferrel Phase - ,” *Prog. Theor. Phys.* **43**, 27 (1970).
- [115] M. Decroux and Ø. Fischer, in “ Superconductivity in Ter nary Compounds, Part ll,” edited by M. B. Maple and Ø. Fischer (Springer, Heidelberg, 1982), p. 57.
- [116] H. Adachi and R. Ikeda, “Effects of Pauli paramagnetism on the superconducting vortex phase diagram in strong fields ,” *Phys. Rev. B* **68**, 184510 (2003).
- [117] H. Shimahara, “Fulde-Ferrell state in quasi-two-dimensional superconductors ,” *Phys. Rev. B* **50**, 12760 (1994).
- [118] R. Modler, P. Gegenwart, M. Lang, M. Deppe, M. Weiden, T. Lhmann, C. Geibel, and F. Steglich, “First-Order Transition between Weak and Strong Pinning in Clean Superconductors with Enhanced Spin Susceptibility ,” *Phys. Rev. Lett.* **76**, 1292 (1996).
- [119] A. Yamashita, K. Ishii, T. Yokoo, J. Akimitsu, M. Hedo, Y. Inada, and Y. Onuki, E. Yamamoto, Y. Haga, and R. Kadono, “Anomalous Field Dependence of Magnetic Penetration Depth in the Vortex State of CeRu₂ Probed by Muon Spin Rotation ,” *Phys. Rev. Lett.* **79**, 3771 (1997).
- [120] K. Gloos, R. Modler, H. Schimanski, C. D. Bredl, C. Geibel, F. Steglich, A. I. Buzdin, N. Sato, and T. Komatsubara, “Possible Formation of a Nonuniform Superconducting State in the Heavy-Fermion Compound UPd₂Al₃ ,” *Phys. Rev. Lett.* **70**, 501 (1993).

- [121] C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, and P. Monthoux, “Heavy-fermion superconductivity in CeCoIn₅ at 2.3 K ,” J. Phys.: Condens. Matter **13**, L337 (2001).
- [122] K. Kumagai, M. Saitoh, T. Oyaizu, Y. Furukawa, S. Takashima, M. Nohara, H. Takagi, and Y. Matsuda, “Fulde-Ferrell-Larkin-Ovchinnikov State in a Perpendicular Field of Quasi-Two-Dimensional CeCoIn₅ ,” Phys. Rev. Lett. **97**, 227002 (2006).
- [123] A. Bianchi, R. Movshovich, N. Oeschler, P. Gegenwart, F. Steglich, J. D. Thompson, P. G. Pagliuso, and J. L. Sarrao, “First-Order Superconducting Phase Transition in CeCoIn₅ ,” Phys. Rev. Lett. **89**, 137002 (2002).
- [124] C. F. Miclea, M. Nicklas, D. Parker, K. Maki, J. L. Sarrao, J. D. Thompson, G. Sparn, and F. Steglich, “Pressure Dependence of the Fulde-Ferrell-Larkin-Ovchinnikov State in CeCoIn₅ ,” Phys. Rev. Lett. **96**, 117001 (2006).
- [125] C. Martin, C. C. Agosta, S. W. Tozer, H. A. Radovan, E. C. Palm, T. P. Murphy, and J. L. Sarrao, “Evidence for the Fulde-Ferrell-Larkin-Ovchinnikov state in CeCoIn₅ from penetration depth measurements ,” Phys. Rev. B **71**, 020503(R) (2005).
- [126] T. Watanabe, Y. Kasahara, K. Izawa, T. Sakakibara, Y. Matsuda, C. J. van der Beek, T. Hanaguri, H. Shishido, R. Settai, and Y. Onuki, “High-field state of the flux-line lattice in the unconventional superconductor CeCoIn₅ ,” Phys. Rev. B **70**, 020506(R) (2004).
- [127] K. Kakuyanagi, M. Saitoh, K. Kumagai, S. Takashima, M. Nohara, H. Takagi, and Y. Matsuda, “Texture in the Superconducting Order Parameter of CeCoIn₅ Revealed by Nuclear Magnetic Resonance ,” Phys. Rev. Lett. **94**, 047602 (2005).
- [128] K. Kumagai, H. Shishido, T. Shibauchi, and Y. Matsuda, “Evolution of Paramagnetic Quasiparticle Excitations Emerged in the High-Field Superconducting Phase of CeCoIn₅ ,” Phys. Rev. Lett. **106**, 137004 (2011).

- [129] A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, “Crystal and Electronic Structures of a New Molecular Superconductor, κ -(BEDT-TTF) $_2$ I $_3$,” Chem. Lett. **6**, 459 (1987).
- [130] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, “Shubnikov-de Haas effect and the Fermi surface in an ambient-pressure organic superconductor [bis(ethylenedithio) tetrathiafulvalene] $_2$ Cu(NCS) $_2$,” Phys. Rev. B **38**, 938 (1988).
- [131] M. Lang, F. Steglich, N. Toyota and T. Sasaki, “Fluctuation effects and mixed-state properties of the layered organic superconductors κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ and κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br,” J. Phys. Soc. Jpn. **76**, 051005 (2007).
- [132] R. Lortz, Y. Wang, A. Demuer, P. H. M. Böttger, B. Bergk, G. Zwicknagl, Y. Nakazawa, and J. Wosnitza, “Calorimetric Evidence for a Fulde-Ferrell-Larkin-Ovchinnikov Superconducting State in the Layered Organic Superconductor κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$,” Phys. Rev. Lett. **99**, 187002 (2007).
- [133] B. Bergk, A. Demuer, I. Sheikin, Y. Wang, J. Wosnitza, Y. Nakazawa, and R. Lortz, “Magnetic torque evidence for the Fulde-Ferrell-Larkin-Ovchinnikov state in the layered organic superconductor κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$,” Phys. Rev. B **83**, 064506 (2011).
- [134] S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, “Magnetic-field-induced superconductivity in a two-dimensional organic conductor,” Nature **410**, 908 (2005).
- [135] M. A. Tanatar, T. Ishiguro, H. Tanaka, and H. Kobayashi, “Magnetic field-temperature phase diagram of the quasi-two-dimensional organic superconductor λ -(BETS) $_2$ GaCl $_4$ studied via thermal conductivity,” Phys. Rev. B **66**, 134503 (2002).
- [136] D. E. Sheehy, and L. Radzihovsky, “BEC-BCS crossover, phase transitions and phase separation in polarized resonantly-paired superfluids,” Annals of Physics **322**, 1790 (2004).

- [137] Y. Chen, Z. D. Wang, F. C. Zhang, and C. S. Ting, “Exploring exotic superfluidity of polarized ultracold fermions in optical lattices ,” *Phys. Rev. Lett.* **79**, 054512 (2009).
- [138] Y. L. Loh, and N. Trivedi, “Detecting the Elusive Larkin-Ovchinnikov Modulated Superfluid Phases for Imbalanced Fermi Gases in Optical Lattices ,” *Phys. Rev. Lett.* **104**, 165302 (2010).
- [139] Simone Chiesa, and Shiwei Zhang, “Phases of attractive spin-imbalanced fermions in square lattices ,” *Phys. Rev. A* **88**, 043624 (2013).
- [140] Peter Rosenberg, Simone Chiesa and Shiwei Zhang, “FFLO order in ultra-cold atoms in three-dimensional optical lattices ,” *J. Phys. Cond. Matt.* **27**, 225601 (2015).
- [141] Y. Matsuda, K. Izawa, and I. Vekhter, “Nodal structure of unconventional superconductors probed by angle resolved thermal transport measurements,” *J. Phys.: Condens. Matter* **18**, R705 (2006).
- [142] G. E. Volovik, “Superconductivity with lines of GAP nodes: density of states in the vortex,” *JETP Lett.* **58**, 469 (1993).
- [143] J. Lowell and J. Sousa, “Mixed-state thermal conductivity of type II superconductors,” *J. Low Temp. Phys.* **3**, 65 (1970).
- [144] C. Proust, E. Boaknin, R. W. Hill, L. Taillefer, and A. P. Mackenzie, “Heat Transport in a Strongly Overdoped Cuprate: Fermi Liquid and a Pure d-Wave BCS Superconductor,” *Phys. Rev. Lett.* **89**, 147003 (2002).
- [145] A. V. Sologubenko, J. Jun, S. M. Kazakov, J. Karpinski, and H. R. Ott, “Thermal conductivity of single-crystalline MgB_2 ,” *Phys. Rev. B* **66**, 014504 (2002).
- [146] E. Boaknin, M. A. Tanatar, J. Paglione, D. Hawthorn, F. Ronning, R. W. Hill, M. Sutherland, L. Taillefer, J. Sonier, S. M. Hayden, and J. W. Brill, “Heat conduction

- in the vortex state of NbSe₂: Evidence for multiband superconductivity,” Phys. Rev. Lett. **90**, 117003 (2003).
- [147] M. Yamashita, N. Nakata, Y. Senshu, S. Tonegawa, K. Ikada, K. Hashimoto, H. Sugawara, T. Shibauchi, and Y. Matsuda, “Thermal conductivity measurements of the energy-gap anisotropy of superconducting LaFePO at low temperatures,” Phys. Rev. B **80**, 220509(R) (2009).
- [148] Y. Kasahara, T. Iwasawa, H. Shishido, T. Shibauchi, K. Behnia, Y. Haga, T. D. Matsuda, Y. Onuki, M. Sigrist, and Y. Matsuda, “Exotic superconducting properties in the electron-hole-compensated heavy-fermion semimetal URu₂Si₂,” Phys. Rev. Lett. **99**, 116402 (2007).
- [149] S. Vishveshwara and M. P. A. Fisher, “Critical dynamics of thermal conductivity at the normal-superconducting transition,” Phys. Rev. B **64**, 134507 (2001).
- [150] R. Okazaki, Y. Kasahara, H. Shishido, M. Konczykowski, K. Behnia, Y. Haga, T. D. Matsuda, Y. Onuki, T. Shibauchi, and Y. Matsuda, “Flux line lattice melting and the formation of a coherent quasiparticle Bloch State in the ultraclean URu₂Si₂ Superconductor,” Phys. Rev. Lett. **100**, 037004 (2008).
- [151] L. W. Gruenberg, and L. Gunther, “Fulde-Ferrell Effect in Type-II Superconductors ,” Phys. Rev. Lett. **16**, 996 (1966).
- [152] L. N. Bulaevskii, “Inhomogeneous state and the anisotropy of the upper critical field in layered superconductors with Josephson layer interaction ,” Sov. Phys. JETP **38**, 634 (1974).
- [153] H. Shimahara, and D. Rainer, “Crossover from Vortex States to the Fulde-Ferrell-Larkin-Ovchinnikov State in Two-Dimensional *s*- and *d*-Wave Superconductors ,” J. Phys. Soc. Jpn. **66**, 3591 (1997).
- [154] A. V. Chubukov, I. Eremin, and D. V. Efremov, “Superconductivity versus bound-state formation in a two-band superconductor with small Fermi energy: Applications to Fe pnictides/chalcogenides and doped SrTiO₃,” Phys. Rev. B **93**, 174516 (2016).

Main works

1. **T. Watashige**, S. Arsenijević, T. Yamashita, D. Terazawa, T. Onishi, L. Opherden, S. Kasahara, Y. Tokiwa, Y. Kasahara, T. Shibauchi, H. v. Löhneysen, J. Wosnitza, and Y. Matsuda, “Quasiparticle Excitations in the Superconducting State of FeSe Probed by Thermal Hall Conductivity in the Vicinity of the BCS-BEC Crossover ”, J. Phys. Soc. Jpn. **86**, 014707 (2017).
2. **T. Watashige**, Y. Tsutsumi, T. Hanaguri, Y. Kohsaka, S. Kasahara, A. Furusaki, M. Sigrist, C. Meingast, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, “Evidence for Time-Reversal Symmetry Breaking of the Superconducting State near Twin-Boundary Interfaces in FeSe Revealed by Scanning Tunneling Spectroscopy ”, Phys. Rev. X **5**, 031022 (2015).
3. S. Kasahara, **T. Watashige**, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, “Field-induced superconducting phase of FeSe in the BCS-BEC cross-over ”, Proc. Nat. Acad. Sci. USA **111**, 16309-16313 (2014). (The 1st. and 2nd. authors contributed equally to this work.)

Published works (including main works)

1. **T. Watashige**, S. Arsenijević, T. Yamashita, D. Terazawa, T. Onishi, L. Opherden, S. Kasahara, Y. Tokiwa, Y. Kasahara, T. Shibauchi, H. v. Löhneysen, J. Wosnitza, and Y. Matsuda, “Quasiparticle Excitations in the Superconducting State of FeSe Probed by Thermal Hall Conductivity in the Vicinity of the BCS-BEC Crossover ”, J. Phys. Soc. Jpn. **86**, 014707 (2017).

2. S. Kasahara, T. Yamashita, A. Shi, R. Kobayashi, Y. Shimoyama, **T. Watashige**, K. Ishida, T. Terashima, T. Wolf, F. Hardy, C. Meingast, H. v. Löhneysen, A. Levchenko, T. Shibauchi, and Y. Matsuda, “Giant superconducting fluctuations in the compensated semimetal FeSe at the BCS-BEC crossover ”, *Nature Commun.* **7**, 12843 (2016).
3. A. Yagil, Y. Lamhot, A. Almoalem, S. Kasahara, **T. Watashige**, T. Shibauchi, Y. Matsuda, and O. M. Auslaender, “Diamagnetic Vortex Barrier Stripes in Underdoped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ”, *Phys. Rev. B* **94**, 064510 (2016).
4. J. P. Sun, K. Matsuura, G. Z. Ye, Y. Mizukami, M. Shimozawa, K. Matsubayashi, M. Yamashita, **T. Watashige**, S. Kasahara, Y. Matsuda, J.-Q. Yan, B. C. Sales, Y. Uwatoko, J.-G. Cheng, and T. Shibauchi, “Dome-shaped magnetic order competing with high-temperature superconductivity at high pressures in FeSe ”, *Nature Commun.* **7**, 12146 (2016).
5. S. Hosoi, K. Matsuura, K. Ishida, H. Wang, Y. Mizukami, **T. Watashige**, S. Kasahara, Y. Matsuda, and T. Shibauchi, “Nematic Quantum Critical Point without Magnetism in $\text{FeSe}_{1-x}\text{S}_x$ Superconductors ”, *Proc. Natl. Acad. Sci. USA* **113**, 8139-8143 (2016).
6. T. Terashima, N. Kikugawa, S. Kasahara, **T. Watashige**, Y. Matsuda, T. Shibauchi, and S. Uji, “Magnetotransport study of the pressure-induced antiferromagnetic phase in FeSe ”, *Phys. Rev. B* **93**, 180503(R) (2016).
7. T. Terashima, N. Kikugawa, A. Kiswandhi, D. Graf, E.-S. Choi, J. S. Brooks, S. Kasahara, **T. Watashige**, Y. Matsuda, T. Shibauchi, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. v. Löhneysen, and S. Uji, “Fermi surface reconstruction in FeSe under high pressure ”, *Phys. Rev. B* **93**, 094505 (2016).

8. Y. Hu, X. Ren, R. Zhang, H-q. Luo, S. Kasahara, **T. Watashige**, T. Shibauchi, P. Dai, Y. Zhang, Y. Matsuda, and Y. Li, “Nematic magnetoelastic effect contrasted between $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ and FeSe ”, Phys. Rev. B **93**, 060504(R) (2016).
9. Y. Suzuki, T. Shimojima, T. Sonobe, A. Nakamura, M. Sakano, H. Tsuji, J. Omachi, K. Yoshioka, M. Kuwata-Gonokami, **T. Watashige**, R. Kobayashi, S. Kasahara, T. Shibauchi, Y. Matsuda, Y. Yamakawa, H. Kontani, and K. Ishizaka, “Momentum-Dependent Sign Inversion of Orbital Order in Superconducting FeSe ”, Phys. Rev. B **92**, 205117 (2015).
10. Y. Sun, S. Pyon, T. Tamegai, R. Kobayashi, **T. Watashige**, S. Kasahara, Y. Matsuda, and T. Shibauchi, “Enhancement of Critical Current Density and Mechanism of Vortex Pinning in H^+ -Irradiated FeSe Single Crystal ”, Appl. Phys. Express **8**, 113102 (2015).
11. Y. Sun, S. Pyon, T. Tamegai, R. Kobayashi, **T. Watashige**, S. Kasahara, Y. Matsuda, and T. Shibauchi, “Critical Current Density, Vortex Dynamics, and Phase Diagram of Single-Crystal FeSe ”, Phys. Rev. B **92**, 144509 (2015).
12. **T. Watashige**, Y. Tsutsumi, T. Hanaguri, Y. Kohsaka, S. Kasahara, A. Furusaki, M. Sigrist, C. Meingast, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, “Evidence for Time-Reversal Symmetry Breaking of the Superconducting State near Twin-Boundary Interfaces in FeSe Revealed by Scanning Tunneling Spectroscopy ”, Phys. Rev. X **5**, 031022 (2015).
13. T. Terashima, N. Kikugawa, S. Kasahara, **T. Watashige**, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhrer, F. Hardy, C. Meingast, H. v. Löhneysen, and S. Uji, “Pressure-Induced Antiferromagnetic Transition and Phase Diagram in FeSe ”, J. Phys. Soc. Jpn. **84**, 063701 (2015).

14. Y. Lamhot, A. Yagil, N. Shapira, S. Kasahara, **T. Watashige**, T. Shibauchi, Y. Matsuda, and O. M. Auslaender , “Local Characterization of Superconductivity in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ”, Phys. Rev. B **91**, 060504(R) (2015).

15. S. Kasahara, **T. Watashige**, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, “Field-induced superconducting phase of FeSe in the BCS-BEC cross-over ”, Proc. Nat. Acad. Sci. USA **111**, 16309-16313 (2014). (The 1st. and 2nd. authors contributed equally to this work.)

16. T. Terashima, N. Kikugawa, A. Kiswandhi, E.-S. Choi, J. S. Brooks, S. Kasahara, **T. Watashige**, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhrer, F. Hardy, C. Meingast, H. v. Löhneysen, and S. Uji, “Anomalous Fermi Surface in FeSe Seen by Shubnikov-de Haas Oscillation Measurements ”, Phys. Rev. B **90**, 144517 (2014).

17. M. Shimozawa, S. K. Goh, R. Endo, R. Kobayashi, **T. Watashige**, Y. Mizukami, H. Ikeda, H. Shishido, Y. Yanase, T. Terashima, T. Shibauchi, Y. Matsuda, “Control-lable Rashba Spin-Orbit Interaction in Artificially Engineered Superlattices Involving Heavy Fermion Superconductor CeCoIn_5 ”, Phys. Rev. Lett. **112**, 156404 (2014).

18. M. Shimozawa, **T. Watashige**, S. Yasumoto, Y. Mizukami, M. Nakamura, H. Shishido, S. K. Goh, T. Terashima, T. Shibauchi, and Y. Matsuda , “Strong suppression of superconductivity by divalent ytterbium Kondo holes in CeCoIn_5 ”, Phys. Rev. B **86**, 144526 (2012).

Acknowledgments

I would like to acknowledge Prof. Yuji Matsuda for guidance and encouragement. I also would like to acknowledge Prof. Takasada Shibauchi in Univ. of Tokyo for valuable advice and discussion. I also would like to appreciate Dr. Shigeru Kasahara for teaching experimental technique. From my master's degree, they have spent a significant amount of time and energy on my work. Without their guidance and stimulation, this work would not have been possible.

I wish to express my great appreciation Dr. Tetsuo Hanaguri in RIKEN especially for providing extensive advice with regards to the experiments using the scanning tunneling microscopy. I stayed in his laboratory two times for a total of seven months to carry out STM measurements.

For the thermal transport measurements, I would like to appreciate to the collaborators in the HLD-EMFL in Dresden, Dr. Stevan Arsenijević, Mr. Lars Opherden and Prof. Jochen Wosnitza for their support during my stay.

I also would like to acknowledge the collaborators, Dr. Yuhki Kohsaka, who supported me to make analysis programs, Dr. Taichi Terashima, Dr. Shinya Uji, who conducted the SdH measurements, Dr. Yuta Mizukami, who performed the penetration depth measurements, Dr. Yasumasa Tsutsumi, Dr. Akira Furusaki, Prof. Manfred Sigrist, Dr. Kazushi Aoyama, Prof. Hiroaki Ikeda, who worked on the project on theoretical side, Dr. Thomas Wolf, Prof. Christoph Meingast, and Prof. Hilbert von Löhneysen, who provided me clean single crystals and taught me how to fabricate the single crystals.

I would like to thank Prof. Yuichi Kasahara, Prof. Yoshifumi Tokiwa, Prof. Takahito Terashima and Dr. Masahiro Haze for experimental supports and helpful discussion. I also would like to appreciate the collaborators in Kyoto Univ., Mr. Daiki Terazawa and Mr. Takafumi Onishi for their efforts to support my research.

I am deeply indebted to members of Prof. Matsuda group, Mr. Tomohiro Ishi, Mr. Yohei Torii, and Mr. Tomoya Taniguchi.

I would like to specially thank Mr. Takuya Yamashita, who is my colleague and friend from the undergraduate degree. Thanks to his help and support, I could overcome difficulties.

I wish to acknowledge the financial support provided by the Research Fellowship of the Japan Society for Promotion of Science for Young Scientists.

Finally, I would like to express my gratitudes to my parents, my brother, my grandparents and the rest of my family for their supports and warm encouragement.