Superconductivity in Fe-chalcogenides

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\textbf{Abstract}

FeSe, which has the simplest crystal structure among the Fe based superconductors, and related chalcogenide superconductors are ideal candidates for investigating the detailed mechanism of the iron-based superconductors. Here, we summarize recent studies on the Fe-chalcogenides, with the goal to address some unresolved questions such as what is the influence of chemical stoichiometry on the phase diagram, what is the exact parent phase of FeSe system, and why can $T_c$ be so dramatically enhanced in FeSe based superconductors? Recent developments in novel synthesis to prepare chalcogenide crystals, nanoparticles and thin films allow the community to begin to address these issues. Then we review physical properties of the Fe chalcogenides, specifically focusing on optical properties, scanning tunneling spectroscopy and angle-resolved photoemission spectroscopy (ARPES) results. These measurements along with recent theories provide a framework for better understanding the origin of superconductivity in FeSe and Fe-chalcogenides.

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1. Introduction

Since the discovery of Fe chalcogenide superconductors in 2008, many research groups have made unprecedented advancement in understanding these materials. Several review articles have summarized efforts to date [1–4], however, many critical issues remain unresolved. The extremely sensitive correlation of superconductivity with chemical stoichiometry of \( \beta \)-FeSe [5,6] is still not fully understood, raising the question what is the exact phase diagram of this system [7,8]?

Recent developments in novel synthesis of chalcogenide crystals, nano-materials and thin films may help to address this question. Iron vacancies and three types of vacancy orders have been observed in a series of nano-dimensional tetragonal \( \beta \)-Fe\(_{1-x}\)Se\(_x\) and superconducting-like feature with \( T_c \) close to 40 K were observed in nano-particle samples [9]. Similar issues remain in the alkali/alkaline metal intercalated iron selenide (\( A_x \)Fe\(_2\)Se\(_2\), where \( A = K, Rb, Cs, Ti \)), and the molecular beam epitaxy (MBE) grown monolayer FeSe on SrTiO\(_3\) (FeSe/STO) [10–12]. \( A_x \)Fe\(_2\)Se\(_2\) superconductors exhibit high \( T_c \) (up to 46 K) [13] as well as an intrinsic multiphase nature, with the presence of iron vacancy order in the non-superconducting regime [14–18]. FeSe/STO displays rich behavior that can be controlled via annealing. Furthermore, despite varying reports of \( T_c \) measurements on these nanoparticles, as shown in 3(b), show that the mixture at 160 °C was gradually cooled to room temperature. Fig. 3(a) displays the superconducting energy gap of \( \sim 20 \) meV puts \( T_c \) higher than other Fe based superconductors, suggesting very unconventional pairing mechanisms.

This review intends to summarize recent advancements in Fe-chalcogenides, beginning with the latest developments in materials synthesis. Careful control of the material then allows for a systematic structure characterization, which we discuss next. Then we review physical properties of the Fe chalcogenides, specifically focusing on optical properties and angle-resolved photoemission spectroscopy (ARPES) results. These measurements along with recent theories provide a framework for better understanding the origin of superconductivity in FeSe and Fe-chalcogenides.

2. Materials synthesis

Several novel approaches have been developed to prepare Fe-chalcogenide materials that exhibit exciting new results. These materials include the alkali–metal doped FeSe superconductor with \( T_c \) above 40 K, the extremely high \( T_c \) ultra-thin film, and materials in nano-dimensional forms, which allow more detailed study its chemical stoichiometry and phase diagram in this intriguing superconducting system.

2.1. Alkali metal–organic solvent intercalated FeSe superconductors

Krzton-Maziopa et al. [19] reported a new synthesizing method to intercalate alkaline metal to FeSe, with the general formula \( A(xC_5H_5N)Fe_2Se_2 \) (\( A = Li, Na, K, Rb \)) that shows superconducting onset \( T_c \sim 45 \) K. The reaction was carried out at 40 °C until the disappearance of the alkaline metal solution. Post-annealing of intercalated material \( Li(xC_5H_5N)Fe_2Se_2 \) at elevated temperatures drastically enlarges the c-parameter of the unit cell (\( \sim 44\% \)) and increases the superconducting shielding fraction to nearly 100%. It is noted that samples prepared this way typically exhibit two phases based on resistivity measurements.

2.2. Methods to prepare materials in nano-dimensional forms

2.2.1. Two-dimensional nanosheets

Oyler et al. [20] reported a low-temperature solution chemistry route to the synthesis of \( \beta \)-FeSe, \( \beta \)-FeTe, FeTe\(_2\), and several members of the \( \beta \)-Fe(Se,Te) solid solution. Consistent with the layered crystal structures, the products are predominantly two-dimensional single-crystal nano-sheets with thicknesses of approximately 2–3 nm and edge lengths ranging from 200 nm to several micrometers from TEM images, as displayed in Fig. 1. Chang et al. [21] independently developed a chemical process to prepare similar Fe-chalcogen nano-sheets. Proper amount of ethylene glycol was mixed with PVP, NaOH and SeO\(_2\) powder. The mixture was heated to 160 °C, followed by adding hydrazine hydrate as reducing agent. The Fe precursor solution, which was made by dissolving FeCl\(_2\) in ethylene glycol, was then injected to the above mixture at 160 °C and kept for 12 h for the formation of FeSe nanosheets.

Chemical composition analysis shows these nanosheets are typically Fe-deficient, with stoichiometry such as Fe\(_x\)Se\(_y\). SAED patterns of the nanosheets reveal a tetragonal lattice along the [001] zone-axis direction, as shown in Fig. 2. Magnetic susceptibility measurements of as-grown Fe\(_x\)Se\(_y\) nanosheets are not superconducting, however, superconductivity results after further annealing in 700 °C for a few hours.

2.2.2. \( \beta \)-FeSe nano-particles

Chang et al. [9] also reported a solvent-less Reaction under Autogenesis Pressure at Elevated Temperature (RAPET) process to synthesize superconducting Fe–Se nanoparticles using iron and selenium powders as the starting materials. The typical reaction temperature was 700 °C for a few hours, and then the reactor was gradually cooled to room temperature. Fig. 3(a) displays the micrographs of the nanoparticle obtained. Detailed magnetization measurements on these nanoparticles, as shown in 3(b), show that in addition to the superconducting transition at \( \sim 10 \) K, an anomaly suggesting the presence of superconducting transition occurs at \( \sim 40 \) K. The superconducting volume fraction depends on the

![Fig. 1](image)
2.2.3. FeSe nanowires

Mishra et al. [22] developed a method using catalyst-aided vapor transport reaction at 800 °C in an inert atmosphere to synthesize superconducting FeSe nanowires. They used the element Se and iron acetylacetonate [Fe(II)(C₅H₈O₂)]₃ as the precursors. These materials vaporized very easily, thereby facilitating transport, and contributed to the formation of a carbonaceous shell encapsulating the FeSe nanowires. The superconductivity of these nanocables was confirmed with a $T_c$ of 24 K. The length of FeSe filling inside the carbon nanofibers could be varied by controlling the reaction conditions while the diameter of nanowires was dependent on the thickness of Au–Pd coating used as a catalyst.

We have also developed a simple process [23] to grow highly crystalline FeSe nanowires (NWs) by annealing FeSe thin film, which is prepared by pulsed laser deposition on MgO substrate. Fig. 4(a) shows the SEM image of the as-grown β-FeSe NWs on substrate. The high-resolution transmission electron microscope (HRTEM) images show excellent crystalline tetragonal structure in these NWs. However, surprisingly, these Fe₀.₈Se NWs exhibit either semiconducting or metallic behavior by resistive measurements, as shown in Fig. 4(c). No superconducting transition is observed in both NWs. From EDS results, all NWs have good uniformity in composition but are found with Fe/Se ratio of 4:5.

2.3. FeSe₁₋ₓTex thin films

Several groups have reported growth of superconducting β-FeSe₁₋ₓTex thin films by Pulse-Laser-Deposition (PLD) technique [1,24–28]. Thin films were synthesized with other approaches such as metal–organic chemical vapor deposition (MOCVD) [29,30], molecular beam epitaxy (MBE) [31], and electrochemical synthesis [32]. In general it is found that β-FeSe₁₋ₓTex can be easily grown in a wide temperature range (250–600 °C) on various substrates such as MgO, LaAlO₃, SrTiO₃, Si, SiO₂/Si, GaAs, R-Al₂O₃, CaF₂, and LSAT.

Wang et al. reported that the superconductivity of FeSe films is strongly thickness and orientation dependent [33]. Schneider et al. demonstrated the existence of a thickness dependent superconducting-insulator quantum phase transition (QPT) in FeSe thin film, and estimated the critical thickness to be ~300 nm [34].
the QPT phenomenon possibly results from the non-superconducting grain boundaries, one expects to fine-tune the critical thickness by optimizing the deposition condition. However, as far as we know there are no reports on (001)-oriented thin film with thickness <100 nm with observable superconducting transition except the recently discovered monolayer FeSe film on special treated SrTiO$_3$ substrate.

Most Te-substituted films were grown on substrate along (001) orientation. Similar to bulk samples, non-uniform Te distribution, resulting in a broadening of X-ray diffraction peaks, was observed in low Te-substituted films [1]. The $T_c$ of films has a similar trend as the bulk samples. However, Zhuang et al. reported recently the enhancement of superconductivity on Fe-deficient films on CaF$_2$ substrates [35]. The $T_c$ of film can be up to 21 K, as in Fig. 5, by using Fe$_{0.8}$Se$_{0.5}$Te$_{0.5}$ targets. Their results reveal that the Fe-vacancy plays an important role in the $T_c$ enhancement. It was a real surprise to the community when Wang et al. reported the unexpected high $T_c$ > 50 K, Fig. 6, in monolayer FeSe thin film [9] grown by molecular beam epitaxy (MBE) on SrTiO$_3$ substrate. With the protecting layer of FeTe, the film has an extremely large critical current density $j_c$ ~ $1.7 \times 10^6$ A/cm$^2$, about two orders of magnitude higher than that in the bulk FeSe [36]. The tunneling spectrum reveals two gap structures around 10 and 20 mV, which corresponds to a superconducting transition temperature higher than 77 K. However, another surprise was superconductivity disappeared in bilayer film. Other groups later confirmed the gap structure using angle-resolved photoemission spectroscopy (ARPES) studies, which show that the electronic structure of one unit cell FeSe film changes with the annealing condition [11,38].

3. Structural studies of Fe-chalcogenides

3.1. $A_{1-x}$Fe$_x$Se$_2$ ($A = K, Cs, Rb, Tl$)

Potassium intercalated FeSe superconductor with a $T_c = 30$ K showed a crystal structure adopting the ThCr$_2$Si$_2$ type tetragonal lattice (space group I4/mmm) [38]. Latter studies revealed that the $A_{x}$Fe$_{1-x}$Se$_2$ system shows strong phase separation in superconducting samples including crystals [13,39–41,40–42] A charge balanced compound with a formal oxidation state close to +2 for Fe was realized to be $A_{0.8}$Fe$_{1.2}$Se$_2$ (or $A_x$Fe$_{2-x}$Se$_2$). Approximately 20% Fe vacancies in $A_{0.8}$Fe$_{1.2}$Se$_2$ exhibit an order that could be described by $\sqrt{5} \times \sqrt{5} \times 1$ supercell (a tetragonal I4/m unit cell) below an ordering temperature $T_S = 500$–578 K depending on the intercalated metal A [13,42–44]. A block antiferromagnetic order developed slightly below $T_c$ ($T_{N1} = 471$–559 K) with an ordered magnetic moment ~3.3 $\mu_B$/Fe at 10 K [44].

The superconducting phase in $A_1$Fe$_2$Se$_2$ system is controversial. Apart from the stable $A_x$Fe$_{3-x}$ non-superconducting matrix in superconducting crystals, a separated phase with an expanded c-axis [14,45–47] and a composition close to $A_x$Fe$_{2-x}$Se$_2$ [15,46,48–50] was assigned to be the superconducting phase with $T_c$ ~ 29–32 K. Others attribute the superconductivity to originate from a parent phase of semiconducting antiferromagnetic $A_x$Fe$_2$Se$_4$ with rhombus ($\sqrt{2} \times \sqrt{2}/2$ Fe-vacancy order [51], of $A_x$Fe$_2$Se$_4$ parallaglogram structure [47], or of $A_x$Fe$_2$Se$_4$ instead of the well known insulating antiferromagnetic $A_x$Fe$_2$Se$_4$ with $\sqrt{5} \times \sqrt{5}$ Fe-vacancy order.

3.2. FeSe nano-materials

Fig. 8B shows the SAED pattern taken from a tetragonal FeSe nanowire, with clear superstructure spots on the reciprocal a’–b’ plane that could be unambiguously identified as the $\sqrt{5} \times \sqrt{5} \times 1$ Fe-vacancy order by the unique superstructure wave vector $q_1 = (1/5, 3/5, 0)$ and $q_2 = (3/5, 1/5, 0)$. This order is exactly the same as the one found in $A_x$Fe$_2$Se$_4$. This observation resolved the puzzle of the absence of superconductivity in these FeSe nanowires. A follow-up question was whether this Fe-vacancy order exists in other FeSe materials? Indeed, after careful examination, the presence of $\sqrt{5} \times \sqrt{5} \times 1$ Fe-vacancy order was observed in nanoparticles and nanosheets prepared using hydrothermal process [21], crystals grown at high pressure, and in samples from K$_2$Fe$_3$Se$_5$ crystals after extracting K by iodine [21].

Besides the $\sqrt{5} \times \sqrt{5} \times 1$ Fe-vacancy order, at least two different types of Fe-vacancy order were found: $\sqrt{2} \times \sqrt{2}$ with d$_{100}$ shift every other (001) plane and $\sqrt{10} \times \sqrt{10}$ with d$_{210}$ shift every other (001) plane. Tetragonal FeSe with $\sqrt{5} \times \sqrt{5} \times 1$ Fe-vacancy order, namely Fe$_2$Se$_4$, is not superconducting (Fig. 8A) and is instead an antiferromagnetic insulator [21], the same as $A_x$Fe$_2$Se$_4$. This suggests that the rich-phases found in $A_{1-x}$Fe$_x$Se$_2$ are not exclusive cases in iron-based superconductors.

Based on the above observations, a temperature-doping phase diagram for Fe–Se superconducting system was proposed [21]. The magnetic and insulating/superconducting phases of $A_{1-x}$Se with Fe-vacancy orders may serve as the parent phase of FeSe superconductor, instead of the previously argued $A_{1-x}$Te [21], which shows different magnetic and electronic features compared to Fe$_1$Se [10.53–54]. The superconducting Fe$_{1.0}$Se with $T_c = 8.5$ K could be in the overdoped regime in this proposed phase diagram.
It has been suggested that disorder of Fe vacancies or suppression of the Fe-vacancy orders may bring the re-emergence of superconductivity in K$_{1-x}$Fe$_2$Se$_2$. The efforts to examine the correlation between the suppression of Fe-vacancy orders and superconductivity in Fe$_{1-x}$Se are currently in progress.

3.3. Pressure effects on structure

Among the Fe chalcogenides, FeSe has the most dramatic response to applied pressure, with $T_c$, onset = 12 K at ambient pressure to 37 K at 4–6 GPa [58–61]. The normal state resistivity drops with applied pressure, and the superconducting transition is reported to be sharper at 1 GPa than at ambient pressures. This implies FeSe undergoes significant electronic, magnetic and structural changes under pressure. Starting at 1 GPa, the Se height from the Fe layer suddenly drops from 1.45 Å to ~1.42 Å and $T_c$ dramatically increases [62] with this anion height change. Above 6 GPa, FeSe undergoes an orthorhombic to hexagonal transition. The $T_c$ begins to drop at this pressure induced structure transition. In order to understand the electronic and magnetic changes involved in the higher $T_c$, nuclear magnetic resonance studies were done and showed that the antiferromagnetic fluctuations are also enhanced under pressure [63]. At ambient pressures, the antiferromagnetic fluctuations start to increase above $T_c$. This increase is pushed to higher temperatures under pressure, strongly suggesting superconductivity in FeSe is correlated with magnetic fluctuations.

Monoclinic FeTe is antiferromagnetically ordered below 70 K, and applying pressures of 1–2 GPa suppresses this ordering [64,65]. However, no superconductivity was found to emerge with applied pressure despite suppression of the antiferromagnetic ordering.

The pressure response of mixed phase FeTe$_{1-x}$Se$_x$ depends on whether the system is Se or Te rich. For Te rich systems, the pressure effect tends to suppress superconductivity, while for Se rich systems applying pressure increases $T_c$, following the trend for FeSe [66–68]. FeTeSe systems undergo a structure change from orthorhombic to monoclinic at 2–3 GPa, similar to FeTe and in contrast to FeSe.

$T_c$s of alkali metal intercalated FeSe are found to monotonically decrease with applied pressure beyond the point of optimal pressure [69]. However, at pressures above 11.5 GPa, a second
superconducting phase emerges, with the $T_c$ of this re-emerging phase significantly higher than $T_c$ at the first maximum. The highest $T_c = 48.7$ K is found for K0.8Fe1.7Se2 at 12.5 GPa, which has a first maximum of 32 K at approximately 1 GPa.

4. Optical spectroscopy

Optical spectroscopy provides valuable insights into the electronic structure, lattice dynamics, and correlation effect in a quantum material [70]. This section reviews the optical experiments that have helped to shape the understanding of iron selenide superconducting systems, with special focuses on Raman and ultrafast optical techniques.

4.1. FeSe$_{1-x}$Te$_x$

Since the first study reported by Xia et al. [71], phonon dynamics in FeSe$_{1-x}$Te$_x$ were examined by several groups using Raman spectroscopy [72–76]. Fig. 9 shows the polarized Raman spectrum of FeSe$_{0.96}$ single crystal [72]. With quasi-back-scattering configuration, the Raman spectrum exhibits two distant peaks at 182 cm$^{-1}$ for $A_{1g}$(Se) mode and 206 cm$^{-1}$ for $B_{1g}$(Fe) mode. Besides, weak lines with frequencies around 236, 290, and 357 cm$^{-1}$ appear in (xx) polarized spectra at low temperatures, which were assigned to $B_{2g}/B_{3g}$ modes in the orthorhombic phase. From the temperature-dependent frequency shifts of the phonon modes (inset of Fig. 9), a large (~6.5%) hardening of the $B_{1g}$(Fe) mode was observed and attributed to the suppression of local fluctuations of the iron spin state with a gradual decrease of the iron paramagnetic moment.

The temperature-dependent phonon hardening and alternation in the electronic structure can also be identified via other spectral features in the Raman spectrum [73,74]. Fig. 10 shows the unpolarized Raman spectrum of a polycrystalline FeSe$_{0.82}$ sample at 3 K [73]. The four Raman-active modes can be addressed at 106, 160, 223, and 234 cm$^{-1}$ for the $E_g$(Fe), $A_{1g}$(Se), $B_{1g}$(Fe), and $E_g$(Se), respectively (marked as S1–S4 in the figure). This temperature-dependent study indicated a 5% increase in the frequency of $E_g$(Fe) due to the phonon hardening at $T < T_S$. In addition, the spectrum exhibits two additional high-frequency peaks at ~1350 and 1600 cm$^{-1}$, which are thought to be from electronic Raman scattering from $(x^2-y^2)$ to $xzyz$ $d$-orbitals of Fe. Detailed measurements as a function of temperature to confirm this hypothesis is still lacking.

Systematic Raman studies on FeSe$_{1-x}$Te$_x$ with different Te substitutions ($x = 0.56–1$) were reported by Um et al. [74]. Except in pure FeTe, all Te doped samples show hardening of both $A_{1g}$ and $B_{1g}$ modes as the temperature is decreased. It is also worth noting a monotonic phonon mode sharpening, i.e., prolongation of phonon lifetime, in FeSe$_{1-x}$Te$_x$ with increasing Se content, argued to be a consequence of spin-phonon coupling. Different from FeSe$_{1-x}$Te$_x$ with $x > 0.56$, the non-superconducting FeTe exhibits magnetic ordering below $T_N \sim 67$ K, resulting in different phonon property of FeTe. The $B_{1g}$ mode of FeTe hardens and broadens with decreasing temperature down to $T_N$ and then softens and narrows at $T < T_N$. The renormalization of the phonon frequency below $T_N$ was also observed by others [76], as well as in iron pnictides, and explained by a phonon modulation of the magnetic interactions, including superexchange, direct exchange, and anisotropy.

Beyond the steady-state properties, optical spectroscopy with ultrafast laser pulses provides a unique tool to probe the dynamic evolution of electrons and phonons in superconductors, including the cooling of the nonequilibrium quasiparticle plasma through electron–electron and electron–phonon interactions.

![Fig. 9. Polarized Raman spectra of FeSe at 7 K. The left inset shows a comparison between FeSe and FeTe at 50 K. The right inset shows the temperature evolution of the (aa) polarized spectra [73].](image_url)

![Fig. 10. Unpolarized-Raman spectrum of FeSe at 3 K. Thick solid line (red) shows the total fit and thin solid lines (blue) show the individual fit. Insets show the S1 mode at two temperatures and the eigen-vectors of the calculated phonon modes [74]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image_url)
Quasiparticle dynamics in FeSe$_1$−$x$Te$_x$ has been studied by the transient reflectivity spectroscopy [77–79,65–67]. An orientation dependent ultrafast investigation revealed distinct carrier–phonon thermalization rate for electrons with different interplane wavevectors in FeSe$_{1-x}$ [77]. In addition, the carrier–phonon coupling strength was found to be suppressed with increasing Te substitution in FeSe$_{1-x}$Te$_x$ [79].

Sub-picoscnd relaxation of quasiparticles in the transient reflectivity of FeSe$_{1-x}$ [77] below 130–140 K reflects the appearance of new electronic structure near the Fermi level. A temperature-dependent study of this spectral feature suggested its origin to be gap-like quasiparticles, with the effective gap size estimated to be ~36 meV. This high-temperature energy gap was observed above the structural phase transition and explained by the short-range orbital and/or charge orders. Similar energy gap was reported soon with angular-resolved photoemission spectroscopy (ARPES) in FeSe/SrTiO$_3$ thin films at ~125 K, while the authors argue its magnetic origin [80].

4.2. $A_x$Fe$_{2-y}$Se$_2$

Raman spectra of $A_x$Fe$_{2-y}$Se$_2$ generally exhibit two digit numbers of phonon peaks below 300 cm$^{-1}$, compared to only four Raman-active phonon modes in FeSeTe. Zhang et al. performed systematic Raman studies on K$_{0.5}$Fe$_{1.5}$Se$_2$, Tl$_{0.3}$K$_{0.7}$Fe$_{1.7}$Se$_2$, and Tl$_{0.3}$Rb$_{0.7}$Fe$_{1.3}$Se$_2$, together with first-principles calculations [81], showing that the abundant phonon modes in $A_x$Fe$_{2-y}$Se$_2$ are the consequence of the superstructure with ordered iron vacancies, which can be assigned by the calculation reasonably well. In the high-energy region, the Raman spectra of $A_x$Fe$_{2-y}$Se$_2$ exhibit a broad, asymmetric peak around 1600 cm$^{-1}$, which was identified as a two-magnon process involving optical magnons [82]. The intensity of the two-magnon peak falls sharply on entering the superconducting phase, suggesting a complete mutual proximity effect occurring within a microscopic structure based on nanoscopic phase separation.

Terahertz (THz) spectroscopy on superconducting Rb$_{1.2}$Fe$_{2.8}$Se$_2$ was recently reported [83]. The temperature dependence of the optical conductivity and dielectric constant exhibits an isobestic point at 90 K ($T_{\text{meas}}$), indicating a metal-to-insulator-type, orbital-selective transition. At $T_{\text{gap}}$ = 61 K, a gap-like suppression of the optical conductivity was observed and followed by the occurrence of the superconducting transition at $T_c$ = 32 K. This hierarchy of temperature $T_c < T_{\text{gap}} < T_{\text{meas}}$ tends to imply that the quasiparticle in the $d_{xy}$ band are more strongly correlated. The quasiparticle dynamics examined by polarized optical pump–probe technique could be helpful to inspect this issue, whereas ultrafast optical experiments in $A_x$Fe$_{2-y}$Se$_2$ system are still lacking so far.

5. Scanning Tunneling Microscopy (STM)

The first scanning tunnel microscopy studies of Fe chalcogenides focused on the FeSeTe crystals due to difficulty with cleaving FeSe [84–88]. From topography and spectroscopy of FeTe$_{1-x}$Se$_x$ with Te $\sim$12–15 K it was concluded that samples had significant nanoscale inhomogeneity. Remarkably, no electronic phase separation was seen, suggesting that the systems maintain electronic homogeneity despite the nanoscale chemical phase separation. Later, FeSe was grown by MBE techniques on bilayer graphene [89]. Regions of the sample surface with excess Se were reported to exhibit a $\sqrt{5} \times \sqrt{5}$ reconstruction, and STM spectroscopy shows an asymmetric gap with no superconducting features. Annealing the sample at higher temperature (~420°C) returned the surface to square-like lattice with lattice parameters matching those of bulk FeSe, and a superconducting gap was then measurable in the dI/dV spectra. Several studies addressed the superconducting pairing symmetry. Hanaguri et al. argue for s+-order parameter in Fe(Se,Te), and the gapped spectra observed suggested no nodes in the order parameter, though there is still likelihood for gap anisotropy [86]. In contrast, Fridman et al. observed a V-shaped gap in FeTeSe, which would provide evidence for nodes [87]. More evidence for nodal order parameter in Fe chalcogenides was observed by Song et al. in MBE grown FeSe with extremely low defect density [80]. A V-shaped gap was observed at lowest temperatures of 0.4 K, providing clear evidence of nodal superconductivity. This discrepancy in observed behavior can be understood by considering the interlayer coupling. In FeTeSe, the interlayer coupling is reduced due to the Se atoms being closer to the Fe plane than Te atoms. This is consistent with the smaller interlayer coupling observed in FeSe, which leads to more likelihood of d-wave order parameter.

The earliest STM studies of the alkali metal iron selenides were performed on thin films of K$_{x}$Fe$_2$−$y$Se$_2$ grown by MBE [91,92]. The STM results showed that the samples can consist of rich mixture of phases, for example $\sqrt{5} \times \sqrt{5}$ Fe vacancy order, $\sqrt{2} \times \sqrt{2}$ charge order or even $\sqrt{2} \times \sqrt{5}$. Typically the Fe vacancy ordered phase is insulating/semiconducting and has antiferromagnetic band nature from first principles calculations. The phase without vacancy order is the superconducting one. In the K$_{x}$Fe$_2$−$y$Se$_2$ samples, for example, the insulating phase had $\sqrt{5} \times \sqrt{5}$ iron vacancy order while the superconducting state existed in K$_{x}$Fe$_2$−$y$Se$_2$, which was later suggested to be the parent compound for K$_{x}$Fe$_{2-y}$Se$_{2-x}$ samples [93].

6. Angle Resolved Photoemission Spectroscopy (ARPES)

Earlier Angle-Resolved Photoelectron Spectroscopy (ARPES) studies on iron-chalcogenides focused on Fe$_{1+y}$Te$_x$ compounds in Te-rich regime [53,94–99]. ARPES studies on FeSe were rather limited [100] due to the difficulty of cleaving FeSe single crystal, and only recently with MBE grown monolayer FeSe film on STO substrate were more ARPES studies reported [10,11,37,101]. ARPES investigations on alkaline–metal iron selenides ($A_x$Fe$_{2-y}$Se$_2$) reveal the absence of hole pockets at the Fermi surface (FS) [102–104]. This striking result challenges the widely believed FS nesting picture. In this section, we review the ARPES studies on $A_x$Fe$_{2-y}$Se$_2$ and the ultrathin FeSe films.

6.1. Alkali metal iron selenides $A_x$Fe$_{2-y}$Se$_2$

Chen et al. [95] identified various phases in K$_{x}$Fe$_{2-y}$Se$_2$ by ARPES and found that the insulating phase exhibits magnetic and vacancy order. These observations are consistent with the well-documented results that $A_x$Fe$_{2-y}$Se$_2$ shows the tendency of mesoscopic phase separation into superconducting, semiconducting or AFM insulating phase [41]. Electron-like Fermi pockets were observed at the corner of the Brillouin zone (BZ), at the zone center, and the hole-like bands were absent [103–105]. However, there is a small electron-like feature enclosing at $k_z$ = $\pi$ (Fig. 11). Regarding the missing hole pocket, Qian et al. reported that the top of the hole band at $\Gamma$ sinks to 90 meV below the Fermi level [103]. Without hole pockets at the center, the idea of Fermi nesting will no longer be the same as which occurs in other iron-based superconductors. However, the same group [103] also suggested that the Fermi nesting in $A_x$Fe$_{2-y}$Se$_2$ might still happen between the circular electron pockets through interband scattering. Owing to the inequivalent S potential with respect to the wave vector connecting the two electron pockets, such interband scattering will favor the opposite signs of the pairing parameter. ARPES of (Tl, $K_{1-x}$Se) [106] also supports a similar Fermi nesting picture. Nevertheless, whether
Fermi surface nesting is responsible for superconductivity in the iron-based family [107] remains an open question. A nodeless, isotropic superconducting gap of 10–15 meV was observed at the electron like pockets at the BZ corner in $A_xFe_2-ySe_2$ [103,104,106,107]. Xu et al. [107] reported a small electron pocket at Z with an isotropic superconducting gap of comparable size (8 meV). A similar 6.2 meV isotropic superconducting gap at the Z-centered electron pocket was also observed in (Tl,K)Fe$_{1.78}$Se$_2$ [18]. Mou et al. [108] observed a small electron like band in the zone center accompanied with an inner small gapless hole band, which barely crosses the Fermi level. The superconducting gaps at both electron pockets at C and M are isotropic, with the values of 15 meV and 12 meV respectively. Whether the superconducting gap is nodeless is still debatable, albeit ARPES results generally report isotropic gaps. The complexity of the bulk and surface related behavior may stimulate more theoretical and experimental work.

6.2. FeSe monolayer and multilayer thin films

The first reported $T_c$ close to 70 K in monolayer FeSe film on STO was based on the in situ scanning tunneling microscopy (STM) measurements [10]. The origin of the remarkable enhancement in $T_c$ is attributed to the charge transfer between the pretreated STO substrate and the FeSe layer [10,11]. The films showed neither sign of Se vacancy ordering, nor any phase inhomogeneity [10,11,37]. The electronic structure of monolayer FeSe consists of only electron band near the BZ corner, and no other Fermi surface observed at the BZ center [11,12,37] as shown in Fig. 12 [37]. Liu et al. [11] reported that FeSe monolayer is a two-dimensional system. However, recent ARPES result on FeSe crystal, by Maletz et al. [100], the hole pockets in the zone center still exhibit clear three-dimensionality.

ARPES studies on the monolayer FeSe exhibit a superconducting gap with a size of 15 meV, corresponding to a $T_c$ $\sim$ 55 K [11,37]. Based on a series of ARPES measurements to investigate the effect of film thickness on the electron structure, Tan et al. [37] found the FSs of the monolayer FeSe film and the multilayer FeSe film were significantly different (Fig. 12). They subsequently proposed a phase diagram for FeSe as a function of lattice constant (Fig. 13a), and then argued that the reason for superconductivity only observed in monolayer film originated from the competition between SDW and superconductivity, with the “lattice constant” as the tuning parameter. The same group was able to enhance $T_c$ of the monolayer FeSe grown on top of the Nb:STO epitaxial film grown on KTaO$_3$ substrate, which expanded the lattice parameter to 3.99 Å [86].

Another effort by He et al. [12] was to post anneal the as grown monolayer FeSe film to change the carrier concentration (Fig. 13b) [12]. They identified three phases and the corresponding band structure: the initial non superconducting N phase, the superconducting S phase forming at the final annealing stage and the intermediate phase as a mixture of N phase and S phase. Neither the N phase nor the S phase shows bands crossing Fermi level in the BZ center. The authors also found that under optimized annealing conditions, the highest $T_c$ can be enhanced to 65 K.

All the ARPES results seem to imply that superconductivity closely associate with the interface between the substrate and the thin film interface such the lattice mismatch induced strain, the charge carrier transfer and pretreatment of the substrate play vital role. Meanwhile, what has been changed during the annealing process is another issue. More effects need to be considered such as, the selenium or oxygen vacancies forming during the annealing and the rearrangement the substrate-film interface.

7. Theory on Fe chalcogenide superconductors

On the theoretical side, enormous efforts have been made to investigate the interplay between the structural phase transition, magnetism, and superconductivity in iron-based superconductors. At first glance, the structural phase transition seems to be an

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**Fig. 11.** (a) The Fermi surface topology of $K_xFe_2-ySe_2$ superconductor in the three-dimensional BZ. (b) The photoemission intensity map for the Fermi surface at $k_z = \pi$ taken with $h\nu = 31$ eV at 35 K [107].

**Fig. 12.** The thickness dependence of the FS of FeSe thin films, taken at 30 K [37].
accidental coincidence of the possible lattice instability due to phonons. This viewpoint, however, has been challenged because the anisotropy in several physical properties below the structural phase transition is experimentally found to be too large to be explained by the small change in the lattice constants [109–112]. This suggests the structural phase transition is driven by the electron correlation [113,114], and the corresponding fluctuations might also be related to the pairing mechanism of superconductivity [115,116]. One natural candidate for the many-body state responsible for the structural phase transition is the electronic nematicity [117–119]. Generally speaking, the electronic nematicity is a charge analogue of Stoner’s ferromagnetism at higher angular momentum. A ‘distortion’ of Fermi surfaces is possible if there exists interaction at higher angular momentum, such as in p-wave or d-wave cases. Because the interaction at high angular momentum is anisotropic in nature, the corresponding Fermi surface distortion is also anisotropic. It is then allowed to have anisotropic spin-independent Fermi surface distortion in principle, and the resulting state is a non-magnetic ordered state in charge channel that breaks the rotational symmetry spontaneously. These instabilities of Fermi surface have been first investigated decades ago by Pomeranchuk in 1958 [120].

The electronic nematicity is the state breaking $C_4$ rotational symmetry due to a d-wave interaction [117]. The Fermi surface in the nematic state is elongated along one particular direction, leading to the strong anisotropy in physical properties along $x$ and $y$ directions. For iron-based superconductors, experimentally measurable 'order parameters' include the difference in lattice constant along $x$ and $y$ directions [121], the difference in occupation number in $xz$ and $yz$ orbitals ($n_{\text{nem}} = n_{xz} - n_{yz}$) [110], and the magnetic torque measurement that is related to the difference in the zero-frequency spin susceptibility along ($q_x,0$) and ($0,q_y$) directions ($\chi_{\text{nem}} = \chi(q_x,0) - \chi(0,q_y)$) [122]. While the first order parameter is related to the lattice degrees of freedom, the later two are both of electronic origins but with very different microscopic mechanisms. Non-zero $n_{\text{nem}}$ arises from the strong charge interactions between electrons on different orbitals, leading to an orbital ordering in $xz$ and $yz$ orbitals [123,124]. $\chi_{\text{nem}}$, on the other hand, is a consequence of degenerate spin fluctuations around momenta ($\pi,0$) and ($0,\pi$), and the ground state of the system breaks this degeneracy due to the strong quadrupole spin–spin interactions [113,114,125]. The main difficulty in resolving this debate experimentally lies in the fact that whenever one of these order parameters is non-zero, all others become non-zero simultaneously, for all of them break exactly the same $C_4$ rotational symmetry [126,127]. Therefore, typical thermodynamic properties used to characterize symmetry-breaking phases are blind to the orbital and the spin scenarios, and further experimental identifications have been proposed and measured to differentiate them. For the orbital scenario, Lee et al. have proposed that the orbital fluctuations can lead to a non-Fermi liquid behavior in the region of the phase diagram in proximity to the structural phase transition [126,128]. Such a non-Fermi liquid behavior has been interpreted as the cause of a novel zero-bias peak in the point contact spectroscopy observed in a variety of iron based superconductors [129].

The diversity of the behaviors from family to family might indicate that both orbital and spin scenarios are necessary to fully understand the iron based superconductors. The theoretical approaches combining both itinerant electrons with strong orbital characters and the local spin interactions have been pursued. Based on the LDA+DMFT formalism, Yin et al. have proposed that the electronic correlations in iron based superconductors are controlled by the strength of the Hund’s rule coupling $J_H$ instead of Hubbard onsite interaction $U$ [130]. Lv et al. proposed to use the double exchange model, a model consisting of $d_{xz}$ and $d_{yz}$ itinerant electrons as well as local spins, as a better starting model for the iron pnictides [131]. Other models of similar nature have been employed to understand the phase transitions [132,133].

Recently, more and more experimental evidence suggest that Fe chalcogenide superconductors might lean toward the orbital scenario. Moreover, they could be more correlated among the iron-based superconductors because the $T_c$ can be enhanced dramatically by various experimental controls. Several theories have been suggested to explain the origin of the extremely large superconducting gap in monolayer FeSe film on SrTiO3. Xiang et al. [134] proposed that the pairing strength of FeSe is enhanced due to the coupling between the screened ferroelectric phonons of SrTiO3 and the electrons in FeSe. It is further suggested that ...FeSe) (STO)n/FeSe/(STO)n... superlattices could be an artificial material with high $T_c$.

To understand the high $T_c$ in $A_2$Fe$_2$Se$_2$ and FeSe/STO which both have only electron pockets, Yang et al. [135] wrote down an effective Hamiltonian containing key features of existing models [113–118,121,123–125]. They conclude: (1) Hole pockets
introduce frustration in Cooper pairing, due to the existence of band vorticity around the hole Fermi surface. Removing the hole pockets releases pairing frustration [119]. This explains why Cooper pairing in AxFe2–ySe2 and FeSe/STO is stronger. Furthermore, screening effect can further enhance \( T_c \) in FeSe/STO substrate [120]; (2) The static orbital order have large effect on superconducting state. Thus, the long pending investigation. It is believed that the iron selenides and related compounds will provide essential information to understand the origin of superconductivity in the iron-based superconductors, and possibly the conducting cuprates.

8. Summary

Here we summarize recent studies on the Fe-Chalcogenide superconductors, focusing on the alkaline–metal intercalated FeSe system, Fe-chalcogenide nanomaterials and the MBE grown monolayer FeSe on SrTiO3 thin film. The absence of hole pockets in the high \( T_c \) FeSe/STO and FeSe/STO implies that Fermi Surface nesting between electron may not be that essential to understand the magnetic and superconducting states in Fe-chalcogenides. Observation of various Fe-vacancy orders in \( \beta_{\text{FeSe}} \). \( \beta_{\text{Se}} \) suggests that the rich-phases similar to those in \( A_{x} \). \( A_{x} \). \( A_{x} \). \( A_{x} \). \( A_{x} \) may be more prevalently found in Fe superconductors. The magnetic, non-superconducting \( \beta_{\text{FeSe}} \). \( \beta_{\text{Se}} \) phases with iron-vacancy order have been shown to behave like Mott insulators from resistivity measurements. Non-superconducting FeSe/STO becomes a superconductor after high temperature annealing. This strongly indicates that one of the Fe-vacancy ordered \( \beta_{\text{Fe}}, \beta_{\text{Se}} \) is the insulating parent compound of the superconducting state. Thus, the long pending question whether magnetic and superconducting state are competing or cooperating for cuprate superconductors may also apply to the Fe-chalcogenide superconductors. For one, phase separation in alkaline–metal intercalated FeSe superconductors reminds us of the situation in the superconducting cuprates. Furthermore, optical spectroscopy measurements imply similar correlated normal state behavior in FeSe system and the cuprates. Could the Fe-vacancy order to disorder transition be associated with the presence of superconductivity? This issue is currently under investigation. It is believed that the iron selenides and related compounds will provide essential information to understand the origin of superconductivity in the iron-based superconductors, and possibly the conducting cuprates.

References


