An overview of the Fe-chalcogenide superconductors

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Topical Review

An overview of the Fe-chalcogenide superconductors

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Received 5 January 2015, revised 14 April 2015
Accepted for publication 30 April 2015
Published 10 July 2015

Abstract

This review intends to summarize recent advancements in FeSe and related systems. The FeSe and related superconductors are currently receiving considerable attention for the high critical temperature ($T_c$) observed and for many similar features to the high $T_c$ cuprate superconductors. These similarities suggest that understanding the FeSe-based compounds could potentially help our understanding of the cuprates. We begin the review by presenting common features observed in the FeSe- and FeAs-based systems. Then we discuss the importance of careful control of the material preparation allowing for a systematic structure characterization. With this control, numerous rich phases have been observed. Importantly, we suggest that the Fe-vacancy ordered phases found in the FeSe-based compounds, which are non-superconducting magnetic Mott insulators, are the parent compounds of the superconductors. Superconductivity can emerge from the parent phases by disordering the Fe vacancy order, often by a simple annealing treatment. Then we review physical properties of the Fe chalcogenides, specifically the optical properties and angle-resolved photoemission spectroscopy (ARPES) results. From the literature, strong evidence points to the existence of orbital modification accompanied by a gap-opening, prior to the structural phase transition, which is closely related to the occurrence of superconductivity. Furthermore, strong lattice to spin coupling are important for the occurrence of superconductivity in FeSe. Therefore, 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 superconducting cuprates.

Keywords: Fe-based superconductor, Fe-vacancy order, orbital ordering

(Some figures may appear in colour only in the online journal)

I. Introduction

The study of Fe-based high temperature superconductors has become one of the most active areas of research in condensed matter physics since 2008. In particular, the rapid rise of Tc’s reported in the FeSe based materials motivates this review. Fe-based superconductivity started with the discovery of superconductivity at 26 K in F-doped LaFeAsO (1111) [1]. Soon after
this discovery several other superconductors with a similar structure were synthesized [2–9], including the FeSe system, which has the simplest crystal structure of all the Fe based compounds. The FeAs or FeSe tetrahedral layers in these materials are the key component of these Fe-based superconductors, and these layers are believed to play similar role to the CuO2 layers in the cuprate superconductors [10, 11]. The FeAs-based superconductors, despite the metallic nature of the parent compounds that is in contrast to the Mott insulators found in the cuprates, may share a common underlying physics as the cuprates from the point of view of crystal structure, phase diagrams, the interplay of antiferromagnetism and superconductivity, and the unconventional nature of the superconductivity in these materials.

In the FeSe based compounds, there is no universally accepted phase diagram up to date, and it is not certain what is the exact parent compound in this system. FeSe compounds crystallize in an anti-PbO type tetragonal lattice (space group P4/mnm) at room temperature [3]. The crystal structure comprises layers of FeSe, which is similar to the FeAs, with Fe atoms arranged in a checkerboard pattern at the same height. The superconducting FeSe undergoes a slight “twist” structural deformation to an orthorhombic lattice (space group Cmmm) at ~105 K [3, 4, 12, 13]. The application of high pressure are known to dramatically increase the critical temperature of FeSe system, and the observation of non-bulk superconductivity at temperature above 30K in FeSe nano-particle seem to suggest the existence of the non-bulk superconductivity at temperature above 30 K, where the Seebeck coefficient changes from positive to negative value [figure 1(a) bottom curve], and an anomalous downturn in resistivity at ~100 K at which the Seebeck coefficient exhibits a maximum (negative) value. It has been shown that the resistive anomaly observed at ~105 K in FeSe is associated with a tetragonal to orthorhombic structural distortion using high-resolution x-ray diffraction experiments at low temperature [3, 4, 13, 19]. Another common feature can be seen in figure 2, which shows the temperature dependence of thermopower for LaFe1−xCoxAsO (1111) [20] and (CaPr)Fe2As2 (122) [18] superconductors. There exists a maximum thermopower in FeSe at ~105 K (the structure distortion temperature), and maximum at ~155 K and ~120 K for LaFe1−xCoxAsO and (CaPr)Fe2As2, respectively. The maxima for the latter two compounds occur at the structure transition temperatures, showing a very common characteristic for these Fe-based superconductors. The anomalous change in the thermopower is due to the change in the electronic state when the system undergoes the structural phase transition. It is noted that such a drastic change only occurs in the superconducting samples, and not in the non-superconducting compounds, as shown in figure 2(a).

II. Physical properties of the Fe-chalcogenide and Fe-pnictide superconductors

There are several common features in FeSe and the FeAs-family if we carefully examine their physical properties. Figure 1(a) displays the temperature dependence of electrical resistivity and Seebeck coefficient (thermopower) of FeSe superconductor, and figure 1(b) is the resistivity curve for an electron-doped (CaPr)Fe2As2 (122) single crystal [18]. It is obvious the similarity of the normal state resistivity in these two compounds. The resistivity shows a broad bump at ~230 K, where the Seebeck coefficient changes from positive to negative value [figure 1(a) bottom curve], and an anomalous downturn in resistivity at ~100 K at which the Seebeck coefficient exhibits a maximum (negative) value. It has been shown that the resistive anomaly observed at ~105 K in FeSe is correlated with a tetragonal to orthorhombic structural distortion using high-resolution x-ray diffraction experiments at low temperature [3, 4, 13, 19]. Another common feature can be seen in figure 2, which shows the temperature dependence of thermopower for LaFe1−xCoxAsO (1111) [20] and (CaPr)Fe2As2 (122) [18] superconductors. There exists a maximum thermopower in FeSe at ~105 K (the structure distortion temperature), and maximum at ~155 K and ~120 K for LaFe1−xCoxAsO and (CaPr)Fe2As2, respectively. The maxima for the latter two compounds occur at the structure transition temperatures, showing a very common characteristic for these Fe-based superconductors. The anomalous change in the thermopower is due to the change in the electronic state when the system undergoes the structural phase transition. It is noted that such a drastic change only occurs in the superconducting samples, and not in the non-superconducting compounds, as shown in figure 2(a).

To understand the electronic and magnetic changes involved in the superconductivity of FeSe, nuclear magnetic resonance studies were done and showed that there are antiferromagnetic fluctuations near the structural distortion temperature [21]. At ambient pressures, the antiferromagnetic fluctuations start to increase above Tc, strongly suggesting superconductivity in FeSe is correlated with magnetic fluctuations.

Figure 3 shows the temperature dependence of the zero field cool (ZFC) and field cool (FC) susceptibilities with the external applied field parallel or perpendicular to (101) directions. It is clear that strong anisotropy exists in β-FeSe1−x, suggesting the charges parallel to (101) may behave more like itinerant electrons, whereas those perpendicular to (101) are more localized [22]. Additionally, the ZFC and FC curves separate at ~230K, suggesting an additional anomaly occurs at this temperature. One possible origin to account for this observation is the presence of orbital modification at this temperature.

Additional evidence for high Tc in chalcogenides was seen with high pressure studies. Among all Fe-based superconductors, FeSe has the most dramatic response to applied pressure, with Tc increasing from TC,ambient = 12 K at ambient pressure to 37 K at 4–6 GPa [23–26]. Note that FeSe undergoes an orthorhombic to hexagonal transition at ~6 GPa, resulting in a drop of Tc at pressures above the transition. To better understand the electronic and magnetic changes involved in the higher Tc, nuclear magnetic resonance studies were done and showed that the antiferromagnetic fluctuations are also enhanced under pressure [21]. This observation further supports the picture that superconductivity in FeSe is correlated with magnetic fluctuations.
In order to gain more insight into the exact stoichiometry and structure of the FeSe superconductors, Chang et al. [16] developed a rapid, solvent-less Reaction under Autogenic Pressure at Elevated Temperature (RAPET) process to synthesize superconducting Fe-Se nanoparticles. The obtained nanoparticles are mainly the superconducting $\beta$-FeSe phase. Detailed magnetization measurements on these nanoparticles show that most of these nano-particles show superconducting transition at ~10 K. Surprisingly, nanoparticles with slightly different chemical compositions become superconducting with an onset transition temperature at ~20 K as shown in figure 4, though a full superconducting volume fraction on these higher $T_C$ samples has not been achieved yet. This method provides one route to better understand the physics behind the observation of the sensitive stoichiometry [3, 13], the dramatic $T_C$ enhancement in FeSe by applying pressure, and the exact phase diagram of the FeSe system [27, 28].

In addition to external pressure, chemical substitutions of alkali metals in between iron selenide layers (A$_x$Fe$_{2-y}$Se$_2$, where A = K, Rb, Cs, Tl) were shown to have relatively high $T_C$ and complex phases [29–31]. Potassium intercalated FeSe superconductor with a $T_C$ of 30 K showed a crystal structure adopting the ThCr$_2$Si$_2$ type tetragonal lattice (space group $I4/mmm$) [32]. Latter studies revealed that the A$_x$Fe$_{2-y}$Se$_2$ system exhibits strong phase separation in superconducting samples and crystals [33–36]. The phase separation of the superconductor forming a network pattern was clearly observed in SEM, TEM, and STM images [37–39]. X-ray diffraction confirmed the structural inhomogeneity in the superconducting sample [40]. It is relevant to notice the presence of a K$_2$Fe$_4$Se$_5$ (245) phase, which exhibits an iron-vacancy order that could be described by a $\sqrt{5} \times \sqrt{5} \times 1$ supercell below an ordering temperature $T_S = 500$–578 K depending on the intercalated metal A [41–44]. A block antiferromagnetic order developed slightly below $T_S$ ($T_N = 471$–559 K) with an ordered magnetic moment ~3.3 $\mu_B$/Fe at 10 K [43, 44].

Post-growth heat treatments could effectively control the superconducting volume fraction [37]. However, the superconducting phase in A$_x$Fe$_{2-y}$Se$_2$ system is controversial. In addition to the stable A$_x$Fe$_2$Se$_3$ non-superconducting matrix in superconducting crystals, a phase with an expanded c-axis [37, 45–47] and a composition close to A$_x$Fe$_2$Se$_2$ [46, 48–51] was assigned to be the superconducting phase with $T_C \sim 29$–32 K. Other attributions include that the superconductivity may originate from either a parent phase of semiconducting antiferromagnetic A$_x$Fe$_2$Se$_4$ with rhombus ($\sqrt{2} \times 2 \sqrt{2}$)
Fe-vacancy order [52], of A₂Fe₇Se₈ parallelogram structure [49], or of A₃Fe₄Se₆ instead of the well known insulating antiferromagnetic A₂Fe₄Se₅ with \( \sqrt{5} \times \sqrt{5} \) Fe-vacancy order.

Under applied external pressure, Svitlyk et al found no structural transition up to ~12 GPa for AₓFe₁₋ₓSe₂ (A = Cs, Rb, K) samples [53]. Figure 5 is the result of the pressure study by Sun et al [54]. They reported that \( T_C \) decreases monotonically with increasing pressure for K₀.₈Fe₁₋ₓSe₂ and Tl₀.₆Rb₀.₄Fe₁.₆₇Se₂ and was completely suppressed at a critical pressure of ~10 GPa [55]. Surprisingly, above 10 GPa, a new superconducting phase with higher \( T_C \) (~48 K) appeared and again was suppressed above 13.2 GPa [54]. Guo et al showed that K₀.₈Fe₁₋ₓSe₂ superconductors transformed from antiferromagnetic state with \( I\bar{4}/m \) symmetry to paramagnetic state with \( I\bar{4}mm \) symmetry in the pressure range of 9.2–10.3 GPa, in which superconductivity tends to disappear [55]. On the other hand, the non-superconducting 245 insulator was shown to transform into an intermediate metallic state and coexisted with the insulating state over a significant range of pressure up to ~10 GPa [56], the same pressure range at which the superconductivity of superconducting samples vanished. The Fe-vacancy order was fully suppressed at 11 GPa in non-superconducting K₀.₈Fe₁₋ₓSe₂ [57], similar to the pressures where the second superconducting phase in K₀.₈Fe₁₋ₓSe₂ samples re-emerged.

Due to the neutrality of FeSe₄ tetrahedral layers, it is more difficult for intercalation in FeSe-based chalcogenides than in FeAs-based pnictides. Ying et al showed that by an ammonothermal method, both alkali and alkaline earth metals were intercalated with \( T_C \) of 30–46 K [58]. It was later shown that the superconducting phases were not AₓFe₂Se₂ but AₓFe₂Se₂(NH₃), and \( T_C \) strongly depended on x while NH₃ had little, if any, effect on superconductivity [57]. Burrard-Lucas et al demonstrated that the reaction of FeSe with a solution of lithium in liquid ammonia yielded a new superconductor Li₃(NH₃)₂(NH₄)₁₋ₓFe₂Se₂ with \( T_C \sim 43 \) K [59].
Figure 6. (a) TEM image of a FeSe nanowire (NW). Inset shows temperature-dependent resistance of the same NW. (b) The SAED pattern of the NW, revealing a tetragonal lattice along the [001] zone-axis direction. Superstructure wave vectors $q_1 = (1/5, 3/5, 0)$ and $q_2 = (3/5, 1/5, 0)$ are indicated by red arrows. Reproduced with permission from [63]. Copyright 2014 PNAS.

Li$_x$(C$_5$H$_5$N)$_2$Fe$_{2−x}$Se$_2$ by Krzton-Maziopa et al with $T_C = 45$ K [60] and LiFeO$_2$Fe$_2$Se$_2$ with $T_C = 43$ K [61] by Lu et al were reported using a similar method. An interesting novel approach has been developed to synthesize materials with higher $T_C$. These methods use reaction at low temperature ~40°C until the discoloration of the alkali metal solution. Post-annealing of intercalated material (Li$_x$(C$_5$H$_5$N)$_2$Fe$_{2−x}$Se$_2$) at elevated temperatures drastically enlarges the c-parameter of the unit cell (~44%) and increases the superconducting shielding fraction to nearly 100%. However, it is noted that samples prepared this way still exhibit two phases.

Following the observation of relatively high $T_C$ in nanoparticle FeSe, Chen and Chang [62, 63] looked into the physical properties of FeSe in different nano-dimensional forms. Figure 6 displays the SEM and high-resolution transmission electron microscope (HRTEM) images of the $\beta$-FeSe nanowires (NWs), showing excellent crystalline tetragonal structure [62]. Most FeSe NWs measured are insulators as shown in the inset of figure 6(a). From energy-dispersive spectroscopy (EDS) results, the NWs are uniform in composition but are surprisingly found to have Fe/Se ratio of 4/5. In addition, the results of HRTEM and X-ray diffraction demonstrate tetragonal crystal structure with lattice constants of $a = 3.728$ Å and $c = 5.363$ Å, which are much smaller than that of $\beta$-FeSe$_x$ (x = 1) bulk sample ($a = 3.7734$ Å and $c = 5.5258$ Å). In addition, the selected area electron diffraction (SAED) pattern of the NW exhibit superstructure wave vectors $q_1 = (1/5, 3/5, 0)$ and $q_2 = (3/5, 1/5, 0)$, surprisingly indicating the presence of $\sqrt{5} \times \sqrt{5}$ Fe-vacancy order as that observed in Fe$_9$Se$_{10}$ ($x = 0.1$). This superstructure has not been observed in $\beta$-Fe$_{1−x}$Se, though it is not necessary to be unique in $\beta$-Fe$_{1−x}$Se. The above results confirm that through unconventional routes PhO-type tetragonal $\beta$-Fe$_{1−x}$Se compound exists in a composition range far beyond the previous reported range [13, 64, 65], to a region with great deficiency of iron (maximum $x = 0.25$ so far). Based on the above observations, Chen et al [63] proposed a temperature-doping phase diagram for the Fe-Se superconducting system, as illustrated in figure 10, which is very similar to the phase diagram of the superconducting La$_2$CuO$_{4+y}$ [66]. The magnetic and insulating/semiconducting phases of $\beta$-Fe$_{1−x}$Se with Fe-vacancy orders act as the parent phase of FeSe superconductor, instead of the
previously argued $\beta$-Fe$_{1+\delta}$Te [27], which shows different magnetic and electronic features compared to $\beta$-Fe$_{1+\delta}$Se [67–70]. The superconducting $\beta$-Fe$_{1.0}$Se with $T_c = 8.5$ K is proposed to be in the overdoped regime as it was demonstrated that it could result from the $\beta$-Fe$_2$Se$_5$ nanosheets by annealing at 700 $^\circ$C in vacuum and then quenching to room temperature.

Wang et al [17] first reported the superconductivity in single unit-cell FeSe films on SrTiO$_3$ with a surprising $T_c$ around 70 K based on STM gap measurements. This discovery of large gap structure in one unit cell FeSe thin film was a real surprise to the community. Two gap structures of 10 and 20 mV in the tunneling spectrum were observed, with the larger gap energy corresponding to a superconducting transition temperature higher than 77 K if the $2\Delta/k_B T_c$ ratio is same as that in bulk sample, ~5.5. Similar gap sizes are seen from ARPES results, and in FeSe monolayer deposited on Nb-doped BaTiO$_3$ [Peng 2014]. The TiO$_2$ termination seems to be critical to observing such features, and the gaps are no longer seen in films thicker than two unit cells. By depositing a protection layer of FeTe on top of FeSe, the films could be removed from the high vacuum system for additional measurements. The one unit cell FeSe shows an onset $T_c$ around 40 K as measured by transport with zero resistance $T_c$ of 23.5 K and an extremely large critical current density $J_C \sim 1.7 \times 10^6$ A cm$^{-2}$ [71].

Although the signature of superconductivity at high temperature was observed by STM and ARPES [72], $T_c$ higher than 50 K has yet to be demonstrated in transport or susceptibility measurement. However, recently Ge et al [73] carried out a novel in situ four-point-probe technique to measure the transport properties of FeSe monolayer with magnetic field up to 11 T without moving the sample out of ultrahigh vacuum chamber. They report resistance-versus-temperature plots extracted from $I$–$V$ measurements of the 4 separate probes.
The data show a resistive transition at temperature higher than 100 K. While these results have yet to be verified, it is certainly intriguing and suggests there is more to come from this exciting system.

Several groups proposed the interface effect of FeSe on SrTiO3 substrate as the origin for the observed high $T_c$ in the monolayer FeSe. The TiO2-terminated surface couples with FeSe layer by dipole-dipole interaction. The one unit cell FeSe behaves like a slightly doped semiconductor with collinear antiferromagnetic (CFA) state [74]. With oxygen vacancies on the top TiO2, the FeSe layer is strongly bonded to the substrate. Then the FeSe layer is significantly electron-doped, which suppresses the CFA states and make it favorable for high-temperature superconductivity [75, 76]. In addition, because of the strong coupling between SrTiO3 substrate and FeSe single layer, the phonon from SrTiO3 substrate could interact with electrons in FeSe layer. Xiang et al pointed out that the SrTiO3 ferroelectric phonons could significantly enhance the energy scale of Cooper pairing and even change the pairing symmetry [77]. More recently ARPES measurements suggest a high energy oxygen optical phonon mode from the SrTiO3 may couple to the FeSe electrons and be responsible for the enhanced gap opening temperature [78].

When examining in more detail the existing literature, the superconductivity of the molecular beam epitaxy (MBE)-grown monolayer FeSe films could be completely destroyed by Se doping [79]. The films were semiconducting where the extra Se dopants were ordered into $\sqrt{5} \times \sqrt{5}$ superstructure at high doping concentration [79]. Such an observation is consistent with the presence of Fe vacancies in a Se-rich growth environment and ordering into superstructures in these ultrathin FeSe films.

### III. Competition among states in Fe chalcogenides

Clearly, the Fe-chalcogenide superconductors exist numerous rich and competing magnetic, nematic, and superconducting phases, as well as other effects, such as orbital ordering and structural phase transition. The large anisotropy of properties found below the structural phase transition experimentally [80–83] suggests the structural phase transition is driven by the electron correlation [84, 85], and the corresponding fluctuations might also be related to the
pairing mechanism of superconductivity [86, 87]. One candidate for the many-body state responsible for the structural phase transition is the electronic nematicity [88–90]. Another candidate as the underlying common mechanism for the structural and antiferromagnetic transitions in the Fe-based superconductors is the orbital ordering [91]. Recently, an orbital selective Mott transition has been suggested to occur in the normal-state phase of iron-selenide superconductors [92–95], where some of the five $d$ orbitals independently undergo metal-to-insulator-like transitions. ARPES results on the single crystal FeSe [96] indicated a strongly orbital dependent renormalization. Maletz et al [96] found comparable renormalization for the $d_{x^2-y^2}$, while the $d_{xy}$ shows a three times larger renormalization.

In this aspect, the $d_{xy}$ band shows the most peculiar behaviour: it is not subject to $k_z$ dispersion, shows a stronger renormalization than the other two bands, and is shifted to higher binding energies, thus not taking part in the formation of the Fermi surface. In section III, we present several experimental results that address the importance of these competing orders.

III-1. Transport and Magnetic Properties

At temperature close to 230 K the magnetic susceptibility of superconducting FeSe exhibits an anomalous behavior that the FC data is different from the ZFC result; and there is a strong anisotropy between external applied field along (1 0 1) and perpendicular to (1 0 1) plane, as shown in figure 3. The temperature where the FC and ZFC data diverges is the same temperature where the Seebeck coefficient changes sign and where the bump in resistivity versus temperature occurs. This feature is most likely related to the orbital modification due to the hybridization of Fe-$d$ and Se-$p$ orbitals [4, 22]. Furthermore, at around 150 K, the rapid increase in Hall coefficient on cooling suggests changes in density of states near the Fermi level, also a result from the orbital modification. This orbital renormalization has been confirmed by other spectroscopic techniques, which we discuss next.

III-2. Optical spectroscopy

Wang et al [97] reported a hierarchy of temperatures $T_C < T_{gap} < T_{met}$ in superconducting Rb$_{1-x}$Fe$_{2-y}$Se$_2$ by THz spectroscopy (where $T_C$ is superconducting critical temperature, $T_{gap}$ is excitation gap open temperature, and $T_{met}$ is metallic response temperature). The temperature dependence of the optical conductivity and dielectric constant exhibits an isosbestic point at 90 K ($T_{met}$), indicating a metal-to-insulator-type, orbital-selective transition. At $T_{gap} = 61$ 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 $T_C < T_{gap} < T_{met}$ tends to imply that the quasiparticle in the $d_{xy}$ band are more strongly correlated.

Quasiparticle dynamics in FeSe$_{1-x}$Te$_x$ has been studied by the transient reflectivity spectroscopy [98–100]. Figure 11(a) shows the optical reflectivity of superconducting FeSe$_{1-x}$ changes on the picosecond timescale after a pulsed laser excitation. It is found that the high-temperature traces can be well described by a single relaxation, whereas an additional sub-picosecond relaxation was observed at low temperatures. The picosecond relaxation is attributed to carrier-phonon (c-p)
thermalization that is ubiquitous at all temperatures and reflects the c-p coupling strength. It was noticed that the measured c-p thermalization rate depends sensitively on the film orientation [98], indicating the anisotropy of the probe transition matrix element as well as different dynamics of electrons with different interplane wavevectors. Also, a systematic time-resolved study on FeSe1-xTe, indicated that the c-p coupling strength can be sufficiently suppressed with increasing Te substitution [98].

From figure 11, an additional sub-picosecond relaxation process emerges below 130–140 K, reflecting the appearance of new electronic structure near the Fermi level. The amplitude of the sub-picosecond relaxation [Inset of figure 11(b)] is found to gradually increase with decreasing T and saturate at ~70 K. This temperature suggests this process arises from the relaxation of gap-like quasiparticles. A crude approximation gives effective gap size ~36 meV. This high-temperature energy gap was observed above the structural phase transition temperature. There are four Raman phonon modes, as shown in figure 12. The spectra of S11 with two sub-components (S12 and S13 below 130 K).

Lattice dynamics of FeSe1-xTe, were studied by transient reflectivity [98–100] and Raman spectroscopies [102–104]. Both revealed manifest phonon softening/hardening near the structural phase transition temperature. There are four Raman active phonon modes belonging to the irreducible representation A1g + B1g + 2Eg, as shown in figure 12. The spectra were fitted with a sum of Lorentzian functions for deriving the resonant frequencies. At high temperature, the low frequency range (70–400 cm⁻¹) shows four Raman phonon modes, labeled as S1 to S4, and two Raman bands at high frequency range (1300–1700 cm⁻¹), labeled as S10, S11 [102]. At 10 K, all phonon modes show a blue shift. However, the S11 mode is best resolved into two modes S12 and S13, as shown in figure 13 and table 1 [102].

Hsiung et al [102] found the frequency of Eg mode saturates below 90 K, which is consistent with the observation of the structural distortion at that temperature. Kumar et al also reported a similar behavior in polycrystalline FeSe1-xTe [103]. They observed a hardening of ~5% in Eg mode below 90 K, and attributed this hardening to spin-phonon coupling. Hsiung et al also observed a hardening below 200 K in the B1g mode. This can be associated with the aforementioned anomalous magnetic susceptibility bump observed at the same temperature in FeSe crystal with magnetic field parallel to (1 0 1) plane. It is believed this result is closely related to the presence of spin-orbital coupling [22]. Moreover, the A1g mode changes by 3 cm⁻¹, while B1g mode undergoes a large change by 14 cm⁻¹ in the whole temperature interval. Such a large frequency shift has been attributed to spin-phonon coupling [104].

The two high-frequency phonon modes (S10 and S11 at 1423 and 1519 cm⁻¹, respectively) were examined in detail by Hsiung et al [102]. S10 has no obvious change as temperature decreases; however, the S11 mode becomes highly asymmetric at temperatures below 130 K, calling for a spectral fitting of S11 with two sub-components (S12 and S13 below 130 K). The partial density of states calculation of FeSe [105] shows that the z/x/y bands are mostly around 300 meV, which corresponds with the Raman mode near 1519 cm⁻¹. The observed three modes S11, S12, and S13 can be well fit to the energy levels of dz²/R and dz²/R, implying that the splitting of dz²/R and dz²/R orbitals occurs around 130 K. Thus, the structural phase

Figure 13. Sample of K₂Fe₄.1Se₅ annealed at different temperatures showing the change from superconducting to non-superconducting and then superconducting state.

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<th>Assignment</th>
<th>E₉(Se)</th>
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<th>S₃(Fe)</th>
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<td>—</td>
<td>1145</td>
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<td>703</td>
<td>1004</td>
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transition can be understood in terms of the splitting of this orbital ordering. It is worthy to mention that the $d$-orbitals splitting temperature corresponds to the temperature of energy gap opening observed by transient optical spectroscopy [98].

Zhang et al performed systematic Raman studies on K$_{0.3}$Fe$_{1.6}$Se$_2$, Tl$_{0.3}$K$_{0.3}$Fe$_{1.6}$Se$_2$, and Tl$_{0.3}$Rb$_{0.3}$Fe$_{1.6}$Se$_2$, together with first-principles calculations [106]. The results show that the abundant phonon modes in A$_x$Fe$_{2-x}$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$_{2-x}$Se$_2$ exhibit a broad asymmetric peak around 1600 cm$^{-1}$, which was identified as a two-magnon process involving optical magnons [107]. 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.

### III-3. Scanning tunneling microscopy (STM)

Most of the STM studies on Fe-chalcogenides focus either on the topography or the pairing symmetry of the superconducting state, with most works so far carried out on FeSeTe crystals or MBE grown samples [108–113]. The topographic and spectroscopic results of FeTe$_{1-x}$Se$_x$ suggested that the samples had nanoscale inhomogeneity. However, no electronic phase separation was seen, suggesting that the systems maintain electronic homogeneity despite the nanoscale chemical phase separation. STM study on the MBE grown samples FeSe on bilayer graphene [113] showed that sample surface with excess Se exhibited a $\sqrt{5} \times \sqrt{5}$ superstructure as that observed in the Fe$_2$Se$_5$ nano-crystals. STM spectroscopy on these samples shows an asymmetric gap with no superconducting features. Annealing the sample at ~420°C returned the surface to square-like lattice with lattice parameters $a$ = $b$ = $a$ = $b$ = $\sqrt{5}$. Typically the Fe vacancy order is insulating/semiconducting and has antiferromagnetic band nature from first principles calculations. The phase without vacancy order is the superconducting one. In the Fe$_2$Se$_5$ samples, for example, the insulating phase had $\sqrt{5} \times \sqrt{5}$ iron vacancy order while the superconducting state existed in KFe$_2$Se$_2$, which was later suggested to be the parent compound for K$_{0.3}$Fe$_{1.6}$Se$_2$ samples [116].

### III-4. Angle resolved photoemission spectroscopy (ARPES)

Moreschini et al [117] reported ARPES investigation on the broken translational symmetry [118] in the Fe$_{1+x}$Te$_{1-x}$Se$_x$ superconductor. They observed that the spectral weight distribution follows the one-Fe periodicity rather than the conventional Brillouin zone (BZ) defined by the two-Fe unit cell. Consequently, they pointed out that the form of the perturbing potential and the symmetries of the Fe-$d$ orbitals lead to differences in the orbital character of the bands even at the nominally equivalent locations in the reciprocal space.

Chen et al [119] identified various phases in K$_x$Fe$_{2-y}$Se$_2$ by ARPES and found that the insulating phase exhibits magnetic and vacancy order. Moreover, the magnetic, vacancy ordered semiconducting phase is considered as the parent phase, in which the superconductivity can be induced by doping. Electron-like Fermi pockets are observed at the corner of the BZ (M), at the zone center, the hole-like bands are absent [120–122]. However, there is a small electron-like ($\pi$ band) feature enclosing at Z ($k_z = \pi$).

Regarding the missing hole pocket, Qian et al reported that the top of the hole band at $\Gamma$ sinks to ~90 meV below Fermi level [120]. Without the hole pockets in the zone center, the idea of Fermi nesting is no longer applicable to the Fe-Chalcogenide superconductors. Qian et al however, also suggested that the Fermi nesting in A$_x$Fe$_{2-x}$Se$_2$ might still happen between the circular electron pockets at the BZ corner through interband scattering [120]. Due to the inequivalent Se 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 result from the same group on (Tl, K)Fe$_{1.78}$Se$_2$ by Wang et al [123] also supports a similar Fermi nesting picture. Of course, Fermi nesting may, or may not be necessary for the superconductivity in the iron-based family, while the pairing symmetry remains $s$-wave [124]. This subject is still an open question to date.

For the superconducting gap in A$_x$Fe$_{2-x}$Se$_2$, a nodeless, isotropic superconducting gap of 10–15 meV is observed at the electron like pockets at the BZ corner [121, 122, 124, 125]. The Fermi surface (FS) sheet in the BZ center is rather tricky. Xu et al reported a small electron pocket at Z presents an isotropic superconducting gap with comparable size (8 meV) [124]. Similar isotropic superconducting gap (~6.2 meV) at the Z-centered electron pocket is observed in (Tl, K)Fe$_{1.78}$Se$_2$ [123]. The (Tl$_{0.58}$Rb$_{0.42}$)Fe$_{1.72}$Se$_2$ is rather a special case; Mou et al [125] observed a small electron like band in the zone center accompanied with an inner small hole band, which barely crosses the Fermi level. The superconducting gaps at both electron pockets at $\Gamma$ and M points are isotropic, with the values of ~15 meV and ~12 meV respectively, while there is no superconducting gap at the hole-like band at the zone center. Whether the superconducting gap should be nodeless is still under debate. ARPES results generally report isotropic behavior of the superconducting gap, while some bulk sensitive experiments indicate gap anisotropy. The complexity of the bulk and surface related behavior combined with the pairing symmetry issue suggests more theoretical and experimental work to be done.

More ARPES studies on FeSe appeared after MBE grown FeSe film on various substrates [17, 67, 74, 101] were successfully prepared. The electronic structure of monolayer FeSe consists only of electron-like band near the BZ corner, and there is no other Fermi surface observed at the center of BZ [67, 98, 123]. Liu et al [67] reported that FeSe monolayer is a strictly 2D system, which avoids all the complications caused by the band dispersion along $k_z$ [126]. However, it is
noted that in the recent ARPES result on FeSe single crystal reported by Maletz et al. [96], the hole pockets in the zone center still exhibit clear three-dimensionality.

Tan et al. carried out a series of ARPES measurements to investigate the thickness dependence of the electronic structure of the FeSe thin film, including the STO substrate after every pre-treatment process [101]. The FSs of the monolayer FeSe film and the multilayer FeSe film were found to be significantly different. The band structure of the multilayer thin films is very similar to that observed in BaFe$_2$As$_2$ in its spin-density-wave (SDW) state. Temperature dependent measurement further shows that such band reconstruction phenomena disappears at high temperature and proves the existence of SDW in multilayer thin films. Tan et al. proposed a phase diagram for FeSe as a function of lattice constant. Based on this picture, the appearance of SDW and the emergence of superconductivity in FeSe thin films are competing effects with the “lattice constant” instead of “doping” as the tuning parameter. This proposal gives a plausible explanation for why very high $T_C$ can be found in the monolayer, but no superconductivity in the multilayer sample.

Another phase diagram was reported at the same time by He et al. regarding the charge carrier concentration tuning by a series of annealing procedures on the monolayer FeSe films [126]. They identified three phases and the corresponding band structure evolution: the initial non-superconducting N phase, the superconducting S phase formed 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 center of BZ. At the BZ corner, the electronic structure of N phase is very similar to the one of AEFe$_2$As$_2$ (AE = Ba or Sr) at its magnetic state, except the bands are pushed below the Fermi level. On the other hand, the S phase shows two degenerate electron pockets at the BZ corner. He et al. [129] also proposed that the carrier concentration of the S phase could be tuned by simple annealing procedure. These results are consistent with the picture proposed by Chen et al. [63] based on their results on FeSe nano-materials.

**IV. Mechanism of superconductivity in Fe-chalcogenide**

For iron-based superconductors, experimentally measurable “order parameters” for structural phase transition include the difference in lattice constant along $x$ and $y$ directions [127], the difference in occupation number in $xz$ and $yz$ orbitals ($n_{\text{nem}} = n_{xz} - n_{yz}$) [83], 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 ($\chi_{\text{nem}} = \chi(q_x,0) - \chi(0,q_y)$) [128]. 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 $C_3$ rotational symmetry [129, 130]. Therefore, typical thermodynamic properties used to characterize symmetry-breaking phases are blind to the orbital and the spin scenarios. 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 [129, 131]. 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 [132].

As mentioned in previous sections, experimental evidences 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 SrTiO$_3$. Xiang et al. [133] proposed that the pairing strength of FeSe is enhanced due to the coupling between the screened ferroelectric phonons of SrTiO$_3$ 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$_x$Fe$_{2−x}$Se$_2$ and FeSe/STO which both have only electron pockets, current theoretical models can be summarized as follows: Yang et al. [134], based on the existing models [86, 127, 135–142], suggested that: (1) Removing the hole pockets frustration in Cooper pairing plus the screening effect in FeSe/STO substrate lead to strong Cooper pairing in A$_x$Fe$_{2−x}$Se$_2$ and FeSe/STO; (2) The static orbital order has large effect on Cooper pairing, which competes with the AFM fluctuation due to the local correlation; (3) The inter-pocket hybridization tends to favor $s$-wave pairing. Hao and Hu [143] argued the importance of the interaction of monolayer FeSe with the substrate and predicted several strong topological phases in the single layer FeSe. Choubey et al. [144] demonstrated that “geometric dimer” impurity states seen in Fe-based superconductors can be understood as consequence of simple defects located on the Fe site due to the hybridization with the pnictogen/chalcogen states. In terms of both symmetry and higher spatial resolution, the result obtained opens a new window on the theoretical analysis of atomic scale phenomena in superconductors.

Finally, it is noted recent preliminary results on the K$_2$FeSe$_2$ compounds prepared using ultra-fine powder [145] show the possibility to change the sample from non-superconducting state, which exhibits strong Fe-vacancy order, to a superconducting state, in which Fe-vacancy order is completely suppressed. Figure 13 displays the magnetic measurements of the same sample treated in different conditions [145]. These results clearly demonstrate that superconductivity depends on the state of the Fe-vacancy. An ordered Fe-vacancy results in the non-superconducting state, whereas disordered Fe-vacancy gives rise to superconducting transition. This observation is consistent with the picture proposed by Emery et al. [146, 147] that phase separation originated from the strong electron correlation can lead to a mesoscopic phase in which a lightly doped locally AF and a more heavily doped region are in close contact, and this type of inhomogeneity may lead to an optimal superconducting transition temperature.
In this paper, we summarize recent studies on the Fe-Chalcogenide superconductors, focusing on FeSe system including the alkaline-metal intercalated FeSe system, Fe-Se nanomaterials and the MBE grown monolayer FeSe on SrTiO$_3$ thin film. FeSe is shown to be a material with strong correlations, and it is sensitive to the change of the crystal modifications. In this regard, it is highly unusual that the Fe vacancy order to disorder transition is associated with the presence of superconductivity. These results strongly suggest the Fe-vacancy order to disorder transition is completely suppressed after annealing.

The relevance of Fe-vacancy to superconductivity can be used to explain the observation of $\sqrt{5} \times \sqrt{5}$ superstructure in MBE-grown monolayer Se-rich FeSe films, in which superconductivity is completely destroyed by Se doping [79]. Similar results were also reported in a series of annealed monolayer FeSe films [126]. In these films, the authors identified three phases and the corresponding band structure evolution: the initial non-superconducting N phase, the superconducting S phase formed at the final annealing stage and the intermediate phase as a mixture of N phase and S phase. These results are consistent with the picture proposed by Chen et al [63] based on their findings of different Fe-vacancy states in FeSe nano-materials.

Finally, literature provides strong evidences to the existence of orbital modification accompanied by gap-opening, prior to the structural phase transition, which is closely related to the occurrence of superconductivity. Furthermore, strong lattice to spin coupling are important for the occurrence of superconductivity in FeSe. Therefore, it is believed that the iron-selenium and related compounds will provide essential information to understand the origin of superconductivity in the iron-based superconductors, and possibly to the superconducting cuprates.

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