**Colloquium: The unexpected properties of alkali metal iron selenide superconductors**

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The iron-based superconductors that contain FeAs layers as the fundamental building block in the crystal structures have been rationalized in the past using ideas based on the Fermi surface nesting of hole and electron pockets when in the presence of weak Hubbard $U$ interactions. This approach seemed appropriate considering the small values of the magnetic moments in the parent compounds and the clear evidence based on photoemission experiments of the required electron and hole pockets. However, recent results in the context of alkali metal iron selenides, with generic chemical composition $A_xFe_2-ySe_2$ ($A =$ alkali metal element), have challenged those previous ideas since at particular compositions $y$ the low-temperature ground states are insulating and display antiferromagnetic order with large iron magnetic moments. Moreover, angle-resolved photoemission studies have revealed the absence of hole pockets at the Fermi level in these materials. The present status of this exciting area of research, with the potential to alter conceptually our understanding of the iron-based superconductors, is here reviewed, covering both experimental and theoretical investigations. Other recent related developments are also briefly reviewed, such as the study of selenide two-leg ladders and the discovery of superconductivity in a single layer of FeSe. The conceptual issues considered established for the alkali metal iron selenides, as well as several issues that still require further work, are discussed.

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**I. INTRODUCTION**

One of the most active areas of research in condensed matter physics at present is the study of the high-critical-temperature ($T_c$) superconductors based on iron. This field started with the seminal discovery of superconductivity at 26 K in F-doped LaFeAsO (Kamihara *et al.*, 2008). Several other superconductors with a similar structure have been synthesized since 2008 [for a review, see Johnston (2010) and Stewart (2011)]. They all have FeAs or FeSe layers, which are widely believed to be the key component of these iron-based superconductors, just as the CuO$_2$ layers are the crucial ingredients of the famous high-$T_c$ cuprates (Dagotto, 1994; Scalapino, 1995). The many analogies between the iron-based superconductors and the cuprates lie not only in the quasi-two-dimensional characteristics of the active layers, but also in the proximity to magnetically ordered states which in many theoretical approaches are believed to induce superconductivity via unconventional pairing mechanisms that do not rely on phonons. However, at least for the case of the iron superconductors based on As, the parent magnetic compounds are metallic, as opposed to the Mott insulators found in the cuprates, establishing an important difference between cuprates and pnictides.
II. EARLY DEVELOPMENTS

The FeAs tetrahedron is the basic building block of the FeAs layers. Materials such as LaFeAsO belong to the “1111” family, with a record $T_c$ of 55 K for SmFeAsO (Ren et al., 2008). Subsequent efforts unveiled superconductivity also in the doped versions of “122” compounds such as BaFe$_2$As$_2$, “111” compounds such as LiFeAs, and others (Johnston, 2010; Paglione and Greene, 2010; Hirschfeld, Korshunov, and Mazin, 2011; Stewart, 2011; Wang and Lee, 2011).

It is important to remark that there are structurally related materials, known as the “11” family, that display equally interesting properties. A typical example is FeSe, which also superconducts, although at a lower $T_c$ of 8 K (Hsu et al., 2008). FeSe has a simpler structure than the pnictides since there are no atoms in between the FeSe layers. Locally, the iron cations are tetrahedrally coordinated to Se, as it occurs in FeAs$_4$. The critical temperature can be increased dramatically by Te substitution or even more by pressure up to 37 K (Fang et al., 2008; Yeh et al., 2008; Margadonna et al., 2009). The normal state of Fe(Se,Te) is electronically more correlated than that of iron pnictides (Tamai et al., 2010). The study of iron superconductors based on Se (the iron selenides) is less advanced than similar studies in the case of As (the iron pnictides), and it is precisely the goal of this Colloquium to focus on the most recent developments in the area often referred to as the “alkaline iron selenides,” with typically alkali metal elements intercalated in between the FeSe layers. Since many results described in this review use K to intercalate, the compounds in focus here will be generically called “alkali metal iron selenides” to avoid confusion with the “alkaline earth metals” (Be, Mg, Ca, Sr, Ba, and Ra). However, one should be aware that there are exceptions, such as the use of Tl in some layered compounds, Ba in the ladders treated in Sec. VIII, and more recently other alkaline earth metals to further increase $T_c$ as described in Sec. IX. Also the more general term chalcogenides will not be used here since our focus is exclusively on compounds with FeSe layers, not with FeTe layers. At present, the field of alkali metal iron selenides is receiving considerable attention not only because the $T_c$s are now comparable to those of the iron pnictides, but also because some of these selenides are magnetic insulators, potentially bringing closer together the fields of the iron- and copper-based superconductors.

One of the motivations for the use of alkali elements to separate the FeSe layers is that the $T_c$ of the iron-based superconductors appears to be regulated by the “anion height,” i.e., the height of the anion above the iron-square planes (Mizuguchi et al., 2010; Garbarino et al., 2011). Alternatively, it has been proposed that the closer Fe(anion)$_4$ is to the ideal tetrahedron, the higher $T_c$ becomes (Qiu et al., 2008). Then via chemical substitutions or intercalations $T_c$ could be further enhanced since that process can possibly optimize the local structure.

In this Colloquium, this active field of alkali metal iron selenides will be reviewed. Before explaining the organization of this article, it is important to remark that it is not a review of the full field of iron-based superconductors, which would be a formidable task. Instead the focus is on the recent developments for compounds with chemical formulas $A_i$Fe$_{2-y}$Se$_2$ ($A = $ alkali element) that not only show superconductivity at temperatures comparable to those of the pnictides, but also present insulating and magnetic properties at several compositions, establishing a closer link to the cuprates. In fact, many studies reviewed here suggest that a proper description of $A_i$Fe$_{2-y}$Se$_2$ requires an intermediate value of the Hubbard repulsion $U$ in units of the carriers’ bandwidth. This degree of electronic correlation is needed to explain, for instance, the large magnetic moment per iron atom observed in these novel compounds. Last but not least, the notorious absence of Fermi surface (FS) hole pockets in these materials, as also reviewed here, prevents the applicability of the ideas widely discussed for the iron pnictides that rely on the FS nesting between electron and hole pockets. Since there are no hole pockets, an alternative starting point is needed. It is fair to say that pnictides and selenides may be in different classes of magnetic and superconducting materials, even if the pairing arises in both cases from magnetic fluctuations. For instance, the former could be based on itinerant spin density wave states, and the latter on local moments. However, mere simplicity also suggests that pnictides and selenides may share a unique mechanism to generate their magnetic and superconducting states. If this is the case, then learning about the physics of the $A_i$Fe$_{2-y}$Se$_2$ compounds may fundamentally alter the conceptual framework used for the entire field of research centered on the iron-based superconductors.

The organization of this Colloquium is as follows. In Sec. II, the early history of the alkali metal iron selenides is provided, including the ordered states of the iron vacancies. Section III addresses the existence of phase separation into superconducting and magnetic regions, and also the much debated issue of which states should be considered the parent states for superconductivity. Results obtained using a variety of experimental techniques are discussed in Sec. IV. In Sec. V, investigations using angle-resolved photoemission are reviewed, with emphasis on the two most important results: absence of hole pockets at the FS and isotropic superconducting gaps. Section VI contains the neutron scattering results, showing the exotic magnetic states in the presence of iron vacancies, particularly the block antiferromagnetic state. Theoretical calculations, using both first-principles and model Hamiltonian approaches, are given in Sec. VII. The experimentally observed phases, as well as a variety of competing states, are discussed from the theory perspective. Section VIII describes recent efforts focused on two-leg ladder selenides, which display several common aspects with the layered iron selenides. Finally, in Sec. IX several closely related topics are discussed, including the discovery of superconductivity in a single layer of FeSe. Because of length constraints some topics that would make this review self-contained, such as the crystallography of the materials of focus here, cannot be included. However, recent reviews (Johnston, 2010; Stewart, 2011) can be consulted to compensate for this missing information. A recent brief review about the alkali metal iron selenides (Mou, Zhao, and Zhou, 2011) can also be consulted for a broader perspective on this topic.

II. EARLY DEVELOPMENTS

The report that started the field of alkali metal iron selenides was published by Guo et al. (2010). In this publication,
results were presented for polycrystalline samples of K$_{0.8}$Fe$_2$Se$_2$ (nominal composition).

The crystal structure is shown in Fig. 1. It contains layers of an alkali metal element, such as K, separating the FeSe layers. As in the 122 pnictide structures based on, e.g., Ba, the FeSe layers are the “conducting layers” while the K$^+$ ions provide charge carriers. The K layers increase the distance between the FeSe layers, magnifying the reduced dimensionality characteristics of the material.

The resistance versus temperature is shown in Fig. 2. Upon cooling, insulating behavior is observed first (a resistance that grows with decreasing temperature), followed by a broad peak at 105 K where a metallic like region starts. At $\sim 30$ K, the resistance abruptly drops to zero, leading to a superconducting (SC) state. To explain the high value of the critical temperature as compared to the $T_c$ of FeSe (8 K) or Te-doped FeSe (15.2 K), Guo et al. (2010) argued that the Se-Fe-Se bond angle is close to the ideal FeSe$_4$ tetrahedral shape and also the interlayer distance is large compared to that of FeSe.

Subsequent work employing single crystals reported that the broad resistivity peak of K$_{0.8}$Fe$_2$Se$_2$ is actually located above 200 K, i.e., at a higher temperature than in polycrystals, and its SC critical temperature is 33 K (Mizuguchi et al., 2011). Related efforts showed that the hump in the normal-state resistivity was related to the iron-vacancy ordering process (D. M. Wang et al., 2011) that was shown to exist in parts of the sample, as discussed in Sec. III devoted to phase separation (i.e., some of the early samples were later shown to contain two phases, at either the nanoscopic or the microscopic length-scale levels). There was no correlation between the hump and the SC critical temperatures.

Similar properties were observed in other compounds. For instance, Krzton-Maziopa, Shermadini et al. (2011) reported a $T_c = 27$ K for C$_{80.8}$(FeSe$_{0.98}$)$_2$. Superconductivity at $T_c = 32$ K was also found in Rb$_{0.88}$Fe$_{1.81}$Se$_2$ (A. F. Wang et al., 2011). Other studies using K and Cs as alkali elements were reported by Ying et al. (2011), superconductivity at 32 K was reported for (Tl, Rb)Fe$_2$Se$_2$ by Hangdong Wang et al. (2011), and using a mixture (Tl,K) by M. H. Fang et al. (2011). The latter also contains an interesting phase diagram varying the amount of iron in (Tl,K)Fe$_2$Se$_2$, constructed from the temperature dependence of the resistivity. This phase diagram displays the evolution from insulating to SC phases in the (Tl,K)Fe$_2$Se$_2$ system, resembling results in the cuprates. From anomalies in magnetic susceptibilities, several of these efforts also reported the presence of antiferromagnetic (AFM) order in regimes that are insulating at all temperatures (M. H. Fang et al., 2011; Bao et al., 2013). Based on previous literature on materials such as TlFe$_2$S$_2$, M. H. Fang et al. (2011) concluded that there must be regularly arranged iron vacancies when Se replaces S, and also a concomitant AFM order. The expected iron-vacancy order is shown schematically in Fig. 3 for the cases of $x = 1.5$, 1.6, and 2.0 in the chemical formula (Tl,K)Fe$_2$Se$_2$ (M. H. Fang et al., 2011). In this context, Bao et al. (2013) argued that decorating the lattice with iron vacancies can produce the SC state.

![FIG. 1](color online). Crystal structure of AFe$_x$Se$_2$. All the other compounds described here have a similar structure. A is an alkali metal element (K in the figure). If $x < 0.5$, iron vacancies are present. From Bao et al., 2013.

![FIG. 2](color online). Temperature dependence of the electrical resistance of polycrystalline K$_{0.8}$Fe$_2$Se$_2$. The dominant features include the SC transition temperature at $\sim 30$ K, with the inset containing better-resolution details of that transition. The peak slightly above 100 K, later found using single crystals at higher temperatures (Mizuguchi et al., 2011), is caused by the iron-vacancy ordering (D. M. Wang et al., 2011). The coexistence of features related to iron vacancies and superconductivity was later explained based on phase separation (see Sec. III). From Guo et al., 2010.

![FIG. 3](color online). (Left panel) Iron-vacancy order corresponding to AFe$_{1.5}$Se$_2$. The solid circles are iron atoms. The open circles are vacancies. Each iron atom has either two or three iron neighbors. This type of order is called the $2 \times 4$ iron-vacancy order since along the horizontal (vertical) axis the vacancies are separated by 2 (4) Fe-Fe lattice spacings. (Center panel) The case of AFe$_{1.8}$Se$_2$ with its $\sqrt{5} \times \sqrt{5}$ iron-vacancy distribution. All iron atoms have three iron neighbors. The label refers to the distance between nearest-neighbor vacancies which is $\sqrt{5}$ in two perpendicular directions, in units of the Fe-Fe lattice spacing. (Right panel) State with no iron vacancies, corresponding to AFe$_2$Se$_2$, where $A = (Tl,K)$, believed to be of relevance for the SC state. From M. H. Fang et al., 2011.
with vacancies offers a new route to high-$T_c$ superconductivity by modifying the FS and altering the balance between competing tendencies. Using x-ray diffraction and single crystals, the iron-vacancy arrangement sketched in the central panel of Fig. 3, i.e., the so-called $\sqrt{5} \times \sqrt{5}$ arrangement, was shown to be present in SC samples by Zavalij et al. (2011) (and those samples have phase separation; see Sec. III). Transmission electron microscopy results also provided evidence of this type of vacancy order (Z. Wang et al., 2011).

All these early discoveries established the field of alkali metal iron selenides, and the subsequent work reviewed here provided a microscopic perspective on the properties of these compounds.

III. TENDENCIES TO PHASE SEPARATION

Recent investigations showed that the often puzzling properties of several alkali metal iron selenides can be understood by realizing that phase separation occurs in these compounds. As happens in manganites and cuprates, in the materials reviewed here several length scales are involved in the phase coexistence. The two competing (or maybe cooperating) states are the SC and magnetic states, the latter with ordered iron vacancies. The coexistence of free-of-vacancies magnetism and superconductivity was also reported in pnictides (Julien et al., 2009; Johnston, 2010). Next a summary of results on phase separation in selenides is presented, ordered by technique but also approximately chronologically.

A. Muon-spin rotation

The microscopic coexistence of magnetism and superconductivity was reported via muon-spin spectroscopy investigations of Cs$_{0.8}$FeSe$_{0.98}$ (Shermadini et al., 2011) and $A$Fe$_2y$Se$_2$ ($A$ = Rb, K) (Shermadini et al., 2012). Additional evidence for phase separation was provided by simultaneous angle-resolved photoemission spectroscopy (ARPES) and muon-spin rotation ($\mu$SR) analysis of Rb$_{0.77}$Fe$_{1.61}$Se$_2$ with $T_c$ = 32.6 K (Borisenko et al., 2012). This study showed that the results can be rationalized via a macroscopic separation into metallic ($\sim$12%) and insulating ($\sim$88%) phases. The metallic component appears associated with RbFe$_2$Se$_2$, and Borisenko et al. (2012) believed that the insulating component is a competing order, not relevant for superconductivity. Instead, they argued that van Hove singularities are the key ingredient for superconductivity. On the other hand, studies of the resistivity and magnetic susceptibility of A$_0.3$Fe$_2y$Se$_2$ are also interpreted as coexisting superconductivity and antiferromagnetism (Liu et al., 2011) but not simply competing with each other. While phase separation between magnetic and SC states is experimentally proven, the implications are still under debate. If antiferromagnetism and superconductivity coexist microscopically, or at least are so close in space that they can influence one another, does AFM induce or suppress SC?

B. Raman scattering, transmission electron microscopy, and x rays

Phase separation with mutual exclusion between insulating and SC states, at the micrometer scale, was also proposed from the analysis of Raman scattering experiments on A$_{0.17}$Fe$_{1.6}$Se$_2$, where the intensity of a two-magnon peak decreases sharply upon entering the SC phase (Zhang, Liu et al., 2012; Zhang, Xiao et al., 2012). Transmission electron microscopy (TEM) on K$_{0.8}$Fe$_2$Se$_2$ and KFe$_2$Se$_2$ by Z. Wang et al. (2011) also provided evidence of nanoscale phase separation (i.e., not a coexistence of the two states but physical separation), including the formation of stripe patterns at the micrometer scale together with nanoscale phase coexistence between magnetic and SC phases (Z. W. Wang et al., 2012). Percolative scenarios involving weakly coupled SC islands were also discussed by Shen et al. (2011) and Z. W. Wang et al. (2012).

X-ray absorption and emission spectroscopy applied to K$_{0.9}$Fe$_{1.6}$Se$_2$ also reported coexisting electronic phases and found superconductivity to have glassy (granular) characteristics (Simonelli et al., 2012). Using scanning nanofocus x-ray diffraction, studies of the same compound focusing down to a size of 300 nm collected thousands of diffraction patterns that allowed for the construction of a real-space imaging of the $k$space results obtained by diffraction. These results provided explicit images of the intrinsic phase separation below 520 K, and they contain an expanded lattice, compatible with a magnetic state in the presence of iron vacancies, and a compressed lattice with nonmagnetic characteristics (A. Ricci et al., 2011) (see Fig. 4). Micrometer-sized regions with percolating magnetic or nonmagnetic domains form a multiscale complex network of the two phases.

Note that, for phase separation at large length scales, x-ray diffraction techniques are sufficient to observe two structurally distinct phases (Bosak et al., 2011; X. G. Luo et al., 2011; Lazarević et al., 2012; Y. Liu et al., 2012; Pomjakushin et al., 2012). This shows that the SC phase is a real bulk phase rather than an interfacial property. It is for shorter lengths scales that more microscopic techniques are needed to clarify the interplay between the two phases.

C. ARPES and phase separation

Using ARPES and high-resolution TEM applied to K$_{0.9}$Fe$_{2-y}$Se$_2$, evidence was provided for a mesoscopic phase separation at the scale of several nanometers between the SC and semiconducting phases and the AFM insulating phases (F. Chen et al., 2011). One of the insulators has the $\sqrt{5} \times \sqrt{5}$ iron-vacancy pattern. A sketch of these results is shown in

FIG. 4 (color online). Spatial distribution of the ratio of the compressed and the expanded phases in a region of size $22 \times 55 \ \mu m^2$ of a K$_{0.8}$Fe$_{1.6}$Se$_2$ crystal. Illustration of several length scales involved in the phase-separated state, resembling those found in cuprates and manganites. From A. Ricci et al., 2011.
FIG. 5 (color online). Cartoon of the phase separation in superconducting K$_x$Fe$_{2-x}$Se$_2$, obtained via photoemission and TEM techniques. The upper insets are the photoemission signals for the two regions: the left region corresponds to the $\sqrt{5} \times \sqrt{5}$ vacancy order, while the right region is the density of states of a superconductor. From F. Chen et al., 2011.

Fig. 5. F. Chen et al. (2011) remarked that the insulators are mesoscopically separated from the SC or semiconducting phases, and they believe that the semiconducting phase (free of magnetic and vacancy order) is the parent compound that upon electron doping leads to superconductivity.

D. Scanning tunneling microscopy and neutron diffraction

Using thin films of K$_x$Fe$_{2-x}$Se$_2$ grown using molecular-beam epitaxy techniques, scanning tunneling microscopy (STM) results were interpreted as caused by the samples containing two phases: an insulating one with the $\sqrt{5} \times \sqrt{5}$ iron vacancies and a SC state with the composition KFe$_2$Se$_2$ free of vacancies (Li et al., 2012a). The densities of states (DOS) of the two phases measured via scanning tunneling spectroscopy (STS) are in Fig. 6. It is interesting that the SC phase is associated with the 122 rather than the 245 composition that contains the ordered iron vacancies, which naively was expected to be the parent compound.

In related STS studies of K$_{0.73}$Fe$_{1.67}$Se$_2$ by Cai et al. (2012), a SC gap was found microscopically coexisting with a so-called $\sqrt{2} \times \sqrt{2}$ charge-density modulation. The iron-vacancy order was actually not observed, and Cai et al. (2012) argued that it is not a necessary ingredient for superconductivity. In fact, their results in the region of the charge modulation are compatible with a ferromagnetic block state in the absence of the $\sqrt{5} \times \sqrt{5}$ iron-vacancy order, as predicted by Li, Dong et al. (2012); see Fig. 17. Other STM studies of K$_{x}$Fe$_{2-x}$Se$_{2-x}$ (Li et al., 2012b) concluded that KFe$_2$Se$_2$ is the parent compound of superconductivity (with this state being induced by Se vacancies or via the interaction with the nearby 245 regions perhaps by modifying the doping concentration). This STM study concluded that the phase with the $\sqrt{2} \times \sqrt{2}$ charge ordering is not superconducting, since the density-of-states dip still has a nonzero value at the minimum and the results are temperature independent from 0.4 to 4.2 K, and for superconductivity to arise a contact with the $\sqrt{5} \times \sqrt{5}$ is needed. The length scale unveiled in this effort is mesoscopic (Li et al., 2012b). The 122 phase charge modulation is compatible with a block spin order without iron vacancies (Li, Dong et al. (2012)), since the distance between equivalent ferromagnetic blocks (with spins pointing in the same direction) is $2\sqrt{2}$ times the Fe-Se distance. Li et al. (2012b) also reported an exotic $\sqrt{2} \times \sqrt{5}$ charge ordering superstructure [see Fig. S3 of Li et al. (2012b)].

Recently another possibility was presented. Using neutron diffraction techniques for K$_{x}$Fe$_{2-x}$Se$_2$, Zhao et al. (2012) proposed the state in Fig. 3 (left panel), with a rhombus-type iron-vacancy order, as the parent compound of the SC state. In this state the iron spins have parallel (antiparallel) orientations along the direction where the iron vacancies are separated by four (two) lattice spacings. This state has ideal composition KFe$_{1.5}$Se$_2$, iron magnetic moments 2.8$\mu_B$, and an AFM band-semiconductor character, as in the first-principles calculations by Yan et al. (2011b). FS nesting is not applicable in this state and the large moments suggest that correlation effects cannot be neglected. The semiconducting nature of this state is also compatible with ARPES experiments (F. Chen et al., 2011) that also proposed a semiconductor as the parent compound.

E. Optical spectroscopy

Optical spectroscopy studies of K$_{0.75}$Fe$_{1.75}$Se$_2$ by Yuan et al. (2012) revealed a sharp reflectance edge below $T_c$, at a frequency much below the SC gap, on an incoherent electronic background. This edge was interpreted as caused by a Josephson-coupling plasmon in the SC condensate. This study provided evidence for nanoscale phase separation between superconductivity and magnetism. The coupling between the two states can be understood if it occurs at the nanometer scale, since at this scale there is a large fraction of phase boundary in the sample, while at a longer length scale a very weak coupling between the states exists (Yuan et al., 2012). Infrared spectroscopy studies of K$_{0.83}$Fe$_{1.53}$Se$_2$ were also presented (Z. G. Chen et al., 2011), revealing abundant phonon modes that could be explained by the iron-vacancy ordering. Studies of the complex dielectric function of Rb$_2$Fe$_4$Se$_5$ (Charnukha et al., 2012b) also concluded that
there are separated SC and magnetic regions in this compound. Investigations via optical microscopy and muon-spin rotation reported an intriguing self-organization of this phase-separated state into a quasiregular heterostructure (Charnukha et al., 2012a).

Other optical studies (Homes et al., 2012a) initially characterized $K_{0.8}Fe_{2-y}Se_2$ as a phase-separated Josephson phase, with inhomogeneous characteristics. However, more recent studies (Homes et al., 2012b) distinguished between the volume-average measurements of the original report (Homes et al., 2012a) and the results arising from an effective-medium analysis (EMA) to determine which fraction of the material is actually metallic or superconducting. The volume-average case has a normal resistance too high for coherent transport, locating this case in the Josephson-coupling region, as shown in Fig. 7 which contains a scaling plot previously used to discuss cuprates and other iron-based superconductors. However, the material is not homogeneous and the EMA shows that only 10% is metallic or SC. Homes et al. (2012b) then concluded that if a sample could be constructed composed of just this phase, then it would be a coherent metal, falling closer to the other iron-based materials as shown also in Fig. 7. This is in agreement with the conclusions by C. N. Wang et al. (2012) using muon-spin rotation and infrared spectroscopy. The use of the EMA to rationalize results in phase-separated systems was also suggested by Charnukha et al. (2012a, 2012b).

In summary, the discussion regarding the characteristics of the parent compound of the superconducting $KFe_2Se_2$ state is still very fluid, defining an intriguing and exciting area of research of much importance. Several candidate states have been proposed for the parent composition of the SC state.

IV. RESULTS USING NUCLEAR MAGNETIC RESONANCE, TEM, MÖSSBAUER, AND SPECIFIC HEAT TECHNIQUES

$^{77}$Se nuclear magnetic resonance (NMR) studies and Knight-shift studies of $K_{0.32}Fe_{1.6}Se_2$ and $K_{0.68}Fe_{1.6}Se_2$ below $T_c$ have demonstrated that the superconductivity is in the spin-singlet channel, although without coherence peaks in the nuclear spin-lattice relaxation rate below $T_c$, suggesting that the state is probably nonconventional (Weiqiang Yu et al., 2011). These results are similar to those known from the pnictides. Moreover, above $T_c$, the temperature dependence of $1/T_1$ indicates that the system behaves as a Fermi liquid, suggesting the absence of strong low-energy spin fluctuations at the Se site (Weiqiang Yu et al., 2011). Other $^{77}$Se NMR measurements of $K_{0.65}Fe_{1.41}Se_2$ (Torchetti et al., 2011) and $^{77}$Se and $^{87}$Rb NMR studies of $T_{1/2}Fe_{1.63}Se_2$ (Male et al., 2011) arrived at similar conclusions. Torchetti et al. (2011) also suggested that the K vacancies may have a superstructure and the symmetry of the Se sites is lower than the tetragonal fourfold symmetry of the average structure. In addition, transmission electron microscopy experiments on $K_{1.74}Fe_{1.6}Se_2$ suggested the ordering of the K ions in the $a$-$b$ plane, and also addressed the resistivity hump anomaly in the iron-vacancy ordering (Li et al., 2011; Song et al., 2011). Using $^{77}$Se NMR, the absence of strong AFM spin correlations was also reported for superconducting $K_{0.8}Fe_{2}Se_2$, with a nonexponential behavior in the nuclear spin-lattice relaxation rate $1/T_1$ which does not indicate a single isotropic gap (Kotegawa et al., 2011, 2012). $^{77}$Se and $^{87}$Rb NMR studies of $Rb_{0.74}Fe_{1.6}Se_2$ also reported two coexisting phases (Texier et al., 2012), and the SC regions do not have iron vacancies or magnetic order.

Mössbauer spectroscopy studies of superconducting $Rb_{0.8}Fe_{1.8}Se_2$ also report the presence of 88% magnetic and 12% nonmagnetic Fe$^{2+}$ regions (Ksenofontov et al., 2011), compatible with previously discussed reports. The magnetic properties of superconducting $K_{0.8}Fe_{1.76}Se_2$ were also studied using Mössbauer spectroscopy (Ryan et al., 2011). Magnetic order involving large iron magnetic moments is observed from well below the $T_c \sim$ 30 K to the Neél temperature $T_N = 532$ K.

Via the study of the low-temperature specific heat, nodeless superconductivity and strong-coupling characteristics were reported by Zeng et al. (2011) for single crystals of $K_{1.74}Fe_{1.6}Se_2$, compatible with results found using ARPES techniques. On the other hand, thermal transport results for superconducting $K_{0.65}Fe_{1.41}Se_2$ were interpreted as corresponding to a weakly or intermediate correlated superconductor by Wang, Lei, and Petrović (2011a, 2011b). A numerical study of the thermal conductivity and specific heat angle-resolved oscillations in a magnetic field for $A_1Fe_2Se_2$ superconductors addressed the gap structure and presence of nodes (Das et al., 2012), concluding that care must be taken in the interpretation of results using these techniques since even for isotropic pairing over an anisotropic FS, thermodynamic quantities can exhibit oscillatory behavior.

V. ARPES

Several photoemission experiments have been carried out for the alkali metal iron selenides. Their common result is the
the magnetic susceptibility to be enhanced, and nesting involving only electron pockets may not be sufficient to address the magnetic states. The same group also studied Tl$_{0.63}$K$_{0.37}$Fe$_{1.78}$Se$_2$ arriving at similar conclusions with regard to the electron pockets at ($\pi$,0) and (0,$\pi$) (iron-sublattice convention), but in addition they also observed an unexpected electronlike pocket at $\Gamma$. This electron pocket has a SC gap of value comparable to that at the zone boundary pockets (X.-P. Wang et al., 2011).

Studies of (Tl$_{0.58}$Rb$_{0.42}$)Fe$_{1.72}$Se$_2$ using ARPES also led to similar conclusions (Mou et al., 2011), including the presence of small electronlike FS sheets around the $\Gamma$ point (see Fig. 10) and a nearly isotropic SC gap of value $\sim$12 meV at the $M$ points. While the SC gap at the larger $\Gamma$-point sheet is also nearly isotropic, for the inner small $\Gamma$-sheet pocket there is no SC gap. The same group also reported ARPES studies for K$_{0.65}$Fe$_{1.79}$Se$_2$ ($T_c$ = 32 K) and (Tl$_{0.45}$K$_{0.55}$)Fe$_{1.83}$Se$_2$ ($T_c$ = 28 K) (Lin Zhao et al., 2011). These results establish a universal FS topology and SC gap in the A$_x$Fe$_{2-y}$Se$_2$ materials: there are no FS holelike pockets at $\Gamma$ (thus there is no FS nesting as in some pnictides) and the SC gaps at the FS electron pockets are isotropic (nodeless). Recent ARPES studies of K$_x$Fe$_{2-y}$Se$_2$ focused on the SC gap of the small electron Fermi pocket around the Z point. An isotropic SC gap $\sim$8 meV was reported in that pocket (see Fig. 11), and Xu et al. (2012) concluded that the symmetry of the order parameter must be $s$ wave since a $d$ wave should
have nodes in that Z-centered pocket. Similar ARPES results were independently presented for Ti$_{0.63}$K$_{0.37}$Fe$_{1.78}$Se$_2$ (X.-P. Wang et al., 2012). In this case the Z-centered electron FS has an isotropic SC gap ~6.2 meV. Both efforts conclude that $d$-wave superconductivity appears to be ruled out in these materials. However, the doping effects of Co on a pnictide (not a selenide) such as KFe$_2$As$_2$ have been interpreted via a $d$-wave SC state (A.F. Wang et al., 2012), since the critical temperature rapidly decreases with increasing Co concentration, similarly as in cuprates. Thermal conductivity also suggests $d$-wave symmetry for the same material (Reid et al., 2012).

Thus, if some pnictides appear to be $d$-wave superconductors, the symmetry of the SC state in the alkali metal iron selenides of focus here still needs to be further investigated.

How do all these ARPES results compare with similar pnictide investigations? The ARPES pnictides effort is large and will not be described here, but interested readers can consult Richard et al. (2011) for a recent review. In fact, there are many similarities between pnictides and selenides if it is simply accepted that the chemical potential for the case of Se is above the entire hole pocket band located at $\Gamma$. Thus, a transition occurs from a combination of hole and electron pockets for the pnictides to only electron pockets for the selenides.

These results are important for the FS nesting theories that may work for pnictides but not for selenides due to the absence of hole pockets. Thus, pairing mechanisms alternative to those based on weak-coupling spin-density-wave scenarios are needed for a proper description of the iron-based superconductors, such as purely electronic theories where the Hubbard coupling $U$ is not small or theories where the lattice is involved in the Cooper-pair formation. Recent Lanczos investigations of the two-orbital Hubbard model in a broad range of Hubbard $U$ and Hund $J_H$ couplings and electronic density $n \sim 2$ (two electrons per Fe) concluded that $s$-wave pairing induced by magnetism is found not only at weak and intermediate couplings, but also at larger couplings where the parent compound becomes an insulator (Nicholson et al., 2011) and there is no simple visual representation of the paired state based on a metallic FS. Then, while FS nesting may not be needed in the iron superconductors (Dai, Hu, and Dagotto, 2012) the pairing symmetry may still be $s$ wave.

Returning to ARPES, the widely reported isotropic nature of the nodeless SC gaps is similar in both pnictides and selenides. However, in pnictides many bulk experiments suggest the presence of nodes in the SC state (Johnston, 2010; Stewart, 2011). Since ARPES is a surface-sensitive technique, the surface and the bulk could behave differently in these materials (Hirschfeld, Korshunov, and Mazin, 2011). Another important aspect to consider is that, for the special case of LiFeAs, recent ARPES experiments (Allan et al., 2012; Umezawa et al., 2012, and references therein) reported a moderate gap anisotropy along the FS, suggesting that complex anisotropic interactions are involved in the SC pairing, together with strong-coupling superconductivity since $2\Delta/k_BT_c$ can be larger than 6. Additional work is clearly needed to fully clarify the symmetry of the SC state for both pnictides and selenides.

VI. NEUTRON SCATTERING

Neutron scattering studies of the alkali metal iron selenides have revealed an unexpected and complex magnetic state in the presence of the ordered iron vacancies. The details are as follows.

A. Elastic neutron scattering

The first powder neutron diffraction studies of the alkali metal iron selenides were presented for K$_{0.8}$Fe$_{1.6}$Se$_2$ (Bao et al., 2011), with Fe in a valence state $2^+$. These investigations confirmed the presence of the $\sqrt{5} \times \sqrt{5}$ vacancy superstructure, compatible with results reviewed in Sec. II such as the single-crystal x-ray diffraction studies (Zavalij et al., 2011). Other neutron diffraction studies of Cs$_x$Fe$_{2-x}$Se$_2$, A$_x$Fe$_{2-x}$Se$_2$ ($A = $ Rb, K), and Rb$_x$Fe$_{1.6+x}$Se$_2$ also concluded that there is a $\sqrt{5} \times \sqrt{5}$ iron-vacancy superstructure in the insulating state of these materials (Pomjakushin, Pomjakushina et al., 2011; Pomjakushin, Sheptyakov et al., 2011; Meng Wang et al., 2011).

More importantly, Bao et al. (2011) reported a novel and exotic magnetic order in this compound that is stable in the iron-vacancy environment. This magnetic order contains $2 \times 2$ iron superblocks, with their four moments ferromagnetically aligned (see Fig. 12). These superblocks display an AFM order between them; thus the state will be referred to as the “block-AFM” state hereafter. The individual magnetic moments are $3.31 \mu_B$/Fe, the largest observed in the family of iron-based superconductors. These neutron results, particularly the large magnetic moments, again challenge the view that these compounds are electronically weakly coupled and that FS nesting explains their behavior. While pnictides and selenides may have different Hubbard $U$ coupling strengths, thus explaining their different properties, it could also occur that the view of the pnictides as weakly correlated materials is incorrect. More work is needed to clarify these matters. Adding to the discrepancy with the weak-coupling picture, an unprecedented high Néel temperature of Fe vacancy order site

![Fig. 12 (color online). In-plane crystal and magnetic structure of K$_{0.8}$Fe$_{1.6}$Se$_2$. The open squares are the iron vacancies and the dark circles with the “+” or “−” denote the occupied iron sites with the orientation of their spins. The open circles correspond to Se, while the K atoms are small open circles. From Bao et al., 2011.](image-url)
Inelastic neutron scattering studies of $A_2\text{Fe}_4\text{Se}_5$ [$A = \text{Rb, Cs, (Tl, Rb), and (Tl, K)}$] by Ye et al. (2011) found the same iron-vacancy order and magnetic block-AFM states as observed in $K_2\text{Fe}_4\text{Se}_5$. The order-disorder transition occurs at $T_S = 500–578$ K, and the AFM transition at $T_N = 471–559$ K with a low-temperature magnetic moment $-3.3 \mu_B/\text{Fe}$. Ye et al. (2011) showed that all 245 iron selenides share a common crystalline and magnetic structure, which is very different from those of other iron-based superconductors such as the pnictides.

Neutron diffraction studies of $\text{TlFe}_{1.8}\text{Se}_2$ (Cao et al., 2012; May et al., 2012) unveiled spin arrangements that may deviate from the block-AFM order, compatible with theoretical calculations (Q. Luo et al., 2011; Yin, Lin, and Ku, 2011; Yu, Goswami, and Si, 2011), where several spin states were found close in energy to the block-AFM state (see Sec. VII for details).

Moreover, neutron (Meng Wang et al., 2011) and x-ray (Alessandro Ricci et al., 2011) diffraction studies of the SC state also provided evidence for phase separation between the above-mentioned regular distribution of iron vacancies and another state with a $\sqrt{2} \times \sqrt{2}$ superstructure, as reported in other investigations reviewed in Sec. VII (theory). The important issue of phase separation was already discussed in Sec. III.

**B. Inelastic neutron scattering**

Inelastic neutron scattering studies (Miaoyin Wang et al., 2011) showed that the spin waves of the insulating antiferromagnet $\text{Rb}_{0.89}\text{Fe}_{1.58}\text{Se}_2$, with the block-AFM order and Néel temperature of $\sim 500$ K, can be accurately described by a local-moment Heisenberg model with iron nearest-neighbor (NN), next-NN (NNN), and next-NN (NNNN) interactions, as reviewed by Dai, Hu, and Dagotto (2012). These results are in contrast to those for the iron pnictides, with As instead of Se, where contributions from itinerant electrons are needed to understand their spin-wave properties (Zhao et al., 2009). Moreover, $\text{Rb}_{0.89}\text{Fe}_{1.58}\text{Se}_2$ has three spin-wave branches, while all other materials studied with neutrons have only one. However, as the energy of the spin excitations grows the neutron results of Miaoyin Wang et al. (2011) also show (see Fig. 13) an evolution from a low-energy state with eight peaks, as expected from the block-AFM state after averaging the two chiralities of the iron-vacancy distribution, to a high-energy state with spin waves very similar to those of pnictides such as $\text{BaFe}_2\text{As}_2$ in spite of their different Néel temperatures. This observation reveals intriguing common aspects in the magnetism of selenides and pnictides. In addition, a fitting analysis of the neutron spin-wave spectra shows that in these materials and others the effective NNN Heisenberg couplings (i.e., the coupling along the diagonal of an elementary iron plaquette) are all of similar value. Since in the same analysis the effective NN couplings (i.e., at the shortest Fe-Fe distance) vary more from material to material, even changing signs, the effective NNN coupling may be crucial to understanding the common properties of the iron-based superconductors (Miaoyin Wang et al., 2011). In fact, a robust real (as opposed to effective) NNN superexchange coupling comparable to or larger in strength than the real NN superexchange is needed for the stability of the magnetic state with magnetic wave vector $(\pi, 0)$, in the iron-sublattice notation, that dominates in many iron-based superconductors. Recent results for superconducting $\text{Rb}_{0.82}\text{Fe}_{1.68}\text{Se}_2$ (Miaoyin Wang et al., 2012) also suggest that the magnetic excitations arise from localized moments. For details see the recent review by Dai, Hu, and Dagotto (2012). Note that the spin-wave spectra have also been addressed using an ab initio linear response by Ke, Schillfgaarde, and Antropov (2012b).

Since its discovery in the context of the high-$T_c$ Cu oxide superconductors, an aspect of the inelastic neutron scattering data that is considered of much importance is the neutron spin resonance (Scalapino, 2012). In superconducting $\text{AFe}_{2-y}\text{Se}_2$ the presence of neutron spin resonances was reported by Park et al. (2011), Friemel, Liu et al. (2012a), Friemel et al. (2012b), and Taylor et al. (2012) [see also Inosov et al. (2011)]. The energies of the resonances for many compounds are summarized in Fig. 14, showing that the normalized resonance energy is similar in all of the iron-based superconductors. The neutron results showing a resonance are

![Fig. 13](image_url)  
**Fig. 13 (color online).** Wave vector dependence of the spin-wave excitations of $\text{Rb}_{0.89}\text{Fe}_{1.58}\text{Se}_2$ at two representative energies (Miaoyin Wang et al., 2011). (a) Eight peaks of the $\sqrt{5} \times \sqrt{5}$ iron distribution when the two chiralities are averaged; (b) is similar to results for $\text{BaFe}_2\text{As}_2$.

![Fig. 14](image_url)  
**Fig. 14 (color online).** Normalized resonance energy of several iron-based superconductors, from inelastic neutron scattering. RFS stands for $\text{RbFe}_2\text{Se}_5$, BFNA for $\text{BaFe}_{1-y}\text{Ni}_y\text{As}_2$, and the rest of the abbreviations are for 122, 111, or 1111 materials. From Park et al., 2011.
compatible with the expectation arising from FS nesting involving the electron pockets for the case of a $d$-wave-symmetric condensate (Scalapino, 2012). However, the discussion is still open since FS nesting may not be sufficient to explain the properties of the iron-based superconductors, not even the pnictides (Dai, Hu, and Dagotto, 2012). Perhaps an intermediate Hubbard $U$ coupling is a more appropriate starting point for the pnictides while the selenides may require an even stronger coupling. Also ARPES experiments reviewed in Sec. V tend to favor $s$-wave superconductivity due to the absence of nodes in the small electron pocket at $\Gamma$. Thus, the $d$ vs $s$ pairing symmetry of the alkali metal iron selenides remains an open and fascinating question.

VII. THEORY

A. Band structure in the presence of iron vacancies

The magnetic state of the alkali metal iron selenides has been investigated from the perspective of theory using a variety of techniques. For example, employing first-principles calculations and comparing several magnetic configurations, the ground state of (K,Tl)$_2$Fe$_{1.5}$Se$_{2}$ was found to be the magnetic configuration with antiferromagnetically coupled $2 \times 2$ Fe blocks (Cao and Dai, 2011a), as reported in neutron scattering experiments. For $y = 0.8$ and K as the alkali element, a band gap $\sim 600$ meV opens, leading to an AFM insulator (Cao and Dai, 2011a). For $y = 1$, the Fermi level is near the top of the band gap of $y = 0.8$, leading to a metallic state with a $\sim 400$–550 meV gap slightly below the Fermi energy. Other $ab$ initio calculations by Xun-Wang Yan et al. (2011) agree with these results, and band structure calculations for K$_3$Fe$_2$Se$_2$ can also be found in Shein and Ivanovskii (2010) and Yan et al. (2011a). The block-AFM ground-state band structure is shown in Fig. 15. In addition, via studies of K$_{0.7}$Fe$_{1.0}$Se$_2$ and K$_{0.9}$Fe$_{1.0}$Se$_2$, i.e., varying the concentration of K to affect the valence of iron and the associated carrier concentration, it was found that the band structure and magnetic order almost do not change in that range of doping. Then K$_{0.4}$Fe$_{1.6}$Se$_2$ could be considered as a parent compound which becomes superconducting upon electron or hole doping (Xun-Wang Yan et al., 2011). This is relevant since in (Tl,K)$_2$Fe$_{1.5}$Se$_2$ superconductivity already occurs at $x = 1.7$ or higher (M. H. Fang et al., 2011). However, the issue of phase separation discussed in Sec. III renders the identification of the parent compound far more complicated than naively anticipated.

B. Influence of electron-electron correlations

First-principles calculations for the related material TlFe$_{1.5}$Se$_2$ (i.e., with Fe$_{1.5}$ instead of Fe$_{1.6}$) and with a different distribution of iron vacancies) using the generalized gradient approximation (GGA) $+ U$ method were also reported by Cao and Dai (2011b). The conclusion is that the magnetic state, a spin-density wave, becomes stable because of an effective increase of $U/W$ due to the reduction in the bandwidth $W$ caused by the loss of electronic kinetic energy in a background with iron vacancies (Cao and Dai, 2011b; Chen, Cao, and Dai, 2011). This is similar to the conclusion of model calculations that addressed the stability of the block-AFM state for the case Fe$_{1.6}$ (Q. Luo et al., 2011; Yin, Lin, and Ku, 2011; Yu, Zhu, and Si, 2011). In fact, the value $U \sim 2$ eV used by Cao and Dai (2011b) is similar to the $U \sim 3$ eV needed in the model Hamiltonian calculations (Q. Luo et al., 2011) to stabilize the block-AFM spin state [for a recent experimental discussion on the $U/W$ strength for the 1111 and 122 pnictides, see Vilmercati et al. (2012)]. The relevance of Mott physics, as opposed to an insulator caused by band structure effects, was also remarked by Craco, Laad, and Leoni (2011) using band structure plus dynamical mean-field theory. In fact, a more general study of the influence of correlations, not only in selenides but in pnictides as well, arrives at the conclusion that the weak-coupling Fermi surface nesting picture is incomplete and the intermediate-$U$ coupling regime is more realistic (Yin, Haule, and Kotliar, 2011; Dai, Hu, and Dagotto, 2012).

Model calculations have been carried out using the multi-orbital Hubbard model. While using five orbitals offers the most realistic description of pnictides and selenides, the complexity of this many-body problem involving interacting electrons often requires a reduction in the number of orbitals to increase the accuracy of the calculations. Thus, one must often balance these two aspects. Using a three-orbital Hubbard model in the random-phase approximation (RPA), Huang and Mou (2011) also concluded that for Fe$_{1.6}$ the block-AFM spin state is caused by electron correlation effects, although at a smaller $U \sim 1.5$ eV than discussed previously. This is understandable since the three-orbital model requires a smaller $U$ to represent the same physics as a five-orbital model (adjusting the electronic densities $n$ for a proper comparison), due to the reduction in the bandwidths when reducing the number of orbitals. This value of $U$ is also compatible with results by Luo et al. (2010) using a three-orbital model and electronic density per Fe orbital $n = 4/3$, but in the context of pnictides. Note that in the paper by Huang and Mou (2011) the ratio $J_H/U$ is 0.2, similar to the 0.25 found by Q. Luo et al. (2011). Studies for pnictides also suggest a similar ratio for $J_H/U$ (Luo et al., 2010). Moreover, the importance of a robust $J_H$ leading to a
so-called “Hund’s metal” state has been remarked from the dynamical mean-field theory perspective (Georges, Medici, and Mravlje, 2013, and references therein) as well as from the orbital differentiation perspective [see Bascones, Valenzuela, and Calderón (2012), and references therein; for recent experimental results see Yi et al. (2013)], where some orbitals develop a gap with increasing $U$ while others remain gapless, leading to a coexistence of localized and itinerant degrees of freedom. In addition, in the work by Q. Luo et al. (2011), and also via mean-field approximations and the three-orbital model by Lv, Lee, and Phillips (2011), it was concluded that for a sufficiently large $U$ an orbitally ordered state should be stabilized for the iron-vacancies-ordered state, with the population of the $d_{xz}$ and $d_{yz}^*$ orbitals different at every iron site.

C. Competing states

The issue of the magnetic states that compete with the $2 \times 2$ block-AFM state [shown in Fig. 16(a)] has been addressed using a variety of techniques. Via first-principles calculations, the usual collinear AFM metallic phase [i.e., the phase with magnetic wave vector $(\pi,0)$ with regard to the iron sublattice] was found to be stable if a pressure of 12 GPa is applied (Lei Chen et al., 2011). This state corresponds to the same $(\pi,0)$ magnetic order (C-AFM) as the 122 and 1111 families, simply removing the spins corresponding to the location of the iron vacancies [see Fig. 16(c)]. On further increasing the pressure to 25 GPa a nonmagnetic metallic state is reached (Lei Chen et al., 2011). These results are qualitatively compatible with those found by Q. Luo et al. (2011) via Hartree-Fock (HF) approximations to the five-orbital Hubbard model at electronic density $n = 6$ (six electrons/Fe), since increasing pressure corresponds to increasing the hopping amplitudes in tight-binding Hamiltonians, thus increasing the carrier bandwidth $W$. Since the Hubbard $U$ is local, it should not be affected by these effects as severely as $W$. Thus, a pressure increase amounts to a decrease in $U/W$ in Hubbard model calculations. Indeed, working at a fixed $J_H/U = 0.25$, Q. Luo et al. (2011) found that reducing $U/W$ at a constant $J_H/U$ led to transitions from the block-AFM state [Fig. 16(a)] to the C-AFM state [Fig. 16(c)], and then eventually to a nonmagnetic state. If $J_H/U$ is reduced, then the state shown in Fig. 16(b) could also be reached, with staggered order within the $2 \times 2$ blocks. The full HF phase diagram of the model is shown in Fig. 16(d). Also both the model and first-principles calculations agree on the reduction of the magnetic moment when moving from the block-AFM state to the C-AFM state.

As an alternative to the model Hamiltonian results, the first-principles calculations by Lei Chen et al. (2011) showed that the stabilization of the block-AFM state is caused by a lattice tetramer distortion; otherwise, the C-AFM state would be stable. This effect is not considered in the Hubbard model calculations where the block-AFM state is stabilized by an increase in $U/W$ (Q. Luo et al., 2011). Thus a combination of lattice distortions and electronic correlation effects may be needed to stabilize the block-AFM state in the presence of iron vacancies.

Note, however, that other first-principles simulations for $A_{0.8}Fe_{1.6}Se_2$ reported that pressure induces a transition from the block-AFM state to the metallic “Néel-FM” state where each $2 \times 2$ block has staggered magnetic order (Cao, Fang, and Dai, 2011). The differences between these first-principles calculations are currently being jointly addressed by Cao, Fang, and Dai (2011) and Lei Chen et al. (2011) (C. Cao, private communication). As already remarked, note also that the model Hamiltonian calculations (Q. Luo et al., 2011; Yin, Lin, and Ku, 2011) have unveiled several competing magnetic configurations that become stable in different regions of the $J_H/U$ phase diagram [see Fig. 16(d)]; thus small variations in the first-principles calculations can lead to different states. These differences highlight the complexity of the phase diagram of various materials, displaying several competing phases when in the presence of iron vacancies.

From the strong-coupling-limit perspective, calculations based on localized spin models for $A_{0.8}Fe_{1.5}Se_2$ also revealed many competing states, including the magnetic arrangement found in neutron experiments (Yu, Goswami, and Si, 2011; Fang et al., 2012). A similar competition of states was found for $A_{0.8}Fe_{1.5}Se_2$, i.e., with $Fe_{1.5}$ instead of $Fe_{1.6}$ (Yu, Goswami, and Si, 2011). Note also that Li, Dong et al. (2012) predicted an insulating block-AFM spin state even
in the absence of iron vacancies, for instance, for KFe$_2$Se$_2$. This state is sketched in Fig. 17. The dominant magnetic instability of vacancies-free KFe$_2$Se$_2$ was also studied by Cao and Dai (2011c), reporting a state similar to that of pnictides and a FS with only electronlike pockets without nesting, and by Da-Yong Liu et al. (2012).

D. Pairing symmetry

As discussed, the states with chemical composition $A_{0.3}$Fe$_{1.6}$Se$_2$, AFe$_{5}$Se$_2$, and AFe$_{2}$Se$_2$ have received considerable attention both experimentally and theoretically. Predicting the pairing symmetry of the SC state in these materials has been one of the areas of focus. Using a slave-spin technique to study the Mott transition of a two-orbital Hubbard model, and an effective perturbation theory once the system is in the Mott state, the superconductivity of slightly doped (Tl, K)Fe$_{1.5}$Se$_2$ was studied, unveiling a competition regulated by $J_H$ between a $d$-wave state (with a positive order parameter in two of the electronlike pockets and negative in the other two) and an $s$-wave state with the same sign of the order parameter in the electron pockets (there are no hole pockets in these materials) (Yi Zhou et al., 2011). The importance of superconductivity mediated by spin fluctuations was also analyzed using spin-fermion models, i.e., mixing itinerant and localized degrees of freedom as opposed to directly using a Hubbard model (Zhang, Lu, and Xiang, 2011). For K$_x$Fe$_{2-y}$Se$_2$, the fluctuation exchange approximation applied to a five-orbital Hubbard model (Maier et al., 2011) leads to $d$-wave superconductivity due to pair scattering between the electron pockets. The RPA enhanced static susceptibility has a broad peak at $(\pi, \pi)$ in the Fe sublattice notation. A similar $d$-wave pairing was found using the two-orbital model within the RPA (Das and Balatsky, 2011), and a possible $s + id$ pairing was also discussed by Rong Yu et al. (2011). The results of Maier et al. (2011) contain a robust dependence of the SC gap with a wave vector along the electron pockets.

However, ARPES results seem to be in disagreement with $d$-wave pairing (X.-P. Wang et al., 2012; Xu et al., 2012). In addition, the calculations that lead to $d$-wave superconductivity have been criticized because they are based on the “unfolded” Brillouin zone (BZ), neglecting the symmetry lowering of the staggered Se atom positions (Mazin, 2011). Based on this consideration, Mazin (2011) argued that the $d$-wave states should develop nodal lines at the folded BZ electron pockets, which are not observed experimentally. It was then concluded that either a conventional same-sign $s$-wave state, with the same sign for the SC order parameter in all the FS pockets, or another form of the $s_{+}$ state, different from the one proposed for the pnictides, should be the dominant symmetry (Mazin, 2011; You et al., 2011); for details and references on the possible pairing channels discussed in the literature, see Johnston (2010); for another form of $s_{+}$ pairing for AFe$_2$Se$_2$, see Khodas and Chubukov (2012)). The dominance of $s$-wave pairing was also concluded from mean-field studies based on magnetic exchange couplings (Chen Fang et al., 2011). They remarked that $s$-wave pairing can exist even without the electron and hole pockets needed in weak coupling. Lanczos calculations by Nicholson et al. (2011) reached similar conclusions. The $d$-wave versus $s$-wave competition, the latter with the same sign in all pockets, was also studied by Saito, Onari, and Kontani (2011) via orbital and spin fluctuations in models for KFe$_2$Se$_2$. For the orbital fluctuations a small electron-phonon coupling is needed. In the phase-separation context, the differences between $d$-wave and $s$-wave pairing for the superconducting proximity effect in the magnetic state and the suppression of the magnetic moments were also addressed via two-orbital models and mean-field approximations (see Jiang et al., 2012); a related work to test the pairing symmetry via nonmagnetic impurities was proposed by Wang, Yao, and Zhang (2013).

E. Other topics addressed by theory

Several other topics have been addressed using theoretical techniques. For example, (i) the effect of disordered vacancies on the electronic structure of K$_x$Fe$_{2-y}$Se$_2$ was studied using new Wannier function methods (Berlijn, Hirschfeld, and Ku, 2012) and also via the two-orbital Hubbard model in the mean-field approximation (Tai et al., 2012). Also in this context and to distinguish between the $d$-wave and $s$-wave pairing channels in the absence of hole pockets, it was argued that the influence of nonmagnetic impurity scattering needs to be considered (Zhu and Bishop, 2011). Similar issues were addressed by Zhu et al. (2011). In addition, it has been argued that adding Fe atoms to K$_x$Fe$_{4-z}$Se$_5$ creates impurity bands that have common features with iron pnictides, thus addressing the coexistence of superconductivity and magnetic states (Ke, Schilfgaarde, and antropov, 2012a). (ii) Band structure calculations have shown that the stoichiometric KFe$_2$Se$_2$ has a rather different FS than Ba122, but still the $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals dominate at the Fermi energy (Nekrasov and Sadovskii, 2011).

VIII. TWO-LEG LADDERS

A. Introduction and experiments

Considering the vast interest in the alkali metal iron selenides summarized in the previous sections, and also considering that deviations from an iron square lattice, as in the presence of iron-vacancy order, lead to interesting physics, other crystal geometries are worth exploring. In this section, recent experimental efforts (Caron et al., 2011; Krzton-Maziopa, Pomjakushina et al., 2011; Lei, Ryu, Frenkel, ...
and Petrovic, 2011; Saparov et al., 2011; Caron et al., 2012; Nambu et al., 2012) in the study of selenides with the geometry of two-leg ladders (sometimes also referred to as double chains) are reviewed. A typical compound in this context is $\text{BaFe}_2\text{Se}_3$ containing building blocks made of $[\text{Fe}_2\text{Se}_3]^{2-}$ that when assembled along a particular direction lead to an array of two-leg ladder structures, as sketched in Fig. 18.

The ladders in $\text{BaFe}_2\text{Se}_3$ can be considered as cutouts of the layers of edge-sharing $\text{FeSe}_4$ tetrahedra of the two-dimensional selenides (see Fig. 19). Each ladder has a long direction ("legs") and a short direction involving two Fe atoms ("rungs"). A field of research involving similar ladder structures, but with spin-$\frac{1}{2}$ copper instead of iron, is also very active since in that context two interesting effects were found: a spin gap and superconductivity upon doping (Dagotto, Riera, and Scalapino, 1992; Dagotto and Rice, 1996). For instance, $\text{SrCu}_2\text{O}_3$ is a material analogous to $\text{BaFe}_2\text{Se}_3$ (Dagotto, 1999).

$\text{BaFe}_2\text{Se}_3$ is an insulator with a gap $0.14-0.18$ eV (Lei, Ryu, Frenkel, and Petrovic, 2011; Nambu et al., 2012). This material has long-range AFM order at $\sim 250$ K, low-temperature magnetic moments $\sim 2.8 \mu_B$, and short-range AFM order (presumably along the leg directions) at higher temperatures (Caron et al., 2011; Lei, Ryu, Frenkel, and Petrovic, 2011; Saparov et al., 2011). Establishing an interesting analogy with the alkali metal iron selenides, neutron diffraction studies (Caron et al., 2011; Nambu et al., 2012) reported a dominant order involving $2 \times 2$ blocks of ferromagnetically aligned iron spins, with these blocks antiferromagnetically ordered, as shown in Fig. 20 (lower panel). These building blocks are the same as in the block-AFM state of the $\sqrt{5} \times \sqrt{5}$ iron-vacancy arrangement. Thus, understanding one case may lead to progress in the other. When the Ba atoms of $\text{BaFe}_2\text{Se}_3$ are replaced by K, eventually arriving at $\text{KFe}_2\text{Se}_3$, the magnetic order changes to that in Fig. 20 (upper panel), with spins along the rungs coupled ferromagnetically, and with an AFM coupling along the legs (Caron et al., 2012).

**B. Theory**

The theoretical study of selenide ladders is only at an early stage. First-principles calculations and spin model studies (W. Li, Setty et al., 2012) showed the dominance of the block-AFM state found experimentally. The band structure calculation in this magnetic state was presented by W. Li, Setty et al. (2012) [see also Saparov et al. (2011)] and it contains a gap of 0.24 eV (see Fig. 21).

![FIG. 18](image1.png) (color online). The two-leg ladder substructures of $\text{BaFe}_2\text{Se}_3$, with their legs oriented perpendicular to the figure. From Lei, Ryu, Frenkel, and Petrovic, 2011.

![FIG. 19](image2.png) (color online). Relation between a complete $\text{FeSe}$ layer and the structure of the ladders. The dark spheres are the Se atoms and the light spheres are the Fe atoms. The ladders simply amount to the removal of every third iron atom from the layers. From Saparov et al., 2011.

![FIG. 20](image3.png) (color online). Magnetic order of the two-leg ladders for the cases of $\text{KFe}_2\text{Se}_3$ and $\text{BaFe}_2\text{Se}_3$ obtained using neutron diffraction. From Caron et al., 2012.

![FIG. 21](image4.png) (color online). Electronic band structure of the block-AFM state of the two-leg ladder $\text{BaFe}_2\text{Se}_3$. The gap is 0.24 eV. From W. Li, Setty et al., 2012.
IX. RELATED AND RECENT DEVELOPMENTS

An exciting recent result is the report of superconductivity in a single-unit-cell FeSe film grown on SrTiO$_3$ (Q.-Y. Wang et al., 2012), displaying signatures of the SC transition above 50 K, and a SC gap as large as 20 meV. The electronic structure of this single-layer FeSe superconductor was studied via ARPES techniques by Defa Liu et al. (2012). The FS is shown in Fig. 23 and it consists only of electron pockets near the zone corner, without any indication of even a small pocket at the zone center. This is contrary to the band structure calculations reported in the same publication that predicted a pocket at $\Gamma$. Thus, there are no scattering channels between the $\Gamma$ and $M$ points of the Brillouin zone. The top of the holelike band at $\Gamma$ is 80 meV below the Fermi level. The critical temperature is $\sim 55$ K and the SC gap was found to be large and nearly isotropic, and since this is a strictly two-dimensional system, the presence of nodes along the $z$ axis is ruled out. From first-principles calculations Liu, Lu, and Xiang (2012) concluded that the single- and double-layer FeSe films are weakly doped AFM semiconductors, i.e., for the monolayer FeSe to be superconducting doped electrons may be needed via O or Se vacancies. Clearly, the in-depth study of this single-layer system contributes significantly to the understanding of the SC state of the iron superconductors.

While completing this Colloquium two new results were reported: (1) the SC $T_c$ of the single-layer FeSe film grown on a SrTiO$_3$ substrate was optimized to $T_c = 65 \pm 5$ K via an annealing process (He et al., 2012), establishing a new $T_c$ record for the iron superconductors. Photoemission studies indicate a FS with electron pockets at the $M$ points of the Brillouin zone. The top of the holelike band at $\Gamma$ is 80 meV below the Fermi level. The critical temperature is $\sim 55$ K and the SC gap was found to be large and nearly isotropic, and since this is a strictly two-dimensional system, the presence of nodes along the $z$ axis is ruled out. From first-principles calculations Liu, Lu, and Xiang (2012) concluded that the single- and double-layer FeSe films are weakly doped AFM semiconductors, i.e., for the monolayer FeSe to be superconducting doped electrons may be needed via O or Se vacancies. Clearly, the in-depth study of this single-layer system contributes significantly to the understanding of the SC state of the iron superconductors.

There are several other exciting recent topics of research in these materials. As discussed, the insulating characteristics of some of the alkali metal iron selenides suggests that Mott physics may be important for understanding their properties. For instance, the iron oxychalcogenides La$_2$O$_2$Fe$_2$O(Se, S)$_2$ were studied theoretically, and the conclusion is that they are Mott insulators because of enhanced correlation effects caused by band narrowing (Zhu et al., 2010). The importance of Mott localization was also addressed for K$_{0.8}$Fe$_{1.7}$S$_2$ and K$_{0.8}$Fe$_{1.7}$SeS (Guo et al., 2011), and also for BaFe$_2$Se$_2$O (Han et al., 2012; Lei et al., 2012). Lei, Abeykoon, ...
Bozin, Wang et al. (2011) studied the phase diagram of K$_x$Fe$_{2−y}$Se$_2$, showing that $T_c$ is suppressed as the S concentration increases [see also Lei, Abeykoon, Bozin, and Petrovic (2011) and Lei, Bozin et al. (2011)].

In a related context, the K$_{0.8}$Fe$_2$Co$_{0.2}$Se$_2$ phase diagram was discussed by T. T. Zhou et al. (2011). A small amount of Co suppresses the superconductivity of the undoped material, and at $x = 0.03$ there is no longer a zero-resistivity state. They argued that this behavior is similar to that of Cu oxide superconductors and for this reason the alkali metal iron selenides are better described by localized 3$d$ spins than by itinerant electrons.

Also among the most recent developments is the study of the phase diagram of $A_x$Fe$_{2−y}$Se$_2$ ($A = K$, Rb, and Cs) versus the valence of iron (Yan et al., 2012). This iron valence was controlled by systematically varying $x$ and $y$. The resulting phase diagram is shown in Fig. 24 and it contains three AFM insulating states (characterized by different iron-vacancy superstructures) and a SC state. Since the SC phase is surrounded by insulators, Yan et al. (2012) concluded that the SC phase must have those insulating states as parent compounds.

Another interesting result is the discovery of a second “reemerging” SC phase (Sun et al., 2012) for $\text{Tl}_{0.9}\text{Rb}_{0.1}\text{Fe}_{1.67}\text{Se}_2$, $\text{K}_{0.8}\text{Fe}_{1.7}\text{Se}_2$, and $\text{K}_{0.8}\text{Fe}_{1.75}\text{Se}_2$, with critical temperatures $T_c \sim 48−49$ K, when the pressure is increased to 11.5 GPa (see Fig. 25). The changes of $T_c$ with increasing pressure may be caused by structural variances within the basic tetragonal unit cell, and the $\sqrt{5} \times \sqrt{5}$ iron-vacancy order may be destroyed by pressure-driving the system into a disordered lattice. The possibility of a novel quantum critical point in this material was also discussed by Guo et al. (2012).

Along similar lines with regard to increases in $T_c$, superconductivity at 30–46 K in $A_x$Fe$_2$Se$_2$ using small-size alkali metals and alkaline earth atoms ($A = \text{Li, Na, Ba, Sr, Ca, Yb, and Eu}$) was recently observed by Ying et al. (2012). Compatible with these results, superconductivity at 44 K in $A_x$Fe$_{2−y}$Se$_2$ was also recently reported (Zhang, Xia et al., 2013). At these temperatures a sharp drop in resistivity and susceptibility was observed. The 44 K SC phase is close to an ideal 122 structure, but with an unexpectedly large $c$-axis lattice parameter 18.10 Å; Zhang, Xia et al. (2013) showed a plot that $T_c$ increases with the distance between neighboring FeSe layers. Related to these results, superconductivity at 43 K in $\text{Li}_x(\text{NH}_3)_y(\text{NH}_2)_z\text{Fe}_2\text{Se}_2$ ($x = 0.6; y = 0.2$) (Burrrad-Lucas et al., 2012), at 44 K in $\text{Li}_x\text{Fe}_2\text{Se}_2(\text{NH}_3)_y$ (Scheidt et al., 2012), and at 45 K in $\text{Li}_x(\text{C}_2\text{H}_5\text{N})_y\text{Fe}_2\text{Se}_2$ (Krzton-Maziopa et al., 2012) was also recently observed.

**FIG. 24 (color online).** The phase diagram of $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$ vs the iron valence. The SC phase appears sandwiched between AFM insulators. The Fe valence state was systematically controlled by varying the $x$ and $y$ concentrations in $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$. From Yan et al., 2012.

**FIG. 25 (color online).** Superconducting $T_c$ vs pressure for the compounds indicated. Two SC phases were found. SC-II has a $T_c \sim 48.7$ K. From Sun et al., 2012.

**FIG. 24 (color online).** The phase diagram of $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$ vs the iron valence. The SC phase appears sandwiched between AFM insulators. The Fe valence state was systematically controlled by varying the $x$ and $y$ concentrations in $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$. From Yan et al., 2012.

**FIG. 25 (color online).** Superconducting $T_c$ vs pressure for the compounds indicated. Two SC phases were found. SC-II has a $T_c \sim 48.7$ K. From Sun et al., 2012.

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**FIG. 25 (color online).** Superconducting $T_c$ vs pressure for the compounds indicated. Two SC phases were found. SC-II has a $T_c \sim 48.7$ K. From Sun et al., 2012.

**X. CONCLUSIONS**

In this Colloquium the “hot” topic of alkali metal iron selenides was reviewed. The main reasons for the current excitement in this area of research include the realization that these materials do not have hole pockets at the $\Gamma$ point, conceptually altering the dominant conception that originated in the pnictides about the importance of FS nesting between electron and hole pockets to understand the magnetic and SC states. This conclusion is compatible with the recent accumulation of evidence that FS nesting and a weak-coupling perspective are not sufficient for the pnictides (Dai, Hu, and Dagotto, 2012). Moreover, via ARPES techniques applied to some alkali metal iron selenides, the small electron (not hole) pocket at $\Gamma$ was investigated and in the SC state this pocket does not present nodes, removing the $d$-wave state as a possibility (although this issue is still under discussion). Thus, the menu of options for the symmetry of the SC order parameter in these selenides appears reduced to a conventional same-sign $s$-wave state (via a coupling of the electrons to the lattice), or a more exotic form of the $s_{++}$ state (Mazin, 2011), different from the $s_{++}$ state proposed for the pnictides (Johnston, 2010). Also note that the same-sign $s$ wave may not explain the neutron spin resonances in the alkali metal iron selenides (Scalapino, 2012). Thus, only further work can clarify this subtle matter.

Another reason for the excitement in this area of research is the possibility of having an insulating parent compound of the SC state, perhaps a Mott insulator. Candidate states with an ordered distribution of iron vacancies have been identified at particular compositions of iron. Some of these states display an exotic magnetic state that contains $2 \times 2$ blocks of aligned iron moments, with an AFM coupling between
blocks. Other states have also been proposed as parent compounds, and a final answer has not been given to this matter.

In this same context of exploring Mott insulators in the iron-superconductor arena, note that iron has been replaced by other transition metal elements, such as Mn, leading to interesting results including AFM insulators and metallic states upon doping, although not yet to superconductivity. For the case of BaMn$_2$As$_2$, see Johnston et al. (2011) and Pandey et al. (2012), and references therein. This line of exploration is promising and it should be further pursued.

Finally, the presence of phase separation has also attracted considerable attention. Are the magnetic and SC states competing or cooperating? This is also a recurrent open question for the SC copper oxides as well. Note that such competition or cooperation is relevant only if the states can influence one another either by sharing the same volume element, i.e., microscopically coexisting, or by forming an inhomogeneous state at such short length scales that one state can still affect the other and vice versa. In fact, in several FeAs-based materials there is evidence that the two competing states share the same volume element (Johnston, 2010), while in the selenides the situation is still evolving with regard to the length scales involved in the phase-separation process.

In summary, the young subfield of alkali metal iron selenides is challenging the prevailing ideas for the pnictides. It might be that selenides and pnictides harbor different pairing mechanisms, or they may have different strengths in their Hubbard $U$ couplings. After all, the pnictides have AFM metallic states as parent compounds of superconductivity, while the selenides may have AFM insulators as parent compounds, based on the discussion presented here. However, by arguments of simplicity it is also reasonable to assume that a unique qualitative mechanism could be at work simultaneously in both families of compounds. Perhaps short-range AFM fluctuations may be similarly operative as the pairing mechanism in the context of both metallic and insulating parent states. All these important issues are still under much discussion, and by focusing on the new alkali metal iron selenides several intriguing conceptual questions raised by the discovery of the iron-based superconductors may soon converge in an answer.

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