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Superconductivity and magnetism in 11-structure iron chalcogenides in relation to the iron pnictides

David Joseph Singh

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056, USA
E-mail: singhdj@ornl.gov

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Abstract
This is a review of the magnetism and superconductivity in ‘11’-type Fe chalcogenides, as compared to the Fe-pnictide materials. The chalcogenides show many differences from the pnictides, as might be anticipated from their very varied chemistries. These differences include stronger renormalizations that might imply stronger correlation effects as well as different magnetic ordering patterns. Nevertheless the superconducting state and mechanism for superconductivity are apparently similar for the two classes of materials. Unanswered questions and challenges to theory are emphasized.

Keywords: superconductivity, magnetism, 11-structure iron chalcogenides, iron pnictides

1. Introduction

The discovery of high-temperature superconductivity (\(T_c \sim 26\) K) in electron-doped \(\text{LaFeAsO}_{1-x}\text{F}_x\) \([1]\) has resulted in widespread interest and exploration of related materials, some of which have \(T_c\) exceeding 55 K. This represented the first finding of superconductivity above 50 K in a non-cuprate material. Furthermore, while important differences from cuprates emerged over time, these iron-based superconductors were found to have similarities with the cuprates as well, particularly the presence of superconductivity ‘near’ magnetism \([2]\). This is in contrast to other high-temperature superconductors discovered after the cuprates, such as \((\text{Ba,K})\text{BiO}_3\) \([3, 4]\), \(\text{MgB}_2\) \([5]\) and probably \(\text{A}_x\text{C}_6\) \([6, 7]\) (in the last case, antiferromagnetism does exist \([8]\) but may not be very intimately connected with superconductivity; most likely it is a competing phase to electron–phonon superconductivity).

This makes the Fe-based materials perhaps the most interesting new superconductors since the discovery of the cuprates. Key questions include of course the mechanism and nature of the superconductivity, the relationship with the cuprates, and the chemistry of the superconductivity, i.e., what range of compounds display this phenomenon and what is the relationship between the superconductivity and the chemical composition and structure. At present there is strong interest in finding new high-temperature Fe-based superconductors and especially in finding materials with higher critical temperature.

As mentioned above, high-temperature Fe-based superconductivity was first discovered in electron-doped \(\text{LaFeAsO}_{1-x}\text{F}_x\). Subsequently, high-temperature superconductivity was also found in various iron-based oxyarsenides by replacing La with other rare-earth metals \([9–13]\), as well as oxygen-free arsenides such as doped \(\text{BaFe}_{2}\text{As}_2\) \([14, 15]\), \(\text{SrFe}_{2}\text{As}_2\) \([16]\), \(\text{CaFe}_{2}\text{As}_2\) \([17, 18]\) and \(\text{LiFeAs}\) \([19–21]\). The common structural feature of this family of materials is the appearance of Fe–As layers. These consist of an Fe square planar sheet tetrahedrally coordinated by As atoms above and below the Fe planes.

In addition, superconductivity of an apparently similar nature occurs in doped \(\text{LaFePO}\) \([22–24]\). This shows that As is not essential to the superconductivity, although it should be noted that the \(T_c\) is much lower in the phosphide. There are no known Fe-based superconductors based on Sb, although not surprisingly there has been speculation
about this possibility and compounds that might realize it [25, 26]. Low-temperature superconductivity has also been found in isostructural Ni compounds, including LaNiPO [27], LaNiAsO [28], LaNiBiO [29], BaNi$_2$As$_2$ [30] and SrNi$_2$As$_2$ [31, 32]. However, while like Fe, Ni is a 3d elemental ferromagnet, these Ni-based materials are readily explained as conventional electron–phonon superconductors [33–35], while, as was shown by direct calculations of the electron–phonon coupling, the Fe-based materials are not [36, 37].

The cuprates are a large family of high-$T_c$ superconductors. They are layered compounds containing CuO$_2$ square planes, with Cu near, but doped away from, the nominal 2+ oxidation state. Many different superconducting compounds that contain stacks of these CuO$_2$ layers with other blocks have been discovered. However, substitution of Cu or the in-plane O is not compatible with high-$T_c$ superconductivity. Similarly, in the case of the Fe-based materials it was known very soon that they also are a large family of materials, and are based on Fe square planes coordinated by As, or with much weaker superconductivity, by P. In contrast with the cuprates, superconductivity can be induced by partial substitution of Fe with dopants such as Co or Ni [38–41] or with isovalent impurities like Ru [42], which suppresses magnetism without doping [43, 44]. This retention of superconductivity with very substantial Fe substitution is most remarkable for an unconventional superconductor and is still not fully understood.

The chemistry of chalcogens is very different from that of the pnictides, and in particular selenides are generally different in properties from arsenides. For example, Se is rather more electronegative than As or P (Pauling scale, 2.55 versus 2.18 or 2.19). Thus it came as a surprise when PbO, so-called ‘11’ structure FeSe$_{1+x}$ [45–47], was discovered to be a superconductor. Direct calculations showed that similar to the pnictides [36], this is not an electron–phonon superconductor [48].

Similar to the pnictides, Fe$_{1+y}$Se features an Fe square lattice and a tetrahedral coordination of the Fe, though not with As, as shown in figure 1. Furthermore, the critical temperature of Fe$_{1+y}$Se (initially written as FeSe$_{1-x}$) increases strongly with either Te substitution [49] or pressure, reaching $\sim 37$ K under pressure [46, 50–53]. The high values of $T_c$ under pressure imply a relationship with the Fe-As superconductors. Here we overview some aspects of the superconductivity and related properties of these 11-structure compounds, mainly from a theoretical perspective.

2. Features of Fe-pnictide superconductors

It is useful to very briefly mention some general aspects of the Fe-pnictide superconductors to set the stage for the discussion of the chalcogenides. A particularly detailed review may be found in [54], while a summary of the electronic structures, which are a focus here, can be found in [55]. Sefat and Singh [56] present the chemistry of these materials. As mentioned above, the Fe-based superconductors have the highest known $T_c$ outside of the cuprates, and a generic cuprate phase diagram is shown in figure 2. It contains a prominent antiferromagnetic Mott insulating state at zero doping that is suppressed by doping and gives way to a high-temperature superconducting state. This Mott insulating phase is universal, and doping is essential to destroy it in favor of superconductivity.

It was recognized early on that the Fe-based materials also have antiferromagnetism that is in apparent competition with a high-$T_c$ superconducting state [2, 57]. However, the antiferromagnetic state of the Fe-based materials is very different from that of the cuprates. First of all, it is unambiguously metallic as seen from spectroscopy [57], transport [58] and quantum oscillations [59]. Furthermore, as shown in figure 3, the order is different from the nearest-neighbor antiferromagnetism of the cuprates, implying more subtle interactions. The particular order observed in the arsenides is a zone-corner ordering, which in the unit cell containing two Fe atoms means a magnetic cell involving four Fe atoms. This order consists of alternating spin-up and spin-down chains of Fe atoms, and lowers the symmetry from tetragonal to orthorhombic. These systems have substantial magnetoelastic coupling and so this symmetry lowering is readily observed in the lattice parameters below the ordering temperature. Remarkably, while in some cases the structural transition and the magnetic

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**Figure 1.** Crystal structure of the ‘11’ Fe-chalcogenides showing the site for the additional Fe as small spheres.

**Figure 2.** Generic high-$T_c$ cuprate phase diagram as a function of doping. Note the prominent antiferromagnetic Mott insulating phase at zero doping.
ordering transition are coincident, in many cases, including the first material studied, LaFeAsO, the structural distortion precedes the magnetic ordering as the temperature is lowered [2, 60, 61]. While various explanations have been offered for this symmetry breaking before magnetic order, i.e., nematic behavior, the details remain unclear [62–65].

In the cuprates, the Mott insulating antiferromagnet is destroyed by doping, giving way to a conducting state. At least at high doping levels this state is a Fermi liquid, while at low doping levels there is nanoscale inhomogeneity. In the Fe-based materials, the antiferromagnetic and superconducting states appear to be more intimately connected. In particular, superconductivity and magnetic order coexist in the phase diagrams [66] and there is a rather continuous evolution of the spin fluctuations seen in nuclear magnetic resonance (NMR) spectra of the magnetic to the superconducting phases [67]. Also, unlike cuprates, the antiferromagnetic order in the Fe-based superconductors can be suppressed in favor of superconductivity by various means, such as pressure, isovalent alloying, etc—not only doping as in cuprates.

Turning to the superconducting state, the electronic structure of Fe pnictides is also very different from that of the cuprates. Initially it as assumed that Coulomb correlations may be dominant and play a role similar to the cuprates, producing Hubbard bands and a nearby antiferromagnetic Mott insulating state [68, 69]. However, early experiments quickly showed differences from cuprates. They revealed a metallic state exhibiting quantum oscillations [59, 70, 71] and metallic-like band dispersions around $E_F$ [72, 73], and lacking the Hubbard bands [74].

More recent theoretical results obtained by incorporating correlations are in good accord with these experimental data. The essential aspects are that the effective Hubbard interaction $U$ is weaker than in the cuprates, the multi-orbital nature of the electronic structure works against Mott states, and the on-site Hund’s interaction $J$ plays a stronger role [75–78].

This is not to say that the materials are uncorrelated. Photoemission does show significant renormalizations relative to standard density functional theory (DFT) calculations [72] and this is also seen in a reduction of the optical Drude weight [79]. Depending on doping level a renormalization of ~1.4–2.7 was needed to bring local density approximation (LDA) calculations into agreement with angle-resolved photoemission (ARPES) results for (Ba,K)Fe$_2$As$_2$ and Ba(Fe, Co)$_2$As$_2$ [80]. The difference from the cuprates is that this represents a redistribution of spectral weight in the Fe d bands, rather than a transfer to Hubbard bands (consistent with an important role for the Hund’s coupling) and furthermore, the renormalization is momentum dependent. Note that in a paper on FeSe based on dynamical mean field calculations, Aichhorn et al [81] referred to this redistribution of spectral weight inside the Fe d bands due to Hund’s coupling as producing a lower Hubbard band, although plainly the feature is not a Hubbard band in the sense that is normally reserved for that characterization.

The band structure and Fermi surfaces have been calculated by many authors. In these compounds Fe occurs...
nominally as Fe$^{2+}$, i.e. with six d electrons. The Fermi surfaces of all the materials consist of compensating electron and hole sheets derived from Fe d bands. This was first found by Lebegue [82] who studied the superconductor LaFePO finding hole-like Fermi surfaces around the tetragonal zone center and compensating electron-like sheets around the zone corner. Studies following the discovery of high-temperature superconductivity in arsenides showed similar structures in the various compounds [55, 83–88]. Therefore, the pnictides have a semimetallic electronic structure consisting of disconnected electron and hole sheets of Fermi surface.

Importantly, the Fermi surface structure is not dominated by a single orbital as in the cuprates, but rather contains contributions from several orbitals. The electron sheets have the same $d_{xz}/d_{yz}$ mixed character in all compounds, while the hole sheets differ more. However, in all cases they contain sections of $d_{xz}/d_{yz}$ character mixed with or in addition to sections of other d orbital character [88]. Therefore, the multiorbital nature of the electronic structure is an essential feature of these materials.

Returning to cuprates, the Mott insulating state is not described by standard band structure calculations, and from a band structure point of view these materials are incorrectly described as not being close to magnetism. The pnictides on the other hand have relatively low Fermi velocities [83] that lead to high densities of states $\sim 1$ eV$^{-1}$ on a per Fe per spin basis. This does put them near itinerant magnetism. In fact, they are very magnetic within standard DFT calculations [89]. The strong overestimate of the magnetic moments in such calculations is an unusual feature of these materials, and may be a consequence of strong competition between different magnetic states leading to renormalization by quantum fluctuations [90]. Another possibility that has been discussed is a more complex magnetic state involving intra-atomic non-collinearity [91]. In any case, from an electronic point of view, these are metals with low carrier concentrations and high densities of states, which approach band magnetism.

As mentioned above, the Fermi surfaces consist of disconnected electron and hole parts, with the hole parts around the zone center and the electron parts around the zone corner. These have similar orbital character and are separated by a 2D wavevector, $\left(\frac{1}{4}, \frac{1}{4}\right)\pi/a$, where $a$ is the in-plane lattice parameter. This leads to a nesting that is reflected in the susceptibility (figure 4). The dominant magnetic instability in iron pnictides is a zone-corner instability corresponding to this connection vector, and is known as the spin density wave (SDW) ordering [2], although this does not mean that the instability comes only from states very close to the Fermi energy [92], as in classical descriptions of weak spin density waves. This ordering pattern, as mentioned above, consists of lines of Fe-atoms with parallel spins, as shown in the middle panel of figure 3, and is the ground state predicted by density functional calculations [37, 93–95]. Various experiments [54] showed an intimate connection between the magnetism and the superconductivity of these materials.

Within a picture of spin-fluctuation mediated superconductivity a susceptibility peaked at the connection vector between such disconnected Fermi surfaces can lead to singlet superconductivity provided that the sign of the order parameter is opposite on the electron and hole sheets. Considering the small sizes of the Fermi surfaces this favors a sign-changing s-wave state, denoted $s^\pm$, while other states that do not have this sign change are disfavored [37, 85]. This sign-changing s-wave superconductivity is strongly supported by a variety of experiments as discussed in [96]. Perhaps most important is the observation of the predicted [97, 98] neutron resonance around $(\pi/a, \pi/a)$ [99], which is an inelastic neutron scattering peak seen in the superconducting state at energies above the superconducting gap and at momenta connecting parts of the Fermi surface where the order parameter has opposite sign.

3. Iron chalcogenides: similarities and differences from the pnictides

Phase diagrams as a function of pressure and composition of the ‘11’ Fe-chalcogenides are shown in figure 5. Two notable features are (i) a strong increase to $\sim 37\,\text{K}$ in the critical temperature of nominal Fe$_{1+4}$Se under pressure, so that this is very much a high-temperature superconductor [46, 50–53], and (ii) the only ordered magnetic phase is that near Fe$_{1+4}$Te, and it has a different magnetic order [100–102] than the SDW-type order seen in pnictides such as LaFeAsO.

One complication is that the ‘11’ Fe-chalcogenides generally form with excess iron, particularly when Te rich, and so the chemical formula should be written as, e.g. Fe$_{1+4}$Te [107, 108]. The superconductivity, especially for the selenide, which has a low $T_c$, is very sensitive to stoichiometry [109]. The excess Fe occurs roughly in the chalcogen plane, in sites that can be regarded as the complementary positions to the chalcogen atoms, i.e. partially occupying the corners of the tetrahedron that would be obtained by an inversion about the center of the chalcogen tetrahedron (see figure 1).

Density functional calculations for Fe$_{1+4}$Te with excess Fe [110] showed that the excess Fe has a valence of...
approximately 1+ and therefore provides electron doping, and furthermore that the excess Fe is strongly magnetic. It provides local moments that interact with the Fe in the planes. Various experiments also show effects of excess Fe on the magnetic and other properties. As mentioned above, the superconductivity of Fe$_{1+x}$Te is very sensitive to stoichiometry [109]; this is also the case in other parts of the phase diagram including both the Te-rich side [111], and the region near the maximum $T_c$ [112, 113].

Han and Savrasov [114] performed band structure calculations for FeTe and noted that a nesting feature would arise at the wavevector of the observed double-stripe magnetic state if the electron count were 0.5 per formula unit higher, which they ascribed to the excess Fe. This explanation is almost certainly incorrect, first of all because other studies showed the double stripe to be the ground state without excess Fe [92, 100], and because the 8+ valence state of the excess Fe (i.e. Fe$^{8+}$) assumed by Han and Savrasov is clearly unphysical and is not supported by calculations [110, 115].

Neutron scattering studies on Fe$_{1+y}$Te$_{1−x}$Se$_x$, $x = 0.38$ showed that the interstitial Fe induces a magnetic Friedel-like oscillation, extending over ~50 Fe sites [116]. This indicates that the excess Fe introduces moments that interact substantially with the Fe planes. Inelastic measurements on samples with different Fe concentrations at $x = 0.3$ showed changes in the magnetic scattering correlated with a decrease in the superconducting volume fraction [117], and changes are also seen in the magnetic behavior at $x = 0$ [118]. Liu et al [119] reported transport, susceptibility and specific heat measurements for samples with different amounts of excess Fe at both $x = 0.4$ and 0. They found both a suppression of superconductivity due to excess Fe and evidence for carrier localization, which they interpreted as reflecting a magnetic interaction between the excess Fe and the Fe planes and leading to local magnetic order. This conclusion is supported by annealing experiments [120]. Interestingly, first principles calculations show that anion vacancies in FeSe, i.e. in FeSe$_{1−x}$, also induce magnetism on at least eight neighboring Fe atoms [121].

Besides magnetic effects, x-ray experiments for $x = 0$ showed strong diffuse scattering indicative of strong local distortions caused by the excess Fe [122]. We note that these materials show strong coupling between magnetism and structure, as seen for example in the strong lattice distortions upon or preceding magnetic order [2], and so these structural distortions may be important for understanding the interplay between the excess Fe and the magnetism of the Fe planes.

Another complication is the structural distortion of superconducting Fe$_{1+x}$Se at $T_c \sim 90$ K depending on composition [123, 124]. Experiments on thin films with different orientations, which affect the structure distortion, show sensitivity of the superconductivity to the structure transition [125], although the sensitivity of superconductivity to strain (as seen, e.g., in the pressure dependence) hinders evaluation of the effect of tetragonal to orthorhombic transition. In any case, this structure distortion lowers the symmetry from tetragonal to orthorhombic, as does the nematic transition in e.g. LaFeAsO, but in Fe$_{1+x}$Se it is not followed by magnetic ordering at lower temperatures, nor is the transition itself caused by magnetic order. It is, however, accompanied by a resistivity anomaly, although not nearly as strong as that in, for example, LaFeAsO [123]. This tetragonal to orthorhombic transition then seems to be different in nature from the transition in the pnictides and at this time is poorly understood.

This tetragonal to orthorhombic distortion on the Se-rich side of the alloy system is also different from the distortion seen for Fe$_{1+y}$Te, which is directly connected with and coincident with the double-stripe magnetic order [102, 104]. The Fe$_{1+y}$Te structural transition is suppressed both by Te alloying and by pressure, by both of which increase the superconducting $T_c$.

Photoemission experiments in comparison with LDA calculations show stronger renormalization in Fe$_{1+y}$Se than in the arsenides, and in particular a larger mass enhancement, $Z^{-1} \approx 3.6$ [126]. The renormalization in Fe$_{1+y}$Se is nearly a factor of two larger than that in doped LaFeAsO [127]. As in the arsenides, there is a large Fe 3d spectral weight in the vicinity of the Fermi level with a clear Fermi edge. In contrast to the pnictides, substitutions on the Fe site are detrimental to the superconductivity of the ‘11’ phases [106, 128], although in the case of Cu-substituted Fe$_{1+y}$Se, which is electron doped [129], superconductivity can be restored under pressure [130]. Density functional calculations show that Cu substitution is highly disruptive to the electronic structure and induces local moments around the Cu site [129].

Therefore, from the points of view of renormalization seen in the electronic structure, sensitivity to substitutions on the Fe site and observed ordered magnetism, the Fe-chalcogenide superconductors appear different from the pnictides. However, both these classes of materials have square lattices of Fe and similarly high $T_c$ values.

Density functional calculations performed shortly after the discovery of superconductivity in Fe$_{1+y}$Se showed some similar aspects to the electronic structure of the chalcogenides and pnictides [48, 131], as illustrated in figures 6 and 7. In particular, the density of states shows predominant Fe character involving multiple orbitals near $E_F$, with a high density of states. It also shows that the Se occurs nominally as Se$^{2−}$, so that the Fe is in a d$^8$ configuration. Also, there is a dip in the density of states at this electron count, in contrast to what would be expected in a tetrahedral crystal field, where the d bands would split into a lower-lying manifold holding four electrons per Fe and an upper manifold of six. This result was supported by photoemission experiments [126, 131], showing that the calculated assignment of partial density of states (Fe and Se) is in accord with measurements, although stronger renormalization near the Fermi energy was found in comparison to the pnictides [126]. Also, first principles calculations show a tendency towards the same type of magnetic order in FeSe as in the pnictides [48, 132, 133]. Again there is substantial coupling to the lattice reflected in static distortion and sizable shifts of phonon frequencies at least at the level of static magnetism [132, 134].

Dynamical mean-field theory calculations, using realistic parameters obtained from first principles via a...
constrained random-phase approximation method, found a spectral function in qualitative accord with this stronger renormalization in relation to the pnictides [77, 81]. The calculations also found a feature at higher binding energy, though still within the Fe d bands that was identified as a lower Hubbard band, which is nomenclature usually applied to correlated materials with Mott physics, as in the cuprates. The parameters obtained by the constrained random-phase approximation method do suggest stronger correlation than in the pnictides $U = 4.01 \text{ eV}$ and $J = 0.91 \text{ eV}$ as compared to $U = 2.7 \text{ eV}$ and $J = 0.8 \text{ eV}$ for LaFeAsO [77, 135].

This result is consistent with the larger renormalizations in the chalcogenide. However, it is to be noted that the origin of the lower band is still with the Hund’s coupling rather than the Coulomb $U$, and so this may be viewed as a redistribution of spectral weight inside the d-bands due to Hund’s (magnetic) coupling rather than a conventional Hubbard band. Unlike a Mott system, features, which are qualitatively similar to this spectral weight at higher binding energies in the d-bands, do occur in standard DFT calculations when magnetism is included [92]. However, this comes at the expense of sizable stable ordered moments that do not exist in experiment. Therefore the issue may relate to understanding why and how the large moments in DFT calculations, which could be regarded for this purpose as a static mean field like method, are suppressed. As mentioned above, one possibility is that the suppression of the magnetic moments is due to quantum fluctuations as is the case in materials near a magnetic quantum critical point [89, 90].

Band structure calculations show disconnected Fermi surface sections, with hole sections around the zone center and electron sections at the zone corner, very similar to the pnictides. It should be noted that recent ARPES experiments see the electron sheets but not the predicted zone center hole sheets [136]. However, this may be an artifact of the measurements; such an electronic structure, if correct, would strongly violate Luttinger’s theorem implying that there are unseen compensating hole sections. The disconnected sheets observed in the pnictides are essential for the $s^+$ superconducting state.

In any case, the calculated electronic structure suggests similar magnetic behavior to the pnictides as was noted early on [48], but experiment did not see the SDW order and instead revealed a different order in Fe$_{1+\delta}$Te. This is the so-called ‘double-stripe’ order, as shown in figure 3. While this different order is also given by standard density functional calculations [92, 100], it does raise the question of whether the superconductivity could really be similar between these two different families within a spin-fluctuation framework given that the observed magnetic order is not the same.

Many experiments showed a similar type of superconductivity in the pnictides and the chalcogenides. Early muon spin rotation ($\mu$SR) measurements indicated gapless $s$-wave superconductivity, with two gaps [137]. Also, similar to the pnictides, NMR experiments on Fe$_{1+\delta}$Se do not detect a Hebel–Slichter peak, indicating unconventional superconductivity, and furthermore they show a connection between antiferromagnetic fluctuations and superconductivity as the spin fluctuations are enhanced approaching $T_c$, and also under pressure, where $T_c$ increases [138]. More directly, the superconducting resonance characteristic of a sign change in the order parameter at $(\pi/\alpha, \pi/\alpha)$ was observed in several inelastic neutron scattering experiments on various samples at different alloy compositions [139–143].

Neutron scattering studies of the evolution of the spin excitations as a function of composition in Fe$_{1+\delta}$Te$_{1-x}$Se$_x$.
showed that even though Fe$_{1+}$Te has a different magnetic order than the pnictides, when this order is suppressed by Se alloying, magnetic fluctuations characteristic of proximity to the SDW-type order emerge showing qualitative similarity to the pnictides [117, 139, 144, 145]. Bulk superconductivity was associated with the appearance of the SDW-type magnetic scattering in the experiments, while the competing double-stripe-type magnetism was found to be antagonistic to superconductivity [145]. Additionally, scattering was observed at wavevectors that correspond to nearest-neighbor magnetism as in the cuprates [144], suggesting that besides the double stripe, nearest-neighbor antiferromagnetism is a competing phase. This was also suggested by DFT calculations for TiFe$_2$Se$_2$ [146], which is a strongly antiferromagnetic compound [147].

Thus it seems that the superconductivity of the ‘11’-phase chalcogenides is similar both in nature (i.e. order parameter) and in relation to magnetism to that of the pnictides in spite of the fact that SDW magnetic order is not seen in the chalcogenides.

4. Some open questions

The superconductivity of the ‘11’ Fe-chalcogenides is clearly closely related to that of the pnictides, but as discussed, shows some key differences. These differences may be particularly useful for understanding Fe-based superconductivity, and perhaps more generally high-temperature superconductivity. In this regard, it is important that large high-quality single crystals can be made, especially of the Se–Te alloy [120, 148, 149].

One set of important questions about the Fe-based superconductors revolve around the nature of the magnetism in these materials. As discussed above, both the chalcogenides and pnictides show strongly reduced magnetism in ordered form relative to density functional calculations, and both show evidence of strong spin fluctuations. However, the driving force for the fluctuations as opposed to ordered magnetism has not yet been properly clarified. Furthermore, while the magnetism and spin fluctuations clearly couple to electrons near the Fermi surface, as seen for example in resistivity, the extent of the coupling and the role of the Fermi surface in the magnetism remain controversial. One aspect that could be important is competition of different magnetic states. In contrast to the pnictides, where SDW order dominates the phase diagrams, phases such as the double stripe are seen in the chalcogenides, as is nearest to nearest-neighbor antiferromagnetism; understanding these nearby phases, the fluctuations associated with them and their role in competing with the SDW type magnetism may be very helpful.

Another set of questions revolves around the strength, nature and role of electron correlations. No Mott insulating state that is plausibly close to the Fe-based superconductors has been identified, and as discussed above it is also not clear whether electronic features characteristic of Mott–Hubbard physics (e.g. Hubbard bands) exist in these materials. However, electron correlations are important as seen for example in the renormalizations of the bands. These correlations or at least their manifestations are different from those in cuprates. The multiorbital nature of the electronic structure may be a critically important aspect of the physics for understanding these differences. The multiple orbitals available at low energy can open channels for inter-orbital charge fluctuations that work against the Mott state. Such effects were approximately quantified by Gunnarsson et al. [150], who arrived at an approximate factor $1/\sqrt{N}$ to be multiplied by $U/W$ when assessing the proximity of a material to a Mott transition ($U$ is the effective Coulomb repulsion, $W$ is the band width and $N$ is the number of orbitals). In any case, as discussed above, the chalcogenides appear to be more strongly correlated than the pnictides and may therefore offer a more convenient window into the correlated electron physics of the Fe-based superconductors.

5. Summary and outlook

This article provided a brief overview of some aspects of the ‘11’-type Fe-based superconductors, which will hopefully stimulate research addressing the many outstanding questions about the physics of these materials. As noted above chalcogens are very different from pnictogens from a chemical point of view. The fact that the maximum $T_c$ of the chalcogenides is not much lower than that of the pnictides provides opportunities for better understanding Fe-based superconductivity as well as hope that additional materials may be found. Thus we may anticipate discoveries of new families of high-temperature superconductors related to the known Fe-based superconductors.

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References
