

Layered Iron High-Temperature Superconductors

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Superconductivity in the high-temperature iron-based materials can be mostly understood as a consequence of the repulsion mediated by spin fluctuations. When the spin susceptibility acquires a maximum around a Fermi surface nesting vector it can lead to a superconducting state with a gap that changes sign between the two nested parts of the Fermi surface. Based on the details of the band structure this can lead to wildly different results. Theoretical efforts have focused on predicting the symmetry and anisotropy of the gap, and while the definitive proof of an exotic new s_{\pm} sign-changing gap in many of these materials is still not found there is now little doubt about its validity. For now itinerant electron models that emphasize the on-site couplings appear to be favoured over strong-coupling models that start from (next)-nearest-neighbour couplings.

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1. Unconventional superconductivity	3	I. INTRODUCTION	
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E. Heisenberg localized antiferromagnetism	3	Since its discovery superconductivity has been an intriguing phenomenon. Its spectacular consequences such as eternally flowing currents and the total expulsion of magnetic fields seem counter-intuitive and are certain to capture the mind of aspiring physicists.	
F. Spin susceptibility itinerant magnetism	3	A theory explaining this phenomenon was proposed by Bardeen, Cooper and Scheiffer. In superconductors described by the BCS theory - also called conventional superconductors - lattice vibrations play a crucial role, which is clearly demonstrated by the isotope effect - the critical temperature in conventional superconductors scales with the frequency of lattice vibrations, which depends on the nuclear mass. The small energy scale of lattice interactions seemed to forbid superconductivity at room temperature and ambient pressure.	
1. Spin density wave order	4	The first major failure of the BCS theory was superconductivity in heavy fermion materials with partly filled f-shells. These necessitated the development of a new framework, in which the superconducting state can be highly anisotropic.	
III. Iron-based superconductors	4	Still it came as a surprise when superconductivity up to 35K was discovered in lanthanum barium copper oxide in 1986, quickly followed by the discovery of superconductivity in many more layered cuprate ceramics. In these materials, it is generally believed that not electron-phonon interactions but electron-electron interactions are the cause of superconductivity. The strong electronic interactions also manifest themselves through the antiferro-	
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magnetic transition that is close to the superconducting phase. Since electrons in the cuprates are localized the superconducting state has to be described in a different way than in the conventional superconductors, where the electrons delocalize over the lattice and form a Fermi surface. This has hampered its theoretical explanation, since the different electrons are so strongly correlated that the different degrees of freedom can not be treated independently.

In 2009 there was a new surprise for the field of superconductivity. Yet another class of high-temperature superconductors was found, this time not based on copper but on iron. The iron pnictide and iron chalcogenide superconductors were immediately compared to the cuprates. Strong parallels exist - the materials have a layered crystal structure and are prone to become antiferromagnetic. However there is one important difference. Even though electron interactions are relatively strong in this class of materials they are not strong enough to localize the electrons, and the normal state is not an insulator but a metal.¹

II. BACKGROUND THEORY

A. Fermi liquid theory

In any material with a half-filled conduction band there is a tradeoff between two effects. In metals the electrons in the half-filled levels delocalize over the entire crystal, forming a Fermi surface and lowering their kinetic energy. Even when there is some interaction between the electrons there is a way to describe the behaviour in terms of quasiparticles, excitations of the system with a well defined energy and momentum that are relatively stable and to first order non-interacting. This phase of material is the Fermi-liquid model, and describes most metals relatively well.

B. Strongly correlated systems

But this electron delocalization comes at some penalty to the potential energy, since there will now be some probability of finding two electrons in the same orbital at the same site in the crystal. This repulsion is called the Coulomb repulsion or Hubbard U . If it outweighs the kinetic energy gain from electron delocalization the material the electrons remain localized and the material becomes a so-called Mott insulator. The case of complete electron localization is called a strongly-correlated system. A theoretical description of strongly-correlated systems is more difficult than of Fermi-liquid materials. Because electrons are spread out in space in a metal they interact with a very large number of other electrons, and it is no big approximation to replace the exact configuration of the other electrons by an average. Localized electrons interact only with a few other electrons on neigh-

bouring sites, but between these electrons the interaction is much stronger. Therefore the correlation - that is to say, the way the fluctuations of the position of one electron are related to those of neighbouring atoms - are essential to the description of the electronic state, and it is insufficient to treat the other electrons as an average. There are also intermediate situations, where electron-electron interactions are important but not strong enough to localize the electrons. In such cases the material is metallic, but quasiparticles scatter each other so strongly that they cannot be treated separately. These are so-called non-Fermi-liquid materials.

C. Superconductivity

During the superconducting transition some fraction of the conduction electrons is bound into Cooper pairs. These pairs have integer spin and therefore behave like bosons, and immediately form a superfluid-like condensate, in which they are in a coherent superposition.

It is instructive to compare the superconducting wavefunction to the wavefunctions of a H_2 molecule. Depending on the sign with which the electron orbitals on the different atoms are combined the resulting wavefunction can be bonding or antibonding. Because there is an interaction the single-electron orbitals to contribute to the ground state wavefunction with a well-defined phase relation. Also, not only is the energy of the ground state lowered, there is also a corresponding increase in the energy of the first excited state which must be orthogonal to the ground state.

The superconducting condensate arises in a similar way, but in this case all electrons near the Fermi surface contribute to the superconducting ground state wavefunction. The wavefunction is not built out of single-electron states but from pairs of electron states. Those states are paired, in the sense that in the ground state the state with momentum k and spin s and the state with momentum $-k$ and spin $-s$ momentum are always both occupied or both unoccupied. If the energy of the single particle states - measured from the Fermi surface - is ξ_k the energy of the pair before the superconducting transition is $2\xi_k$. The total many-particle wavefunction superimposes all these electron pairs with a certain amplitude and a well-defined phase. The superconducting ground state is then

$$|BCS\rangle = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger}) |0\rangle \quad (1)$$

where all pair states are empty with amplitude $u_{\mathbf{k}}$ and filled with amplitude $v_{\mathbf{k}}$. The $c_{\mathbf{k}\uparrow}^{\dagger}$ and $c_{\mathbf{k}\uparrow}$ operators are respectively the creation and annihilation operators of an electron with momentum k and spin up. Because of the pairing interaction single-particle states with different energy and momentum become mixed. In the normal state at $T=0$ the occupancy instantly changes from fully occupied to fully unoccupied at the Fermi surface. In the

superconducting state due to the mixing of one-electron states above and below the Fermi surface the occupancy smoothly drops from one to zero in some energy range around E_F . The excited states must be orthogonal to the ground state, and hence are raised in energy. The energy of quasiparticle excitations in the presence of the superconducting condensate becomes $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}$. Δ acts as a binding energy, lowering the energy of the electron pair state with momenta $\pm\mathbf{k}$ in the presence of a condensate of electron pairs at other momenta. There are no states in an energy range between $-\Delta_{\mathbf{k}}$ and $+\Delta_{\mathbf{k}}$. The lowest energy excitation with momentum \mathbf{k} will create both an electron and a hole, and will cost energy $2\Delta_{\mathbf{k}}$. At nonzero temperatures there will also be unpaired electrons, and at the transition temperature T_c the superconducting condensate disappears and there are no paired electrons. This also implies $\Delta_{\mathbf{k}} = 0$ everywhere above T_c .

1. Gap equation

The form of the gap function $\Delta_{\mathbf{k}}$ follows from the shape of the Fermi surface and the interaction potential. A general form of the Hamiltonian in single band superconductors is

$$H = \sum_{\mathbf{k}} 2\xi_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow} + \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} U_{\mathbf{k}, \mathbf{k}'} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger c_{\mathbf{k}\uparrow} c_{-\mathbf{k}'\downarrow} \quad (2)$$

The first term gives rise to the energy $\xi_{\mathbf{k}}$ of the electrons pairs without considering the interaction while the second term corresponding to the scattering of pairs, representing the process where the electrons in a Cooper pair interact, so their momenta are changed from $\pm k$ to $\pm k'$. A negative value of $U_{\mathbf{k}, \mathbf{k}'}$ corresponds to an attractive force in real space. The superconducting wave function which is given by $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ is directly related to the gap function $\Delta_{\mathbf{k}}$. In the mean-field approximation the gap function at different values of k is related by the pairing interaction.

It is related to the attractive interaction $U_{\mathbf{k}, \mathbf{k}'}$ by the gap equation:

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{k}'} \frac{U_{\mathbf{k}, \mathbf{k}'} \Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} = - \sum_{\mathbf{k}'} \frac{U_{\mathbf{k}, \mathbf{k}'} \Delta_{\mathbf{k}'}}{2\sqrt{\Delta_{\mathbf{k}}^2 + \xi_{\mathbf{k}}^2}} \quad (3)$$

D. Conventional superconductivity

In conventional superconductors this state is energetically favourable because electrons near the fermi surface can attract each other by exchanging phonons. The attraction of this interaction can overcome the shielded repulsive coulomb interaction for small momentum transfers, because in these cases the response of the lattice is much slower than the speed of the electrons. Therefore

two electrons do not have to be at the same position simultaneously. The retardation of the lattice response is crucial, since without it the Coulomb repulsion would be stronger than the lattice-mediated attractive interaction. From equation 3 with $U_{\mathbf{k}, \mathbf{k}'}$ negative everywhere and maximal for values of \mathbf{k} and \mathbf{k}' close together it can be seen the gap is the same on all points of the Fermi surface. This shows that the superconducting state is rotationally invariant and hence that the Cooper pairs have zero orbital angular momentum. Such a superconductor is called conventional or s-wave.

1. Unconventional superconductivity

Surprisingly there can also be a superconducting stability if the pairing potential $U_{\mathbf{k}, \mathbf{k}'}$ is positive and hence repulsive for all momentum transfers, and has its maximum at some finite value of $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. In those cases there can be a solution where the wavevector \mathbf{q} connects two different parts of the Fermi surface. If the gap function has the opposite sign on those different Fermi surface components there can be a nontrivial solution.²³ This can be visualized as the electrons in some way becoming correlated in order to minimize their repulsive interaction, and thereby lowering their energy. This situation can lead to a gap function that transforms nontrivially under rotations of the crystal lattice. An example is the d-wave superconducting state in cuprates which has two nodal planes through the origin. Often the presence of nodal planes means the superconducting gap is zero on some part of the Fermi surface, but if the Fermi surface consists of different parts this is not always necessary.

2. Multiband superconductivity

The treatment of superconductivity can be generalized to situations where multiple orbitals are involved and multiple bands cross the Fermi level, like happens in a semimetal.

E. Heisenberg localized antiferromagnetism

Antiferromagnetism can occur in insulators if there are unpaired spins. This can be described using a Heisenberg spin-spin hamiltonian coupling the spins on various lattice sites.

F. Spin susceptibility itinerant magnetism

In an itinerant system the electrons are localized in momentum space, and the Fermi surface is the surface in momentum space that separates the occupied from unoccupied states. Introducing a spin wave, that is, a periodic modulation of the density of spin-up and spin-down

electrons, therefore corresponds to a redistribution of the electrons close to the Fermi surface. This redistribution costs kinetic energy.

1. Spin density wave order

Nesting of the Fermi surfaces can cause antiferromagnetic order, where states differing by a wavevector q mix together and a gap opens, having spin-polarized occupation for these parts of the Fermi surface. This instability can be calculated from a self-consistent field interaction, and is probable when the nesting vector connects parts of the Fermi surface with a high density of states, and corresponds to a large spin susceptibility. The ordering wavevector can be commensurate or incommensurate. The partial gap partially suppresses the scattering, and hence decreases resistivity. Since the AFM SDW order is suppressed by a magnetic field a positive magnetoresistance is expected.⁴

III. IRON-BASED SUPERCONDUCTORS

A. Crystal structures

The most important structure, that is shared between all high- T_c iron-based superconductors in this class, are tetragonal layers of iron atoms coordinated tetrahedrally to pnictogen (As or P) or chalcogen (S, Se or Te) atoms laying in a checkerboard pattern alternatingly above and below the squares. These layers of iron ions are the source of most electronic properties of these materials. In some cases the tetragonal lattice is distorted at lower temperatures and becomes orthorhombic. Between these iron pnictogen there can be different layers.

1. Iron pnictides

There are various classes of FeSC's with the pnictogen As or P coordinated to the iron layers. All of these derive from a non-superconducting antiferromagnetically ordered parent compound, that becomes superconducting when the magnetic order is suppressed by doping. In the literature these classes are often referred to by the stoichiometric indices of the parent compound. High T_c superconductivity in iron pnictides was first discovered in LaFeAsO upon doping by substituting F for O. The lanthanum atom can be replaced by various other atoms, giving the class of 1111 FeSC's.

Another class of iron pnictides in which superconductivity can be induced has stoichiometry 122. These materials derive from BaFe₂As₂ where Ba can be sometimes replaced by Sr, Ca or K. These materials can be electron doped by substituting cobalt for iron, or hole doped by doping K for Ba. Since their discovery this class of FeSC's was widely studied because it is relatively easy to

grow large single crystals.

AFeAs is an example of the 111 class, where A stands for Li or Na.

Often the arsenide can be partially replaced by phosphorous.

2. Iron selenides

Iron-chalcogen superconductors have a similar structure. The most well-studied class is known by its stoichiometry 11. It consists of only stacked FeSe or FeTe layers, possibly with S substitutions. There are also chalcogenide superconductors with layers of for example intercalated K, Rb or C with the 122 stoichiometry, or more complicated materials with the stoichiometry 234 and 245 where mesoscopic phase-separation of iron vacancies appears to occur, so the crystals show simultaneous AFM and superconductivity, but they do not co-exist microscopically.⁵

B. Electronic structure

The electronic structure of FeSC's can be predicted using density functional theory. The only partially occupied levels are the 3d levels of the iron atoms. In the undoped state the configuration is $3d^6$. The tetrahedral crystal field lowers the two e_g levels, so most of the density at the Fermi level originates from three partially occupied t_{2g} . However, accurately describing the electronic structure requires the consideration of all five 3d orbitals. The p band of the pnictogen or chalcogen above and below the iron plane is roughly 2eV lower in energy, and its contribution to the Fermi levels can almost always be ignored.

1. Fermi surface

Because the electronic overlap and therefore the hopping in the z direction is much weaker than the in-plane hopping the Fermi surfaces are almost cylindrical, and show little dispersion in the out-of-plane direction. Therefore the electronic structure is often approximated by a two-dimensional Fermi surface.

2. Band structure

The real unit cell of all iron superconductors contains two Fe ions, so calculations considering all five 3d orbitals on both atoms would have to consider 10 bands. However the two atoms are almost equivalent, and connected by a glide symmetry in the iron plane. In calculations that do not involve the dispersion of the band along the z

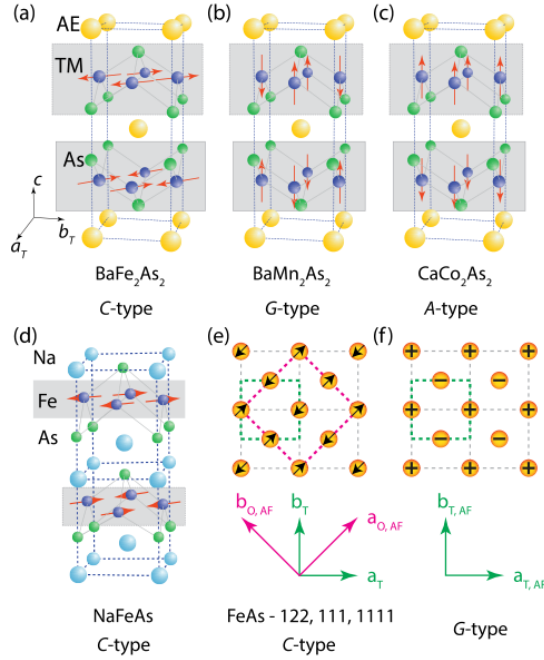
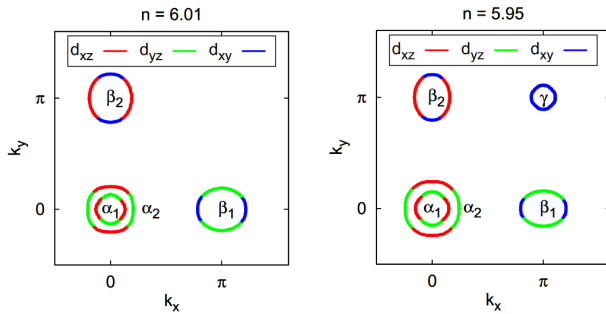


Figure 1. 122 type structure

Figure 3. Predicted Fermi surface of LaFeAsO. Reproduced with permission from ⁶

direction the distinction between these two atoms is irrelevant. In such cases it is often easy to consider a unit cell containing only one Fe atom. The Brillouin zone will be twice as big as the real 2-Fe unit cell. It can be obtained by unfolding the Brillouin zone as shown in figure 4. For experiments like ARPES the real folded Brillouin zone has to be considered.

The shape of the Fermi surface is shown in figure 3. It consists of two hole-like parts near the Γ point, and an electron-like part near the X/Y point. In the hole-doped materials there can appear an extra hole-like component.

3. Fermi surface nesting

An important consequence of the two-dimensional nature of the Fermi surface is that the bands are almost par-

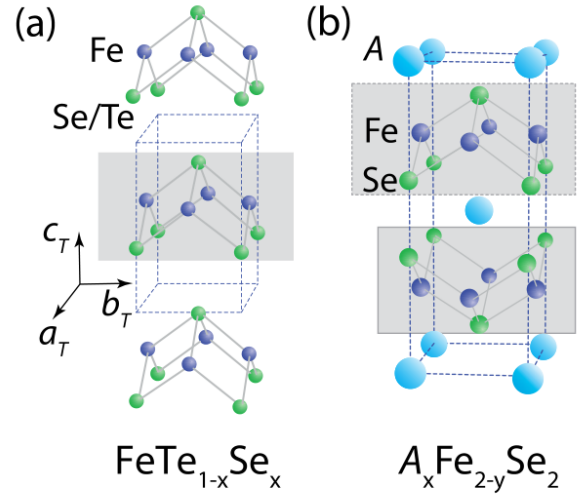
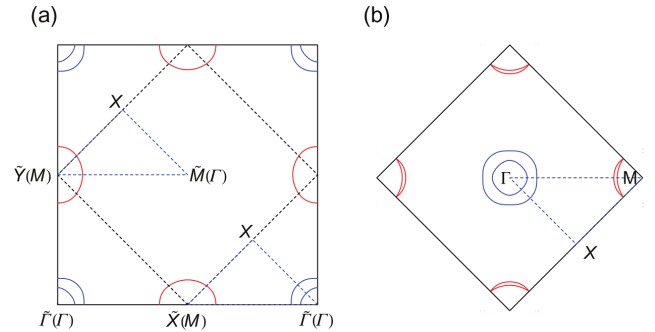


Figure 2. a) 11 type structure b) 122 type structure

Figure 4. a) Two-dimensional cut through the unfolded 1-Fe Brillouin zone b) Cut through the real 2-Fe Brillouin zone. Reproduced with permission from ⁷

allel in one direction. When two parts of the Fermi surface are parallel there may exist a wavevector q that connects many states on the different parts of the Fermi surface. The presence of good Fermi surface nesting favours the formation of instabilities such as a charge or spin density wave. The vectors connecting the center of one of the electron pockets to a hole pocket or connecting the two electron pockets have good Fermi surface nesting.

4. Doping and pressure.

Electronic doping can be achieved by substituting the atoms in the layers above and below the iron layers, or by replacing iron by differently charged ions. This has

the effect of moving the fermi level. Electron doping will expand the electron pockets and shrink the hole pockets, hole doping has the opposite effect.

The distance between iron atoms plays an important role, because it determines the orbital overlap. The distance can be changed by applying pressure, or by chemical substitutions. For example partially substituting As with P in the iron pnictides or Te with S in the iron calcogenides.

C. Magnetic structure

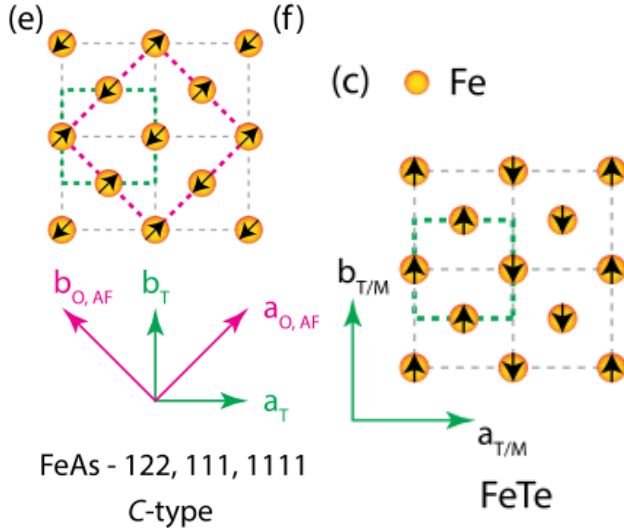


Figure 5. Magnetic structure in BaFe_2As_2 and FeTe . Reprinted from⁵

A stripe-type SDW antiferromagnetic order occurs in the parent compound of the superconducting iron pnictogens. $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ material.⁴

IV. PHASE DIAGRAMS AND COMPETING ORDERS

A. Iron pnictogens

In all pnictogens where superconductivity has been observed it displays a phase diagram like 6, and is adjacent to a antiferromagnetically ordered SDW state. The superconducting state occurs in a region of the phase diagram where the AFM order is suppressed by doping the parent compound. The superconducting state then occupies a dome shaped region in the phase diagram. Different kinds of substitutions in BaFe_2As_2 can induce superconductivity. These include hole doping to $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ or $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{Se}_2$, electron doping to $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Se}_2$ or $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{Se}_2$ or isoelectronic doping by substituting P for As or Ru for Fe.

In these compounds the antiferromagnetic order is accompanied by an orthorhombic distortion of the iron sub-

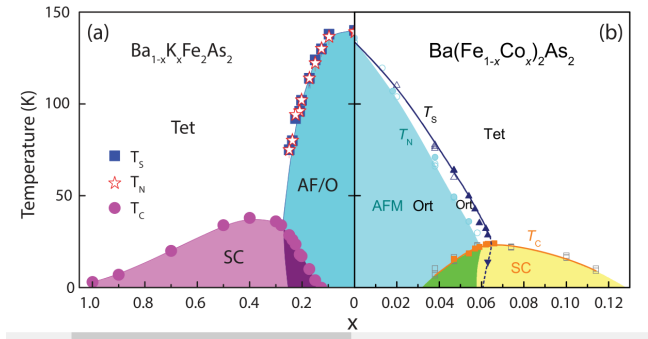


Figure 6. Superconductivity occurs in BaFe_2As_2 when it is sufficiently hole doped (a) or electron doped (b)⁵. (a) Reprinted with permission from⁸. (b) Reprinted with permission from⁹

lattice, accompanied by an anisotropy in various optical and transport properties.

B. Iron selenide or related compounds

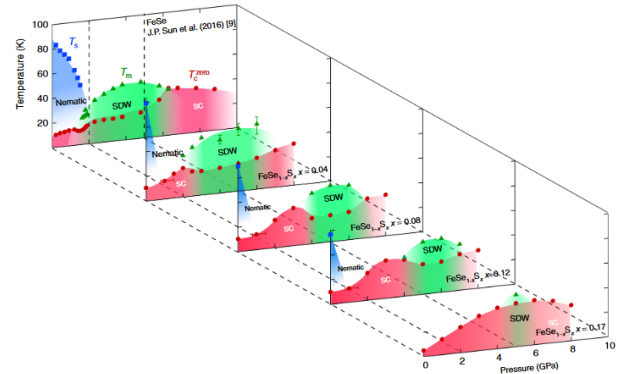


Figure 7. Upon cooling FeSe first undergoes a nematic phase transition, and later becomes superconducting. Pressure first suppresses the nematic phase and later induces a spin density wave state.¹⁰

Böhmer and Kreisel have written an up-to-date review on the competition of different types of ordering in FeSe ¹¹.

V. PAIRING MECHANISM

A. Singlet or triplet pairing

In conventional superconductors Cooper pairs are formed from electrons with opposite spin, so the pairs have total spin zero. In some superconductors electrons with the same spin will pair, forming a triplet state with spin one. This can occur when the pairing interaction acts between electrons of equal spin.

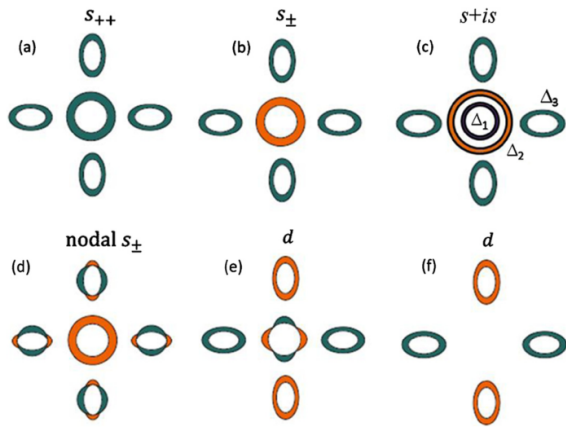


Figure 8. Possible form of nodal and nodeless sign-changing gaps. Reprinted with permission from¹³

Experimentally the total spin of the electrons will not change if triplet pairs are formed, but will disappear if a singlet pair is formed. The difference can be seen from NMR measurements of the Knight shift, which is due to the dynamic spin susceptibility of electrons surrounding a nucleus. A discontinuity of the Knight shift was observed for almost all FeSC's, indicating a singlet spin pairing. Since the total pairing wavefunction of the must obey the antisymmetry condition under particle exchange, and since the singlet is antisymmetric the momentum part of the wavefunction must be symmetric.

B. Shape of the superconducting band gap

The most intuitive way of studying the superconducting gap is ARPES. However it is not sensitive to the sign of the gap, and has problems with surface reconstruction/getting a good resolution. One hallmark of a sign-changing gap is that a loop through a polycrystalline sample can contain half-integer flux quanta. This has been observed for 1111 iron pnictides.¹²

C. Gap nodes

The band gap can be studied in experiments that probe the density of electronic states. If there is a gap at all points on the Fermi surface a minimal amount of energy is required to form an excitation, as can be seen from the quasiparticle spectrum. However, if the gap vanishes at some point on the Fermi surface there will be some density of excitations available at all energies. This can be observed in different measurements, like ARPES or scanning tunneling spectroscopy.¹³

1. s_{\pm} -pairing or d-pairing

The presence of multiple Fermi Spin fluctuations were quickly predicted to cause a band gap that changes sign between different parts of the fermi surface. The band gap can be s_{\pm} if it changes sign between the Γ and the X/Y points, or d-type if it changes sign between the X and the Y point.¹⁴

In some of the materials the band gap vanishes for some angles in Fourier space. This leads to the possibility of exciting quasiparticles in those directions. The phase difference of the band gap can only be determined by a few experimental methods, for example pair tunneling. Large variation of properties with doping/pressure, as compared to cuprates.

D. s_{++} -pairing

Spin-driven s_{\pm} -pairing competes with orbital driven s_{++} -pairing, which is present in some cases.^{13,15}

E. Spin waves and neutron spin resonance

The presence of a superconducting condensate modifies the spectrum of the fluctuations that it interacts with. By comparing the spectrum of fluctuations above and below the critical temperature it can be clearly verified how the spectrum is changed. In FeSC's this leads to the appearance of a broad peak in the spin fluctuation spectrum, whose wavevector corresponds to the Fermi surface pairing. This is accompanied by a decrease in the spectral density of spin fluctuations at different wavevectors. The strength of this resonance has the same order-parameter-like temperature dependence as is expected for the superconducting gap. For example in doped LaFeAsO there is a broad AFM fluctuation (predicted shortly after the discovery of the superconductivity). The broadness of this peak explains why it doesn't lead to magnetic ordering but to a sign changing superconducting state.¹⁶ Inelastic neutron scattering reveals the presence of a collective mode with an appropriate momentum to pair the hole and electron Fermi surfaces.^{16,17} In general the shape of the two Fermi surface components being connected by a nesting vector can be slightly different. If one of the pockets is elongated there can be two different vectors that give optimal nesting. In such cases a corresponding split in the neutron spin resonance to two peaks at slightly incommensurate wavevectors has been observed, confirming that this resonance is indeed best explained in terms of the Fermi surface nesting.

F. Impurity bound states

The presence of mid-gap bound states is evidence in favour of the presence of a sign-changing gap function. If

the gap does not change sign such bound states are not expected.¹³

G. π -loops and half-integer flux quanta

One consequence of superconductivity is the quantization of the amount of magnetic flux passing through a superconducting loop. This quantization is a result of the phase-coherence of the superconducting gap. On going around a loop in a superconductor, the phase change has to be an integral multiple of 2π . A possible way to investigate the symmetry of the gap is by forming a phase-coherent loop containing an unconventional superconductor with a sign-changing gap and a conventional s-wave superconductor. At the junction between the different superconductors there will be phase continuity between the cooper pairs tunneling across the junction. In a d-wave superconductor the cooper pairs with momentum in the x-direction have an opposite sign to those with momentum in the y-direction. Therefore, if a junction is formed to differently oriented phases, there will be an extra factor π on going around the loop, and the flux quanta will be quantized to an integral number plus one half flux quantum.

A similar situation appears in sign changing s-wave superconductors. If one junction has a barrier that favours tunneling to the electron pockets, and the other junction favours tunneling to the hole pockets there will be a half-integer number of flux quanta in the loop. This situation cannot be created reliably, but by testing a large number of junctions such half-integer flux quantization has been found.¹²

H. Bogliubov quasiparticle interference

Scanning tunneling spectroscopy shows interference patterns around impurities. This is due to interference of scattered with unscattered quasiparticle state. The fourier transform of this interference pattern should show a peak at the most likely scattering wavevectors, which are determined by the joint density of states of the scattered and unscattered states. The density of states is largest at those points of the bands where dk/dE is largest: the tips of constant energy curves. Tracing these tips can then directly be used to map the anisotropic energy gap.^{18,19}

An alternative way used to measure the gap is point contact Andreev reflection²⁰.

VI. ELECTRON CORRELATION

A. Closeness to Mott-insulating state

Bad-metal behaviour can be seen in FeSC's from the optical conductivity measurements, or by changing the

interparticle spacing (and hence bandwidth) by substituting smaller atoms. Some authors emphasizes the role of electron correlations in Iron based unconventional superconductors, and their closeness to a Mott insulating state.²¹ The intersite couplings can be elucidated using the spin-statistics theorem, by measuring the dynamical spin susceptibility using inelastic neutron scattering.

B. Electron nematicity

In many iron-based superconductors a small structural tetragonal-to-orthogonal transition in the iron plane occurs. Under electron doping this transition appears shortly before the occurrence of antiferromagnetism, while with hole or isoelectronic doping it occurs simultaneously with the antiferromagnetic transition. Observing this anisotropy requires a detwinned crystal, which can be obtained by applying uniaxial stress while the crystal is cooled through the structural transition temperature²². A proposed explanation involves the "striped phase" antiferromagnetic order. This order has alternating spins along one direction, and parallel spins along the other one (ie column-like). This clearly breaks the C_4 symmetry. It is proposed that this symmetry breaking can occur shortly before the sublattices become completely ordered.²³

1. Nematicity in FeSe

The nematic transition in FeSe can be seen in ARPES as a splitting of the xz and yz bands, so that only one band contributes to the fermi surface density. This splitting is reduced upon chemically doping the material by substituting S for Se (increasing the iron orbital overlap)²⁴ FeSe does not normally form a magnetically ordered SDW state, but it does show a nematic state. Recently a strong x-y anisotropy in the gap on the hole pocket in FeSe was found using BQPI.¹⁸ This is consistent with the predicted gap assuming the pairing interaction strength is different for pair in different orbitals, and strongest for the d_{yz} orbital. Recent ultrafast pump-probe measurements also gave new insight into the nematicity in FeSe, showing nematic fluctuations persist to temperatures far above the structural transition temperature²⁵. Recently a similar effect was seen in iron pnictides.²⁶

VII. OUTLOOK

So far all iron pnictide and iron selenide superconductors appear to have a unified origin. A model where the pairing is a consequence of the exchange of repulsive spin fluctuations that appear close to an antiferromagnetic transition can explain essentially all observations. This can for example explain the shape of the superconducting gap function and its anisotropy, as

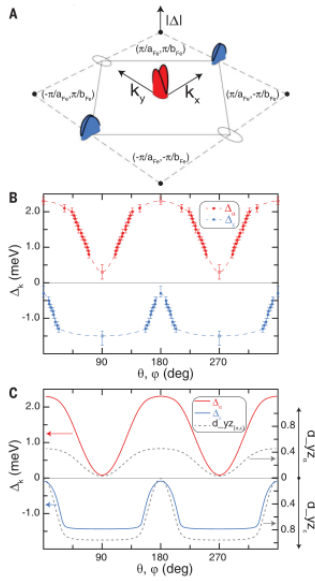


Figure 9. BQPI shows an anisotropy in the superconducting gap for FeSe in its nematic state. The anisotropy doesn't adhere to the C_4 tetragonal symmetry, and can be explained by an orbital-selective pairing interaction. Reprinted with permission from ¹⁸

well as their variation with hole or electron doping. The spin fluctuation spectrum and the position, structure and temperature dependence of the observed neutron spin resonance lends further support to this model. Due to the complicated fermi surface structure and multiorbital nature of these materials the nature of the developed instability can depend sensitively on the details of the material. Importantly, from theory and experiment it is clear that the sign-changing s_{\pm} and the d type superconducting state can both occur depending on the precise size and orbital content of the different electron and hole pockets.

In the 11 type materials derived from FeSe the situation at first appeared rather different, since there is an orbital nematic transition that is not accompanied by antiferromagnetic order except under high pressure. However recent experiments show that the nematic transition is similar to that in iron-pnictides in its specific heat, magnetic susceptibility and resistivity.

The fact that many different terms in the Hamiltonian contribute to similar processes makes it difficult to draw hard conclusions. This is made worse by the fact that all calculations are only approximately correct, casting some doubt on specific predictions. This tension can be seen in attempts to answer the question whether an itinerant model with on-site couplings or a localized model with nearest-neighbour spin couplings is more appropriate. Though it is not impossible these models are to some extent equivalent there is no reason to believe them to be. However both approaches have in many cases found agreement to the same experimental

observations of for example the superconducting gap function and the spin fluctuation spectrum.

It can be hoped that with the increase of computational power and the increasing sophistication of mathematical models the situation can be resolved. However, because there are many possible interaction channels in a material with in principle ten different orbitals contributing and at least four bands crossing the Fermi surface, and with both strong charge fluctuations and orbital instabilities, there is always the risk that models can be easily adjusted to reproduce the observed results. Therefore it will also be of paramount importance to find accurate experimental techniques to determine the various parameters that serve as the starting point for these models.

A. Non-universal behaviour

Only the monolayer FeSe superconductor is clearly different from the others considered, since its a coupling to a phonon mode points to rather different physical processes. With a T_c of 80K this material also reaches the highest superconducting transition temperature of around of all iron-based unconventional superconductors. However this is still far off from the results obtained in cuprate superconductors, and the material does not look very promising for practical applications.

B. Implications for the field of unconventional superconductors

In a way the FeSC's and cuprates are different sides of the same coin. Both involve strongly correlated systems with strong magnetic fluctuations, helped by the low dimensionality of the system. But while the cuprates necessitated a new framework for superconductivity in systems with localized electrons the FeSC's are best understood as itinerant electron materials. It is now clear that all materials with strong electron correlation and fluctuations of any kind have the potential to be new superconductors. Materials with an interesting Fermi surface structure are especially important, and in combination with the fluctuation spectrum it can serve as a starting point in this investigation.

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