Non-cuprate exotics III: The ferropnictide (FeAs) superconductors[1]

Superconductivity in this group of materials was discovered in January 2008: it shows the highest T_c ($\sim$ 55K) of any non-cuprate material. All compounds in this class contain a transition metal (usually Fe)[2] and a pnictide element (same column of periodic table as N), usually As, or a chalcogenide (Se or Te). By now four classes of ferropnictides have been discovered, denoted respectively by "1111", "122", "111" and "11." The 1111 class is derived from a parent compound with the formula

$$\text{(RE)(TM)(PN)O} \qquad \text{RE} \equiv \text{rare earth, TM} \equiv \text{transition metal, PN} \equiv \text{pnictide, O} \equiv \text{oxygen}$$

A typical example is

$$\text{LaFeAsO} \qquad \text{(“iron oxypnictides”)}$$

This class is not superconducting in the parent state, but becomes so when some of the O is replaced by F: $\text{LaFeAsO}_{1-x}\text{F}_x$ and then can have T_c up to $\sim$ 55K ($\text{SmFeAsO}_{1-x}\text{F}_x$, $x \approx 0.15$). (also pure O deficiency)

The second class, "122" has the formula $(\text{AE})(\text{TM})_2(\text{PN})_2$ (AE $\equiv$ alkaline earth): example is BaFe_2As_2. This class is (sometimes) superconducting in the parent state, but with a low T_c (a few K); T_c can be raised to $\sim 38K$ by partial substitution of the AE by an alkali, e.g. $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$. A third class, "111" has the formula A(TM)(PN) (A$\equiv$ alkali), e.g. LiFeAs. In this case, superconducting transition temperatures up to $\sim$ 20K are reached already in the pure stoichiometric material without chemical doping. Finally, there is a class "111" with the simple formula (TM)C (C$\equiv$ chalcogenide), e.g. Fe Se.; note that this class contains no As, although the structure of the Fe Se (etc.) planes seems to be very similar to that of the Fe As planes in the other ferropnictides (on which see below).

In the first year or so of the subject, most experimental work was done on the "1111" compounds; however, following the discovery that unlike these the 122's could be prepared as large single crystals, attention has tended to shift to them. Less work has been done on the 111 and 11 classes, in the latter case partly because the behavior seems extremely sensitive to small variations in doping and disorder.

Structure and chemistry

The 1111 compounds crystallize in the so-called ZrCuSiAs structure; within each unit cell we have a "LaO layer" (roughly, two La planes sandwiching an O plane) and a "FeAs layer" (2 As planes sandwiching an Fe plane). In the tetragonal phase (see below) the ab-plane

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[1] A good partial review, which concentrates on the magnetic properties is Lumsden et.al., J. Phys. Cond. Mat **22**, 203203 (2000)

[2] LaNiPO is superconducting but only at $4-5$K.

lattice constant is ∼ 4 Å, the c-axis l.c. ∼ 9Å (cf. the cuprates). The Fe-Fe spacing is ∼ 2.85Å. In the parent compound (e.g. LaFeAsO) the ionization state[3] is believed to be $(La^{3+}O^{2-})^+(Fe^{2+}As^{3-})^-$, i.e. the LaO layer is (doubly) closed-shell, the As is (roughly) closed-shell and the Fe is $3d^6$. There is believed to be some hybridization between the 5 Fe $3d$ states and the As $4p$'s. When F (Z = 9) is substituted for O (Z = 8), the extra electron is believed to migrate to the FeAs layer, giving (at $x \sim 0.1$) a carrier density (above the parent compound) of $\sim 10^{21}\text{cm}^{-3}$. This number, and also the fact that the "charge reservoir" (in this case the LaO layer) is well separated from the metallic (FeAs) layer, is similar to (some of) the cuprates; however, note that the 1111 series is *electron*-doped.[4]

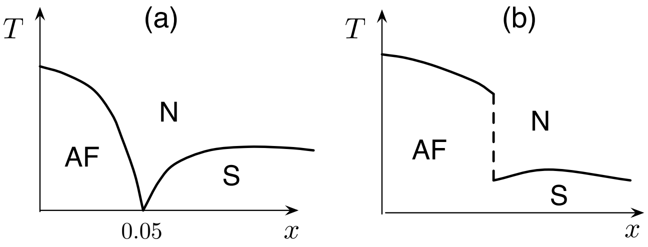
In the 122 compounds (e.g. $CaFe_2As_2$), the unit cell ($a = 3.9$Å, $c = 11.7$Å) contains two similar layers, each of them with two planes sandwiching an Fe plane, separated by an alkaline-earth plane. (Again, the charge reservoir (Ca → K) layer is relatively distant from the Fe atoms.) Note that substitution of an AE by an alkali (e.g. $Ca_{1-x}K_x$) gives *hole* doping, as in the cuprates and again, for $x \sim 0.1$ the (extra) carrier density is $\sim 10^{21}\text{cm}^{-3}$.

Note that in the 1111 compounds many RE's are possible (La, Sm, Ce, Nd, Pr, Gd) (though T_c may be only ∼ a few K, e.g. for Gd); in the 122's Ba, Ca, Sr work.

Phase diagram (preliminary)

At sufficiently high temperatures, for all dopings, both the 1111 and 122 materials are metallic, tetragonal and have no magnetic order. In the parent compounds, at temperatures ∼ 140K (1111) and ∼ 170K (122) one gets a tetragonal → orthorhombic crystallographic transformation, and at a somewhat lower temperature a *spin density wave* forms, in "striped" form (the system is still (somewhat) metallic).

For relatively small doping x (∼ 0.05) both the crystallographic transition and the magnetic one disappear, and for larger values of x the system becomes superconducting at low T. The phase diagram sometimes looks like (a) (2nd order) sometimes like (b) (1st order).



Note that as in the cuprates, the superconducting T_c has a maximum as a function of x (at ∼ 0.12 for La, ∼ 0.15 for Sm), but in contrast to the cuprates it is very "shallow" (i.e. T_c is not very sensitive to x). T_c can sometimes be somewhat increased by pressure: e.g. for La 1111 T_c is 16K at ambient pressure but 43K at 4GPa.

The structure of the AF phase is a major topic in its own right, see Lumsden et.al., op. cit. Briefly, the in-plane magnetic ordering is antiferromagnetic along one axis and ferromagnetic along a perpendicular one, but the axes are diagonal for the 1111 compounds but "square" (i.e. along the crystal axes) for 122 ones.

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[3] Recall: Fe: $3d^6 4s^2$, As: $4s^2 4p^3$, La: $5d6s^2$, Sm: $4f^6 6s^2$.

[4] But hole-doping is also sometimes possible, e.g. La → $La_{1-x}Sr_x$, $T_c = 25$K (cf. cuprates)

There is sometimes a small region of the phase diagram where antiferromagnetism and superconductivity appear to coexist, but it is debated whether this is phase-separated.

Experimental properties

Most experiments are on (1111) or (122) classes. In the following, I will make "default" assumptions that results of experiments done on any one member of a class (e.g. La, Sm . . .) are representative of behavior of class as a whole. However, properties of (1111) and (122) classes may be nontrivially different. When not stated, the doping level corresponds to the region where the superconducting states is stable.

Experimental properties: N state

The *specific heat* fits roughly to the textbook $\alpha T + \beta T^3$ formula, though when there are structural or magnetic transitions the parameters α and β change there. There is a very small anomaly close to T_c and a pronounced anomaly at a few K (attributed to magnetic ordering of the RE ions).

The *susceptibility* $\chi(T)$ is roughly $A + BT$ for 125K $< T <$ 300K for (1111) samples, with $A, B > 0$. For the 122 samples it has a kink (_|¯) around 150 − 200K.

The *dc resistivity* ρ of polycrystalline samples is $\sim 3\text{m}\Omega\,\text{cm}$ at RT (about 10^3 of that of Cu, comparable to (ab-plane) ρ of cuprates). Above T_c it can be fitted approximately to something between $A + BT$ and $A + BT^2$. $(A, B > 0)$

The *Seebeck coefficient* is rather large: for F-doped samples it is $\sim -95\mu$V/K at 100K.

The *Hall coefficient* fits roughly $A + BT$, with $A < 0$, $B > 0$: if we take the value at RT and interpret it according to the naive theory ($R = 1/ne$) it corresponds to negative (electron) carriers with $n \sim 1.8 \times 10^{21}\text{cm}^{-3}$.

The optical properties[5] appear to be qualitatively similar to those of the cuprates; in particular there appears to be a broad"midinfrared" peak centered at around 0.6-0.7 eV. If we attempt to fit it to a Drude form, the inferred plasma frequency is around 1.3-1.4 × 10^4 cm^{-1} (1.6-1.7 eV), comparable to that in the cuprates. It is a very interesting question, which to the best of my knowledge has not been answered explicitly in the existing literature, whether the phase of the dielectric constant in the MIR regime is close to $3\pi/4$ as it is in the cuprates.

Fermiology

Let's start by asking what qualitative predictions we might be able to make about the band structure, and hence the Fermi surfaces(s), on the basis of a naive tight-binding model. For the moment we concentrate on the states deriving from the Fe orbitals (since the other atoms are expected to be mostly in a closed-shall configuration). Recall that in the isolated

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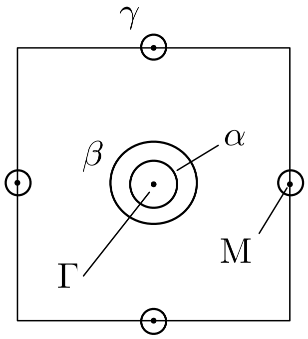
[5] For a partial review which is however already somewhat outdated, Hu et al., Physica C 469, 545 (2009).

Fe^{2+} ion, there are 6 d-shell electrons, which must occupy (some of) the 5 d-orbitals. In the presence of a tetragonal lattice, we expect the states to split into (a) a d_{3z^2-1} state, oriented mainly along the z-axis (normal to the Fe As planes) (b) two states, d_{xy} and $d_{x^2-y^2}$, which are mainly in plane, and (c) two states, d_{xz} and d_{yz}, which have appreciable components both in- and out-of-plane. Note that in an intuitive sense the states (a) and (b) respect the in-plane ($x \leftrightarrow y$) tetragonal symmetry, while the two states (c) explicitly break that symmetry.

When we allow for hopping between Fe atoms, as in a simple tight-binding model, we would expect that the 5 atomic d-orbitals would broaden into the corresponding bands; since the structure of all the ferropnictide classes is strongly layered, we might expect that these bands would be mainly 2-dimensional. A quantitative LDA calculation[6] for 1111, which also takes account of other possibly relevant orbitals such as the As 4p's, confirms this expectation: it predicts that there are 5 relevant bands, of which three are centered at the FBZ center (Γ-point) and two at the zone edges: see the figure, which shows four of the five resulting pieces of the Fermi surface (near optimal doping)



The three bands centered at Γ are all hole-like: two of them (shown in the figure) are strongly 2-dimensional, giving barrel-shaped (nearly cylindrical) 3D Fermi surfaces, while the third, which is not shown in the figure and is derived from the atomic d_{3z^2-1} orbital, is much more 3-dimensional. The two bands centered at the M points are electronlike. Subsequent calculations along similar lines give similar results for the 122 compounds.

It is rather satisfying that both ARPES and quantum-oscillation (Shubnikov-de Haas) data seem to agree well with the theoretical LDA predictions. Thus, in distinction to the case of the cuprates (but similarly to Sr_2RuO_4), the band-structure and Fermiology are more or less noncontroversial, at least in the doping regime where the S state is observed (i.e. where there is no orthorhombic or magnetic ordering).

Experimental properties: S state

In part because their discovery is so recent, and in part because of the number of different families, our present knowledge of the S-state ferropnictides is less systematic than in the case of the cuprates; in particular, there seem to have been few experiments which probe the limiting T → 0 temperature-dependence of quantities such as the spin susceptibility or penetration depth. However, there are a few things one can say with confidence.

(1) Magnetic properties: The ferropnictides are strongly type-II, with values (for 1111) of $\partial H_{c2}/\partial T|_{T_c} \sim 4.9T/K$ for H ∥ ab, 2.5 T/K for H ∥ c, giving an extrapolated

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[6] Singh et al., PRL **100**, 237003 (2008)

value of $H_{c2}^{(ab)}$ T=0) of $\sim$ 55T. (still considerably smaller than for cuprates); if interpreted according to standard GL-type theory this would give $\xi_{ab}(0) \sim 20\mathring{A}$. The low-temperature (ab-plane) Landon penetration depth is typically $\sim$ 1600-3000 $\mathring{A}$, consistent with the estimated carrier density.

Note: (i) the degree of anistropy, as measured by H_{c2}, is rather small compared with that of the cuprates.

(ii) if we take $\Delta(0)/k_R T_c$ to have the BCS value, then (for 1111 compounds). $H_{cz}^{(ab)}(T)$ exceeds the CC limit already at T $\sim$ T$_c$/2. On the other hand, for the 111 compound $K_xFe_{1-y}Se$ Torchetti et al* find that H$_{c2}$ is definitely CC-limited.

(2) Susceptibility and nuclear relaxation: at least for K FeSe, the spin susceptibility drops steeply below T_c, as does the quantity $(T_1T)^{-1}$(no HS peak). The low-temperature asymptotic behavior is not clear; if anything, indications are that $(T_1T)^{-1}$ follows a power law, but an exponential can probably not be excluded.

(3) ARPES: The most definitive experiment appears to be the recent one of Xu et.al.†, who claim to have measured the complete 3D dependence of $|\Delta(\mathbf{k})|$ on all five sheets. They find that $|\Delta|$ is nonzero for all sheets and all $\mathbf{k}$: for the four "2D" bands they find that $|\Delta|$ is well fitted by the expression

$$|\Delta|(\mathbf{k}) \cong \text{const. } (1 + \eta \cos k_2) \qquad\qquad (k_2 \text{ in units of } \pi/d_c)$$

where η = 0.17, 0.13 and 0.01 for the α, β and γ bands respectively. (Thus, the $\gamma(d_{xz}, d_{yz})$ gaps are almost entirely 2D in character).

(4) Neutron scattering: The most striking new feature observed in the inelastic neutron scattering (INS) spectrum below T_c in the superconducting state is a prominent resonance which appears at approximately $Q = (\frac{1}{2}, \frac{1}{2}, 0)$ (the "antiferromagnetic" RLV).†† This resonance is observed in (at least) the 1111, 122 and 11 families, and in each case occurs at an energy of approximately $5k_BT_c$, which is somewhat similar to that of the famous "41 meV peak" occurring in the cuprates. ($k_BT_c \sim$ 8 meV). However, note that in the cuprates the 41 meV peak has to date been observed only in the odd channel of bilayer compounds, whereas all the ferropnictides are single-layer.

(5) Optics: A very interesting recent experiment by Charnukha et.al.§ measures the spectral weight shift between the N and S states. This is an ellipsometric measurement over the whole range 12 meV - 6.5 eV, on the 122 compound $Ba_{0.68}K_{0.32}Fe_2As_2$. They find, inter alia, an increase in $Re\ \epsilon(\omega)$ above 2.5 eV but a marked decrease

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[*] Phys. Rev. B **83**, 104508 (2011)

[†] Nature Physics **7**, 198 (2011)

[††] see Lumsden et al., op. cit, Sec. 4.3.

[§] Nature Communications **2**, 219 (2011). (Note their sign convention for $\Delta\epsilon$)

below 2.5 eV, at least down to 1.7 eV (data at lower energies is not shown).; this is strikingly similar to the behavior seen in the cuprates, cf. l. 12.

(6) Josephson experiments: To the best of my knowledge there are to date no "planar" Josephson experiments similar to those conducted on the cuprates. However, there is one experiment[‡] in which a Nb pickup coil is moved over the surface of a (presumably polycrystalline) 1111 sample surface, and the flux through the loop detected; the main qualitative result is that half-integral flux jumps as well as integral ones are seen.

(8) Finally, a note on the dependence of T_c on various parameters:

(a) T_c can be enhanced very substantially by pressure (e.g. from 26K at p = 0 to 43K at p = 5 Gpa in $La\ O_{1-x}F_xFeAs$).

(b) If one compares the four currently known families of ferropnictides (cf. Lumsden et al., fig 1) one notices a strong correlation between T_c and the distance between FeAs planes (i.e. greater distance → higher T_c). In fact, by inserting the spacing layers $SrVO_3$ a T_c of 37 K was reached in a stoichiometric material, suggesting that further improvement may be possible.

(c) T_c appears to be relatively insensitive to replacements not only in the "charge reservoir" layers but, more surprisingly, the FeAs layers themselves: e.g. replacement of some Fe's by Co's can actually induce superconductivity when it was absent in the parent compound. This is in strong contrast to the cuprates, where just about any replacement of the Co's tends to strongly suppress superconductivity.

Nature of the superconducting state

As in the other exotic superconductors, the two most obvious questions are: is the mechanism phononic or electronic, and what is the symmetry of the order parameter?

(a) Phonon or non-phonon mechanism?

To the best of my knowledge, the only isotopic replacement experiments to date are those of Liu et al., Nature **459**, 64 (2009) ($O^{16} \to O^{18}, Fe^{56} \to Fe^{54}$). They report a very small O isotope effect ($\alpha \cong -0.07$, for both T_c and T_s (see below)) but an appreciable effect for $Fe(\alpha \cong 0.35$. At first sight, this suggests a phonon mechanism with the relevant phonons being mainly associated with the FeAs planes. However, they also report an isotope effect of the same magnitude on the spin density wave transition temperature: this might suggest that the mechanism is basically electronic, but the phonons appreciably affect the relevant electronic parameters (e.g. via lattice distortion). The whole question of the relation between structural, phonon and SF effects is at the moment very open. (It would be interesting to see how far one can apply Chester's 1956 arguments to this case . . .)

[‡] Chen et al., Nature **6**, 260 (2010)

(b) Symmetry of the OP:

The magnetic data (in particular the sharp drop in χ below T_c) suggest rather strongly that the spin state of the Cooper pairs is a singlet, so the question reduces to the orbital symmetry. There one has to be a bit careful, and distinguish clearly between those operations (e.g. rotation of the crystal through $\pi/2$) which correspond to the operations of the relevant symmetry group C_{4v}, and those (such as interchange of the α and γ bands) which do not. Thus, in general, the behavior of F_k as we go around a given sheet of the Fermi surface (e.g. the γ-sheet) would not be expected to correspond to a symmetry operation and therefore is not expected to be classified as s, d etc. (the exception is the α and β bands centered on Γ, where say a $\pi/2$ rotation does correspond to a symmetry operation).

The observation of a nonzero value of $|\Delta(k)|$ everywhere on the α and β sheets would, if correct, definitely rule out both d-wave and $s^-(A_{2g})$ symmetry, leaving only s^+. However, it does not tell us anything about the relative phase of F_k on the different sheets, which indeed need not a priori even be 0 or π. (However, the $\gamma(d_{xz})$ and $\delta(d_{yz}$ sheets must each have a uniform ($\mathbf{k}$-independent) sign because of the observation of a nonzero gap everywhere on them, and it must then be the same from the overall s-symmetry). Thus the question reduces to the relative phases of the gap on the α, β and $\gamma - \delta$ sheets (and the fifth, "3D", sheet). The general belief among theorists is that the phase can be chosen as 0 for the three Γ-central sheets and α for the $\gamma - \delta$ sheets; this is the so-called s^{+-} state. The reasons for this belief primarily have to do with ensuring that the large-q part of the Coulomb interaction gives an effective attractive contribution to the pairing energy (cf. l. 12). It is a major challenge, currently taken up by many, to devise experiments which will test the s^{+-} hypothesis against that of simple s-pairing (phase identical on all sheets).