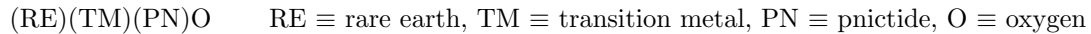
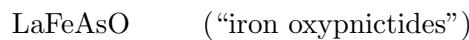


Non-cuprate exotics III: The ferropnictide (FeAs) superconductors¹

Superconductivity in this group of materials was discovered in January 2008: it shows the highest T_c ($\sim 55\text{K}$) 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. The ferropnictides fall into two main classes, denoted respectively as “1111” and “122”. The 1111 class is derived from a parent compound with the formula



A typical example is



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 $\sim 55\text{K}$ ($\text{SmFeAsO}_{1-x}\text{F}_x$, $x \approx 0.15$). (also pure O deficiency)

The second class, “122” has the formula $(\text{AE})(\text{TM})_2(\text{PN})_2$ ($\text{AE} \equiv$ 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 $\sim 38\text{K}$ 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 contains e.g. LiFeAs ($T_c \sim 18\text{K}$ in present state); there is also by now at least one non-pnictide containing Fe, namely FeSe ($T_c \sim 18\text{K}$). Most experimental work has been done on the (1111) materials, and unless otherwise stated I refer to those.

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 lattice constant is $\sim 4 \text{ \AA}$, the c-axis l.c. $\sim 9 \text{ \AA}$ (cf. the cuprates). The Fe-Fe spacing is $\sim 2.85 \text{ \AA}$. In the parent compound (e.g. LaFeAsO) the ionization state³ is believed to be $(\text{La}^{3+}\text{O}^{2-})^+(\text{Fe}^{2+}\text{As}^{3-})^-$, 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

¹General reviews: Johrendt and Pöttgen, *Angew. Chem. Int. Ed.* **47**, 4782 (2008); M.R. Norman, *Physics* **1**, 21 (2008).

² LaNiPO is superconducting but only at 4 – 5K.

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

metallic (FeAs) layer, is similar to (some of) the cuprates; however, note that the 1111 series is *electron-doped*.⁴

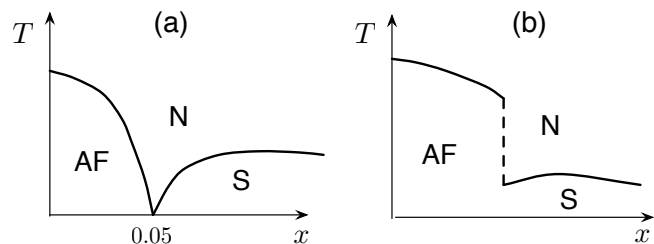
In the 122 compounds (e.g. CaFe_2As_2), the unit cell ($a = 3.9\text{\AA}$, $c = 11.7\text{\AA}$) contains two similar layers, each of them with Ca and As planes sandwiching an Fe plane. (Again, the charge reservoir (Ca \rightarrow K) layer is relatively distant from the Fe atoms.) Note that substitution of an AE by an alkali (e.g. $\text{Ca}_{1-x}\text{K}_x$) 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 \sim a few K, e.g. for Gd); in the 122's Ba, Ca, Sr work.

Phase diagram

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 $\sim 140\text{K}$ (1111) and $\sim 170\text{K}$ (122) one gets a tetragonal \rightarrow 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.

Experimental properties

Caution: experiments in the first few months mainly on *polycrystalline* (powder) samples: single-crystal samples available only recently. Most experiments are on (1111) class. In the following, I will make “default” assumptions that results of experiments done on any one member of this 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.

Experimental properties: N state

The *specific heat* fits roughly to a $\alpha T + \beta T^3$ formula, though when there are structural and magnetic transitions the parameters α and β change there. There is a very small

⁴But hole-doping is also sometimes possible, e.g. $\text{La} \rightarrow \text{La}_{1-x}\text{Sr}_x$, $T_c = 25\text{K}$ (cf. cuprates)

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 $125\text{K} < T < 300\text{K}$ for (1111) samples, with $A, B > 0$. For the 122 samples it has a kink ($_|_$) around $150 - 200\text{K}$.

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 $A + BT^2$. ($A, B > 0$)

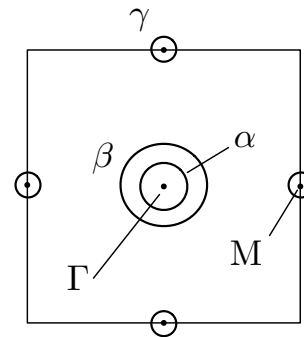
The *Seebeck coefficient* is rather large: for F-doped samples it is $\sim -95\mu\text{V}/\text{K}$ at 100K .

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 *static compressibility* is one of the few unusual properties of the N state: it changes by $\sim 30\%$ between 100 and 300K].⁵

Spectroscopy: ARPES experiments seem consistent with theoretical (LDA) band-structure calculations, which predict (for both 1111 and 122) two medium-sized nearly cylindrical pockets of Fermi sea around the Γ point (zone center) and smaller pockets around the M points. Quantum oscillation (SdH) experiments in the SDW phase of Sr 122 are also consistent with this picture.

[Nb. Beware of different conventions for plotting the “unit cell” in the presence and absence of a SDW!]



More inferences from ARPES: Oh et al., arxiv: 0806.0078

(actually AIPES) measure T and x -dependence of raw data in $\text{SmFeAsO}_{1-x}\text{F}_x$, and from it infer a *doping-independent* suppression of the DOS, at all T up to highest reached, over an energy scale $\sim 80\text{meV}$. Below $\sim 100\text{K}$ they observe a smaller energy scale, $\sim 10\text{meV}$, which eventually (below T_c) merges with the superconducting gap.

Other spectroscopic probes: In very recent (Nov 08) work, Park et al. (arxiv: 0811.2224) studied single-crystal $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0.41$) by a combination of μSR , neutron scattering, MFM and XRPD measurements. From this they conclude that when we are below T_c (hence also T_N) this material *phase separates* into alternating domains of SDW and SC phases, on a scale $\sim 680\text{\AA}$. If this is right it must surely affect the interpretation of at least some of the earlier experiments.

In summary, the N-state data overall look pretty much consistent with “textbook” behavior, with the complication of several different pieces of Fermi surface (cf. MgB_2 , Sr_2RuO_4).

Experimental properties: S state

Magnetic properties: the ferropnictides are strongly type-II, with (at optimal doping) with values of $dH_{c2}^{ab}/dT \sim 4.9\text{T}/\text{K}$, $dH_{c2}^{(c)}/dT \sim 2.5\text{T}/\text{K}$, giving an extrapolated value of $H_{c2}^{ab}(T = 0)$ of $\sim 55\text{T}$. Note:

⁵This statement was made in a recent seminar, but I have been unable so far to confirm it.

- (a) From this data, the degree of anisotropy is small ($\gamma \sim 1.5 - 2$)
- (b) The CC limit is already exceeded by $T = T_c/2$ (assuming $g = 2$ and $\Delta(0)/k_B T_c =$ BCS value.)

The inferred value of $J_c^{ab}(T) \sim 4 \times 10^5 \text{ A/cm}^2$. Values of $\lambda_{ab}(0)$ are somewhat scattered, but mostly in range $1600 - 2400 \text{ \AA}$. The value of $\xi_{ab}(0)$ inferred from H_{c2} is $\sim 20 \text{ \AA}$.

Two obvious questions:

1. Is the mechanism phononic? Isotopic effect: Line et al., arxiv: 0810.2694 perform isotope-effect measurements for both the SDW and SC transitions on Sm 1111, replacing ^{16}O with ^{18}O and ^{56}Fe with ^{54}Fe .

Their findings:

- (1) In both cases, $\alpha_{\text{SDW}} \cong \alpha_{\text{SC}}$. ($\equiv \alpha$)
- (2) For O, $\alpha \cong -0.07$
- (3) For Fe, $\alpha \cong +0.4$

Obvious inference: mechanism is phononic, but relevant phonons mainly involve vibrations of Fe ions, little of O ions (not implausible, since “action” presumably mainly associated with Fe planes).

*Problem: phonon-based theory apparently cannot generate $T_c \sim 55\text{K}$!

2. What is the gap symmetry?
 - (a) Temperature-dependencies in limit $T \rightarrow 0$:
 - λ : Martin et al. arxiv: 0807.0876 (Nd 1111, single-crystal) find low- T behavior exponential, well-fitted by BCS theory with s -wave gap with anisotropy $\lesssim 20\%$ (but find $\Delta/k_B T_c$ only $\sim 1.2!$)
 - T_1^{-1} : Grafe et al., PRL **101**, 047003 (La 1111) find $T_1^{-1} \propto T^3$ in superconducting state (suggestion of line nodes, cf. cuprates)
 - (b) ARPES: data somewhat mutually inconsistent, but more recent work (Kondo et al., PRL **101**, 147003, on Nd 1111) finds a “pull-back” from the Fermi edge corresponding to full gapping $\sim 15 \pm 1.5\text{meV}$, of the Γ pocket, with an anisotropy $< 20\%$.
 - (c) Other: Chen et al., Nature **453**, 1224 (Sm 1111) performed detailed Andreev-reflection experiments and deduced that $\Delta(0) \cong 6.5\text{meV}$ (close to “BCS” value for $T_c \sim 55\text{K}$)⁶
 - (d) Josephson: no experiments to date.

⁶Note $1\text{meV} \approx 12\text{K}$ so BCS value is $\approx 1.75 \times 4.5\text{meV} \approx 7.7\text{meV}$.

The above refers to some kind of “overall/average” gap. How is it distributed between the different pockets of the FS? This is not entirely clear, though there seems *no* evidence for anything resembling the “2-band” picture of MgB₂. One possibility is the so-called s_{\pm} state, where (with the conventional choice of relative phase of the single-electron states) the gap changes sign between the Γ and M pockets.

Conclusion: At present no convincing experimental evidence against “default” hypothesis, namely phonon-induced *s*-wave pairing, but (a) details unclear (b) theoretical (microscopic) understanding shaky.