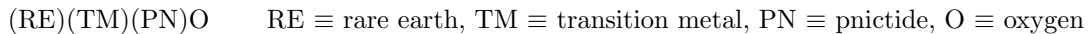
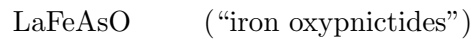


Non-cuprate exotics III: The ferropnictide (FeAs) superconductors¹

Superconductivity in this group of materials was discovered in January 2008: it shows the highest T_c ($\sim 55\text{K}$, but see also below) 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



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, “111” has the formula $\text{A}(\text{TM})(\text{PN})$ ($\text{A} \equiv$ alkali), e.g. LiFeAs . In this case, superconducting transition temperatures up to $\sim 20\text{K}$ are reached already in the pure stoichiometric material without chemical doping. Finally, there is a class “11” with the simple formula $(\text{TM})\text{C}$ ($\text{C} \equiv$ chalcogenide), e.g. FeSe ; 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. However, recently FeSe monolayers have attracted considerable interest (see below).

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”

¹A good early review, which concentrates on the magnetic properties is Lumsden et.al., J. Phys. Cond. Mat **22**, 203203 (2010). For a more recent partial review, see E. Dagotto, RMP **85**, 849 (2013)

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

(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). See Figs. 1 and 2 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 metallic (FeAs) layer, is similar to (some of) the cuprates; however, note that the 1111 series is *electron-doped*.⁴

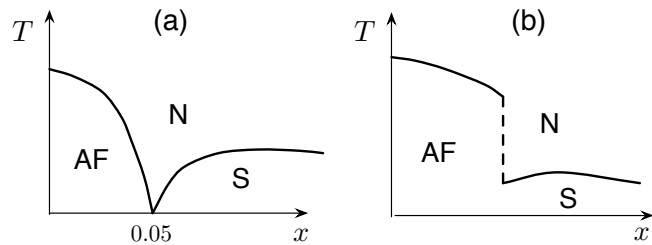
In the 122 compounds (e.g. CaFe_2As_2), the unit cell ($a = 3.9 \text{ \AA}$, $c = 11.7 \text{ \AA}$) contains two similar layers, each of them with two planes sandwiching an Fe plane, separated by an alkaline-earth plane. (Again, the charge reservoir (Ca \rightarrow K) layer is relatively distant from 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 (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 $\sim 140 \text{ K}$ (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.

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

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

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)

but “square” (i.e. along the crystal axes) for 122 ones.

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 the “default” assumption 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 $125\text{K} < T < 300\text{K}$ 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 $\sim -95\mu\text{V/K}$ 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 properties⁵ appear to be qualitatively similar to those of the cuprates; in particular there appears to be a broad “midinfrared” peak centered at around $0.6\text{-}0.7\text{ eV}$. If we attempt to fit it to a Drude form, the inferred plasma frequency is around $1.3\text{-}1.4 \times 10^4\text{ cm}^{-1}$ ($1.6\text{-}1.7\text{ eV}$), 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

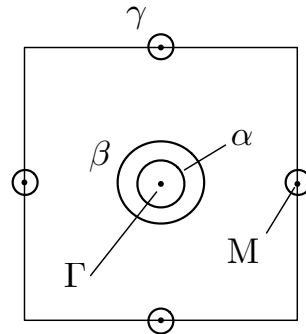
Let’s start by asking what qualitative predictions we might be able to make about the band structure, and hence the Fermi surfaces(s), on the basis of a naive tight-binding model. For the moment we concentrate on the states deriving from the Fe orbitals (since the other

⁵A fairly up-to-date review is A. Charnukha, J. Phys. Cond. Mat. 20, 253203 (2014)

atoms are expected to be mostly in a closed-shell configuration). Recall that in the isolated 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 calculation⁶ 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 $T \rightarrow 0$ 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)

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

of $\partial H_{c2}/\partial T|_{T_c} \sim 4.9T/K$ for $H \parallel ab$, 2.5 T/K for $H \parallel c$, giving an extrapolated 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 $\xi_{ab}(0) \sim 20\text{\AA}$. The low-temperature (ab-plane) London penetration depth is typically $\sim 1600\text{-}3000\text{\AA}$, consistent with the estimated carrier density, and comparable to that of the cuprates..

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

(ii) if we take $\Delta(0)/k_B T_c$ 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

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

where $\eta = 0.17, 0.13$ 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 $5k_B T_c$, which is somewhat similar to that of the famous “41 meV peak” occurring in the cuprates. ($k_B T_c \sim 8$ 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 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

*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 $\Delta\epsilon$)

find, inter alia, an increase in $Re \epsilon(\omega)$ above 2.5 eV but a marked decrease 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.

- (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 \rightarrow 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 Cu’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) ($O^{16} \rightarrow O^{18}$, $Fe^{56} \rightarrow Fe^{54}$). 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

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

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 ...)

(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 π 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. 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).

Orbital ordering

A rather important idea which has emerged from both experiment and theory in the study of the FeAs materials is the notion of "orbital fluctuations" and the associated spontaneous nematicity. On the experimental side, transport experiments seem to show a substantial degree of (ab-plane) anisotropy even at temperatures substantially above the $T \rightarrow O$ transition. On the theoretical side, one notices that the atomic d_{xz} and d_{yz} states are degenerate from symmetry, and thus provided the crystallographic symmetry is not broken (T phase) the strongly 2D bands derived from them have the same degeneracy; thus, fluctuations of (say) the relative number of electrons in these two bands should have a very low frequency, and possibly at some temperature one might get spontaneous "orbital ordering" (spontaneous nematicity); if one looks at this transition at zero temperature as a function

of doping or pressure, it might correspond to a quantum critical point. One interesting suggestion is that, analogously to what is believed by some to happen in the cuprates, the low-energy fluctuations associated with this QCP may provide the “glue” for the formation of Cooper pairs and thus for the onset of superconductivity. As of Nov. 2015 these ideas are still in flux.)

FeSe monolayers⁷

The properties of the compound FeSe are even more strongly dependent on doping, crystallographic state etc. than the rest of the FeAs family. Stoichiometric FeSe in bulk has a modest T_c (12K), but this rises sharply under pressure to ~ 37 K at 4-6 GPa. Because it is prone to phase separation, it is still not entirely clear whether the “parent” compound is indeed simple FeSe or something more complicated (cf. the current situation with H_2S). In any case, it was a surprise when STM and ARPES measurements on a single-unit-cell layer of FeSe deposited on $SrTiO_3$ appeared to show two superconducting-like gaps, respectively ~ 10 and 20 MeV, occurring below a temperature of ~ 70 K; if we interpret the latter as the T_c for superconductivity, this (the 20 MeV gap) corresponds to a 2Δ value $\sim 5k_B T_c$ (similarly as in bulk FeSe). This behavior appears to occur only when the monolayer is deposited on a perovskite crystal of the composition $(AE)TiO_3$. Some transport measurements appear to give a lower onset temperature $T_c \sim 40$ K, but with a very large critical current $J_c \sim 1.7 \times 10^6 A/cm^2$. However, recently there have also been conducted 4-probe measurements on the film which have been interpreted as showing the onset of superconductivity (in the sense of vanishing resistance) at a temperature as high as 110K. These results need to be confirmed; irrespective of this, the question of what is going on in these monolayers, and in particular what is the role being played by the $SrTiO_3$ substrate, is at the time of writing hotly debated.

⁷M-K. Wa et al., J. Phys. D **48**, 323001 (2015)

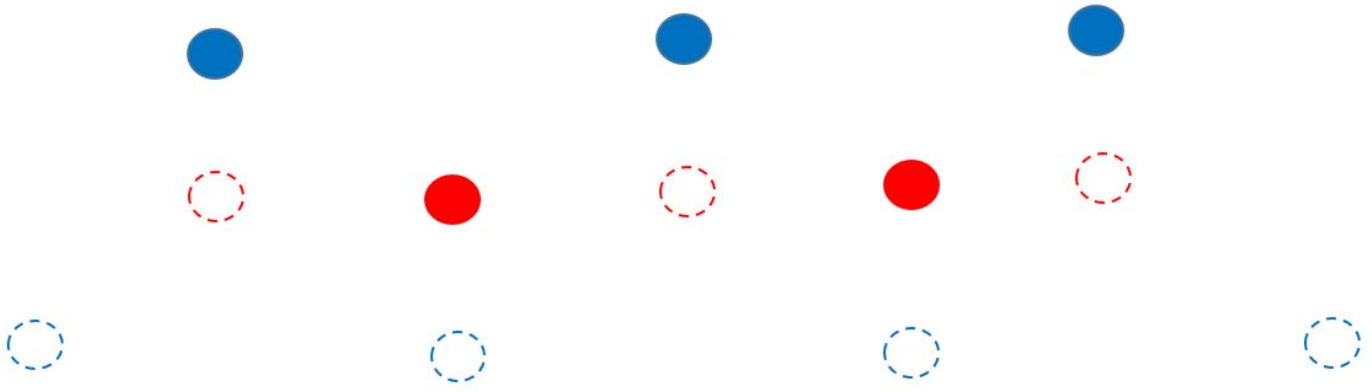


Fig. 3. Characteristic structure of the FeAs bilayer. ●, ○ = Fe, ●, ○ = As (or Sa),

(a) pecked atoms offset by 1/2 a lattice spacing relative to solid ones

(b) iterated indefinitely in direction \perp to plane of paper



Fig 4. Structures of ferropnictide families