LnOMPn Superconductors

Basic Chemistry/Structure

Ln= Y, Rare Earth
M= Later Transition Metal (Mn, Fe, Co, Ni)
Pn= Pnicogen (P, As)

-Tetragonal P4/nmm (#129)

-Alternating layers of LnO and MPn

-MPn Layer: Transition metal tetrahedrally coordinated by the Pnicogen forming layer of edge sharing tetrahedra in a square lattice.

-LnO Layer: Oxygen terahedraly coordinated by Ln would also form layer of edge sharing tetrahedral.

-Sometimes represented as alternating layers of $(Ln^{3+}O^{2-})^{+}$ and $(MPn)^{-}$ or $(Ln^{3+}O^{2-})^{\delta+}$ and $(MPn)^{\delta-}$ because it is thought that the layers are charged, with the bonding in the LnO being mostly ionic and mostly covalent in the MPn layer. The idea of isolated charged layers is supported by the fact that the tetrahedra in the layers are compressed and the distance between the layers is relatively large.

Discovery of Superconducting Phases

-Much of the work done in Japan at the Tokyo Institute of Technology

-LaOFeP: Discovered to be superconducting in 2006 with T_c ~5 K (LaONiP T_c ~3 K)
(Y. Kamihara, *et al.*, J. Am. Chem. Soc. **128**, 10012 (2006))

-$La[O_{1-x}F_x]FeAs$: Just discovered in January 2008 to have T_c~26 K
(Y. Kamihara, *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008))

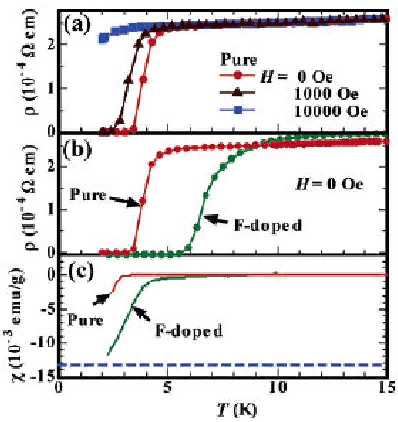
-Like in the cuprates, the conduction electrons are believed to be confined in a 2D layer, the MPn layer in this case. The conducting layer looks quite different, having edge sharing tetrahedral coordination rather than corner sharing square pyramidal units of the cuprates.

-Also like the cuprates the conducting layer can be modulation doped by impurities/defects in the LaO layer, i.e. Fluorine doping on the Oxygen site. Unlike the cuprates, these superconducting phases are electron doped rather than hole doped.

-In LaOFeP F doping raises the transition by a few degrees.

-Undoped LaOFeAs does not have superconducting transition, but as F is added the transition is increased above 0 K, plateaus around 26K at about 5% F , but then falls again above 11%.

Figure 2. Electrical resistivity (ρ) versus temperature (T) for pure and F-doped LaOFeP.



(Y. Kamihara, *et al*., J. Am. Chem. Soc. **128**, 10012 (2006))

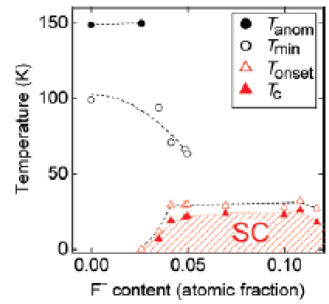
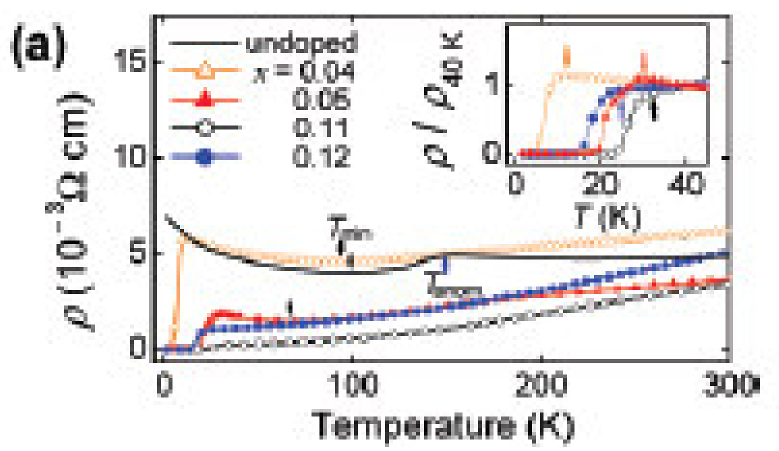


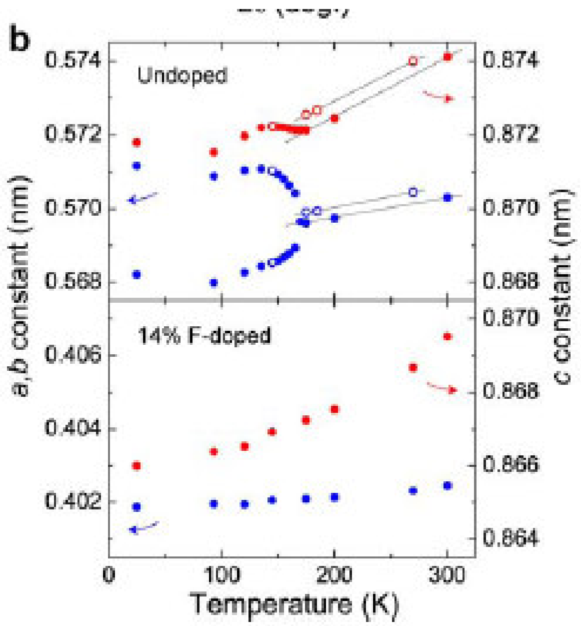
Figure 3. T_c, T_{onset}, and T_{min} in the ρ-T curves as a function of F^- content (x) for $La[O_{1-x}F_x]FeAs$. T_c is defined as the temperature where the ρ value becomes half of that at T_{onset}. T_{anom} values for the undoped and $LaO_{0.97}F_{0.03}$-FeAs are also shown. Dotted curves are guides for eyes.

(Y. Kamihara, *et al*., J. Am. Chem. Soc. **130**, 3296 (2008))

-"Underdoped" $La[O_{1-x}F_x]FeAs$ has other low temperature anomalous behavior that may be preventing superconducting transition. It goes through resistivity maximum at around 150 K and then a minimum around 100 K before increasing again at lower temperatures. (Similar ρ vs. T behavior to 50% 2^+ alkaline earth/3^+ rare earth manganates) Has been found to be accompanied by structural phase transition to orthorhombic Cmma structure at around 150 K. (T. Nomura, *et al.,* arXiv:0804.3569). F doping appears to stabilize the tetragonal structure and prevent this phase transition.



(Y. Kamihara, *et al*., J. Am. Chem. Soc. **130**, 3296 (2008))



(T. Nomura, *et al.,* arXiv:0804.3569)

-It well known in the cuprates superconductors that pressure can be used to increase T_c by increasing charge transfer from the insulating to the conducting layers. For $La[O_{1-0.11}F_{0.11}]FeAs$ the T_c was increased from ~26 K to 43 K by applying ~4 GPa.
(H. Takahashi, *et al.*, Nature **453**, 376 (2008)) This is a good indication that "chemical pressure" will also result in increased T_c. In fact F doping results in a decrease in the cell parameter.

-It was then reported that substitution of La with later, and thus smaller, rare earths also increase T_c. At present F doped SmOFeAs appears to hold the record with a T_c of ~55 K. (Z.A. Ren, *et al*., arXiv:0804.2053)

-Behavior also strongly dependent on transition metal used. Iron and Nickel compounds exhibit superconductivity, but Mn apparently leads to antiferromagnetic insulators, and Co to metallic ferromagnets. Clear that the number of 3d electrons plays a critical role.

-It is clear that much work is being conducted on these materials, and many peer reviewed papers are to be expected soon even though only a few have been published so far. To soon to tell for sure, but it seems likely that research on these materials will lead to a better understanding of the mechanisms behind high temperature superconductivity.