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Overview of High Temperature Superconductivity in Iron Pnictides

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ABSTRACT

The discovery of new superconductor *LaFeAsOi-xFx* with a superconducting critical temperature, *Tc* of 26K in 2008 has quickly renewed interest in the exploration of iron based superconductors. More new superconductors have been discovered with the highest *Tc* of up to 55K being observed in the *SmF eAsO*1-*xFx* compound. High *Tc* have previously only been observed in cuprates, these new iron based superconductors have been added as second member of high *Tc* family. The crystal structur of these compounds contains an almost 2D Fe-As layer formed by *FeS*4 tetrahedrons, which can be separated an ionic layer that provides an extra electron to Fe-As layer superconductivity can be induced by carrier doping, which destroy the antifrromagnetic ground state. The pairing mechanism has been clarified as unconventional and antiferromagnetic (AF) spin fluctuations (SFs) seem to play an important role in making these pairs. In this paper superconducting crystal structure, physical properties of parent compounds, pressure effects, the electronic state of the compounds will be presented.

Keyword: superconductor, Superconductivity, Iron Pnictides

INTRODUCTION

Superconductivity is one of the most peculiar phenomena in nature. Its zero electrical resistance and fully repulsion of magnetic field (known as Meissner effect [1]) have great potential uses in practical applications. The first superconducting phenomenon was discovered in 1911 by Heike Kamerlingh Onnes, [2] who found that the resistance of solid mercury disappeared abruptly at 4.2 K. Since this discovery, scientists have been seeking superconductors with higher temperatures. In 1913, lead was found to superconduct below 7 K and in 1941 niobium nitride was found to superconduct at 16 K. Since the first discovery of superconductivity in mercury in 1911, the underlying mechanism has been a major challenge to condensed matter physics community. In 1935, the brothers F. and H. London [3] explained the Meissner effect as a result of the minimization of the electromagnetic free energy carried by superconducting current. The famous London equations described the two basic electrodynamics properties mentioned above very well. In 1950, Landau and Ginzburg [4] developed the phenomenological Ginzburg-Landau theory by introducing a complex pseudowave function as an order parameter within Landaus general theory of second order phase transitions which led to a Schrodinger like wave function equation. The Ginzburg-Landau theory explained the macroscopic properties of superconductors successfully. By applying the Ginzburg-Laudau theory, Abrikosov [5] showed that superconductors could be grouped into Type I and Type II superconductors in 1957. Also in 1950, Maxwell and Reybold et al.[6, 7] found the isotope effect which showed that the critical temperature of a superconductor depends on the isotopic mass 2

of the constituent element. This important discovery pointed to the electron- phonon interaction as the microscopic mechanism responsible for superconductivity. The complete microscopic theory of superconductivity was finally proposed in 1957 by Bardeen Cooper and Schrieffer known as the BCS theory [8] In the BCS theory, they showed that pairs of electrons (known as Cooper pairs) could form through even a weak attractive interaction

between electrons, such as electron-phonon interaction. The super current is explained as a super fluid of Cooper pairs. The superconductivity phenomenon was explained independently in 1958 by Nikolay Bogoliubov [9] who was able to use a canonical transformation of the electronic Hamiltonian to derive the BCS wave function, which was obtained from a variation method in the original work of Bardeen, Cooper, and Schrieffer. In 1959, Lev Gorkov [10] showed that the Ginzburg-Laudau theory was a limiting form of the BCS theory close to the critical temperature. BCS theory is the most successful theory to explain superconductivity in conventional superconductors. Nevertheless, superconductivity in many superconductors remains unexplained, including high temperature superconductors (HTS, namely, the cuprates), the newly discovered iron-based superconductors, some organic superconductors and heavy fermions superconductors (eg: the 115 materials).

1. **Overview of superconductivity**

Superconductivity occurs when electrical resistivity of the specimen drops to zero when cooled to a sufficiently low temperature also knows as critical (transition) temperature, *TC*. Below *TC* resistivity is zero, not just close to zero. This was, for instance, demonstrated by injection
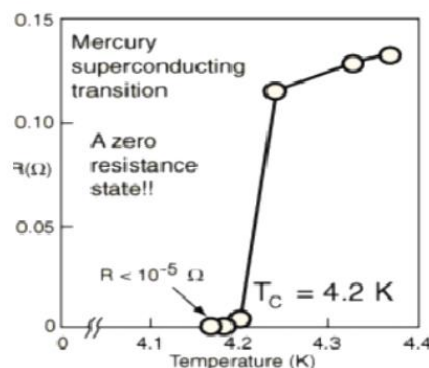

Figure 1.1: Resistance in ohms of a specimen of mercury versus absolute temperature by Kamerlingh Onnes in 1911 [1]

Current into lead superconducting (SC) wire. This SC current persists almost indefinitely as long as $T < TC$. In Figure 1.1 shows the historical electrical measurement of Kamerlingh Onnes, who first reported on a discovery of superconductivity in mercury in 1911. Transition temperature for mercury is 4.2 K (Figure 1.1)

1.1. Meissner-Ochsenfeld effect
When the specimen is placed in a magnetic field, and then cooled, the magnetic flux is expelled from the specimen (Figure 1.2). This is known as Meissner effect. If there would be any magnetic field in superconductor it would change
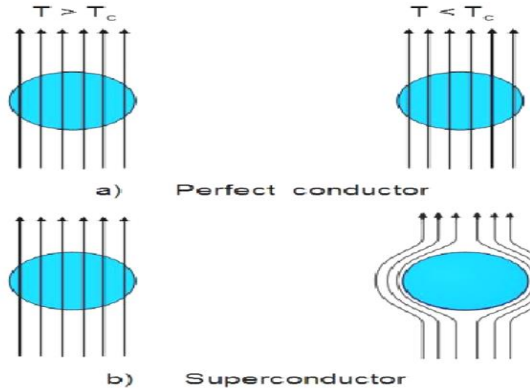

Figure 1.2: Meissner effect in a superconducting sphere, which is cooled in a constant

applied magnetic field; below critical temperature the lines of induction B are ejected from the sphere (a) Perfect conductor, (b) Superconductor.

The flux. According to Lenz's law a current would be generated, which would oppose the flux, and eject any magnetic field from the superconductor. For the case, when magnetic field is expelled from the specimen, we can write

$B = 0 = \mu o(H + M) = \mu o H(1 + \chi)$ ----------------------------2.1

Here M is magnetization and χ, is magnetic susceptibility. Because there is no magnetic field in specimen we can see from equation (1) that $\chi = -1$ A superconductor in magnetic field will act as a perfect diamagnetic.

1.2. London equation describes Meissner effect
London equation can correctly predict magnetic field penetration into the SC material, but cannot give a microscopic picture. Let us assume a two-fluid model [4], where we distinguish between normal electrons and superconducting electrons $n = nN + nS$, where n is the electron density. As it was proved by the BCS theory, nS are Cooper pairs, which are bound states of electron pairs. For superconducting electrons in electric field we can write

$m \frac{\partial v_s}{\partial t} = -e_o E$ ---2.2

If we consider equation for current density and apply it for superconducting electrons

$j_s = -e_o n_s v_s$ --------------------------------------2.3

$\frac{\partial j_s}{\partial t} = \frac{\partial n_s e^2{}_o}{m} E$ ---------------------------------------2.4

Combining this with Faradays law $\nabla x E = -\frac{\partial B}{\partial t}$ we obtain

$\frac{\partial}{\partial t}\left(\nabla x j_s + \frac{n_s s e^2{}_o}{m} B\right) = 0$ ----------------------------2.5

At this stage Fritz London took into account also the Meissners effect i.e. the magnetic

field in superconductor is zero, and derived

$\nabla x j_s = -\frac{n_s s e^2{}_o}{m} B$ ------------------------------2.6

If equation (2.6) is combined with $\nabla x B = \mu_o j_s$ we get

$\nabla^2 B = \frac{\mu_o n_s e^2{}_o}{m} = \frac{1}{\lambda^2} B \to B(x) = B_0 exp\left(-\frac{x}{\lambda}\right)$ **----------2.7**

$\lambda = \sqrt{\frac{mc^2}{4\pi n_s e^2}}$ where is a London penetration depth, which measures the depth of penetration of the magnetic field. Inserting typical values for the density of SC charges for standard superconductors it is in order of 10 nm, while in HTSC it is around 100 nm.

1.3. Type I and type II superconductors
The superconducting state in specimen is destroyed if the specimen is placed in a sufficiently strong magnetic field (critical field, Hc) or if we generate strong enough currents (critical current $> 105 \frac{A}{cm^2}$) Based on this we distinguish two types of superconductors: type I and type II. Type I superconductor expels a magnetic field for $H < Hc$ while for $H > Hc$ superconductivity is destroyed and the field penetrates completely into the sample (Figure 1.3). A type II superconductor expels field in the normal state completely under $Hc1$. When H exceeds $Hc1$ the field is only partially excluded, and the bulk specimen remains to be superconducting. Between $Hc1 and Hc2$ the superconducting state coexists with normal state regions where magnetic field penetrates into the sample.
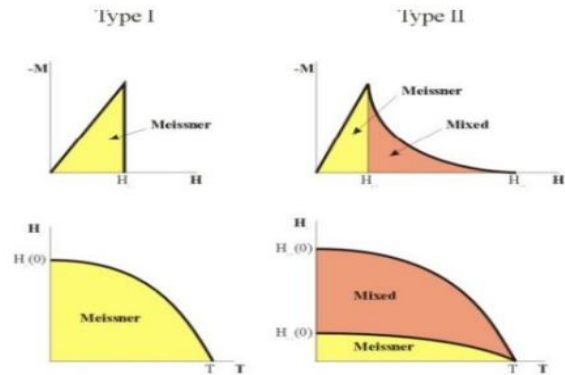

Figure 1.3: Magnetization properties of type I and type II superconductors.

1.4. BCS theory
In 1950, two groups independently found that different isotopes of mercury have different Tc [49, 50] which were later found to obey the relation $TcM^{\beta} =$ constant, where M is the mass of the isotope. Inspired by this isotope effect, Bardeen, Cooper and Schrieffer (BCS) assumed an electron-phonon interaction as the pairing mechanism Although other pairing mechanisms, like spin fluctuation, etc, were hypothesized for nonconventional superconductors, the idea of the formation of Cooper pairs, the key ingredient of superconductivity remains the same. In BCS theory, to simplify the calculation, a lot of assumptions were made, such as constant electron-phonon interaction, Fermi sphere assumption, etc,
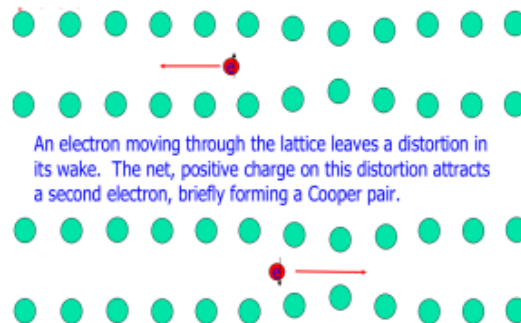

An electron moving through the lattice leaves a distortion in its wake. The net, positive charge on this distortion attracts a second electron, briefly forming a Cooper pair.

Figure 2.1: electron indirect interaction in crystal for pairing mechanisms.

2. Iron pnictides

High *Tc* superconductivity at 26 K was reported by Kamihara et al. in F-doped LaFeAsO [55] that appeared online on 23*rd* of February 2008. This was the discovery of high*Tc* superconductivity in a completely new class of materials that came to be known asiron pnictides. This new discovery has generated a great interest in the materials sciencecommunity opening a new route for the high *Tc* research in addition to that of the cuprates. However, this has also brought new challenges on both experimental and theoretical sidesand added a new problem for material scientists in addition to the long standing problem of cuprates.

2.1. Different families of pnictides

1111 family : Following the discovery of high *Tc* superconductivity in *LaF eAsO*1-xFx ,*Tc* rapidly increased by exchanging lanthanum with rare earth ions of smaller atomic radii in LnFeAsO and appropriate carrier doping or creating oxygen deficiencies, until it reacheda maximum value of $\sim 56K$ until now in *Gd*1*xThxF eAsO* [56]. This family LnFeAsO cameto be known as 1111 family. Note that LaFePO, also discovered by Kamihara et al. in 2006, was the first 1111 compound to show superconductivity, but with very low *Tc* (~ 5 - 7*K*). In addition to *LaF eAsO*1-xFx , the most remarkable 1111 compounds that show high *Tc* superconductivity discovered until now are: (i) *SmFeAsO*1*xFx* (*Tc* $\approx$ 43*K*) [57], (ii) *CeF eAsO*1*xFx* (*Tc* $\approx$ 41*K*) [58], (iii) *NdF eAsO*1*xFx* (*Tc* $\approx$ 51*K*) [59], and (iv) *P rF eAsO*1*xFx*(*Tc* $\approx$ 52*K*) [60]. 122 family: M. Rotter et al. [61]proposed *BaF e*2*As*2 as a potential new parent compound based on the similarities between *BaF e*2*As*2 and LaFeAsO. In fact, both compounds contain identical (FeAs) layers, and have the same charge accordance as follows:

*Ba*2+[(*F eAs*)]2*vs*:(*LaO*)+(*F eAs*) . Partial replacement of Barium with Potassium (hole doping) induced superconductivity at 38 K in *Ba*0:6*K*0:4*F e*2*As*2 [62], the first member of a new family of superconducting iron arsenides known as the 122 family. This discovery was followed by reports of similar compounds with: (i) strontium (*Tc* $\approx$ 37*K*) [63, 64], (ii) calcium (*Tc* $\approx$ 20*K*) [65], and (iii) europium (*Tc* $\approx$ 32*K*). Later electron doping in *BaF e*2*As*2 by the partial replacement of Fe with Co with *Tc* $\approx$ 22*K* was reported by Sefat et al. [67]. 111 famliy X. C. Wang et al. [68] reported the discovery of another new superconducting iron arsenide system LiFeAs (termed 111). Superconductivity with *Tc* up to 18 K was found in these compounds. 11 families F.-C. Hsu et al. [69] reported the observation of superconductivity with zero resistance transition temperature at 8 K in the PbO-type *α*FeSe compound known as 11 families. Although FeSe has been studied quite extensively, a key observation is that the clean superconducting phase exists only in those samples prepared with intentional Se deficiency.

2.2. Crystal structure and physical properties

The crystal structures of the four families of iron pnictides are discussed briefly below: 1111 family LaFeAsO and the 1111 family of iron pnictides crystallizes in the ZrCuSiAs type structure, (space group (*p nmm* 4). In this structure, two dimensional layers of edge-sharing *F eAs*4=4tetrahedra alternate with sheets of edge sharing *LaO*4=4 tetrahedral. Because of the differences between the ionic nature of the Ln-O (Lanthanum oxide) bonds and the more covalent Fe-As (iron arsenide) bonds, a distinctive
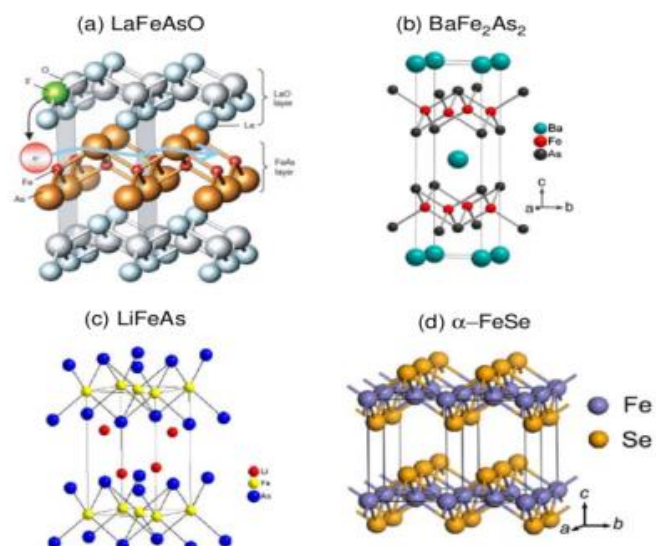

Figure 3.1: Schematic crystal structure of: (a) LaFeAsO [68], (b) *BaF e*2*As*2 [62] (c)
LiFeAs [68] (d) FeSe [69]..

two-dimensional structure forms, where ionic layers of lanthanum oxide (*LaO*)+ alternate
with metallic layers of iron arsenide (*F eAs*)-

122 families

The ternary iron arsenide *BaF e*2*As*2 , with the tetragonal *ThCr*2*Si*2 -type structure space
group (space group I4/nmm) contains practically identical layers of edge-sharing *F eAs*4=4
tetrahedra, but they are separated by barium atoms instead of LaO sheets. This structure
is shown in Fig. 3.1 (b) [62].

111 families

LiFeAs crystallizes into a *Cu*2*Sb*-type tetragonal structure containing [FeAs] layer with an average iron valence *Fe*2+ like those for 1111 or 122 parent compounds. This structure
is shown in Fig. 3.1 (c) [68].

2.3. Resistivity of iron pnictides

Parent compounds of iron pnictides show an anomaly in the resistivity curves at certain temperature that depends on the compound itself. Later, it was found out that this anomaly is due to a structural phase transition. Typical examples of resistivity curves of *LaF eAsO*1*xFx* [19] and *BaFe*2*As*2 [26] are shown in panels a and b of Fig. 3.2
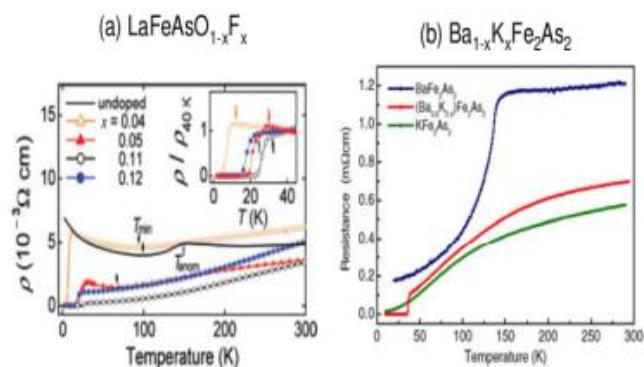

Figure 3.2: Typical resistivity curves of (a) *LaFeAsO*1*xFx* [19] and (b) *(Ba; K)Fe*2*As*2 [62].

2.4. Factors affecting Tc in pnictides

It has been known that electron doping in the 1111 system can be done by substitution

of oxide for fluoride or by oxide vacancies.

- Effect of Rare-earth elements
- Rare earths with smaller ionic radii decreased the lattice constant there by developing inner chemical pressure leading to high *Tc* Doping brings structural modification such as a reduction in cell volume decrease between layers and increase in distance between *Re*3+ and *F* - which enhances spin and charge density fluctuation. As mentioned above, exchanging lanthanum with rare earth ions of smaller atomic radii in *LnF eAsO*1-*y* , *Tc* was found to increase. This effect is summarized in Fig. 3.3 taken from Ref. [72].*Tc* increases from 28 K (Ln=La) to 53 K (Ln=Nd). However, *Tc* stays almost constant from Ln=Nd to Dy and this effect is not completely understood yet.
- Effect of pressure Pressure enhancement increases charge transfer between the insulating *LaO* layer and the conducting FeAs layer, in addition the external pressure induces an anisotropic shrinkage, which considered as the main reason for further increase in onset *Tc*. It was found that pressure has a large effect on iron pnictides so that some parent compounds can become superconducting by simply applying pressure. As an example of the pressure effect, we remark that the *Tc* of the original system *LaF eAsO*1*xFx* went up from $\sim 26K$ to $\sim 43K$ by applying a pressure of $\sim 4GPa$ [37].
- Effect of oxygen deficiency Oxygen deficiency produces more lattice shrinkage and charge carrier thereby increase the density of state (DOS). *Tc* increase abruptly to a maximum with a slight doping of oxygen vacancies and then decreased with further increase in oxygen vacancies.
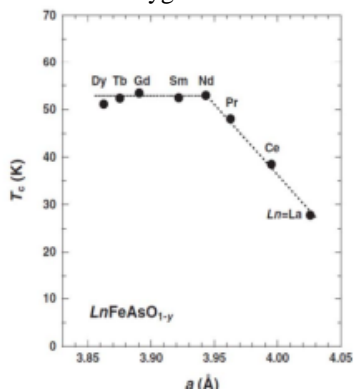

Figure 3.3: Ln-dependence of *Tc* for *LnFeAsO*1*y* system (Ln=La, Ce, Pr, Nd, Sm, Gd,

Tb, and Dy). *Tc* is plotted against the a-axis lattice parameter [72]

2.5. Phase Diagrams

1111 materials

The first evidence for the importance of magnetism in the Fe-based superconductors was the concentration dependent phase diagram presented with the initial discovery of superconductivity in F doped LaFeAsO [73]. An additional phase was clearly present at low F concentration which vanished at doping levels where superconductivity appears although the exact nature of this phase was unclear. It was soon shown that the undoped LaFeAsO parent compound exhibited spin-density wave (SDW) order below about 150 K [74, 75] . Unexpectedly, LaFeAsO also exhibited a structural phase transition [74] at a temperature slightly above the magnetic ordering temperature. There is clear competition between magnetism and superconductivity as the magnetically ordered state is destroyed in the fluorine doped, superconducting

samples [74, 75]. The phase diagram of *RF eAsO*1*xFx* as a function of doping has been carefully studied for R = La [76] (figure 3.4(a)), Ce [77] (figure 3.4(b)), Pr [78] and Sm [79, 80] (figure 3.4(c)). The phase diagrams were experimentally determined using the following techniques: R = La, SR, 57 Fe Messbauer spectroscopy and x-ray diffraction [76]; R = Ce, neutron diffraction, resistivity and magnetization [77]; R = Pr, x-ray diffraction, resistivity and magnetization [78]; R = Sm, typical structural transition at 150 K and SDW ordering at about 140 K. In general, doping causes a suppression of both the structural and magnetic phase transitions and as these are suppressed, superconductivity emerges. The fundamental difference between materials with different rare earths comes in the behavior near the emergence of superconductivity. For R = La and Pr, the structural and magnetic transitions in an abrupt step-like manner as a function of doping at the onset of superconductivity [76, 78], as shown in figure 3.4(a) for the case of R = La. For the case of R = Ce, the magnetic transition appears to vanish continuously to very low temperatures and superconductivity emerges at a concentration where this transition has been completely suppressed [77] (see figure 3.4(b)). However, the structural transition has some range of concentrations where superconductivity coexists with phase transition [77]. Finally, the case or R = Sm, shown in figure 3.4(c), looks similar to R = Ce in that the transitions are suppressed gradually and there appears to be overlap between the structural transition and superconductivity [80]. However, unlike the case of Ce, the Sm phase diagram shows a region where magnetic ordering coexists with superconductivity [79]. The above fig (d) the parent compound *BaFe*2*As*2 contains hole doping (K) and electron doping (Co)on FeAs plane. As the case of the 1111 parent compounds,122 exhibits both structural and phase transition from room temperature *I*4 *mmm* space group to the low temperature to the low temperature orthorhombic Fmmn space group and magnetic transition to a long range order SDW state. Unlike 1111 material both structural magnetic phase transition occurs at the same temperature in 122 parent compound. In electron doping case and hole doping superconductivity emerges as the SDW order is suppressed. Interestingly in both case K and Co doping there is a region of phase diagram where the SDW state and structural transition coexist with superconductivity. This certainly shows a very strong interaction between the superconducting and SDW state. It could be interpreted that this suppression is due to the same electrons participating in both SDW and superconductivity

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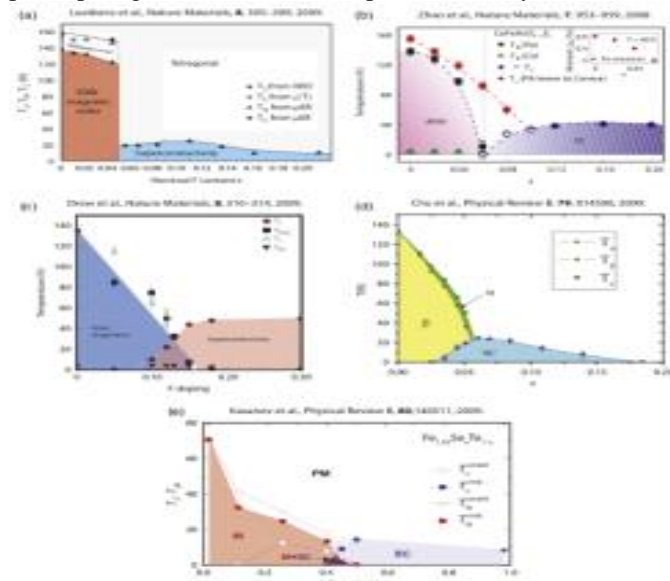
CONCLUSION

Iron pnictides are high critical temperature not exceeding 55K and they took the attention of researchers because of their structural similarities with copper oxides since both have antiferomagnetic phase next to superconductivity. Pnictides are not phonon-mediated superconductors hence, they are unconventional and electron-phonon coupling constant $\lambda = 0.21$ which is too small to express such critical temperature. The microscopic pairing mechanisms for iron pnictide seems spin fluctuation because the nesting of fermi surfaces around $(\pi; 0); (0; \pi)$ and structural distortion and magnetic order vanish in F doping and SDW suppressed before superconductivity for most cases. On the other hand superconductivity can coexist with SDW.This shows that pairing mechanisms for iron pnictide high temperature superconductivity is not general case like BCS theory in conventional superconductivity which is phonon mediated. Pnictides of different families have common general; features like layers of (FeAs) in structure and similar fermi surfaces of electronic structure. Beside this differences may exist with similar families ,the vertical distance of of Pn to Fe plane is different in comparison with the two compounds LaFeAsO and LaFePOwith Tc 26K in the former and $\sim (5K - 7K)$ in the latter LaFeAsO evolves to LaFePO as the height of As to Fe plane decreases .This indicates that another mechanisms can be found in future in addition to known mechanisms of raising Tc.

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