Effective valence as the control parameter of the superconducting iron pnictide T_c

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Abstract

One approach to investigating the superconductivity in the iron-based materials is understanding the chemical and structural parameters that can be used to tune their remarkably high T_c. In this paper, we have demonstrated that the effective valence of iron can be used as the control parameter to tune the T_c of this family of superconducting materials. This is achieved by postulating that our model of spin fluctuation which has been used to successfully account for the superconductivity in the cuprates in Ref. [21] can also be applied to the superconducting iron-based materials.

1.0 Introduction

In January 2008, the group of Hideo Hosono in Japan reported that a layered iron arsenide material (LaOFeAs) is superconducting with a transition temperature (T_c) of 26 K [1]. The two surprising issues here are: (1) it was believed before then that iron ions in many compounds have magnetic moments and consequently form an ordered magnetic state [2] rather than a superconducting state though the Hosono group had earlier obtained a T_c of 5 K in LaOFeP [3]; (2) The T_c of 26 K is higher than any intermetallic compounds except that of 35 K in MgB2 [4]. Thus it has attracted a deluge of experimental and theoretical studies of the iron based compounds commonly called the iron pnictides (pnictides means compounds of the nitrogen group). Today, a T_c of 55 K has been achieved [5] and there are four major classes of this family of superconducting materials: iron oxypnictides/single layered LnOMPn (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y: M = Mn, Fe, Co and Ni: Pn = P and As) ; oxyfree-pnictides/single layered AMPn (A = LnO = Li and Na: M = Mn, Fe, Co and Ni: Pn = P and As); oxyfree-pnictides/double layered ALM_2Pn_2 (AL = Ba, Sr, Ca: M =Mn, Fe, Co and Ni: Pn = P and As) and chalcogen/non-layered MCn (M = Mn, Fe, Co and Ni: Cn = S, Se and Te) (see Table 1.1 for some of these compounds and their T_c) .

An important goal in the study of the iron-based superconductors is to figure out the chemical and structural parameters which can be used to tune their properties and consequently lead to understanding the origin of their remarkably high T_c [6]. This will involve determining

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the mechanism responsible for the formation and propagation of the Cooper pairs hence the superconducting state, as was in the case of the successful story of the BCS theory for the conventional superconductors. The first step in this direction is to identify the key element(s) that control the structural and chemical properties of these materials: here the iron seems to be the most relevant element.

Iron is a transition element and the general form of the configuration of this group of elements is [7]

$$ns^a(n-1)d^b \tag{1.1}$$

hence the valence electrons for the transition elements resides in the ns and (n-1)d subshells. For the iron with a configuration of $3d^6 4S^2$, its ion is either Fe^{2+} for $3d^6$ or Fe^{3+} for $3d^5$ (see Fig. 1). It has been observed that the superconducting T_c of the iron pnictides is critically dependent on extremely small changes in the iron stoichiometry [8]. For example, the non-iron based superconductor, LaONiP is isostructural to LaOFeAs, yet it can be accounted for by electron-phonon coupling [9] while the electron-phonon interaction (EPI) of the iron-based compounds has been shown to be too weak to produce their remarkably high T_c [10,11]. This not only establishes the non-trivial factor of the iron atom for the superconducting iron pnictides but has led to a general consensus that they are non-conventional superconductors [12,13]. This observation in turn led to the speculation that the superconductivity of the iron-based compounds might be related to that of the cuprates which are the first conventional superconductors discovered in 1987 [14] have been actively studied since then. The speculation was boosted by early observation that like the cuprates, the parent compounds of the iron pnictides are antiferromagnetic (AF) and only become superconducting when doped [12,15]. However, more recent studies have shown that the electronic correlations of the iron pnictides is weak as such the undoped compound is a spin density wave (SDW) as the electrons are delocalized [16]. This form of antiferromagnetism is quite different from that in the Mott-insulator state of the undoped cuprates as the electrons are localized (localization here arises because the spins can lower their energy if they are antiparellel to their neigbours) [12,17]. Therefore the scenario now is that though the iron based compounds are quite different from the cuprates, there is growing opinion that magnetic fluctuations may purely be responsible for their transition from normal to superconducting states as still being canvassed by some groups for the cuprates [2,12,16,18-20]. Interestingly, the antiferromagnetism of the parent compound of the iron pnictides is also a nearest neighbor antiferromagnetism and can be related to superexchange [2,20]. In this paper therefore, we shall review the possibility of extending our spin fluctuation model for the cuprates [21] to the iron pnictides in section 2. It will be observed that in making this extension, the control parameter to drive the superexchange interaction in the model is the effective valence of the iron, $3d^{z+}$ in the same spirit as this same parameter provides the 'trigger' for the interaction of the iso-superconductivity model [22]. To gain an insight into how the $3d^{z+}$ influences the interaction, it will be related to the T_c of the iron pnictides in section 3. This will be followed by a summary and a conclusion.

Table 1.1: Some compounds and their T_c

Compounds	Exp T_c	References
PNICTIDES		
OXYPNICTIDES/ *Single layered LnOMPn (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y: M =Mn, Fe, Co and Ni: Pn = P and As)*		

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The 1111		
LaOFeP	4 K	Ref. [3]

Compounds	Exp T_c	References
LaONiP	3 K	T. Watanabe et al., Inorg. Chem. 46, 7719(2007)
LaOFeAs	26 K	Y. Kimihara et al., J.Am. Chem. Soc. 130, 3296 (2008)
SmOFeAs	55 K	Ref. [5]
OXYfree-PNICTIDES/*Single layered* AMPn *(A =LnO= **Li** and Na: M =Mn, **Fe**, Co and Ni: Pn = P and **As**)* *The **111***		
LiFeAs	18 K	Ref. [20]
OXYfree-PNICTIDES/*Double layered* $A_LM_2Pn_2$ *(A_L = **Ba**, Sr, Ca: M =Mn, **Fe**, Co and Ni: Pn = P and **As**)* *The **122***		
$BaFe_2As_2$	40 K	A. D. Christianson et al., Nature 456, 930 (2008)
Non-PNICTIDES/CHALCOGEN		
*Non-layered MCn (M =Mn, **Fe**, Co and Ni: Cn = S, **Se** and **Te*** *The **11***		
FeSe	18 K	arXiv:0807.4315
$FeSe_{0.85}$	8.3 K	R. Khasanov et al., PRB78,220510(2008)
α −FeSe (with PbO structure)	8 K	F. C. Hsu et. al., Proc. Natl. Sci. USA. 105, 14262 (2008)
β−FeSe (with NiAs structure)	8.5 K	Ref. [8]
FeTe	14 K	Ref. [2]

2.0   Possible spin fluctuation model of the iron-based compounds

The issue of the mechanism responsible for the interesting phases of the superconducting cuprates is still very contentious after more than two decades of intense studies [21,23]. For example, the observation of kinks at the phonon frequency in some members of the superconducting cuprates in angle resolved photoemission spectroscopy experiment by Lanzara in 2001 [24] reinvigorated the electron-phonon mechanism group. However, using local density approximation and a realistic phonon spectrum to study $YBa_2Cu_3O_7$, Held et. al. [25] argued that phonons cannot solely produce the well defined kinks. One possible mechanism then is that an interplay between spin fluctuation and EPI may be responsible for the superconducting cuprates [23]. One approach to achieve this is to start with a model of spin fluctuation and then renormalized it with the EPI or verse visa. We have adopted the former by developing a spin fluctuation model which we hope can be enhanced by including the effect of lattice distortion [21].

To develop our model of spin fluctuation, we have started with the Anderson observation that the superconductivity phenomenon involving the copper 3d and oxygen 2p bands of the CuO_2 plane which is believed to be the key to understanding the normal and superconducting properties of the cuprates, can be reduced to an effective single band pairing problem via his doped resonant valence bond (RVB) model [26]. Zhang and Rice generalized the Anderson approach by showing that it is possible to obtain the Cooper pair as a bound singlet state of the CuO_2 plane within a *t-J* model [27]. This has been successfully achieved [21] using the first electron removal (FER) approach [28] and a highly simplified correlated variational aproach [17,29] to obtain a *t-J* model with the interaction part, *J* being the *XY* limit of the anisotropic Heisenberg exchange interaction in second quantization language:

$$H_{t_{pd}} = -t_{pd}\left[\sum_{\{i\}}\sum_{<j,k>\in\{i\}}d^+_{i_r,\sigma}p^+_{j_r,\sigma}d_{i_r,\sigma}p_{k_r,\sigma} + H.C.\right] + J_{dp}\left[\sum_{\{i\}}\sum_{<j,k>\in\{i\}}d^+_{i_r,\sigma}p^+_{j_r,\bar{\sigma}}d_{i_r,\bar{\sigma}}p_{k_r,\sigma}\right] \quad (2.1)$$

where $d^+(d)$ is the creation (annihilation) of the carrier at the $Cu\,3dx^2\text{-}y^2$ orbital and $p^+(p)$ is the creation (annihilation) of the carrier at the O$2p_x$ and O$2p_y$ orbitals and the t_{pd} denotes a hopping between a Cu and O in the same plane.

This model in (2.1) has been used to account for the formation and propagation of the Zhang-Rice singlet leading to a Cooper channel and hence the superconducting state of the cuprates in agreement with FER experiment [28].

The AF order of the SDW state of the iron pnictides is speculated to be a collective effect that emerges from an instability of the paramagnetic Fermi surface [12]. It is expected that during the phase transition, the SDW is suppressed and the Cooper pairs are formed and liberated to achieve the superconductivity. As stated above, EPI is very weak for the iron pnictides and therefore, there is growing consensus that magnetic fluctuations may be solely responsible for the superconductivity of these materials. It follows then that we can extend the spin fluctuation model in Ref. 21 to the iron pnictides. This will require two modifications of the model: first the Gutzwiller renormalization factors [30] have to be eliminated from the model to reduce the effect of strong correlations and secondly, the strong anisotropy of the interaction part of the model has to be reduced since the iron pnictides have very low anisotropy [18,31], unlike the cuprates which are highly anisotropic [12]. It is pertinent to point out that this study which we have started can be viewed as an extension of the BCS theory to magnetic fluctuation in the same spirit as our recent generalization of the conventional BCS model to iso-superconductivity model [22]. As depicted in Fig. 1, whereas the Feynman diagram for electron-electron scattering leading to net attraction (i.e., Cooper pairing) in the BCS model is mediated by virtual phonon exchange (as shown in Fig. 1a), the exchange interaction in the iso-superconductivity model is 'triggered' by a control parameter (i.e. the effective valence) just as in the superexchange interaction in Ref. 21 and the resulting Cooper pairs in both models is the overlapping electron wavefunctions (as shown in Fig. 1b),. Since this parameter is the effective valence, the remaining part of this paper will be focused on obtaining the T_c from it.
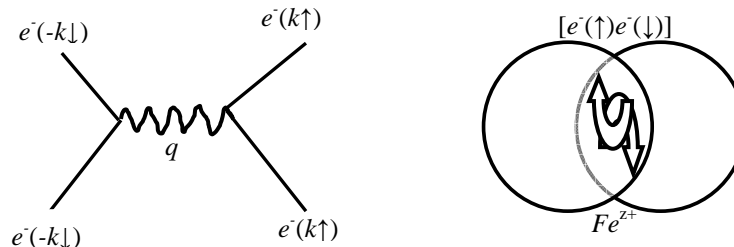

Figure 2.1: Attractive interaction of the electron pair **(a)** due to virtual phonon exchange in the BCS model and **(b)** due to overlapping electron wavefunctions in the superexchange interaction.

3.0   The T_c from the effective valence of the iron

One of the beautiful features of the BCS theory is its ability to predict the T_c of conventional superconductors. Basically, the BCS T_c depends on the electron-phonon coupling

λ, the logarithmically averaged phonon frequency ω_{In}, and the effective Coulomb repulsion μ^{*}:

$$T_c \sim \lambda \omega_{In} \mu^{*} \qquad (3.1)$$

Therefore once these parameters are known for a conventional superconductor, its T_c can be

obtained [16]. This is why the BCS lost its predictive power when the non-conventional superconducting cuprates were discovered because the correlation in these materials is strong and its EPI is weak, though as stated above, the latter factor is still contentious. The inclusion of many body effects as in the Migdal-Eliashberg theory [32] and also vertex corrections [33] could not produce realistic T_c for the nonconventional superconductors. This led to re-expressing (3.1) as [34]

$$T_c \sim \sqrt{\frac{\eta}{M}} \qquad (3.2)$$

where M is an average atomic mass and η is related to the strength of the electronic response of electrons at the Fermi surface to perturbation of the atoms in the crystal.

An interesting feature of (3.2) is that the T_c now depends on parameters which may be determined from the periodic table. Following this line of thinking, Ironkwu [35] empirically obtained a T_c for superconducting materials,

$$T_c = \frac{\chi n k_0}{\sqrt{FW}} \qquad (3.3)$$

where for a material $A_x B_y$ say,

χ is the electronegetivity: $\chi[A_x B_y] = \dfrac{xA_\chi + yB_\chi}{x + y}$;

n is the valence electron count: $n[A_x B_y] = \dfrac{xA_n + yB_n}{x + y}$;

FW is the formula weight: $FW[A_x B_y] = xA_{FW} + yB_{FW}$

and k_0 is an experimentally determined constant which is expected to be specific to the various families of the superconducting materials.

This formula was used to obtain a T_c of 39 K for $MgBr_2$ in agreement with experiment [36] taking $k_0 = 57.1809$. However, using this same value of k_0, one obtain a T_c of 60 K for the $LaFeAsO_{0.89}F_{0.11}$, Tc of 27 K for the $Ba_{0.6}K_{0.4}Fe_2As_2$ and an outrageous T_c of 208 K for the $FeSe_{0.85}$ which are not within the experimental ranges for these compounds (see Table 1). To obtain the experimental T_c values of 26 K for $LaFeAsO_{0.89}F_{0.11}$ and 40 K for $Ba_{0.6}K_{0.4}Fe_2As_2$, one needs $k_0 = 25.63$ and $k_0 = 83.94$ respectively. Therefore (3.3) is not universal and still needs further investigation

The motivating factor here, however, is that the T_c depends on parameters from the periodic table and table of electronegetivity in line with some studies in the literature [2,6,8,12]. For example, the difference between the T_c of LaONiP and LaOFeAs is due to the difference in their electron count and as pointed out in their density functional calculation in [6], the chemical formula in order of electronegativity is $LaFeAsO_{1-x}F_x$ rather than $LaO_{1-x}F_xFeAs$. What this means is that there may be some parameters of the superconducting materials that can be tuned to predict their T_c from data based on these tables. However, it is expected that the general effect of these parameters is to modify the effective valence of the element that drives the formation of the

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Cooper pair in the superconducting compound as discussed in sec. II. Therefore the T_c in (3.3) can be expressed to depend on the $3d^{z+}$ [22]:

$$T_c = 467.0\, z \exp\left(\frac{-13.6}{z}\right) \tag{3.4}$$

where 467.0 is the experimental Debye temperature of iron which a universal quantity and z is to be determined from chemical structure of the superconducting material.

From (3.4), the graph of Figure 3.1 has been plotted to depict the dependence of the T_c on the effective valence of the iron. A number of the superconducting family of the iron pnictides have been inserted for further theoretical and experimental investigation. Also, it is obvious in the graph that the $3d^{z+}$ can be tuned with appropriate material design to achieve higher T_c and probably a T_c at room temperature for $z \approx 5.5 - 6.0$.

Interestingly, a number of studies have shown that there is strong sensitivity of magnetism to the crystal structures of the iron pnictides [2,6,37]. This can easily be illustrated with FeSe which has the simplest structure in the family of superconducting Fe-based compounds and consequently is expected to shed light on the interplay of their structure, magnetism and superconductivity [38]. It has been demonstrated that the sensitivity of the structure and magnetic properties of the FeSe state depends on the Fe:Se ratio [39]. For example, it is observed in a recent study that $FeSe_{0.82}$ has a PbO-type structure belonging to the tetragonal p4/nmm space group and is superconducting while $FeSe_{1.14}$ has a hexagonal structure and is ferrimagnetic [40]. Furthermore, as shown in Table 1, the $\alpha-$ phase of $FeSe_x$ (i.e with $x < \frac{8}{7}$) which superconducts at 8 K is stable in a PbO type structure at room temperature while the β-phase (i.e. with $x > \frac{8}{7} - \frac{4}{3}$) which superconduct at 8.5 K is stable in a NiAs structure at room temperature [37]. This Fe:Se ratio determines the effective valence of the iron atom in the compound.
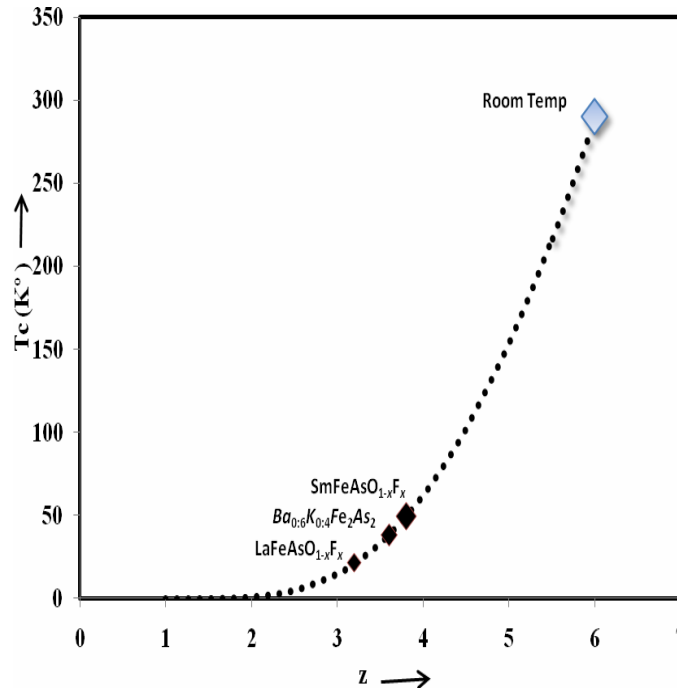

Figure 3.1: A graph showing the relation between the transition temperature T_c and the effective valence $3d^{z+}$ of the iron pnictides.

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4.0   Summary and conclusion

In this paper, it has been pointed out that the spin fluctuation model we developed for the superconducting cuprates [21] can also be modified to account for the magnetic fluctuation leading to superconductivity in the iron pnictides discovered less than two year ago. It was also pointed out that the effective valence of the iron may be responsible for driving the superexchange interaction when the model is applied to the iron pnictides as we have observed from the iso-superconductivity model in a recent study [22]. Therefore, the semiemperical T_c

formula derived from the iso-superconductivity model can also be derived from the spin fluctuation model in Ref. 21. This T_c formula which depends on $3d^{z+}$ is used to predict a room temperature T_c. An obvious open problem now is how to design real materials from the predictive values of the effective valence. This requires further investigation on how parameters from the periodic table database, electronegativity spectrum and material database can be used to obtain the effective valence of iron as a control parameter of the T_c of the superconducting iron pnictides as well as their other properties.

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