Anion height dependence of T_c and density of states in iron based superconductors

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Systematic *ab initio* LDA calculations were performed for all the typical representatives of recently discovered class of iron based high-temperature superconductors: REOFe(As,P) (RE=La,Ce,Nd,Sm,Tb), Ba_2Fe_2As, (Sr,Ca)FFeAs, $Sr_4Sc_2O_6Fe_2P_2$, LiFeAs and Fe(Se,Te). Non-monotonic behavior of total density of states at the Fermi level is observed as a function of anion height relative to Fe layer with maximum at about $\Delta z_a \sim 1.37$Å, attributed to changing Fe – As (P,Se,Te) hybridization. This leads to a similar dependence of superconducting transition temperature T_c as observed in the experiments. The fit of this dependence to elementary BCS theory produces semiquantitative agreement with experimental data for T_c for the whole class of iron based superconductors. The similar fit to Allen – Dynes formula underestimates T_c in the vicinity of the maximum, signifying the possible importance of non – phonon pairing in this region. These results unambiguously demonstrate that the main effect of T_c variation between different types of iron based superconductors is due to the corresponding variation of the density of states at the Fermi level.

Recent discovery of the new class of iron based high-temperature superconductors [1] has ignited almost unprecedented stream of experimental and theoretical studies (for the review of an early work see [2, 3]). Despite the immense progress in understanding of these systems, the nature (mechanism) of superconducting pairing, as well as the reasons for high values of superconducting temperature T_c, are still under debate. In a recent preprint Mizuguhci et al. [4] have established an interesting anion height dependence of T_c for the typical representatives of Fe – based superconductors, demonstrating almost symmetric curve with a peak around $\Delta z_a \sim 1.37$Å. Below we present an explanation of this dependence, attributing it to the effect of the appropriate variation of the total density of states at the Fermi level within standard BCS-like approach.

The main representatives of the class of iron (pnictides, chalcogenides) based superconductors known at the moment are:

1. Doped RE111 (RE=La,Ce,Pr,Nd,Sm,Tb,Dy) with T_c about 25–55 K, with most typical representatives such as $LaO_{1-x}F_xFeAs$ [1, 5 – 12] and $LaO_{1-x}F_xFeP$ [13] with much lower $T_c = 6.6$ K.

2. Doped A122 (A=Ba,Sr), such as $Ba_{1-x}K_xFe_2As_2$ [14 – 17] and T_c about 38 K.

3. $Li_{1-x}FeAs$ with $T_c = 18$ K [18, 19].

4. (Sr, Ca, Eu)FFeAs [20 – 22] with $T_c = 36$ K [23].

5. $Sr_4(Sc,V)_2O_6Fe_2(P,As)_2$ with $T_c = 17$ K [24].

6. $FeSe_x$, $FeSe_{1-x}Te_x$ with T_c up to 14 K [25].

There is now a plenty of papers on LDA (local density approximation) calculation of the band structure of La111 [30 – 32], LaOFeP [33], RE111 series [26], $BaFe_2As_2$ [27, 34, 35], LiFeAs [28, 36], (Sr,Ca)FFeAs [29, 37], Sr42622 [38] and Fe(S,Se,Te) [39]. Below we present some of the results of our continued work on LDA electronic structure, along the lines of Refs. [26, 27, 28, 29], covering all typical representatives of the whole class of iron based superconductors and taking into account some new structural data.

Iron based high-T_c superconductors in general have tetragonal structure with the space group $P4/nmm$ (RE1111, LiFeAs, Sr42622, Fe(Te,Se), SrFFeAs) and the space group $I4/mmm$ (Ba122). For the $P4/nmm$ systems Fe ions occupy positions (2b)(0.75, 0.25, 0.5), and anion ions A=P,As,Se,Te – (2c) $(0.25,0.25,z_a)$ and for Ba122 Fe(4d) (0.5,0,0.25), As(4e)$(0,0,z_a)$. Corresponding experimental lattice parameters and atomic coordinates (used in this work) are collected in Table 1.

Physically important electronic bands (those which cross the Fermi level) are formed by antibonding Fe(3d)-A(p) states of FeA_4 tetrahedron layer. Here A denotes different types of anions: P,As,Se,Te. To calculate electronic structure of compounds listed in Table 1 linearized muffin-tin orbitals method (LMTO) [40] with default settings was employed (except for Re111 systems, where Re-4f states were taken as a pseudocore states). Obtained results are in good agreement with other LDA calculations by other authors.

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Table 1

Experimental crystallographic data for iron based superconductors

| System	Δz_a, Å	a, Å	c, Å	z_{Re}	z_a	$\angle_{a-Fe-a}$
LaOFeP	1.140	3.9636	8.5122	0.1487	0.6339	104.4
$Sr_4Sc_2O_6Fe_2P_2$	1.200	4.0160	15.543	–	0.5772	105.2
LaOFeAs	1.320	4.0353	8.7409	0.1415	0.6512	107.5
CeOFeAs	1.354	3.9959	8.6522	0.1480	0.6565	108.4
SmOFeAs	1.357	3.9270	8.4413	0.1420	0.6608	108.8
NdOFeAs	1.367	3.9476	8.5446	0.1440	0.6600	110.5
TbOFeAs	1.373	3.8530	8.2990	0.1447	0.6654	109.7
SrFFeAs	1.369	4.0110	8.9650	0.1598	0.6527	108.6
$BaFe_2As_2$	1.371	3.9090	13.2122	–	0.3538	109.3
CaFFeAs	1.417	3.8780	8.5920	0.1505	0.6649	110.4
LiFeAs	1.505	3.7914	6.3642	0.8459	0.2635	112.7
Fe(Se,Te)	1.630	3.8215	6.2695	–	0.2599	111.5

Table 2

LDA total DOS N(E_F), calculated and experimental T_c for iron based superconductors

System	Δz_a, Å	N(E_F), states/cell/eV	T_c^{BCS}, K	T_c^{AD}, K	T_c^{Exp}, K
LaOFeP	1.140	2.06	3.2	12	6.6
$Sr_4Sc_2O_6Fe_2P_2$	1.200	3.24	19	27	17
LaOFeAs	1.320	4.13	36	37	28
CeOFeAs	1.354	4.96	54	43	41
SmOFeAs	1.357	4.66	48	37	53
NdOFeAs	1.367	4.78	50	44	54
TbOFeAs	1.373	4.85	52	45	53
SrFFeAs	1.369	4.26	38	39	36
$BaFe_2As_2$	1.371	4.22	38	38	38
CaFFeAs	1.417	4.04	34	36	36
LiFeAs	1.505	3.86	31	34	18
Fe(Se,Te)	1.630	2.02	3	11	14

Motivated by the results of Ref. [4] we present here our LDA calculated total density of states N(E_F) as a function of anion height Δz_a with respect to Fe layer. Corresponding dependence is plotted in Fig.1 with circles. We can see that N(E_F) has an interesting behavior with clear maximum at about $\Delta z_a \sim 1.37$Å (see also Table 2). Such nonmonotonous behavior can be explained by hybridization effects. Namely, as a governing structural parameter characterizing hybridization strength one can chose a-Fe-a angle – an angle between anions (a) and Fe within the same tetrahedron. The value of the angle corresponding to the strongest hybridization is 109.45°, i.e. for an ideal anion tetrahedron with Fe in the very center of it. Other crystal structure parameters which might be marked as important here such as Fe-Fe, Fe-a or a-a distances are not changed

very much from system to system and do not have any transparent dependence of Δz_a. The values of these distances are about following 2.8Å, 2.4Å and 3.85Å with slight lowering for LaOFeP, LiFeAs and Fe(Te,Se) compounds.

From Table 1 one can see that compounds with highest $N(E_F)$ values have the a-Fe-a angle very close to this value. Decrease or increase of this angle leads to $N(E_F)$ drop from this maximum value. This comes from partial DOS behavior. The strongest hybridization corresponds to the strongest bonding-antibonding splitting. Since antibonding band DOS grows monotonically with binding energy [26–29] stronger hybridization will lead to higher values of $N(E_F)$. With lowering of hybridization bonding-antibonding splitting goes down together with $N(E_F)$.
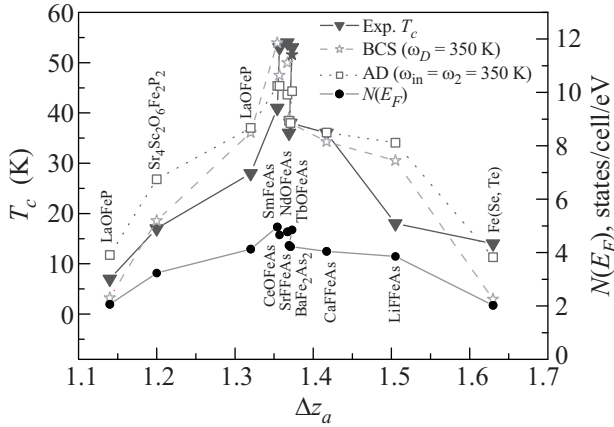
LDA calculated total DOS values $N(E_F)$ (circles, right scale) and superconducting transition temperatures T_c (left scale) obtained from simple BCS (stars) and Allen-Dynes (AD) expressions (squares), as well as experimental T_c values (triangles) versus anion height Δz_a over Fe layer for a number of iron based high temperature superconductors

The Δz_a dependence of $N(E_F)$ inevitably leads to the corresponding dependence of superconducting critical temperature T_c. To estimate this we, first of all, use the elementary BCS expression: $T_c = 1.14\omega_D e^{-1/\lambda}$, where ω_D is the characteristic frequency of collective excitations involved in pairing interaction (phonons, spin fluctuations etc.), and $\lambda = gN(E_F)/2$ is the dimensionless pairing interaction constant (g is the appropriate dimensional coupling constant). In the following we take $\omega_D = 350\,\mathrm{K}$ in rough accord with neutron scattering experiments on phonon density of states for La111 [41] and Ba122[42] systems. We fix g to fit the experimental value of T_c for Ba122 system since this system possesses probably most stable value of T_c (about 38 K) with respect to the way of sample preparation and doping. Thus we obtain the value of dimensionless coupling constant $\lambda = 0.43$. Then just fixing the value of g as for Ba122 we obtain T_c values for all other systems, taking into account the appropriate change of the density of states. Rather surprisingly we observe almost quantitative agreement with experimental data on T_c (see triangles on Figure and Table 2). Note that we can even obtain the right order of T_c values for 1111 systems with different rare-earth elements as due to rather small difference of corresponding densities of states, which were not obtained in our previous work [26], where we just fixed Δz_a to the only known at that time experimental value for LaOFeAs. However, the calculated value of T_c for LaOFeAs system is still rather higher than most typical experimental value of 26–28 K. At the same time, the samples of this system obtained via high pres-

sure synthesis [43] demonstrated much higher values of $T_c \sim 41\,\mathrm{K}$, which is pretty closer to our calculated values. Also the notable deviation of our calculated T_c for LiFeAs system may be attributed both to the crudeness of our model (e.g. our use of a single value of ω_D for all compounds), as well as to probable experimental uncertainties of T_c in this system.

In principle, for the number of systems under consideration we can obtain even better results if we use the multiple band BCS-like approach, along the lines of Ref. [44]. However, to reduce the number of free parameters, the multiple band model fit requires additional information on the relations between energy gaps on different Fermi surface sheets (cylinders), which at present is only availbale for some of 122 systems.

It is well known that the elementary BCS-like expression for T_c has a tendency to overestimate the role of the density of states at the Fermi level. As an alternative we try the same approach estimating superconducting critical temperature T_c using Allen – Dynes interpolation formula (which is probably the best semi-analytic expression for T_c in case of electron-phonon pairing mechanism, including the strong coupling region) [45]:

$$T_c = \frac{f_1 f_2 \omega_{ln}}{1.20} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right), \quad (1)$$

where

$$f_1 = [1 + (\lambda/\Lambda_1)^{3/2}]^{1/3}, \quad \Lambda_1 = 2.46(1 + 3.8\mu^*),$$

$$f_2 = 1 + \frac{(\bar{\omega}_2/\omega_{ln} - 1)\lambda^2}{\lambda^2 + \Lambda_2^2}, \quad \Lambda_2 = 1.82(1 + 6.3\mu^*)(\bar{\omega}_2/\omega_{ln}),$$

and $\bar{\omega}_2 = <\omega^2>^{1/2}$, ω_{ln} are square root average and average logarithm of phonon frequency. Assuming for simplicity $\omega_{ln} \approx \bar{\omega}_2 = 350\,\mathrm{K}$, and taking the optimistic value of Coulomb pseudopotential $\mu^* = 0$, we repeat our previous analysis, fixing first $\lambda = 0.97$ for Ba122 and then changing only the density of states as obtained in our calculations for all other systems. The results for T_c obtained in this way from Allen – Dynes expression (1) are shown in Figure by squares (see also Table 2).

We can see that Allen – Dynes expression produces a kind of a lower bound T_c estimate, with obvious deficit in T_c values in the vicinity of maximum. This deficit may signify the importance of non phonon pairing mechanism to obtain maximal values of T_c in FeAs superconductors. However, our main conclusion on important correlation of T_c with the values of the density of states at the Fermi level remains intact.

In fact we do not adhere at the moment to any specific pairing mechanism. Main objection to electron-phonon pairing in iron based superconductors comes

from microscopic calculations, e.g. those of Ref. [31]. At the same time, there are experiments on isotope effect [46, 47], which support the importance of this mechanism, though the other isotope experiments [48] produce quite opposite picture.

Our choice of characteristic phonon frequencies in the preexponential factor of BCS and Allen – Dynes expressions for T_c is used only as a kind of an estimate. What is important to us, is the well known fact that the dimensionless pairing constant is proportional to the total density of states in almost any BCS-like model of superconducting pairing, with some additional modifications in the case of multiple band models [44].

In conclusion, our results show unambiguous correlation of the values of superconducting T_c and those of the total density of electronic states at the Fermi level for the whole class of iron based superconductors, thus supporting the usual BCS-like pairing mechanism in these systems.

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