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

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Systematic \textit{ab initio} LDA calculations were performed for all the typical representatives of recently discovered class of iron based high-temperature superconductors: REOF(As,P) (\( \text{RE}=\text{La,Ce,Nd,Sm,Tb} \)), \( \text{Ba}_2\text{Fe}_2\text{As}, \) \( \text{Sr}_2\text{Sc}_2\text{O}_6\text{Fe}_2\text{P}_2, \) \( \text{LiFeAs} \) and \( \text{Fe(Se,Te)} \). 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 \( \Delta a \approx 1.37\text{Å} \), 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.

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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 \(^4\) Mizuguhci et al. 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 \( \Delta a \approx 1.37\text{Å} \). 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 (\( \text{RE}=\text{La,Ce,Pr,Nd,Sm,Tb,Dy} \)) with \( T_c \) about 25–55 K, with most typical representatives such as \( \text{LaO}_{1-x}\text{Fe}_{2}\text{As} \) \(^1\)\(^-\)\(^3\) \( \text{LiFeAs} \) \(^4\) \( \text{Sr}_2\text{Sc}_2\text{O}_6\text{Fe}_2\text{P}_2 \) \(^5\)\(^-\)\(^8\) \( \text{Sr}_{1-x}\text{K}_x\text{Fe}_{2}\text{P} \) \(^9\)\(^-\)\(^12\) and \( \text{LaO}_{1-x}\text{Fe}_{2}\text{P} \) \(^13\) with much lower \( T_c \approx 6.6 \) K.

2. Doped A122 (\( \text{A}=\text{Ba,Sr} \)), such as \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_{2}\text{As} \) \(^13\)\(^-\)\(^15\) \( \text{LiFeAs} \) \(^4\) \( \text{Sr}_2\text{Sc}_2\text{O}_6\text{Fe}_2\text{P}_2 \) \(^5\)\(^-\)\(^8\) \( \text{Sr}_{1-x}\text{K}_x\text{Fe}_{2}\text{P} \) \(^9\)\(^-\)\(^12\) and \( \text{Ba}_{1-x}\text{K}_x\text{FeAs} \) \(^16\) \( \text{FeSe} \) \(^4\) \( \text{Sr}_{1-x}\text{K}_x\text{Fe}_{2}\text{P} \) \(^9\)\(^-\)\(^12\) and \( \text{Fe}(\text{Se,Te}) \) \(^39\).

There is now a plenty of papers on LDA (local density approximation) calculation of the band structure of \( \text{La}_{111} \) \(^30\)\(^-\)\(^32\), \( \text{LaFeP} \) \(^33\), RE111 series \(^26\), \( \text{BaFe}_2\text{As}_2 \) \(^27\)\(^-\)\(^30\), \( \text{LiFeAs} \) \(^28\)\(^-\)\(^30\), \( \text{(Sr,Ca)}\text{FeAs} \) \(^29\)\(^-\)\(^37\), \( \text{Sr}_{2622} \) \(^38\) and \( \text{Fe(Se,Te)} \) \(^39\). Below we present some of the results of our continued work on LDA electronic structure, along the lines of Refs. \(^26\)\(^-\)\(^29\), 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 \( P4/nnm \) (RE111, \( \text{LiFeAs} \), \( \text{Sr}_{2622} \), \( \text{Fe(Se,Te)} \), \( \text{Sr}_{2622} \)) and the space group \( I4/mmm \) (Ba122). For the \( P4/nnm \) systems Fe ions occupy positions \( (2b)(0.75, 0.25, 0.5) \), and anion ions \( \text{A}=\text{P,As,Se,Te} – (2c) (0.25,0.25,\Delta a) \) and for Ba122 \( \text{Fe(4d)} \) \( (0.5,0,0.25) \), \( \text{As(4e)(0,0,\Delta a)} \). 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 \( \text{Fe(3d)} \)-\( \text{A(p)} \) states of \( \text{Fe}_4 \) tetrahedron layer. Here \( \text{A} \) denotes different types of anions: \( \text{P,As,Se,Te} \). To calculate electronic structure of compounds listed in Table 1 lin-
earized muffin-tin orbitals method (LMTO) \cite{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.

Motivated by the results of Ref. \cite{4} we present here our LDA calculated total density of states \(N(E_F)\) as a function of anion height \(\Delta z_a\) 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 \(\Delta z_a \sim 1.37\text{Å}\) (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 \(a\text{-Fe-}a\) 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 \(a\text{-a}\) distances are not changed very much from system to system and do not have any transparent dependence of \(\Delta z_a\). 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 \(a\text{-Fe-}a\) 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 \(\Delta E\) and \(\Delta E\) of La111 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 \cite{26}, where we just fixed \(\Delta z_a\) 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 26-28K. At the same time, the samples of this system obtained via high pressure synthesis \cite{33} demonstrated much higher values of \(T_c \sim 41\text{ K}\), 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 \(\omega_D\) 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. \cite{41}. However, to reduce the number of free parameters, the multiple band model fit requires additional information on the relations between energy gaps

\[\lambda = 0.43.\]  

Then just fixing the value of \(\lambda\) 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 Fig. 1 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 \cite{26}, where we just fixed \(\Delta z_a\) 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 26-28K. At the same time, the samples of this system obtained via high pressure synthesis \cite{33} demonstrated much higher values of \(T_c \sim 41\text{ K}\), 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 \(\omega_D\) for all compounds), as well as to probable experimental uncertainties of \(T_c\) in this system.

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on different Fermi surface sheets (cylinders), which at present is only available 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]:

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

where

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

\[
f_2 = 1 + \left( \frac{\bar{\omega}^2/\omega_{ln} - 1}{\Lambda_2} \right)^2, \quad \Lambda_2 = 1.82(1 + 6.3 \mu^*)(\bar{\omega}^2/\omega_{ln}),
\]

and \( \bar{\omega} = \sqrt{\omega^2 - 1/2}, \omega_{ln} \) are square root average and average logarithm of phonon frequency. Assuming for simplicity \( \omega_{ln} \approx \bar{\omega} = 350 \, \text{K} \), 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 [4] are shown in Fig. 1 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 [46,17], 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 [14].

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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Table 1. Experimental crystallographic data for iron based superconductors.

| System          | $\Delta z_a$, 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$_4$Sc$_2$O$_6$Fe$_2$P$_2$ | 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$_2$As$_2$  | 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          | $\Delta z_a$, Å | $N(E_F)$, states/cell/eV | $T_{BCS}^{rel}$, K | $T_{AD}^{rel}$, K | $T_{Exp}^{rel}$, K |
|-----------------|------------------|--------------------------|--------------------|-------------------|---------------------|
| LaOFeP          | 1.140            | 2.06                      | 3.2                | 12                | 6.6                 |
| Sr$_4$Sc$_2$O$_6$Fe$_2$P$_2$ | 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$_2$As$_2$  | 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                  |