

Correlation between T_c and the Cu 4s level reveals the mechanism of high-temperature superconductivity*

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Abstract. Band structure trends in hole-doped cuprates and correlations with T_c are interpreted within the s - d exchange mechanism of high- T_c superconductivity. The dependence of T_c on the position of the copper 4s level finds a natural explanation in the generic Cu 3d, Cu 4s, O 2p_x and O 2p_y four-band model. The Cu 3d–Cu 4s intra-atomic exchange interaction is incorporated in the standard BCS scheme. This dependence of T_c in the whole interval of 25–125 K has no alternative explanation at present, and possibly this quarter of a century standing puzzle is already solved.

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1 Introduction

Quarter of a century after the dramatical discovery of high temperature superconductivity (HTS) the problem of its mechanism remains one of the longest-standing puzzles in the history of science. The cornucopia of ideas is immense – almost every quantum process was tested whether it is the long sought mechanism of HTS. In parallel, the intensive experimental research made cuprates into the most investigated materials. First-principles electronic structure calculations play an important role in understanding the physics of these materials. The Fermi surface of these highly anisotropic crystals is almost cylindrical with rounded-square cross-section. Fifteen years after the beginning of the cuprates era the eye of the professionalist has

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uncovered a subtle correlation [1] between the shape of the Fermi contour and the critical temperature T_c for optimally hole doped cuprates. Pavarini *et al.* [1] considered many hole doped cuprates: $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, La_2CuO_4 , $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_6$, $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{O}_6$, TlBaLaCuO_5 , $\text{HgBa}_2\text{CuO}_4$, $\text{LaBa}_2\text{Cu}_3\text{O}_7$, $\text{La}_2\text{CaCu}_2\text{O}_6$, $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$, $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$, $\text{HgBa}_2\text{CaCu}_2\text{O}_6$; the list can be extended but we believe that a universal correlation was discovered.

In an acceptable approximation the electronic band structure can be described by the four-band Linear Combination of Atomic Orbitals (LCAO) model with on-site energies $\epsilon_s, \epsilon_p, \epsilon_d$, and hopping parameters t_{sp}, t_{pd}, t_{pp} . In this approximation the Hilbert space spans over the Cu $3d_{x^2-y^2}$, Cu 4s, O $2p_x$ and O $2p_y$ valence orbitals. The range parameter $r \equiv 1/2(1 + s)$ which determines the shape of the Fermi contour is determined by the LCAO parameters and the Fermi energy E_F

$$s(E_F) = (\epsilon_s - E_F)(E_F - \epsilon_p)/(2t_{sp})^2. \quad (1)$$

The correlation between T_c and r from the work by Pavarini *et al.* [1] is reproduced in Fig. 1. How such a correlation can possibly exist? Superconductivity is, certainly, created by some interaction, whilst the electronic band structure describes the properties of independent electrons. Is it then possible to uncover an unknown mechanism of interaction investigating only the properties of noninteracting particles? The T_c - r correlation covers the whole temperature range of HTS, but now ten years it remains unexplained. We suppose that this correlation is as important for HTS, as was the isotope effect for the conventional phonon superconductors half a century ago. The aim of the present work is to interpret the correlation reported by Pavarini *et al.* [1] in the framework of some of the models of HTS.

2 T_c - r correlation within the s-d theory

Let us introduce a small modification of the s parameter, $\tilde{s} = \frac{t_{sp}}{t_{pd}}s$. Its reciprocal value

$$\frac{1}{\tilde{s}(\epsilon)} = \frac{4t_{pd}t_{sp}}{(\epsilon_s - \epsilon)(\epsilon - \epsilon_p)}, \quad (2)$$

has an energy denominator typical for the perturbation theory as applied to the secular equation of the generic four-band model

$$\begin{pmatrix} \epsilon_d & 0 & t_{pd}s_x & -t_{pd}s_y \\ 0 & \epsilon_s & t_{sp}s_x & t_{sp}s_y \\ t_{pd}s_x & t_{sp}s_x & \epsilon_p & t_{pp}s_x s_y \\ -t_{pd}s_y & t_{sp}s_y & -t_{pp}s_x s_y & \epsilon_p \end{pmatrix} \begin{pmatrix} D_{\mathbf{p}} \\ S_{\mathbf{p}} \\ X_{\mathbf{p}} \\ Y_{\mathbf{p}} \end{pmatrix} = \epsilon_{\mathbf{p}} \begin{pmatrix} D_{\mathbf{p}} \\ S_{\mathbf{p}} \\ X_{\mathbf{p}} \\ Y_{\mathbf{p}} \end{pmatrix}, \quad (3)$$

where $\epsilon_{\mathbf{p}}$ is the electron energy for the conducting d-band, $s_x = 2 \sin(p_x/2)$, $s_y = 2 \sin(p_y/2)$, and the wave function is normalized $D_{\mathbf{p}}^2 + S_{\mathbf{p}}^2 + X_{\mathbf{p}}^2 + Y_{\mathbf{p}}^2 = 1$.

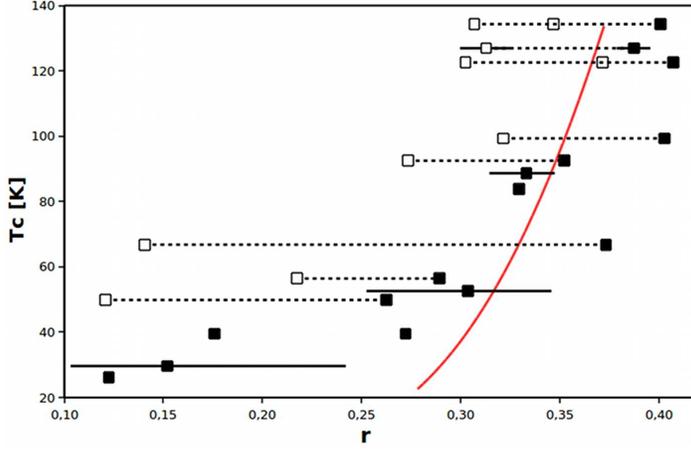


Figure 1. Critical temperature of hole doped cuprates versus band structure parameter r by Pavarini *et al.* [1]. The theoretical curve is calculated according to Eq. (7) (see text for details).

The approximate solution for small hopping amplitudes

$$\begin{pmatrix} D_{\mathbf{p}} \\ S_{\mathbf{p}} \\ X_{\mathbf{p}} \\ Y_{\mathbf{p}} \end{pmatrix} \approx \begin{pmatrix} 1 \\ (s_x^2 - s_y^2) / 4\tilde{s}(\epsilon) \\ \frac{t_{\text{pd}}}{\epsilon - \epsilon_{\mathbf{p}}} s_x \\ -\frac{t_{\text{pd}}}{\epsilon - \epsilon_{\mathbf{p}}} s_y \end{pmatrix}, \quad (4)$$

has a simple interpretation: in the initial approximation we have a pure Cu 3d state with $D_{\mathbf{p}} \approx 1$, in first approximation we have a linear dependence from the t_{pd} amplitude on O 2p levels $X_{\mathbf{p}}$, $Y_{\mathbf{p}} \propto t_{\text{pd}}$, and finally in second approximation, the amplitude on the Cu 4s orbital $S_{\mathbf{p}} \propto t_{\text{pd}} t_{\text{sp}}$ is included by the second virtual transition proportional to t_{sp} . In short, the Cu 4s amplitude of the conduction band can be phrased as 3d-to-4s-by-2p.

As it was concluded by Pavarini *et al.* [1] that materials with lower ϵ_s tend to be those with higher observed values of $T_{c \text{ max}}$. In the materials with higher $T_{c \text{ max}}$ the axial orbital is almost Cu 4s. What is the simplest interpretation of these observations? There is an emerging consensus that superconductivity in cuprates is created by some exchange interaction. The Pavarini *et al* [1] correlation gives that higher $T_{c \text{ max}}$ is determined by the highest Cu 4s amplitude $S_{\mathbf{p}}$. Now we have to recall that the most usual 3d-4s intra-atomic exchange has one of the largest amplitudes in condensed matter physics. We also have to point out that transition metal ion-ion exchange integrals J_{ii} , which create antiferromagnetism in insulator phase are smaller than intra atomic exchange integral J_{sd} .

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The intensive investigations of the Kondo effect have demonstrated that the anti-ferromagnetic sign of the two electrons s–d exchange is the rule and the ferromagnetic sign is an exception. Incorporated in the BCS scheme for the calculation of the order parameter Ξ , the anti-ferromagnetic sign gives pairing in singlet channel with momentum dependent gap

$$\Delta_{\mathbf{p}}(T) = \Xi(T)\chi_{\mathbf{p}}, \quad \chi_{\mathbf{p}} \equiv S_{\mathbf{p}}D_{\mathbf{p}}. \quad (5)$$

This gap is included in the fermion excitation energy

$$E_{\mathbf{p}} \equiv (\eta_{\mathbf{p}}^2 + \Delta_{\mathbf{p}}^2)^{1/2}, \quad \eta_{\mathbf{p}} \equiv \epsilon_{\mathbf{p}} - E_F, \quad (6)$$

and for the temperature dependent order parameter $\Xi(T)$ we have the standard BCS equation

$$2J_{sd} \left\langle \frac{\chi_{\mathbf{p}}^2}{2E_{\mathbf{p}}} \tanh \left(\frac{E_{\mathbf{p}}}{2k_B T} \right) \right\rangle = 1, \quad \langle f_{\mathbf{p}} \rangle \equiv \int_0^{2\pi} \int_0^{2\pi} \frac{dp_x dp_y}{(2\pi)^2} f(\mathbf{p}) \quad (7)$$

where $\langle \dots \rangle$ denotes momentum–space averaging over the Brillouin zone. For a pedagogical derivation of the BSC gap equation in the present notations see the textbook [2] and references therein. Slightly below the critical temperature where the order parameter disappears $\Xi(T_c - 0) = 0$ the gap equation reads

$$\left\langle \frac{\chi_{\mathbf{p}}^2}{\eta_{\mathbf{p}}} \tanh \left(\frac{\eta_{\mathbf{p}}}{2k_B T_c} \right) \right\rangle = \frac{1}{J_{sd}}. \quad (8)$$

Supposing that J_{sd} , being an intra-atomic process, is weakly temperature dependent we can determine its value using band parameters $\epsilon_s, \epsilon_d, \epsilon_p, t_{sp}, t_{pd}, t_{pp}, E_F$ and known T_c . Then we can calculate, for example, the dependence of $T_{c \max}$ by position of the Cu 4s levels ϵ_s . One illustrative example is shown in Fig. 2. The almost linear dependence has to have a simple qualitative interpretation. Let us try to reveal this simplicity using the BCS interpolation formula

$$k_B T_c = 1.14 \hbar \omega_D e^{-1/N(0)V}. \quad (9)$$

In the present case ω_D is an energy parameter of order of the bandwidth, $N(E_F)$ is electronic density of states per spin at the Fermi level and

$$V = J_{sd} \frac{4t_{pd}t_{sp}}{(\epsilon_s - E_F)(E_F - \epsilon_p)} = J_{sd}/\tilde{s}(E_F). \quad (10)$$

The interpolation BCS formula gives

$$\ln(T_c) \approx \ln(1.14\omega_D) - \tilde{s}(E_F)/[N(E_F)J_{sd}], \quad (11)$$

which according to Eq. (2) correlations reported by Pavarini *et al.* [1] are actually correlations between the critical temperature $T_{c \max}$ and the BCS coupling

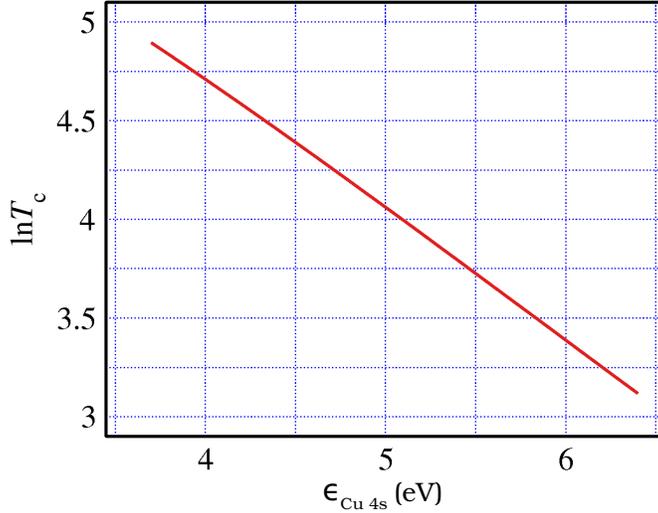


Figure 2. Logarithm of T_c (K) versus $\epsilon_{\text{Cu } 4s}$. Science starts with simplicity – the almost linear behavior corresponds to the well-known BCS formulae given by Eqs. (9) and (11).

constant $J_{sd}/\tilde{s}(E_F)$. This general correlation is typically perturbed by stripes, inhomogeneities, magnetic phenomena, structural phase transition, apex oxygen, chemical substitution, and many other accessories of HTS cuprates. Nevertheless, they can be clearly seen for all hole doped cuprates. This qualitative agreement gives hope that four-band model with incorporated s–d exchange can become a standard model for superconductivity of cuprates. The key role of the $\tilde{s}(E_F)$ parameter reveals why cuprates are unique for reaching high- T_c . Imagine that we can easily tune the position of the Cu 4s level ϵ_s . The pre-exponential factor ω_D is so big that we can easily reach a *sauna-temperature* superconductivity if ϵ_s is small enough. Maximal T_c is reached upon 3d–2p–4s hybridization. For the Cu–O duet we have maximal triple coincidence of levels which ensures the success of the CuO_2 plane. For all other combinations of transition metal with a chalcogenide \tilde{s} is much bigger. For 25 years many ways to decrease ϵ_s were empirically found: apex oxygen, bilayer hopping, pressure, etc. Perhaps only metastable artificial layers are not completely investigated.

3 Computational method

The parent CuO_2 layer is an insulator with a half-filled conduction band. Doping with \tilde{p} holes per Cu atom results in metalization with hole filling $f = \frac{1}{2} + \tilde{p}$. The optimal doping corresponds to $\tilde{p}_{\text{max}} = 0.16$ and $f_{\text{max}} = 0.66$. We will use 66% hole filling for all examples in the present work. The Fermi level is determined

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by the condition

$$f = \langle \theta(\epsilon_{\mathbf{p}} > E_F) \rangle, \quad \text{where} \quad \theta(\epsilon_{\mathbf{p}} > E_F) = \begin{cases} 1 & \text{if } E_{\mathbf{p}} > E_F, \\ 0 & \text{if } E_{\mathbf{p}} < E_F. \end{cases} \quad (12)$$

The parameters of the four-band model can be determined by comparison with first-principles electronic structure calculations. For example, using the Γ point one can determine the on-site energies $\epsilon_d = \epsilon(p_x = 0, p_y = 0)$ for the conduction band. In the present paper we use as an illustration a set of parameters (in eV) similar to Ref. [1]

$$\begin{aligned} \epsilon_s &= 5.4, & \epsilon_p &= -1, & \epsilon_d &= 0, \\ t_{sp} &= 2, & t_{pd} &= 1.5, & t_{pp} &= 0.2. \end{aligned} \quad (13)$$

eV Assuming $T_{c, \max} = 90$ K for $\epsilon_s = 5.4$ we obtain, according to Eq. (8), $J_{sd} = 2.44$ eV. Then for so fixed J_{sd} we can calculate the correlations of $T_{c, \max}$ with the range parameter

$$r \equiv \frac{1}{2(1+s)}. \quad (14)$$

Let us discuss briefly our finding. Within the four-band model one can derive an exact equation for constant energy contours

$$-2t(\epsilon)[\cos(p_x) + \cos(p_y)] + 4t'(\epsilon) \cos(p_x) \cos(p_y) = q(\epsilon), \quad (15)$$

where $t(\epsilon)$, $t'(\epsilon)$ and $q(\epsilon)$ are polynomial functions of energy. The ratio of the effective intra-layer hopping parameters

$$\frac{t'(E_F)}{t(E_F)} \propto r(E_F), \quad (16)$$

describes small variations of the shape of the Fermi contour influenced by the position of the Cu 4s level ϵ_s .

4 Conclusions

Electronic structure experts should be proud that after many years of systematic research band calculations have revealed that T_c depends on the Cu 4s level. This numerical experiment is actually the crucial one for understanding the mechanism of HTS. The r parameter is introduced in electronic structure calculations in such a way, that for the first time we have a mechanism of a physical phenomenon possibly revealed by computer.

We advocate a conventional theoretical explanation of the T_c - r correlations [1] which has no alternative among other theories of HTS. We have to wait for

the appearance of some other descriptions, because this important correlation covers a whole range of HTS. The LCAO model was only a tool for the theoretical analysis of the mechanism of HTS. It should be interesting to determine S_p and D_p directly from partial wave analysis at the muffin spheres directly by the electronic band calculations. The interpolating $\chi_p = S_p D_p$ function can be directly substituted in the BCS gap equation (7) and the equation for T_c , Eq. (8). For the cuprates χ_p well describes the experimental data for the gap anisotropy Δ_p on the Fermi surface. It remains to be seen if this mechanism is applicable only to cuprates.

The iron-based pnictides are suspected to pursue an Oscar for supporting role. It will be extremely interesting to probe if Eq. (8) can describe the common trends for the T_c and gap anisotropy of ferro-pnictides. In this regards, finally we would like to re-analyze the “boost” that the physics of superconductivity got from the iron pnictides. Very recently, Mazin [3] recalled the Matthias’ rules, well known in the physicists folklore: 1) A high symmetry is good; cubic symmetry is the best. 2) A high density of electronic states is good. 3) Stay away from oxygen. 4) Stay away from magnetism. 5) Stay away from insulators. 6) Stay away from theorists.

In order to emphasize the common properties of cuprates and iron pnictides we feel it compelling to rephrase these rules: (1) A high symmetry is good, square symmetry is the best, layered structure ensures empty s-band. (2) Having empty s-band, the Fermi level falls in the narrow d-band which ensures high density of states. (3) The oxygen and pnictide p-orbitals are perfect “go-between” for the transition metal 3d and 4s orbitals. These oxidants create significant 4s polarization of the conduction 3d band. (4) We are just in the epicenter of magnetism; the s-d exchange amplitude which creates the ferromagnetism of iron, possibly creates the superconductivity of iron pnictides and cuprates. (5) Having narrow 3d band in the case of half-filling we observe metal-insulator transition. Transition to insulator phase is a hint for high density of states at the Fermi level for a doped compound. (6) Favorites of great socialists like Lenard, Kapica and Stark, have given similar advice. In order to surmount this weakness it is necessary to remedy the inferiority complex of the band calculators. One Nobel prize is a good initial dose of this treatment. Up to now there is no Nobel prize awarded to computational physics, but the considered in this paper T_c - r correlations are a typical physical phenomenon whose nature is revealed by numerical calculations. Prediction of an artificial structure with high \bar{s} parameter, further synthesis by solid-state chemists and measurement of T_c may successfully initiate a new direction of intensive research.

In conclusion, we briefly re-state the main property of high- T_c superconductivity—the triple coincidence of the d-, s-, and p-levels which ensures big enough BCS coupling constant. This triple coincidence is analogous to the sequence of vernal equinox, full moon, and Sunday (the end of the winter season, the end of the moon month and the end of the week): a triple holiday

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creating the Great-day. In this sense the high- T_c superconductivity is the Easter of condensed matter physics.

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