Band-structure trend in hole-doped cuprates and correlation with $T_{c_{\text{max}}}$.

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By calculation and analysis of the bare conduction bands in a large number of hole-doped high-temperature superconductors, we have identified the energy of the so-called axial-orbital as the essential, material-dependent parameter. It is uniquely related to the range of the intra-layer hopping. It controls the Cu 4$s$-character, influences the perpendicular hopping, and correlates with the observed $T_c$ at optimal doping. We explain its dependence on chemical composition and structure, and present a generic tight-binding model.

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The mechanism of high-temperature superconductivity (HTSC) in the hole-doped cuprates remains a puzzle [1]. Many families with CuO$_2$-layers have been synthesized and all exhibit a phase diagram with $T_c$ going through a maximum as a function of doping. The prevailing explanation is that at low doping, superconductivity is destroyed with rising temperature by the loss of phase coherence, and at high doping by pair-breaking [2]. For the materials-dependence of $T_c$ at optimal doping, $T_{c_{\text{max}}}$, the only known, but not understood, systematics is that for materials with multiple CuO$_2$-layers, such as HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2}$, $T_{c_{\text{max}}}$ increases with the number of layers, $n$, until $n \sim 3$. There is little clue as to why for $n$ fixed, $T_{c_{\text{max}}}$ depends strongly on the family, e.g. why for $n=1$, $T_{c_{\text{max}}}$ is 40 K for La$_2$CuO$_4$ and 85 K for Tl$_2$Ba$_2$CuO$_6$, although the Neel temperatures are fairly similar. A wealth of structural data has been obtained, and correlations between structure and $T_c$ have often been looked for as functions of doping, pressure, uniaxial strain, and family. However, the large number of structural and compositional parameters makes it difficult to find what besides doping controls the superconductivity. Insight was recently provided by Sео et al. [3] who grew ultrathin epitaxial La$_{1.9}$Sr$_{0.1}$CuO$_4$ films with varying degrees of strain and measured all relevant structural parameters and physical properties. For this single-layer material it was concluded that the distance between the charge reservoir and the CuO$_2$-plane is the key structural parameter determining the normal state and superconducting properties.

Most theories of HTSC are based on a Hubbard model with one Cu $d_{x^2-y^2}$-like orbital per CuO$_2$ unit. The one-electron part of this model is, in the $k$-representation:

$$\varepsilon(k) = -2t (\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y$$

$$-2t'' (\cos 2k_x + \cos 2k_y) + \ldots,$$  \hspace{1cm} (1)

with $t$, $t'$, $t''$, ... denoting the hopping integrals ($\geq 0$) on the square lattice (Fig. 1A). First, only $t$ was taken into account, but the consistent results of local-density approximation (LDA) band-structure calculations [4] and angle-resolved photoemission spectroscopy (for overdoped, stripe-free materials) [3], have lead to the current usage of including also $t'$, with $t'/t \sim 0.1$ for La$_2$CuO$_4$ and $t'/t \sim 0.3$ for YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$, whereby the constant-energy contours of expression (1) become rounded squares oriented in respectively the [11]- and [10]-directions. It is conceivable that the materials-dependence enters the Hamiltonian primarily via its one-electron part [1], and that this dependence is captured by LDA calculations. But it needs to be filtered out:

$$1 - u - d(\varepsilon) + (1 + u)p(\varepsilon) = \frac{v^2}{1 - u + s(\varepsilon)}$$ \hspace{1cm} (2)

in terms of the coordinates $u \equiv \frac{1}{2} (\cos k_x + \cos k_y)$ and $v \equiv \frac{1}{2} (\cos k_x - \cos k_y)$, and the quadratic functions

$$d(\varepsilon) \equiv \frac{(\varepsilon - \varepsilon_d) (\varepsilon - \varepsilon_p)}{4t''^2_{pd}} \quad \text{and} \quad s(\varepsilon) \equiv \frac{(\varepsilon_s - \varepsilon) (\varepsilon - \varepsilon_p)}{4t''^2_{sp}}$$
which describe the coupling of $O_a/p_z/y$ to respectively Cu $d_{x^2-y^2}$ and Cu $s$. The term proportional to $p(\varepsilon)$ in (2) describes the admixture of $O_a/p_z$ orbitals for dimpled layers and actually extends the four-orbital model to a six-orbital one. For $\varepsilon$ near the middle of the conduction band, $d(\varepsilon)$, $s(\varepsilon)$, and $p(\varepsilon)$ are positive, and the energy dependence of $d(\varepsilon)$ may be linearized ($d>0$), while that of $s(\varepsilon)$ and of $p(\varepsilon)$ may be neglected. $p=0$ for flat layers and $p=s^2/(1+s)^2$ for layers dimpled so as to yield extended saddlepoints. The bilayer bonding and antibonding subbands have $\varepsilon_s$-values split by $\pm t_{ab}$. Now, if $\varepsilon_s$ were infinitely far above the conduction band, or $t_{sp}$, vanishingly small, the right-hand side of (2) would vanish, with the result that the constant-energy contours would depend only on $u$. The dispersion of the conduction band near the Fermi level would thus be that of the one-orbital model with $t=(1-p)/4d$ and $t'=t''=0$.

For realistic values of $\varepsilon_s$ and $t_{sp}$, the conduction band attains Cu $s$-character proportional to $v^2$, thus vanishing along the nodal direction, $k_x=k_y$, and peaking at $(\pi,0)$, where it is of order 10 per cent. The repulsion from the Cu $s$-band lowers the energy of the van Hove singularities and turns the constant-energy contours towards $[10]$. This same $v^2$-dependence pertains to the interlayer splitting caused by $t_{ab}$ in a multilayer material. In order to go from (2) to (3),

$$\frac{1}{1-u+s} = \frac{2r}{1-2ru}, \quad \text{with} \quad r = \frac{1/2}{1+s},$$

was expanded in powers of $2ru$. This provided explicit expressions, such as: $t = [1-p+o(r)]/4d$, $t' = [r+o(r)]/4d$, and $t'' = \frac{1}{2}t'+o(r)$, for the hopping integrals of the one-orbital model in terms of the parameters of the four(six)-orbital model and the expansion energy $\sim \varepsilon_F$. Note that all intralayer hoppings beyond nearest neighbors are expressed in terms of the range-parameter $r$. Although one may think of $r$ as $t'/t$, this holds only for flat layers and when $r<0.2$. When $r>0.2$, the series must be carried beyond $t''$. Dimpling is seen not to influence the range of the intralayer hopping, but to reduce $t$ through admixture of $O_a/p_z$. In addition, it reduces $t_{pd}$.

Here, we shall generalize this analysis to all known families of HTSC materials using a new muffin-tin-orbital (MTO) method which allows us to construct minimal basis sets for the low-energy part of an LDA band structure with sufficient accuracy that we can extract the materials dependence. This dependence, we find to be contained solely in $\varepsilon_s$, which is now the energy of the axial orbital, a hybrid between Cu $s$, Cu $d_{3z^2-1}$, apical-oxygen O, $p_z$, and farther orbitals on e.g. La or Hg. The range, $r$, of the intralayer hopping is thus controlled by the structure and chemical composition perpendicular to the CuO$_2$-layers. It turns out that the materials with the larger $r$ (lower $\varepsilon_s$) tend to be those with the higher observed values of $T_{c,max}$. In the materials with the highest $T_{c,max}$, the axial orbital is almost pure Cu $4s$.

![FIG. 2. LDA bands calculated with the NMT0 method in the body-centered tetragonal structure. The dashed band was obtained using the Bloch sum of MTOs with N=0 and Cu $d_{x^2-y^2}$ symmetry at the central site. $\Gamma (0,0,0), D (\pi,0,0), Z (2\pi,0,0) = (0,0,2\pi/c), X (\pi,\pi,0)$.](image)

It should be noted that $r$ describes the shape of the non-interacting band in a 1 eV-range around the Fermi level, whose accurate position is unknown because we make no assumptions about the remaining terms of the Hamiltonian, inhomogeneities, stripes, a.s.o.

Fig. 2 shows the LDA bands for the single-layer materials La$_2$CuO$_4$ and Tl$_2$Ba$_2$CuO$_6$. Whereas the high-energy band structures are complicated and very different, the low-energy conduction bands shown by dashed lines contain the generic features. Most notably, the dispersion along $\Gamma$DZ is suppressed for Tl$_2$Ba$_2$CuO$_6$, relatively to La$_2$CuO$_4$, whereas the dispersion along $\Gamma$ZX is the same. This is the $v^2$-effect. The low-energy bands were calculated variationally with a single Bloch sum of Cu $d_{x^2-y^2}$-like orbitals, constructed to be correct at an energy near half-filling. Hence, these bands agree with the full band structures to linear order and head towards the pure Cu $d_{x^2-y^2}$-levels at $\Gamma$ and Z, extrapolating across a multitude of other bands. This was explained in Ref. 3.

Now, the hopping integrals $t$, $t'$, $t''$, ..., may be obtained by expanding the low-energy band as a Fourier series. This yields: $t=0.43\text{eV}$ in both cases, $t'/t=0.17$ for La$_2$CuO$_4$ and 0.33 for Tl$_2$Ba$_2$CuO$_6$, and many further inter- and intralayer hopping integrals.

That all these hopping integrals and their materials-dependence can be described with a generalized four-orbital model, is conceivable from the appearance of the conduction-band orbital for La$_2$CuO$_4$ in the $xz$-plane (Fig. 3). Starting from the central $Cu$ atom and going in the $x$-direction, we see 3$d_{z^2}$ and $d_{x^2-y^2}$ antibond to neighboring $O_a$ 2$p_z$, which itself bonds to 4$s$ and antibonds to 3$d_{3z^2-1}$ on the next Cu. From here, and in the $z$-direction, we see 4$s$ and 3$d_{3z^2-1}$ antibond to O$_b$ 2$p_z$, which itself bonds to La orbitals, mostly 5$d_{3z^2-1}$. In the $y$-direction, 4$s$ antibonds and 3$d_{3z^2-1}$ bonds to O$_b$ 2$p_y$. For Tl$_2$Ba$_2$CuO$_6$, we find about the same amount of Cu 3$d_{z^2}$ and O$_b$/4$p_{z/y}$ character, but more Cu 4$s$, negligible Cu 3$d_{3z^2-1}$, much
less O₂, 2p₂, and Tl6s instead of La₅d₃z²₋₁ character. That is, in Tl₂Ba₂CuO₆ the axial part is mainly Cu 4s.

Calculations with larger basis sets than one MTO per CuO₂ now confirm that, in order to localize the orbitals so much that only nearest-neighbor hoppings are essential, one needs to add one orbital, Cu axial, to the three standard ones [7]. The corresponding four-orbital Hamiltonian is therefore the one described above in Fig. 1 and Eqs. (2)-(4). Note, that we continue to call the energy of the axial orbital c, and its hopping integral with Oₐ/b.pₓ/y tₛp. Calculations with this basis set for many different materials show that, of all the parameters, only c varies significantly [7]. This variation can be understood in terms of the couplings between the constituents of the axial orbital sketched in the right-hand panel of Fig. 3. We first form the appropriate Oₐ.p₂-like 5-atom hybrid Cu₅d₃z²₋₁ - 20c.p₂ - 2La with the energy [7]

\[ c = c + \left(1 + \frac{t_{sc}}{t_{sp}} \right)^2 \frac{4t_{czz}^2}{\epsilon_F - \epsilon_{cz} - 2} - \frac{t_{sc}^2}{\epsilon_F - \epsilon_{La}} \],

and then couple this to the Cu s-orbital to yield the energy c = cₐ + 2tₛ²/\(\epsilon_F - \epsilon_c\) of the axial orbital. Here, the energies of the pure Cu s- and Oₐ.p₂-orbitals are denoted cₐ and c, respectively, while their hopping integral is tₛ. The energy of the Cu d₃z²₋₁-orbital is cₐ, and its hopping integrals to Oₐ/b.pₓ/y and Oₐ.p₂ are respectively tₛp and tₛz². In deriving Eqs. (2)-(4), we have exploited [7] that \( t_{pz}^2/t_{sp}^2 \ll \frac{\epsilon_F - \epsilon_{cz}}{\epsilon_{La} - \epsilon_F} \) and that \( t_{pd}^2/t_{sp}^2 \ll \frac{\epsilon_F - \epsilon_c}{\epsilon_{La} - \epsilon_F} \). Although specific for La₂CuO₄, Eq. (4) is easy to generalize.

FIG. 3. Left: N=0 MTO describing the Cu d₃z²₋₁-like conduction band in La₂CuO₄. The plane is perpendicular to the layers and passes through Cu, Oₐ, Oₐ, and La. Right: Schematic diagram giving the energy c of the axial orbital in terms of the energies of its constituents and their couplings.

In Fig. 4 we plot the r-values for single-layer materials against the distance dₐ-CuO₄ between Cu and apical oxygen. r increases with dₐ-CuO₄ because c is lowered towards \( \epsilon_F \) when the coupling between Oₐ.p₂ and Cu₅d₃z²₋₁/s is weakened. Since \( t_{cz} \propto d_{cu-oₐ} \) and \( t_{sc} \propto d_{cu-oₐ}^2 \), increasing the distance suppresses the Cu₅d₃z²₋₁ content, which is then important in La₂CuO₄, but negligible in Tl₂Ba₂CuO₆ and HgBa₂CuO₄. This is also reflected in the slopes of the lines in Fig. 5 which give r vs. dₐ-CuO₄ for each material. The strong slope for La₂CuO₄ explains the findings of Seo et al. [7], provided that r correlates with superconductivity. That the Bi-point does not fall on the La-line is an effect of Bi being different from La: Bi 6p₂ couples stronger to Oₐ, 2p₂ than does La 5d₃z²₋₁. The figure shows that upon reaching HgBa₂CuO₄, r is saturated, \( c \sim cₐ \), and the axial orbital is almost purely Cu 4s.

FIG. 4. Calculated range parameter, r, for single-layer materials vs. the distance (in Å) between Cu and Oₐ. The lines result from rigid displacements of Oₐ.

FIG. 5. Correlation between calculated r and observed Tₐ max. Filled squares: Single-layer materials and most bonding subband for multilayers. Empty squares: Most antibonding subband. Half-filled squares: Non-bonding subband. Dotted lines connect subband-values. Bars give kₓ-dispersion of r in primitive tetragonal materials. a-m [7]
relate with the observed $T_c \max$. But the experimental uncertainties of both $T_c \max$ and the structural parameters are such that we need better statistics. Therefore, we plot the observed $T_c \max$ against the calculated $r$-values for nearly all known hole-doped HTSCs in Fig. 3 For the single-layer materials, we observe a strong correlation between $r$ and $T_c \max$, which seems to be continued in the bonding subband for the multilayer materials (filled squares). This indicates that the electrons are delocalized over the multilayer, and that $T_c \max$ increases with the number of layers for the same reason that it increases among single-layer materials; the multilayer is simply a means of lowering $\varepsilon_s$ further, through the formation of Cu 4$s$-Cu 4$s$ bonding states. This is consistent with the celebrated pressure-enhancement of $T_c$ in HgBa$_2$CaCu$_2$O$_{6+}$ One might attempt to increase $T_c \max$, say for YBa$_2$Cu$_3$O$_{7-}$, by substituting Y with a smaller cation, e.g. Sc. This has not been done, but a larger cation, La, was recently inserted [2], and that caused $T_c \max$ to drop from 92K to 50K. Using the observed structure of LaBa$_2$Cu$_3$O$_{7-}$, we have calculated the $r$-values and included them in Fig. 3 Here again, the bonding subband is seen to follow the trend! That $T_c \max$ eventually drops for an increasing number of layers, is presumably caused by loss of phase coherence.

Interlayer coupling in bct La$_2$CuO$_4$ mainly proceeds by hopping from O$_c$p$_z$ at (0, 0, zc) to its four nearest neighbors at $(\pm \frac{1}{2}, \pm \frac{1}{2}, \frac{1}{2} - z)c$, and is therefore taken into account by adding to $\varepsilon_s$ on the right-hand side of (4) the term $-8t^\perp_{cc} \cos \frac{\pi}{2} k_x \cos \frac{\pi}{2} k_y \cos \frac{\pi}{2} k_z$. In primitive tetragonal materials, the corresponding term is merely $\infty \cos c k_z$, because the CuO$_2$-layers are stacked on top of each other, e.g. in HgBa$_2$CaCu$_2$O$_{6+}$, the interlayer coupling proceeds from O$_c$p$_z$ at (0, 0, zc) via Hg6s/6p$_z$ at (0, 0, (1 - z)c) Periodic interlayer coupling thus makes $\varepsilon_s$ depend on $k_z$, and this passes onto the conduction band a $k_z$-dispersion $\propto v^2 \cos \frac{\pi}{2} k_x \cos \frac{\pi}{2} k_y \cos \frac{\pi}{2} k_z$ in bct and $\propto v^2 \cos c k_z$ in tetragonal structures. Fig. 5 shows how the $k_z$-dispersion of $r$ decreases with contraction of the axial orbital.

Our identification of an electronic parameter, $r$ or $\varepsilon_s$, which correlates with the observed $T_c \max$ for all known types of hole-doped HTSC materials should be a useful guide for materials synthesis and a key to understanding the mechanism of HTSC. With current $k$-space renormalization-group methods one could for instance investigate the effect of the band shape on the leading correlation-driven instabilities [23]. Moreover, the possibility that a longer hopping-range leads to better screening of the Coulomb repulsion, maybe even to screening, could be studied. Increased diagonal hopping, $t'$, might lead to higher $T_c \max$ by suppression of static stripe order [24]. The Van Hove scenario [25] finds no support in Fig. 3 because it is the saddlepoint of the anti-bonding band which is at the LDA Fermi level in YBa$_2$Cu$_3$O$_7$; the bonding band is about half-filled and enhances spin-fluctuations with $q \approx (\pi, \pi)$ [26]. The propensity to buckling is increased by pushing the conduction band towards the O$_c$/p$_{z}$-level by lowering of $\varepsilon_s$ [4], but recent structural studies [22] as well as Fig. 3 disprove that static buckling enhances $T_c \max$, although dynamical buckling might. The interlayer-pair-tunnelling mechanism [27] is ruled out by the fact that the additional factor $\frac{1}{2} k_x \cos \frac{\pi}{2} k_y$ attained by $t^\perp$ (k) in bct materials suppresses the interlayer-pair-tunnelling in Tl$_2$Ba$_2$CuO$_6$ compared with HgBa$_2$CuO$_4$, and yet, $T_c \max \sim 90K$ in both cases. That the axial orbital is the channel for coupling the layer to its surroundings is supported [28] by the observations that the $k$-dependence of the scattering in the normal state is $v^2$-like [4] and that the $c$-axis transport is strongly suppressed by the opening of a pseudogap [29] with similar $k$-dependence. The axial orbital is also the non-correlated vehicle for coupling between oxygens in the layer. Therefore it seems plausible that contraction of the axial orbital around the CuO$_2$-layer, away from the less perfect doping and insulating layers, will strengthen the phase coherence and thus increase $T_c \max$. Thermal excitation of nodal quasiparticles [30] is, on the other hand, hardly the mechanism by which the superconducting state is destroyed, because the axial orbital does not influence the band in the nodal direction. Finally, we note that the correlation between $r$ and $T_c \max$ does not extend to electron-doped cuprates, where the mechanism for superconductivity thus seems to be different.

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