O.K. Andersen,
Max-Planck Institute for Solid-State Research, Stuttgart:

Band structures of known families of HTSC cuprates;

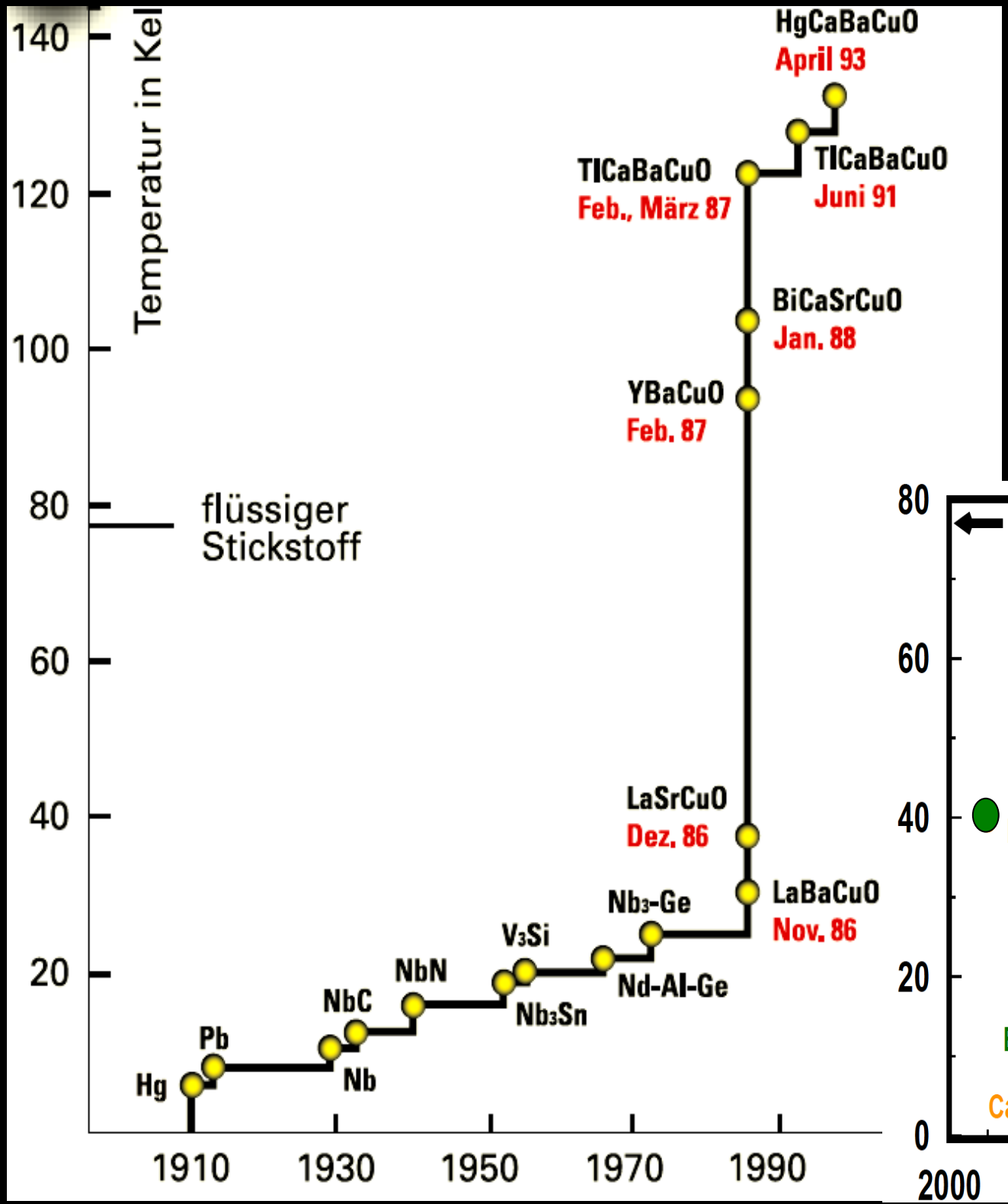
Ove Jepsen, S. Lichtenstein, I. Mazin, I. Dasgupta, E. Pavarini,
T. Saha-Dasgupta.

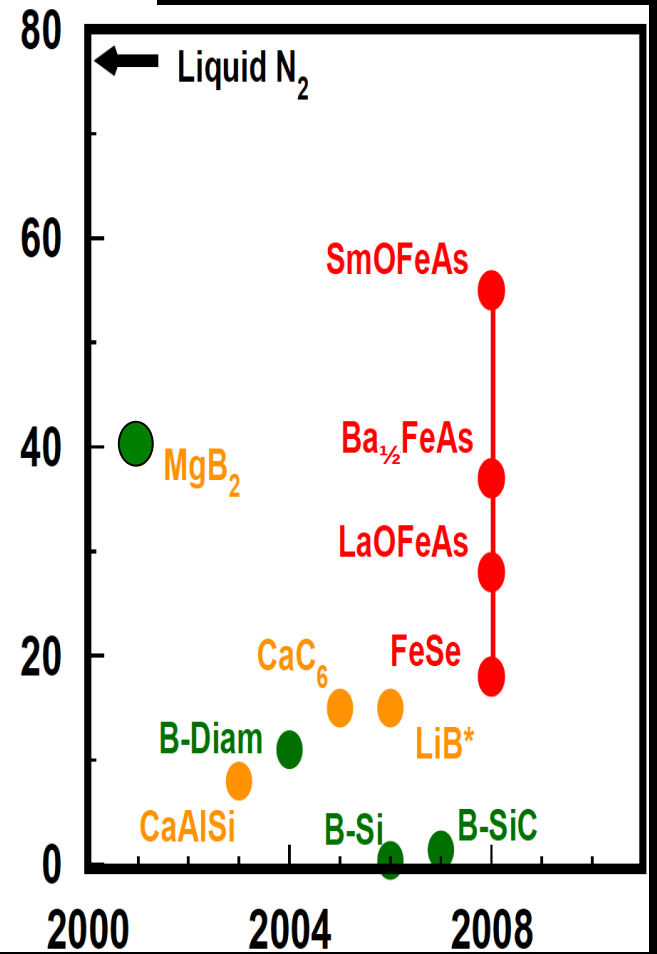
can we engineer them to get further?

Xiaoping Yang, P. Hansmann, A. Toschi, G. Khaliullin, K. Held

The crackpot contribution at the end of an otherwise serious school

The quest for high-temperature super-conductivity





In order to get better superconductors,
do we need to understand the
mechanism?

and if we do,
does it help?

What can be learned about high T_c from the LDA?

1988 Physica C **153-155**; Zaanen, Jepsen, Gunnarsson, Paxton, Andersen, Svane.

1988 - **Presumably nothing, because strong electronic correlations in HTSCs.**

1988 - 91 LDA+U calculations for undoped compounds. Parameters of the 3-band Hubbard model supporting the Emery and t-J models.

1988 - 92 Fermi surfaces for many cuprates. Agreement with positron anihilation and early ARPES.

$YBa_2Cu_3O_7$:
Interband transitions. Agreement with optical spectra for $\omega > 2$eV.
Phonon frequencies and linewidths at high symmetry **q**'s. Consistent with Raman data.
Raman intensities for the various polarizations. Consistent with exp.

1994 - 95 Extract low-energy TB models explaining the "chemistry". Predict t'/t, bi-layer splitting $t_{perp}(k_x,k_y) \alpha (\cos k_x - \cos k_y)^2$ and interplane exch-coupling $J_{perp} \alpha \int t_{perp}(k) t_{perp}(k+Q) dk/U$

1995 - 96 Phonon frequencies and linewidths for all **q**'s in *s*- and *d*-wave channels. Analytical g(**k**,**k**')

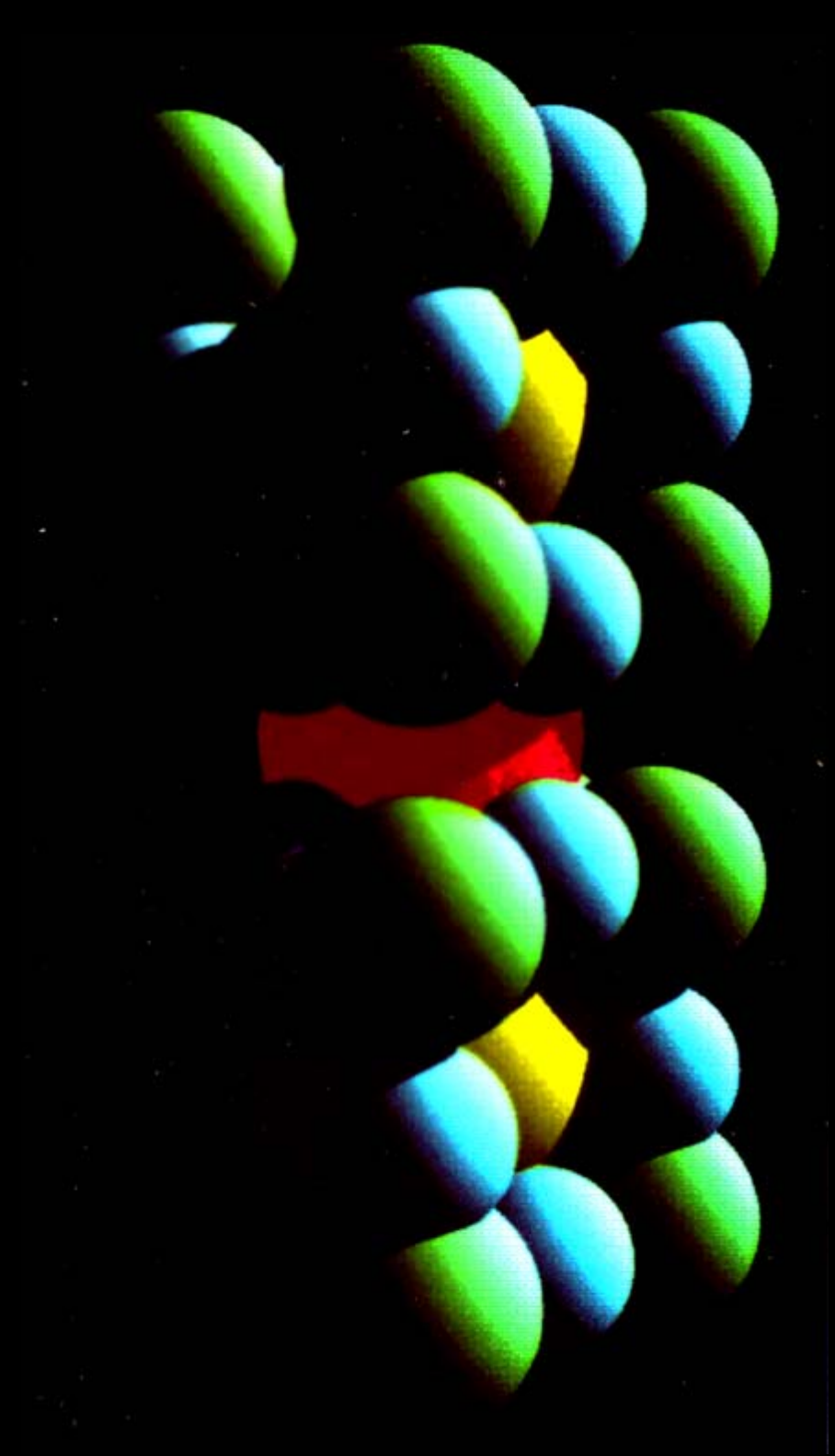
2000- **Who cares! ARPES sees the FS and the dressed band structure!**

We do, because ARPES from overdoped systems do confirm the LDA FS predictions.

2001 t'/t for 15-20 families of HTSC; correlation with $T_{c,max}$

2003- Numerically exact Wannier functions, 1- and 3-band Hubbard Hamiltonians. DMFT, DCA and other many-body calculations.

2009- **After 23 years, the mechanism of HTSC remains an unsolved problem**



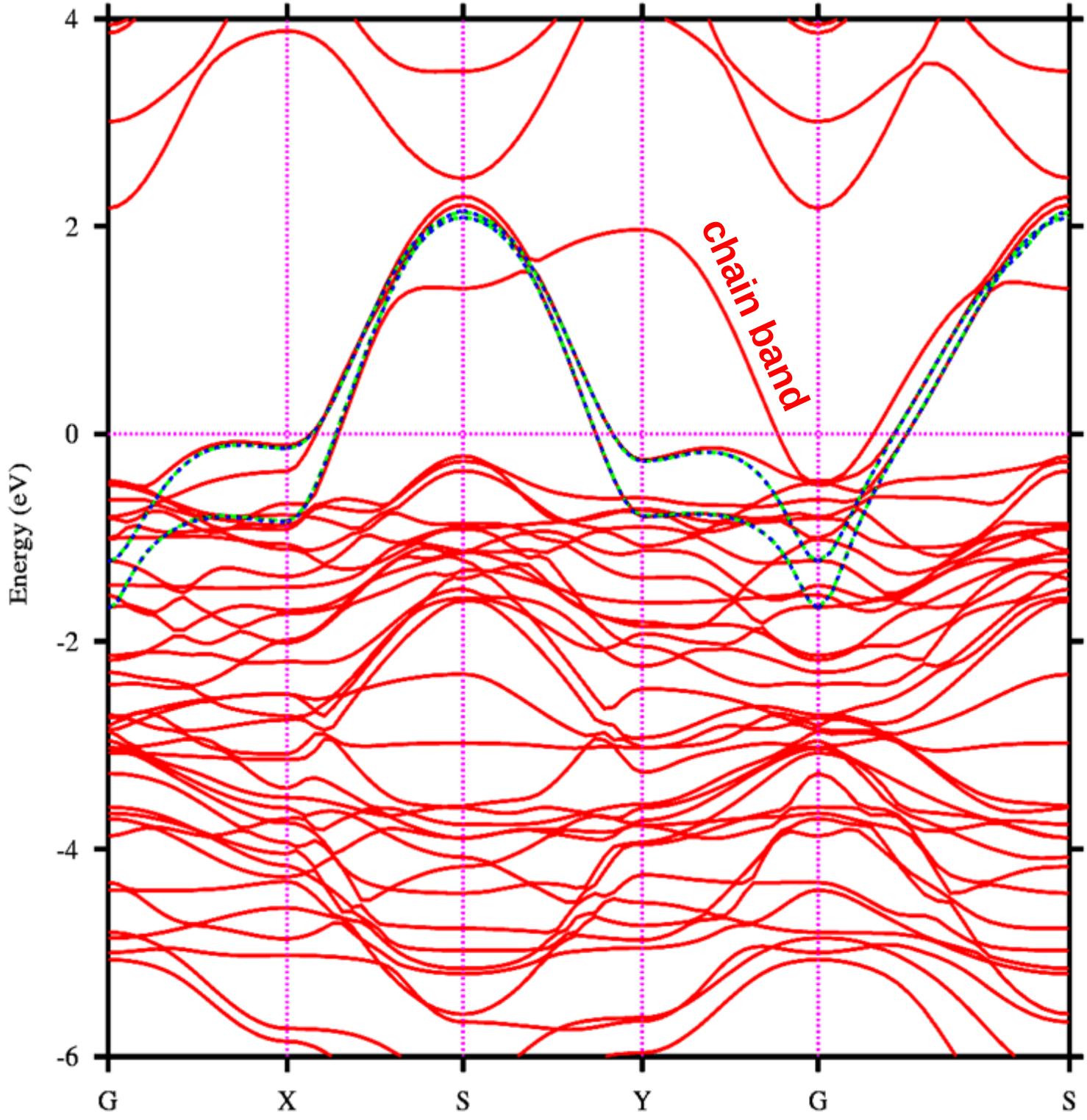
$YBa_2Cu_3O_7$

$YBa_2Cu_3O_7$

Stoichiometric at optimal doping

LDA

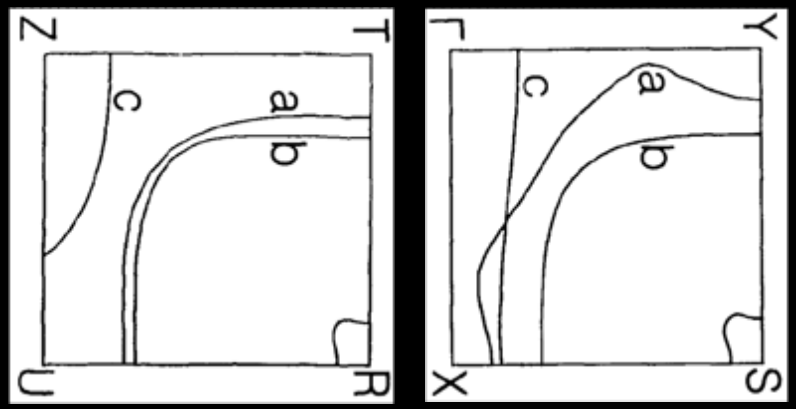
Bi-layer splitting:



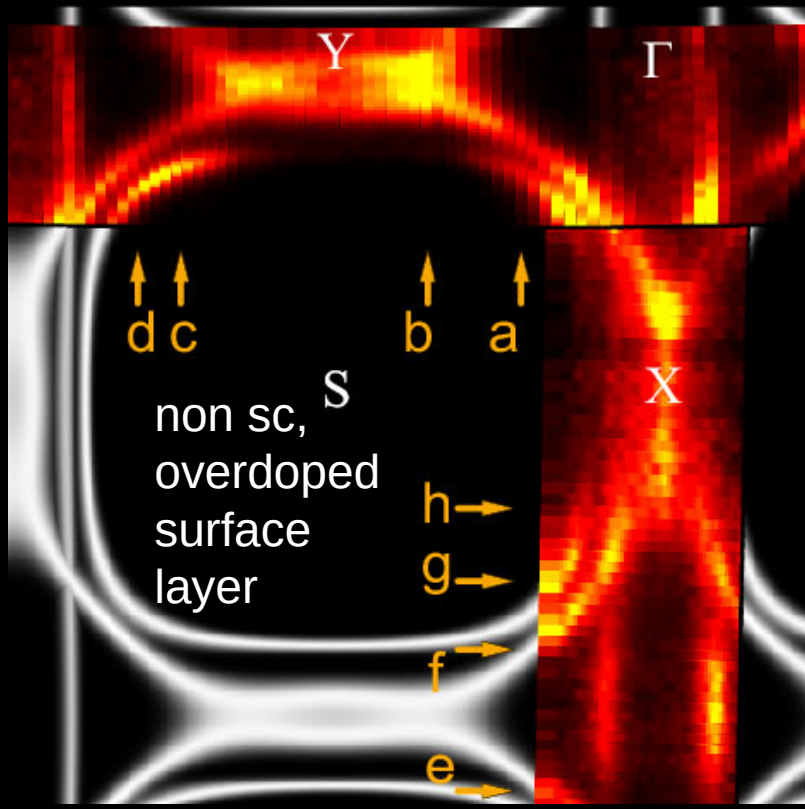
$YBa_2Cu_3O_7$

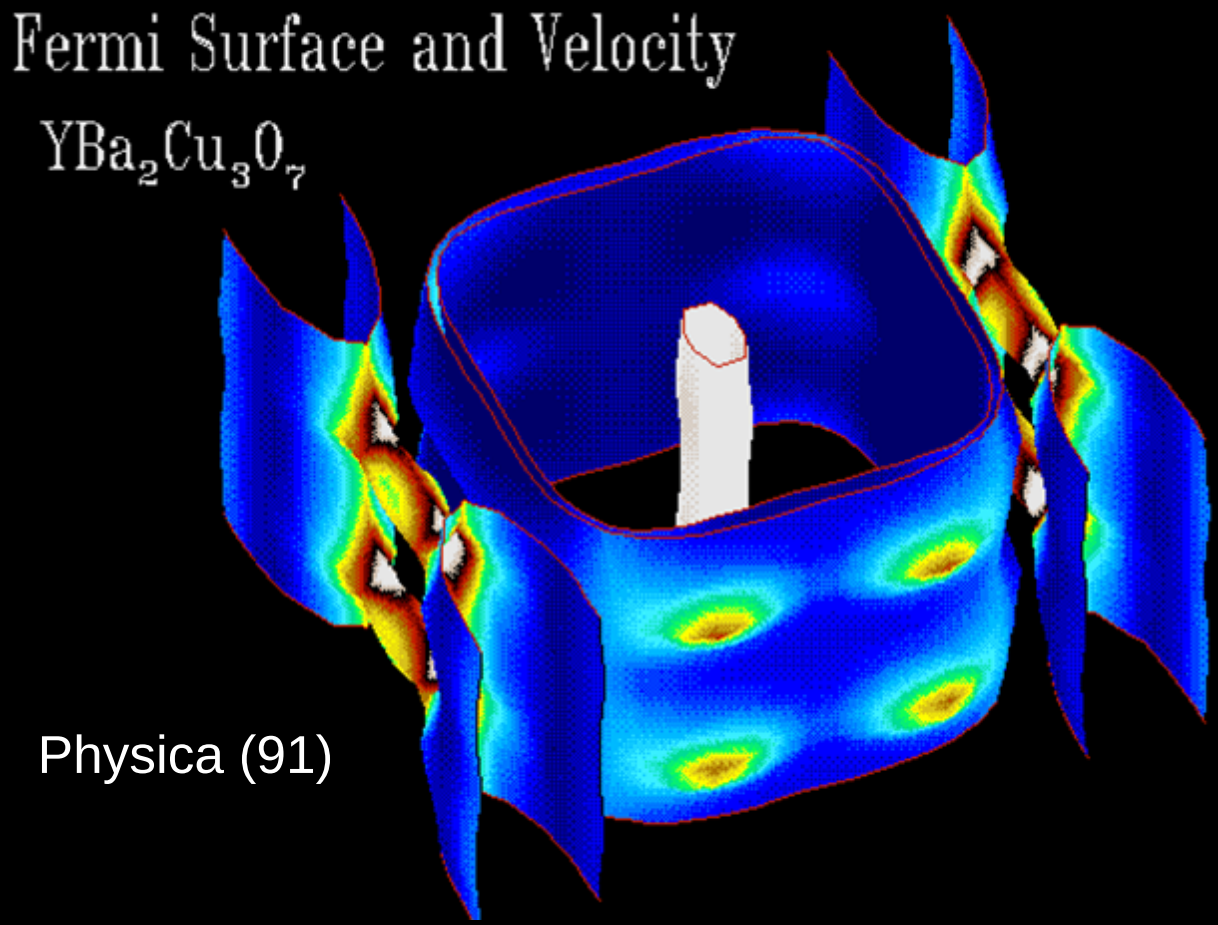
LDA

Andersen, Liechtenstein,... JPhysChemSolids (95)



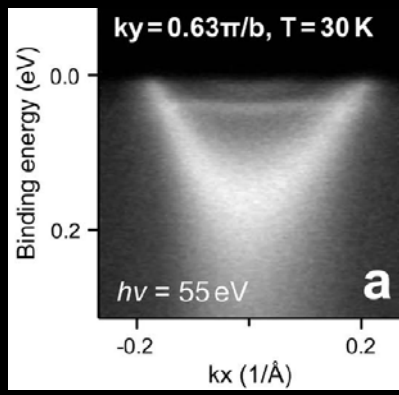
ARPES

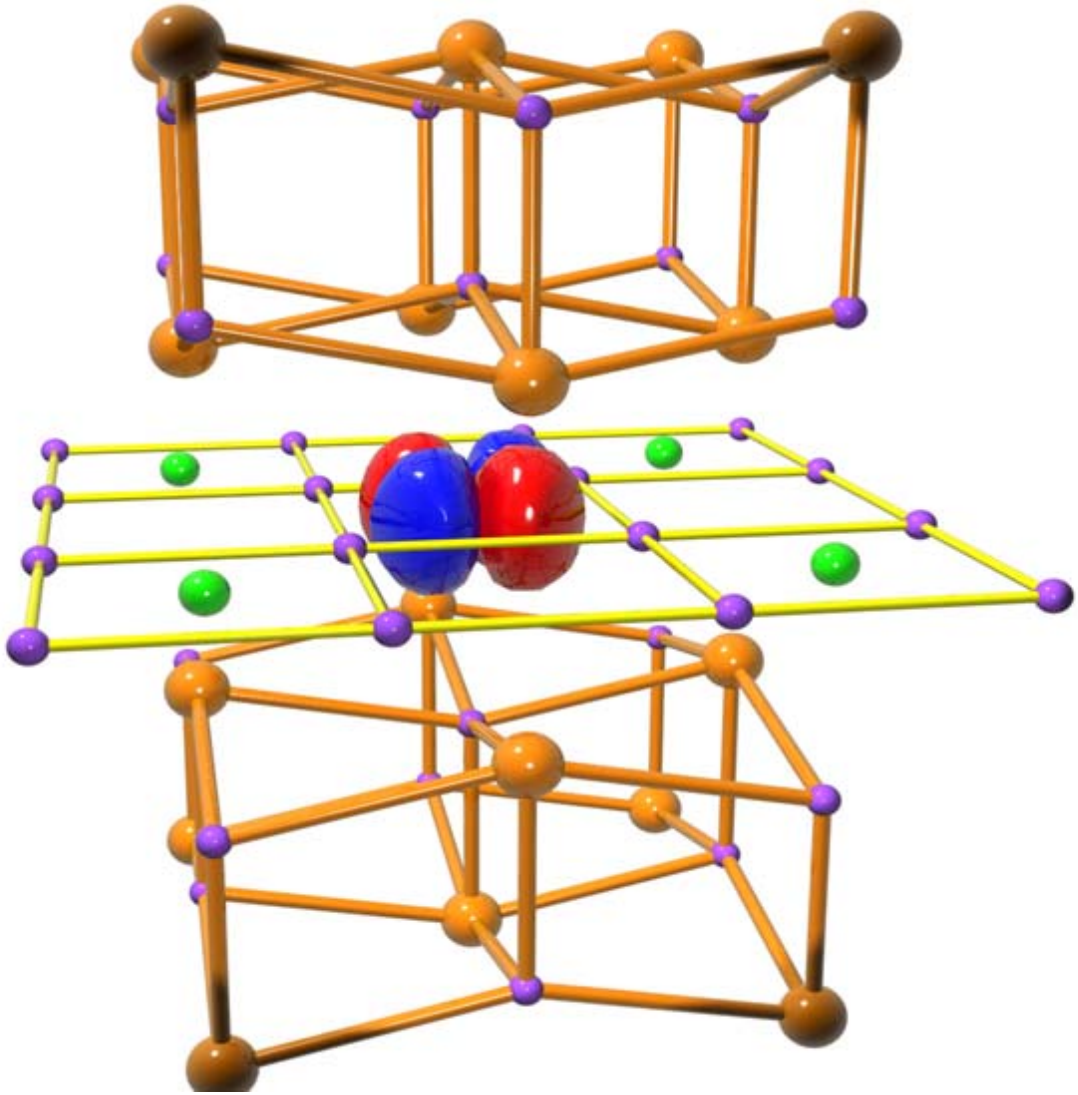


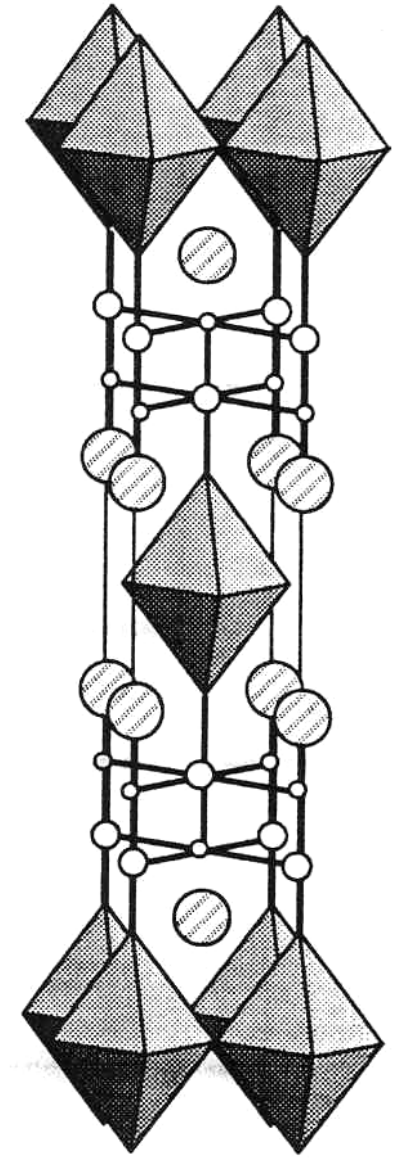


Physica (91)

Zabolotnyy, Borisenko,... PR (07)

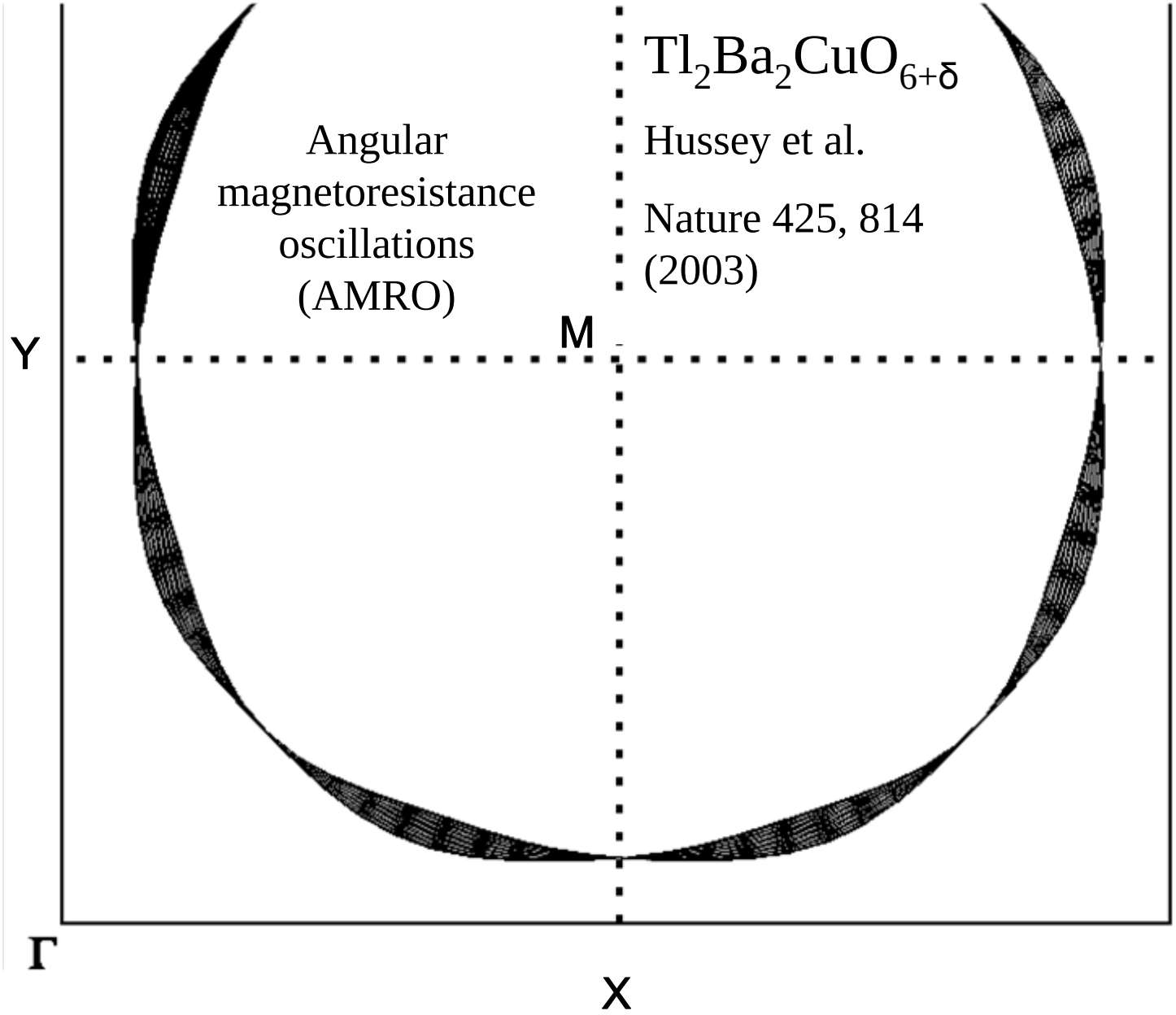


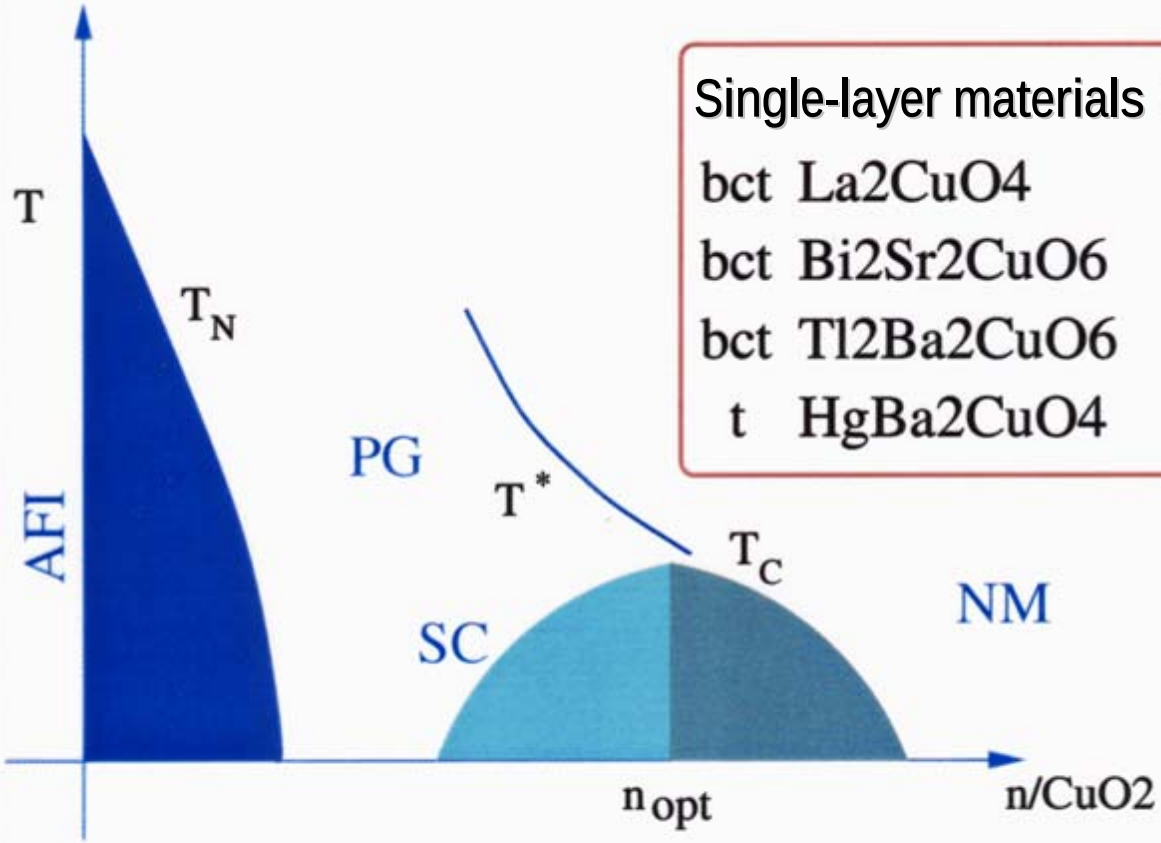




$La_{2-n}Sr_nCuO_4$

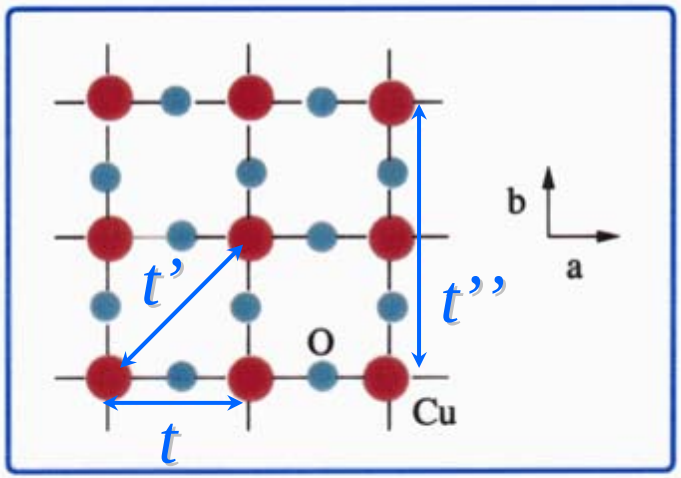
Electron count: $+3\times2 - n + 11 - 2\times4 = 9-n \rightarrow Cu\ d^{9-n}$


$Tl_2Ba_2CuO_{6+\delta}$
Hussey et al.
Nature 425, 814 (2003)
Angular magnetoresistance oscillations (AMRO)
M
Y
Γ
X



Single-layer materials		max Tc
bct	La2CuO4	40 K
bct	Bi2Sr2CuO6	40 K
bct	Tl2Ba2CuO6	90 K
t	HgBa2CuO4	90 K

Where does this materials dependence come from?



There is presently no accepted theory of high-temperature superconductivity in the cuprates

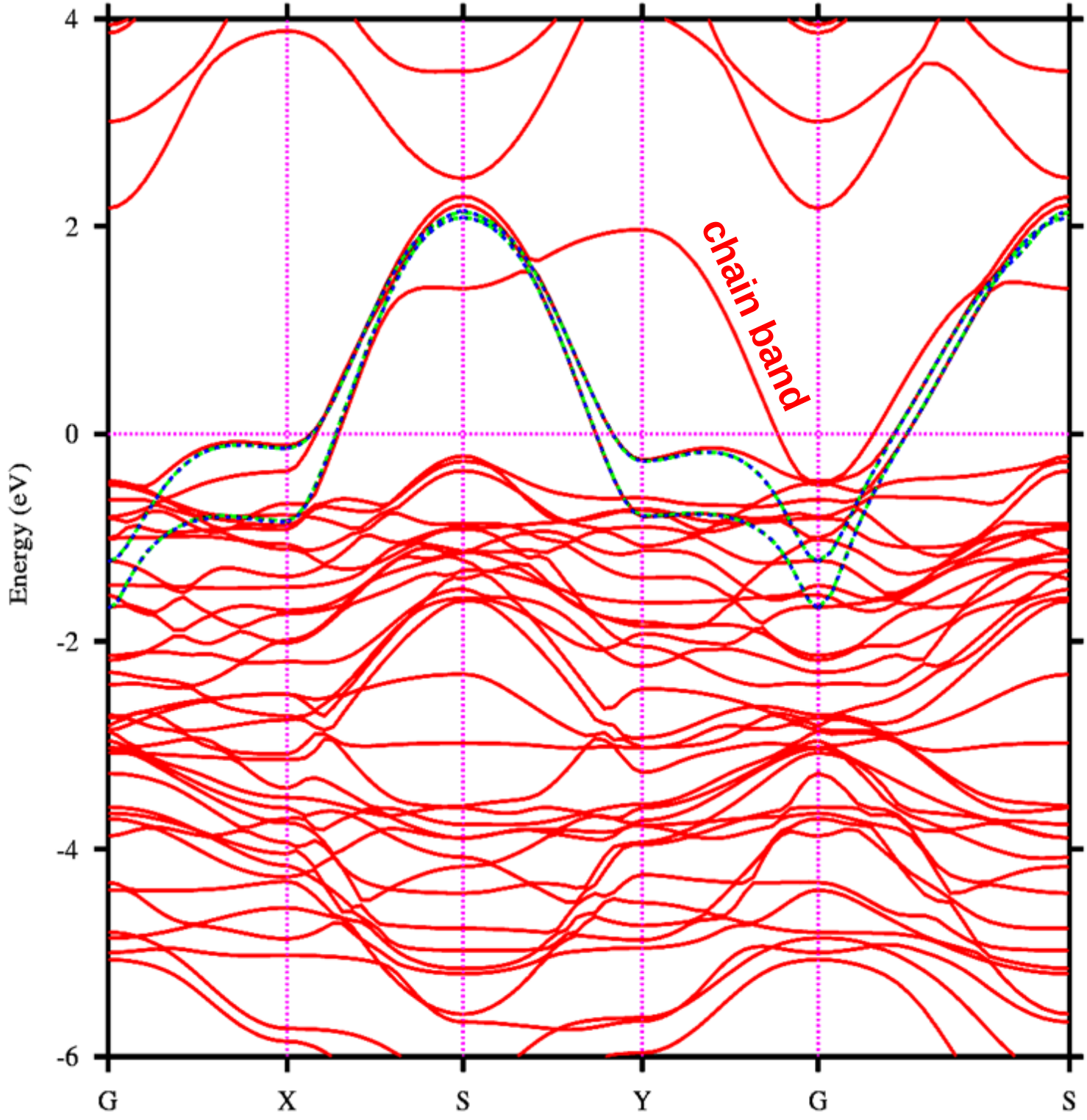
Electronic structure $\rightarrow H = \sum t_{ij} c_i^\dagger c_j + U \sum_i n_{i\uparrow} n_{i\downarrow}$

$YBa_2Cu_3O_7$

Stoichiometric at optimal doping

LDA

Bi-layer splitting:

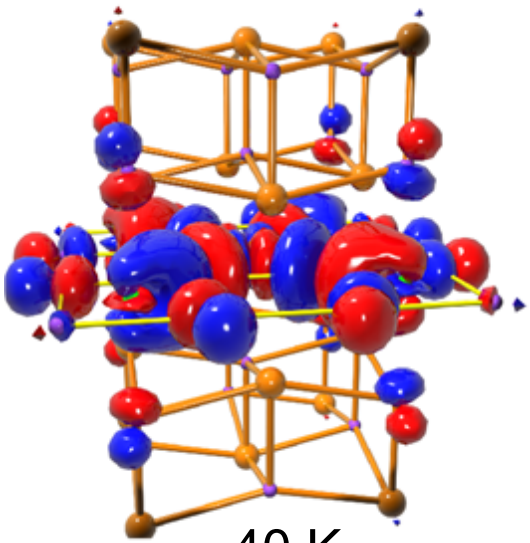


Cuprates $3d^{9-x}$
$= 3d_{x^2-y^2}{}^{1-x}$

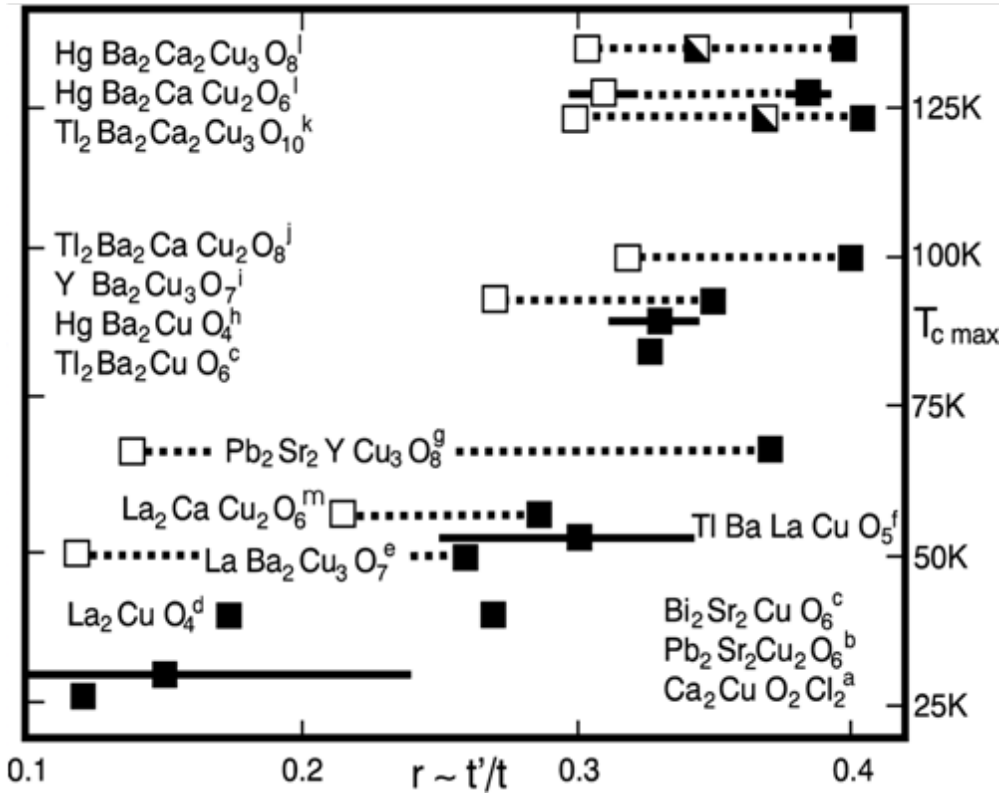
The Materials Trend, PRL **87**, 047003 (2001)

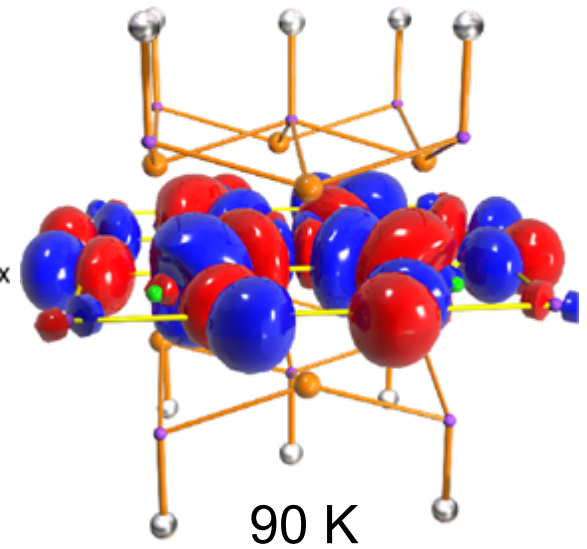
$HgBa_2CuO_4$

La_2CuO_4



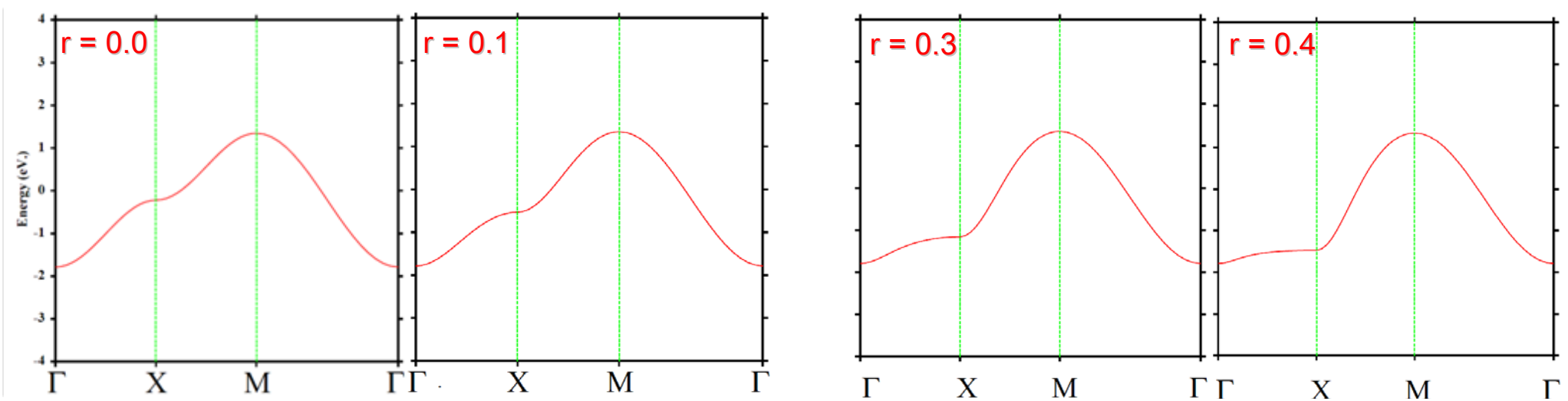
40 K





90 K

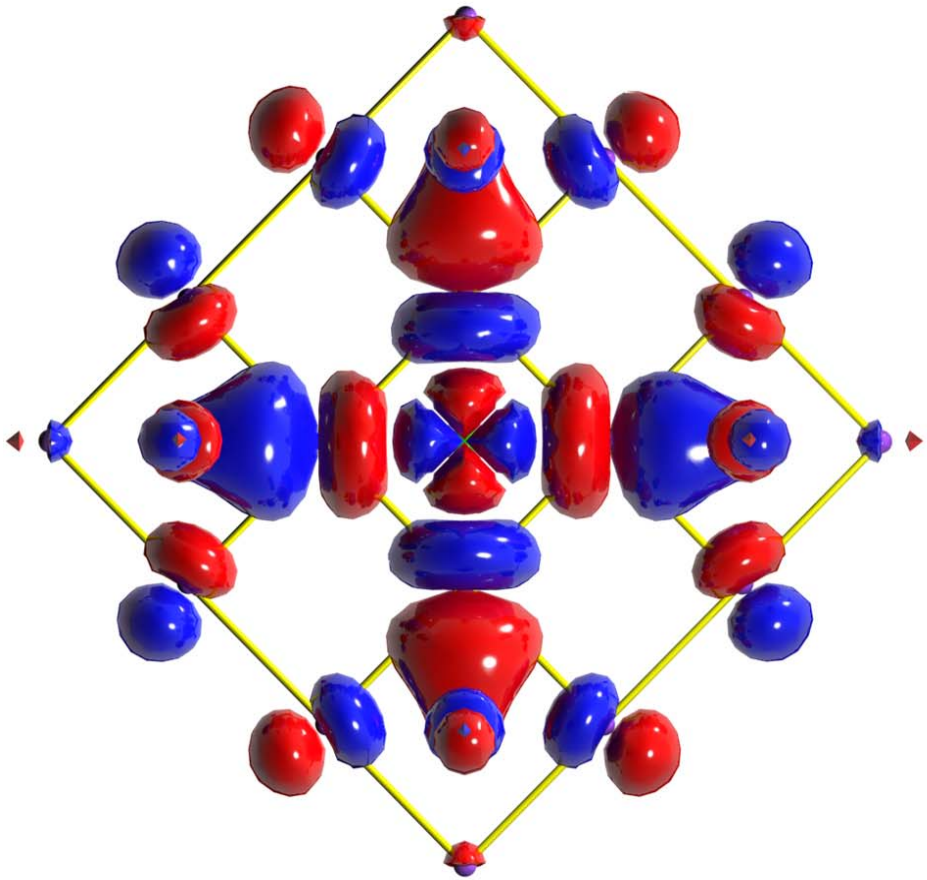
LDA conduction-band (x^2-y^2) shapes and ARPES Fermi surfaces for overdoped HTSCs



Which structural elements determine r ?

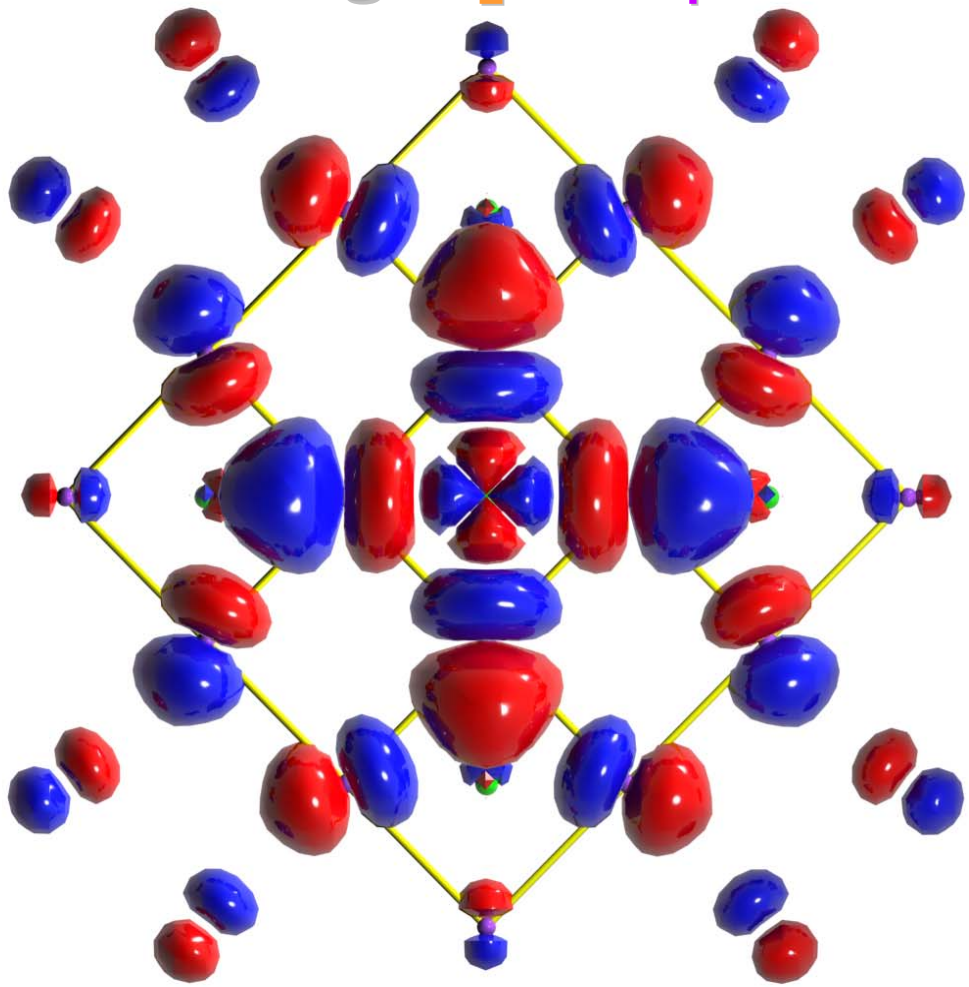
One-orbital LDA Wannier-like function

La_2CuO_4



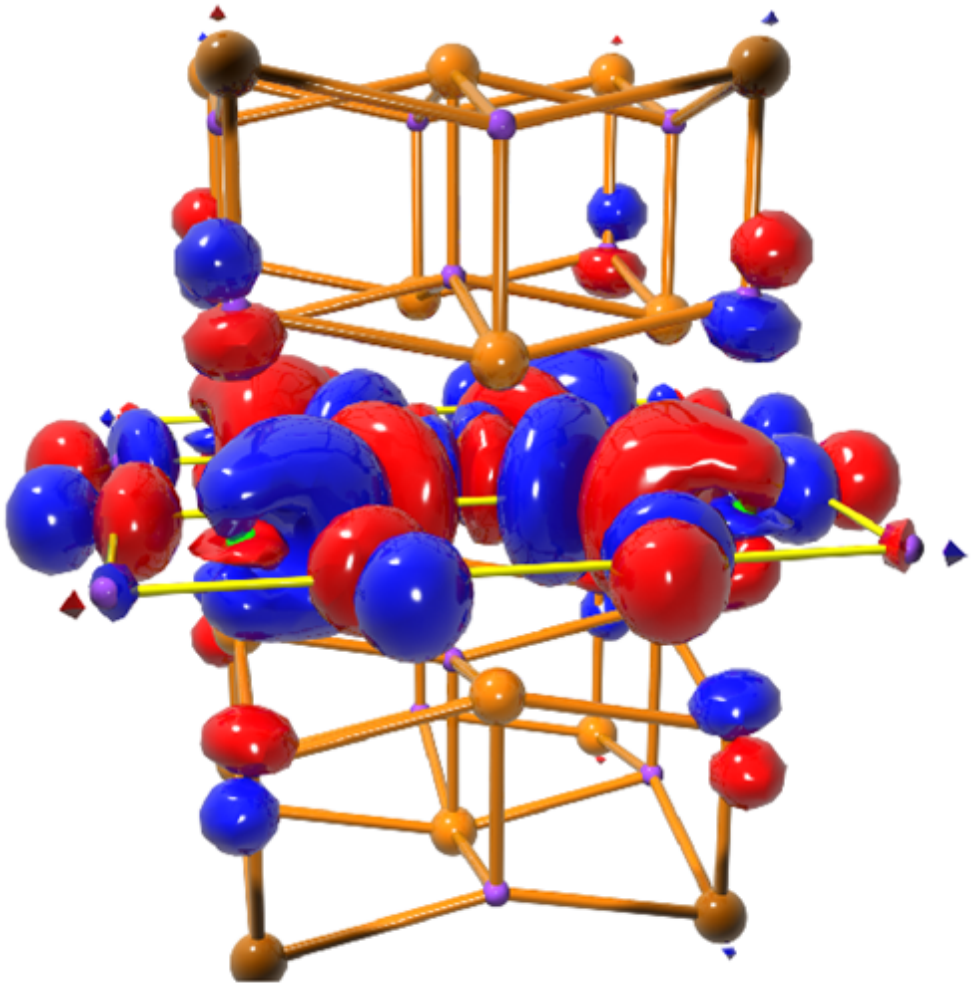
T_c = 40 K, r=0.17

$HgBa_2CuO_4$

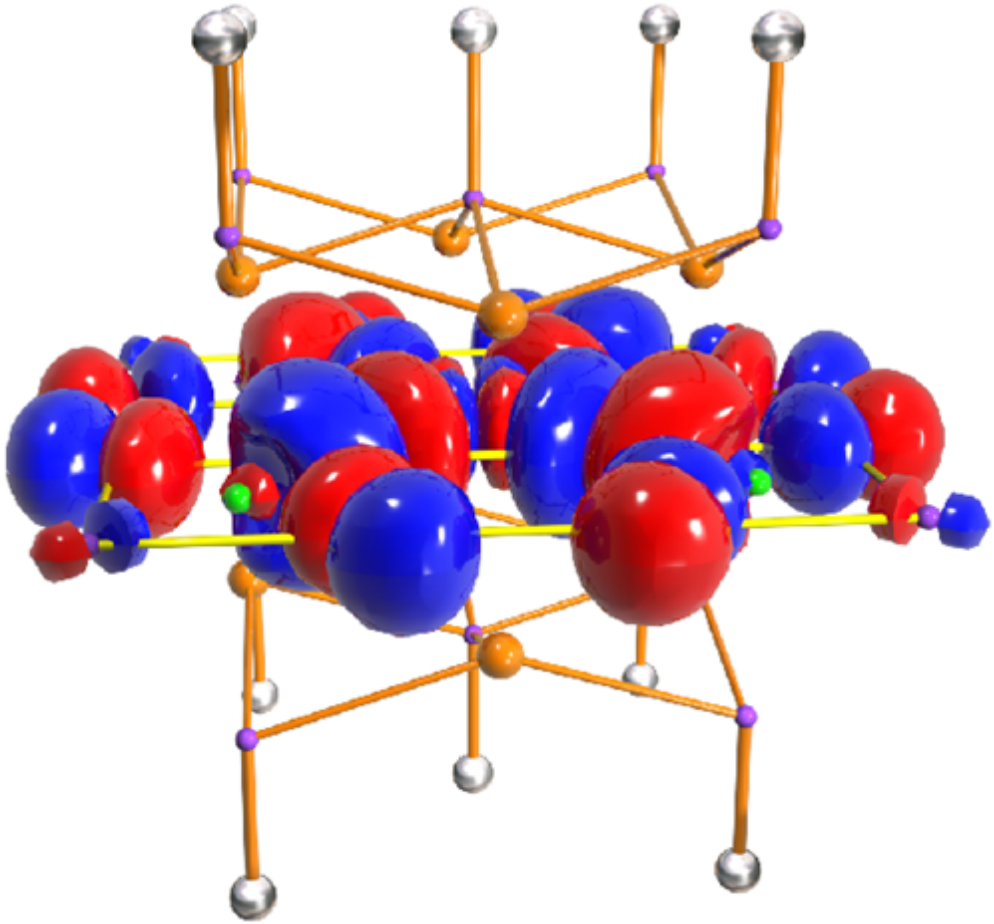


T_c = 90 K, r=0.33

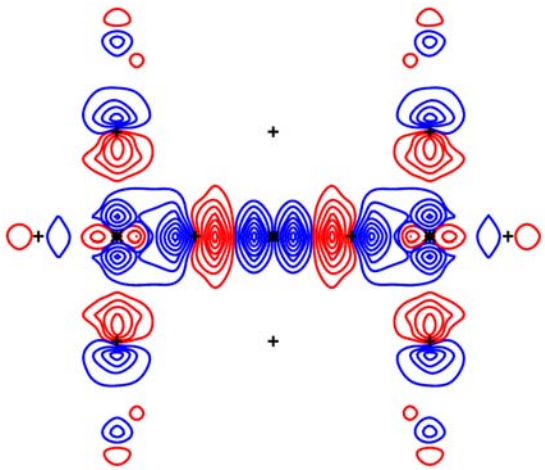
La_2CuO_4

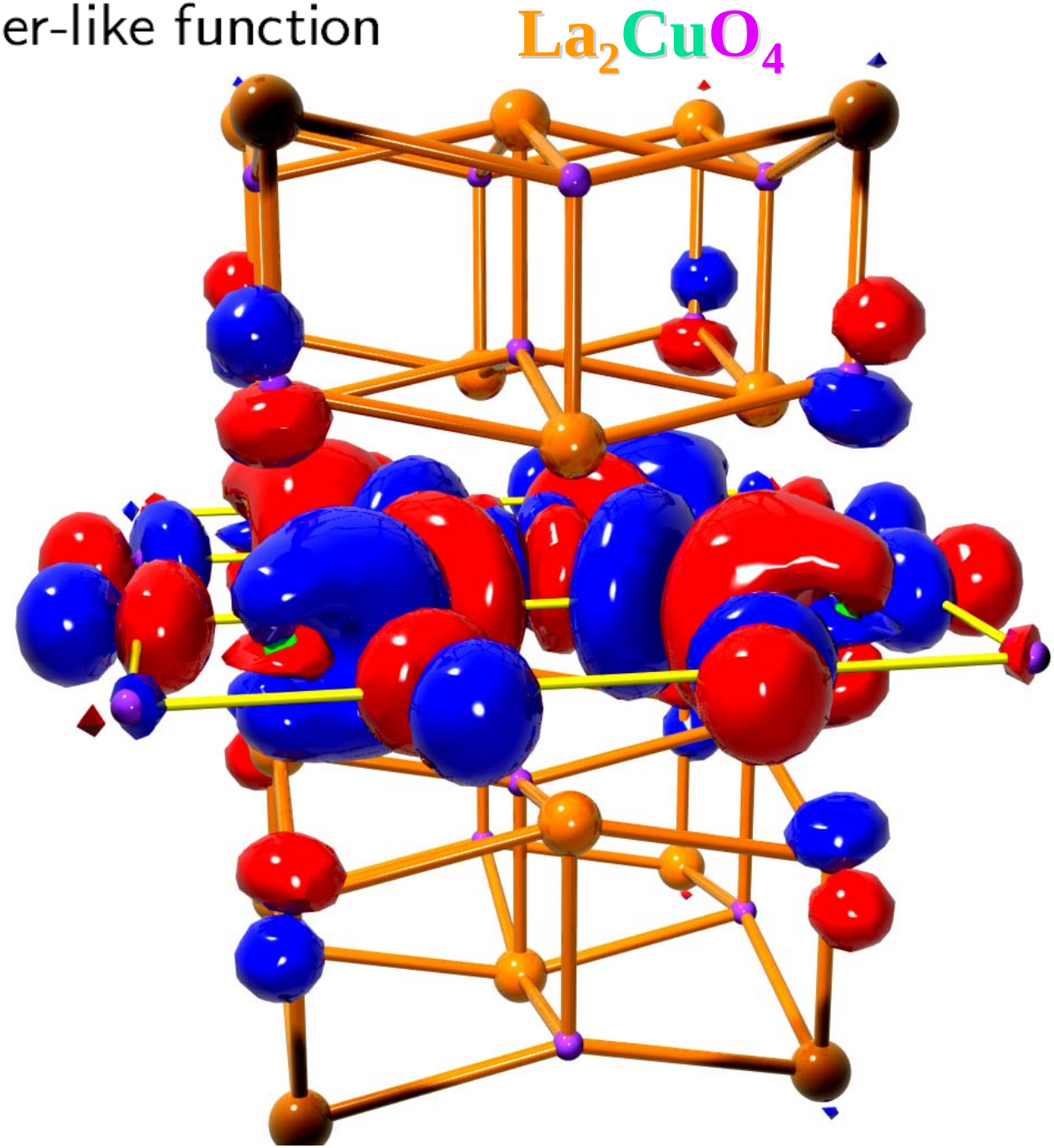


$HgBa_2CuO_4$

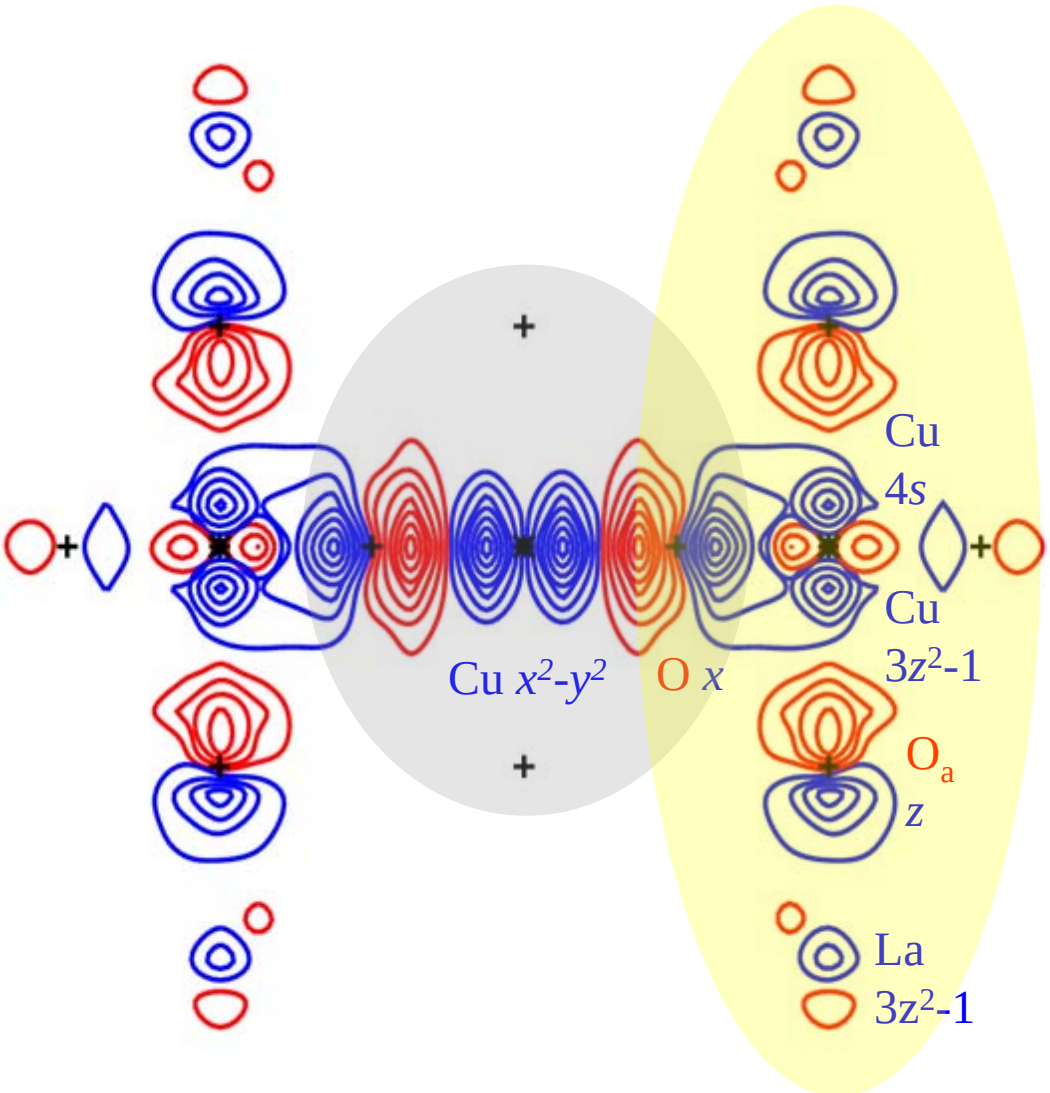


One-orbital LDA Wannier-like function





Wannier function for the cuprate conduction band



La_2CuO_4

The materials trend is best understood in terms of a tight-binding model with two orbitals:

d **= Cu** x^2**-**y^2

dressed with

O *p*

and

s = axial orbital = **Cu 4*s***

dressed with

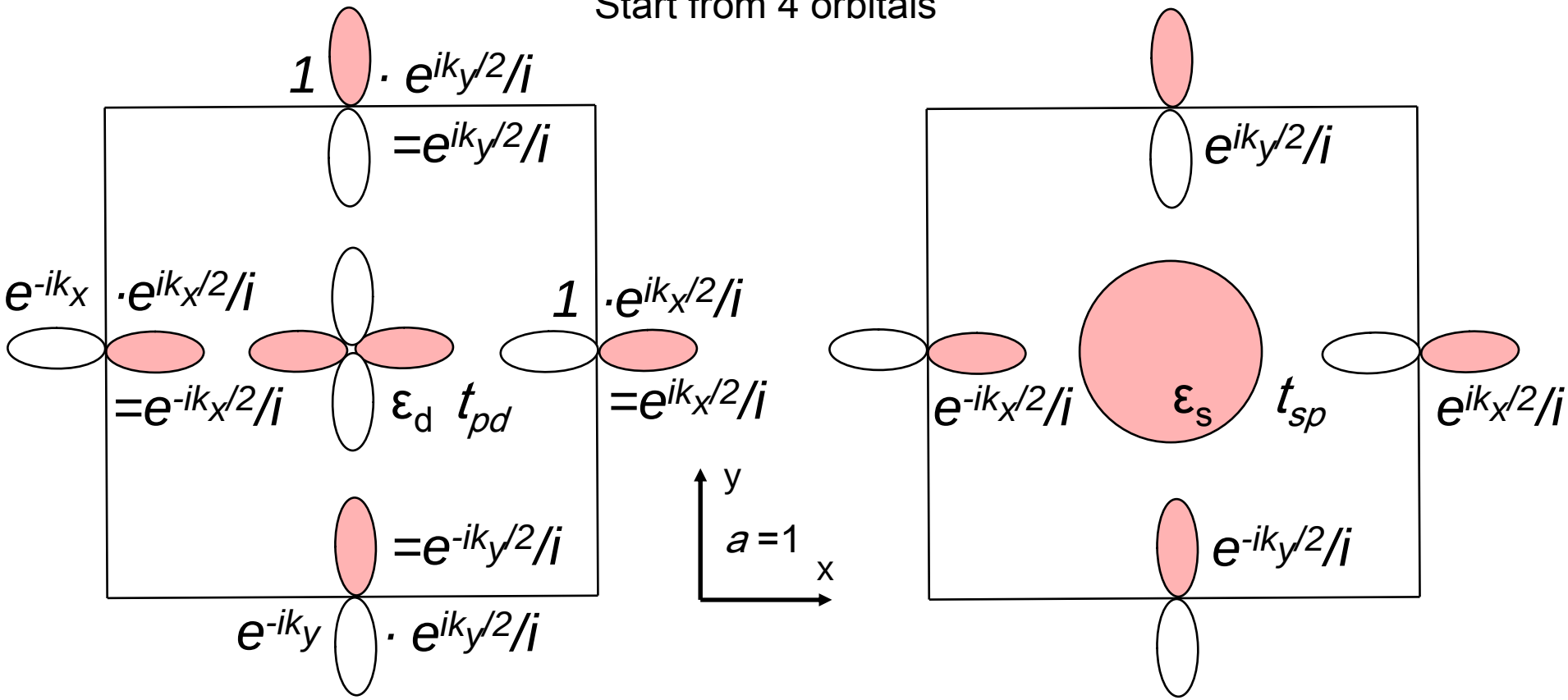
Cu $3z^2$**-1,**

O$_a$ ***z*,**

La $3z^2$**-1, a.s.o.**

The material-dependent parameter is $\varepsilon_s - \varepsilon_F$ (> 0) . The smaller it is, the larger is $r \sim t'/t$.

Start from 4 orbitals



$H4$	$\lvert d,\mathbf{k}\rangle$	$\lvert s,\mathbf{k}\rangle$	$\lvert x,\mathbf{k}\rangle$	$\lvert y,\mathbf{k}\rangle$
$\langle d,\mathbf{k}\rvert$	ϵ_d	0	$2t_{pd}\sin\frac{k_x}{2}$	$-2t_{pd}\sin\frac{k_y}{2}$
$\langle s,\mathbf{k}\rvert$	0	ϵ_s	$2t_{sp}\sin\frac{k_x}{2}$	$2t_{sp}\sin\frac{k_y}{2}$
$\langle x,\mathbf{k}\rvert$	$2t_{pd}\sin\frac{k_x}{2}$	$2t_{sp}\sin\frac{k_x}{2}$	ϵ_p	0
$\langle y,\mathbf{k}\rvert$	$-2t_{pd}\sin\frac{k_y}{2}$	$2t_{sp}\sin\frac{k_y}{2}$	0	ϵ_p

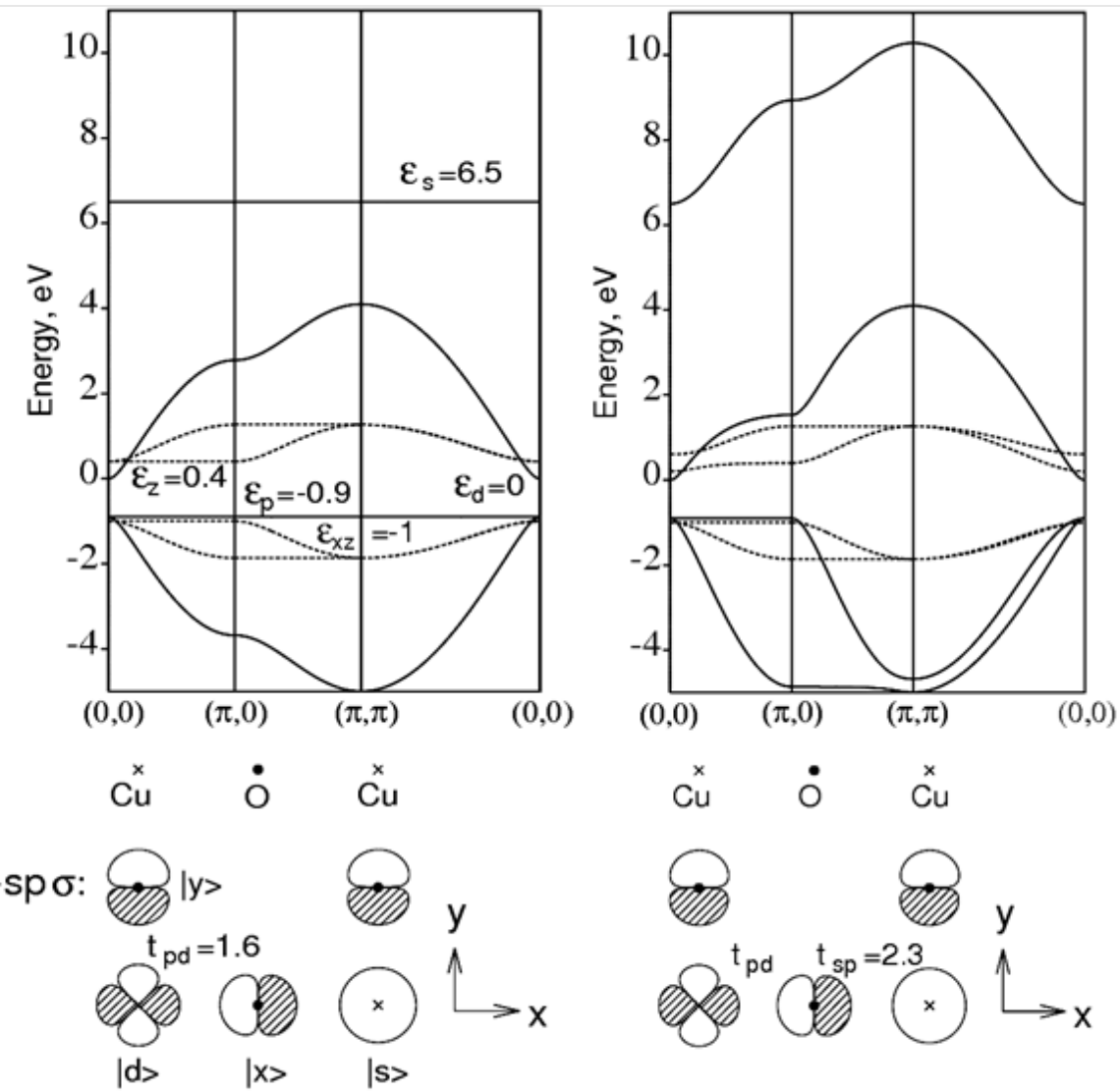
Löwdin downfolding to 2 orbitals:

$H4$	$\lvert d,\mathbf{k}\rangle$	$\lvert s,\mathbf{k}\rangle$	$\lvert x,\mathbf{k}\rangle$	$\lvert y,\mathbf{k}\rangle$
$\langle d,\mathbf{k}\rvert$	ϵ_d	0	$2t_{pd}\sin\frac{k_x}{2}$	$-2t_{pd}\sin\frac{k_y}{2}$
$\langle s,\mathbf{k}\rvert$	0	ϵ_s	$2t_{sp}\sin\frac{k_x}{2}$	$2t_{sp}\sin\frac{k_y}{2}$
$\langle x,\mathbf{k}\rvert$	$2t_{pd}\sin\frac{k_x}{2}$	$2t_{sp}\sin\frac{k_x}{2}$	ϵ_p	0
$\langle y,\mathbf{k}\rvert$	$-2t_{pd}\sin\frac{k_y}{2}$	$2t_{sp}\sin\frac{k_y}{2}$	0	ϵ_p

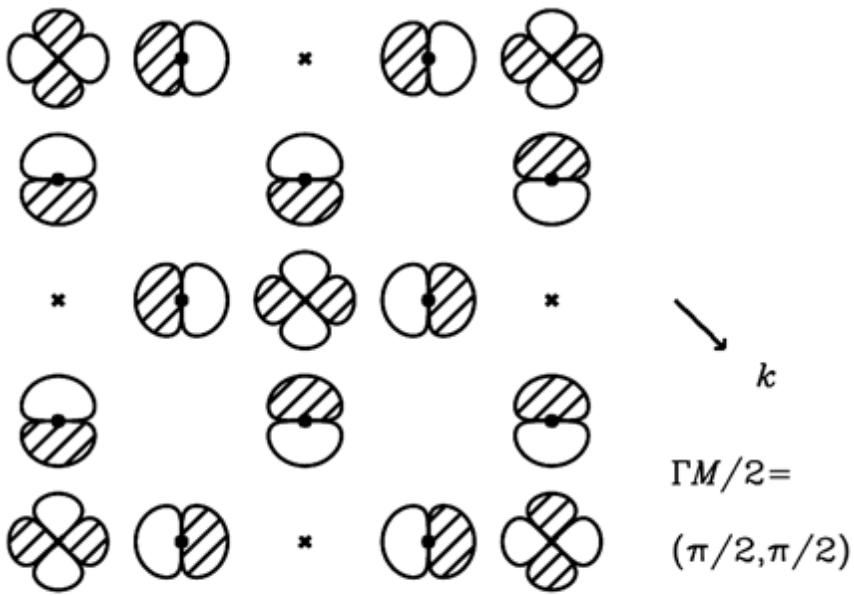
$\longrightarrow$

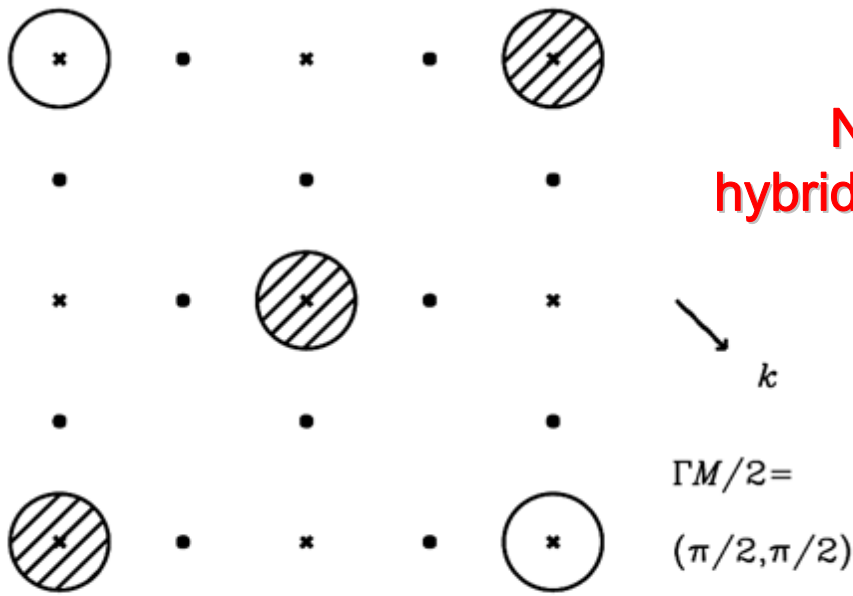
$H2(\varepsilon)$	$\lvert d,\varepsilon,\mathbf{k}\rangle$	$\lvert s,\varepsilon,\mathbf{k}\rangle$
$\langle d,\varepsilon,\mathbf{k}\rvert$	$\epsilon_d+\frac{4t_{pd}^2}{\varepsilon-\epsilon_p}\left(\sin^2\frac{k_x}{2}+\sin^2\frac{k_y}{2}\right)$	$\frac{4t_{sp}t_{pd}}{\varepsilon-\epsilon_p}\left(\sin^2\frac{k_x}{2}-\sin^2\frac{k_y}{2}\right)$
$\langle s,\varepsilon,\mathbf{k}\rvert$	$\frac{4t_{sp}t_{pd}}{\varepsilon-\epsilon_p}\left(\sin^2\frac{k_x}{2}-\sin^2\frac{k_y}{2}\right)$	$\epsilon_s+\frac{4t_{pd}^2}{\varepsilon-\epsilon_p}\left(\sin^2\frac{k_x}{2}+\sin^2\frac{k_y}{2}\right)$

$=$

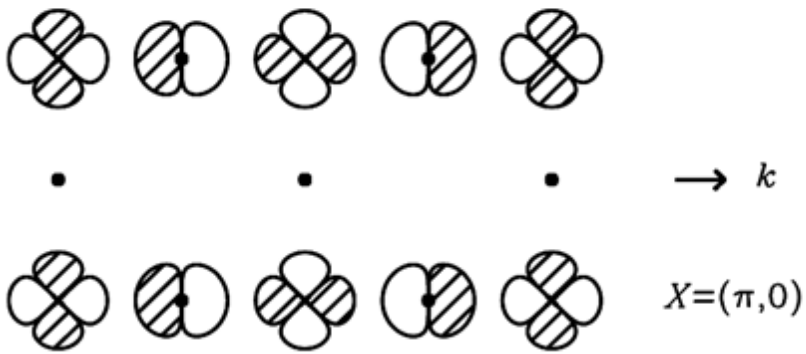


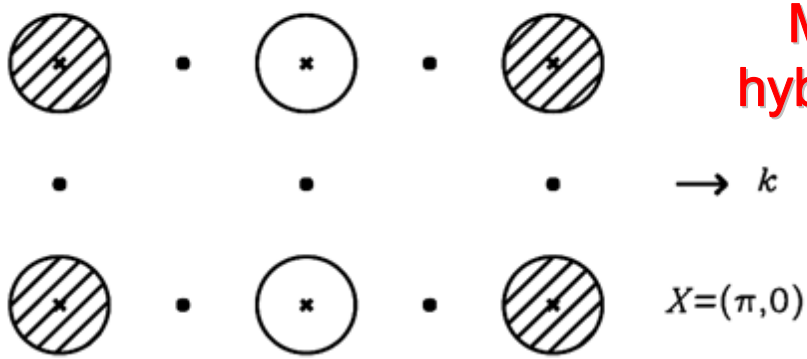
Hybridization betwen x^2-y^2 and axial orbital Cu $4s$, apical O $2p_z$, etc.





No hybridization





Maximal hybridization

Hybridization ~ $(\cos k_x - \cos k_y)^2$

$H2(\varepsilon)$	$\lvert d,\varepsilon,\mathbf{k}\rangle$	$\lvert s,\varepsilon,\mathbf{k}\rangle$
$\langle d,\varepsilon,\mathbf{k}\rvert$	$\epsilon_d + \frac{4t_{pd}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}\right)$	$-\frac{4t_{sp}t_{pd}}{\varepsilon-\epsilon_p}\frac{\cos k_x-\cos k_y}{2}$
$\langle s,\varepsilon,\mathbf{k}\rvert$	$-\frac{4t_{sp}t_{pd}}{\varepsilon-\epsilon_p}\frac{\cos k_x-\cos k_y}{2}$	$\epsilon_s + \frac{4t_{sp}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}\right)$

Downfolding to 1 orbital:

$$H1(\varepsilon) = \left\langle \tilde{d},\varepsilon,\mathbf{k}\right| H \left|\tilde{d},\varepsilon,\mathbf{k}\right\rangle =$$

$$= \epsilon_d + \frac{4t_{pd}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}+\frac{\frac{4t_{sp}^2}{\varepsilon-\epsilon_p}\left(\frac{\cos k_x-\cos k_y}{2}\right)^2}{\varepsilon-\epsilon_s-\frac{4t_{sp}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}\right)}\right)$$

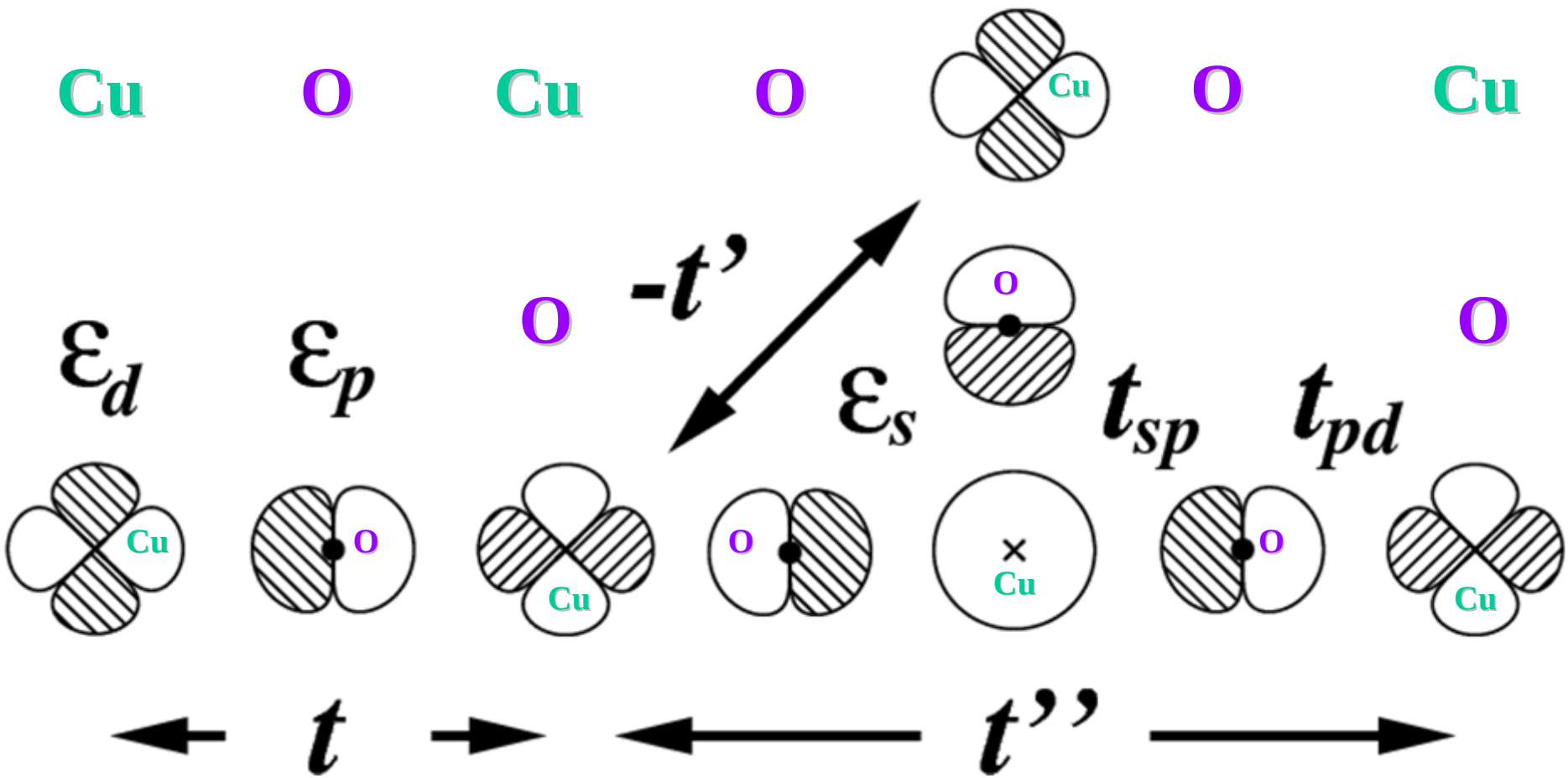
$$= \epsilon_d + \frac{4t_{pd}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}+\frac{\frac{t_{sp}^2}{\varepsilon-\epsilon_p}\left(1-2\cos k_x\cos k_y+\frac{\cos 2k_x+\cos 2k_y}{2}\right)}{\varepsilon-\epsilon_s-\frac{4t_{sp}^2}{\varepsilon-\epsilon_p}\left(1-\frac{\cos k_x+\cos k_y}{2}\right)}\right)$$

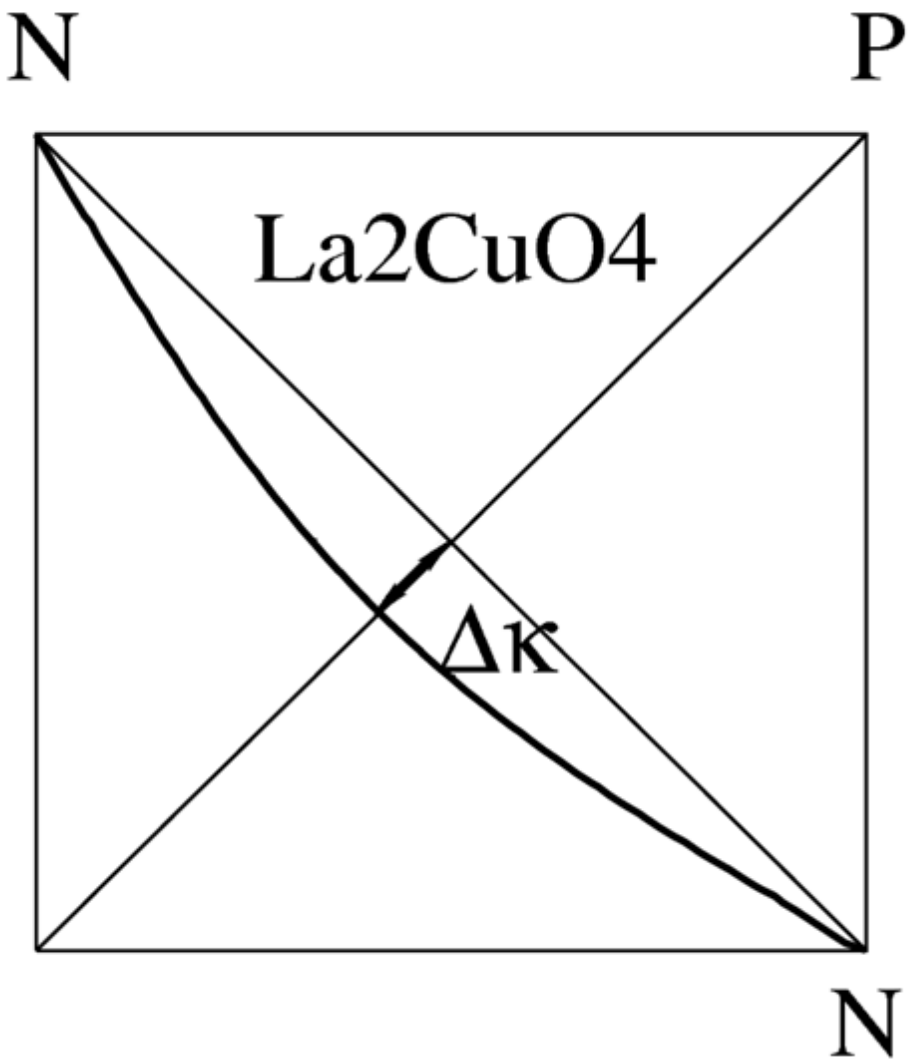
$$\equiv \epsilon_0 - 2t\left(\cos k_x+\cos k_y\right)+4t'\cos k_x\cos k_y-2t''\left(\cos 2k_x+\cos 2k_y\right)+\ldots.$$

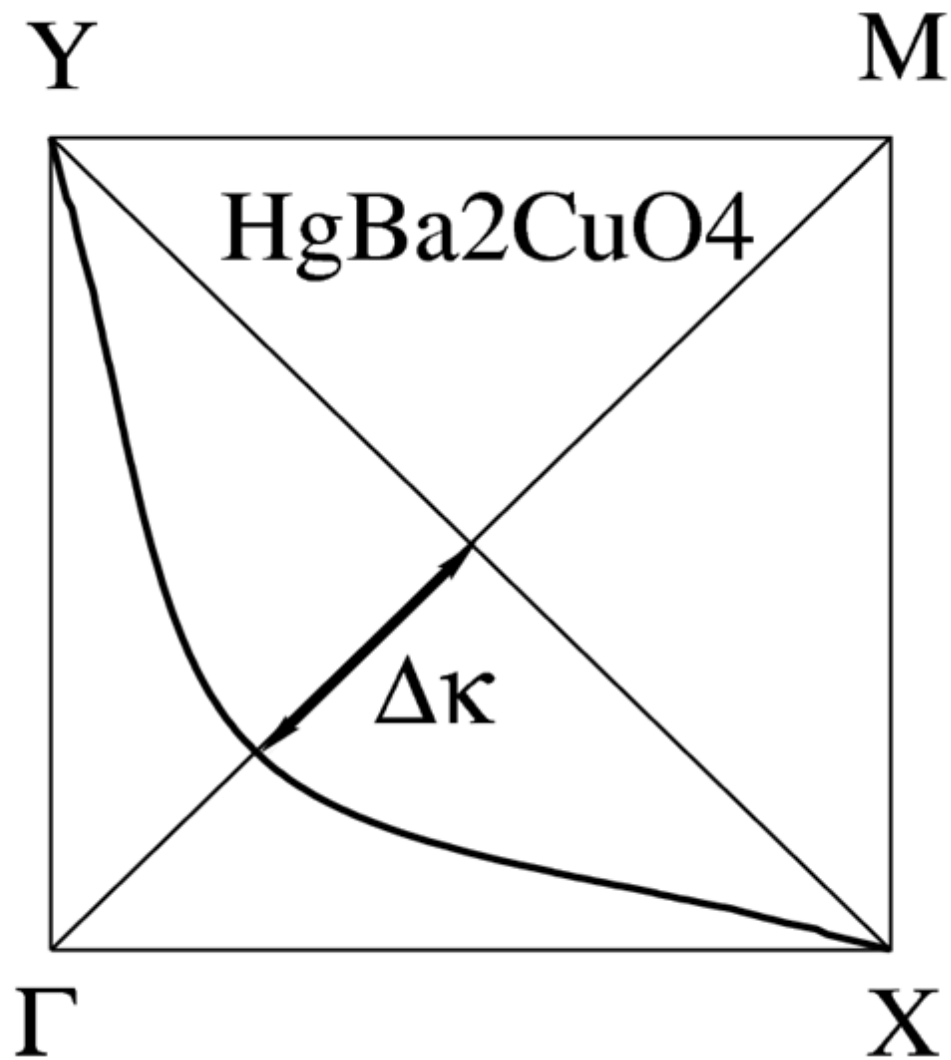
$$t=\frac{t_{pd}^2}{\varepsilon-\epsilon_p},\quad t'/t\approx\frac{\frac{2t_{sp}^2}{\varepsilon-\epsilon_p}}{\epsilon_s-\varepsilon+\frac{4t_{sp}^2}{\varepsilon-\epsilon_p}}\equiv r(\varepsilon),\quad t''/t'=\frac{1}{2}$$

From the nearest-neighbor 4-orbital model (ε_p, ε_d, ε_s, t_{pd}, t_{sp})

to the longer-ranged 1-orbital model (t, t', t'', ...)



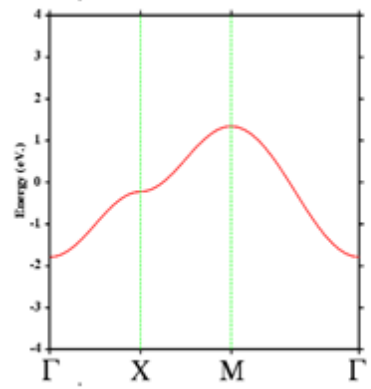




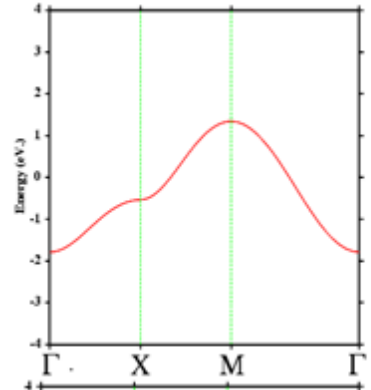
$T_{c\,max}$ = 40K, r = 0.17

$T_{c\,max}$ = 90K, r = 0.33

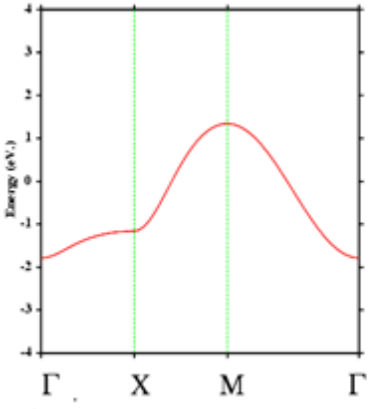
$$r = \frac{1}{2}\sin\left(\pi\Delta\kappa\right)$$



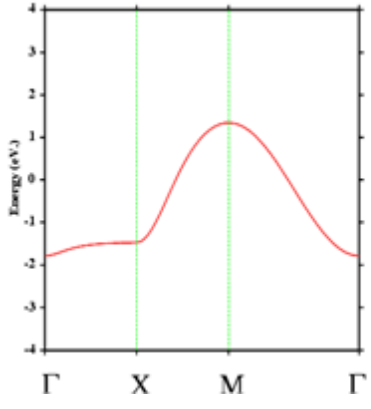
r=0.



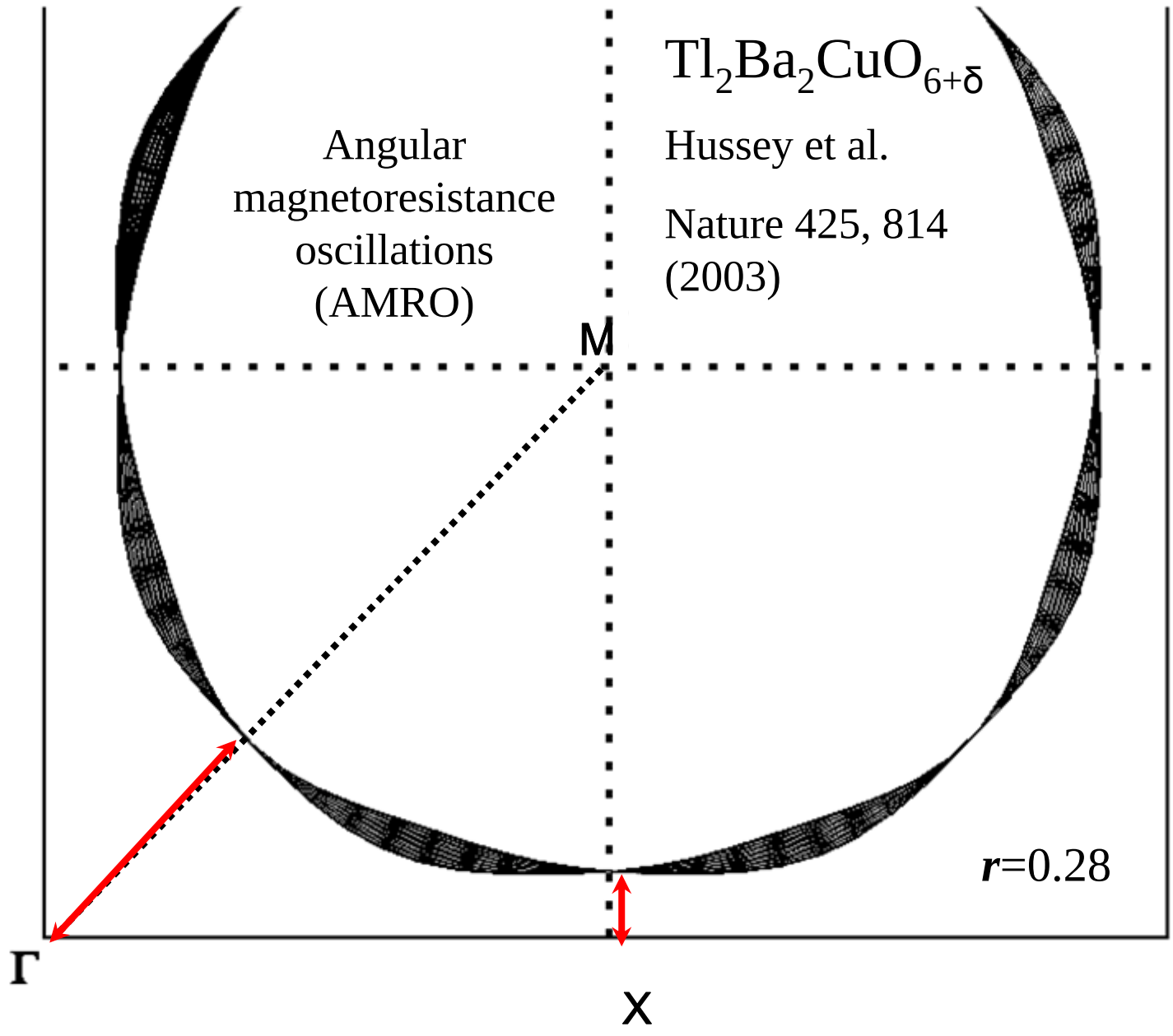
r=0.1



r=0.3

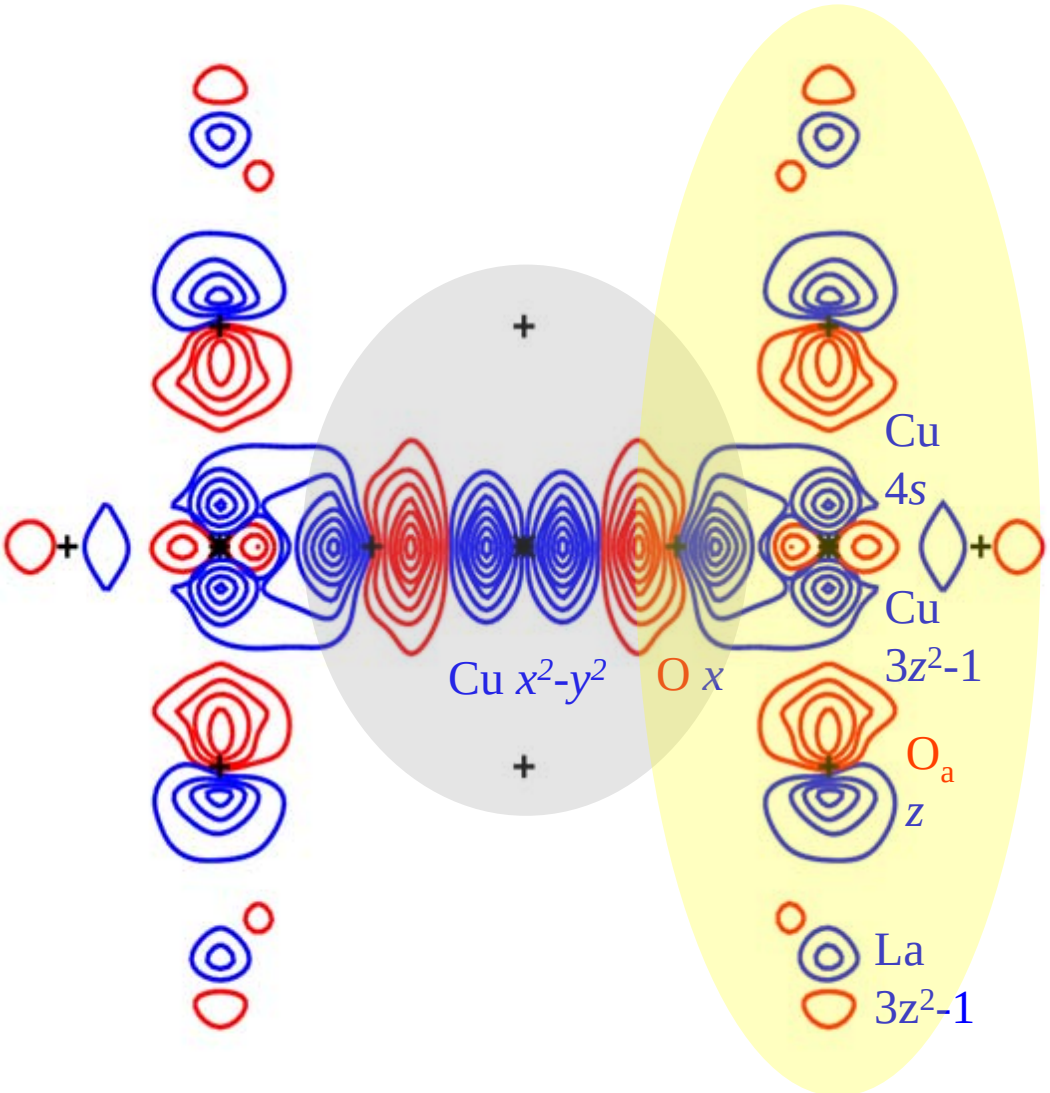


r=0.4



$$r = \frac{1}{2}\,\frac{\cos\left(\pi k_{\Gamma\mathrm{M}}/\Gamma\mathrm{M}\right) + \sin^2\left(\frac{\pi}{2}k_{\mathrm{XM}}/\mathrm{XM}\right)}{1 - \sin^2\left(\frac{\pi}{2}k_{\mathrm{XM}}/\mathrm{XM}\right)\left[2 + \cos\left(\pi k_{\Gamma\mathrm{M}}/\Gamma\mathrm{M}\right)\right]}$$

Wannier function for the cuprate conduction band



La_2CuO_4

The materials trend is best understood in terms of a tight-binding model with two orbitals:

d **= Cu** x^2**-**y^2

dressed with

O *p*

and

s = axial orbital = **Cu 4*s***

dressed with

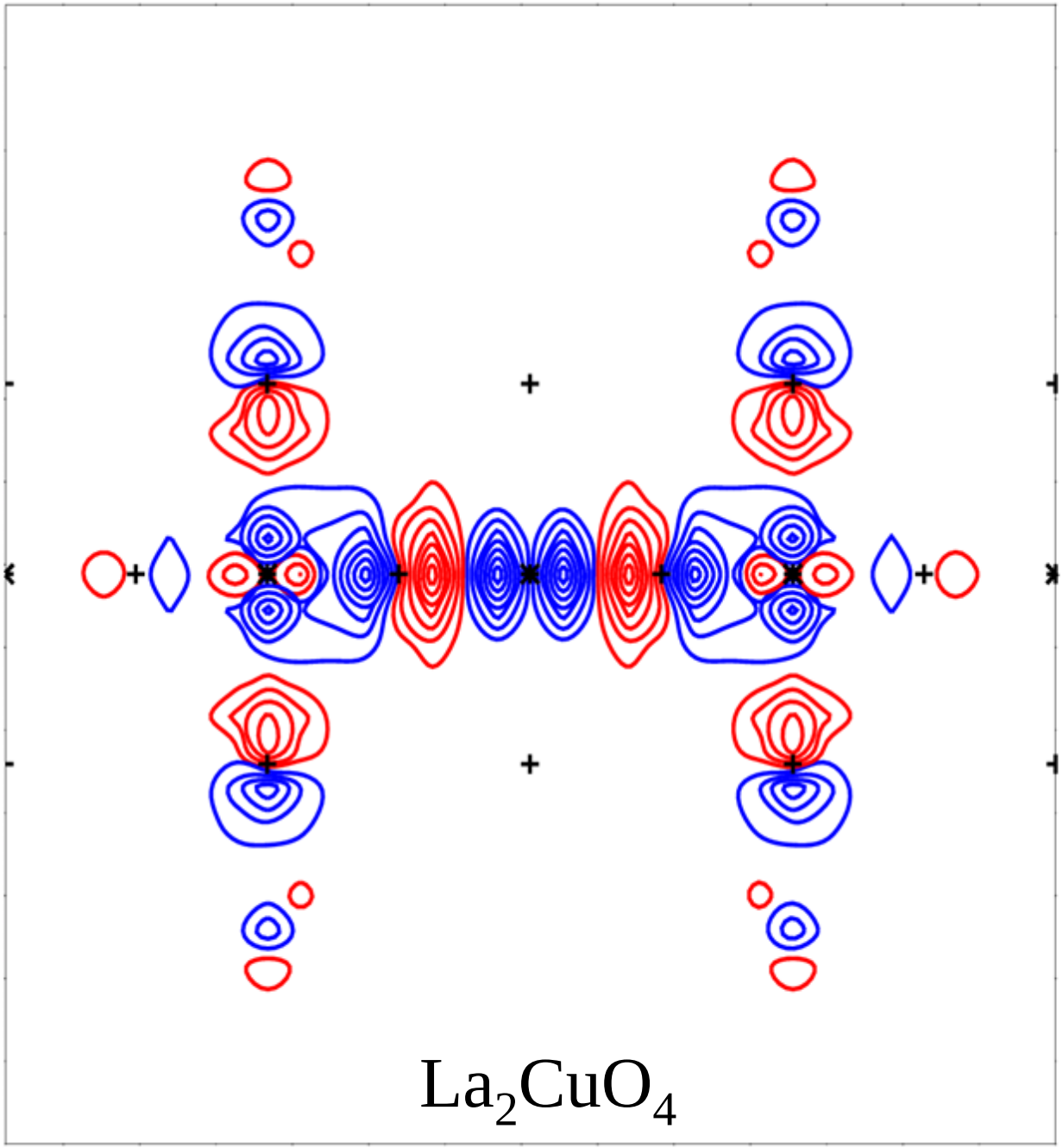
Cu $3z^2$**-1,**

O$_a$ ***z*,**

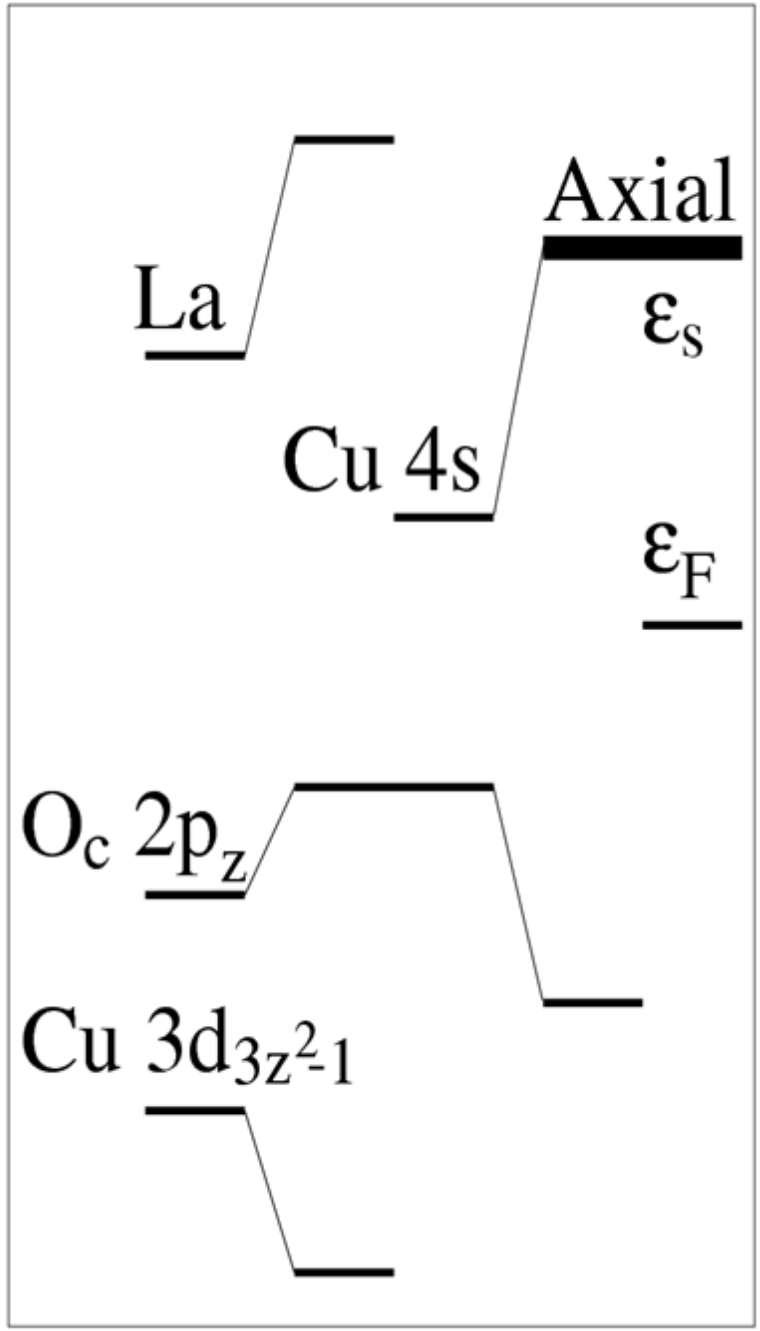
La $3z^2$**-1, a.s.o.**

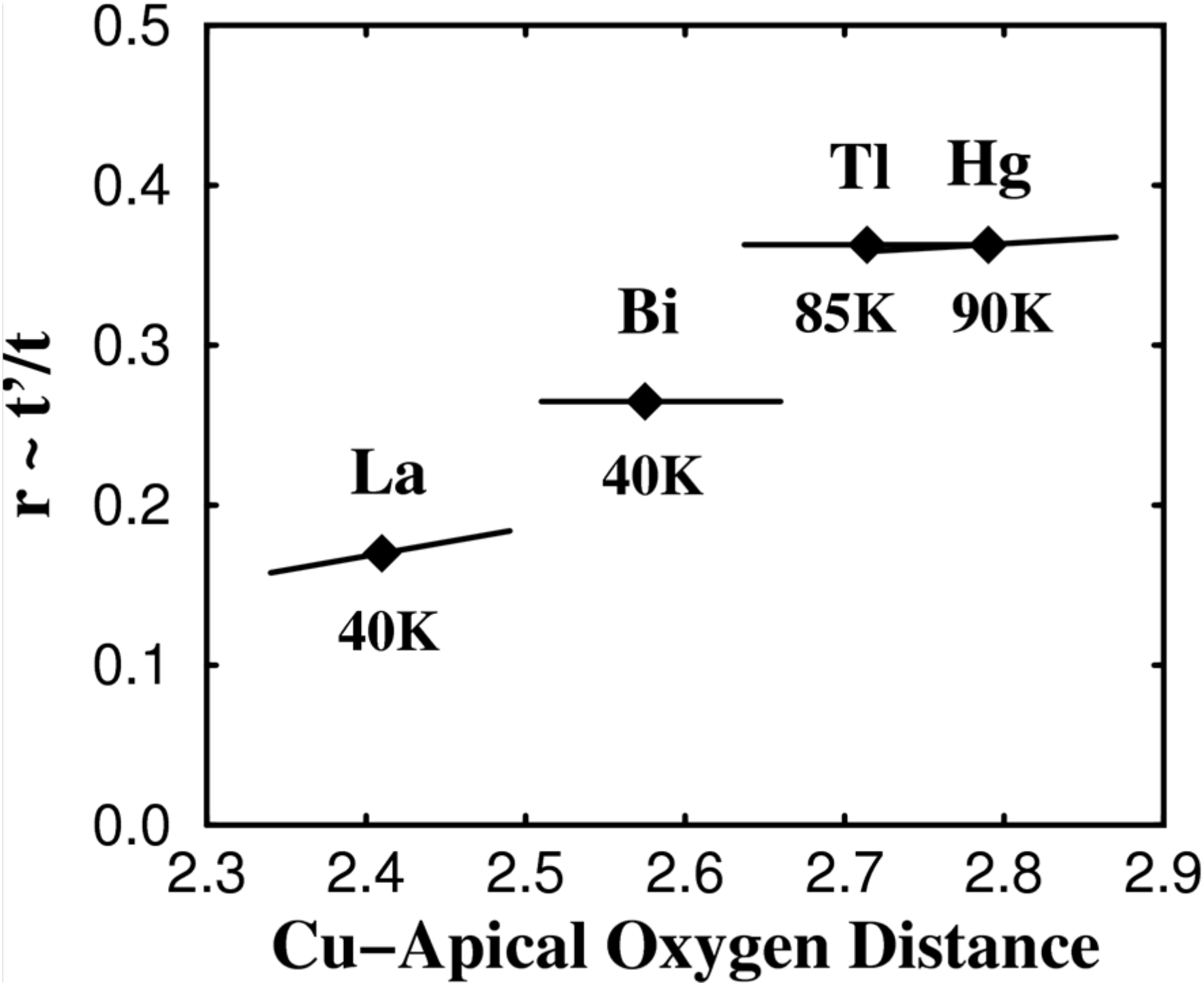
The material-dependent parameter is $\varepsilon_s - \varepsilon_F$ (> 0) . The smaller it is, the larger is $r \sim t'/t$.

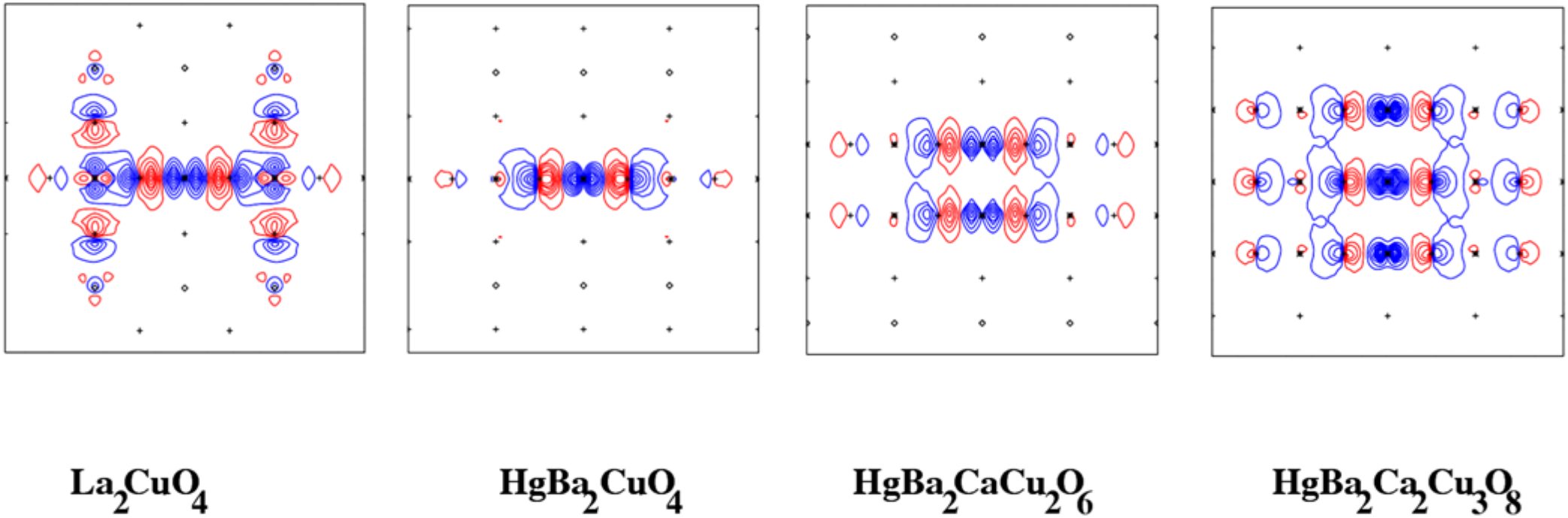
One-orbital LDA Wannier-like function



Four-orbital model

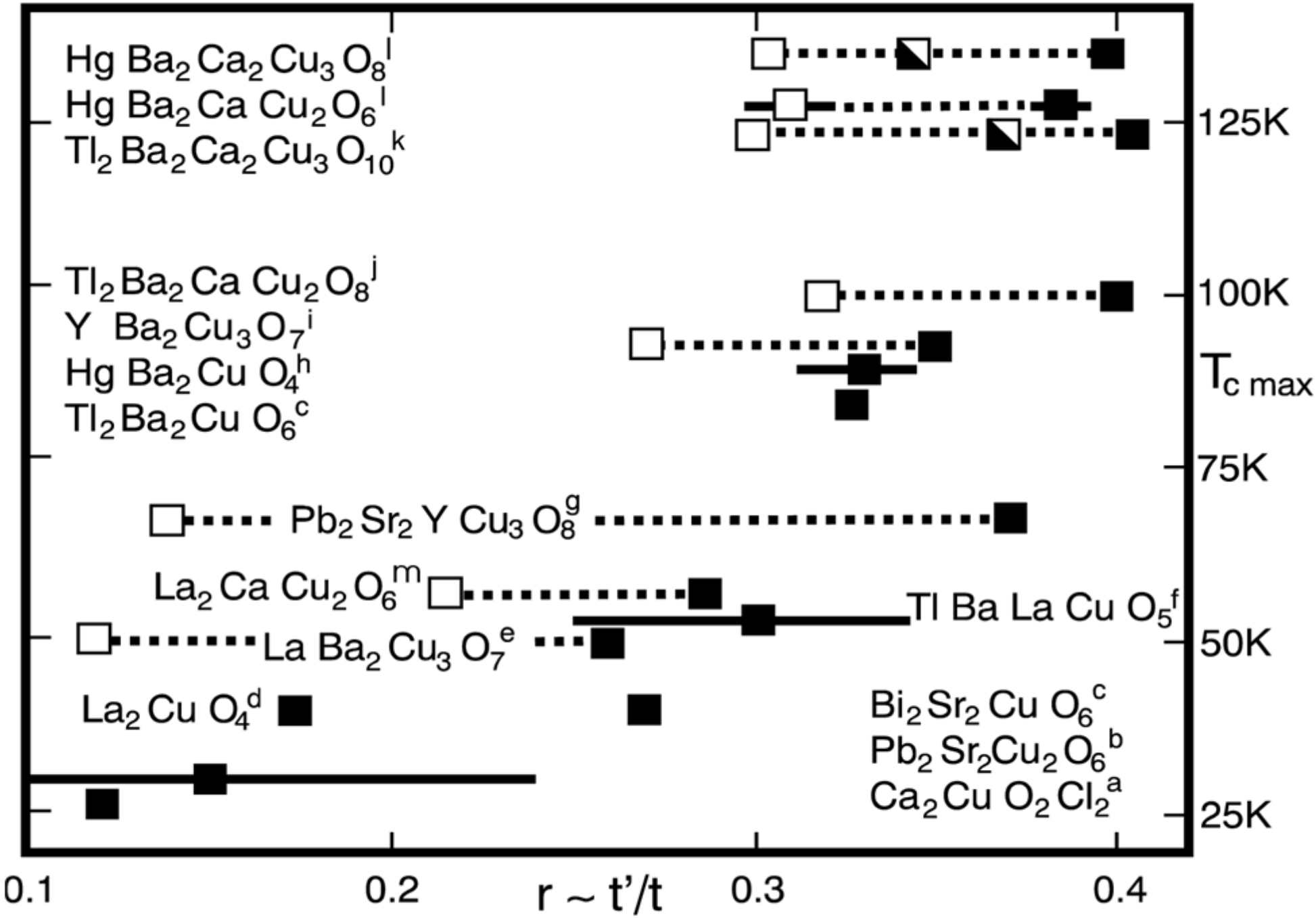



0.5
0.4
0.3
0.2
0.1
0.0
r ~ t'/t
2.3
2.4
2.5
2.6
2.7
2.8
2.9
Cu–Apical Oxygen Distance
La
40K
Bi
40K
Tl
85K
Hg
90K



One-orbital LDA Wannier-like function

The Materials Trend, PRL **87**, 047003 (2001)



That the axial orbital is the channel for coupling the CuO_2 layer to its surroundings is supported by the experimental observations that c-axis transport is strongly suppressed by the opening of a pseudogap with a $(\cos k_x - \cos k_y)^2$-dependence and that the scattering in the normal state has a similar $\mathbf{k}_{\|}$-dependence.

At the same time, the axial orbital is the vehicle for coupling *between* neighboring oxygens *inside* the layer. It therefore seems plausible that contraction of the axial orbital around the CuO_2-layer, away from the non-stoichiometric layers, will strengthen the phase coherence and thus increase $T_{c\,\mathrm{max}}$.

It was completely unexpected that for multi-layer materials, the $T_{c\ \mathrm{max}}$ trend is followed the Fermi-surface sheet with the largest r-value, i.e. with the lowest $\epsilon_{\mathrm{axial}}$ and, hence, with the smallest hole volume.

How r determines $T_{c\,\mathrm{max}}$ remains to be understood.

Computations for materials with strong electronic correlations:

Current approximations to ab inito Density-Functional Theory (LDA) are insufficient for conduction bands with strong electronic correlations, e.g. they do not account for the Mott metal-insulator transition.

On the other hand, LDA Fermi surfaces are accurate for most metals, including overdoped high-temperature superconductors.

Presently, we therefore start with the LDA.

For the few correlated bands, we then construct localized Wannier orbitals and a corresponding low-energy Hubbard Hamiltonian.

The latter is solved in the Dynamical Mean-Field Approximation.

Low-energy multiband Hubbard Hamiltonian

$$\hat{H} = \sum_{im\sigma,i'm'\sigma'} \delta_{\sigma,\sigma'} h_{im,i'm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma'} + \frac{1}{2}\delta_{i,i'} \sum'_{imm'\sigma\sigma'} U_{imm'} \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} - d.c.$$

$h_{im,i'm'}$ is the LDA one-electron part. For the two-electron, on-d-site term, we use:

$$\frac{1}{2} \sum_{m=1} \sum_{m'=1} \sum_{\sigma} \sum_{\sigma'} U_{imm'}\, \hat{n}_{im\sigma}\, \hat{n}_{im'\sigma'} \approx$$

$U_i \sum_m \hat{n}_{im\uparrow}\, \hat{n}_{im\downarrow} +$	for two electrons in same orbital
$(U_i - 2J_i) \sum_m \sum_{m' \neq m} \hat{n}_{im\uparrow}\, \hat{n}_{im'\downarrow} +$	different orbitals and spins
$(U_i - 3J_i) \sum_m \sum_{m' > m} \left(\hat{n}_{im\uparrow}\, \hat{n}_{im'\uparrow} + \hat{n}_{im\downarrow}\, \hat{n}_{im'\downarrow}\right)$	same spin

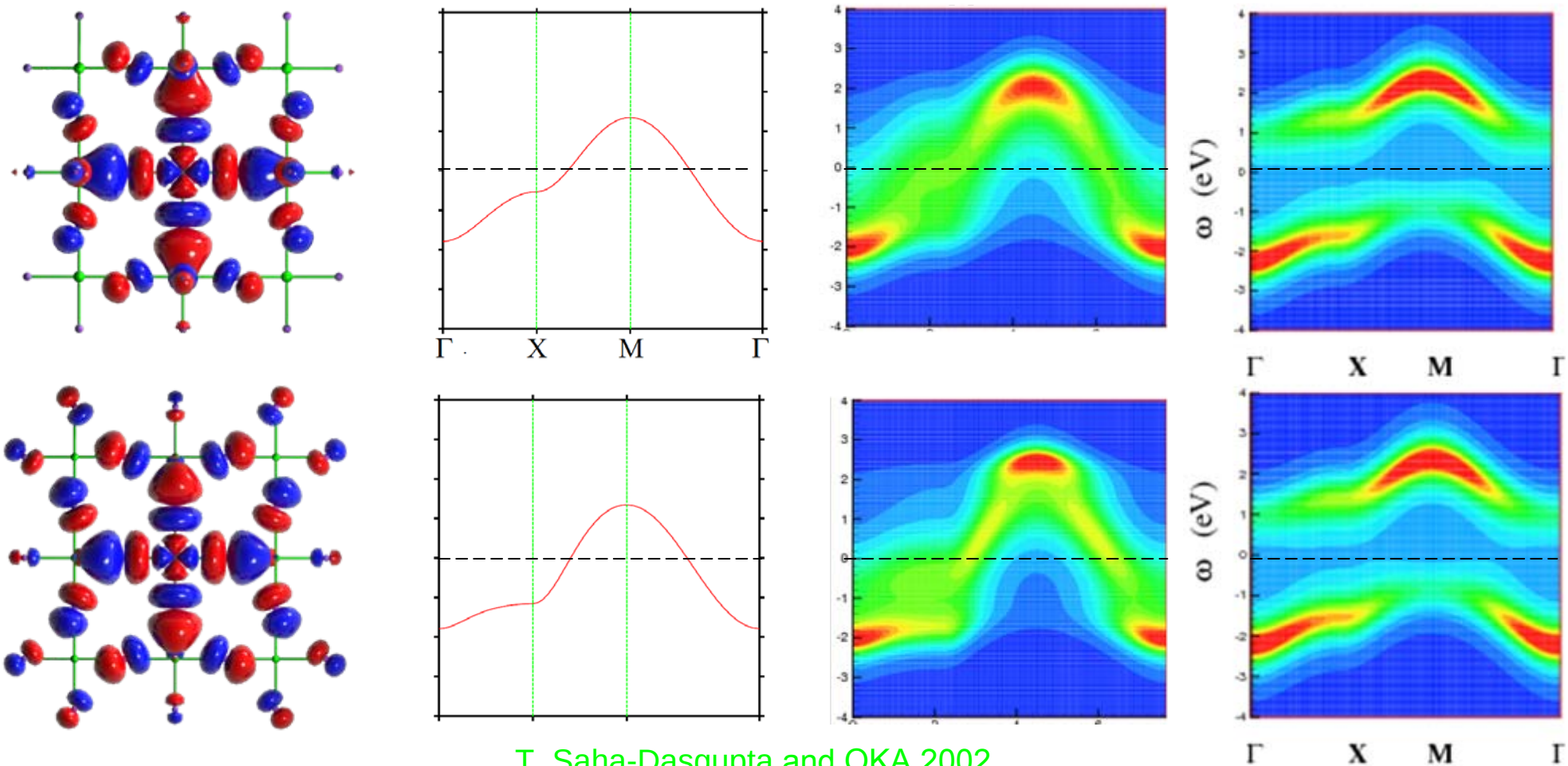
Mott transition in cuprate HTSCs

Wannier orbitals and conduction band, LDA

Hubbard model, LDA+DMFT

T=2000K, undoped

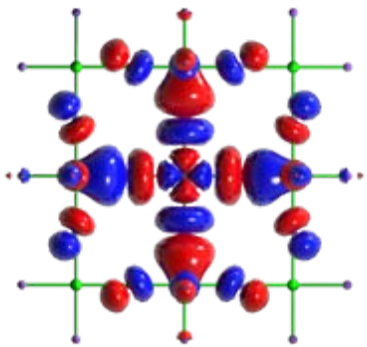
U =2.1 **U = 3.0 eV**

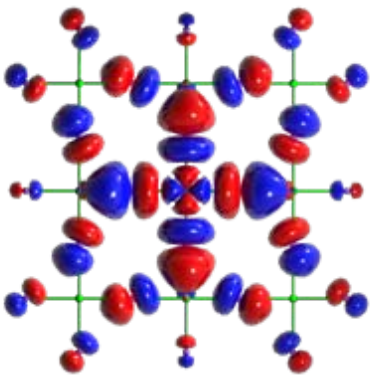


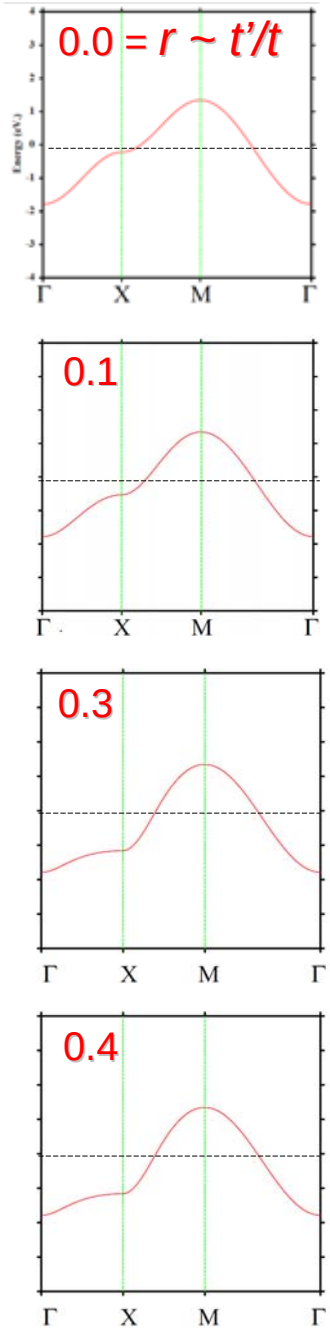
T. Saha-Dasgupta and OKA 2002

Cuprates $3d^{9-x} = 3d_{x^2-y^2}{}^{1-x}$

Conduction band LDA





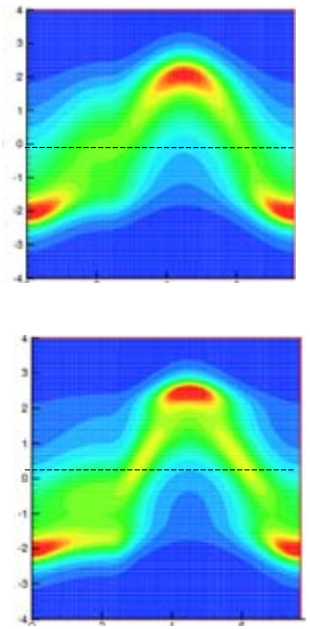


T. Saha-Dasgupta and OKA 2002

One-band Hubbard model LDA+DMFT

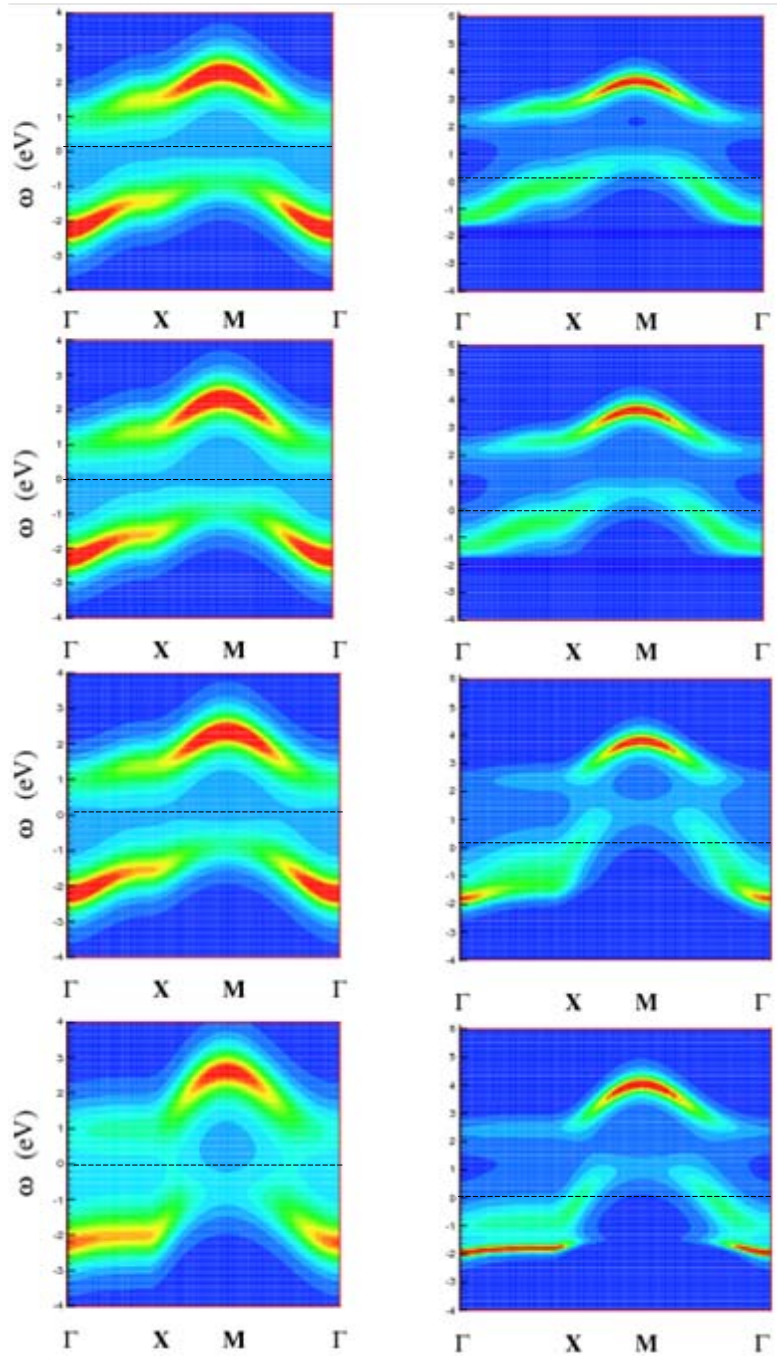
U =2.1 eV

undoped

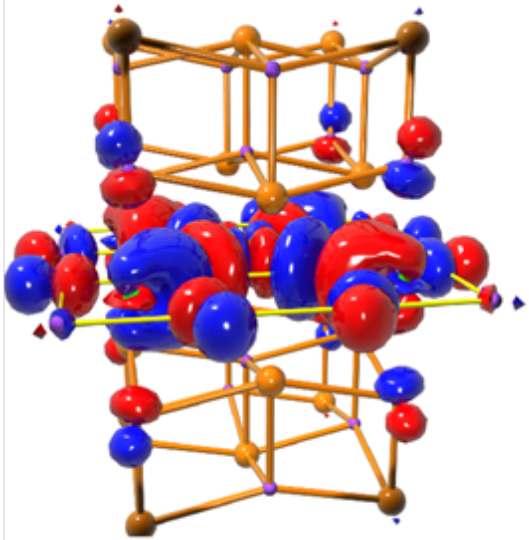


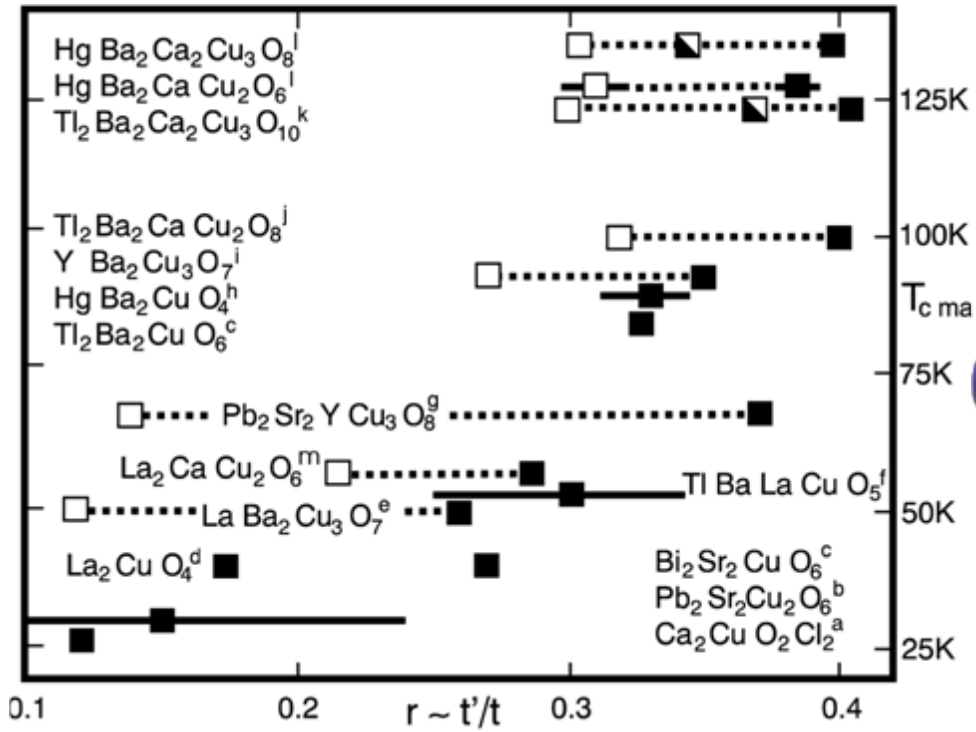
U = 3.0 eV

undoped | 10% doped

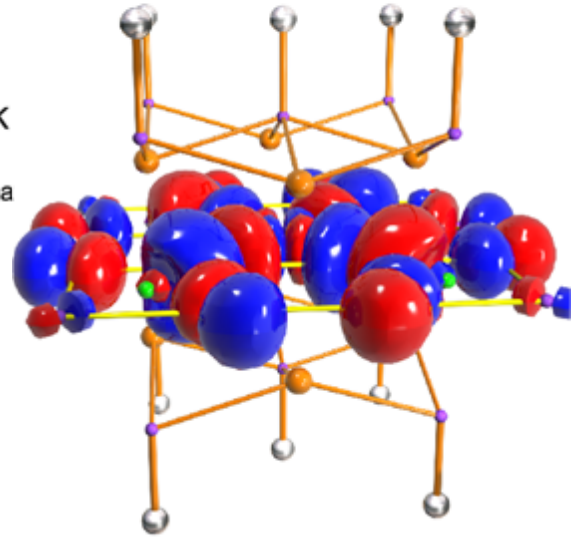


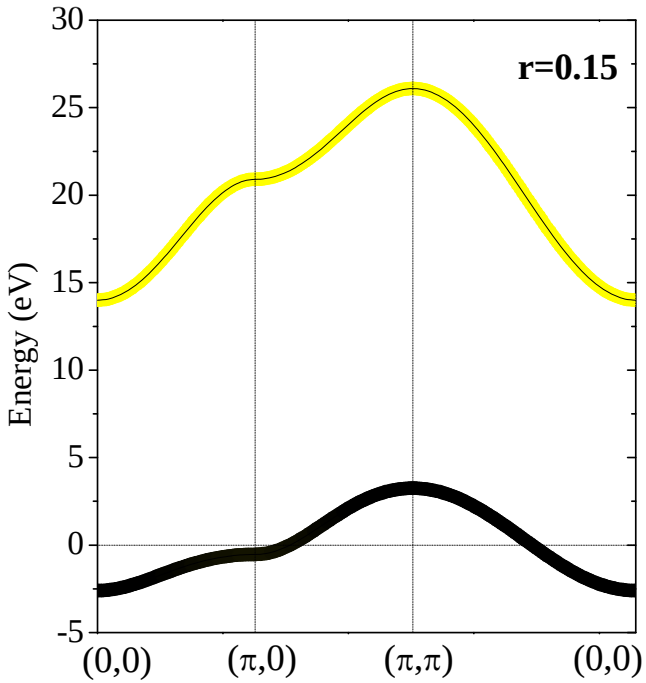
La_2CuO_4





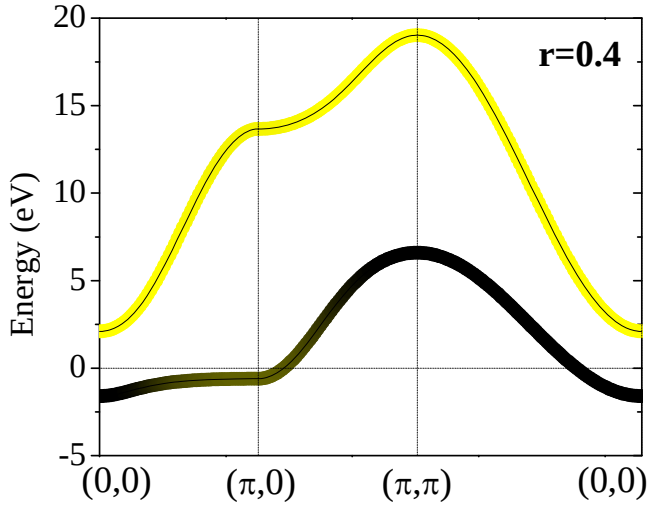
$HgBa_2CuO_4$



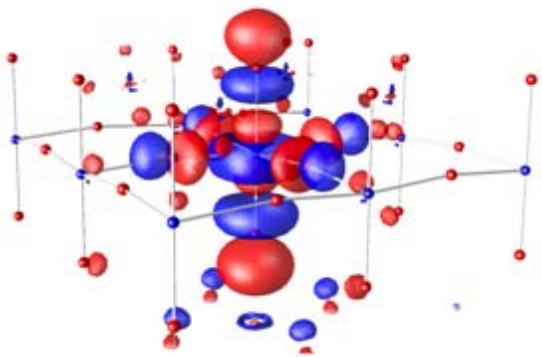


Axial 4*s*-like orbital

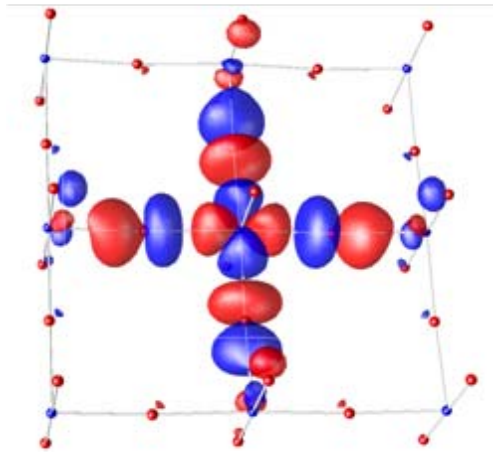
and x^2-y^2



How to make a cuprate Fermi surface out of a nickelate heterostructure, in theory



$3z^2$-1 $\quad$ $3d^7\,(e_g^1)$ $\quad$ x^2-y^2



X. Yang[1], P. Hansmann[2],
A. Toschi[2], K. Held[2],
G. Khaliullin[1], O.K. Andersen[1]

[1] Max-Planck-Institut für Festkörperforschung, Stuttgart
[2] Institute for Solid State Physics, Vienna University of Technology

Khaliullin's idea:

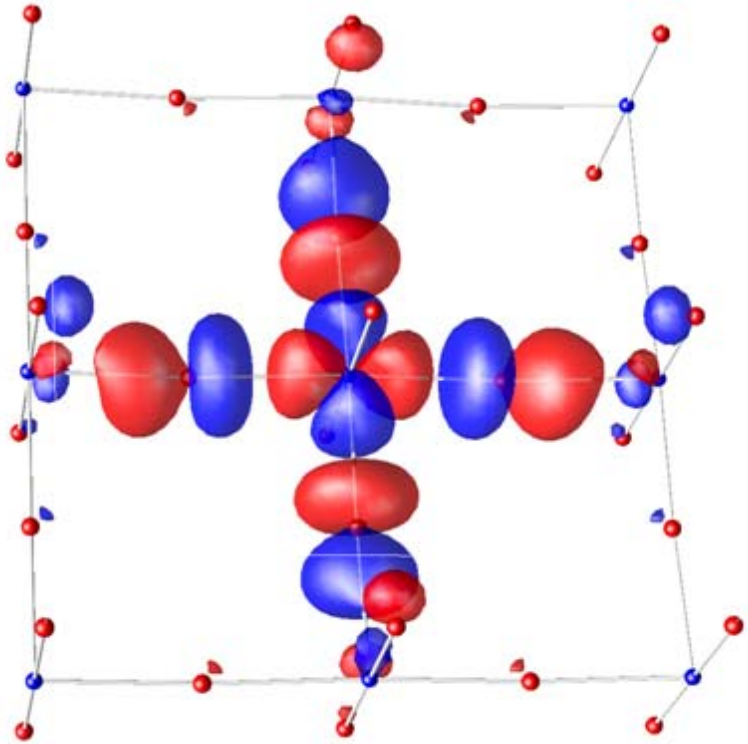
Make $Ni^{3+}(d^7)$-based HTSCs by sandwiching hole doped $LaO\text{-}NiO_2$ layers between insulating layers through heterostructuring (orbital engineering)

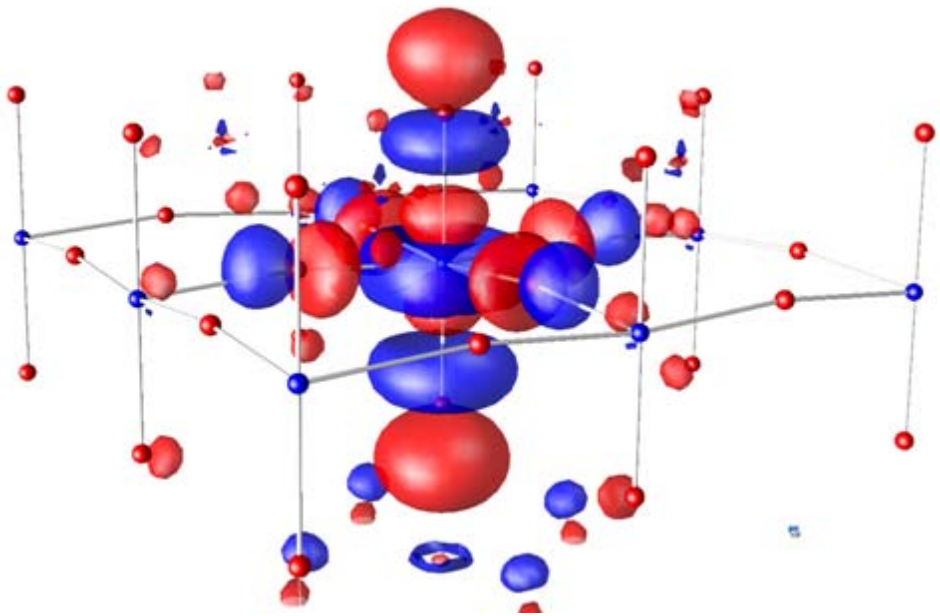
- The confinement together with the electronic correlations should make it possible to localize or empty the $3z^2$-1 band thus leaving the conduction electron in the x^2-y^2 band
- If the $3z^2$-1 orbital can be manipulated to lie *above* x^2-y^2 , it might play the role of the axial orbital in the cuprate d^9 HTSCs
- Charge disproportionation (d^6+d^8) must be avoided

J. Chaloupka and G. Khaliullin, PRL 100, 016404 (2008).

P. Hansmann, Xiaoping Yang, A. Toschi, G. Khaliullin, O.K. Andersen, and K. Held, PRL 103, 016401 (2009).

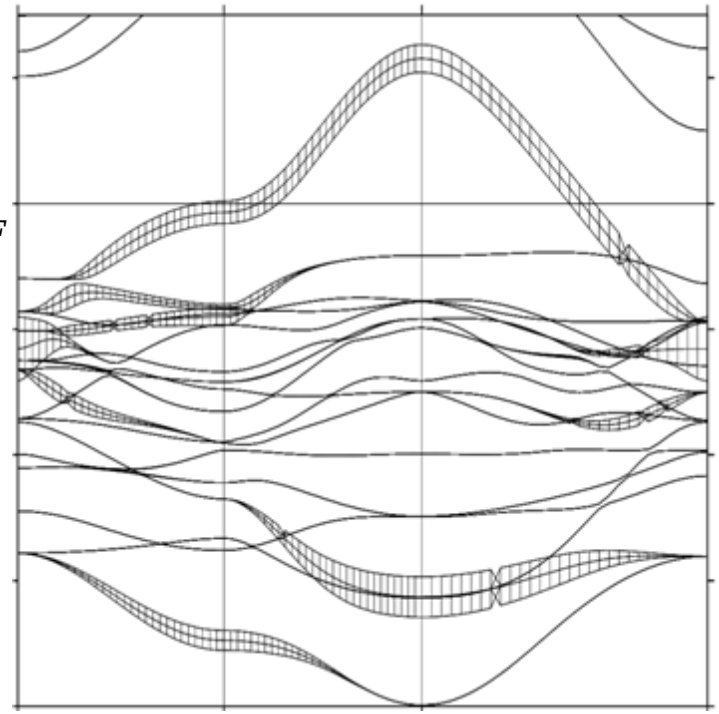
Nickellate **e_g orbitals** **La_2CuO_4**





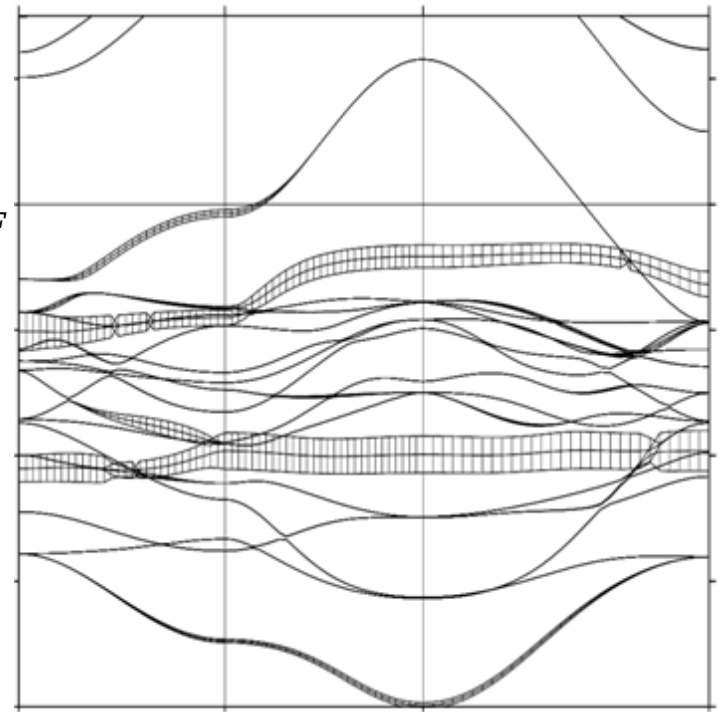
ε_F

x^2-y^2



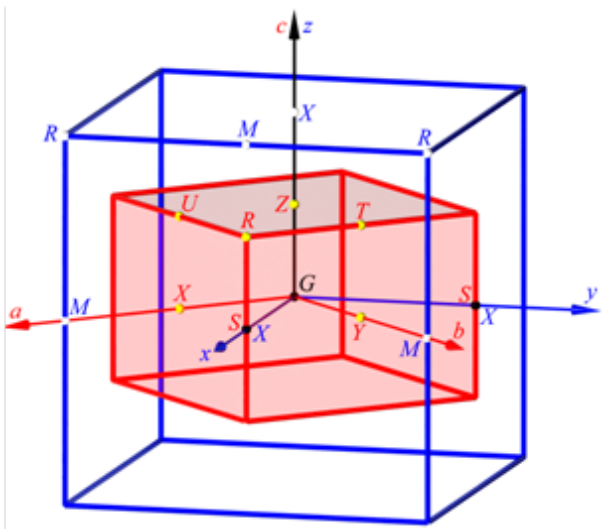
ε_F

$3z^2$-1

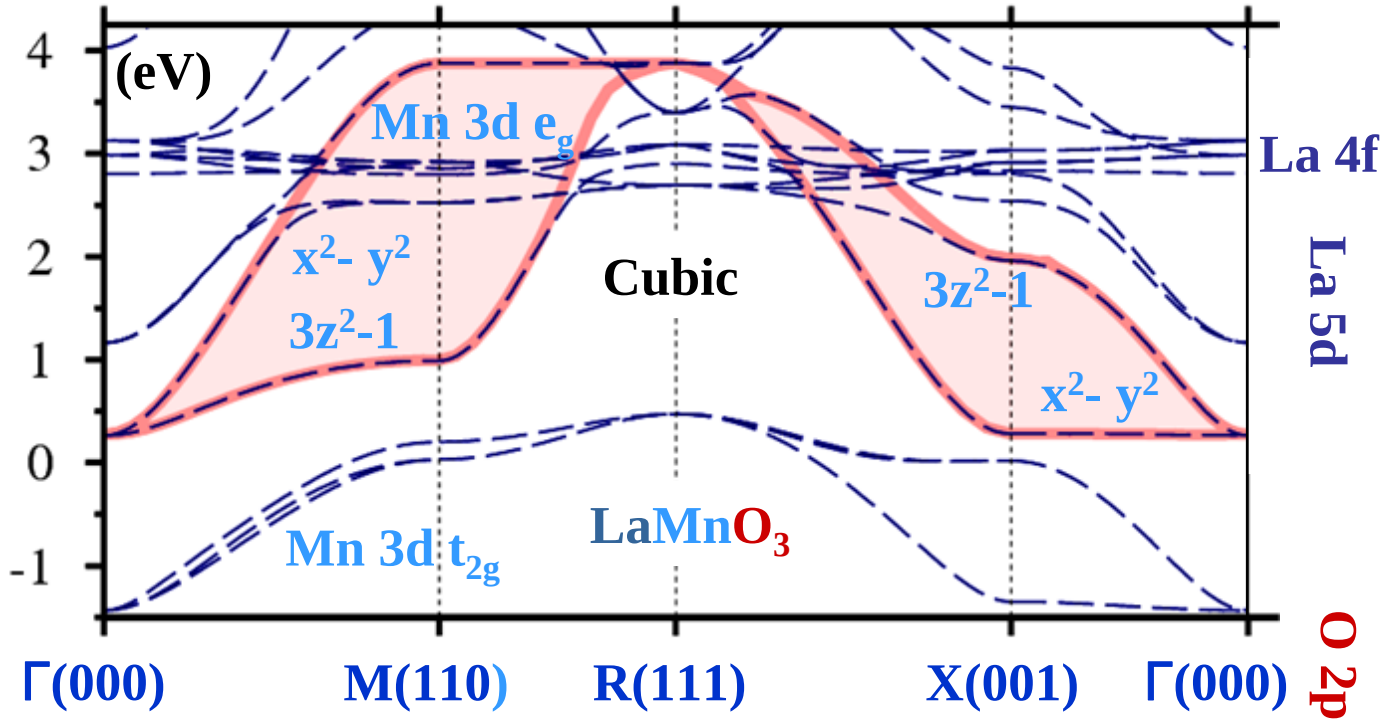


10 eV

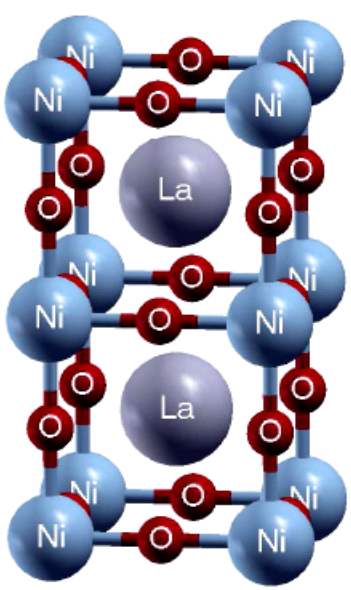
Confinement:

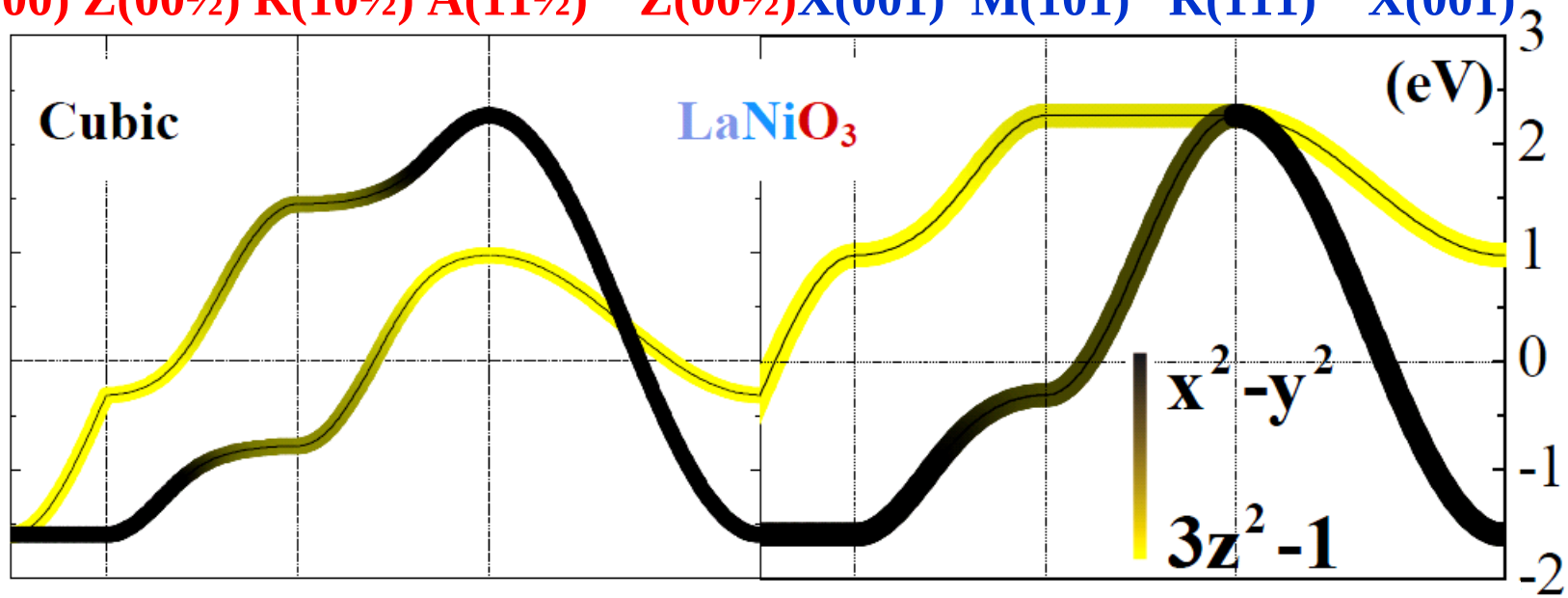


Paramagnetic LDA bands in (1 -1 0) plane



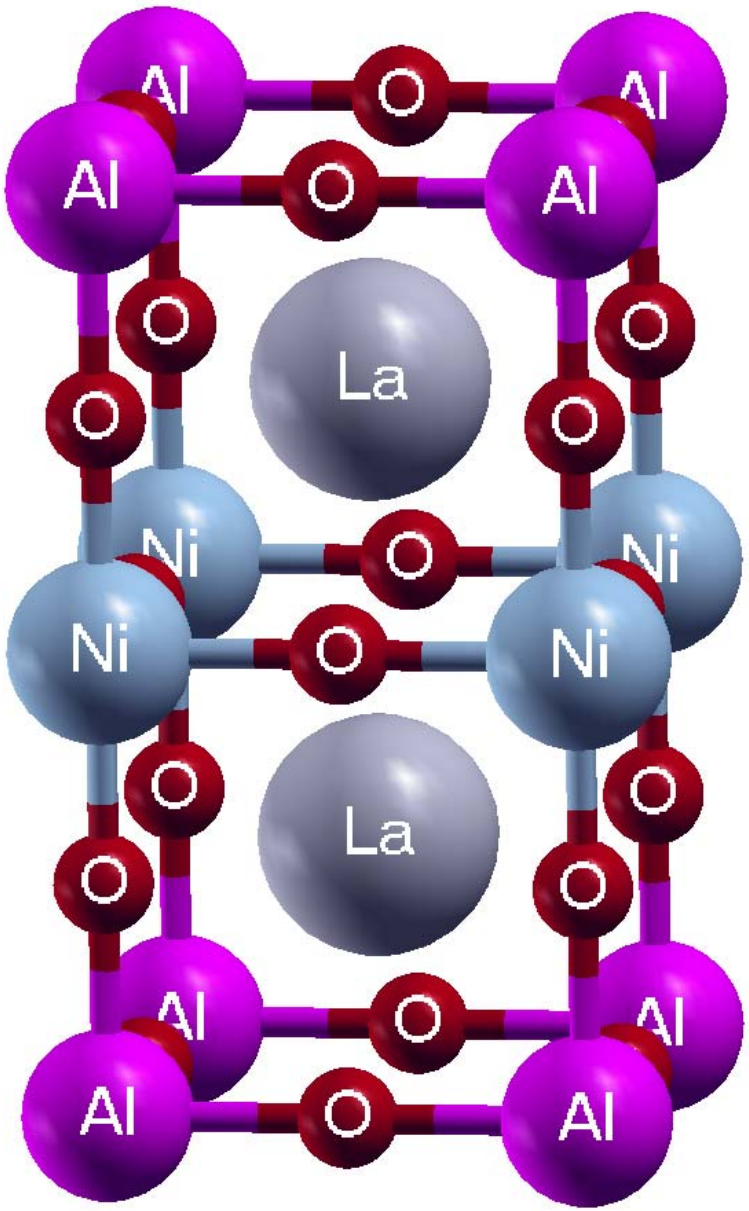
Γ(000) Z(00½) R(10½) A(11½) Z(00½) X(001) M(101) R(111) X(001)

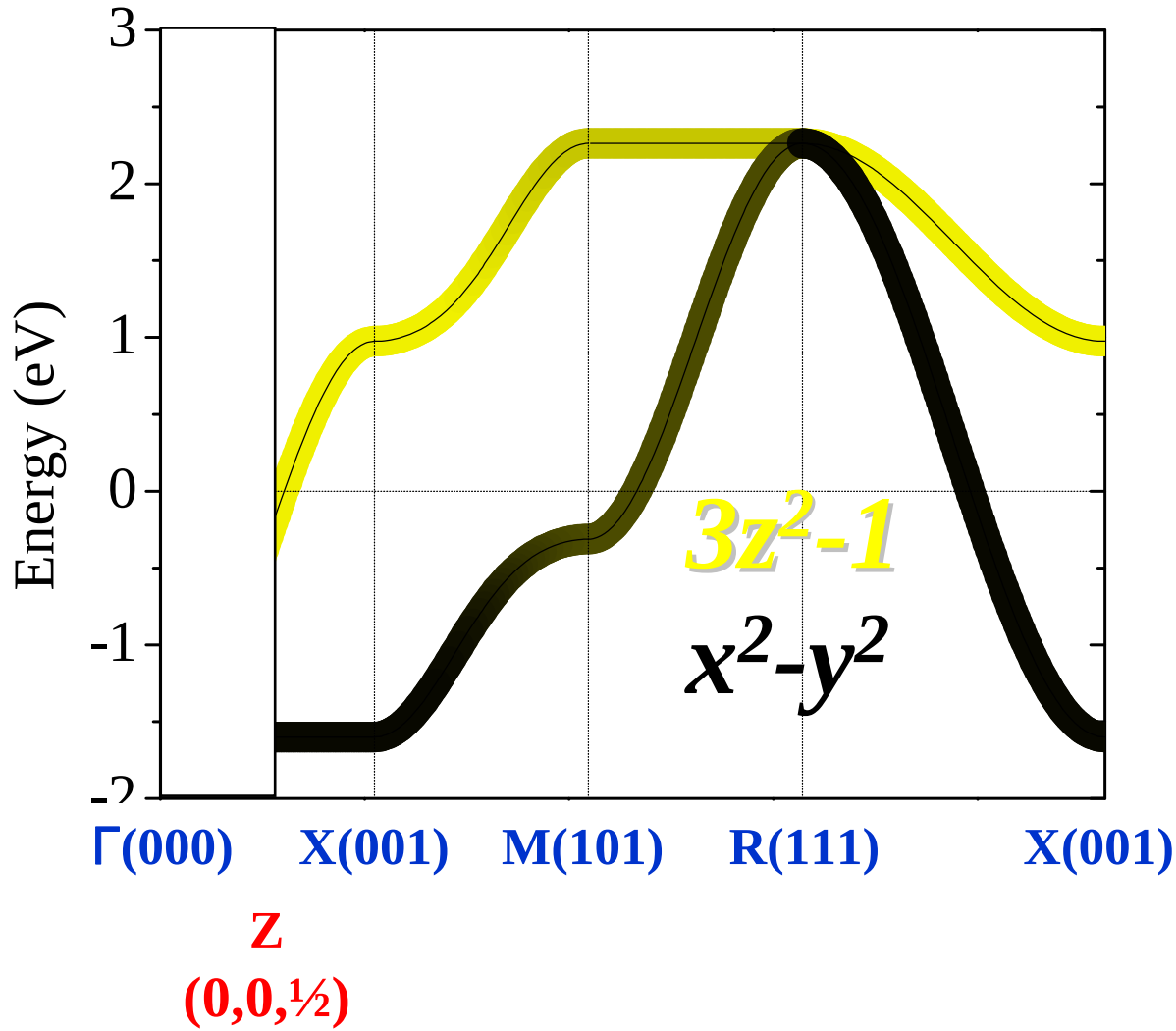


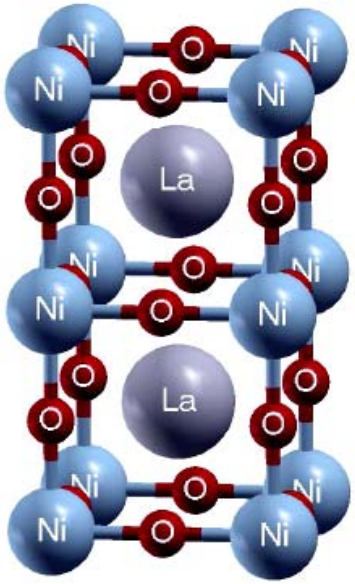


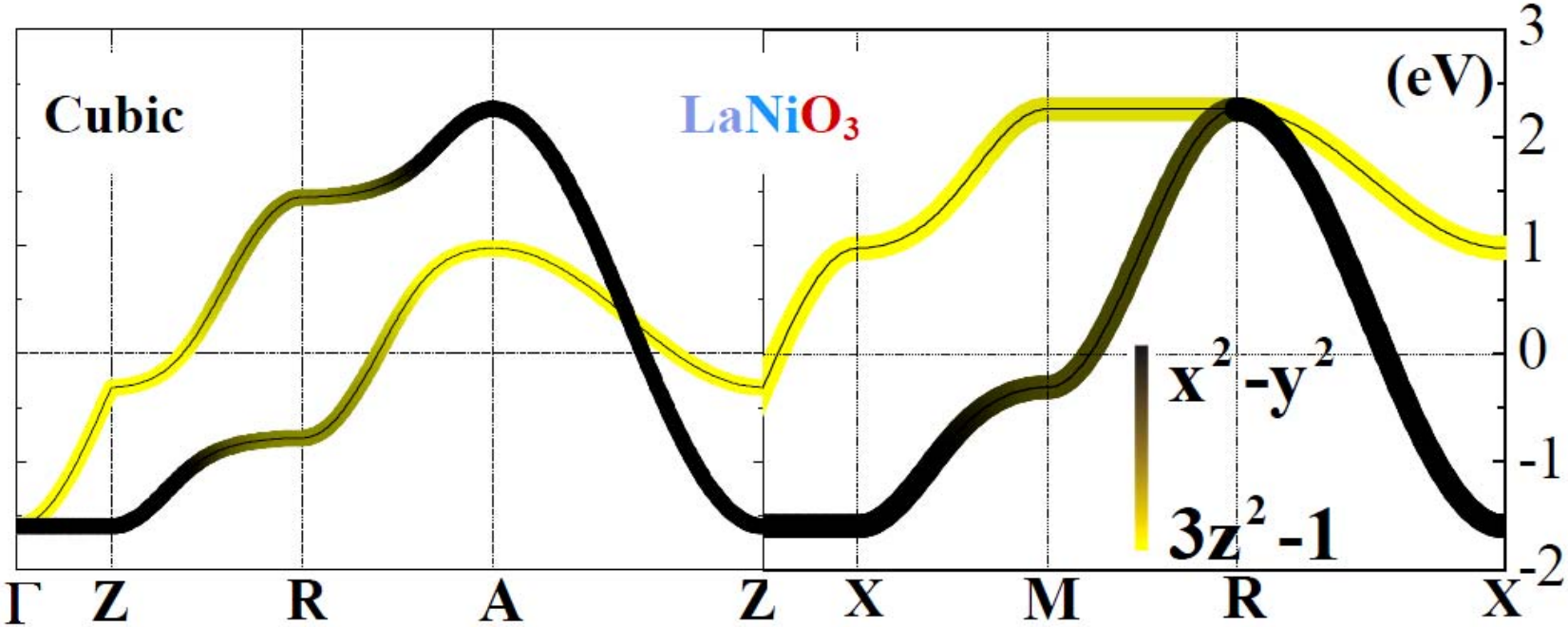
d^7 nickelates

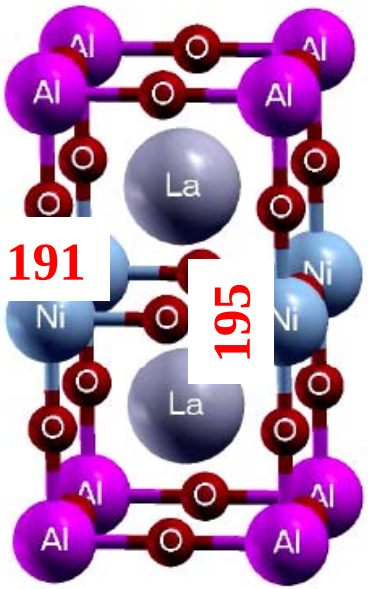
Simplified e_g conduction-band structure in 2D square lattice:

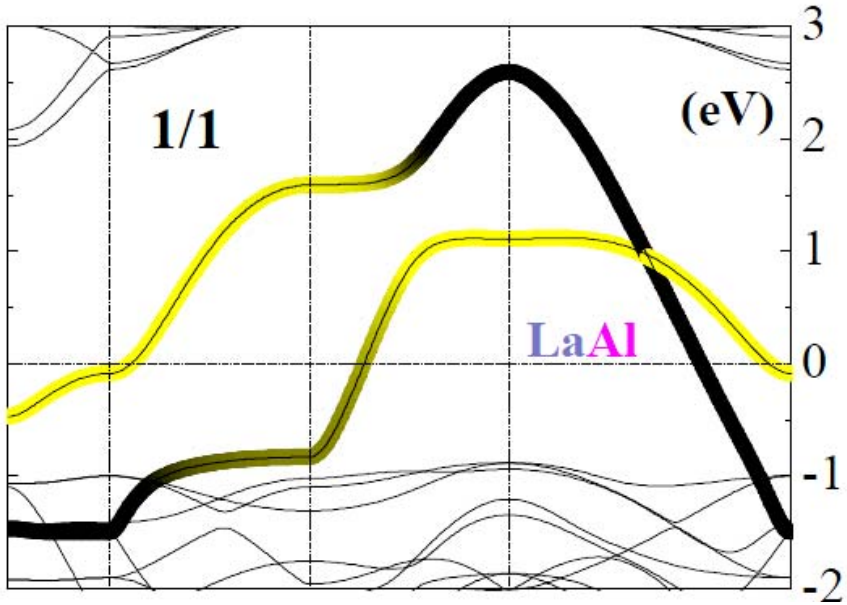












Ni 4s, La 5d, Al 3p

Ni t_{2g}, O 2p, Al 3s

LDA

LDA+DMFT

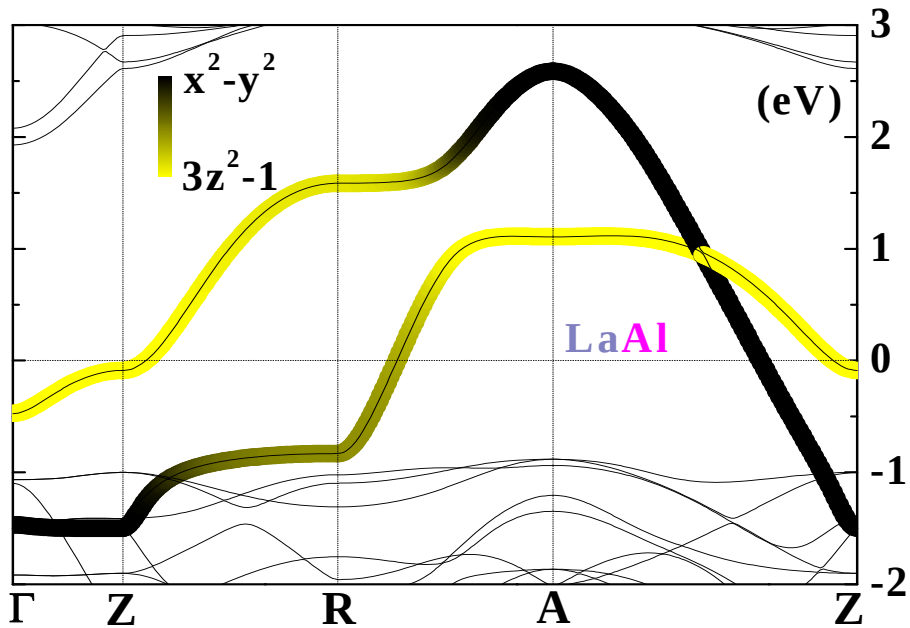
Undoped

U = 6.7 eV

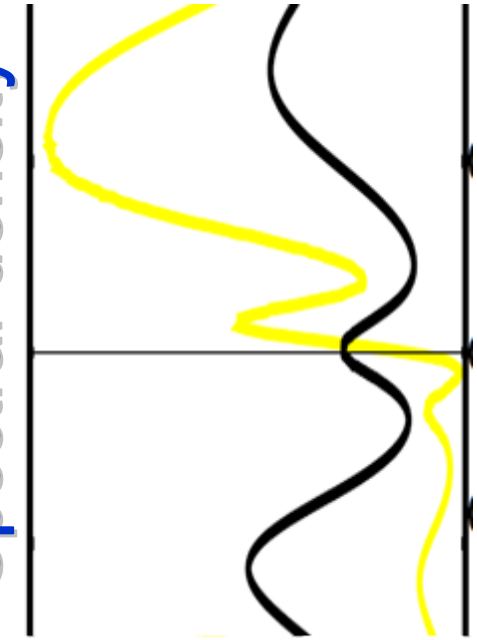
J = 0.7 eV,

T = 1100 K.

Band structure



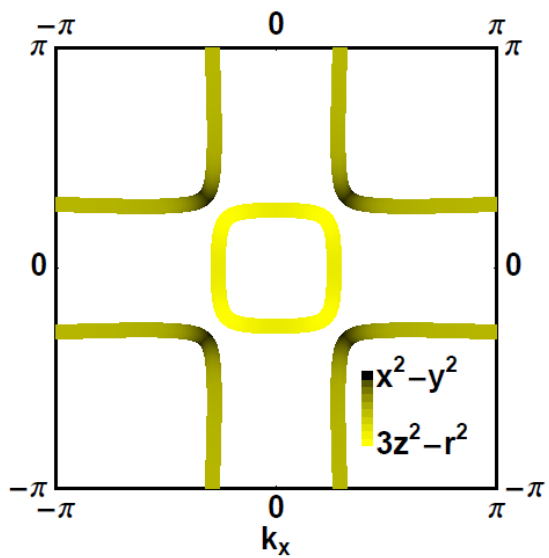
Spectral-density

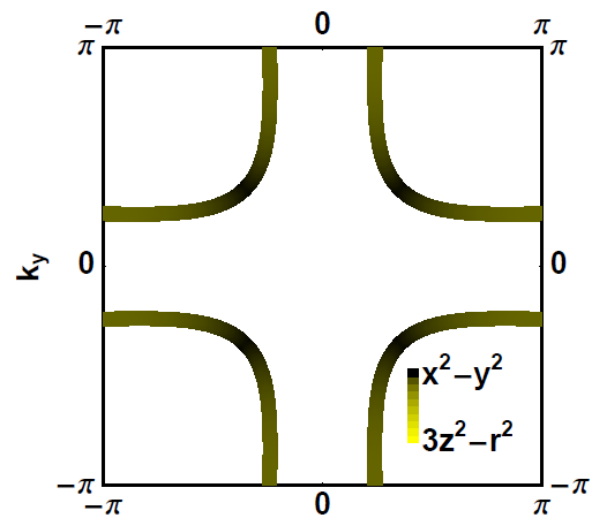


0 < U < 6.4 eV

two FS sheets.

Fermi surface





6.4 < U < 7.4

one FS sheet.

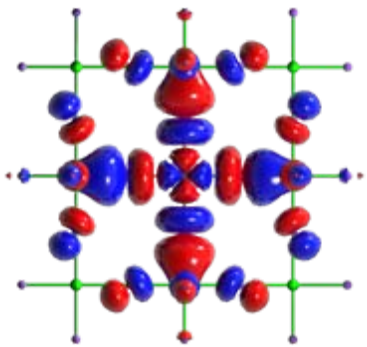
7.4 < U

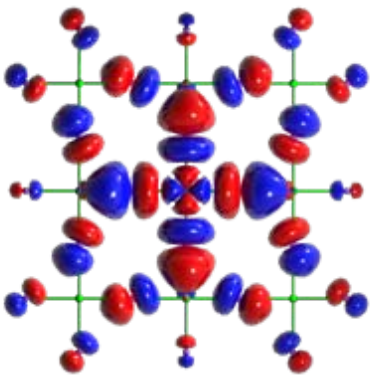
no FS; Mott ins.

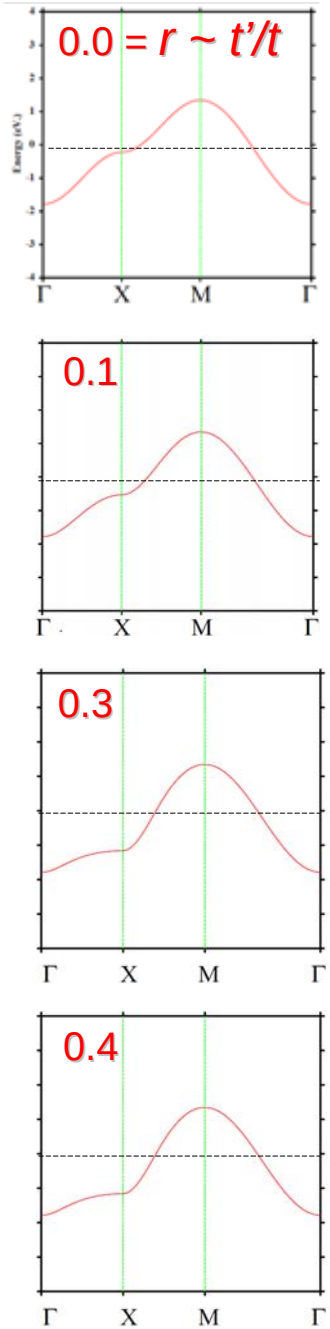
The Coulomb correlations enhance the crystal-field splitting and simplifies the Fermi surface to one sheet when $\varepsilon_{3z^2-1}(\Gamma) > \varepsilon_F$, i.e. with a shape (r ~ ½), like that in the cuprates with the highest T_{cmax}

Cuprates $3d^{9-x} = 3d_{x^2-y^2}{}^{1-x}$

Conduction band LDA





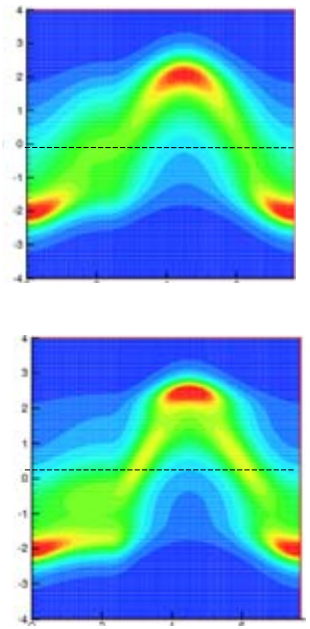


T. Saha-Dasgupta and OKA 2002

One-band Hubbard model LDA+DMFT

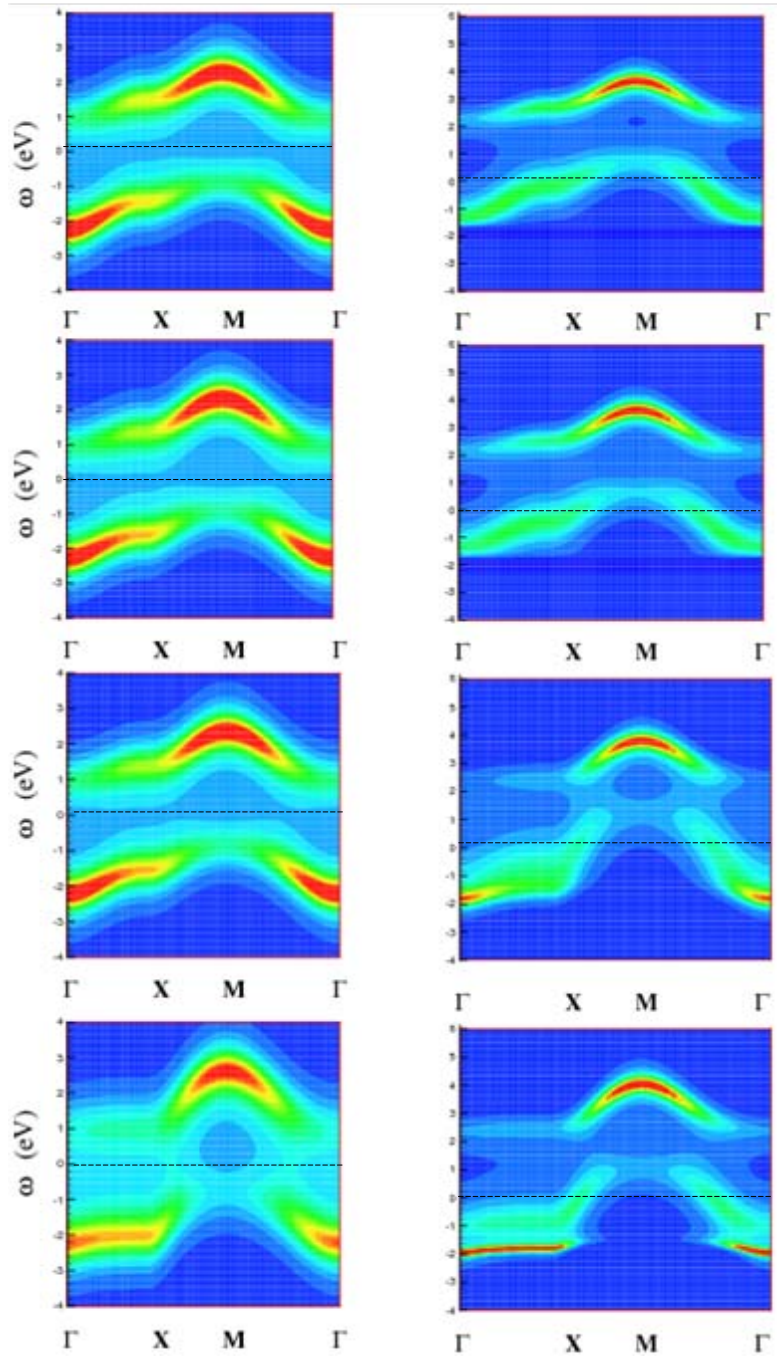
U =2.1 eV

undoped



U = 3.0 eV

undoped | 10% doped



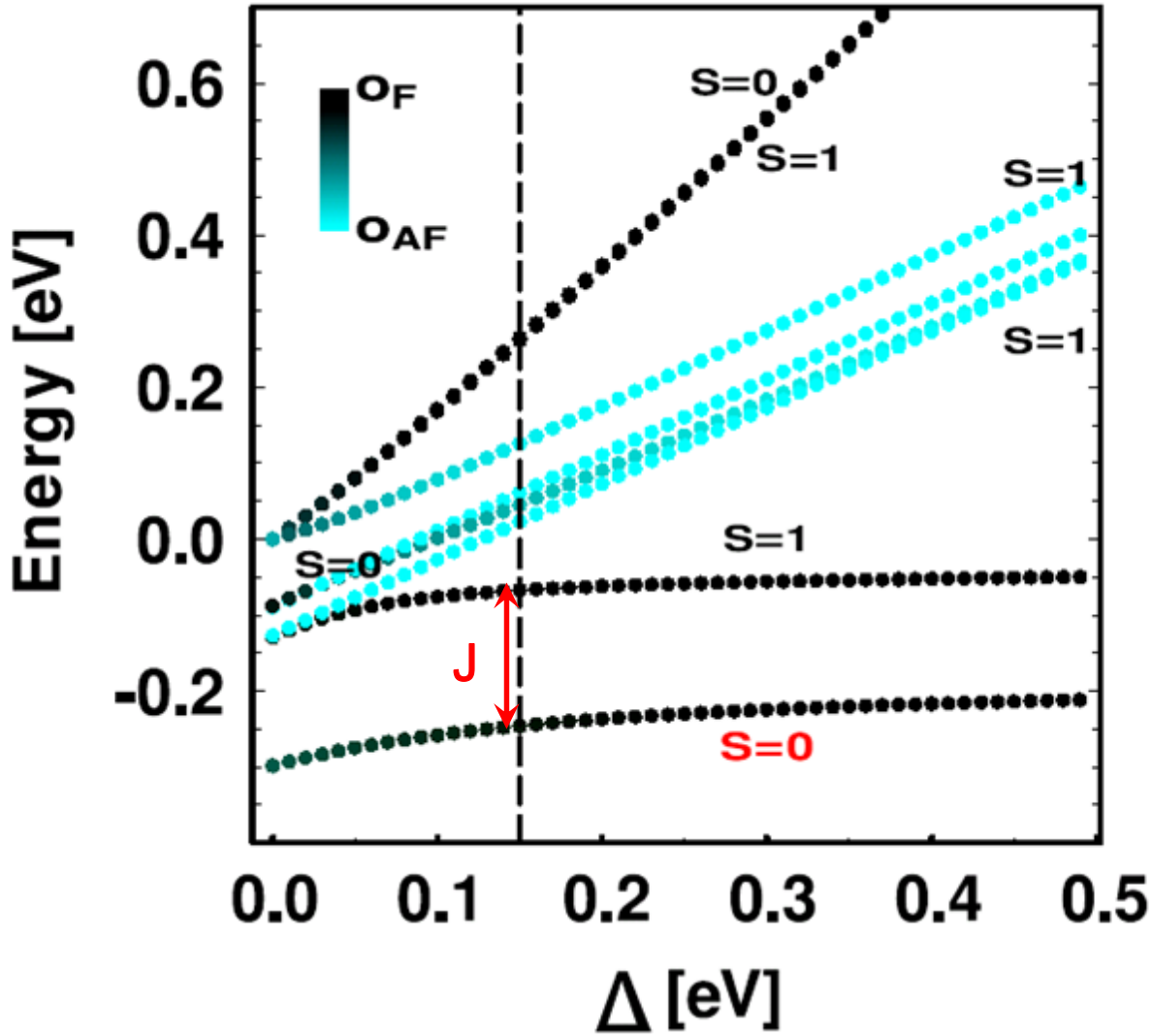
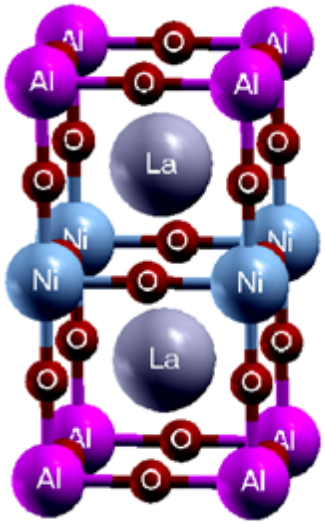
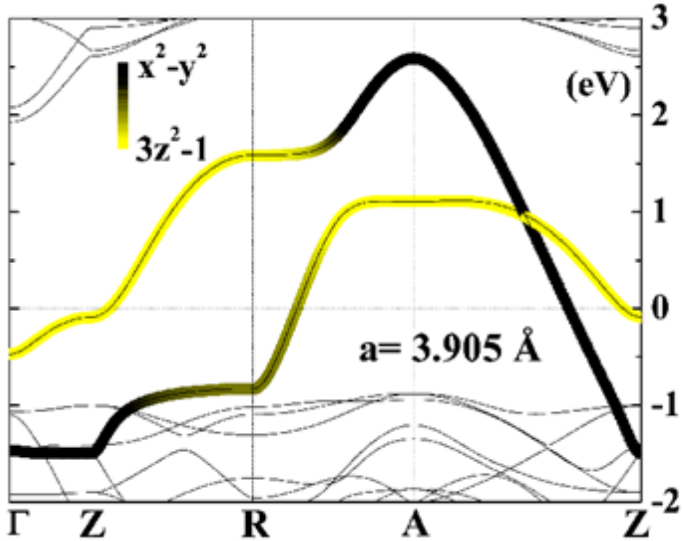
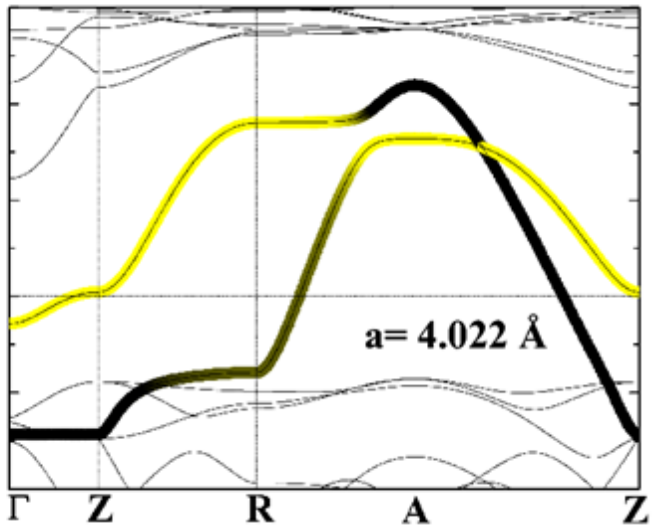


FIG. 3 (color online). Energy levels for the unstrained two-site model with $U = 6.4$ eV as a function of the splitting Δ between the energies of the $3z^2 - 1$ and $x^2 - y^2$ Wannier orbitals. The LDA value of Δ is indicated by the dashed line. O_F (O_{AF}) denotes a configuration with the same (different) orbital(s) on the two sites.

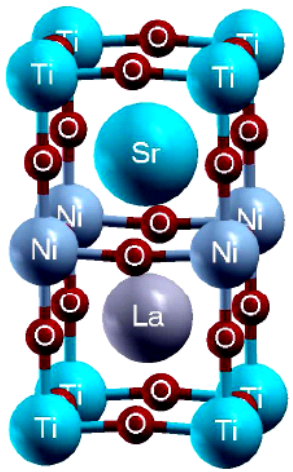


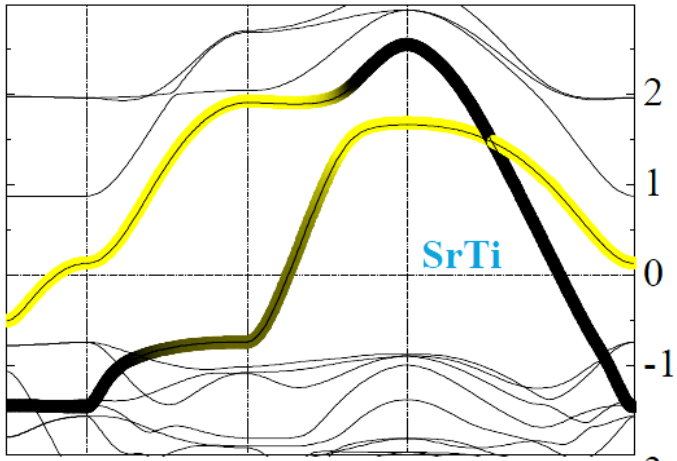


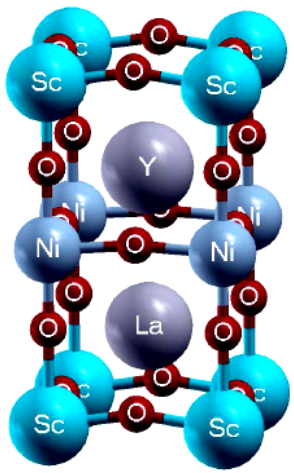


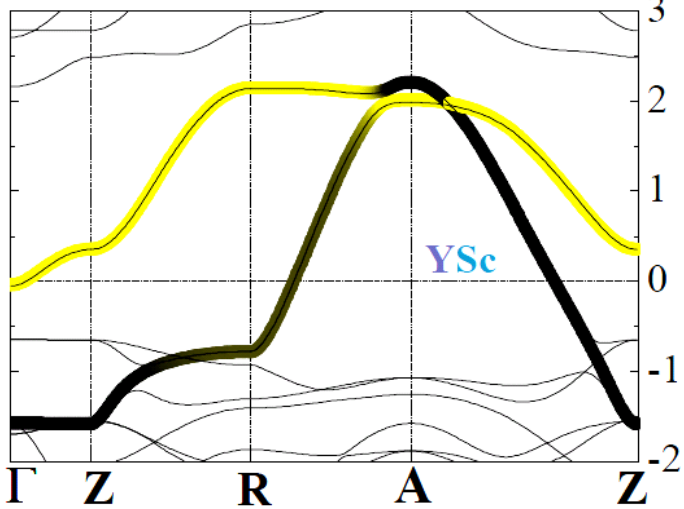
Control by lattice constant of the substrate

1-sheet FS: $5.7 < U < 6.5$ eV

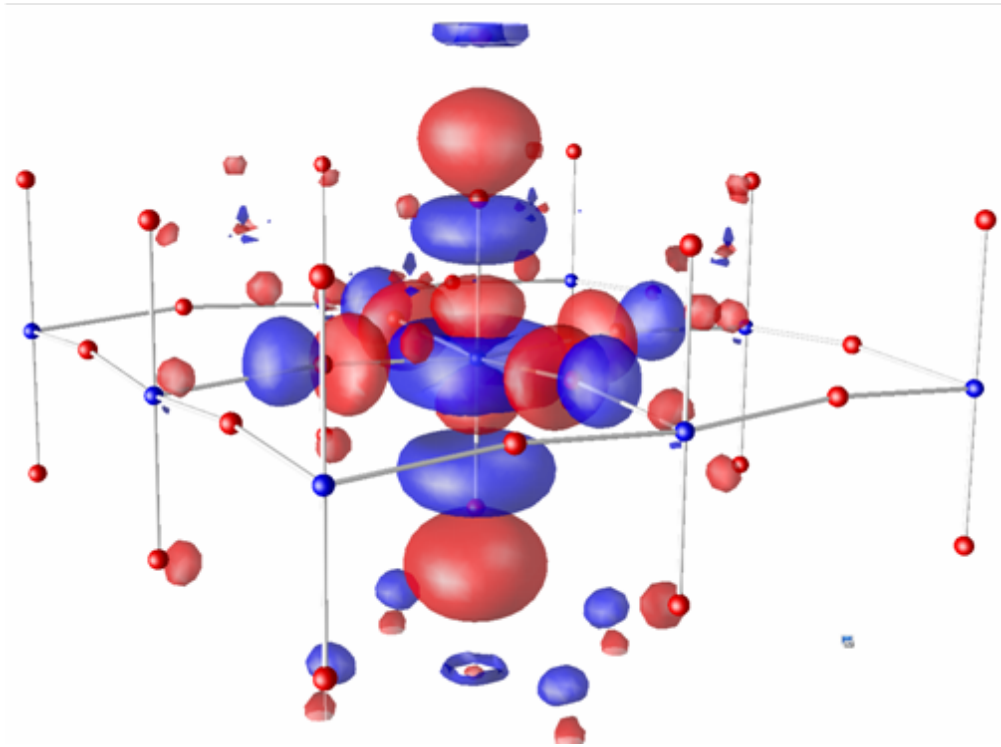








Control by the chemistry (Al, Ti, Sc) of the insulating layers



Phase diagram of 3D $RNiO_3$ perovskites

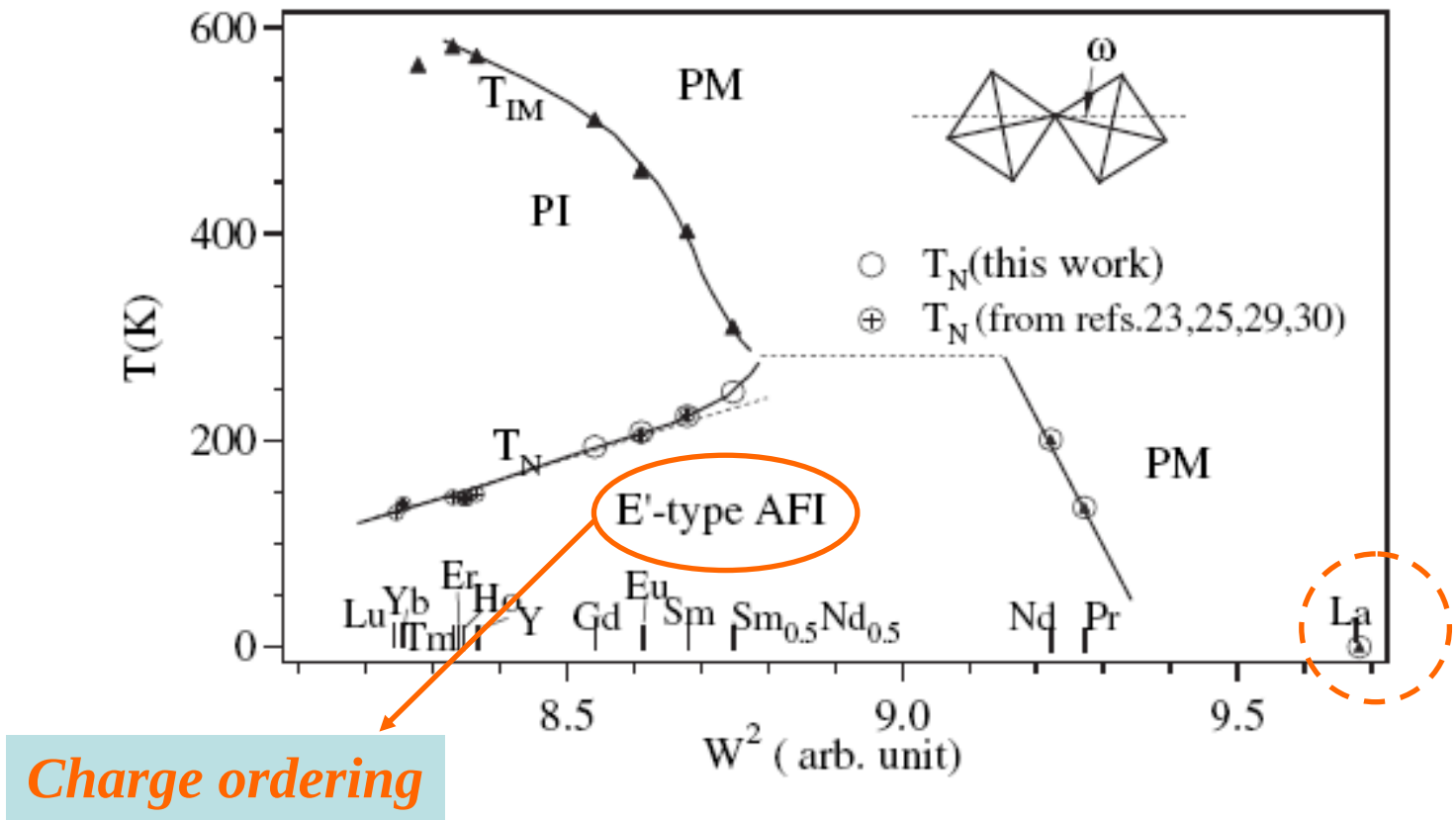
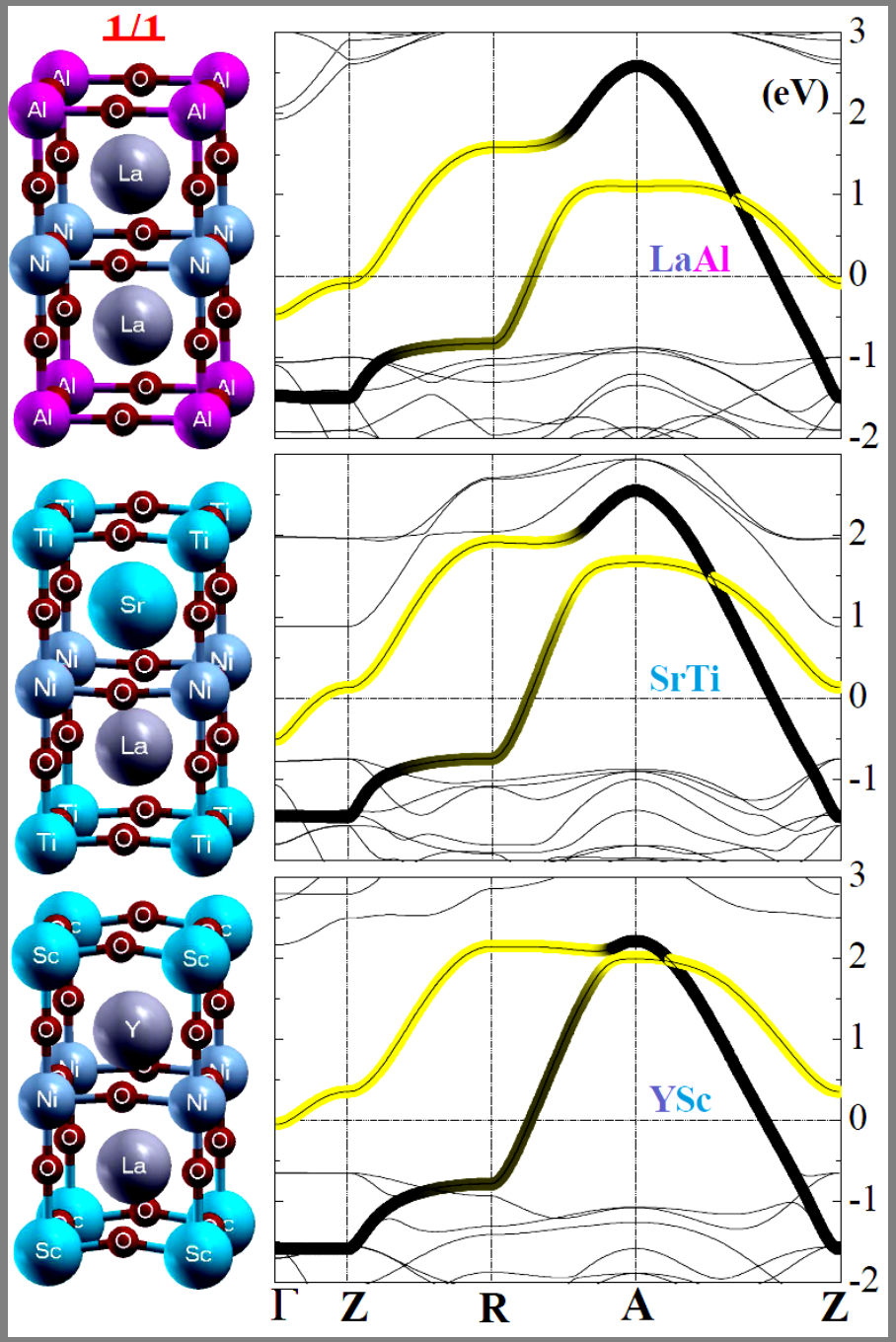
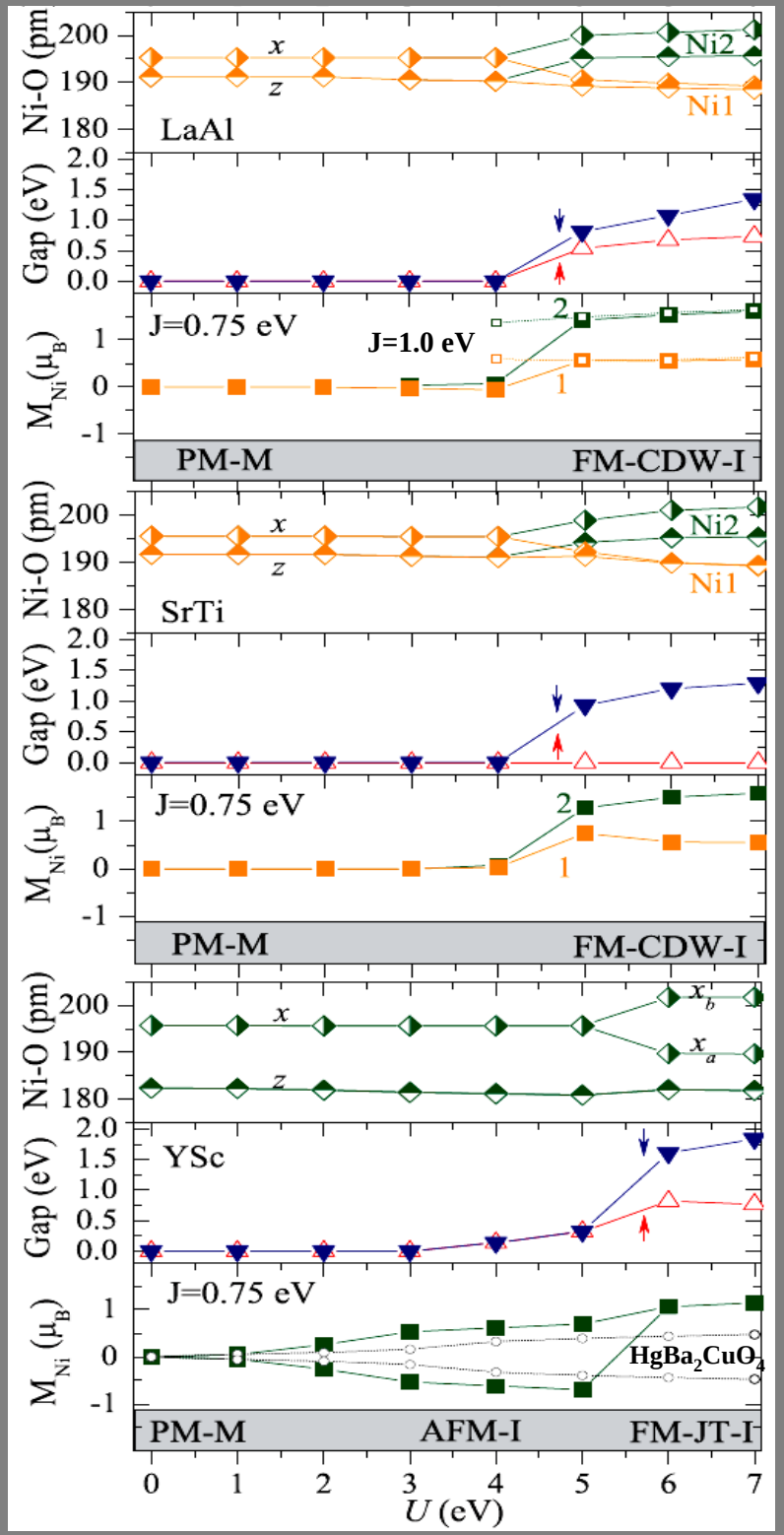


FIG. 5. The phase diagram of transition temperatures vs bandwidth W^2 at room temperature. T_{IM} and T_N are taken from Refs. [23,25,29,30]. Lines inside the figure are guides to the eyes. Inset: definition of the angle ω used to obtain $W \sim \cos\omega/(\text{Ni-O})^{3.5}$.

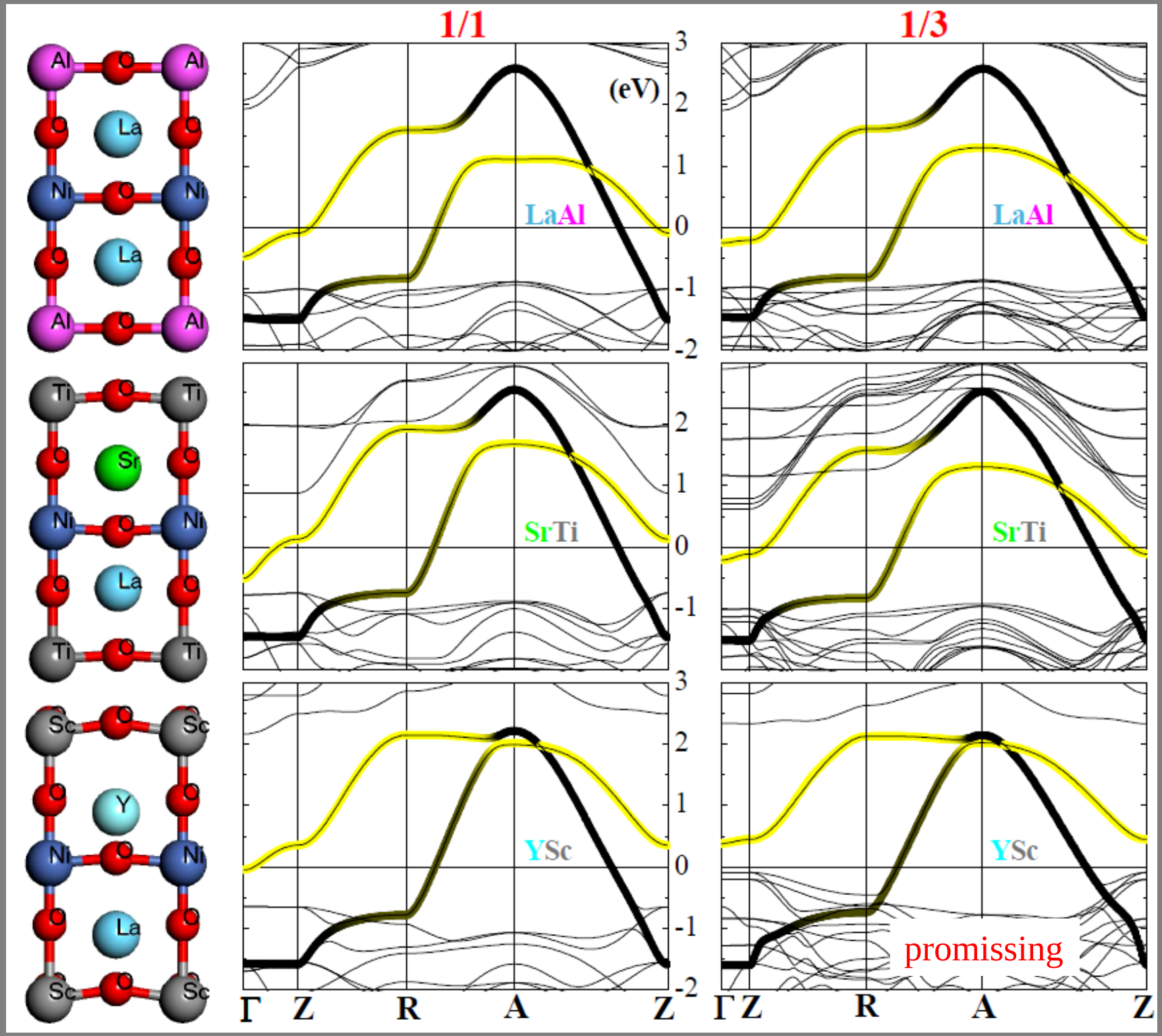
J.S. Zhou *et al*., Phys. Rev. Lett. 95, 127204 (2005)

Chemical control by the A and B cations and the thickness of the insulating layer. This is also a tool for avoiding charge disproportionation.

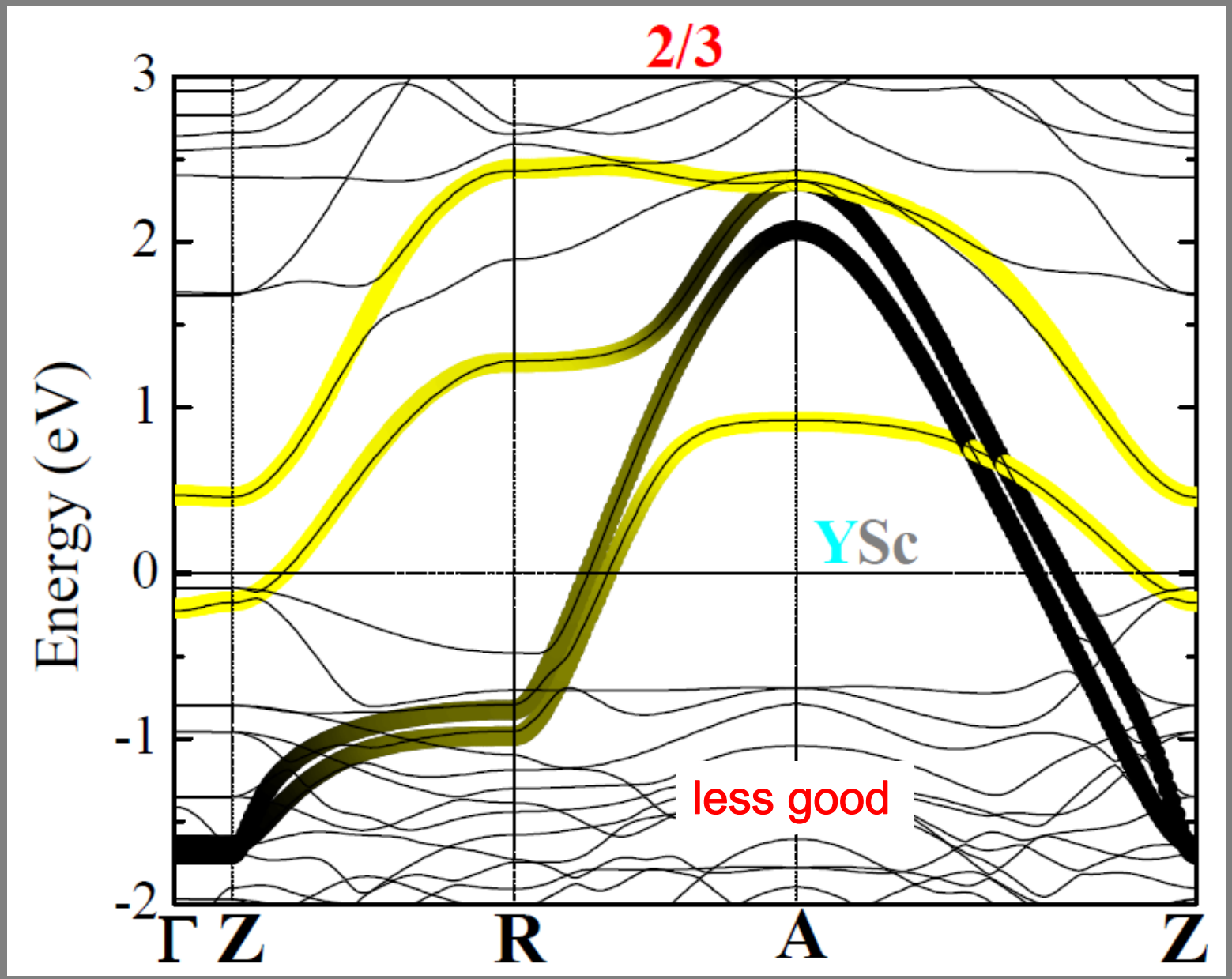


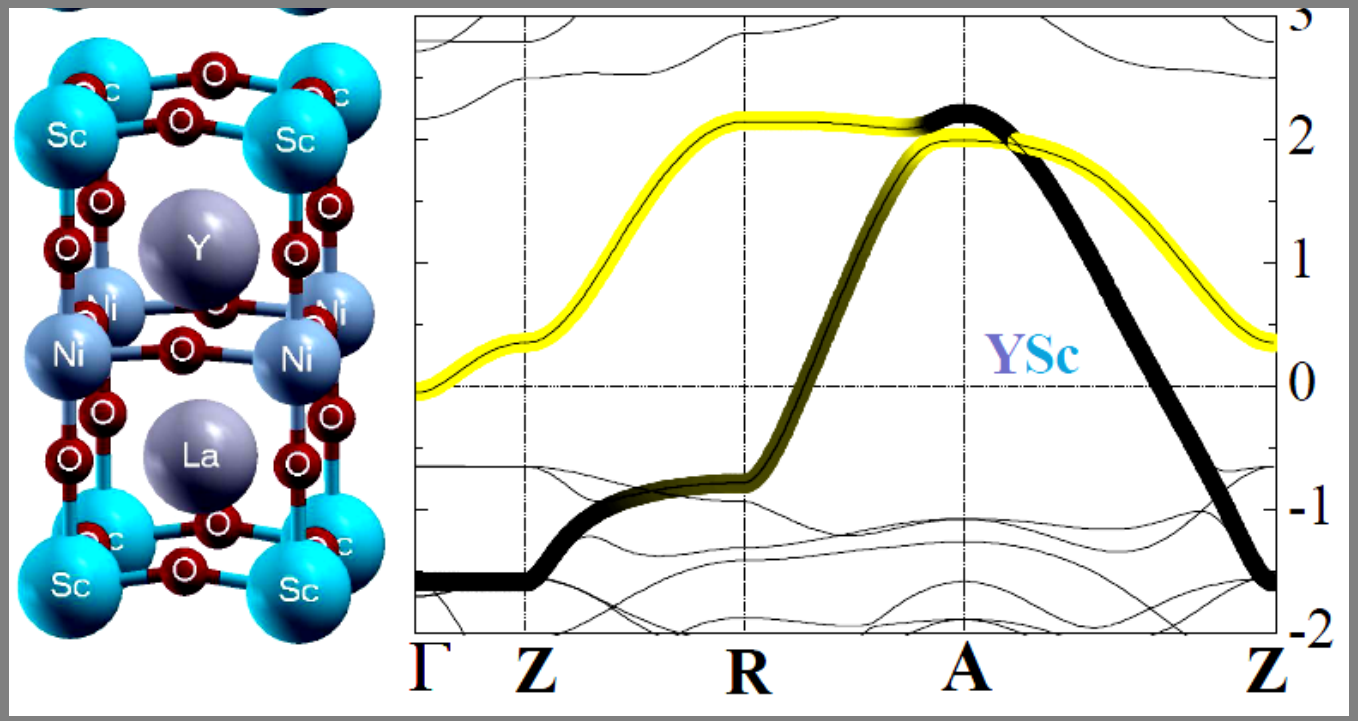


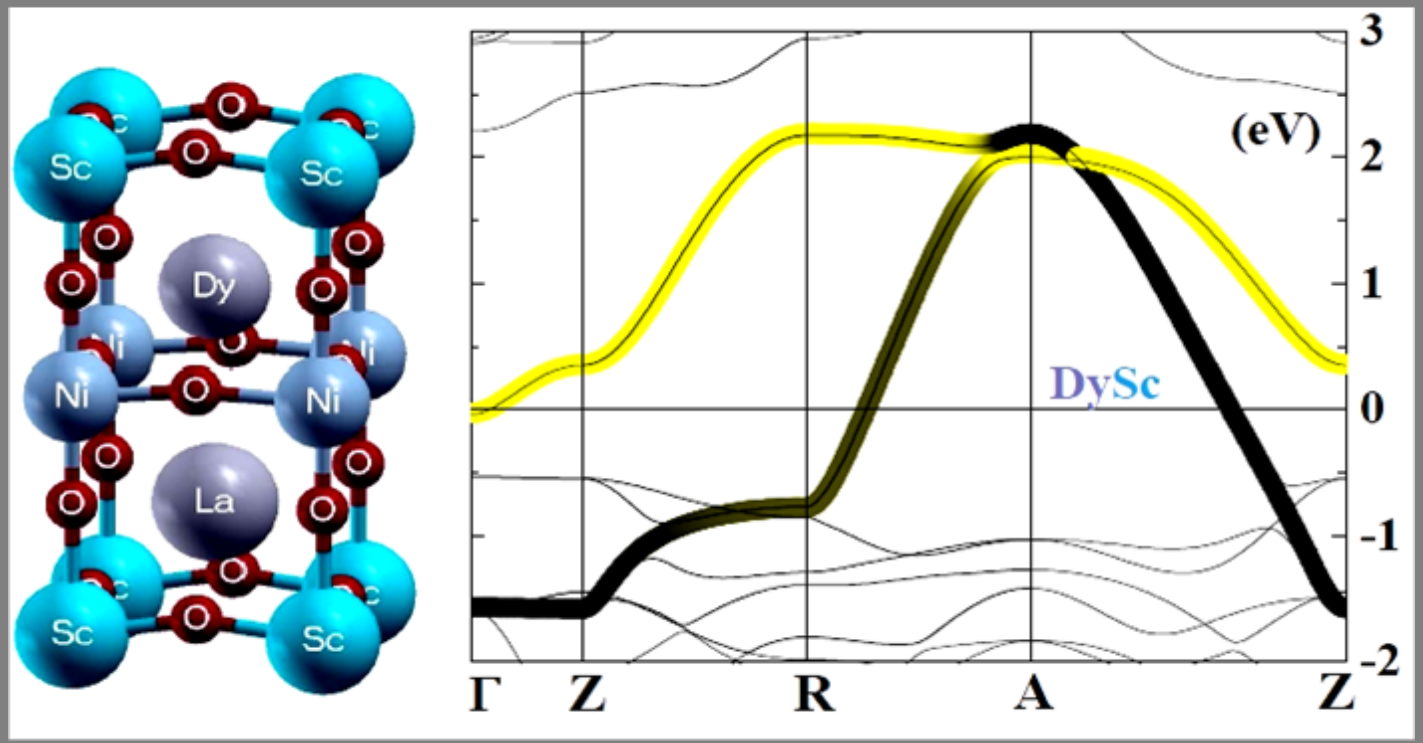
Adding insulating neighbor layers



Adding a NiO_2 nearest-neighbor layer (bilayer)







On stock:

(H-U Habermeier)

Thank you for listening

and

thank you to Nicola, Claudia and Mac for organizing this exciting summer school