Getting the chemistry into Hubbard Hamiltonians via DF Wannier-like functions

1. Electron localization in $3d^1$ perovskites

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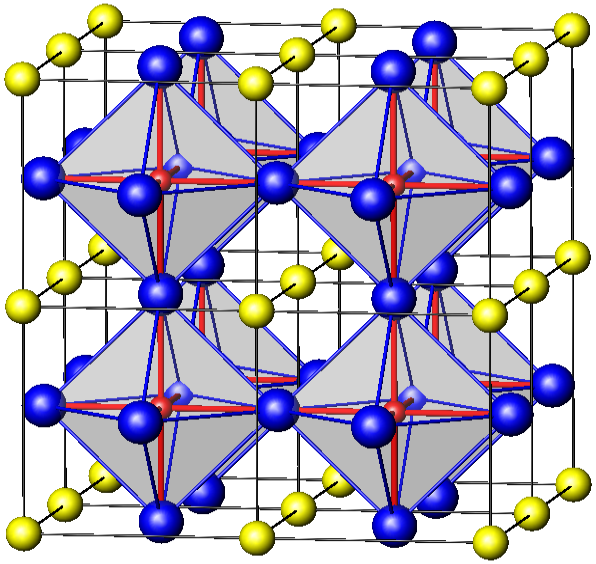
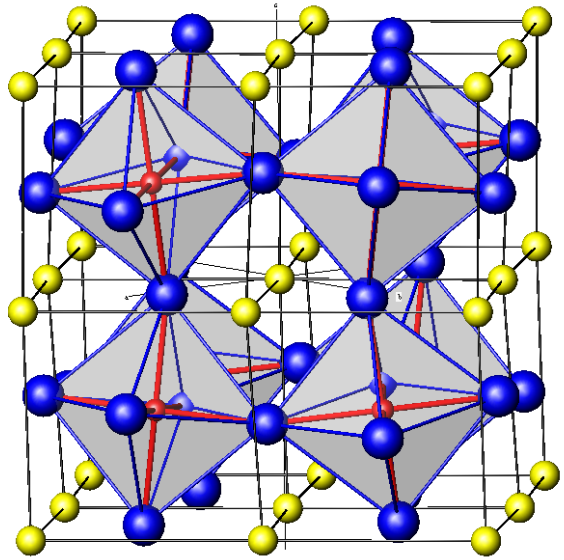
Orthorhombic $3d^1$ Perovskites

$SrVO_3$

Metal

m*/m=2.7





$CaVO_3$

Metal

m*/m=3.6

$LaTiO_3$

Insulator

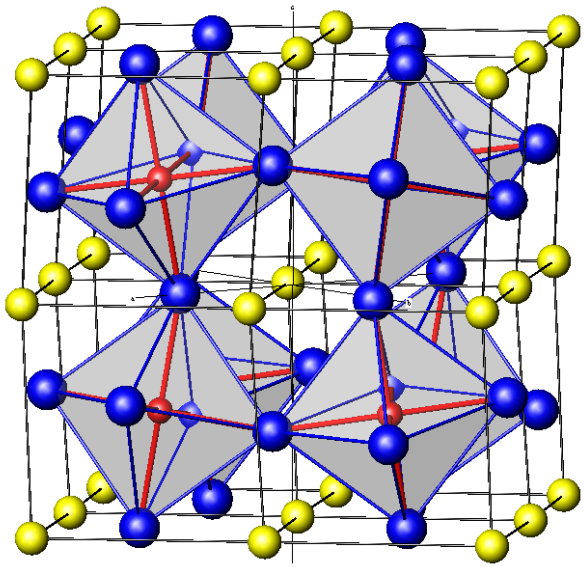
Gap=0.2eV

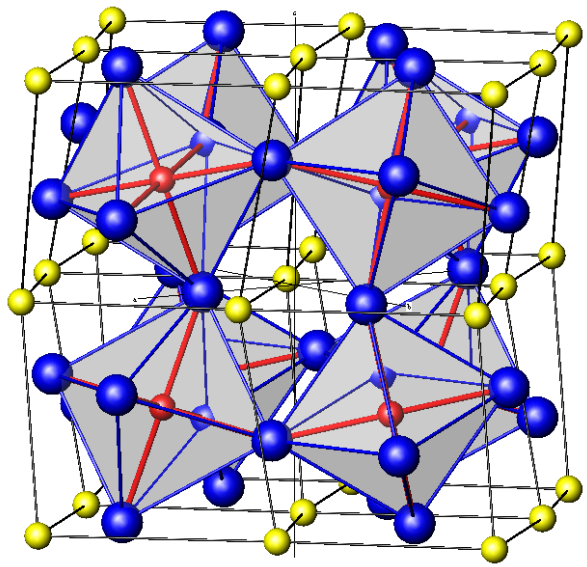
G-type AF

T_N=140K

M=0.45μ_B

Isotropic spin-wave spectrum





$YTiO_3$

Insulator

Gap=1.0eV

F

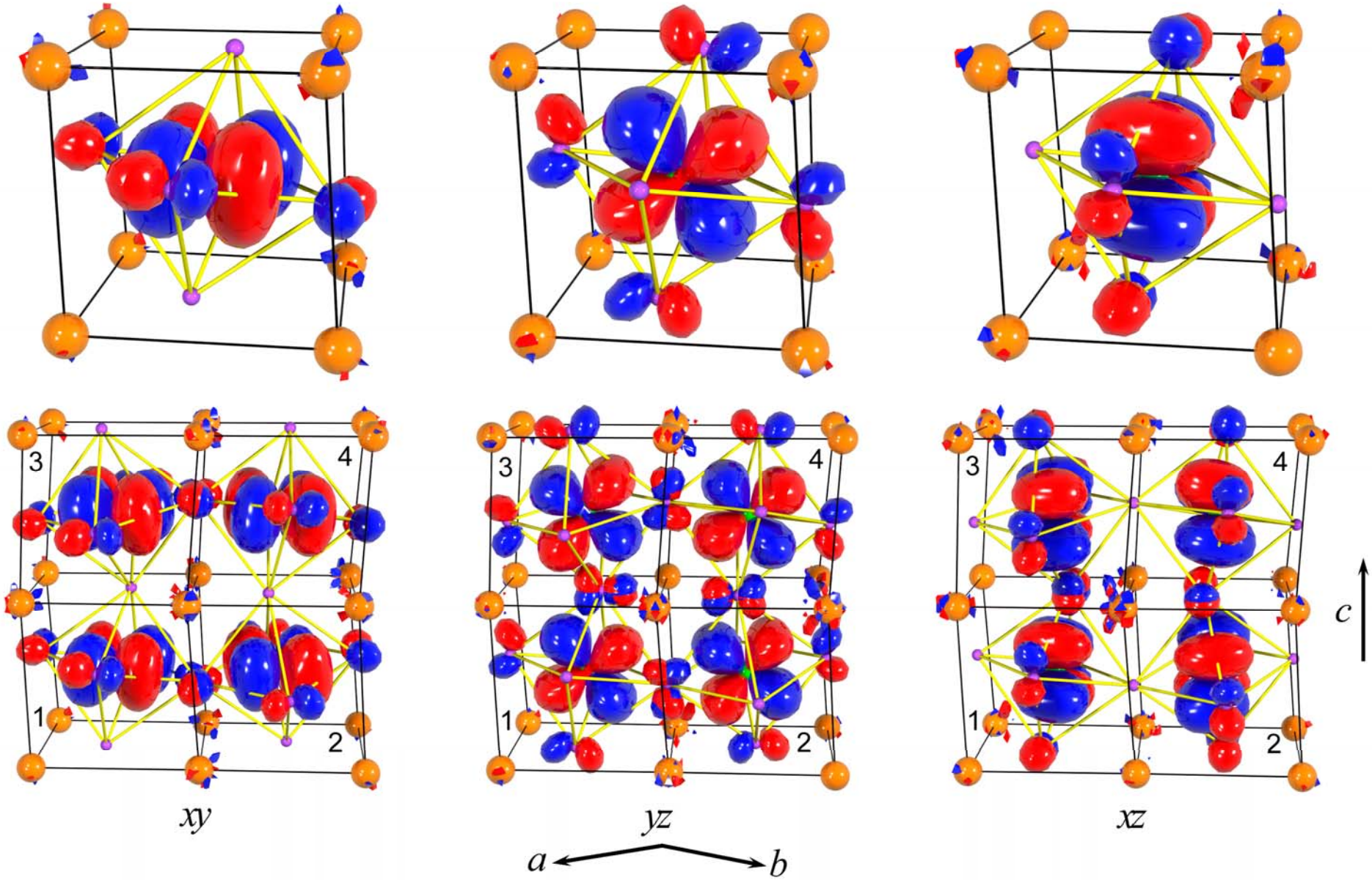
T_C=30K

M=0.8μ_B

Isotropic spin-wave spectrum

Here: High-temperature paramagnetic phases

$LaTiO_3$



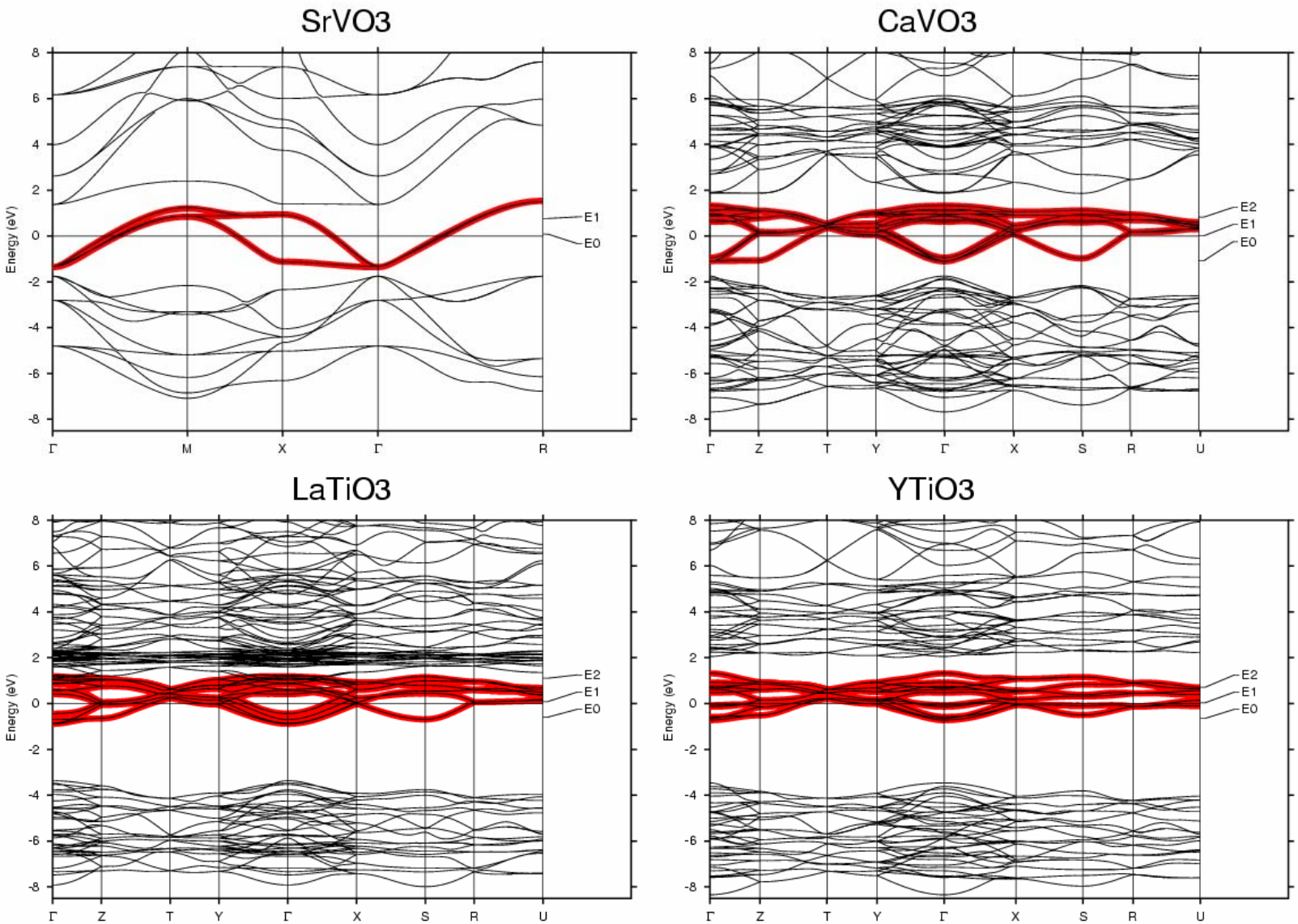
NMTO downfolding to t_{2g} Wannier functions

Sr 4d5s

V 3d e_g

t_{2g}

O 2p



Mostly Experiments:

Pioneering work	Goodenough	*Magnetism and the Chemical Bond* (1963)
Photoemission	Fujimori *et al*	PRL 69, 1796 (1992)
Photoemission in $La_{1-x}Sr_xTiO_3$	Fujimori *et al*	PRB 46, 9841 (1992)
Photoemission in $Y_{1-x}Ca_xTiO_3$	Morikawa *et al*	PRB 54, 8446 (1996)
Review of Mott transitions	Imada,Fujimori,Tokura	RMP 70, 1039 (1998)
Optical gaps in $La/YTiO_3$	Okimoto *et al*	PRB 51, 9581 (1995)
Optical σ, m^*/m in $Sr/CaVO_3$	Makino *et al*	PRB 58, 4384 (1998)
Photoemission in $Ca_{1-x}Sr_xVO_3$	Maiti *et al*	EL 55, 246 (2001)
Photoemission in $Ca_{1-x}Sr_xVO_3$	Sekiyama *et al*	cond-mat/0206471
NMR, OO in $Y\not{\parallel}\not{a}TiO_3$	Itoh *et al*	JPSJ 68, 2783 (1999)
Neutr scat, isotr SW in $LaTiO_3$	Keimer *et al*	PRL 85, 3946 (2000)
Res x-ray, $\not{\phi}\not{\phi}$ in $LaTiO_3$	"	"
Pol neutr scat, OO $YTiO_3$	Akimitsu *et al*	JPSJ 70, 3475 (2001)
Neutr scat, isotr SW in $YTiO_3$	Ulrich *et al*	PRL 89, 167202 (2002)
Orbital Liquid Theory, $LaTiO_3$	Khaliullin, Maekawa	PRL 85, 3950 (2000)
Orbital Liquid Theory, $YTiO_3$	Khaliullin, Okamoto	PRL 89, 167201 (2002)

Computational Method

Such properties may be described by a multi-band Hubbard Hamiltonian:

$$H = H^{LDA} + \frac{1}{2}\sum\nolimits'_{imm'\sigma\sigma'} U_{imm'}\hat{n}_{im\sigma}\hat{n}_{im'\sigma'} - d.c.$$

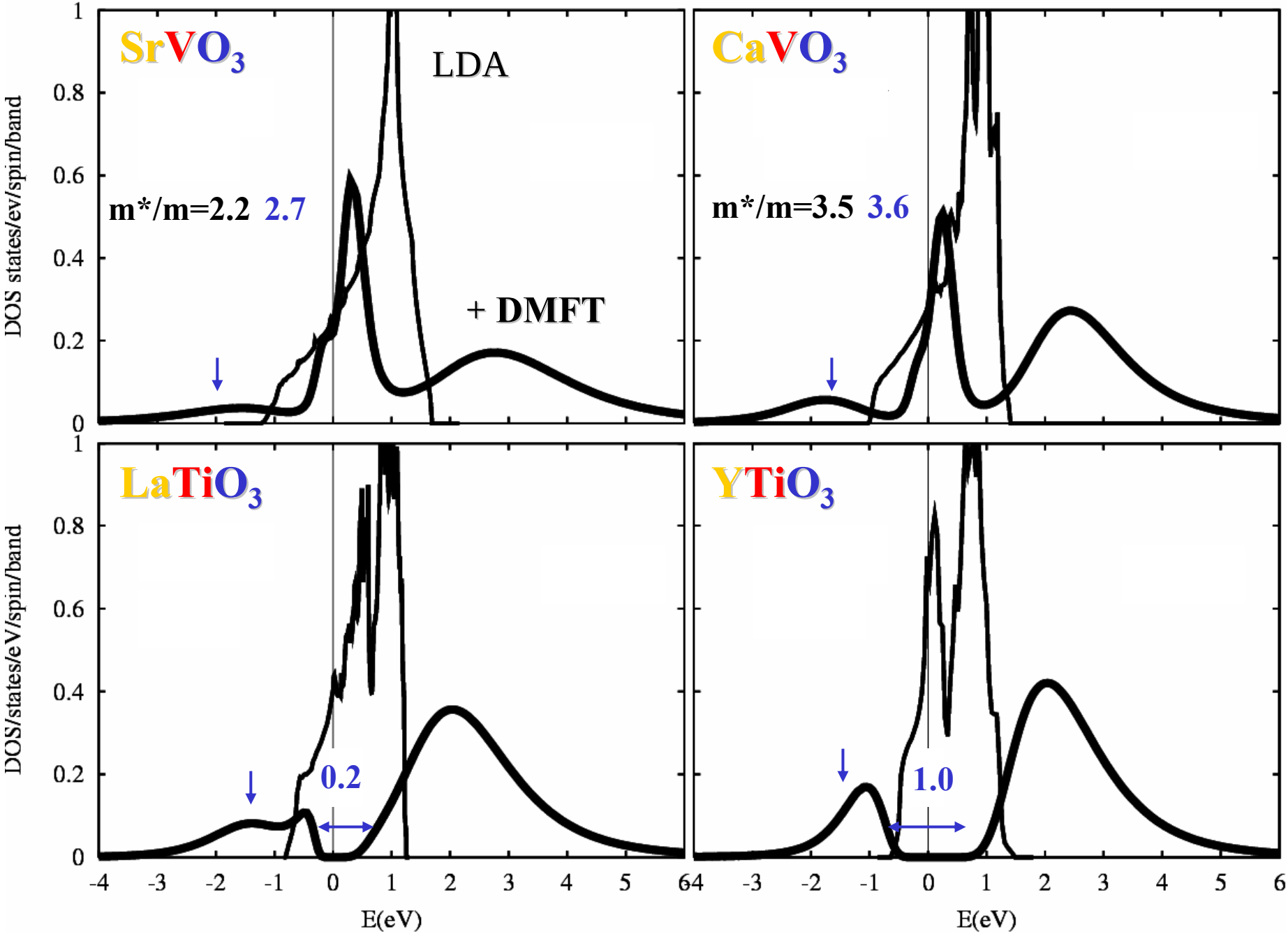
H^{LDA} is the one-electron part given by the local approximation to density-functional theory (LDA), which should provide the proper *chemistry*.
From the Kohn-Sham Hilbert space, we separate a subspace of *localized orbitals* (im) for which the *on-site* (i) *Coulomb interaction* is included.
H depends on how these orbitals are chosen.
We use localized *Wannier functions* generated by downfolding and formation of Nth-order muffin-tin orbitals (NMTOs).[1]
H is solved in the *single-site dynamical mean-field approximation* (DMFT)[2], which is based on the $d = \infty$ limit of the Hubbard model.[3]

[1] Andersen and Saha-Dasgupta, PRB 62, 16219 (2000).

[2] Georges, Kotliar, Krauth, Rozenberg, Rev. Mod. Phys. 68, 13 (1996); Anisimov et al, J. Phys.Cond .Mat. 9, 7359; Liechtenstein and Katsnelson, PRB 57, 6884 (1998)

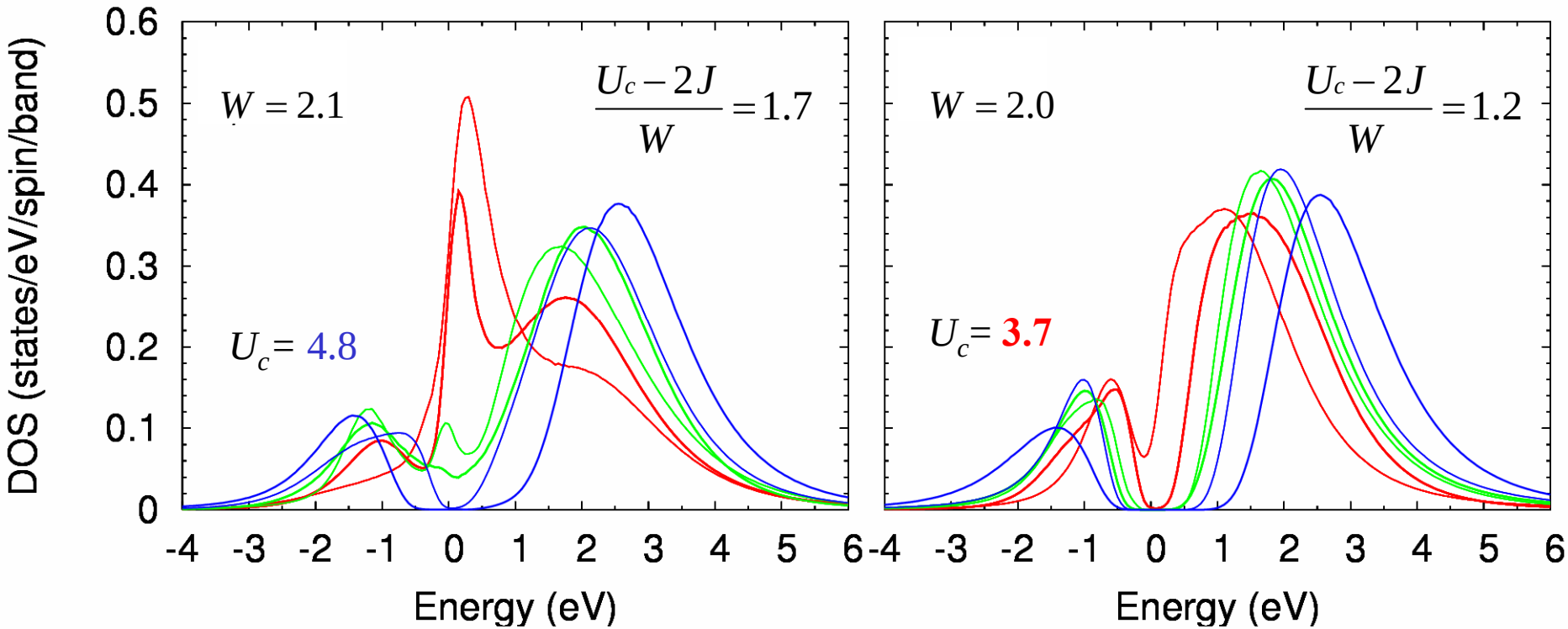
[3] Metzner and Vollhardt PRL 62, 324 (1989).

LDA+DMFT (U=5.0 eV, J_H~0.66 eV, k_BT=0.1) and comparison with experiments



Is the electron localization just caused by the reduction of W ?

LDA+DMFT U=3.5, **4.0,** 4.5, **4.75,** 5.0, **6.0** eV



$LaTiO_3$ **$YTiO_3$**

No, $\frac{U_c - 2J}{W}$ decreases!

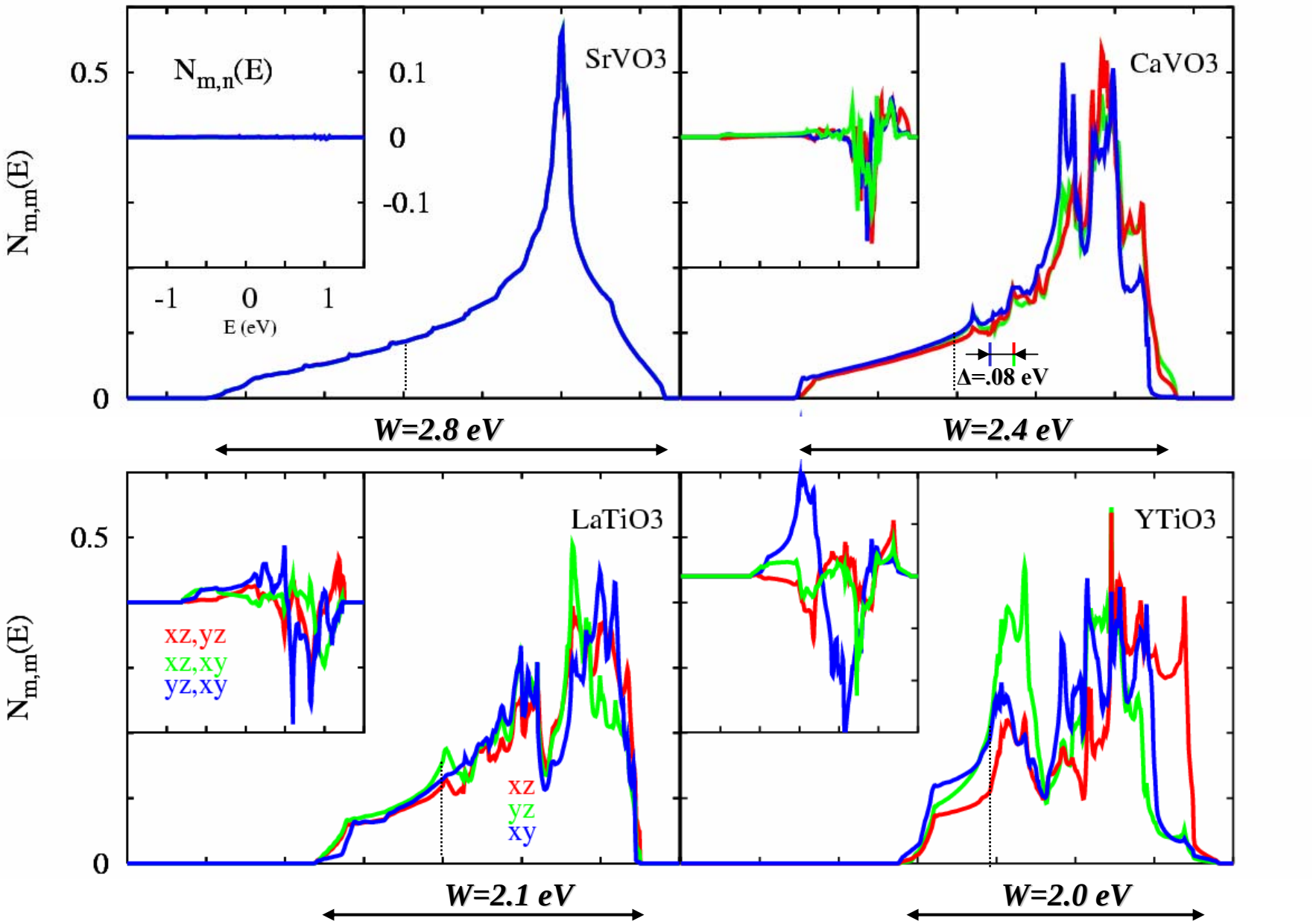
Bandwidths (rms), W, and Critical Coulomb repulsions (average), U_c'

	$SrVO_3$	$CaVO_3$	$LaTiO_3$(Mac)	$LaTiO_3$(Cwik)	$YTiO_3$
W (eV)	2.90	2.43	2.22	2.11	1.91
U_c' (eV)	> 4.6	4.4	3.4		2.5
U_c'/W	> 1.59	1.81	1.53	–	1.31

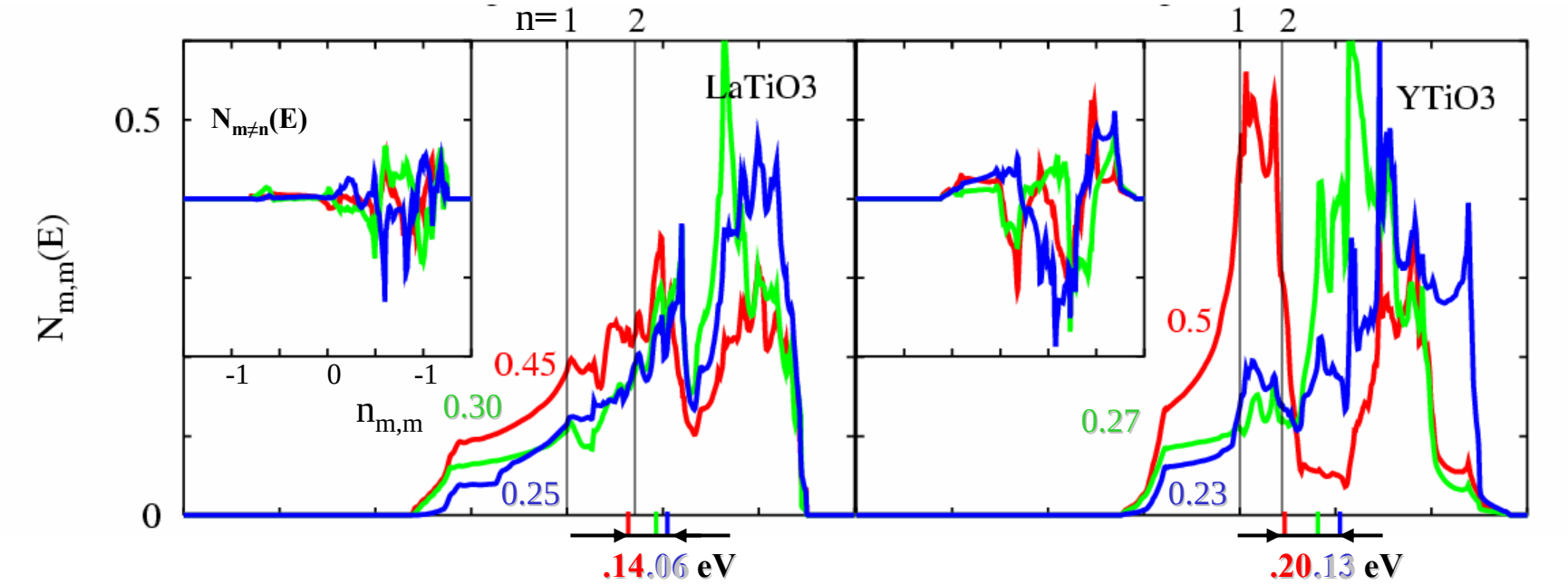
From cubic $SrVO_3$ to distorted $YTiO_3$, U_c'/W **decreases by almost 50%**

Since with increasing degeneracy, there are more possiblities to hop in a many-electron system than in a one-electron system, larger U-values are needed to cause a Mott metal-insulator transition (Gunnarsson et al.). Reversely, splitting of a degenerate band leads to reduction of U_c.

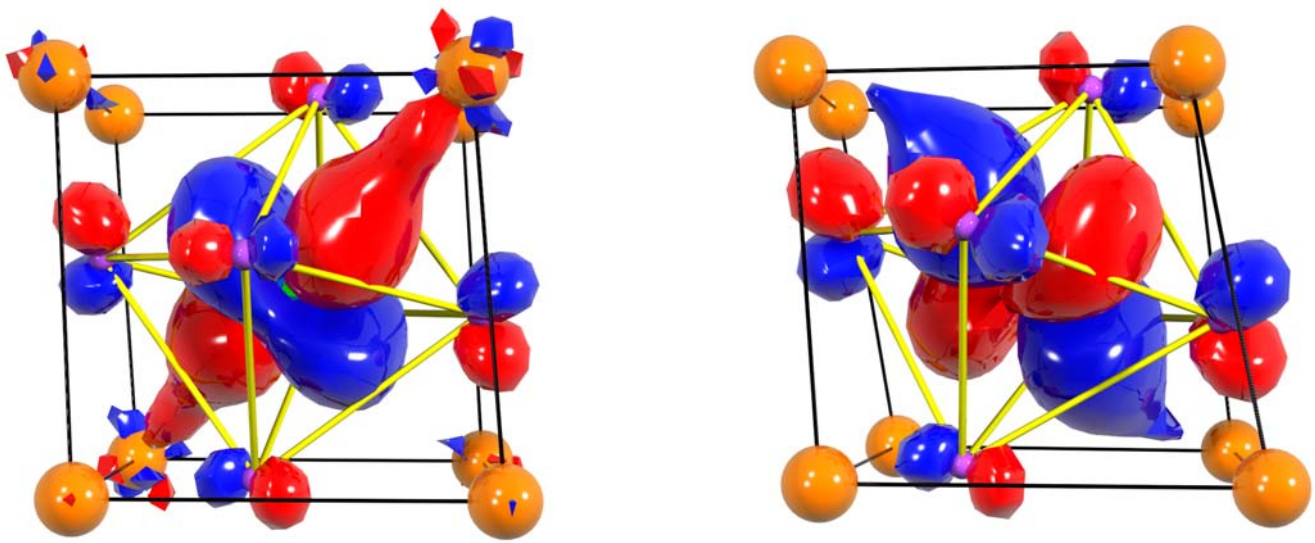
LDA density-of-states matrix in the t_{2g} Wannier representation



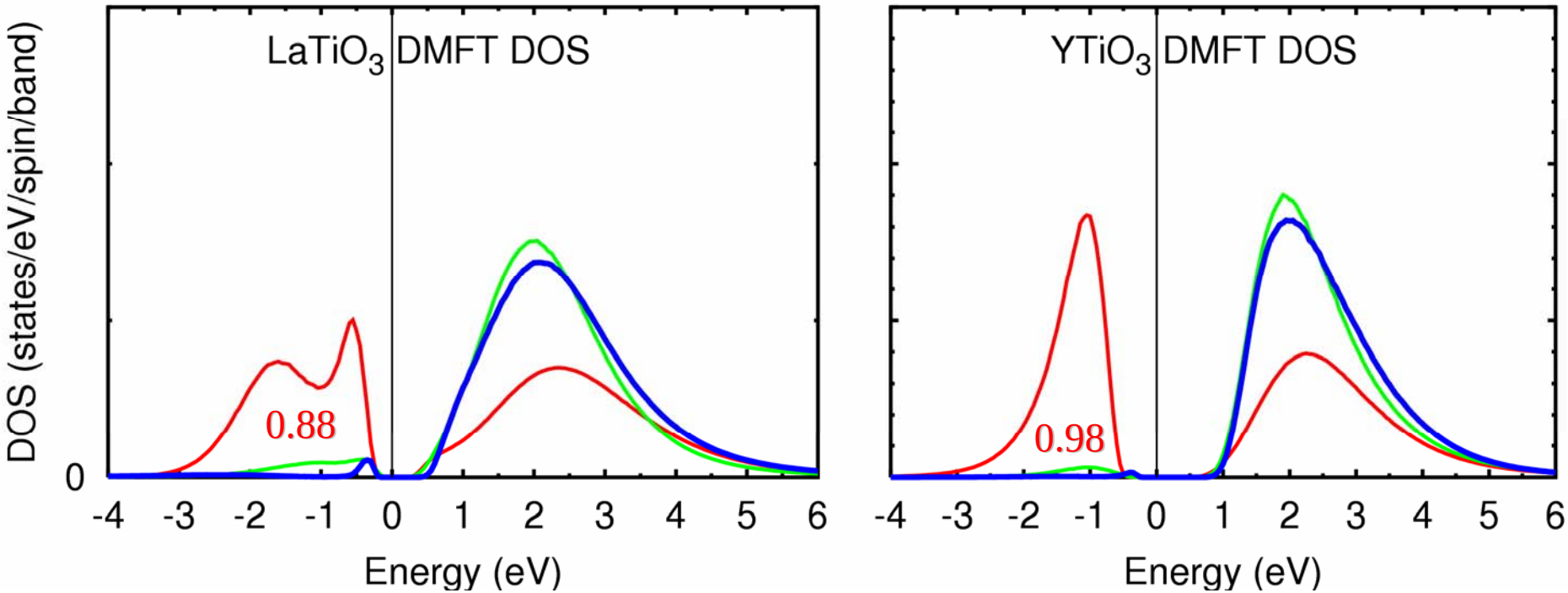
Diagonalize the on-site term of H^{LDA} to get the crystal-field levels and their eigen-orbitals:



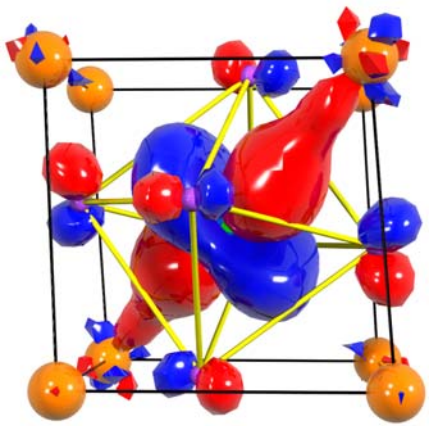
Low contour brings out covalency effects:

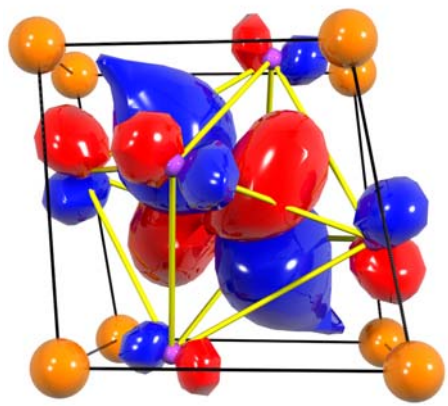


Diagonalize the LDA+DMFT density matrix for the Mott insulators to get orbital occupations:



The most occupied orbital turns out to be the essentially same as the one with the lowest energy (i.e. crystal-field level), but the DMFT increases its occupancy from the LDA value of about 0.5 to about 1, that is, the Coulomb correlations strongly suppress orbital fluctuations:





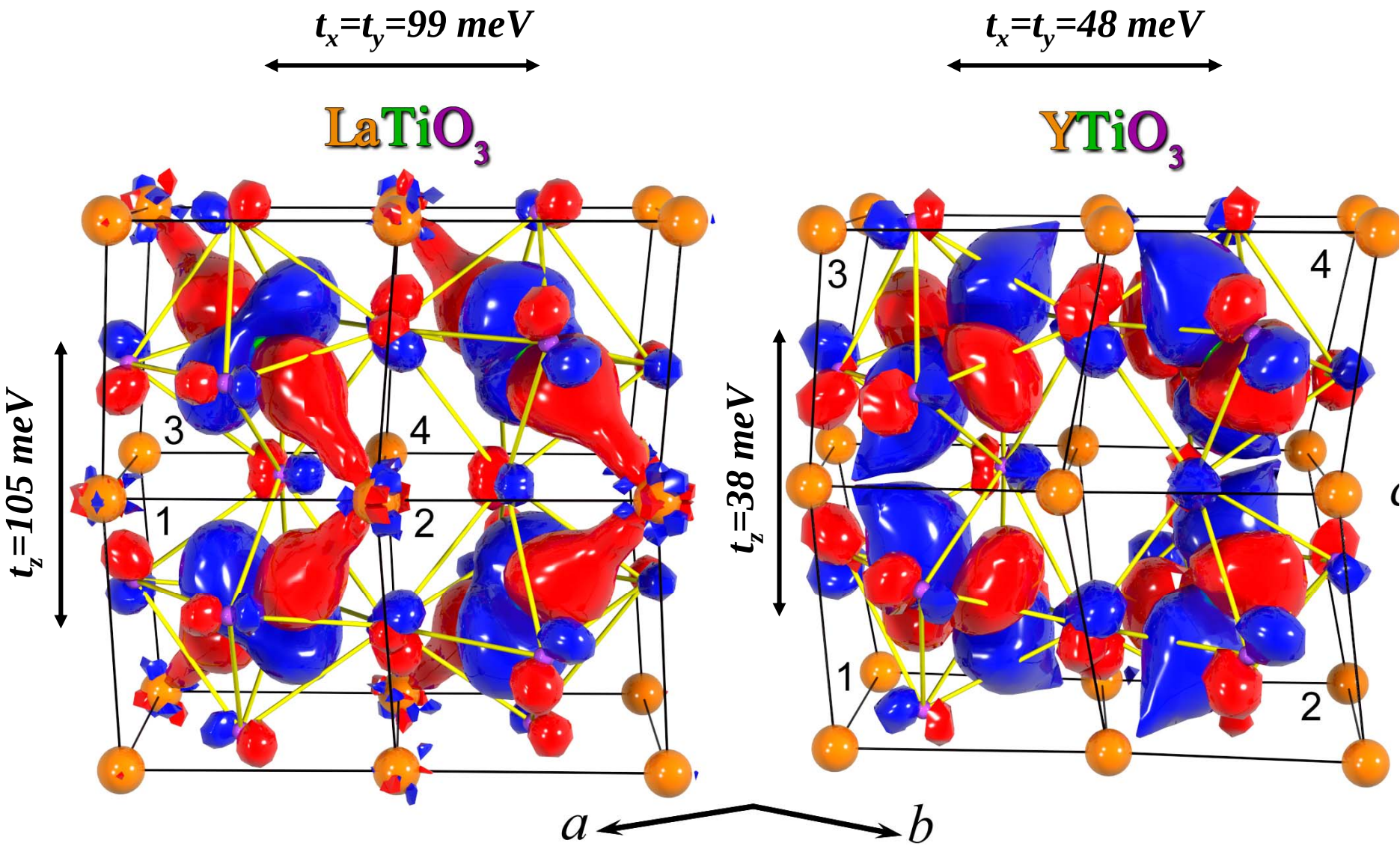
Crystal-field splittings, Δ_{12} and Δ_{23}, of the 3-fold degenerate t_{2g}-band

		$SrVO_3$	$CaVO_3$	$LaTiO_3$(Mac)	$LaTiO_3$(Cwik)	$YTiO_3$
Δ_{12}	(meV)	0	80	140	190	200
Δ_{23}		0	0	70	20	130
Δ_{12}/W		0	3%	6%	9%	10%

The crystal-field splitting needs merely be at the order of the reduced bandwidth: $\Delta \sim ZW = (m/m^*)\,W \sim (1 - U'/U'_c)\,W$ (Manini et al).
The reduction of U'_c/W when going from a 3-fold, 1/6-filled degenerate band to a 1-fold, 1/2-filled degenerate band was estimated by Koch et al. to be 20%
But we found almost 50%.

Orbital and Magnetic Orders

Superexchange: $J_{AF} \sim 4t^2/U$



$$t_{2g}^1 + t_{2g}^1 \longrightarrow t_{2g}^0 + t_{2g}^2$$

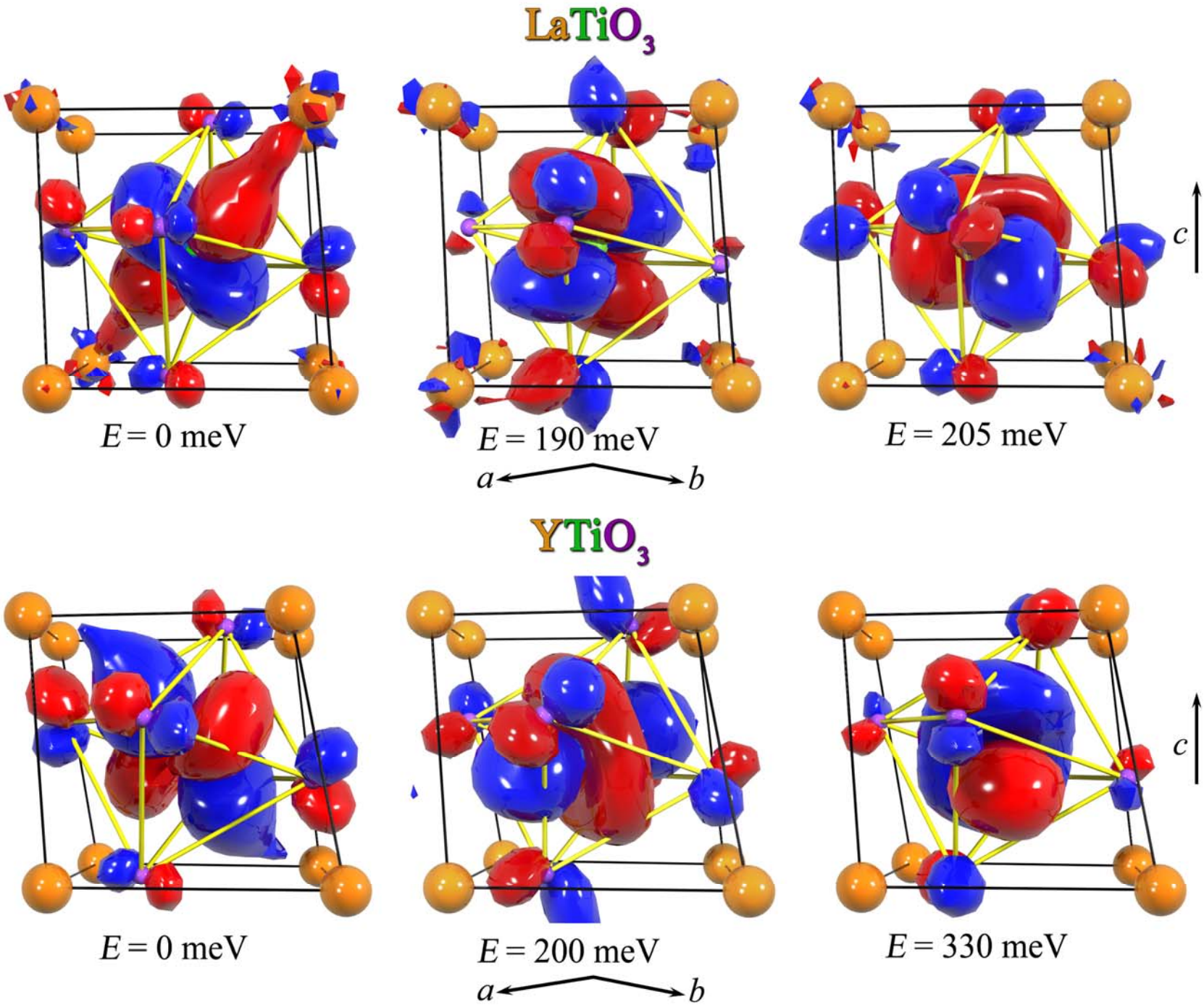
$|1) = \begin{array}{|cc|}\hline - & - \\ - & - \\ \uparrow & \downarrow \\ \hline \end{array}$ $|5) = \begin{array}{|cc|}\hline - & - \\ - & - \\ - & \uparrow\downarrow \\ \hline \end{array}$ $|6) = \begin{array}{|cc|}\hline - & - \\ - & \uparrow \\ - & \downarrow \\ \hline \end{array}$ $|7) = \begin{array}{|cc|}\hline - & \uparrow \\ - & - \\ - & \downarrow \\ \hline \end{array}$

$|2) = \begin{array}{|cc|}\hline - & - \\ - & - \\ \downarrow & \uparrow \\ \hline \end{array}$ $|5) = \begin{array}{|cc|}\hline - & - \\ - & - \\ - & \uparrow\downarrow \\ \hline \end{array}$ $|8) = \begin{array}{|cc|}\hline - & - \\ - & \downarrow \\ - & \uparrow \\ \hline \end{array}$ $|9) = \begin{array}{|cc|}\hline - & \downarrow \\ - & - \\ - & \uparrow \\ \hline \end{array}$

$|3) = \begin{array}{|cc|}\hline - & - \\ - & - \\ \uparrow & \uparrow \\ \hline \end{array}$ $|10) = \begin{array}{|cc|}\hline - & - \\ - & \uparrow \\ - & \uparrow \\ \hline \end{array}$ $|11) = \begin{array}{|cc|}\hline - & \uparrow \\ - & - \\ - & \uparrow \\ \hline \end{array}$ $|14) = \begin{array}{|cc|}\hline - & - \\ - & \uparrow\downarrow \\ - & - \\ \hline \end{array}$

$|4) = \begin{array}{|cc|}\hline - & - \\ - & - \\ \downarrow & \downarrow \\ \hline \end{array}$ $|12) = \begin{array}{|cc|}\hline - & - \\ - & \downarrow \\ - & \downarrow \\ \hline \end{array}$ $|13) = \begin{array}{|cc|}\hline - & \downarrow \\ - & - \\ - & \downarrow \\ \hline \end{array}$ $|15) = \begin{array}{|cc|}\hline - & \uparrow\downarrow \\ - & - \\ - & - \\ \hline \end{array}$

$|16) = \begin{array}{|cc|}\hline - & \downarrow \\ - & \uparrow \\ - & - \\ \hline \end{array}$ $|17) = \begin{array}{|cc|}\hline - & \uparrow \\ - & \downarrow \\ - & - \\ \hline \end{array}$ $|18) = \begin{array}{|cc|}\hline - & \uparrow \\ - & \uparrow \\ - & - \\ \hline \end{array}$ $|19) = \begin{array}{|cc|}\hline - & \downarrow \\ - & \downarrow \\ - & - \\ \hline \end{array}$


LaTiO3
E = 0 meV
E = 190 meV
E = 205 meV
c
a
b
YTiO3
E = 0 meV
E = 200 meV
E = 330 meV
c
a
b

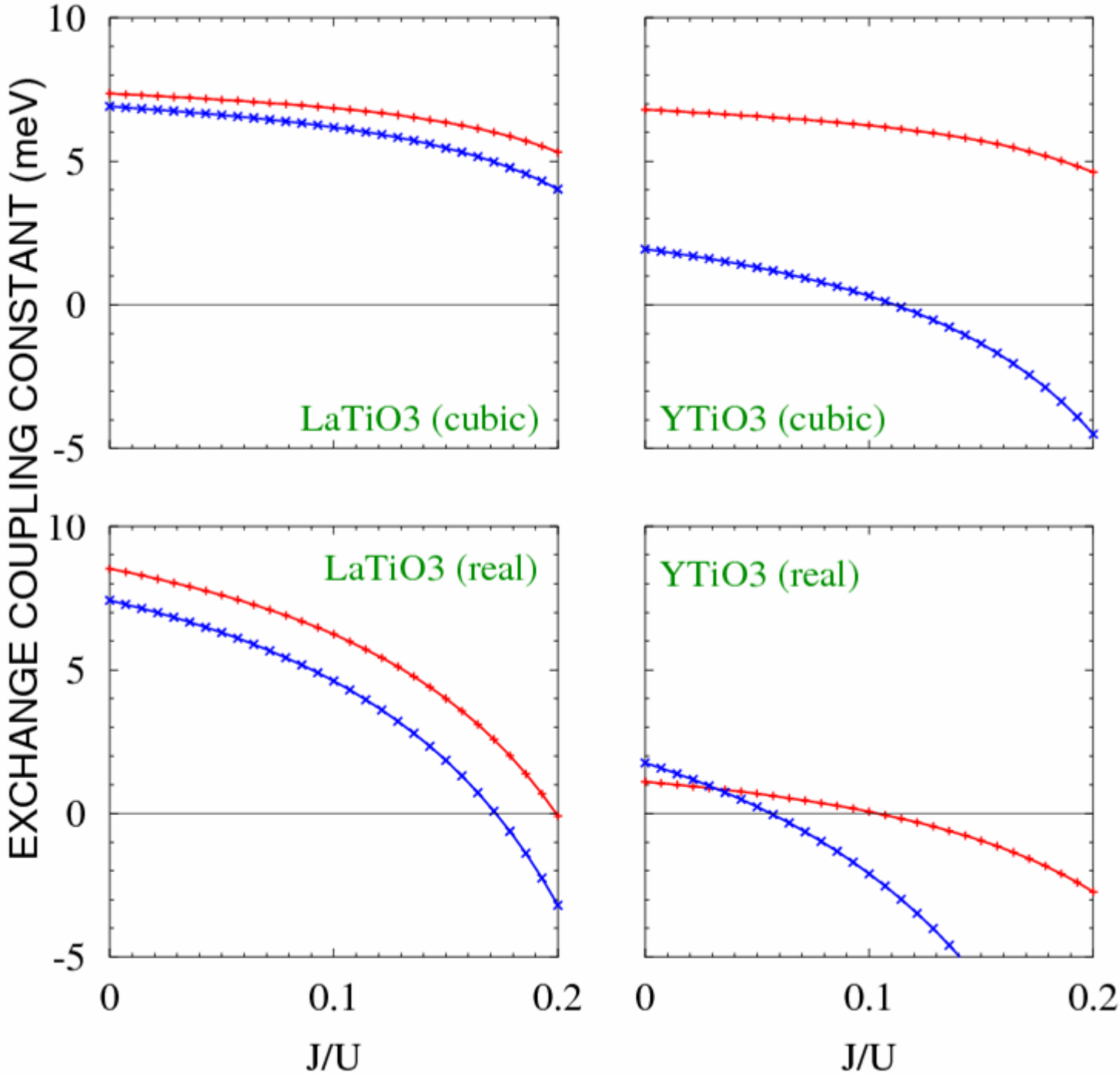
$$
\begin{array}{c|ccccccccc}
 & |.) & |.) & |.) & |.) & |.) & |.) & |10) & |11) & |12) \\
(1| & 3^{-\frac{1}{2}}t_{11} & \left(\frac{2}{3}\right)^{\frac{1}{2}}t_{11} & 2^{-\frac{1}{2}}t_{12} & 2^{-\frac{1}{2}}t_{13} & 2^{-\frac{1}{2}}t_{12} & 2^{-\frac{1}{2}}t_{13} & 0 & 0 & 0 \\
(2| & 3^{-\frac{1}{2}}t_{11} & \left(\frac{2}{3}\right)^{\frac{1}{2}}t_{11} & 2^{-\frac{1}{2}}t_{12} & 2^{-\frac{1}{2}}t_{13} & -2^{-\frac{1}{2}}t_{12} & -2^{-\frac{1}{2}}t_{13} & 0 & 0 & 0 \\
(3| & 0 & 0 & 0 & 0 & 0 & 0 & t_{12} & t_{13} & 0 \\
(4| & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_{12} \\
. & U+2J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
. & 0 & U-J & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
. & 0 & 0 & U-J & 0 & 0 & 0 & 0 & 0 & 0 \\
. & 0 & 0 & 0 & U-J & 0 & 0 & 0 & 0 & 0 \\
. & 0 & 0 & 0 & 0 & U-3J & 0 & 0 & 0 & 0 \\
. & 0 & 0 & 0 & 0 & 0 & U-3J & 0 & 0 & 0 \\
(10| & 0 & 0 & 0 & 0 & 0 & 0 & U-3J & 0 & 0 \\
(11| & 0 & 0 & 0 & 0 & 0 & 0 & 0 & U-3J & 0 \\
(12| & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & U-3J \\
(13| & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
U
$$

$$
(3|\mathcal{H}_{SE}|3)-(1|\mathcal{H}_{SE}|1) = t_{11}^2\left(\frac{\frac{1}{3}}{U+2J}+\frac{\frac{2}{3}}{U-J}\right)+\frac{t_{12}^2+t_{13}^2}{2}\left(\frac{1}{U-J}-\frac{1}{U-3J}\right)
$$

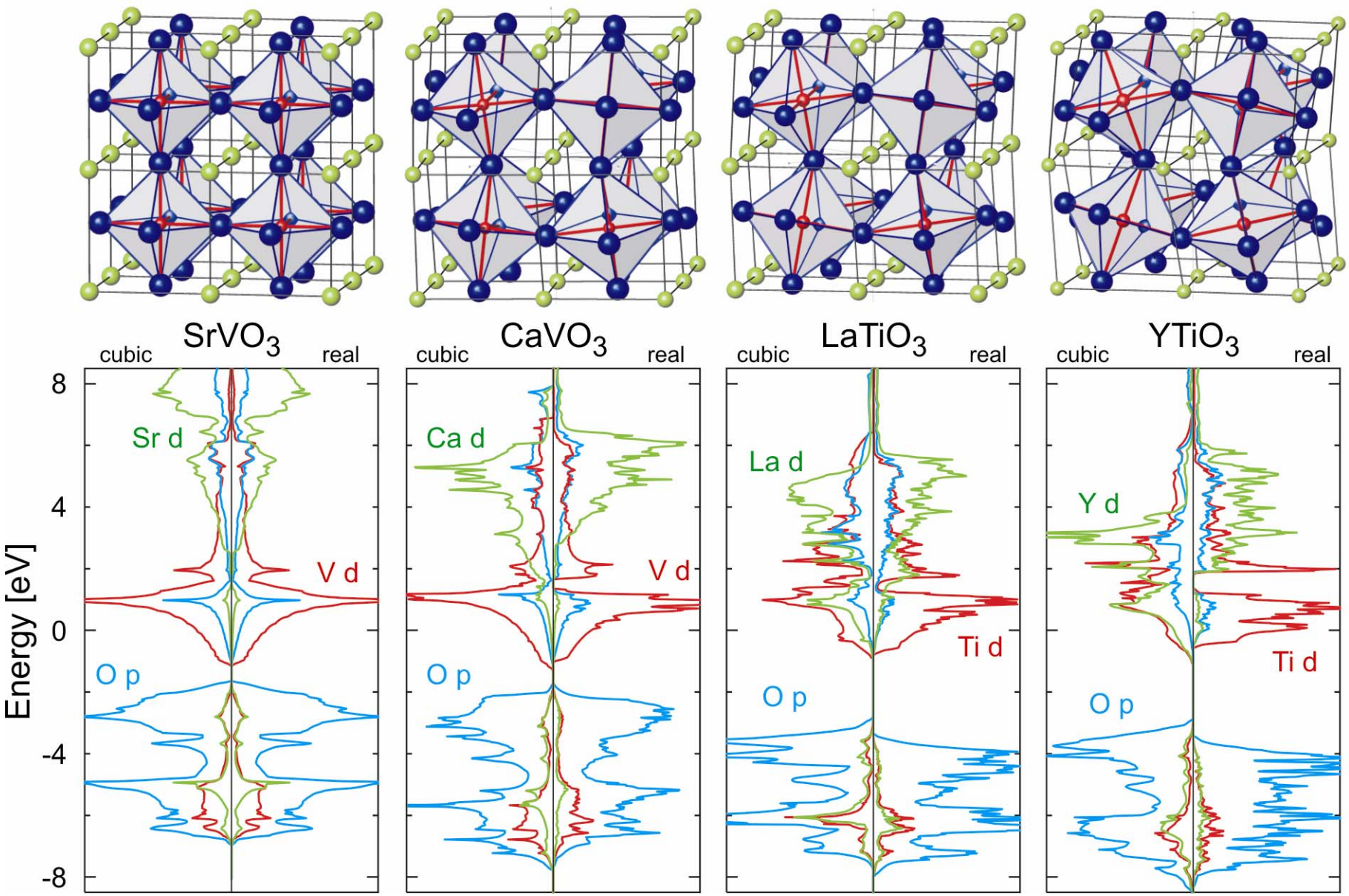
$$(3|\mathcal{H}_{SE}|3)-(1|\mathcal{H}_{SE}|1) = t_{11}^2\left(\frac{\frac{1}{3}}{U+2J}+\frac{\frac{2}{3}}{U-J}\right)+\frac{t_{12}^2+t_{13}^2}{2}\left(\frac{1}{U-J}-\frac{1}{U-3J}\right)$$

Hopping integrals and superexchange couplings in meV

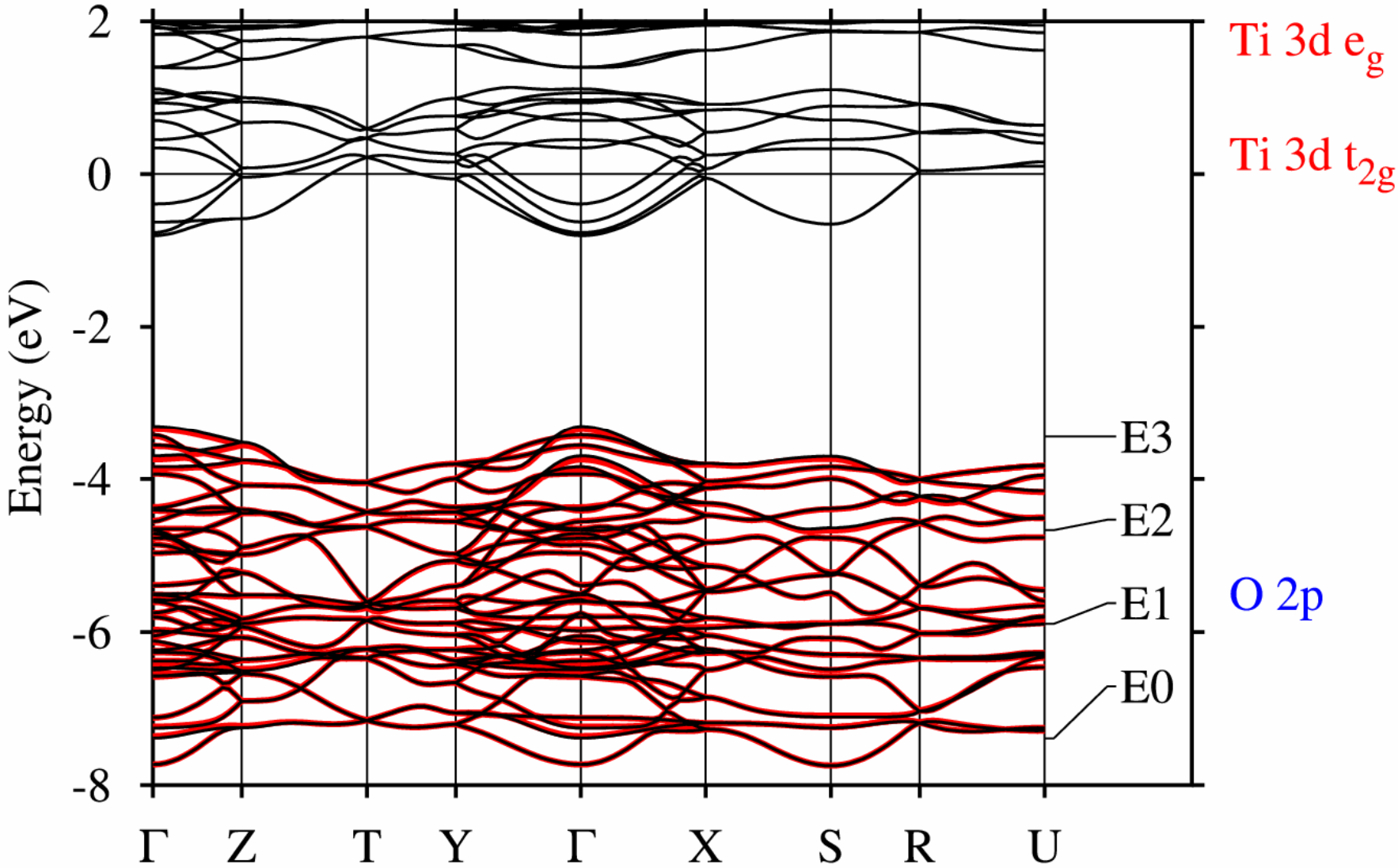
	dir.s$\longrightarrow$	001		010		100		
	levels$\downarrow$	t_{1m}	J_{SE}	t_{1m}	J_{SE}	t_{1m}	J_{SE}	
$LaTiO_3$	$1,1$	105	9.1	-98	7.9	-98	7.9	
	$1,2$	31	-0.2	-192	-7.0	4	-0.0	
	$1,3$	143	-3.9	12	0.0	120	-2.7	
	$\sum J_{SE}$		5.0		0.9		5.2	3.0
	dir.s$\longrightarrow$	001		010		100		
	levels$\downarrow$	t_{1m}	J_{SE}	t_{1m}	J_{SE}	t_{1m}	J_{SE}	
$YTiO_3$	$1,1$	-38	1.2	-48	1.9	-48	1.9	
	$1,2$	-21	-0.1	-191	-7.0	-84	-1.3	
	$1,3$	97	-1.8	-130	-3.2	94	-1.7	
	$\sum J_{SE}$		-0.7		-8.3		-1.1	-4.7

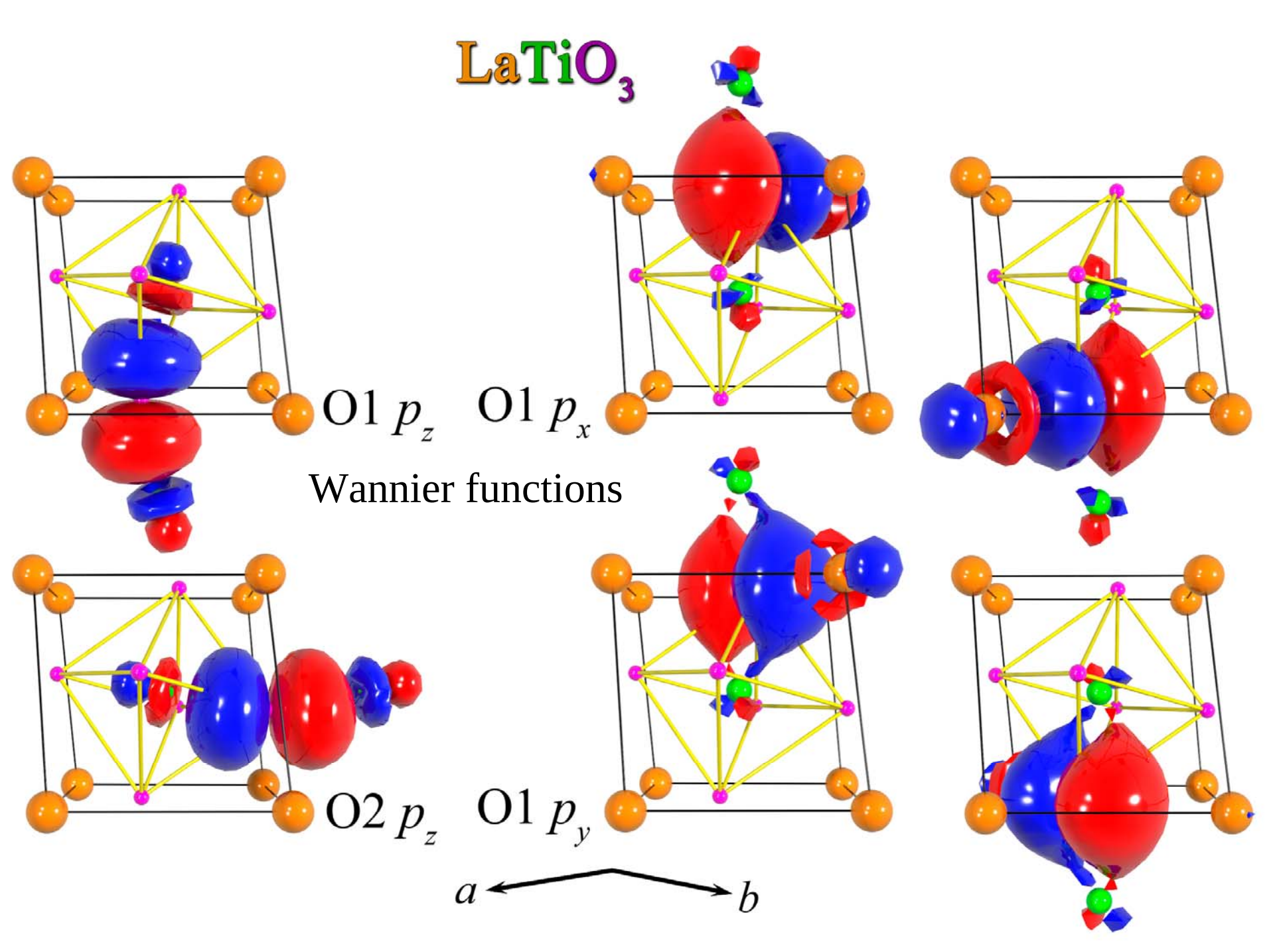

EXCHANGE COUPLING CONSTANT (meV)
10
5
0
-5
LaTiO3 (cubic)
YTiO3 (cubic)
LaTiO3 (real)
YTiO3 (real)
0
0.1
0.2
J/U
J/U

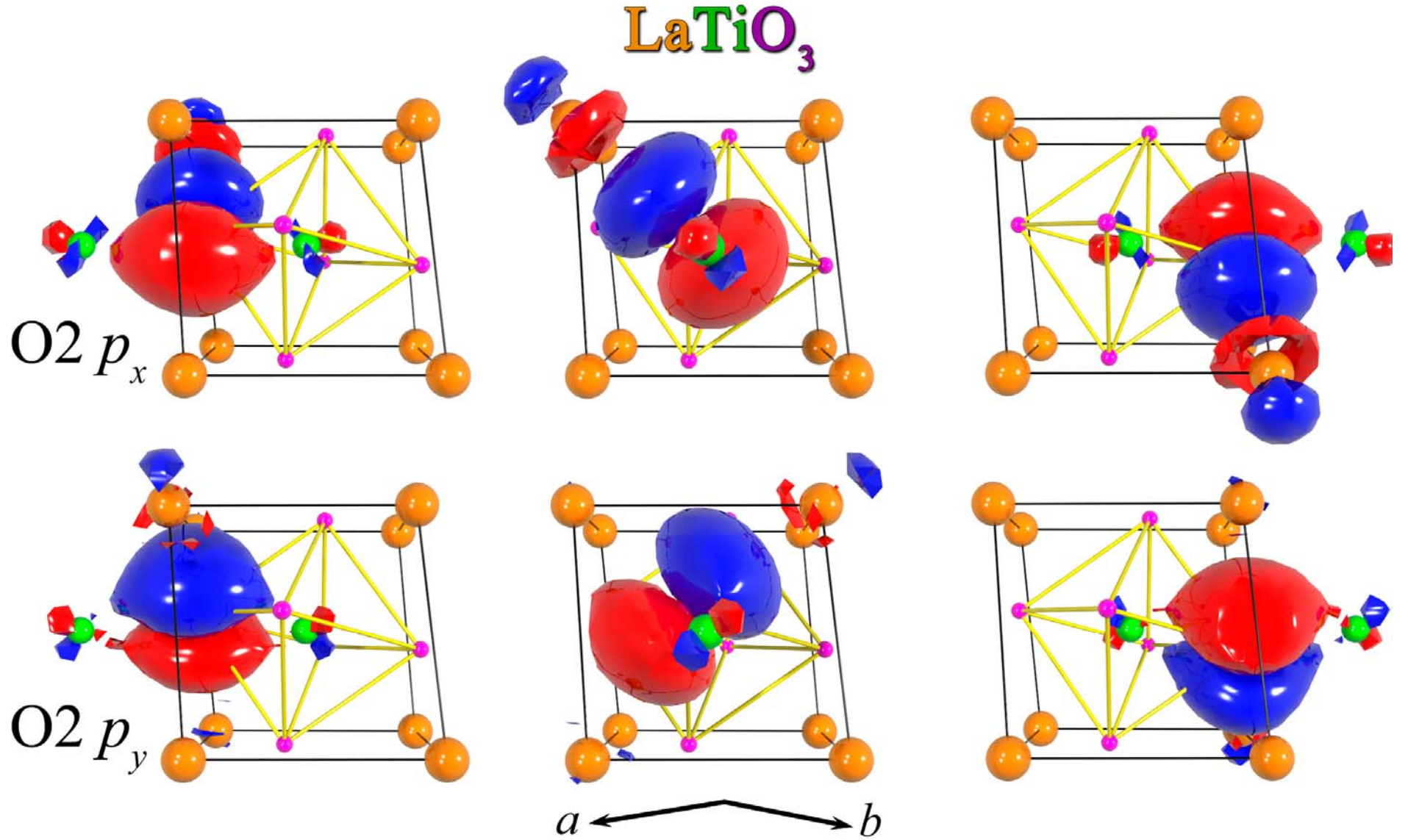
What causes the progressive reduction of t_{2g} bandwidth and splitting of the levels?

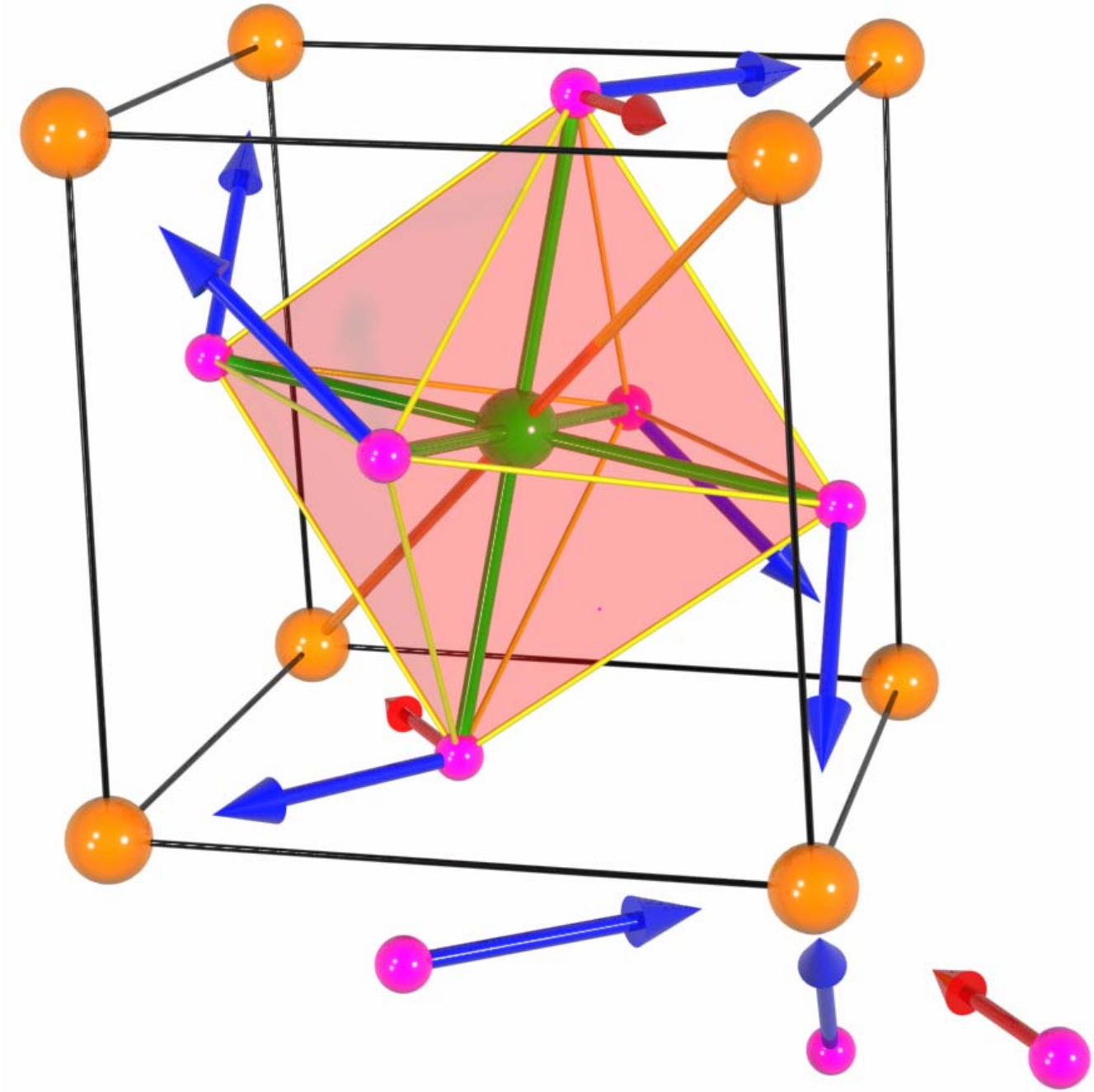


Bandwidth: Cation-oxygen covalency. Level splitting: Cation-transition ion covalency

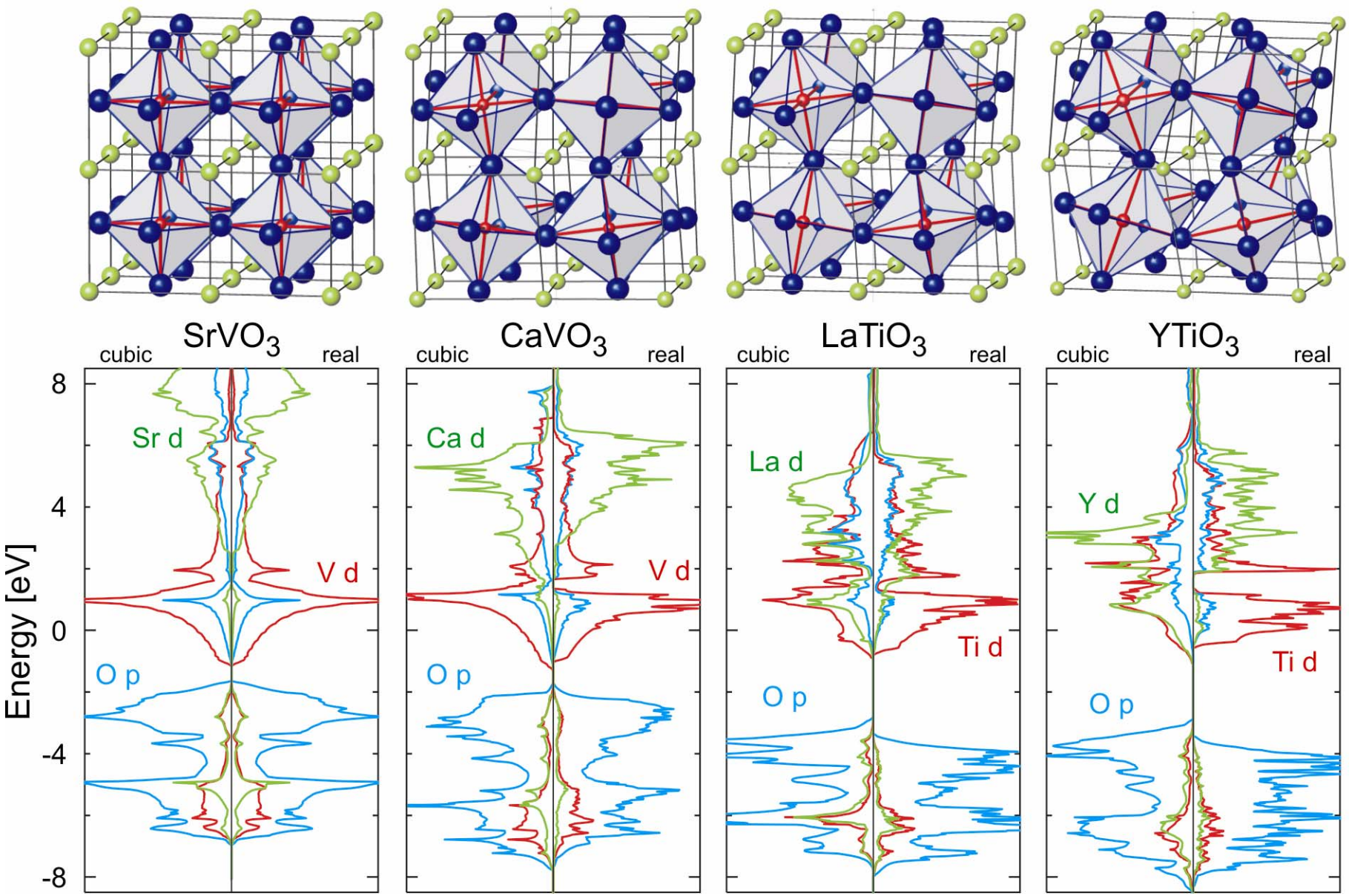

2
0
-2
-4
-6
-8
Energy (eV)
Γ
Z
T
Y
Γ
X
S
R
U
E3
E2
E1
E0
Ti 3d e_g
Ti 3d t_{2g}
O 2p


LaTiO3
O1 pz
O1 px
Wannier functions
O2 pz
O1 py
a
b

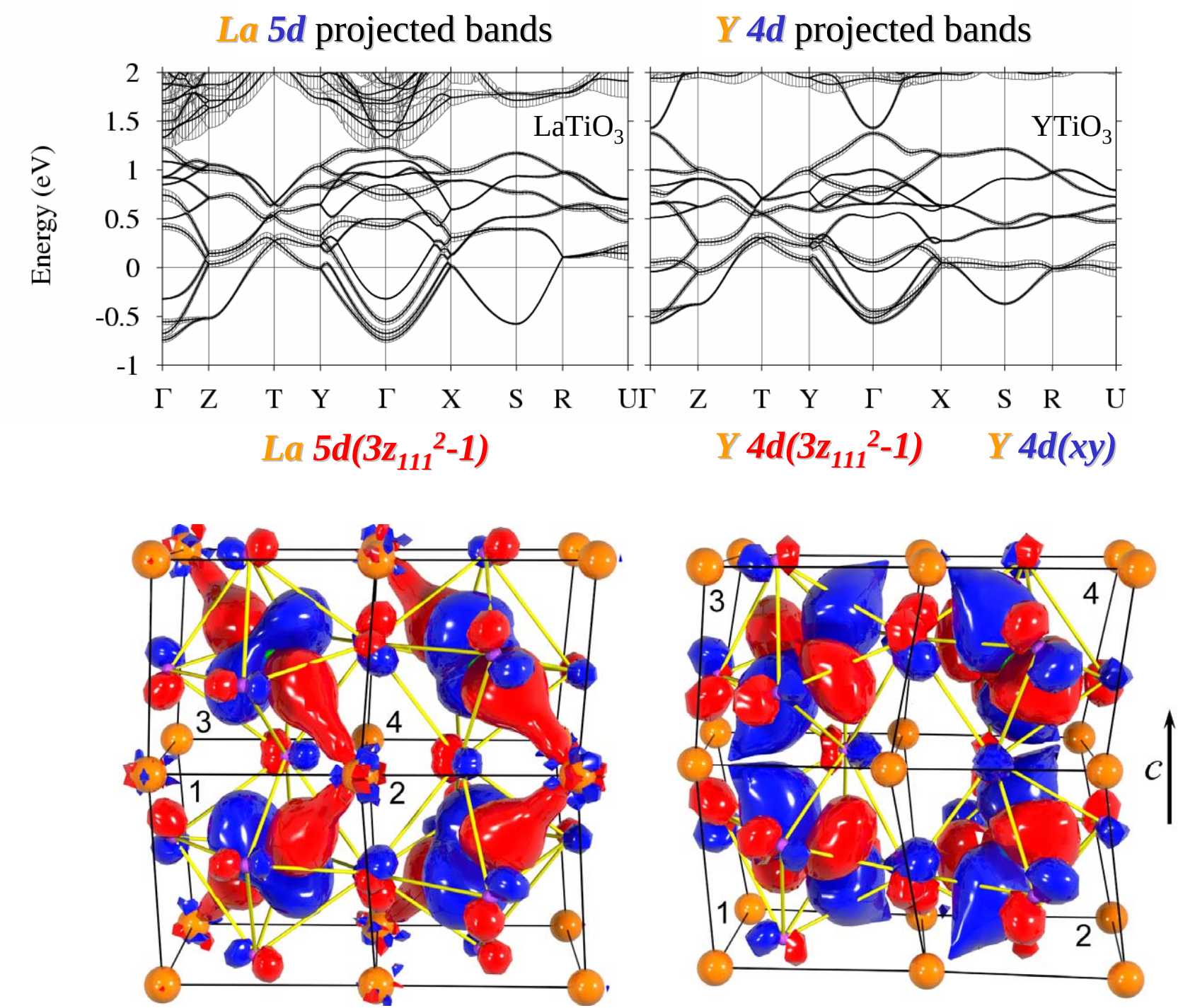

LaTiO3
O2 px
O2 py
a
b

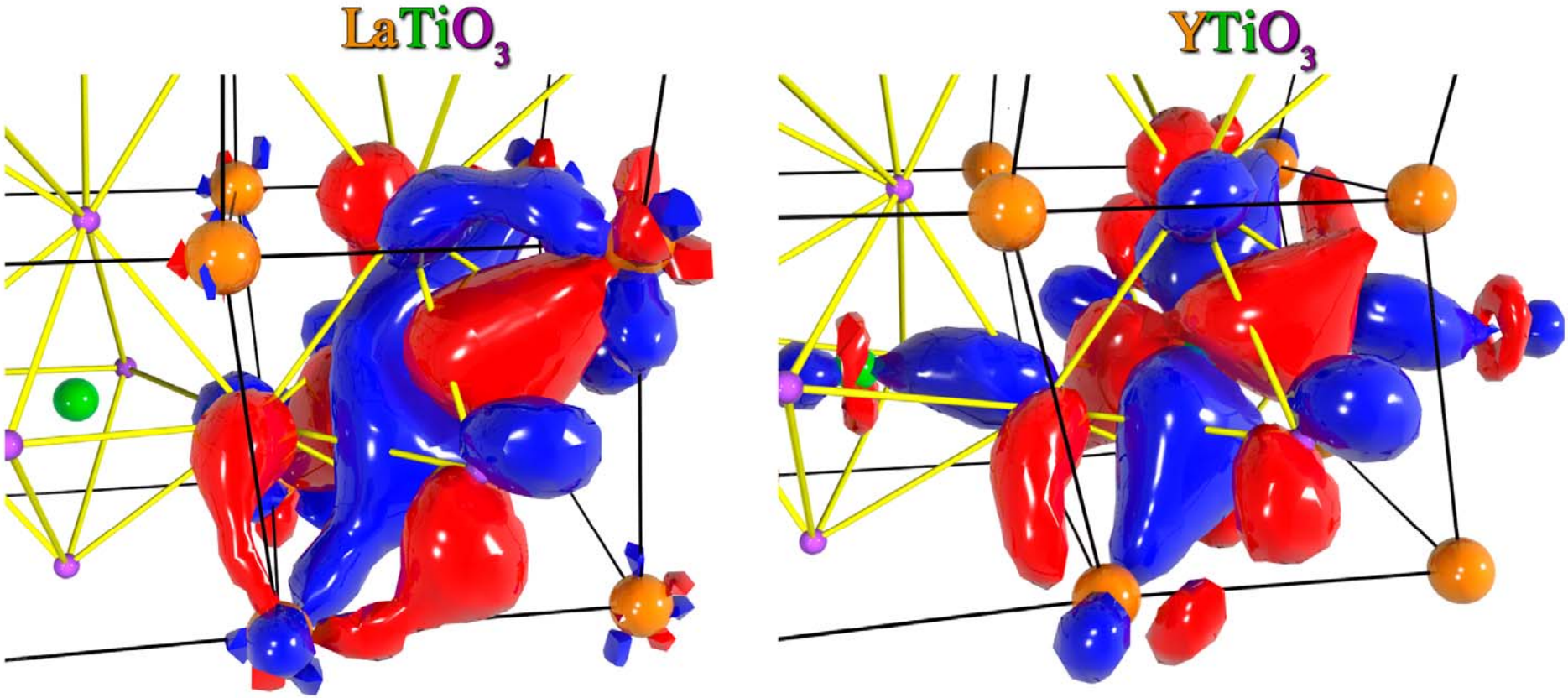


What causes the progressive reduction of t_{2g} bandwidth and splitting of the levels?

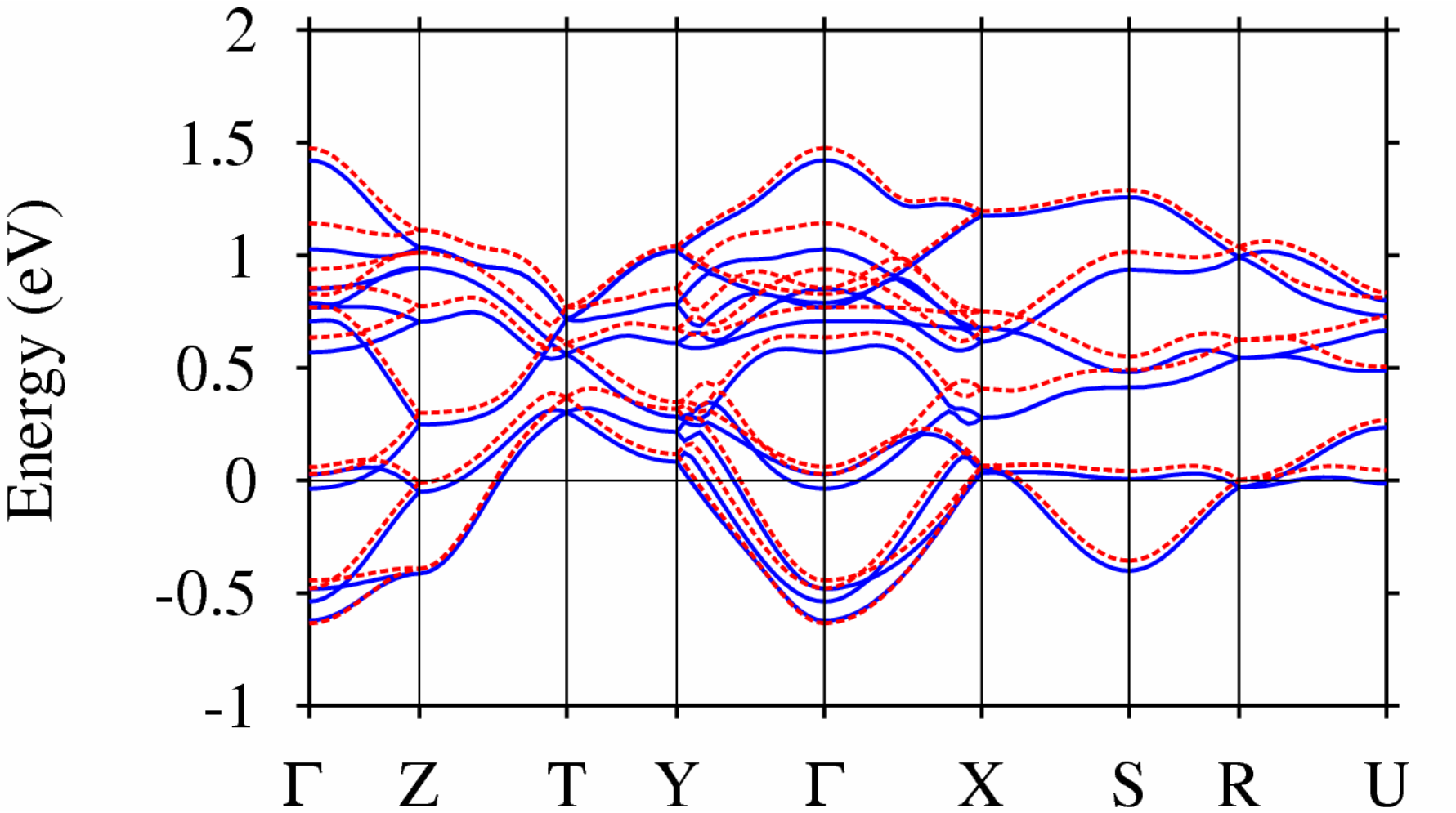


Bandwidth: Cation-oxygen covalency. Level splitting: Cation-transition ion covalency

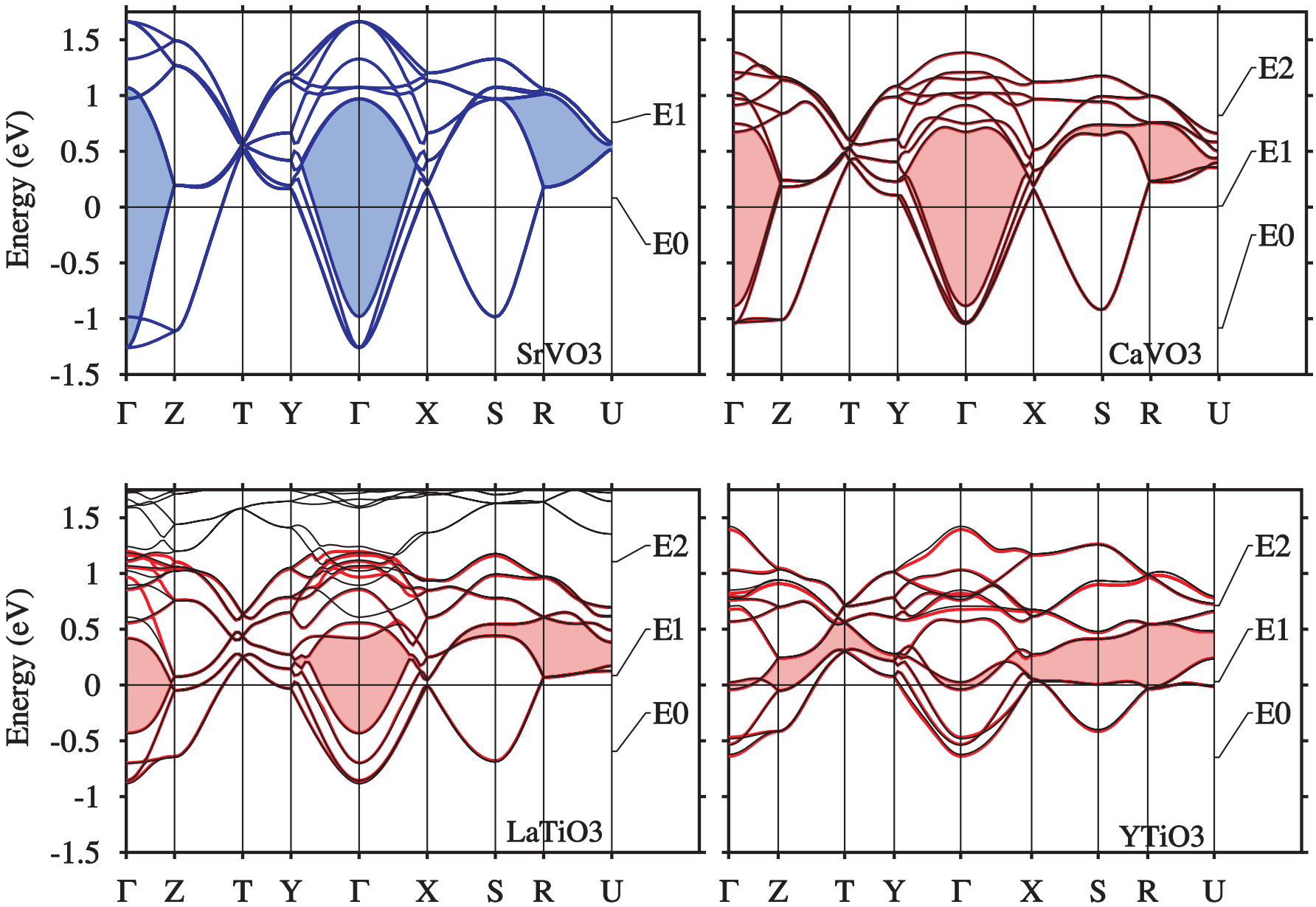

La 5d projected bands
Y 4d projected bands
Energy (eV)
2
1.5
1
0.5
0
-0.5
-1
LaTiO3
YTiO3
Γ Z T Y Γ X S R UΓ Z T Y Γ X S R U
La 5d(3z111^2-1)
Y 4d(3z111^2-1)
Y 4d(xy)
1
2
3
4
c

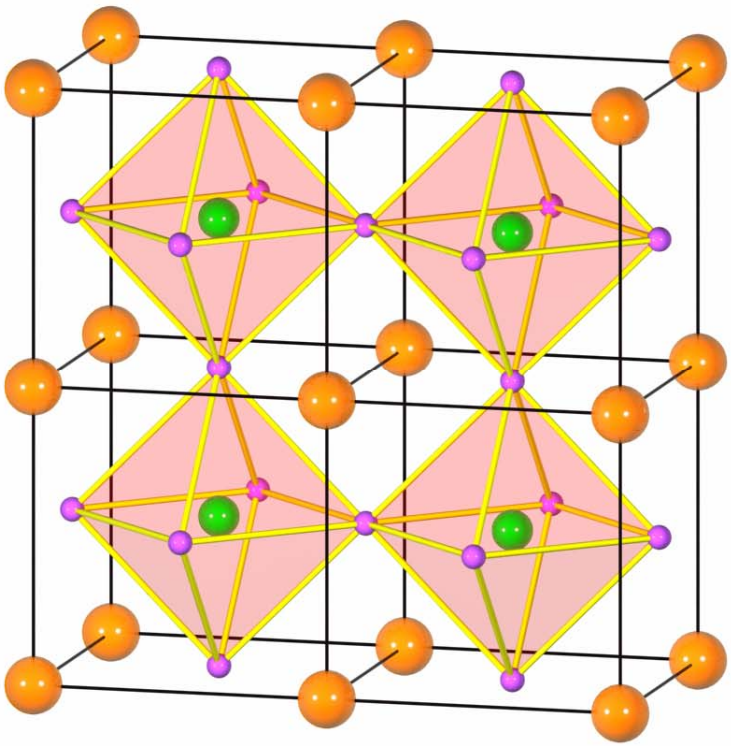

LaTiO3
YTiO3

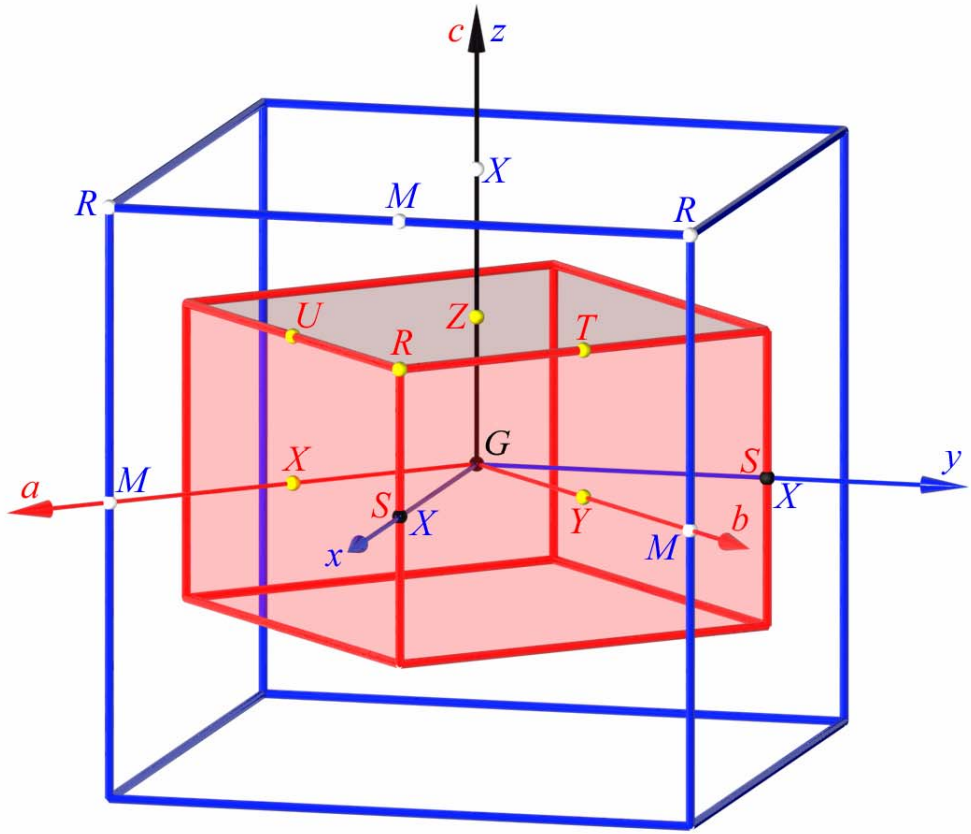
$YTiO_3$ bandstructure with and without the Jahn-Teller distortion:

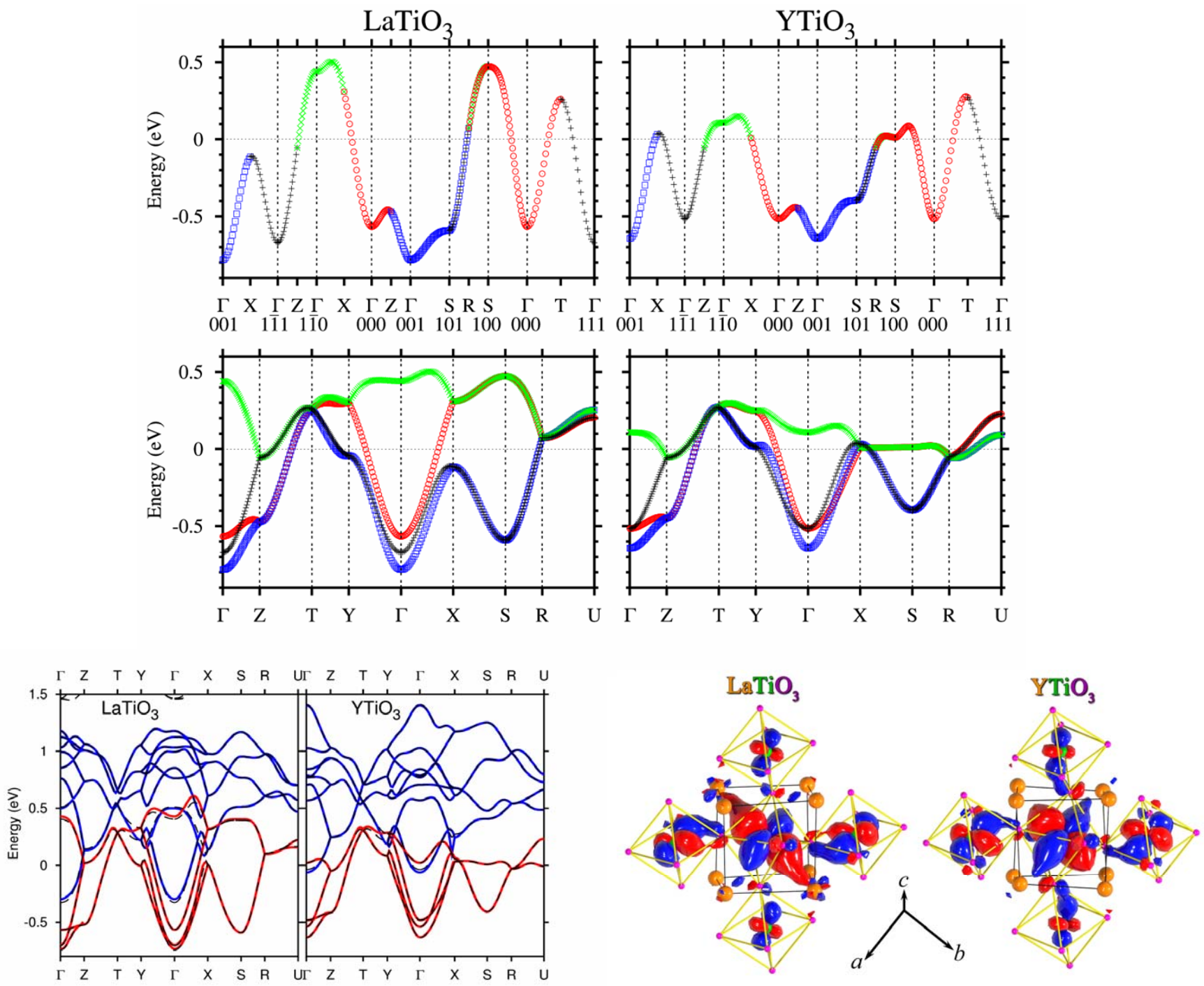


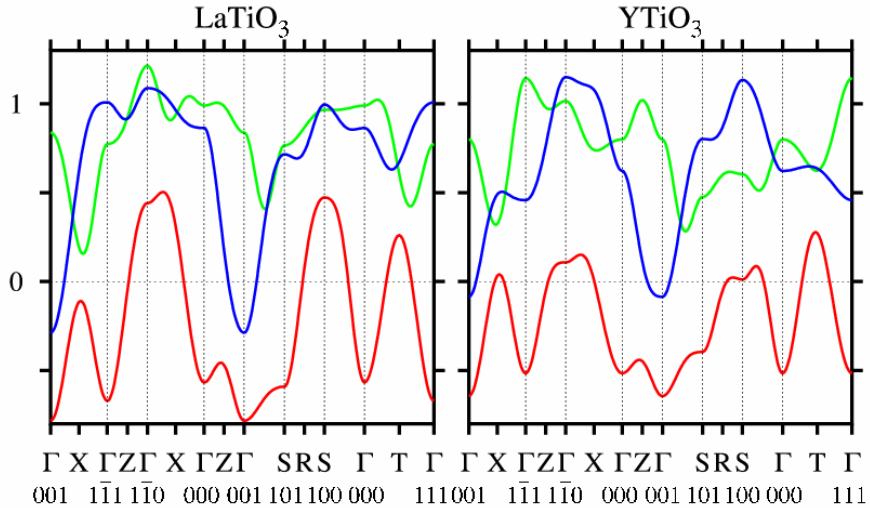
The J-T distortion hardly influences the pseudogap!

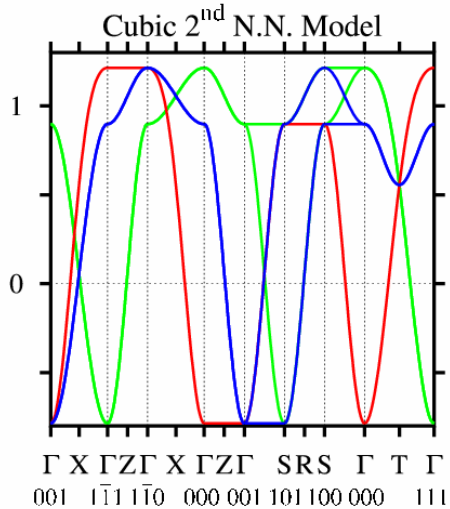

Energy (eV)
1.5
1
0.5
0
-0.5
-1
-1.5
Γ Z T Y Γ X S R U
E1
E0
SrVO3
E2
E1
E0
CaVO3
E2
E1
E0
LaTiO3
E2
E1
E0
YTiO3

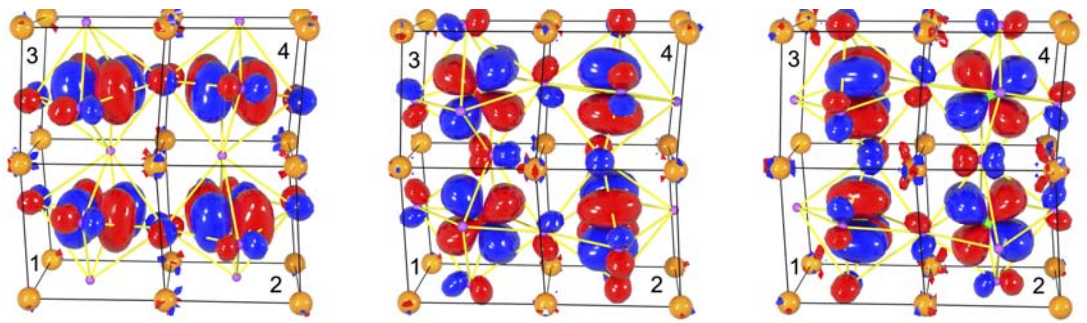



c
z
X
R
M
R
U
Z
T
R
G
X
S
y
a
M
X
S
X
Y
b
M
x


LaTiO3
YTiO3
Energy (eV)
0.5
0
-0.5
Γ X Γ Z Γ X Γ Z Γ S R S Γ T Γ
001 1$\bar{1}$1 1$\bar{1}$0 000 001 101 100 000 111
Γ Z T Y Γ X S R U
1.5
1
0.5
-0.5
c
a
b


LaTiO3
YTiO3
1
0
Γ X ΓZΓ X ΓZΓ SRS Γ T Γ
001 1$\bar{1}$1 1$\bar{1}$0 000 001 101 100 000 111


Cubic 2nd N.N. Model
1
0
Γ X ΓZΓ X ΓZΓ SRS Γ T Γ
001 1$\bar{1}$1 1$\bar{1}$0 000 001 101 100 000 111


3
4
1
2

Most recent work:

m^*/m :		
dHvA of FS, $CaVO_3$	Inoue *et al*	PRL **88**, 236403 (2002)
Photoemission bulk/surface:		
TB+*dia*DMFT, Sr/$CaVO_3$ surf	Liebsch	PRL **90**, 096401 (2003)
Photoemission, LDA+DMFT, Sr/$CaVO_3$	Sekiyama *et al*	cond-mat/0312429
OO in $LaTiO_3$:		
M and specific heat, $LaTiO_3$, orb liquid?	Fritsch *et al*	PRB **65,** 212405 (2002)
X-ray diff, JT in $LaTiO_3$, La-field$\rightarrow$OO	Cwik *et al*	cond-mat/0302087
Ti $L_{2,3}$ x-ray abs., Ti-field = 0.12-0.30 eV	Haverkort *et al.*	cond-mat/0405516
HF model calc, A-field$\rightarrow$OO in $LaTiO_3$	Mochizuki, Imada	PRL **91,** 167203 (2003)
LDA+DMFT, Sr/$CaVO_3$ and La/$YTiO_3$	This work	cond-mat/0309102
LDA+*dia*DMFT, $La_{1-x}Sr_xTiO_3$	Craco *et al*	cond-mat/0309370

The three last calculations reach the essentially the same conclusion concerning the orbital order in LaTiO3