Theoretical studies of oxide heterostructures

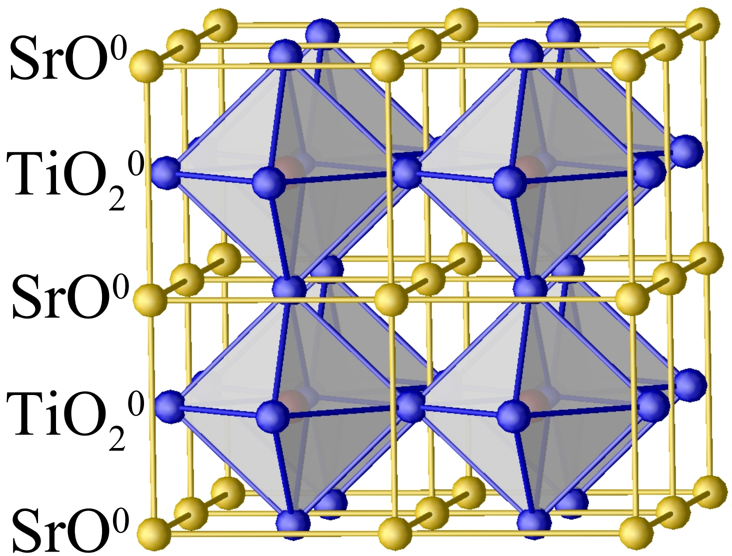
Zhicheng Zhong
Vienna University of Technology, Austria

Acknowledgements:
Prof. Paul J. Kelly;
Prof. Karsten Held

Vienna Computational Materials Laboratory
ViCoM
IFP TU

Bulk $LaAlO_3$ (LAO) and $SrTiO_3$ (STO)

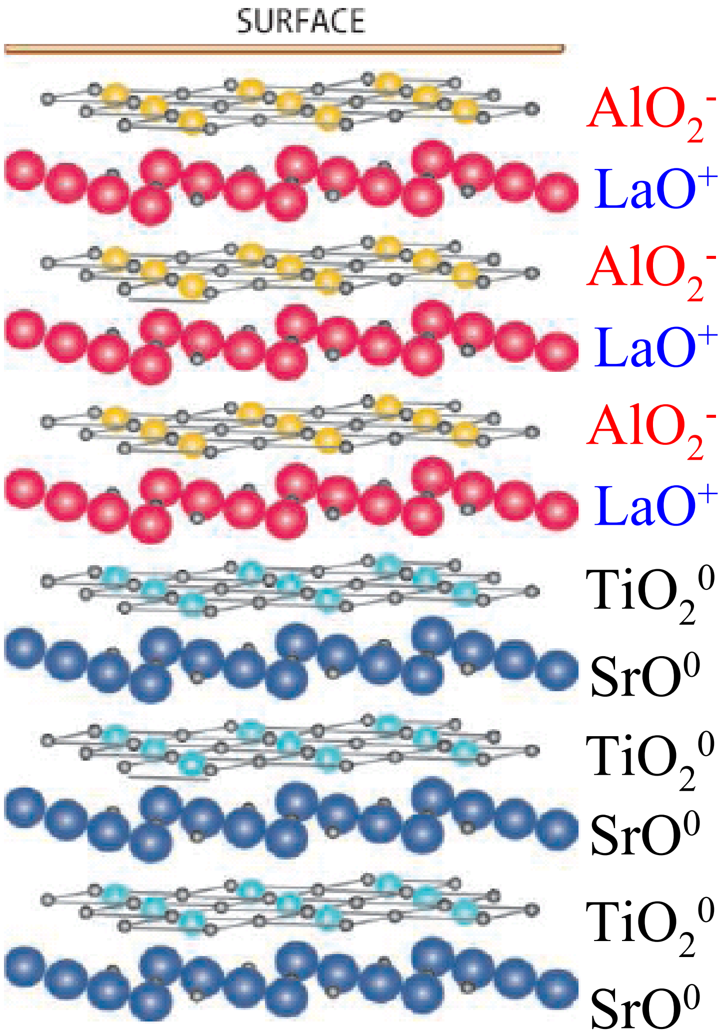
- <u>Perovskite structure</u>
  $SrTiO_3$ 3.905Å;
  $LaAlO_3$ 3.789Å
- <u>Band insulator</u>
  Sr^{2+}, Ti^{4+}, $(O^{2-})_3$ Gap: 3.2eV
  La^{3+}, Al^{3+}, $(O^{2-})_3$ 5.6eV
- <u>No-magnetic</u>



$SrTiO_3$: non-polar SrO^0, TiO_2^0 (charge neutral)

$LaAlO_3$: polar LaO^+, AlO_2^-

Two dimensional electron gas (2DEG) at LAO/STO



Ohtomo and Hwang Nature(2004)

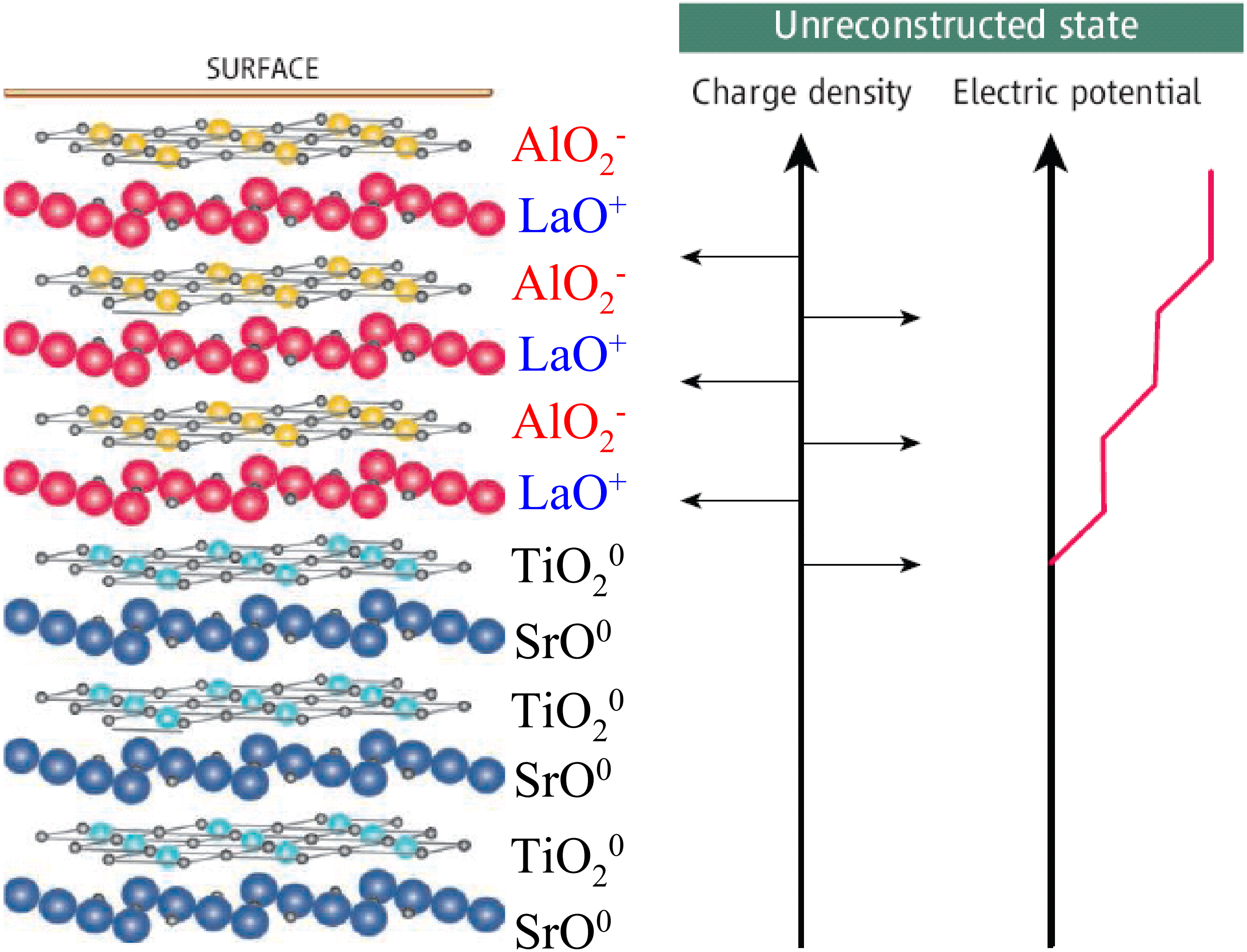
LaO^+/TiO_2^0 interface:
critical thickness ($N_{LAO}>3$,conducting)
magnetic, superconducting, correlated,
spin-orbit coupling....

Semiconductor heterostructures
($GaAs/Al_xGa_{1-x}As$)

- Origins of the 2DEG?
  (i) polar catastrophe
  (ii)polarity induced oxygen vacancies

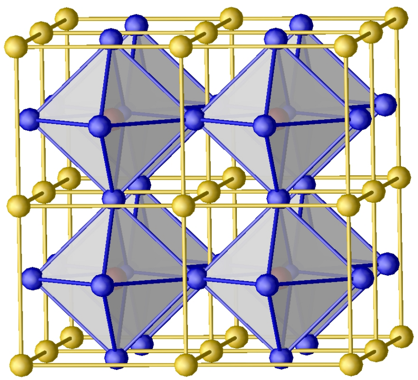
- Properties of the 2DEG?

Origins of 2DEG: (i) polar catastrophe

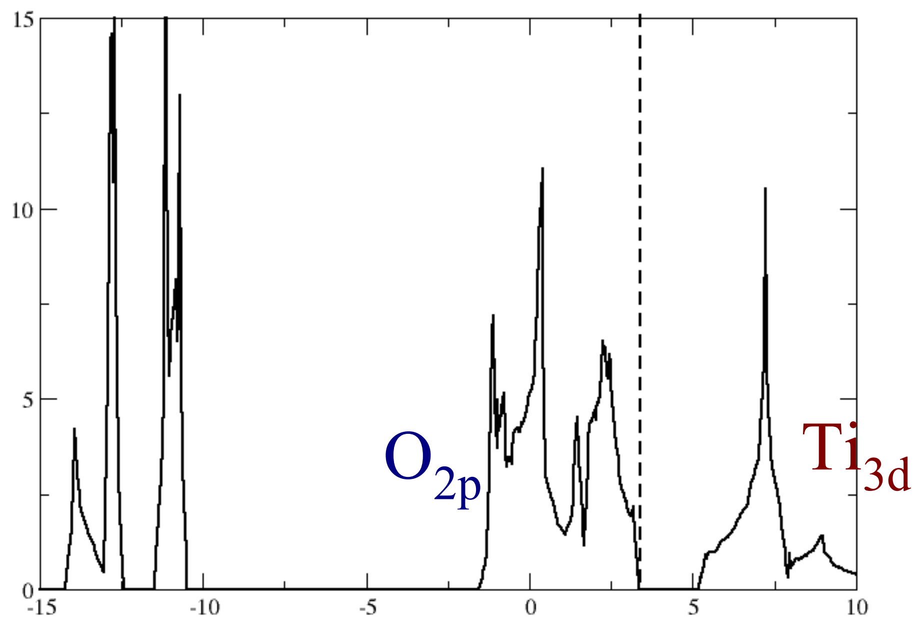


- Charge transfer from surface AlO^-_2 to interface TiO_2

DFT calculation of bulk LAO and STO

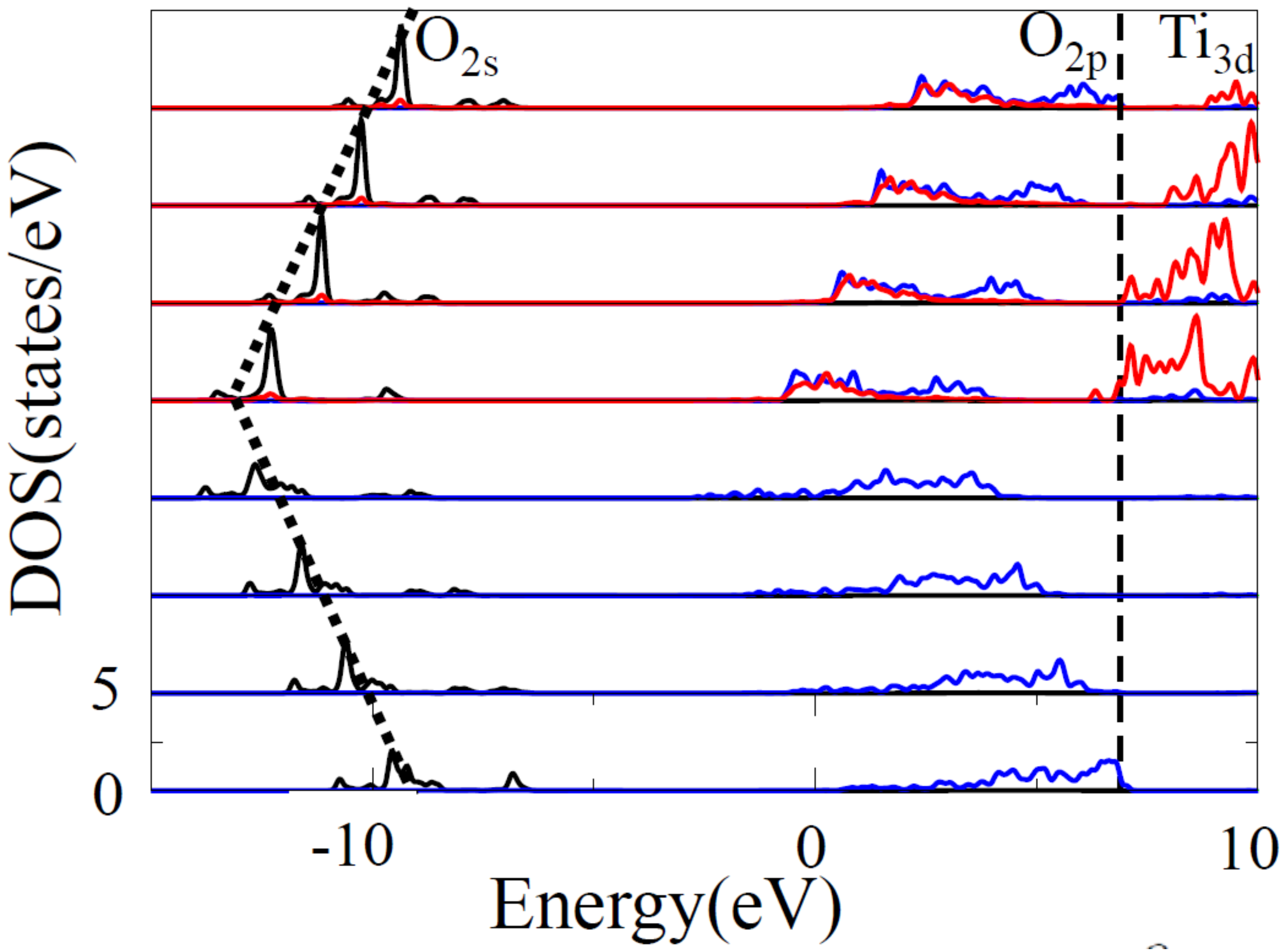


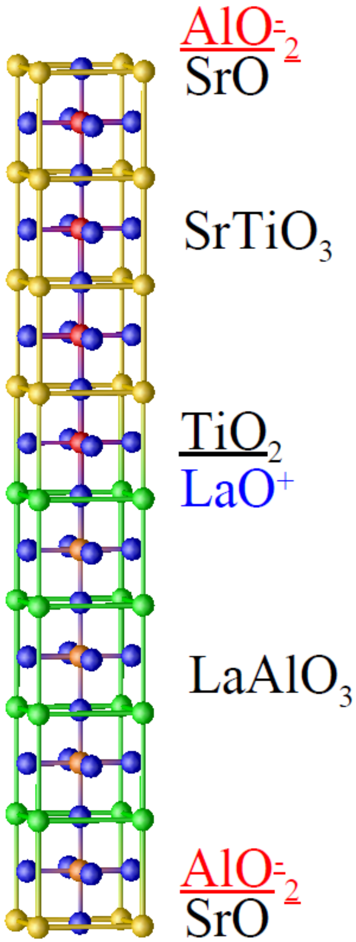
	a (LDA)	*a* (exp)	Gap (LDA)	Gap (exp)
$SrTiO_3$	3.866 Å	3.905 Å	1.88 eV	3.2 eV
$LaAlO_3$	3.754 Å	3.789 Å	3.62 eV	5.6 eV



Density of States of STO

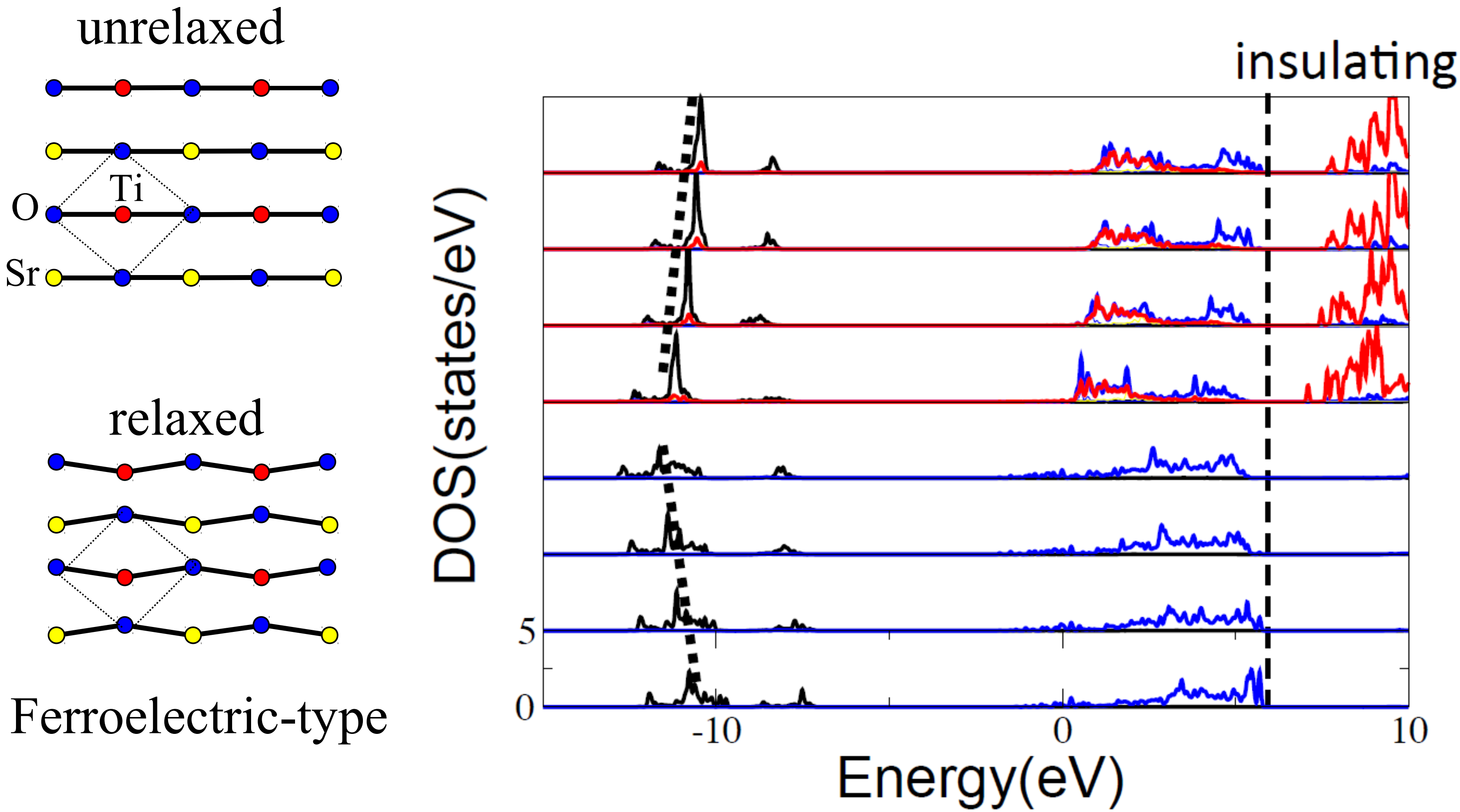
Superlattice LAO/STO (4/4): unrelaxed





➢ A large internal electric field

Superlattice LAO/STO (4/4): relaxed



- Atomic relaxation will suppress the internal electric field

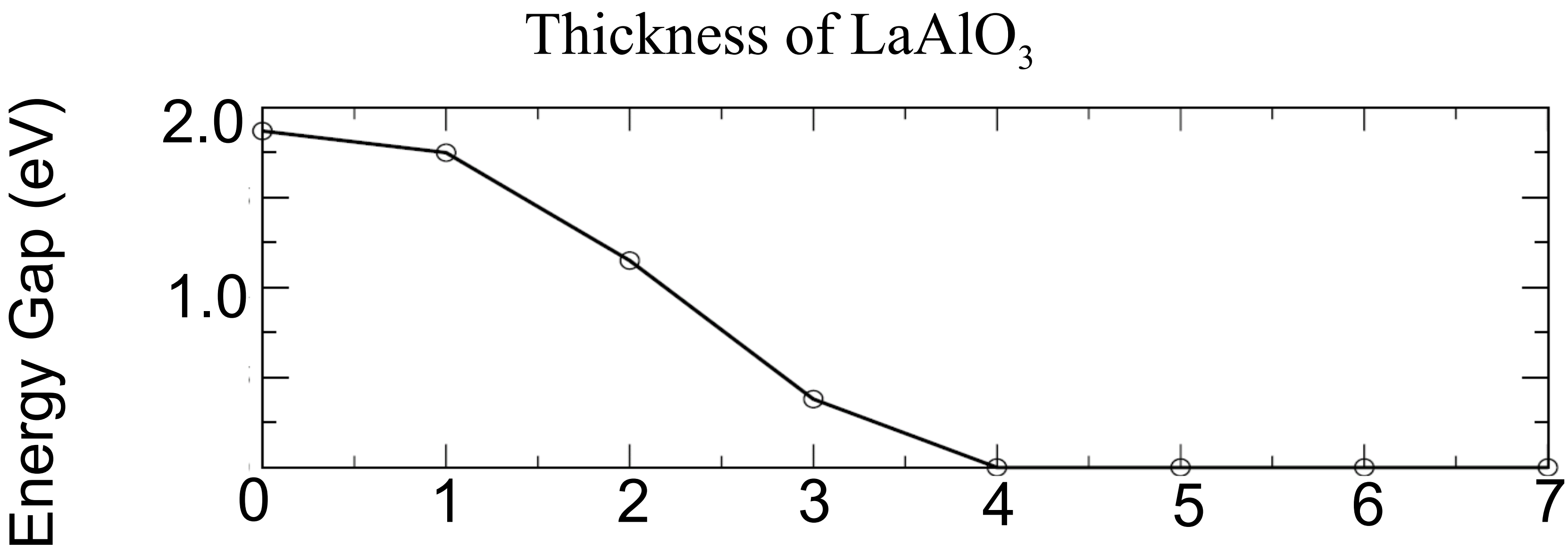
Vacuum/LAO/STO

Assume:

Clean and abrupt interface

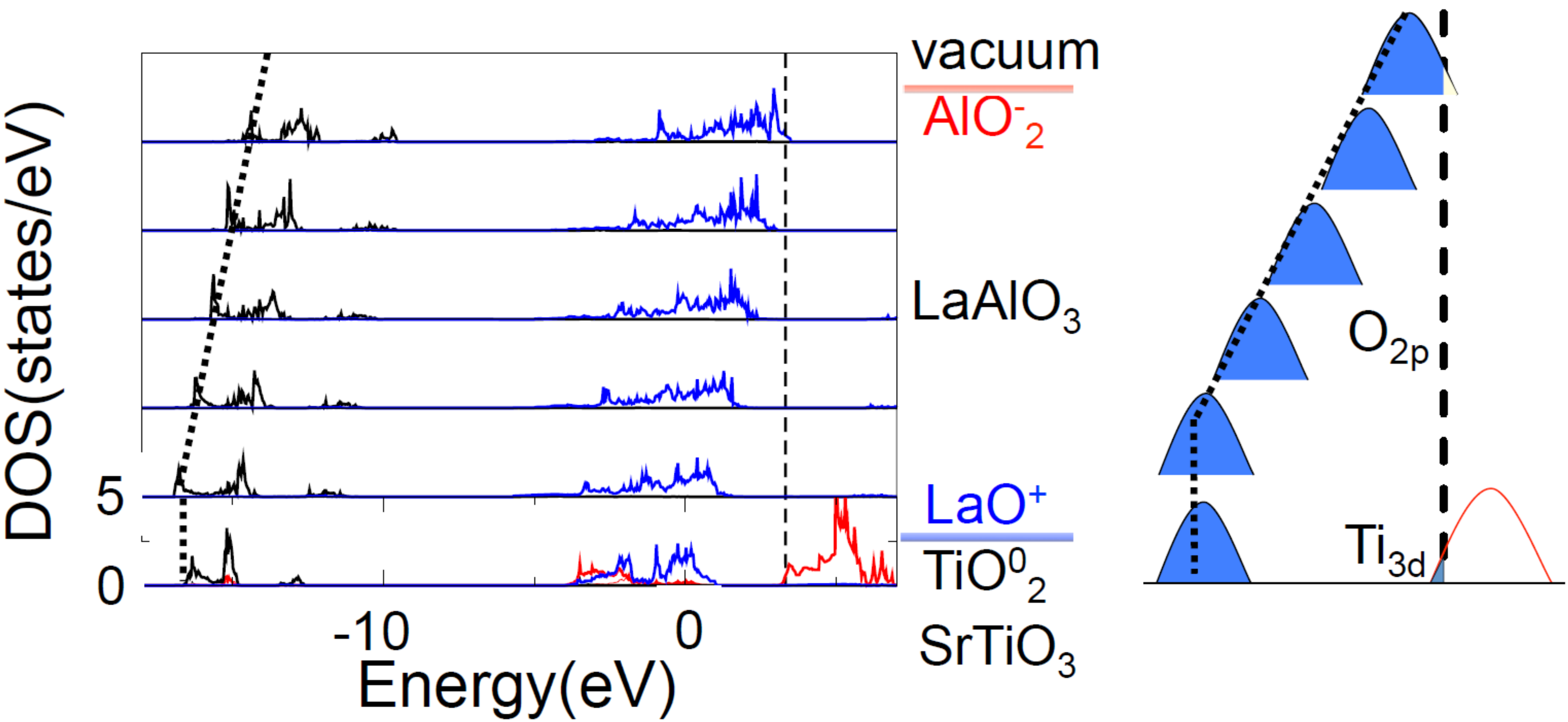
No oxygen vacancy

No surface reconstruction



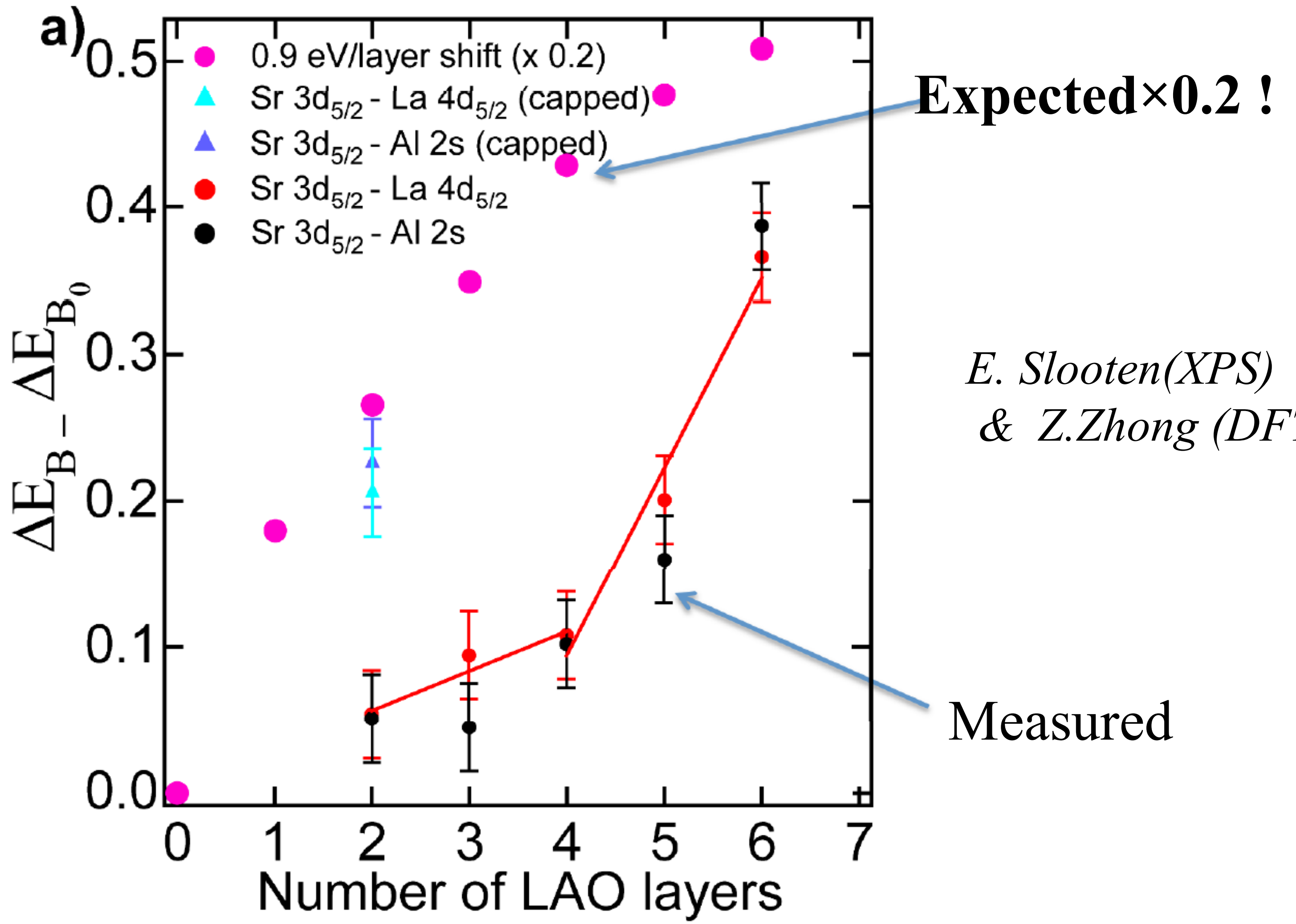
➢ Thickness dependent insulator-metal transition

Vacuum/LAO/STO



- Polar catastrophe seems to be reasonable

However, key evidence is missing......

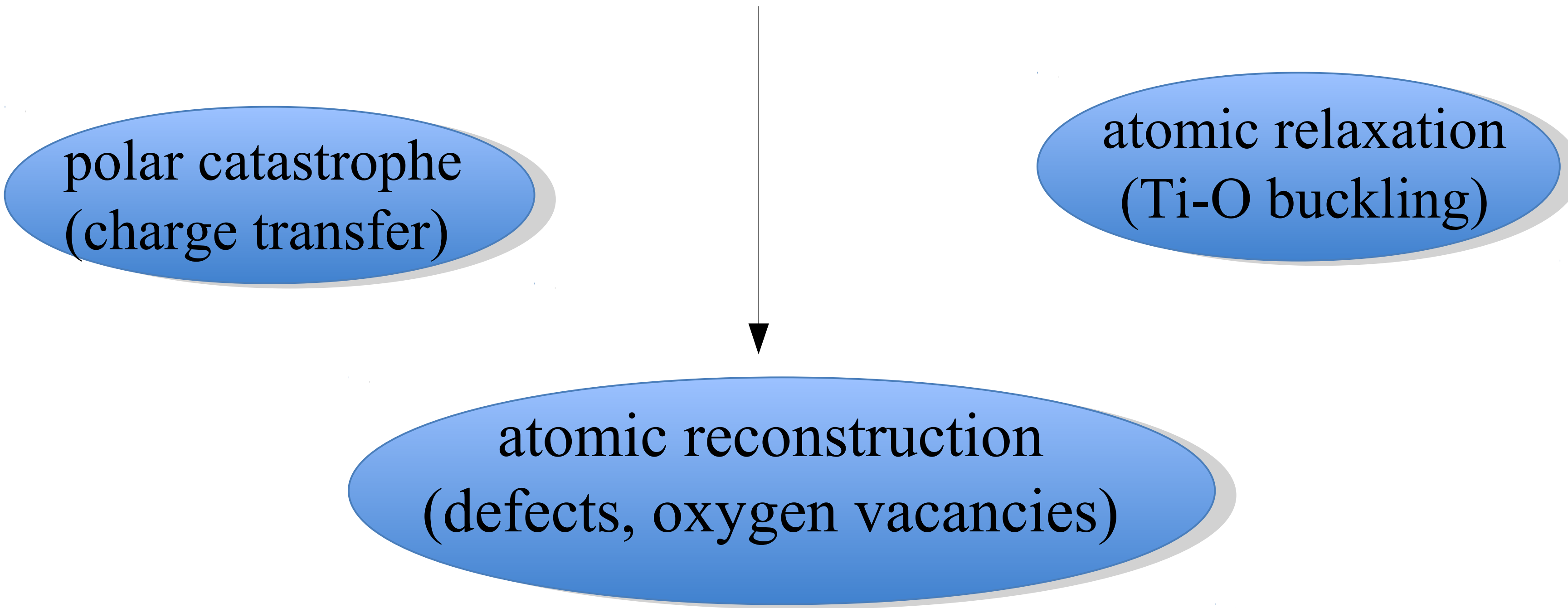


E. Slooten(XPS) & Z.Zhong (DFT)

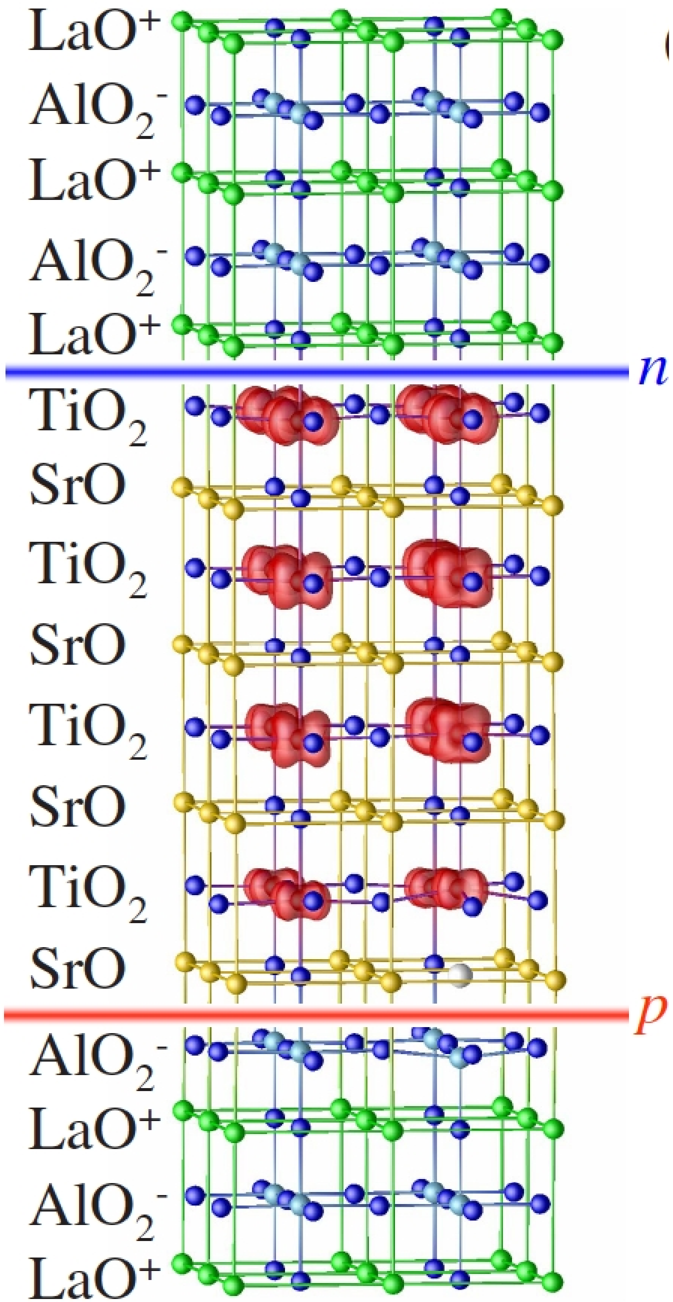
- The internal electric field is much smaller

Origins of 2DEG: (ii) polarity-induced oxygen vacancies

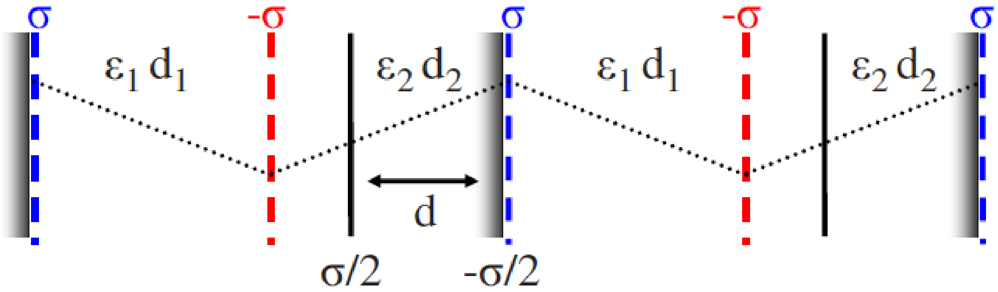
<u>DFT+ model</u> demonstrate the internal electric field.
But it is not observed in experiments.

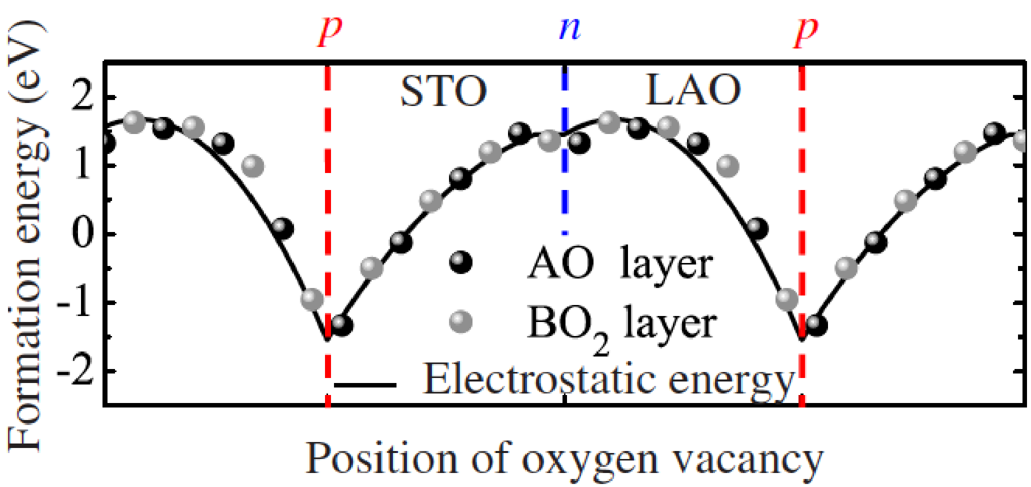


Formation energy of oxygen vacancies in LAO/STO



$$\Omega^{Vac} = E_{SC}^{Vac} - E_{SC} + \underline{\mu_O(T, p_{O_2})}$$



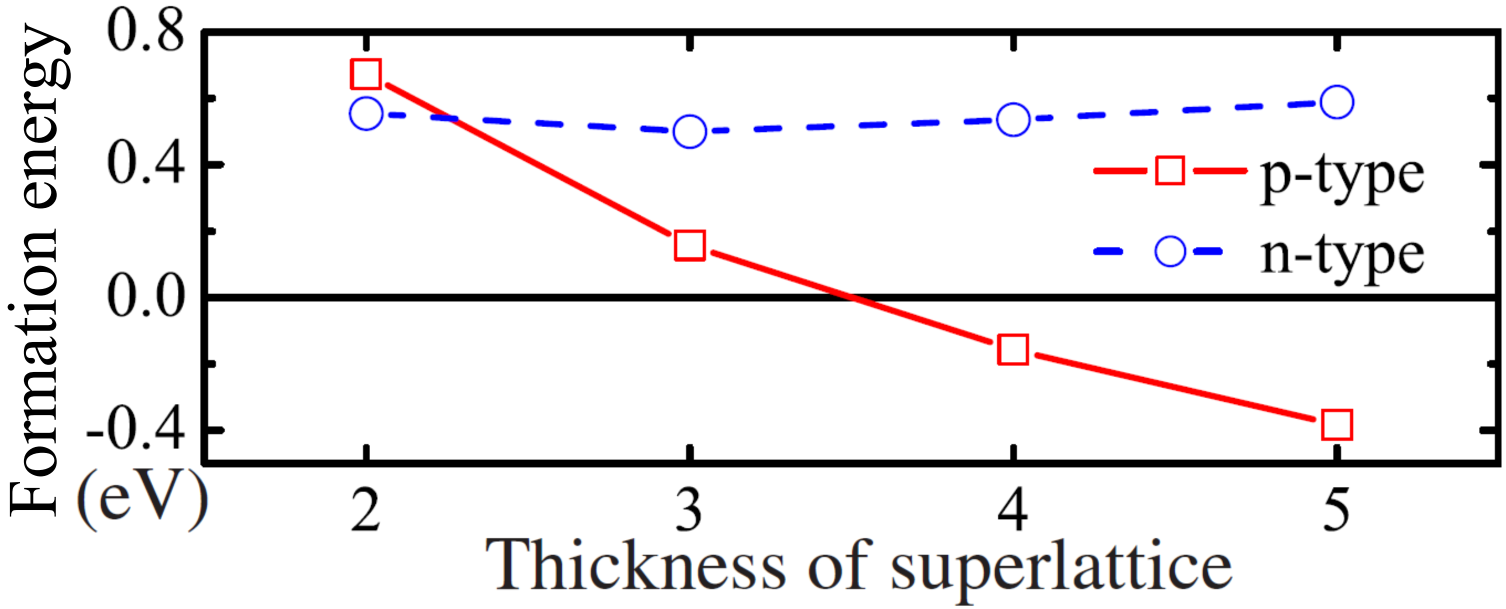


- Asymmetric behavior of ***n*-** and ***p*-** type interfaces

Thickness dependent formation energies

Formation energy of oxygen vacancies

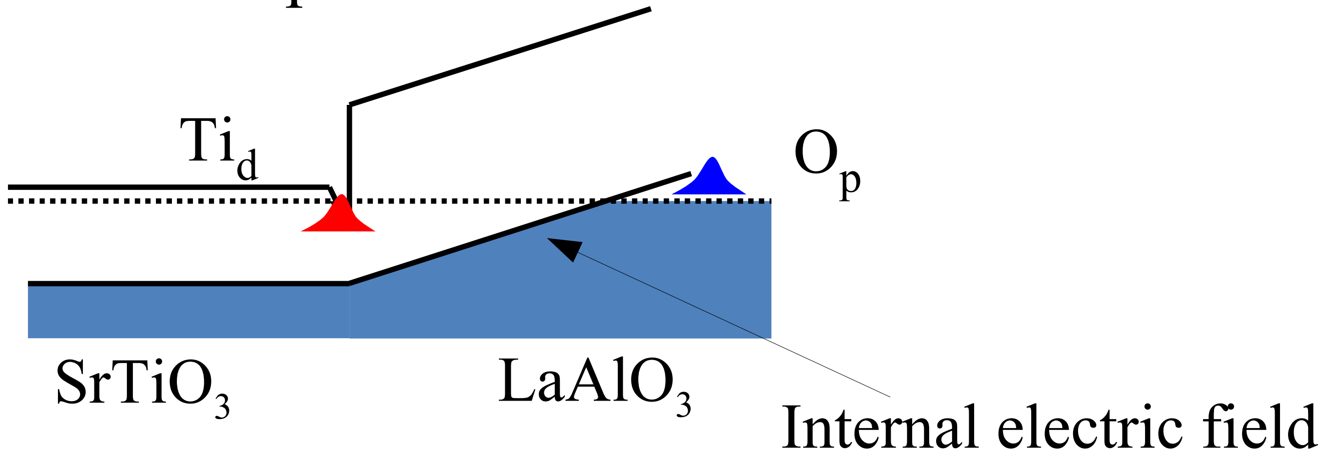
$E_{LAO / STO} < E_{STO}, E_{LAO}$



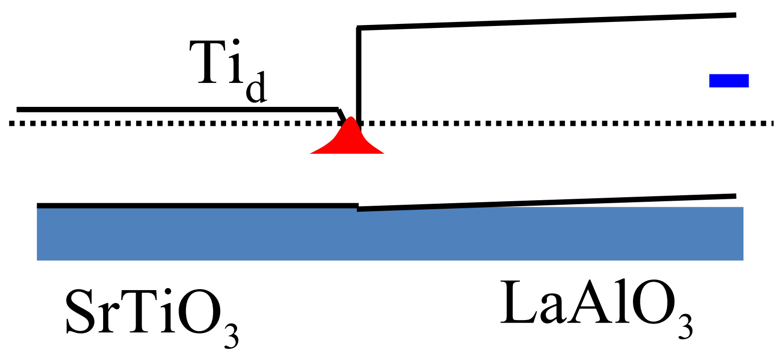
- Oxygen vacancies are spontaneously created by polarity

Origins of the 2DEG

- Polar catastrophe



- Polarity induced oxygen vacancies

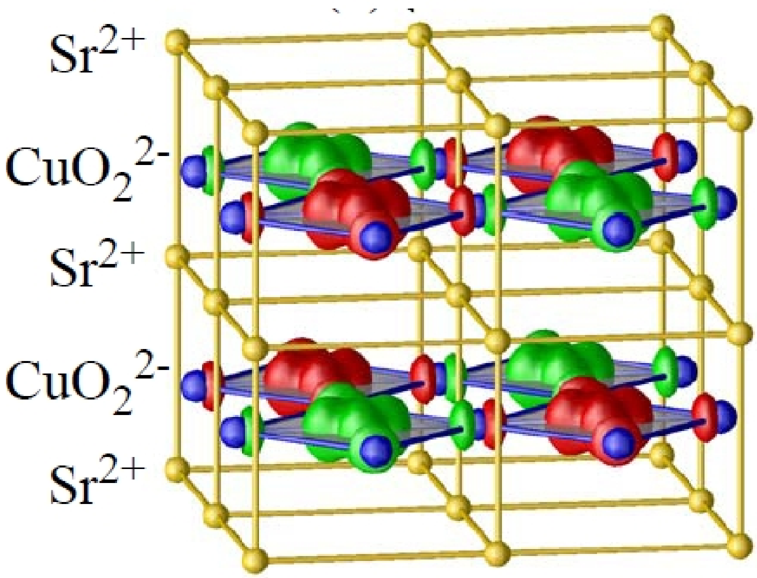


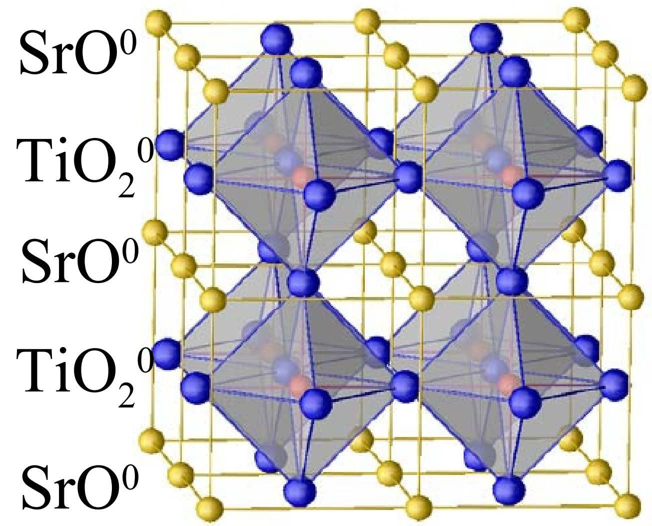
How to confirm?

$$\Omega^{\mathrm{Vac}} = E_{\mathrm{SC}}^{\mathrm{Vac}} - E_{\mathrm{SC}} + \underline{\mu_{\mathrm{O}}(T, p_{\mathrm{O}_2})}$$

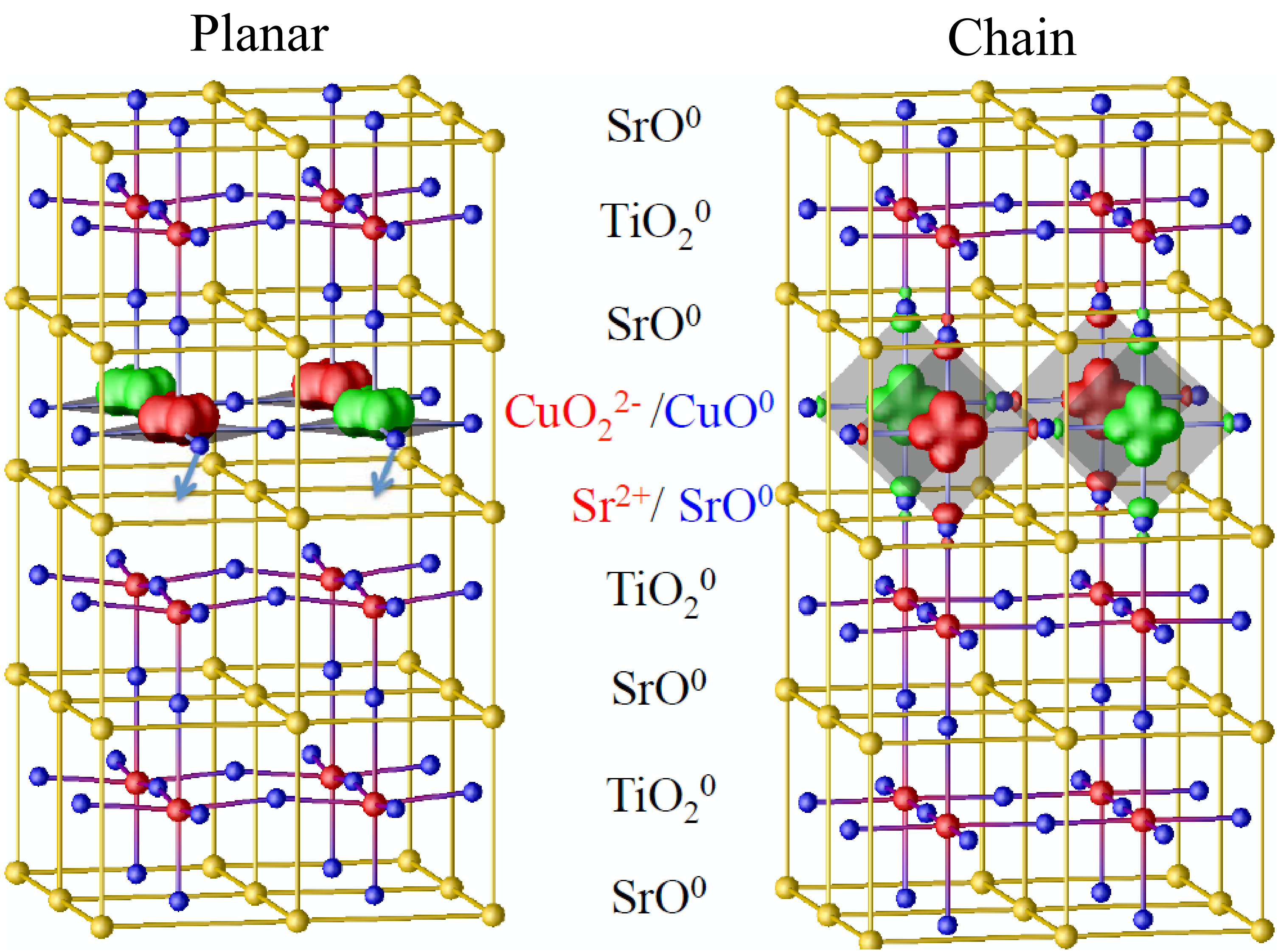
$SrCuO_2$ infinite layer structure

Parent compound of cuprate high-temperature superconductors



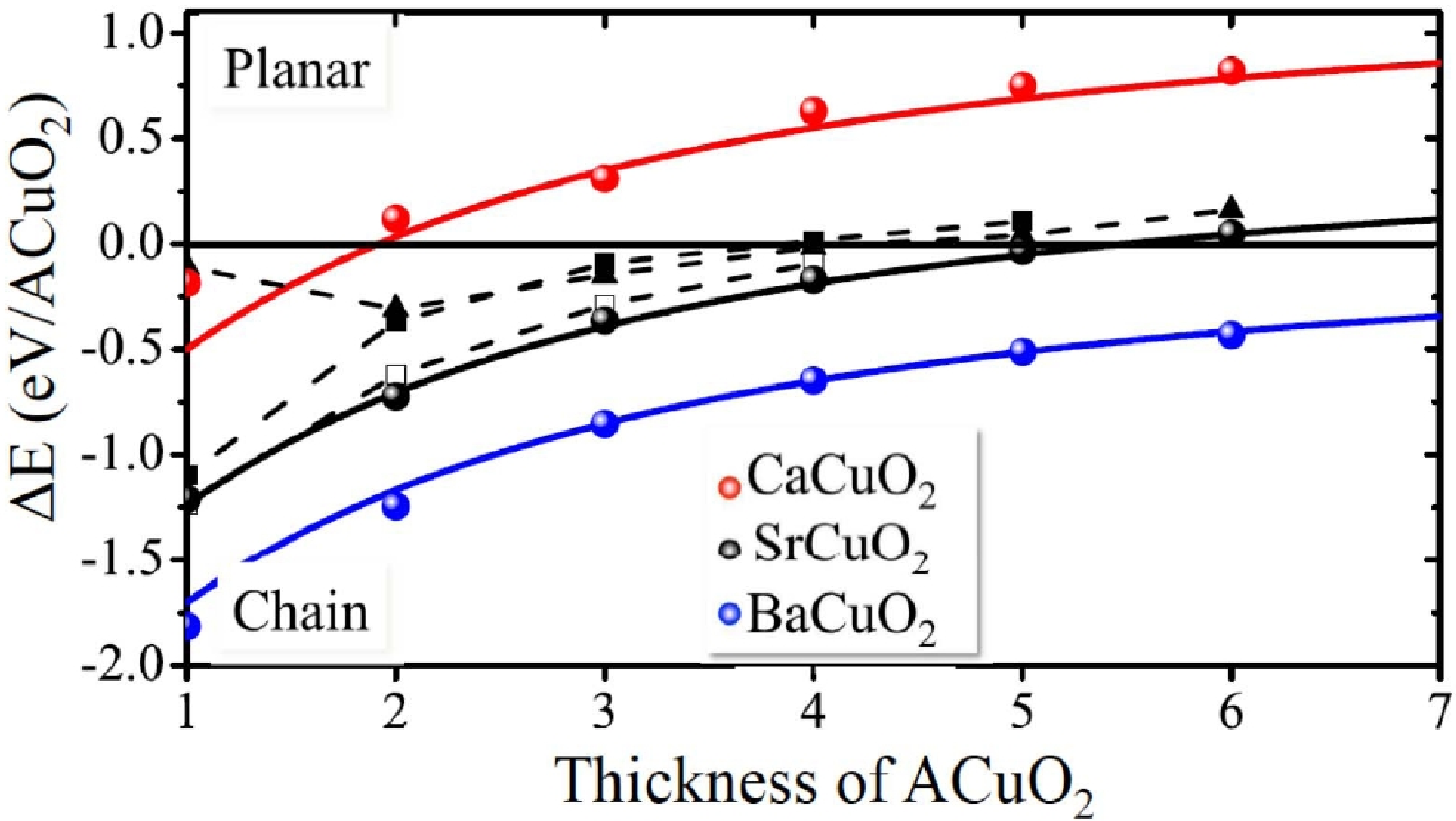


Stoichiometric $SrCuO_2$ thin films



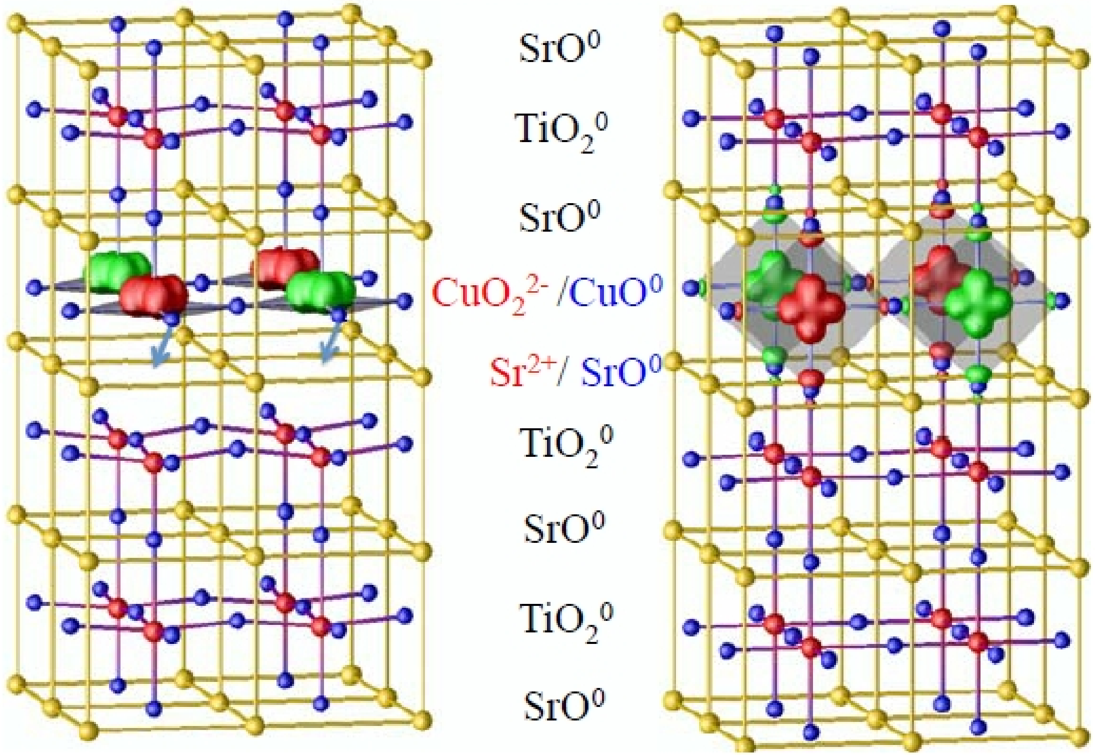
- Moving electrons or Oxygen ions?

Thickness dependence of structural transition



$$\Delta E = -E^{Planar} + E^{Chain}$$

How to prove it?

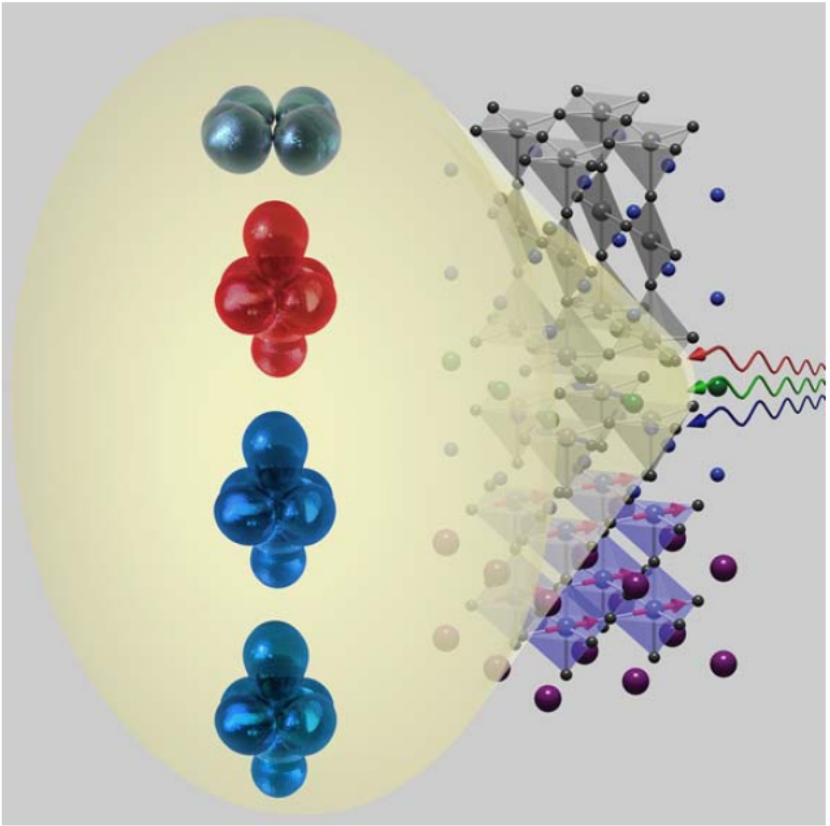


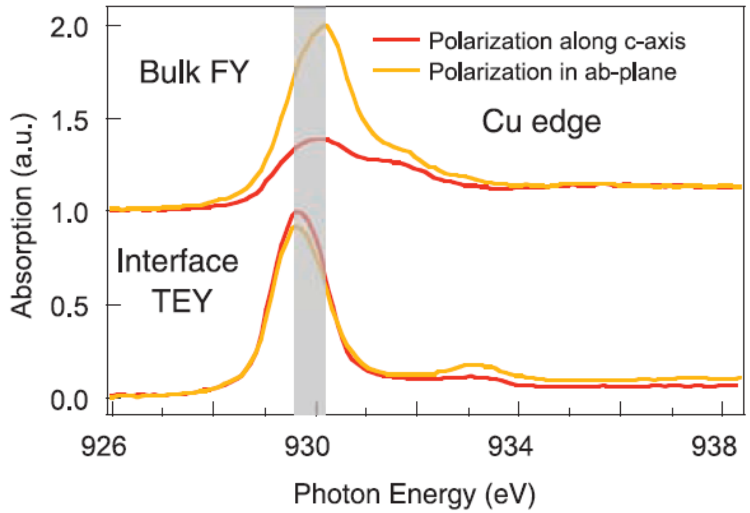
Thickness dependent

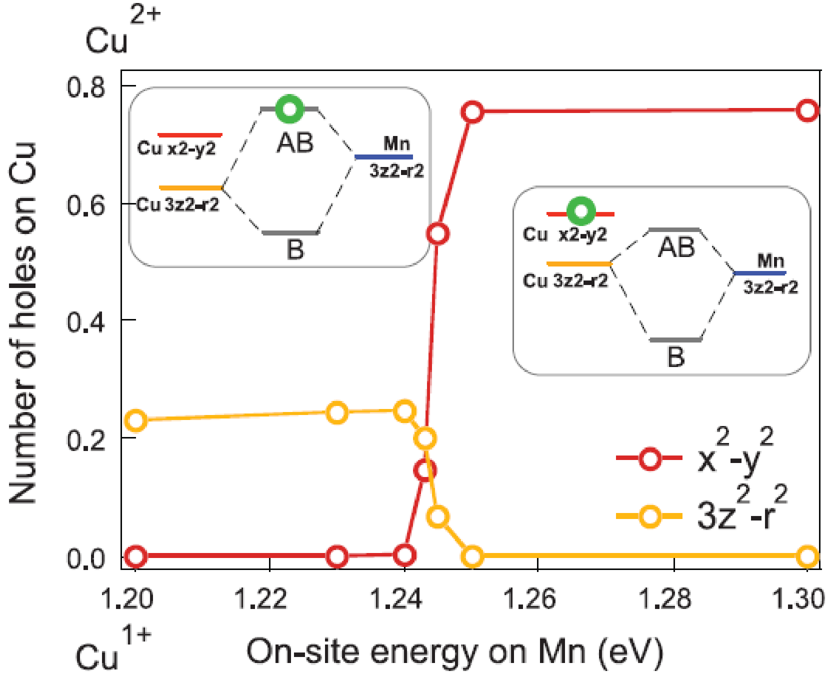
- Enlarged lattice constant along *c* ~ 0.5A
- Out of plane orbital character, z^2

Two experimental groups (Netherlands and Italy) find it

Cuprates heterostructures shoud be revisited



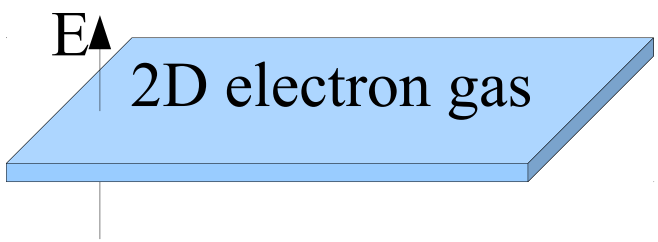


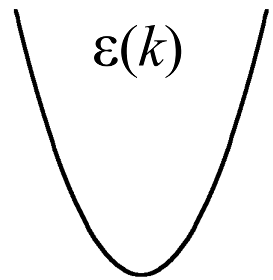


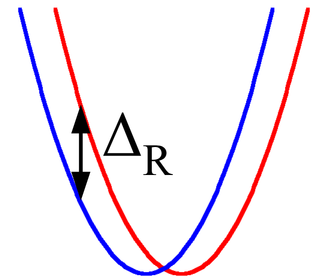
Orbital reconstruction at LCMO/YBCO

J.Chakhalian et.al. Science (2007)

Properties of 2DEG: Rashba spin splitting







(i)Space inversion symmetry $\varepsilon(\vec{k},\uparrow) = \varepsilon(-\vec{k},\uparrow)$ ✗

Time inversion symmetry $\varepsilon(\vec{k},\uparrow) = \varepsilon(-\vec{k},\downarrow)$

(ii)Spin orbit coupling $(\hbar/2m_e^2c^2)(\nabla V \times \vec{p}) \cdot \vec{s}$

free 2DEG: $\Delta_R = 2\alpha_R k \quad \alpha_R = (\hbar/4m^2c^2)\mathrm{d}V(z)/\mathrm{d}z$

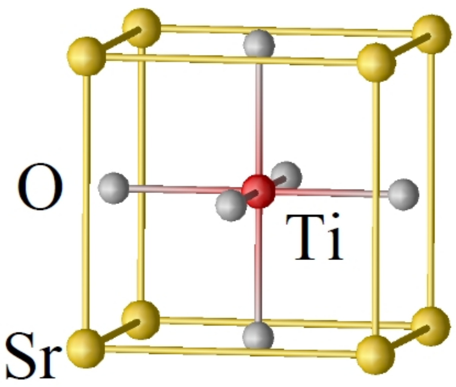
E~100 Volt/mm $\quad \Delta_R \sim 10^{-8}\mathrm{meV}$

- Δ_R~meV
- $2\alpha k$ at $LaAlO_3/SrTiO_3$ interface (*Caviglia et.al.; Ben Shalom et.al.*)

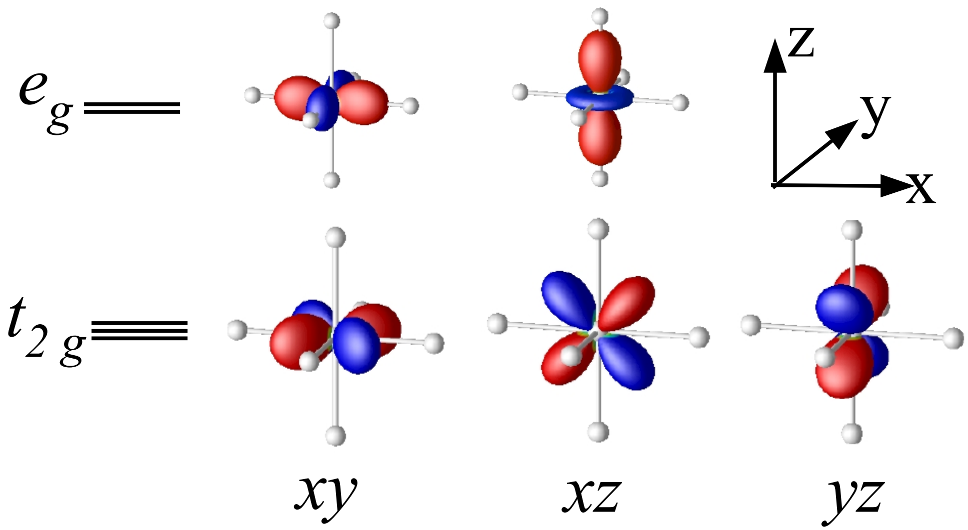
  $2\alpha k^3$ at $SrTiO_3$ surface (*Nakamura et.al.*)

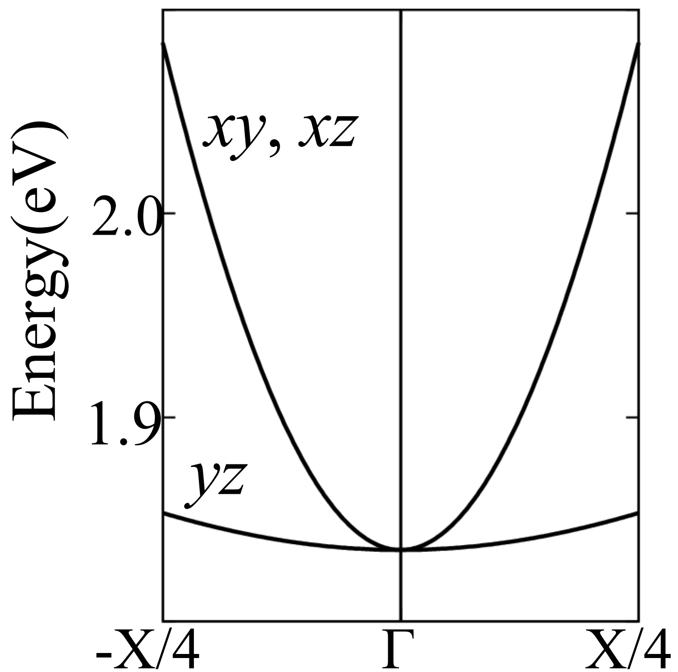
Band structure of bulk $SrTiO_3$

Bulk $SrTiO_3$



TiO_6 crystal field splits Ti *d* orbitals

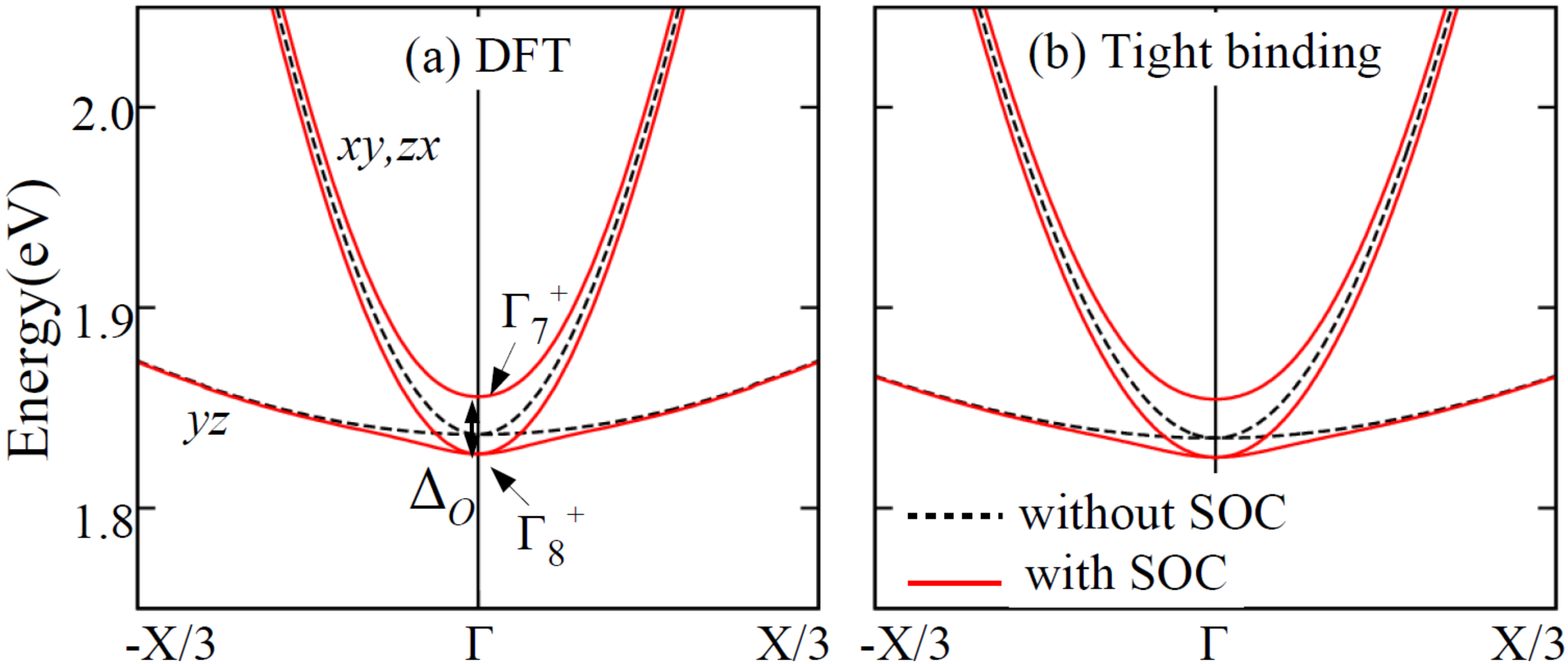




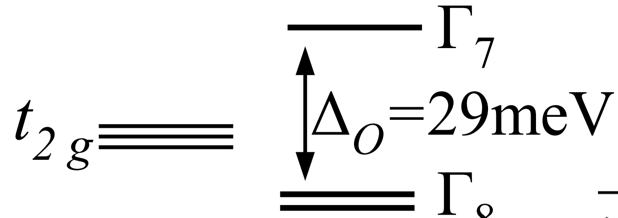
- three degenerate t_{2g} orbitals
- heavy carrier *yz* ($6.8m_e$), two light carriers *xy* and *xz* ($0.41m_e$)

Spin-orbit coupling (SOC) effects on bulk STO

Wien2k -->Wien2Wannier -->Wannier90

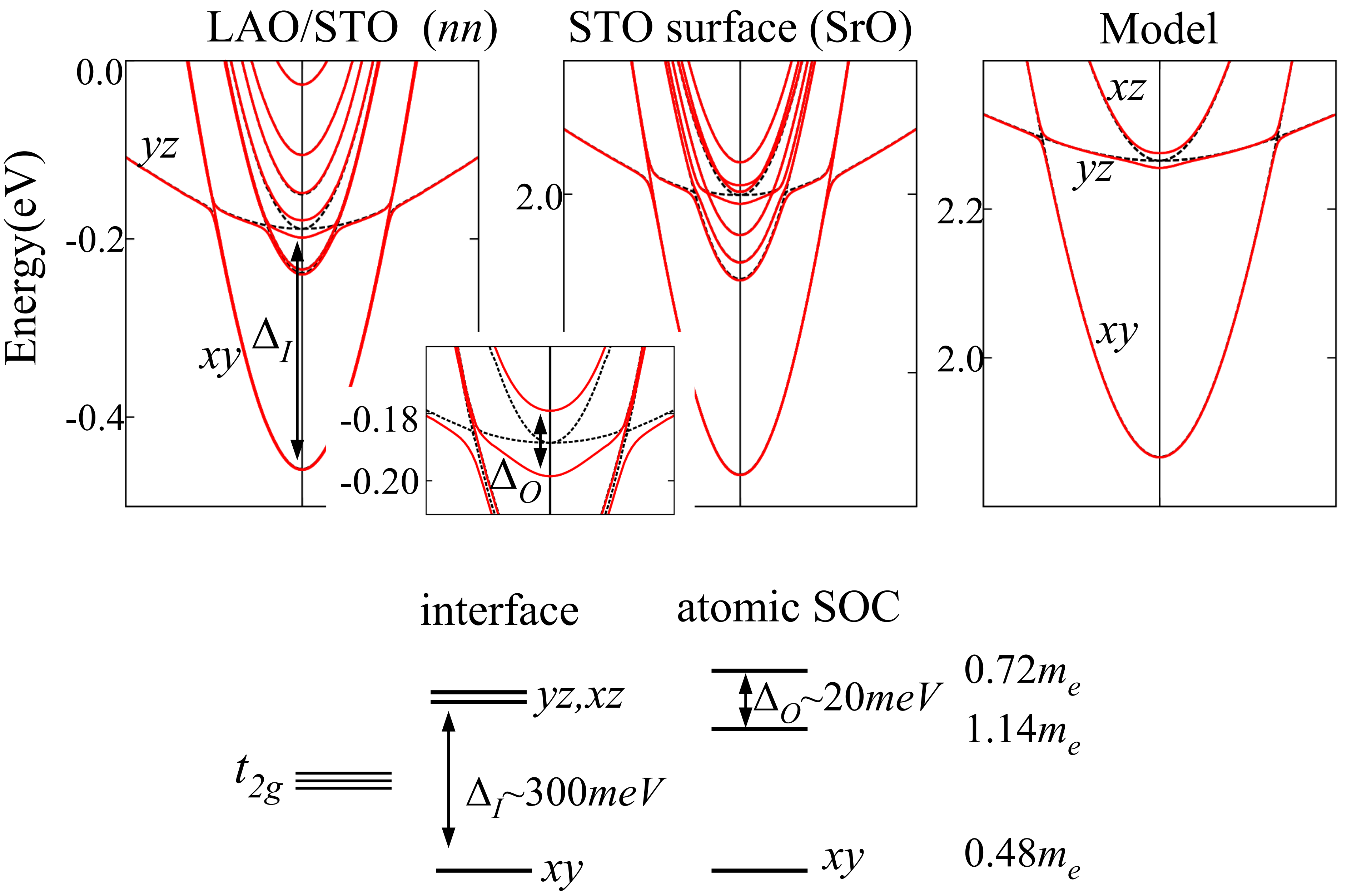


hopping t + atomic SOC $\xi \vec{l} \cdot \vec{s}$



$$\frac{1}{\sqrt{6}}\left(\pm i\, yz|\uparrow,\downarrow\rangle + zx|\uparrow,\downarrow\rangle + 2i\, xy|\downarrow,\uparrow\rangle\right)$$

Orbital splitting at LAO/STO interfaces and STO surfaces



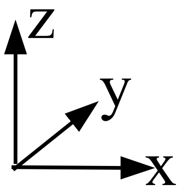
Model for Rashba spin splitting

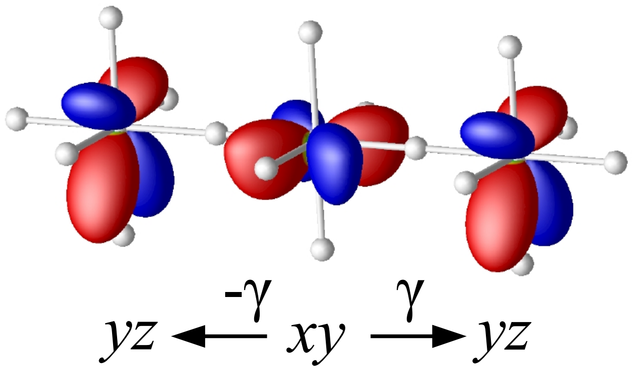
$$H_0^i + H_\xi + H_\gamma$$

Free: $-2t_1 cosk_x - 2t_1 cosk_y - t_2 - 4t_3 cosk_x cosk_y$

atomic SOC: $$\frac{\xi}{2}\begin{pmatrix} 0 & 0 & i & 0 & 0 & -1 \\ 0 & 0 & 0 & -i & 1 & 0 \\ -i & 0 & 0 & 0 & 0 & i \\ 0 & i & 0 & 0 & i & 0 \\ 0 & 1 & 0 & -i & 0 & 0 \\ -1 & 0 & -i & 0 & 0 & 0 \end{pmatrix}$$

interface asymmetry: $$\gamma\begin{pmatrix} 0 & 0 & 2i\sin k_x \\ 0 & 0 & 2i\sin k_y \\ -2i\sin k_x & -2i\sin k_y & 0 \end{pmatrix}$$



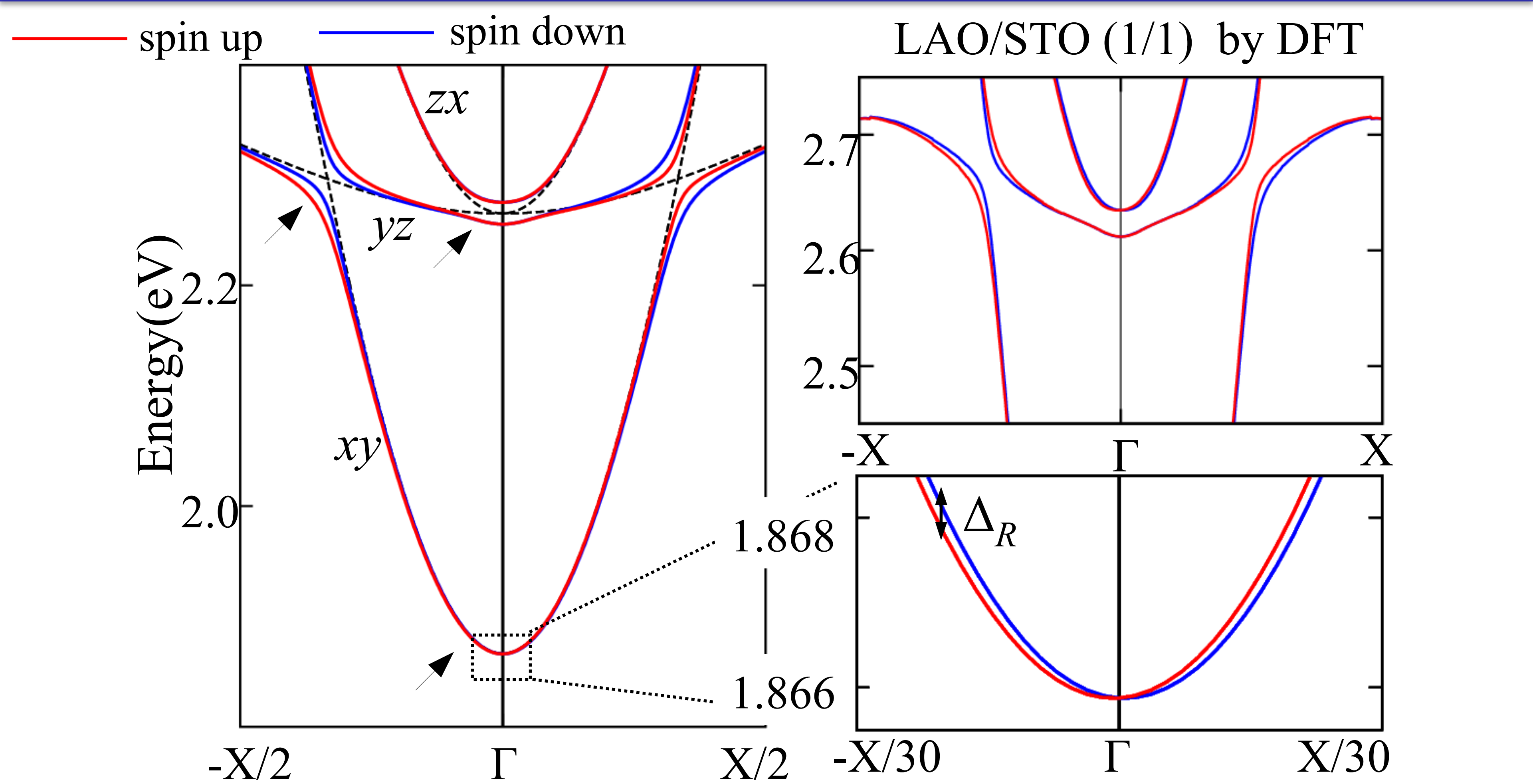


$$\gamma = \langle xy|H|yz(R)\rangle$$

0.02eV, interface layer

s-*p* electrons of Au surfaces *Lashell* et al.(1996); *Peterson* et al.(2000)

Spin splitting

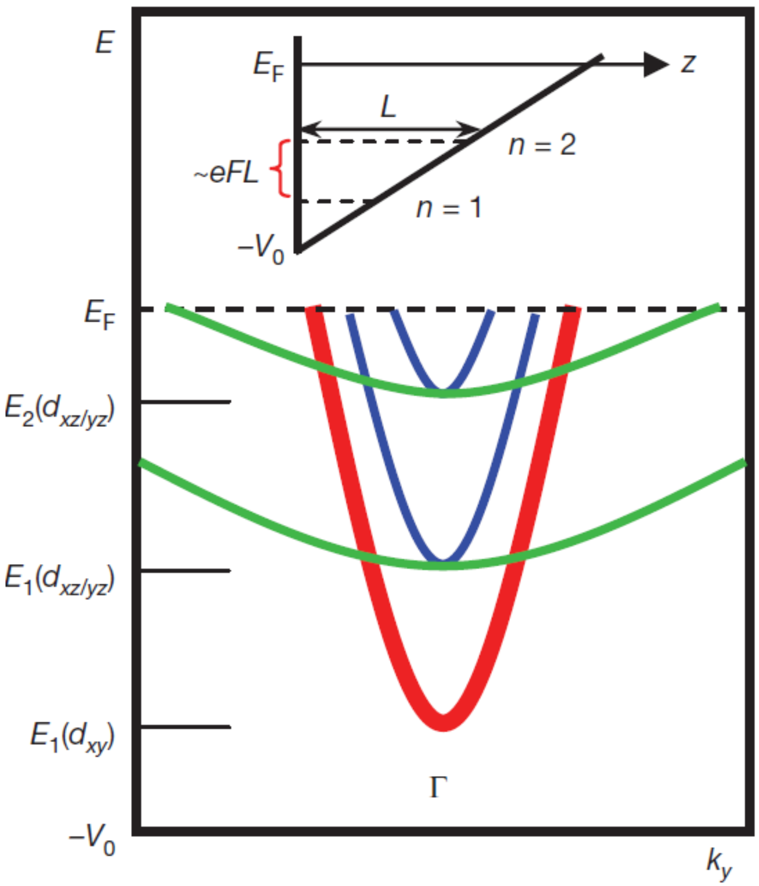


- Γ, *xy* orbital: $\Delta_R = 2\alpha_R k$ $\quad \alpha_R = 2a\xi\gamma/\Delta_I$
- Γ, *yz/xz* mixed orbitals: $2\alpha_3 k^3$
- *xy*-*yz* crossing point

Properties of 2DEG: Quantum Well states

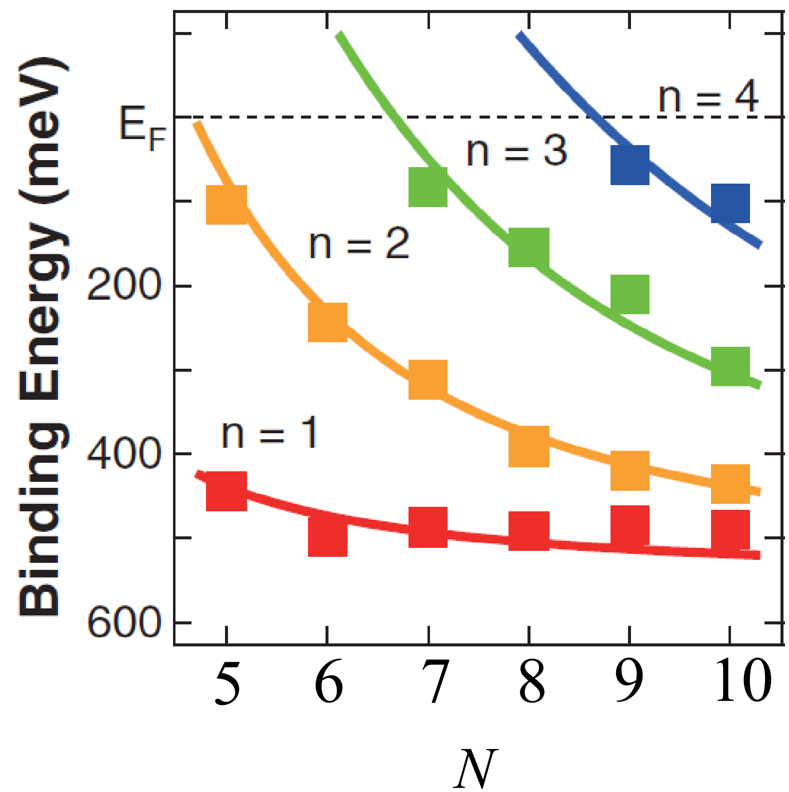
$SrTiO_3$ surfaces

A.F. Santander-Syro et.al. Nature (2011)

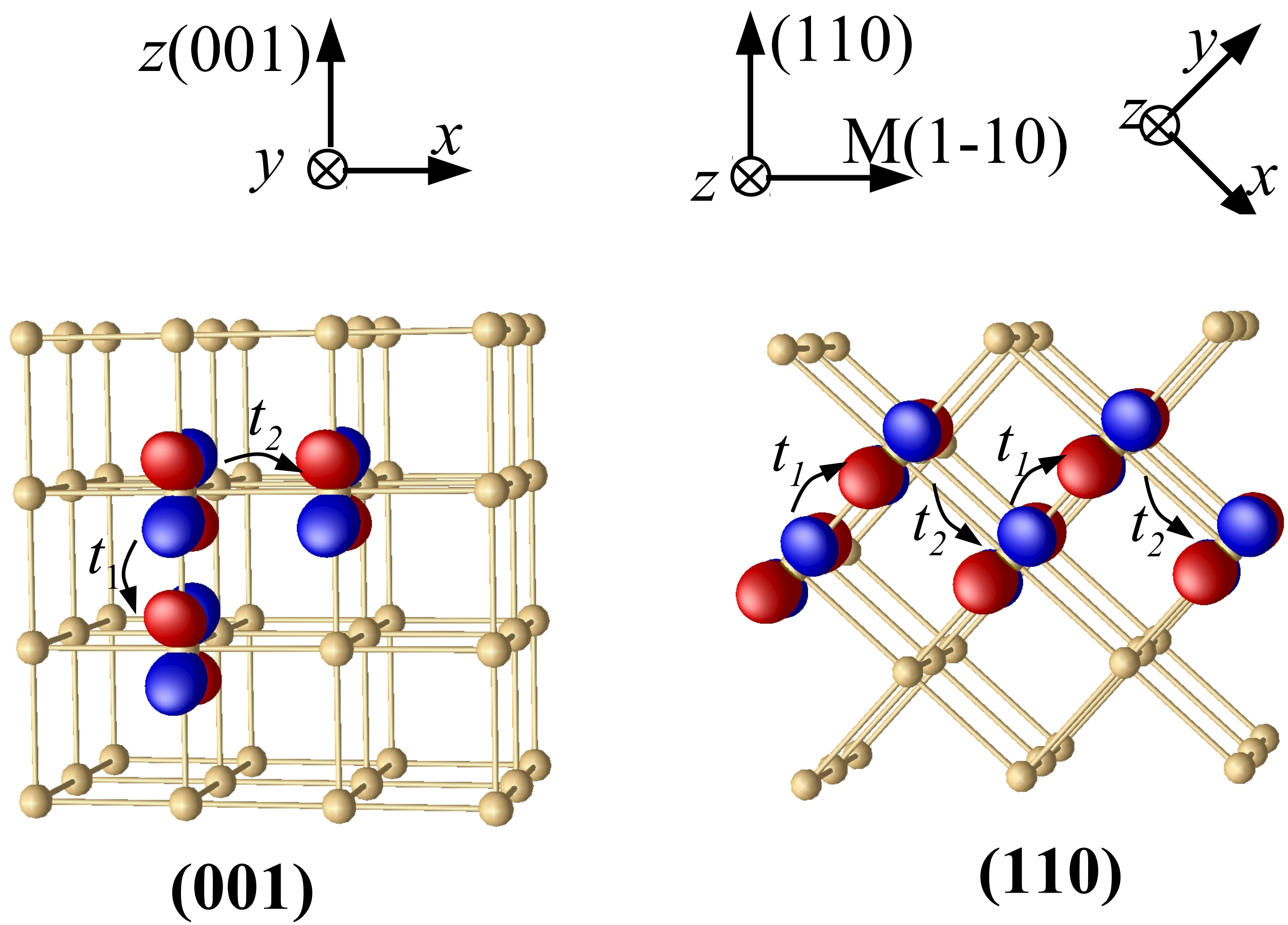


$SrVO_3$ ultrathin films

K. Yoshimatsu *et.al.* Science (2011)



Properties of 2DEG: Quantum Well states along (110) is different

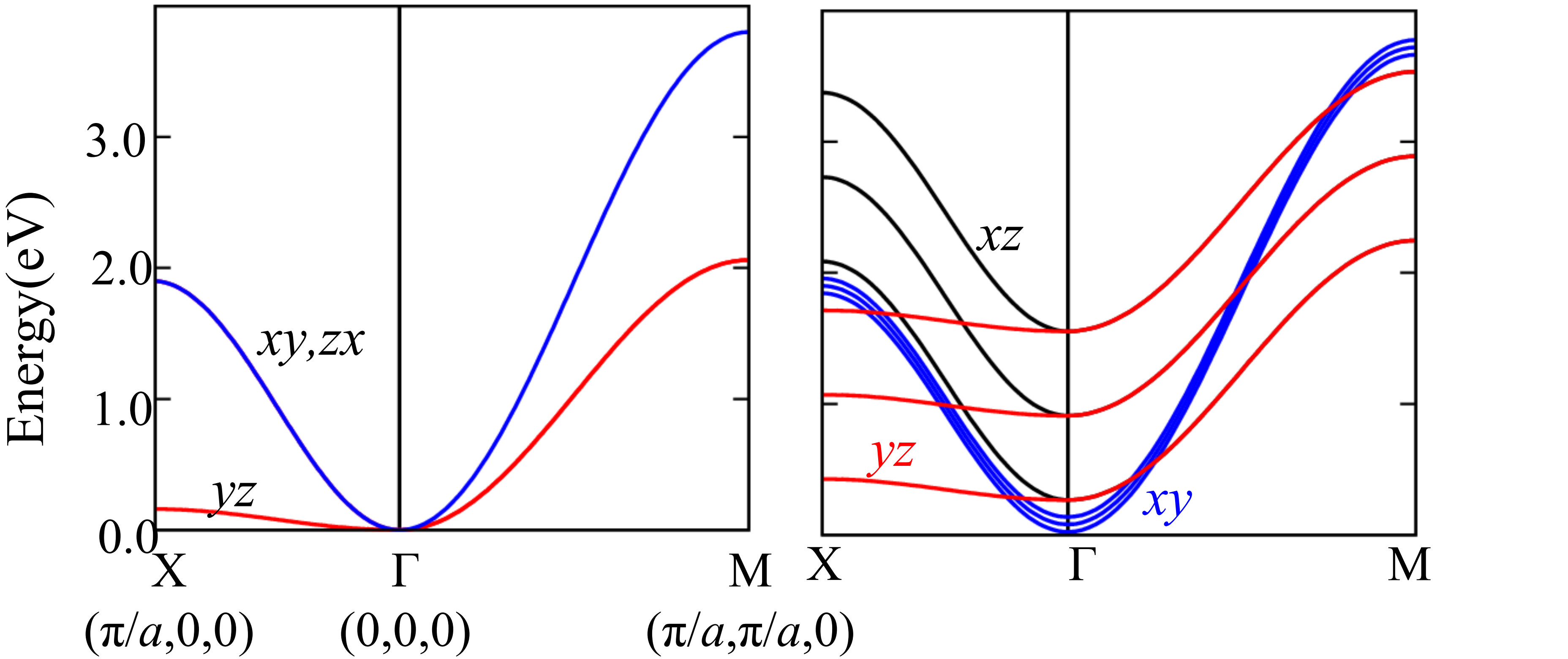


- Nearest neighbor hopping

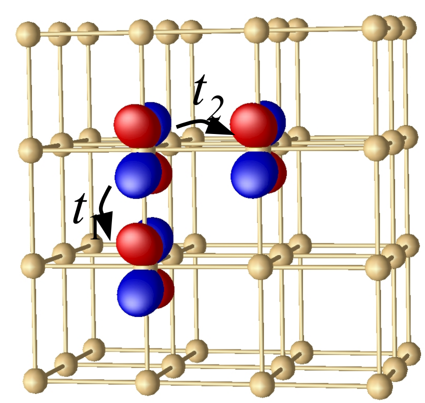
t_1=-0.455eV

t_2=-0.040eV

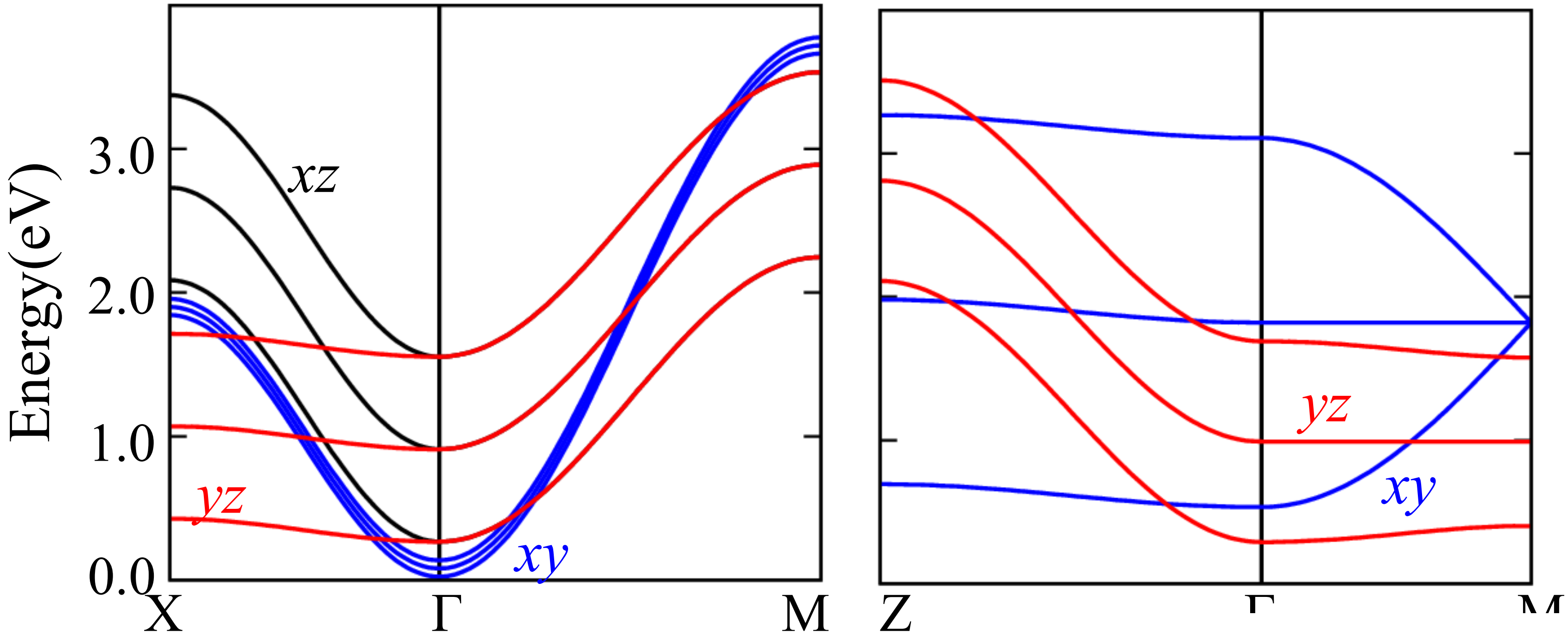
Quantum Well states along (001)



- two light bands *xy*, *zx*, t_1
  one heavy bands *yz*, t_2
- Orbital-selective quantum well states, with <u>constant effective mass</u>

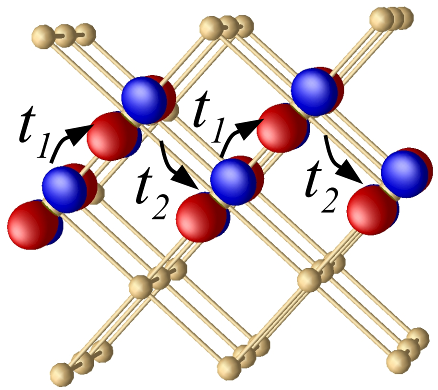


Quantum Well states along (110) are different



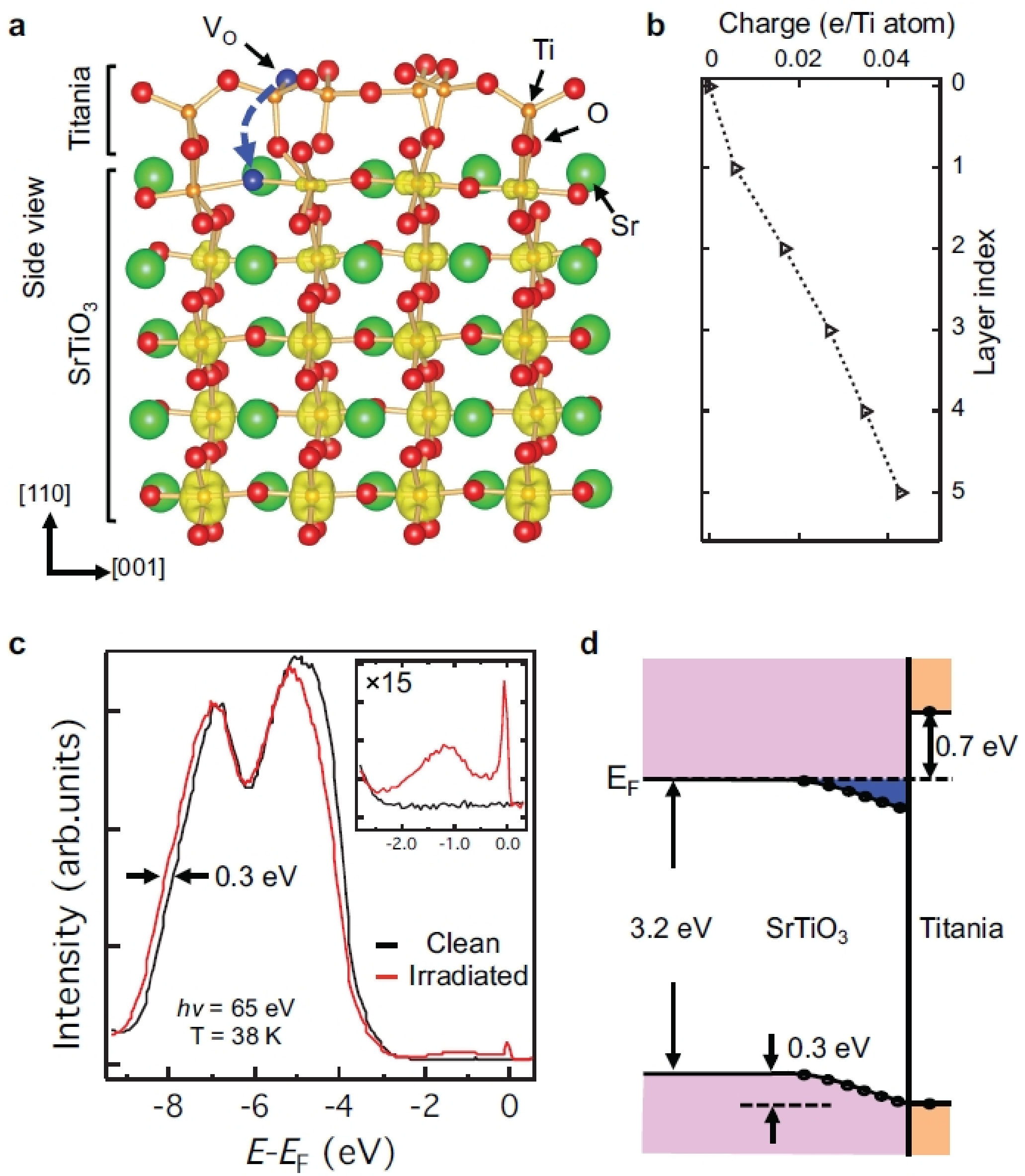
- Effective mass: $\underbrace{\frac{2t_1t_2}{(t_1+t_2)}}_{\text{Anisotropic hopping}}\cos(\underbrace{\frac{\pi n}{N+1}}_{\text{Quantization}})$

Anisotropic hopping   Quantization

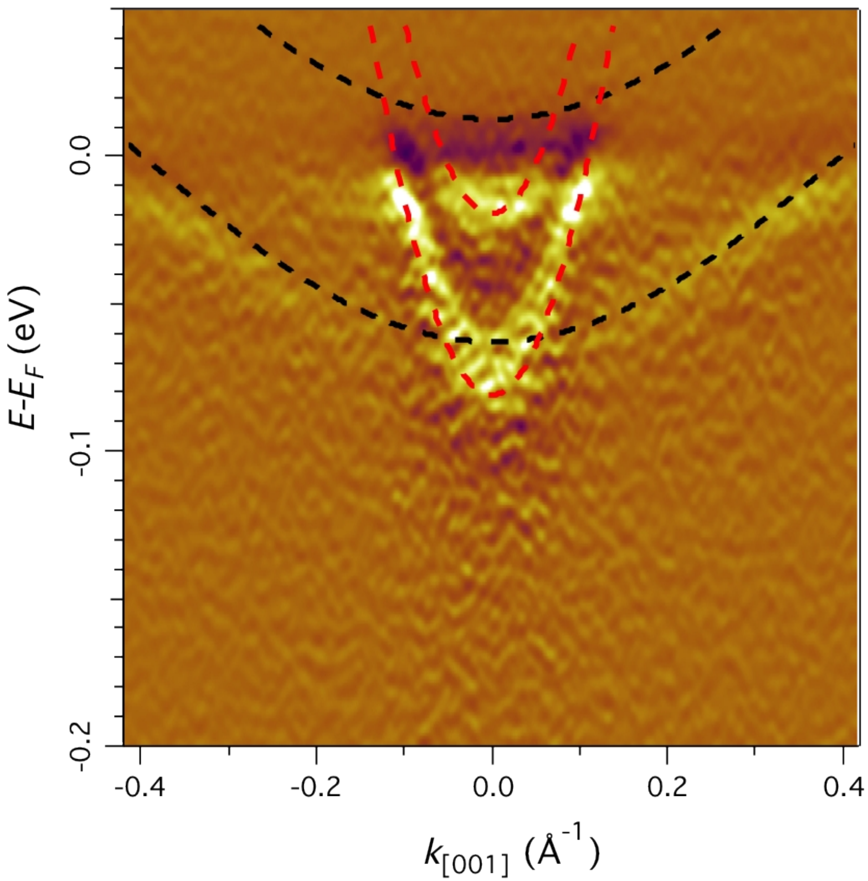


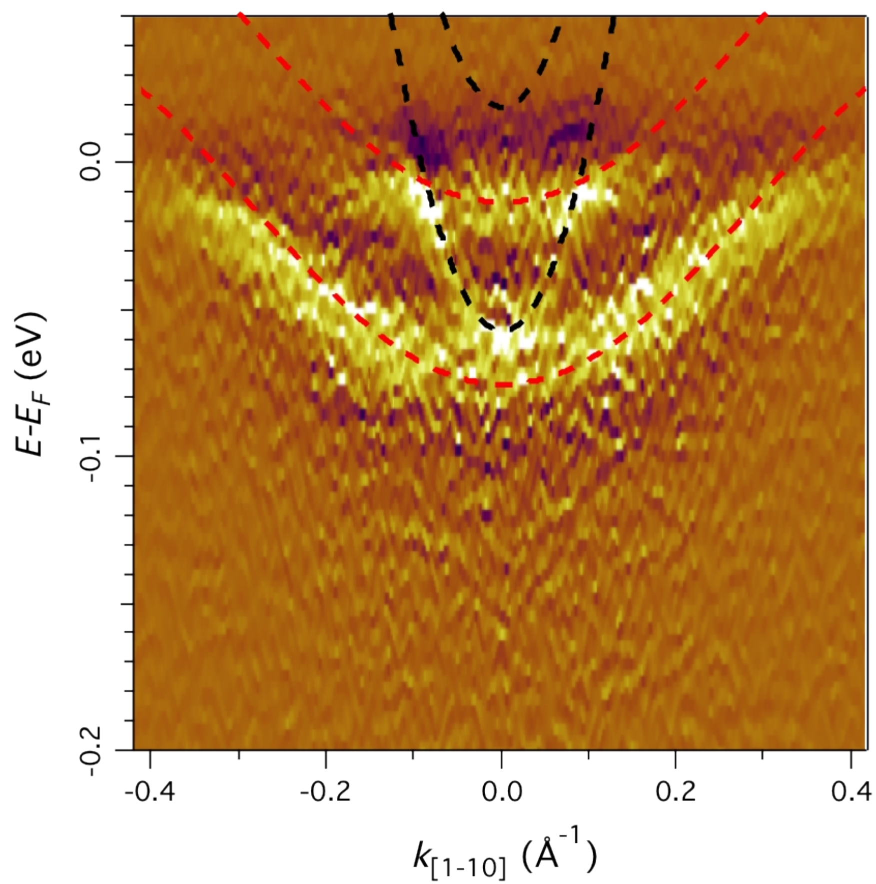
- Semi-heavy band, $2t_2$, when $N \gg n$

$SrTiO_3$ (110) surface



“Semi-heavy” band is observed





m_{xy}=8.25

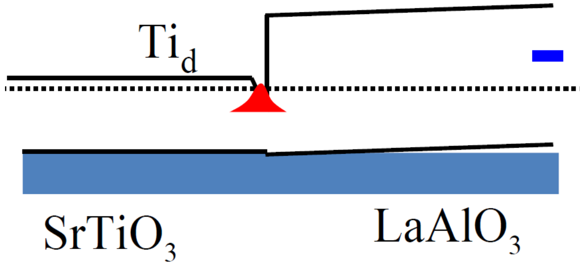
m_{yz}=0.60

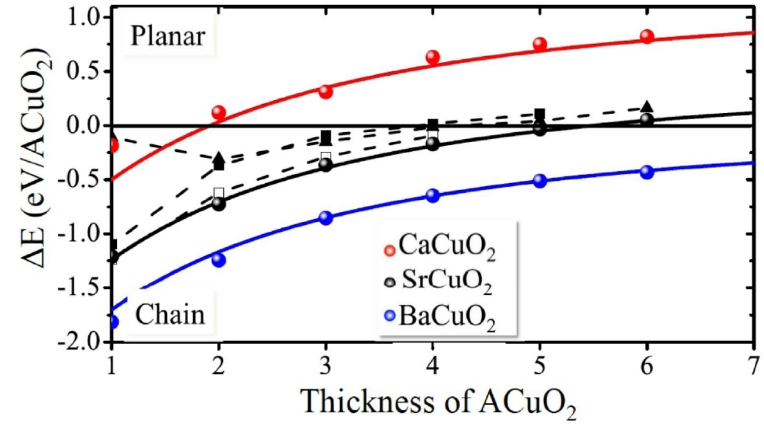
m_{yz}=4.69

m_{xy}=0.60

Conclusion: origins and properties of the 2DEG at $LaAlO_3/SrTiO_3$

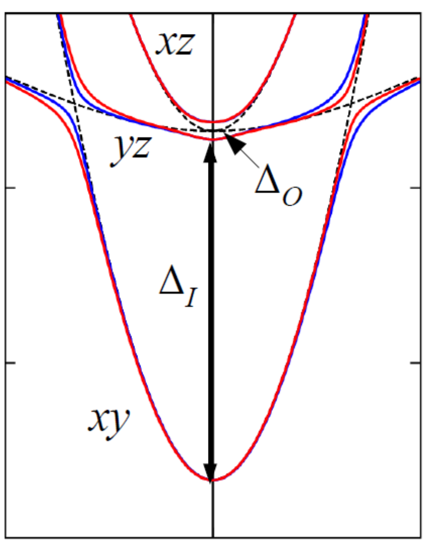
Origin: Polarity-induced oxygen vacancies



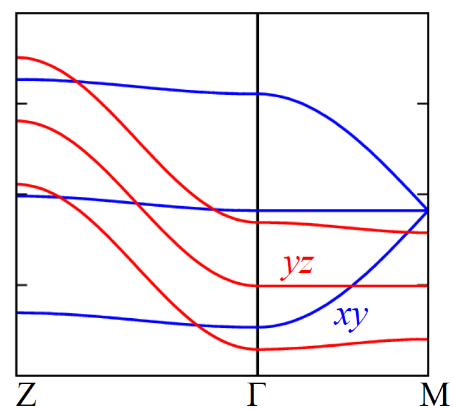


Properties:

spin-orbit coupling

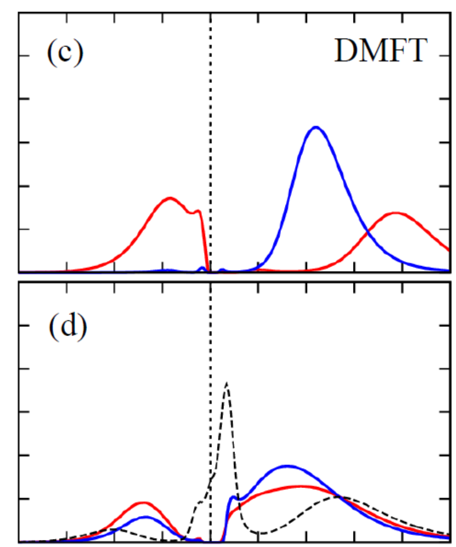


(110) is different



$$\frac{2t_1t_2}{(t_1+t_2)}\cos\left(\frac{\pi n}{N+1}\right)$$

Orbital polarized Mott insulator



Quantum well states in SVO thin film:Nearly Free Electron picture

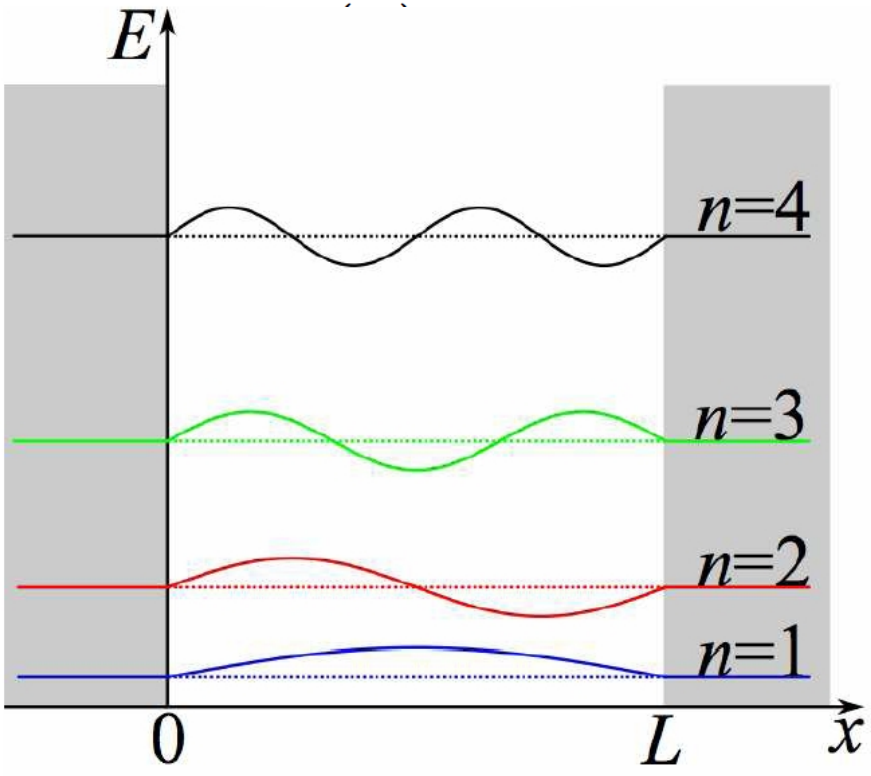
L=Na

(N thickness of SVO; a lattice constant)

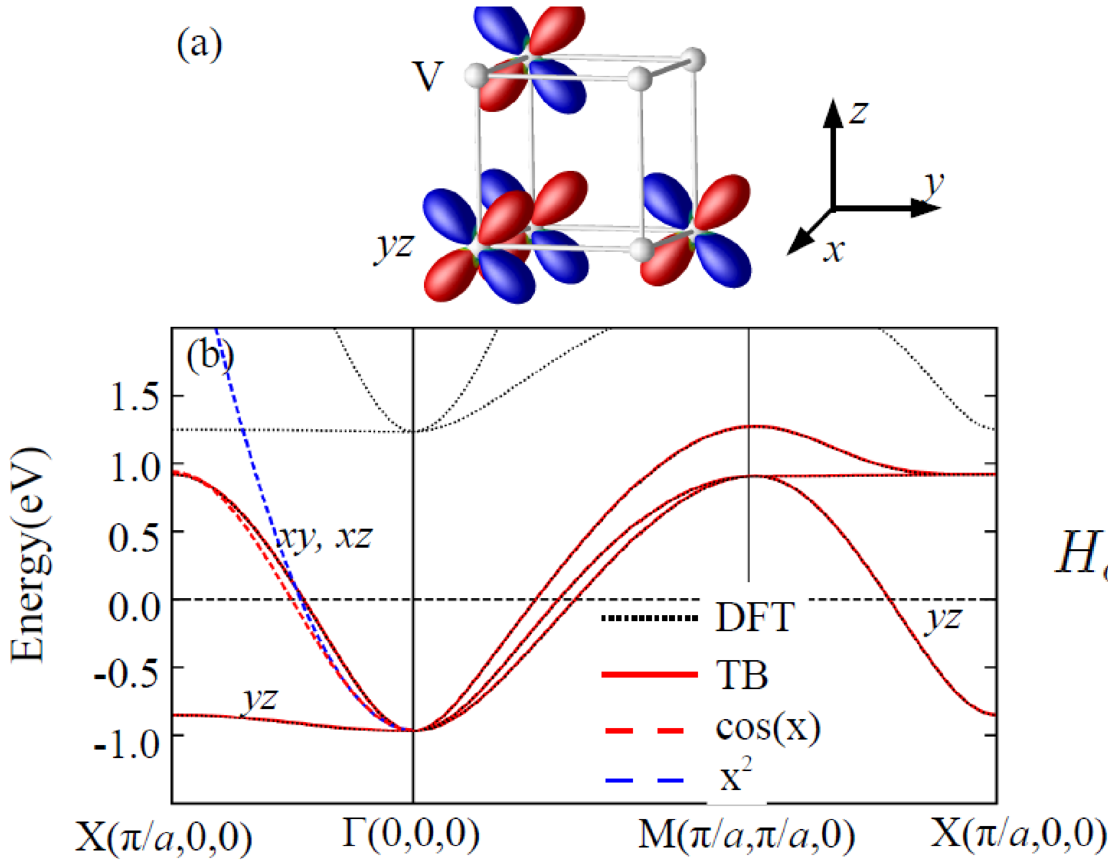
$\psi(0)=\psi(L)=0$

$$\frac{\hbar^2 k^2}{2m^*}$$

$$\frac{\hbar^2 \pi^2 n^2}{2m^* N^2 a^2}$$



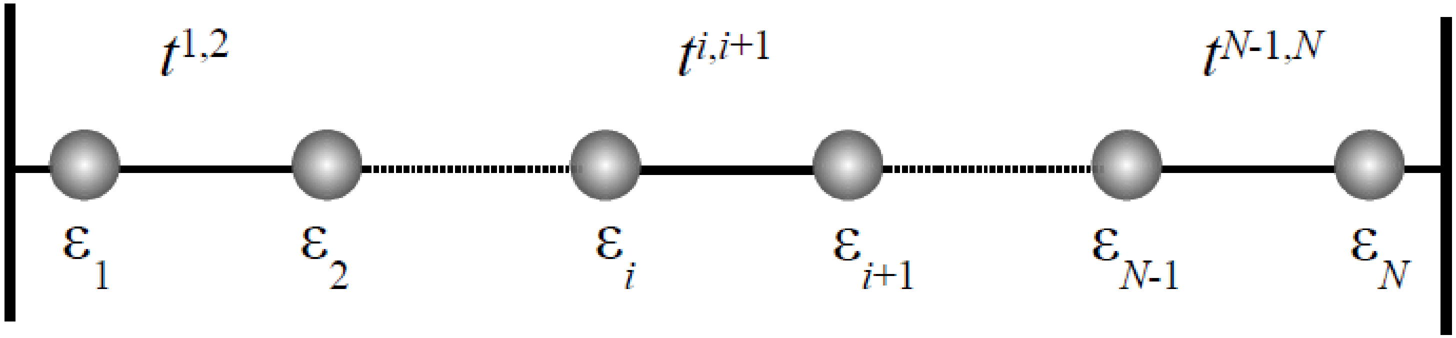
Why not NFE?



$$H_{\alpha\beta}(\vec{k}) = \sum_{\vec{R}} t_{\alpha\beta}(\vec{R}) e^{i\vec{k}\vec{R}}$$

$t_{\alpha\beta}(\vec{R})$	$\vec{R}$=(0,0,0)	(0,0,1)	(0,0,2)	(0,1,1)
xy,xy	0.579	-0.026	0.000	0.005
yz,yz	0.579	-0.259	0.007	-0.082
xz,xz	0.579	-0.259	0.007	0.005
xy,yz	0	0	0.000	0.009

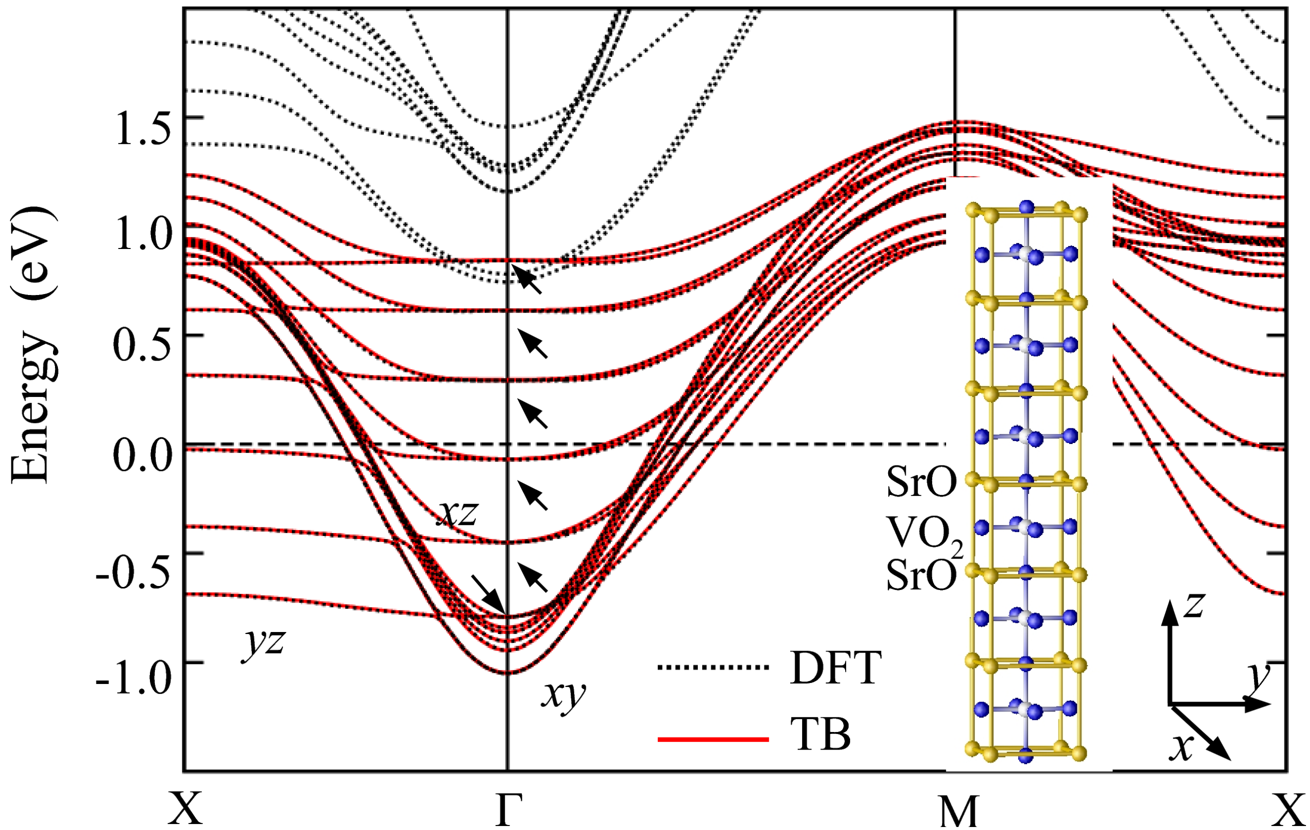
Tight binding description of Geometric confinement



$$\begin{pmatrix} \varepsilon & t & 0 & 0 & 0 & 0 \\ t & \varepsilon & t & 0 & 0 & 0 \\ 0 & t & \varepsilon & t & 0 & 0 \\ 0 & 0 & \dots & \dots & t & 0 \\ 0 & 0 & 0 & t & \varepsilon & t \\ 0 & 0 & 0 & 0 & t & \varepsilon \end{pmatrix}$$

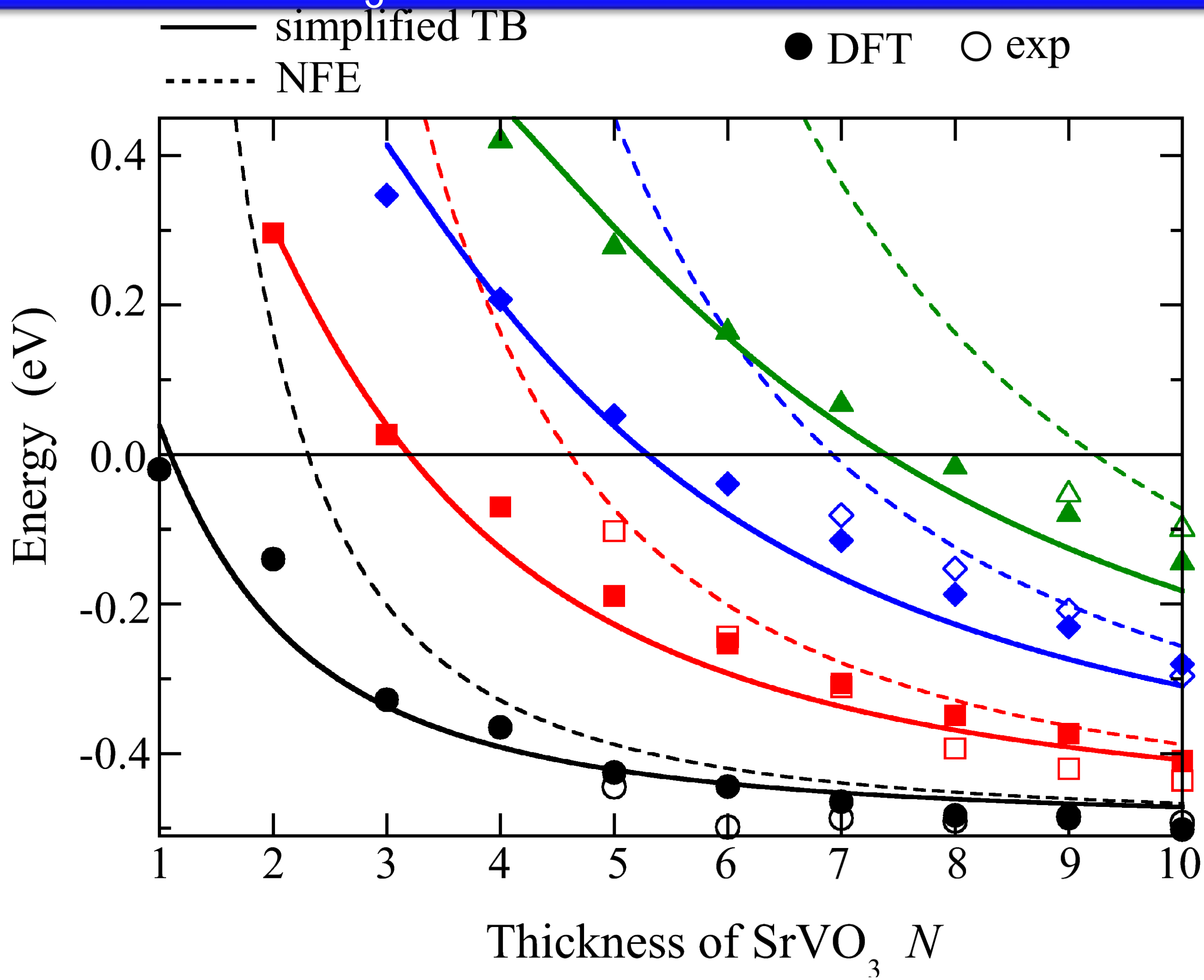
$$\frac{\hbar^2 \pi^2 n^2}{2m^* N^2 a^2} \longrightarrow \varepsilon + 2t\cos\left(\frac{\pi n}{N+1}\right)$$

$SrVO_3$ thin films: Quantum well states



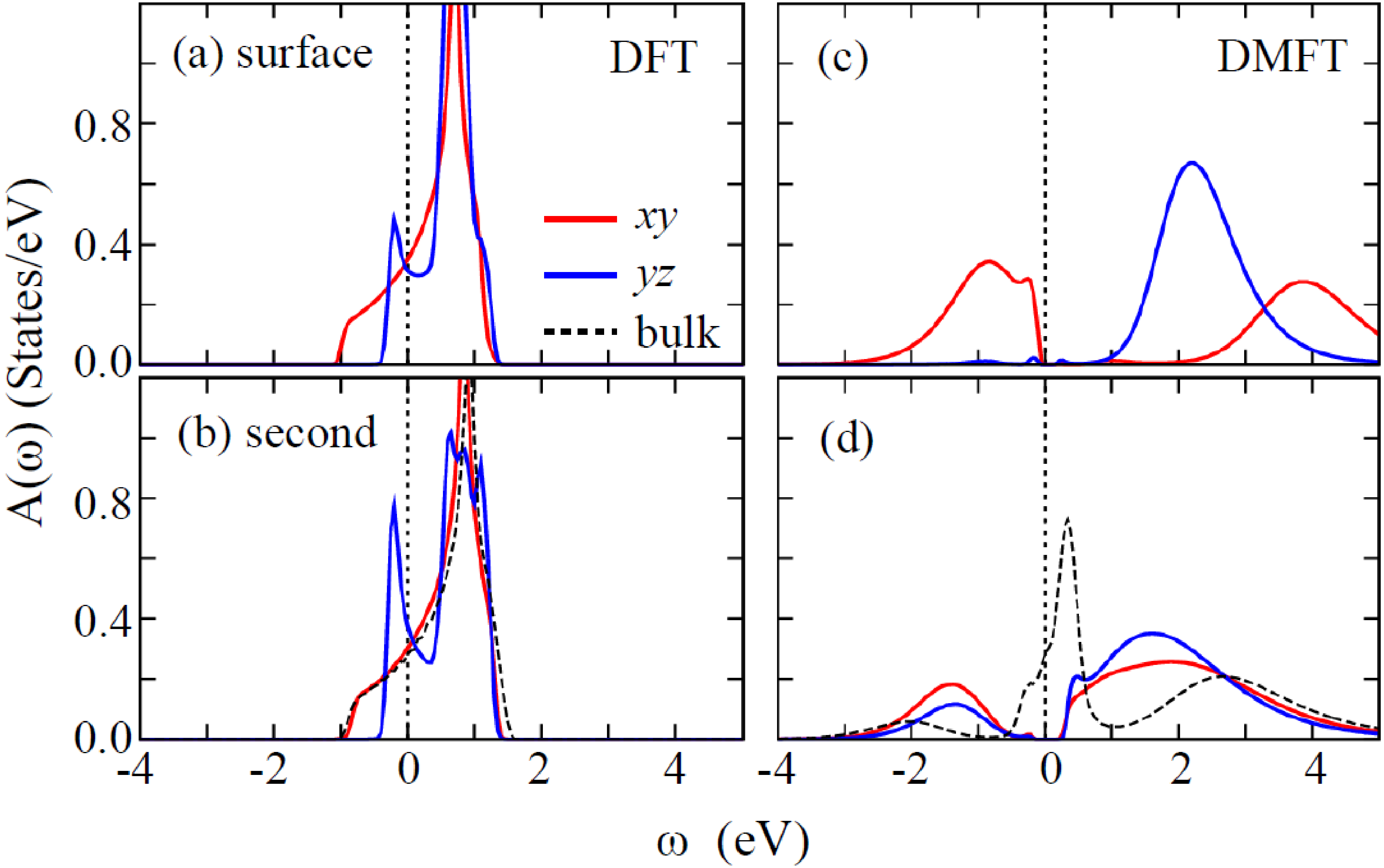
	yz	xy	yz along z	yz along y	xy along y
1st V	0.508	0.436	0	-0.224	-0.260
2nd V	0.599	0.594	-0.242	-0.262	-0.259
3rd V	0.584	0.583	-0.255	-0.258	-0.259

SrVO$_3$ thin films: correlation → Z



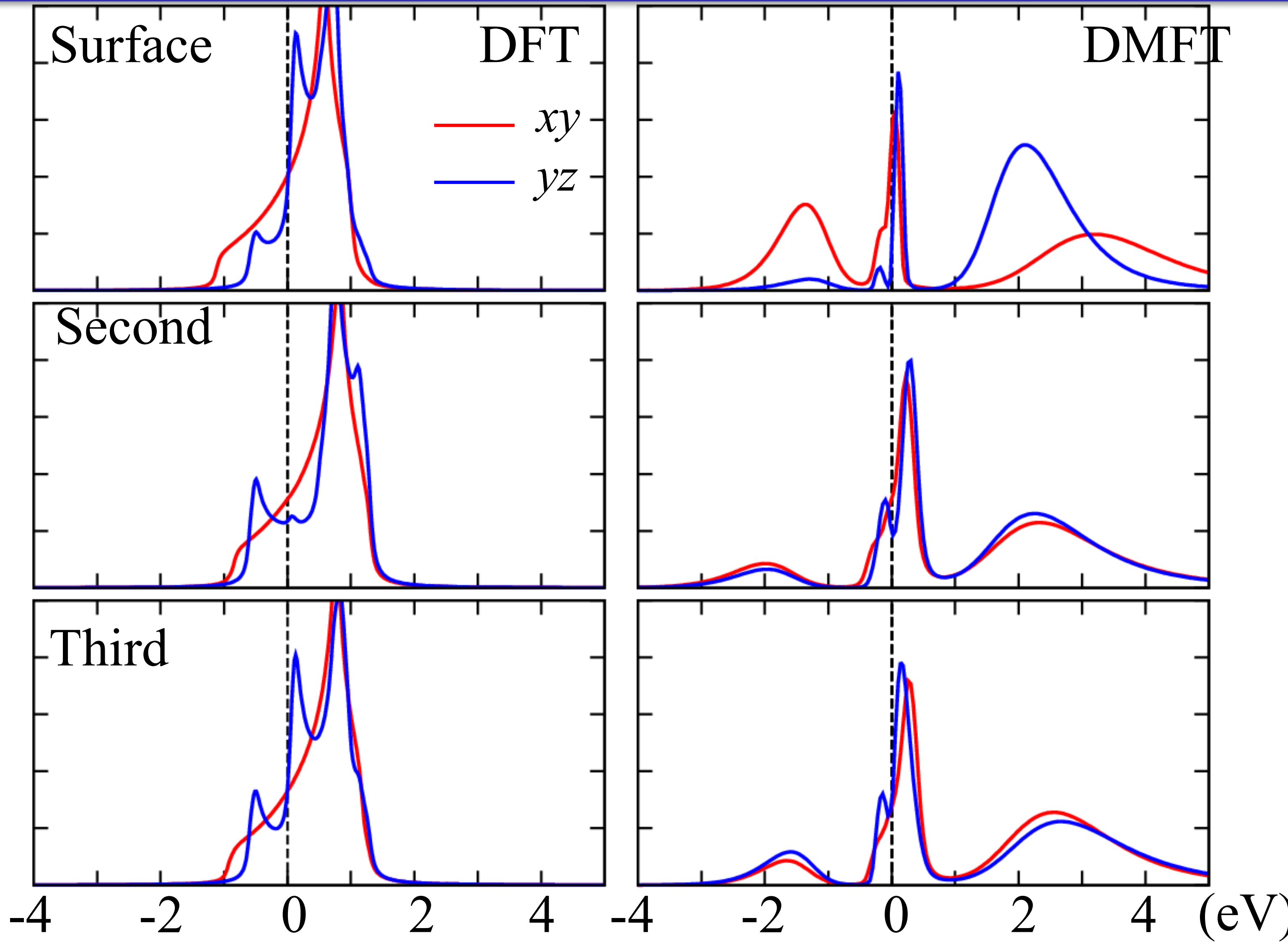
- Quantum confinement in perovskite oxide heterostructures: Tight binding instead of a nearly free electron picture
- Correlation effect : DFT+ Dynamical Mean Field Theory (DMFT)

Insulating state in SVO thin films (N=2) grown on STO substrate



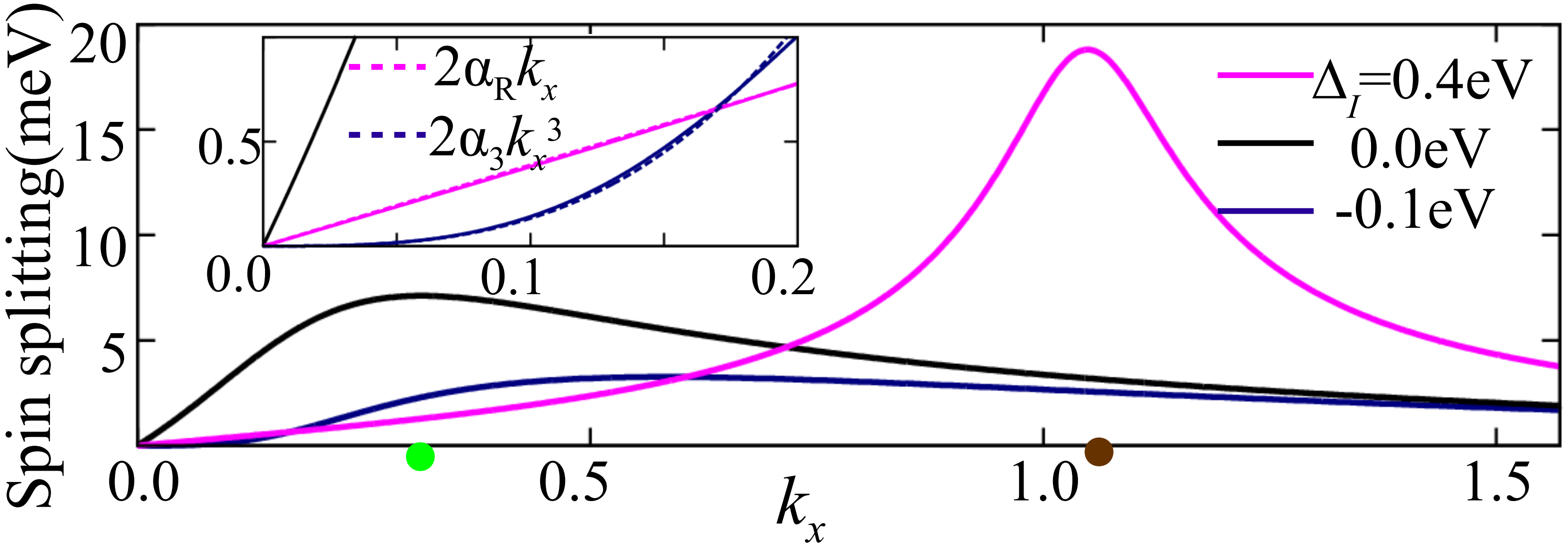
- *yz* orbital is narrowed, but the energy of *xy* is lower.
  Competition: bandwidth ~ orbital splitting
- Surface(Second) layer, strong(weak) orbital polarization.

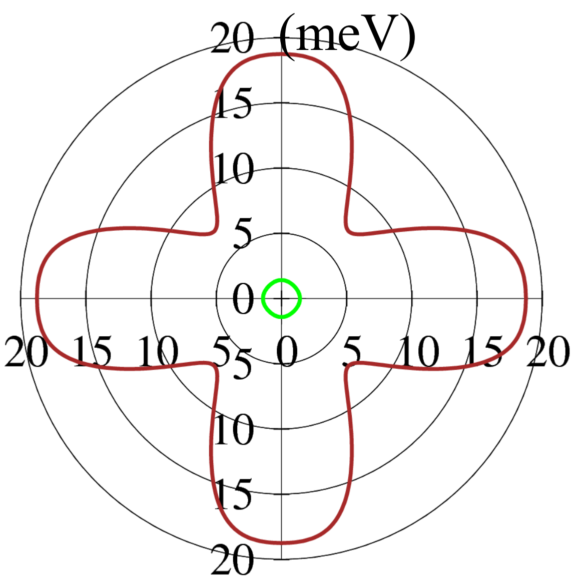
Metallic state in SVO thin films (*N*=3) grown on STO substrate



- The lower Hubbard band of the surface layer: enhanced, shifted, and orbital polarized.

spin splitting





$\Delta_R = 2\alpha_R k$

α_R = 0.76×10^{-2}eVÅ Δ_I=0.4eV

6.0×10^{-2}eVÅ Δ_I=0.0eV

1-5×10^{-2}eVÅ (exp)

$\Delta_R = 2\alpha_3 k^3$

α_3 = 4eVÅ^3

1-2eVÅ^3 (exp)

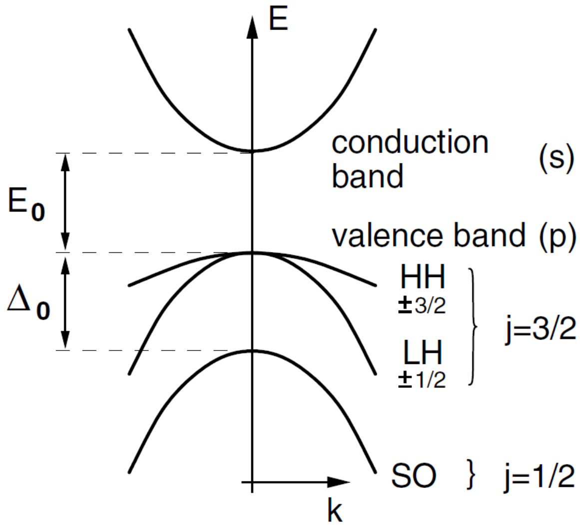
Anisotropic spin splitting->AMR (exp)?

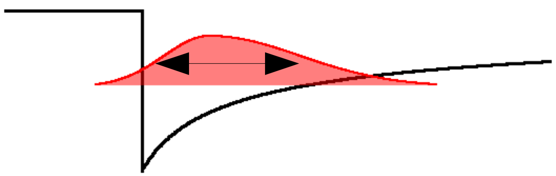
Comparison: semiconductor and oxide heterostructures

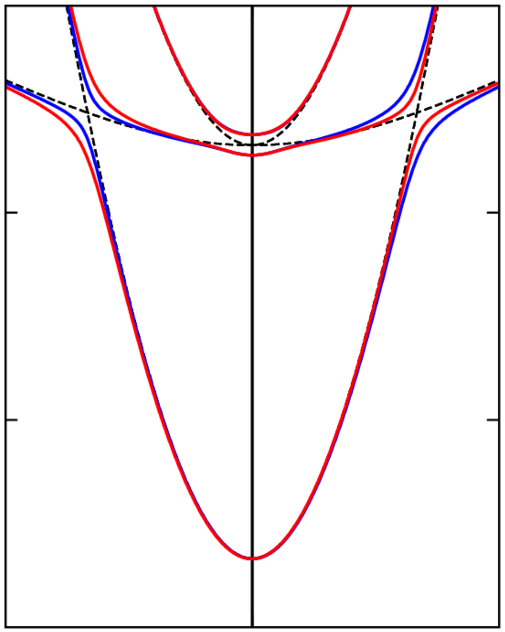
GaAs/$Al_xGa_{1-x}As$

10*nm* 2DEG 1*nm*

LAO/STO







single orbital Rashba
nearly free electron

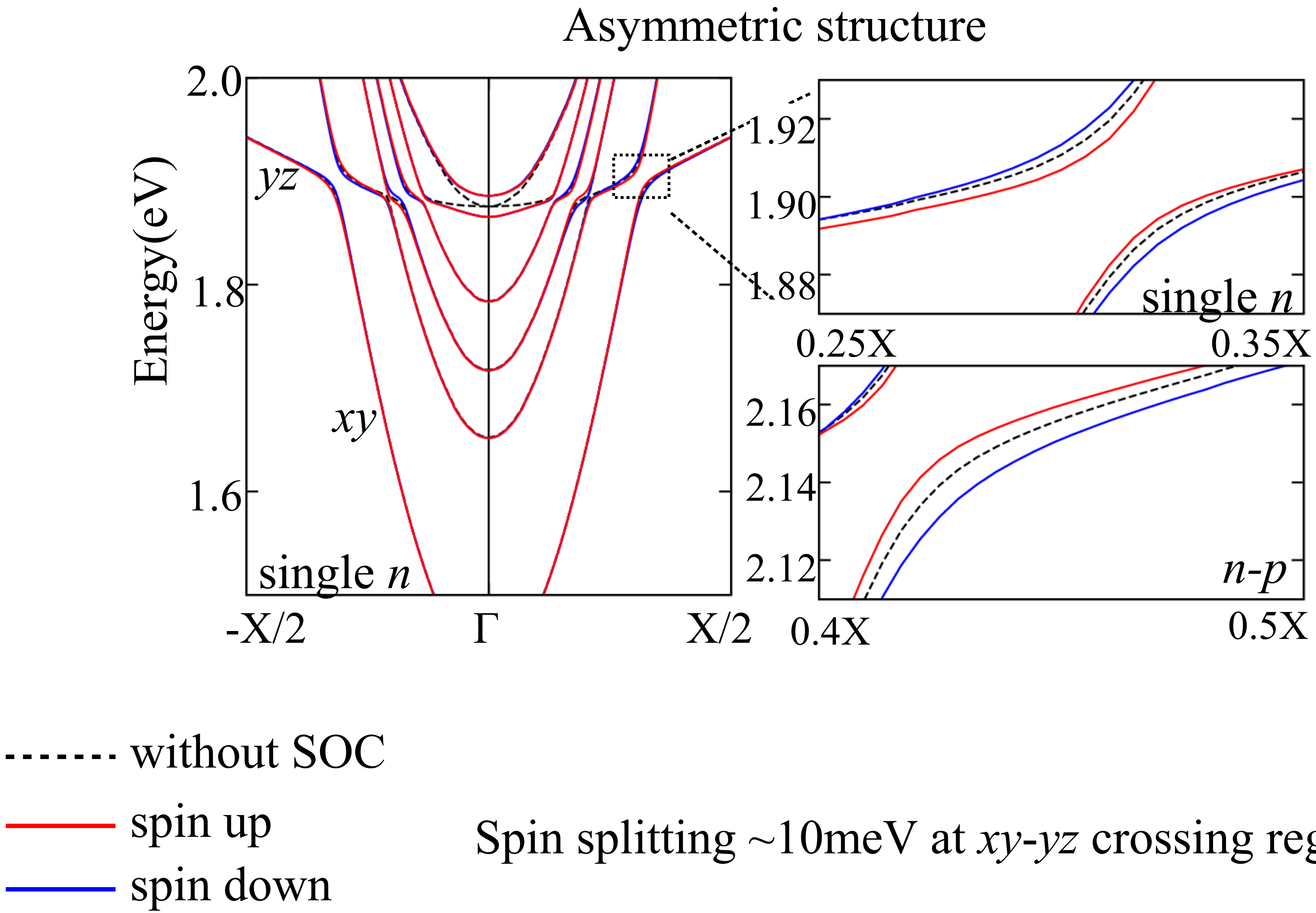
multi-orbital
magnetic, superconducting,
correlated, and spin-orbit coupling

fitting parameter or *kp* method

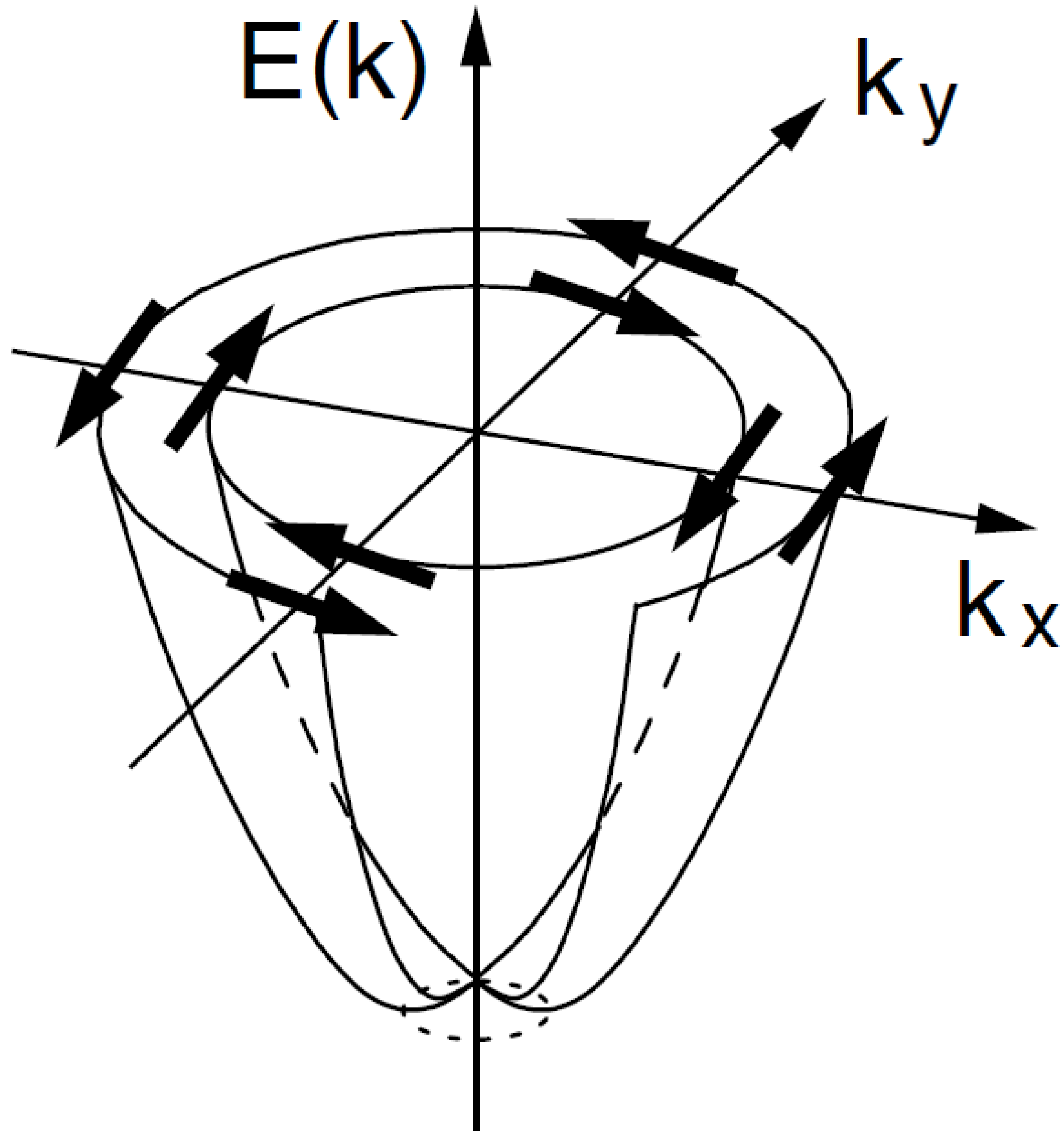
first principle tight-binding

Book "Spin–Orbit Coupling Effects in Two-Dimensional Electron and Hole Systems"
by Winkler (2003)

Spin splitting at LAO/STO interfaces and STO surfaces



Spin splitting ~10meV at *xy*-*yz* crossing region?


E(k)
k y
k x

DFT studies of Bulk properties of $ACuO_2$ (A=Ca, Sr, Ba)

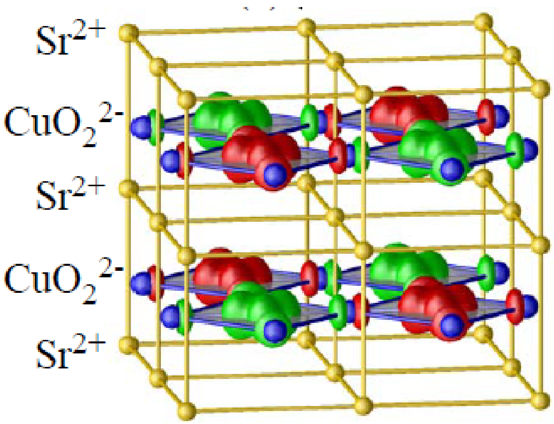
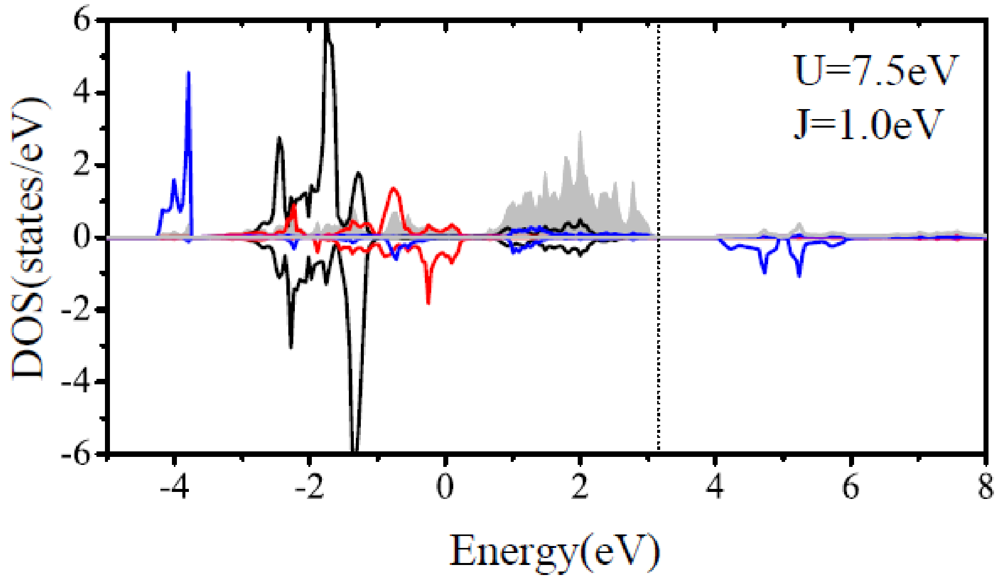
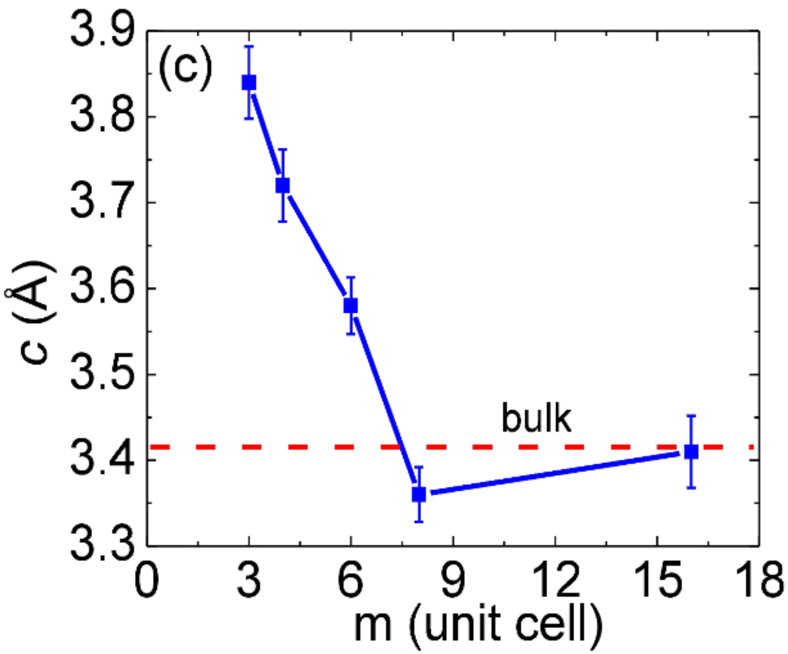


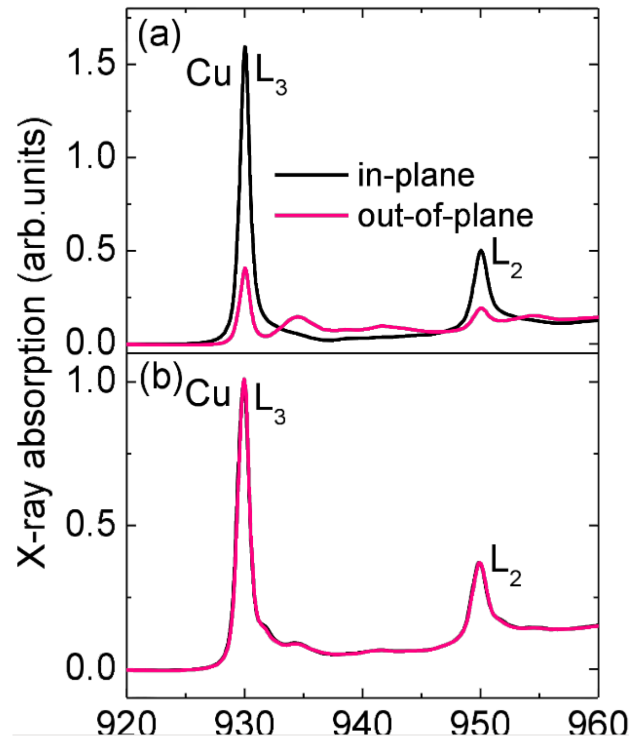
TABLE I. Lattice constants of perovskite $SrTiO_3$ and infinite layer copper oxides $ACuO_2$(A=Ca, Sr, Ba).

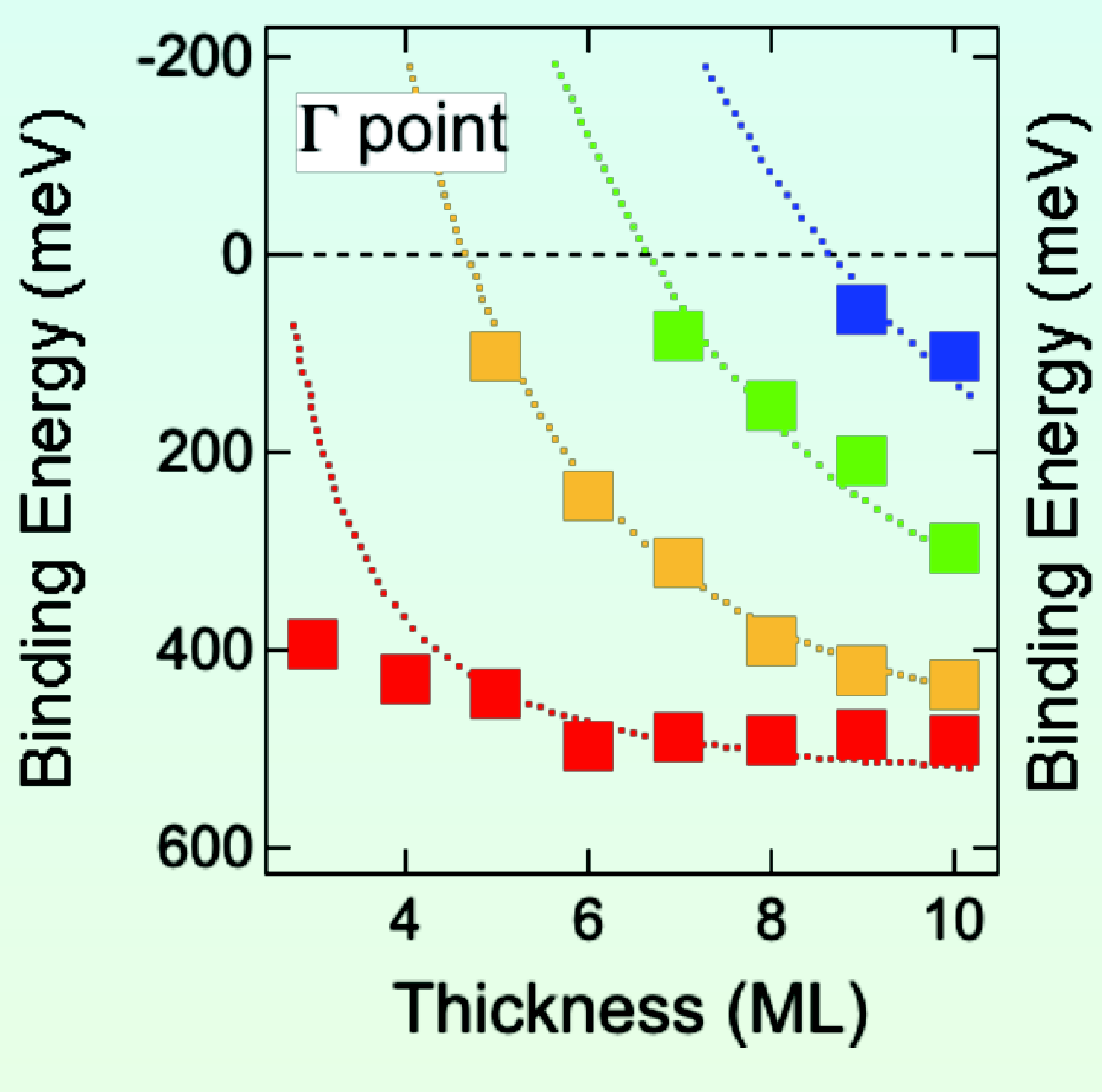
	a^{LDA}	c^{LDA}	a^{GGA}	c^{GGA}	a^{exp}	c^{exp}
$SrTiO_3$	3.87	3.87	3.95	3.95	3.905	3.905
$CaCuO_2$	3.77	3.08	3.87	3.20	3.853 [a]	3.177 [a]
$SrCuO_2$	3.84	3.38	3.95	3.47	3.926 [b]	3.432 [b]
$BaCuO_2$	3.92	3.68	4.03	3.84		

- Lattice constant ***c*** is 10% smaller than ***a***;
- *dx^2-y^2 orbital*




(c)
bulk
c (Å)
m (unit cell)
3.9
3.8
3.7
3.6
3.5
3.4
3.3
0
3
6
9
12
15
18


(a)
Cu L3
L2
in-plane
out-of-plane
(b)
Cu L3
L2
X-ray absorption (arb.units)
1.5
1.0
0.5
0.0
920
930
940
950
960



Γ point
Binding Energy (meV)
-200
0
200
400
600
4
6
8
10
Thickness (ML)
Binding Energy (meV)

Oxide Interfaces—An Opportunity for Electronics

J. Mannhart* and D. G. Schlom*

	GaAs - $Al_xGa_{1-x}As$	$LaAlO_3$ - $SrTiO_3$
Carrier density *n* (without gate field)	several 10^{10} - several $10^{11}/cm^2$	several 10^{13} /cm²
Sheet resistance ρ (*H*=0)	order of 10-100 Ω/□ (low *T*, samples with high-*μ*)	~ 200 Ω/□ (4.2 K) ~ 20 kΩ/□ (300 K)
Thickness *d*	order of 10 nm	~ 10 nm (4.2 K) ≲ 4 nm, possibly 0.4 nm (300 K)
Equivalent volume carrier concentration	order of 10^{17} /cm³	order of 10^{20} /cm³
Typical thicknesses of the host layers in heterojunctions (*e.g.*, cap layers)	tens of nanometer	≥ **1.6 nm** $LaAlO_3$ (4 unit cells)
Hall mobility *μ*	≳ 10^7 cm²/Vs (4.2 K)	≲ 1000 cm²/Vs (4.2 K) ≲ 10 cm²/Vs (300 K)
Effective mass *m* of carriers at interface	$m_e \sim 0.07\ m_0$	$m_e \sim 3\ m_0$
Mean scattering time τ, mean free path	100 psec, order of 100 μm	psec, tens of nm (4.2 K)
v_F	~ 3×10^7 cm/s	several 10^6 cm/s
Magnetic flux density inducing quantum Hall filling factor *v* =1	order of 10 T	order of 1000 T
Energy dependence of density of states *N*(*E*)	step function of 2-DEG (ideal case)	complex function reflecting the *N*(*E*)-dependence of the Ti-, La-, and O-ions

GaAs - $Al_xGa_{1-x}As$	$LaAlO_3$ - $SrTiO_3$
• two-dimensional electron gas (2-DEG); • quantum well induced by band bending; • 2D-subbands of nominally free electrons	• two-dimensional electronic liquid (2-DEL); • metal-insulator transition at a few 10^{12} /cm^2; quantum well structure as shown in Fig. 4; • 2D-subbands composed of ionic orbital states with local character (*e.g.*, Ti 3*d*, La 5*d*, O 2*p*); • 2D-superconducting ground state; • strong spin-orbit coupling.

$$H^{yz}(k_z, k_M) = -4t_1 - 2t_2 + 2t_1 cos(k_z a) - 2(t_1^2 + t_2^2 + 2t_1 t_2 cos(k_M \sqrt{2} a))^{1/2} cos(\frac{\pi n}{N+1})$$

$$H^{xy}(k_z, k_M) = -4t_1 - 2t_2 + 2t_2 cos(k_z a) - 2(t_1^2 + t_1^2 + 2t_1 t_1 cos(k_M \sqrt{2} a))^{1/2} cos(\frac{\pi n}{N+1})$$