Quantum chemistry simulations of $LaAlO_3$/ $SrTiO_3$ interface electronic structure

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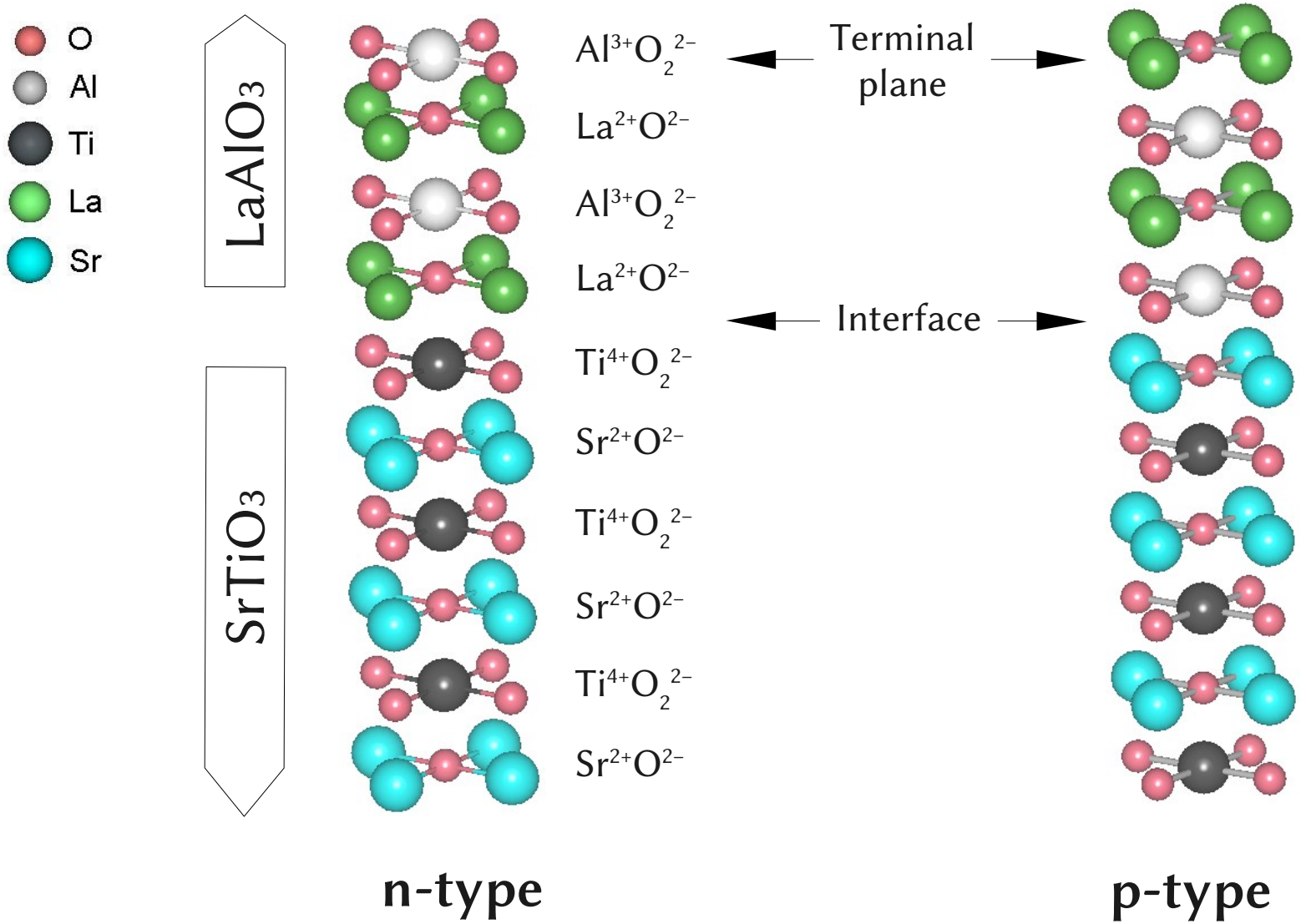
Outline

- Introduction and motivation.
- Thermodynamic stability of $LaAlO_3$ (001) surfaces.
- $LaAlO_3/SrTiO_3$: Electronic structure and charge redistribution.
- Summary and conclusions.

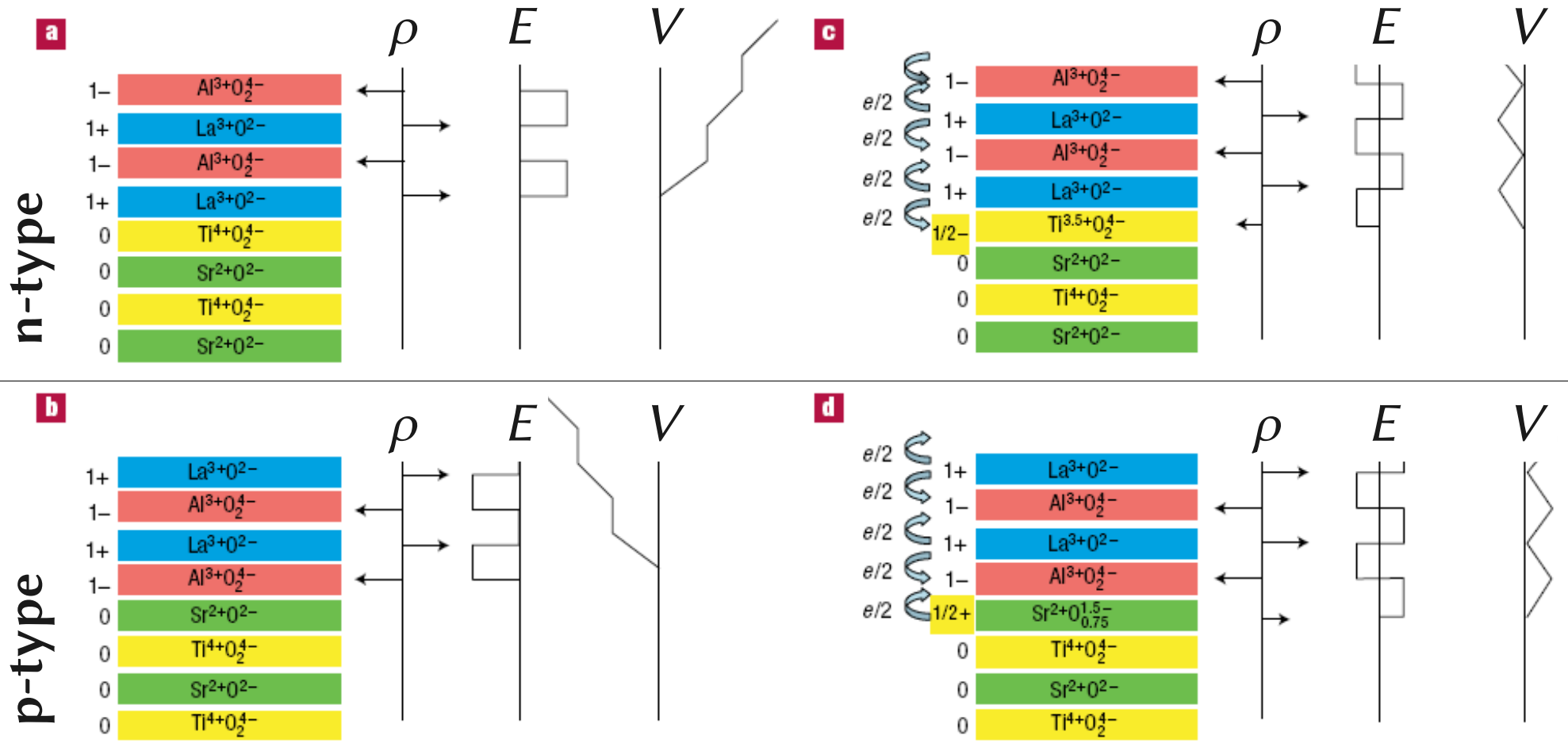
Introduction and Motivation

- Depending on the preparation conditions, the system may be either **insulating** or highly **conducting**!
- In this study we simulated **plane-by-plane** epitaxial **growth** of $LaAlO_3$ (001) films atop $SrTiO_3$ (001) substrate. Calculated charge redistribution in the studied structures allows us to provide deeper insight into the origin of their conductivity.
- Calculated thermodynamic stability of $LaAlO_3$ (001) surfaces offers a possible explanation of insulating behaviour for p-type interfaces.

Structure and types of the interface



The polar catastrophe



Nakagawa, N., *et al.* Why some interfaces cannot be sharp. *Nature Mat.* 5, 25

ρ – charge density in each layer
E – electric field projection on z-axis
V – plane potential with respect to the first LAO plane

Used approaches

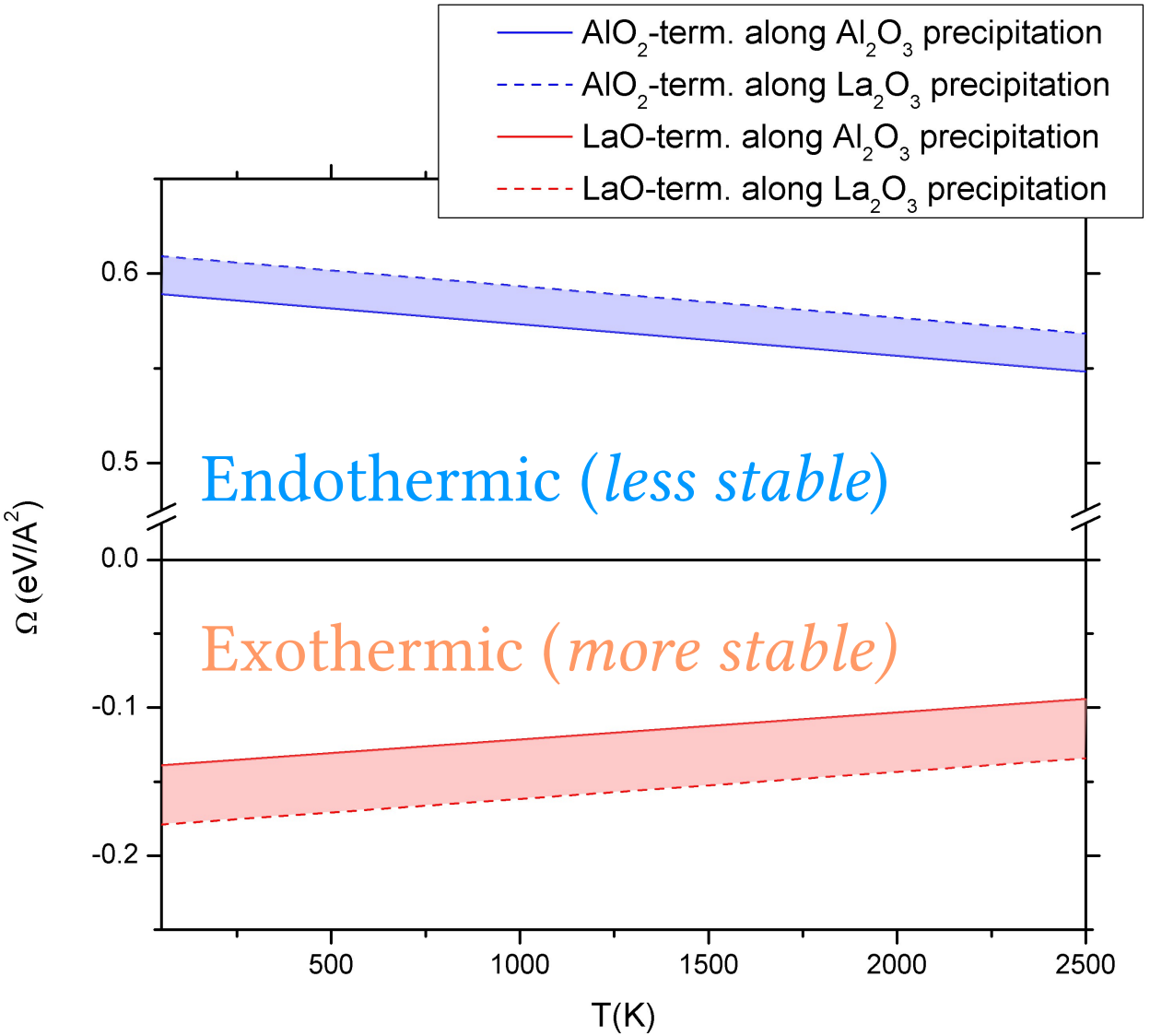
Approach	DFT LCAO	DFT Plane Waves
Functional	Hybrid B3PW	GGA PW91
Comp. code	CRYSTAL09	VASP5

Pre-calculations

Optical band gap as calculated by different Hamiltonians

	LDA	PW GGA	B3PW	HF	Exp
$SrTiO_3$	2.04	1.77	3.63	11.97	3.25
$LaAlO_3$		3.18	6.15		6.5
$BaTiO_3$	1.92	1.84	3.50	11.73	3.2
$PbTiO_3$	1.40	1.56	2.87	10.01	3.4

Thermodynamics of LAO (001) surfaces

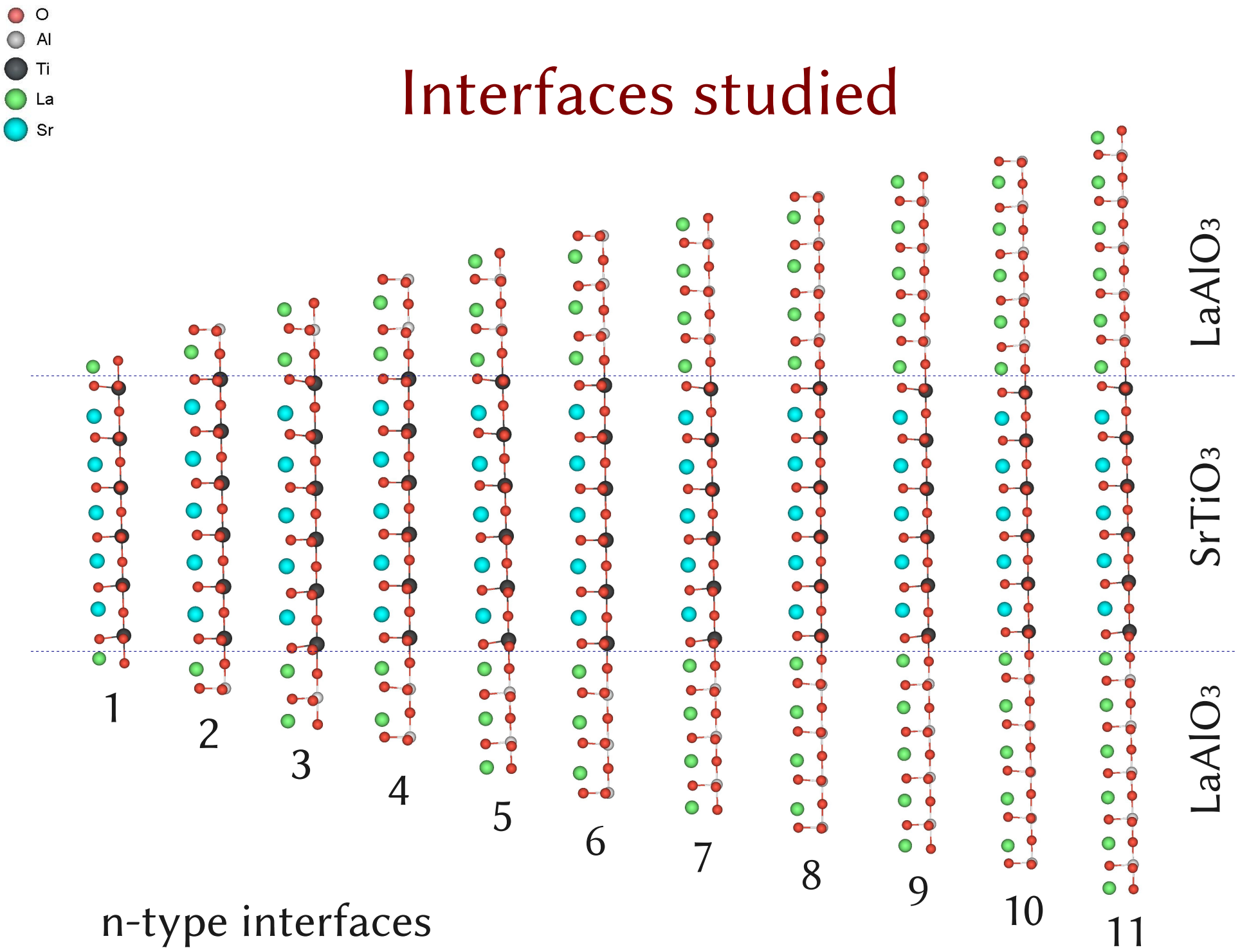


Thermodynamic grand potential as calculated by means of B3PW.

Picture is qualitatively the same for PW91-GGA functional

LaO termination is more favourable.

Interfaces studied

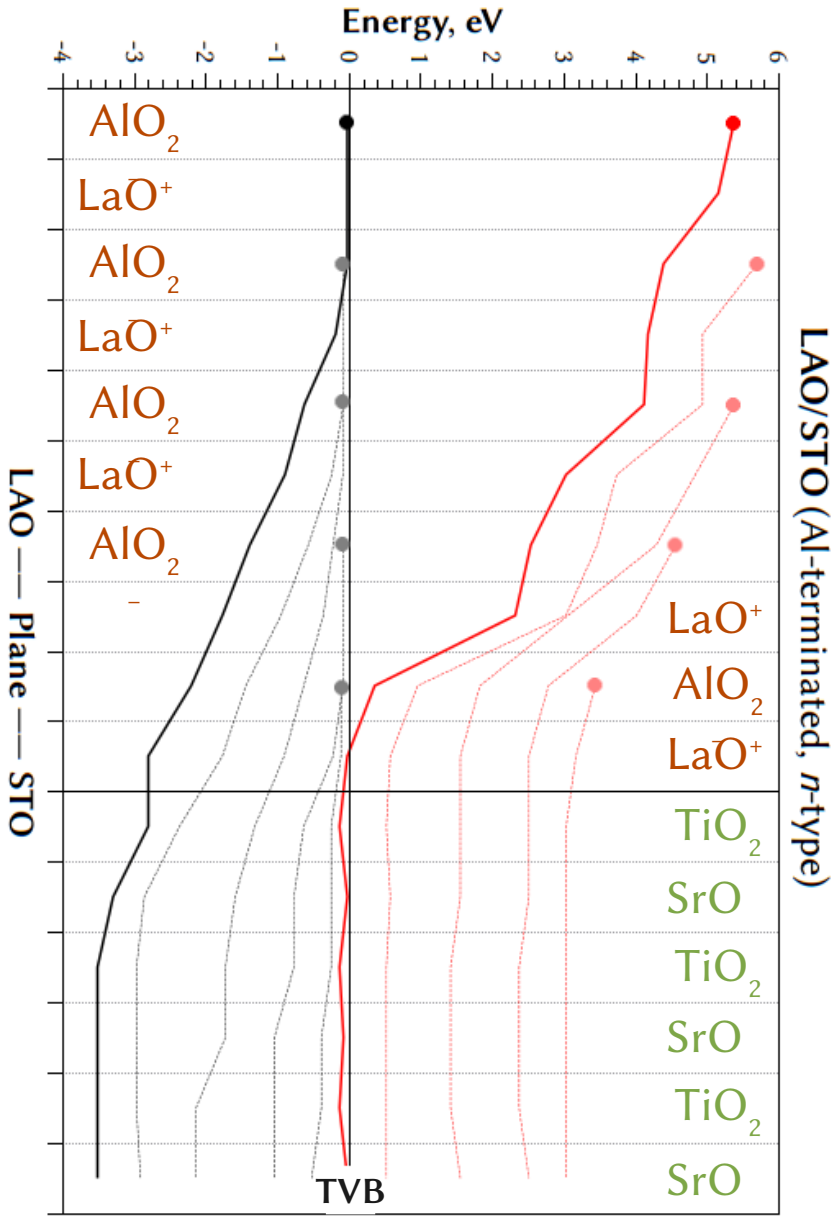


n-type interfaces

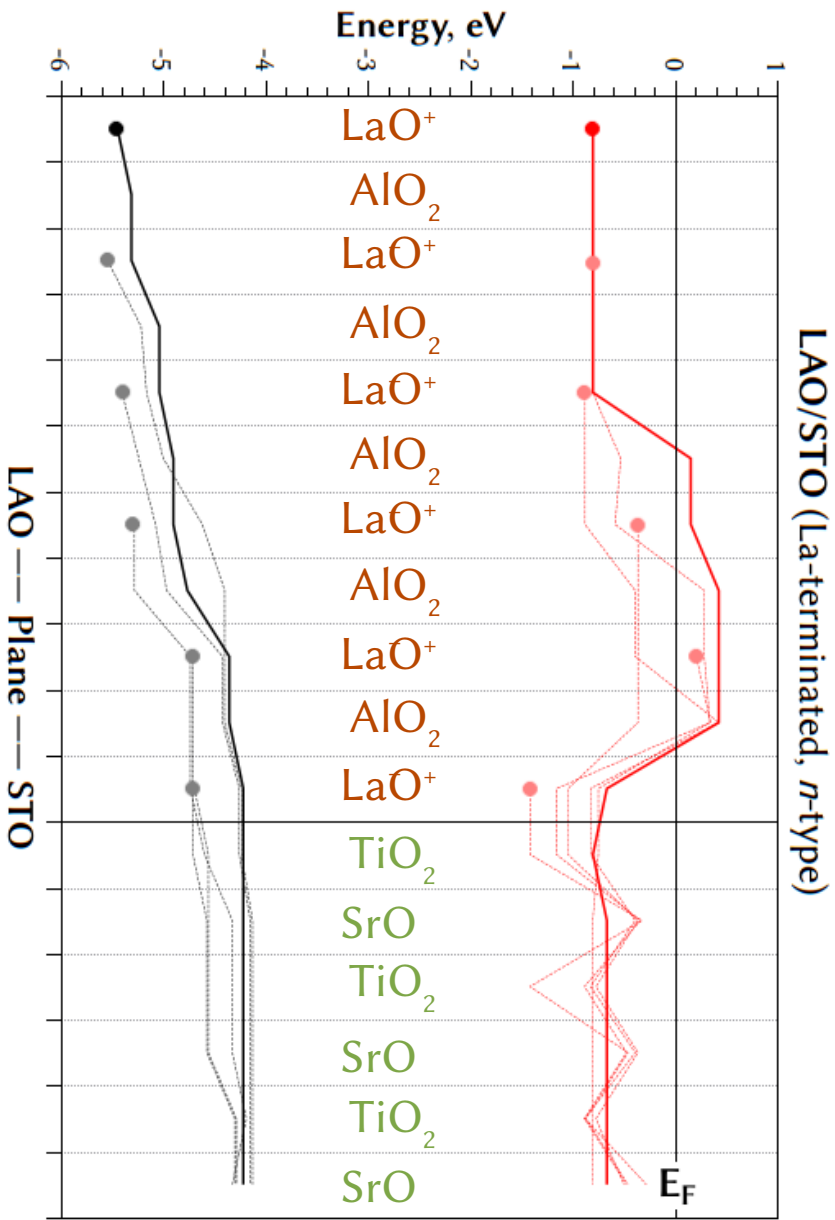
Conductance of the system *vs.* termination

No. of planes	**n-type**	CRYSTAL	VASP	**p-type**	CRYSTAL	VASP
	Termination	Gap, eV	Gap, eV	Termination	Gap, eV	Gap, eV
1	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.
2	AlO_2^-	3.65	1.41	LaO^+	4.00	1.60
3	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.
4	AlO_2^-	2.91	1.03	LaO^+	4.05	1.69
5	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.
6	AlO_2^-	1.96	0.40	LaO^+	4.05	1.51
7	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.
8	AlO_2^-	1.07	0.03	LaO^+	3.80	0.48
9	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.
10	AlO_2^-	**Cond.**	**Cond.**	LaO^+	2.92	0.25
11	LaO^+	Cond.	Cond.	AlO_2^-	Cond.	Cond.

n-Type interfaces: band edges

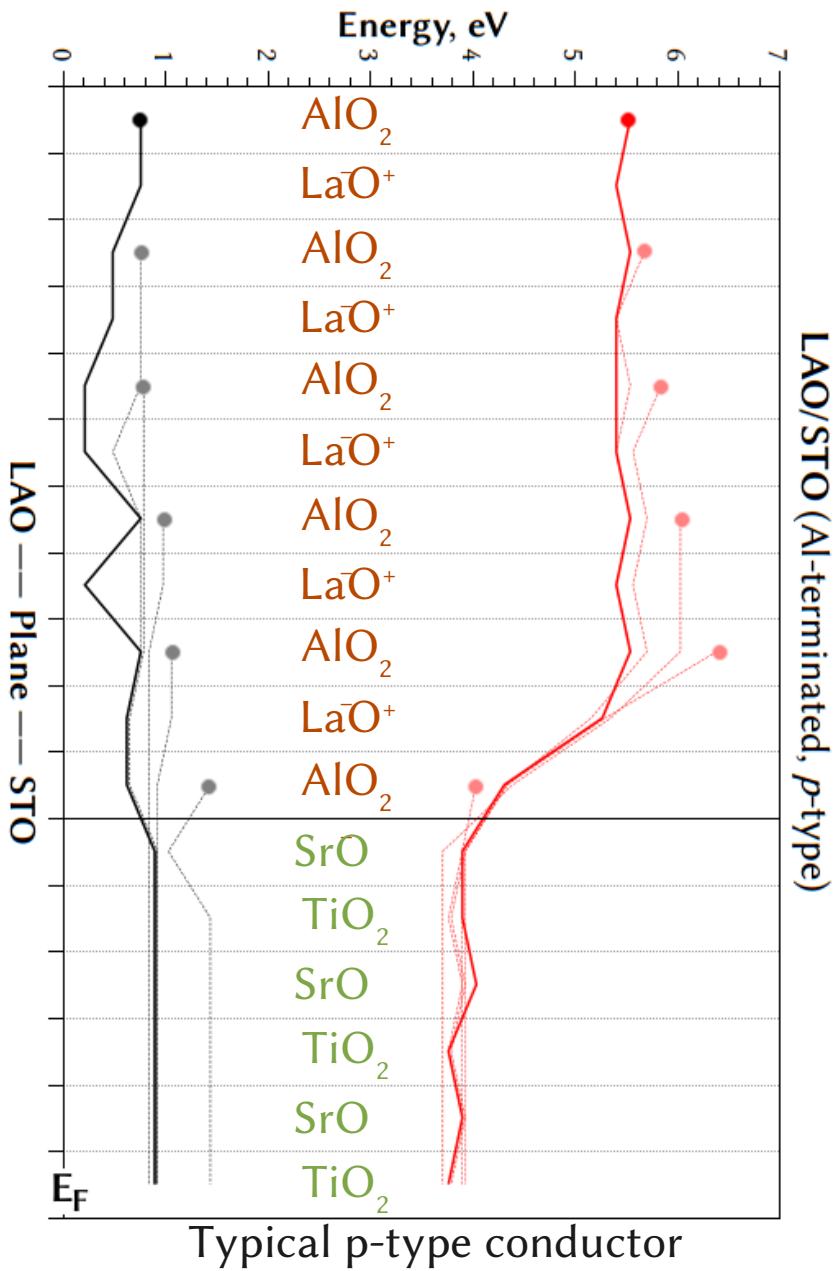


Conductance due to closing the gap

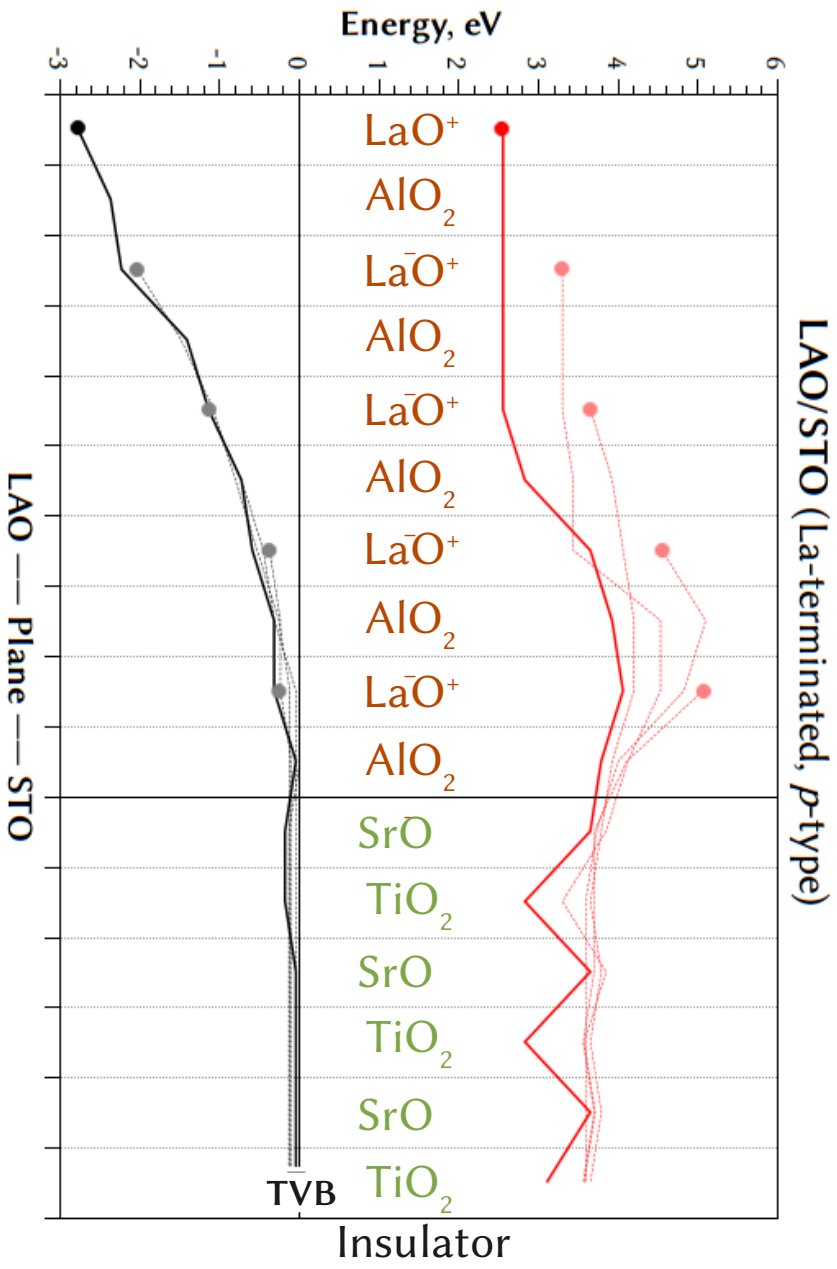


Typical n-type conductor

p-Type interfaces: band edges



Typical p-type conductor



Insulator

Electronic charge redistribution

n-Type			p-Type		
LaO^+		0.19	AlO_2^-		−0.28
AlO_2^-	0.26	−0.50	LaO^+	0.08	0.45
LaO^+	−0.44	0.45	AlO_2^-	−0.38	−0.38
AlO_2^-	0.44	−0.48	LaO^+	0.43	0.42
LaO^+	0.47	0.48	AlO_2^-	−0.39	−0.38
AlO_2^-	−0.46	−0.48	LaO^+	0.39	0.41
LaO^+	0.47	0.49	AlO_2^-	−0.38	−0.38
AlO_2^-	−0.46	−0.47	LaO^+	0.38	0.42
LaO^+	0.48	0.49	AlO_2^-	−0.38	−0.38
AlO_2^-	−0.47	−0.46	LaO^+	0.38	0.46
LaO^+	0.52	0.44	AlO_2^-	−0.42	−0.38
TiO_2	0.04	0.06	SrO	−0.02	−0.01
SrO	−0.05	−0.05	TiO_2	0.02	0.02
	Cond.	Cond.		Insul.	Cond.

Calculated Mulliken effective net charge with respect to bulk for the thickest interfaces explored

Summary and conclusion

- n-Type interfaces exhibit n-type conductance if terminated by LaO plane. If the structure is AlO_2-terminated, conductance appears only if the film is thicker than 5 u.c. in agreement with earlier studies.
- p-Type interfaces are insulators if LaO-terminated and p-type conductors otherwise.
- According to experiment p-Type interfaces are always insulating. This may occur due to the fact that LaO-terminated $LaAlO_3$ (001) surfaces are thermodynamically more stable.
- Charge redistribution shows that an excess of electrons or holes, giving rise to conductivity, is concentrated in the topmost surface layer.