HPC-Europa3 project – assessing the nature and role of band alignment of copper oxides heterostructures

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ARCHER2 webinar series
27/04/2022

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Prof Nicholas Harrison

HPC-Europa3 project – assessing the nature and role of band alignment of copper oxides heterostructures

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Dr Giuseppe Mallia

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HPC-Europa3 Transnational Access programme

- access to world-class HPC systems to academic and industrial researchers
- scientific collaboration with host researchers in any field
- technical support by the HPC centres
- travel and living expenses reimbursed

CINECA (Bologna - IT)

EPCC (Edinburgh - UK) 2021

BSC (Barcelona - SP)

HLRS (Stuttgart - DE)

SURFsara (Amsterdam - NL) 2020

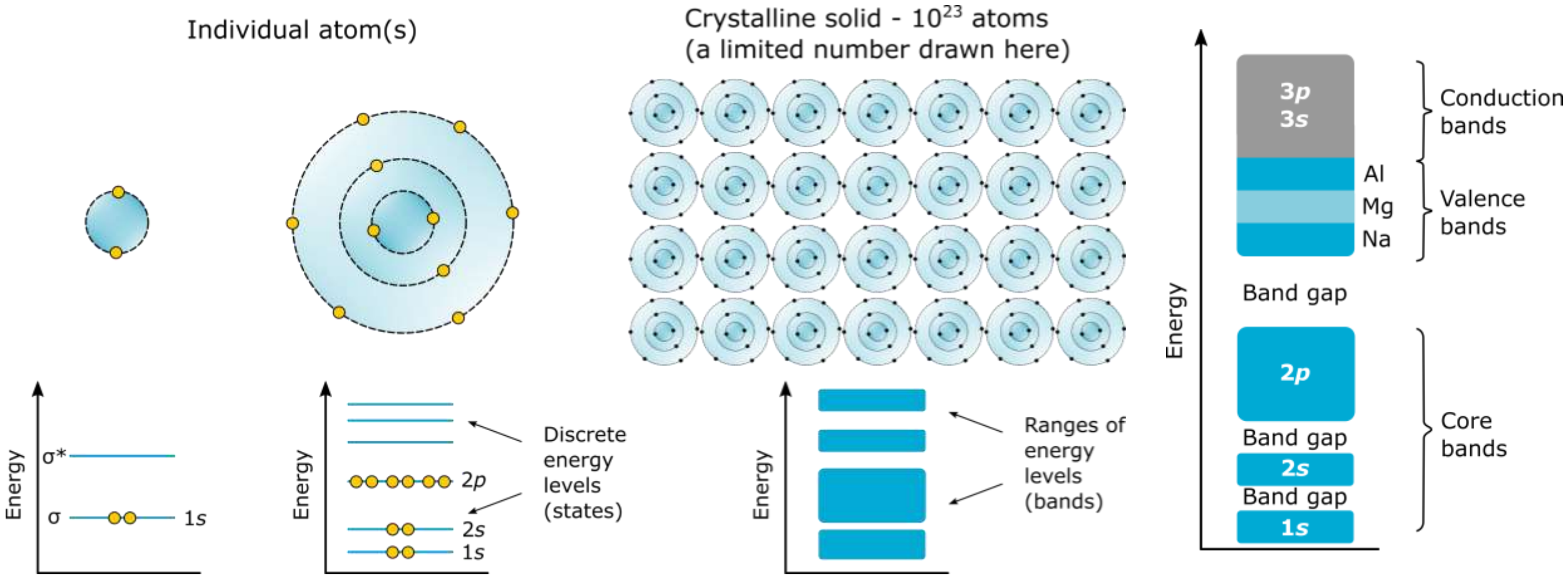
CSC (Helsinki - FIN)

GRNET (Athens, GR)

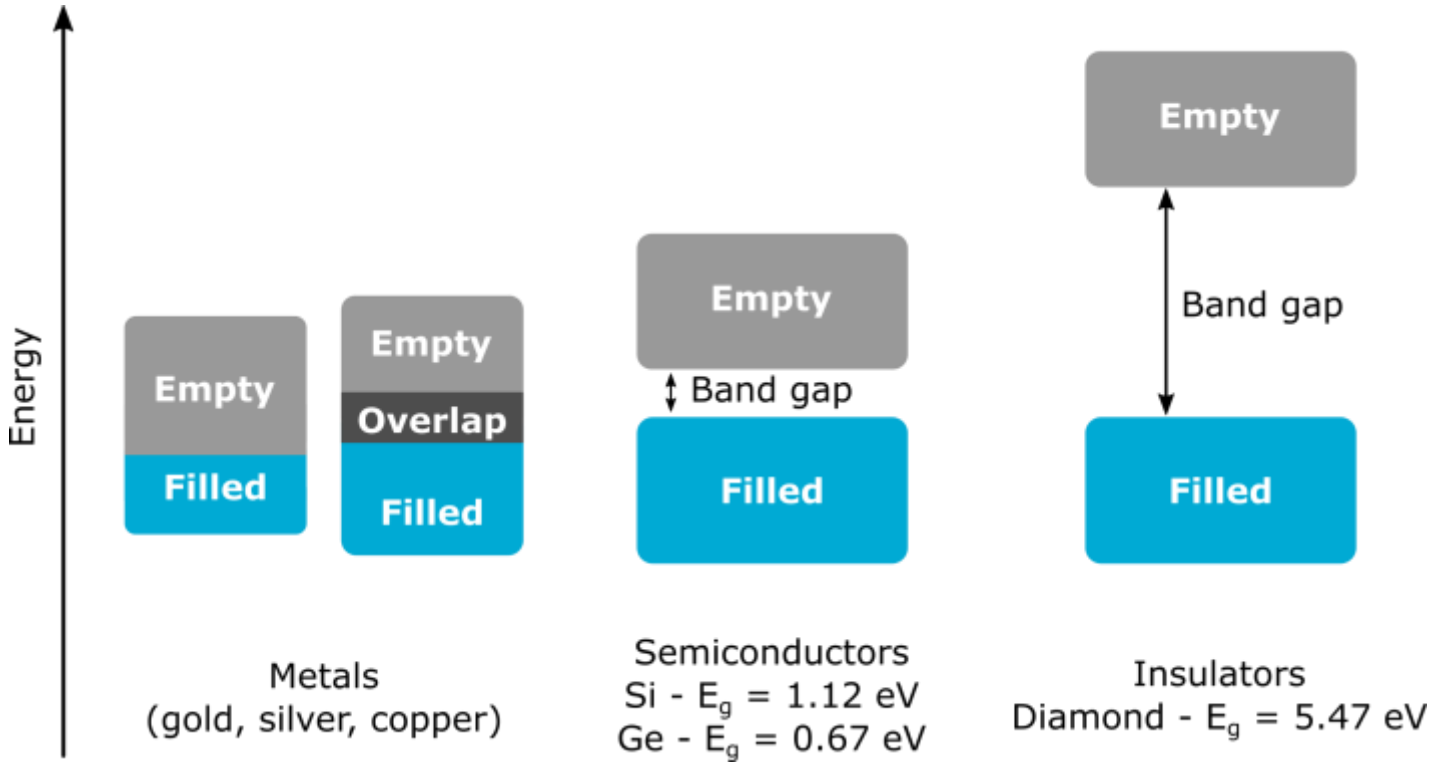
KTH (Stockholm, SE)

ICHEC (Dublin, IE)

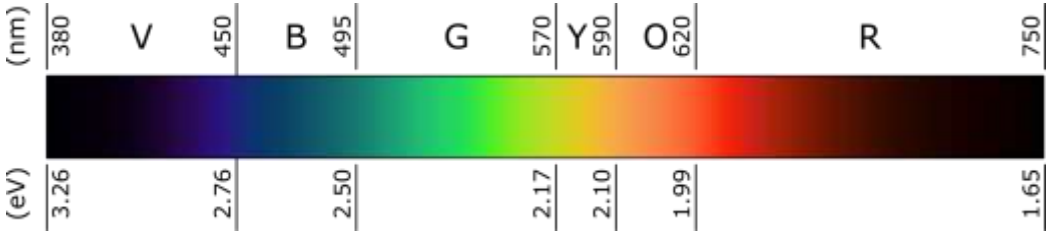
Nuts and bolts of band theory



Nuts and bolts of band theory

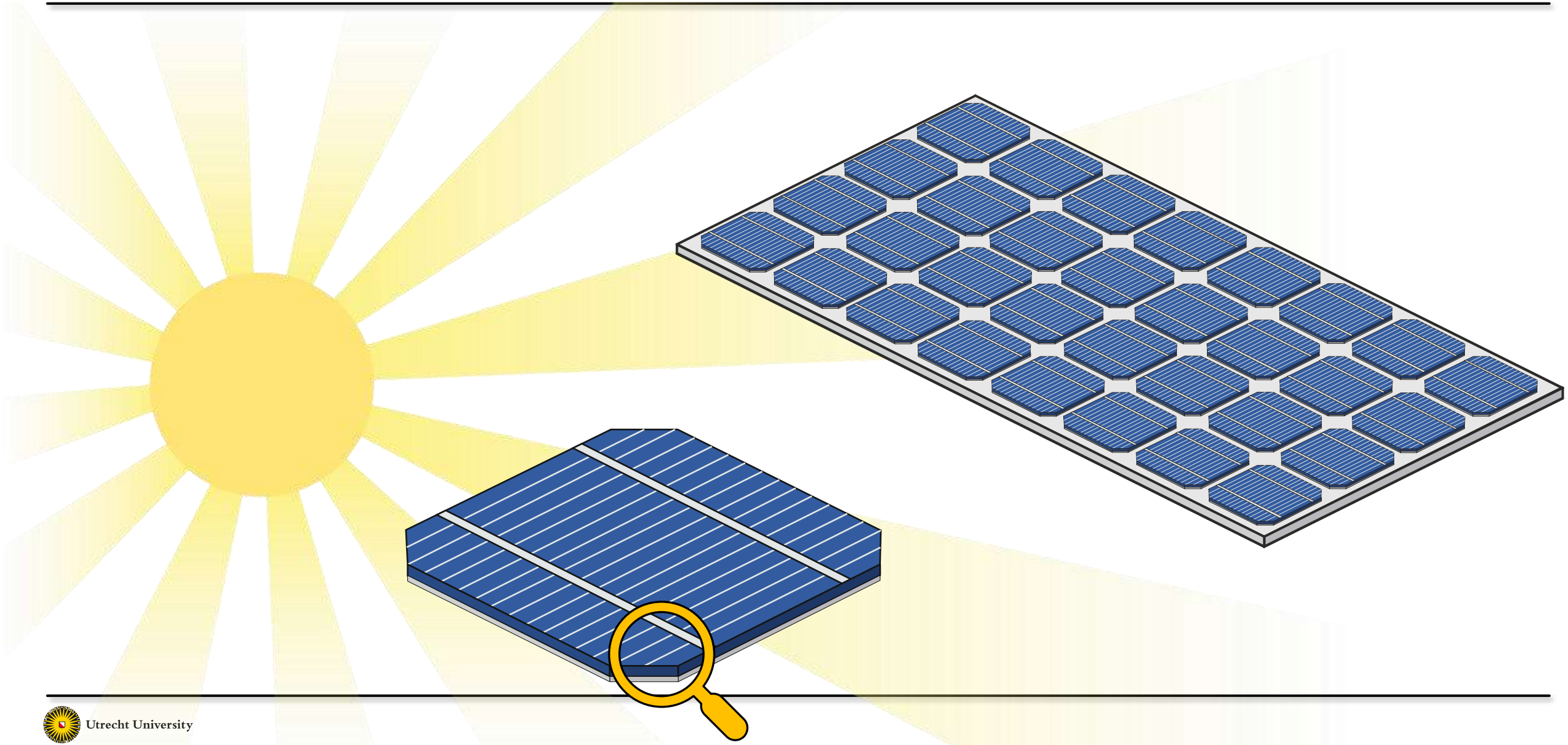


Substance	Mineral	E_g (eV)	Colour
C	Diamond	5.4	Colourless
ZnO	Zincite	3.0	Colourless
CdS	Greenockite	2.6	Yellow
$CdS_{1-x}Se_x$	-	2.3	Orange
HgS	Cinnabar	2.0	Red
HgS	Metacinnabar	1.6	Black
Si	-	1.1	Black
PbS	Galena	0.4	Black

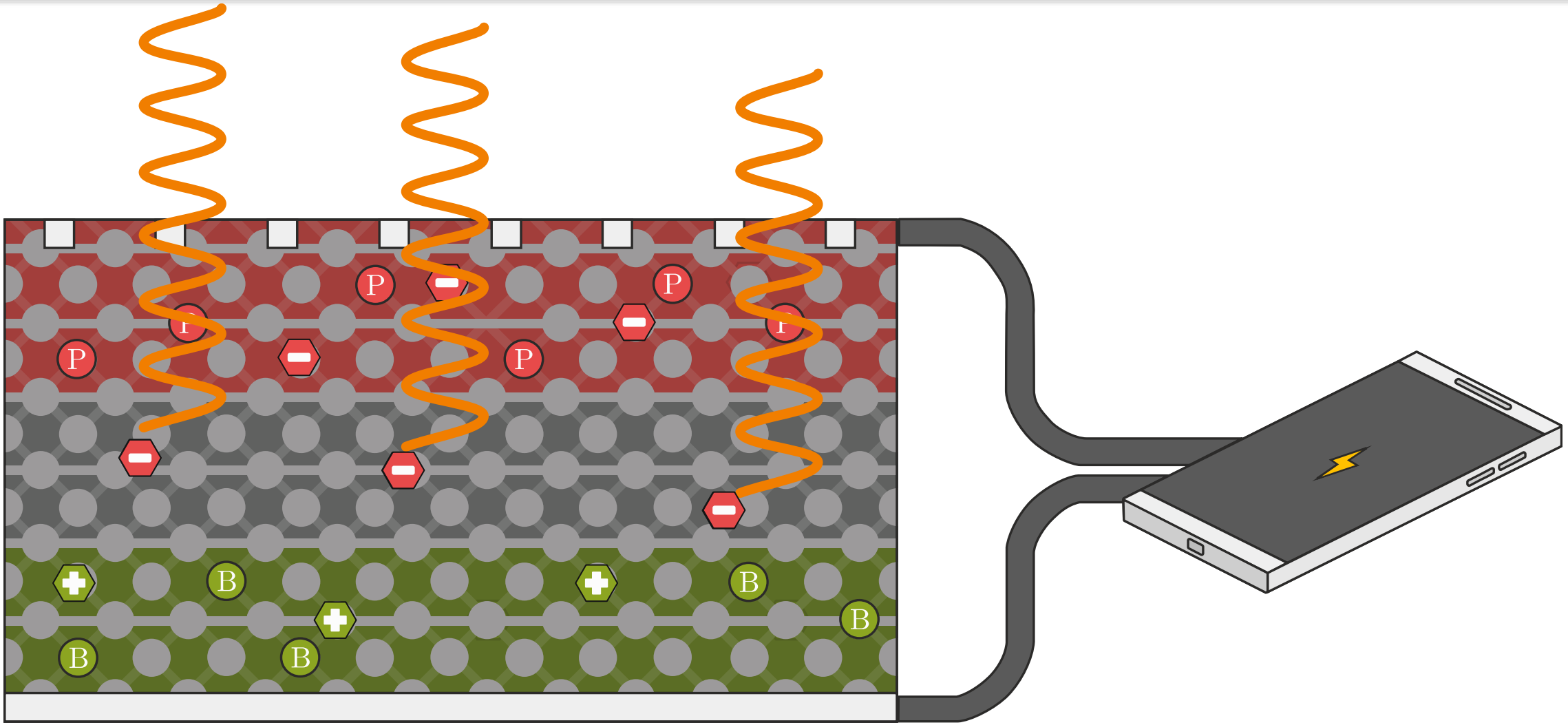


http://www.webexhibits.org/causesofcolor/10.html (22.03.2022)

Photovoltaics - ingredients

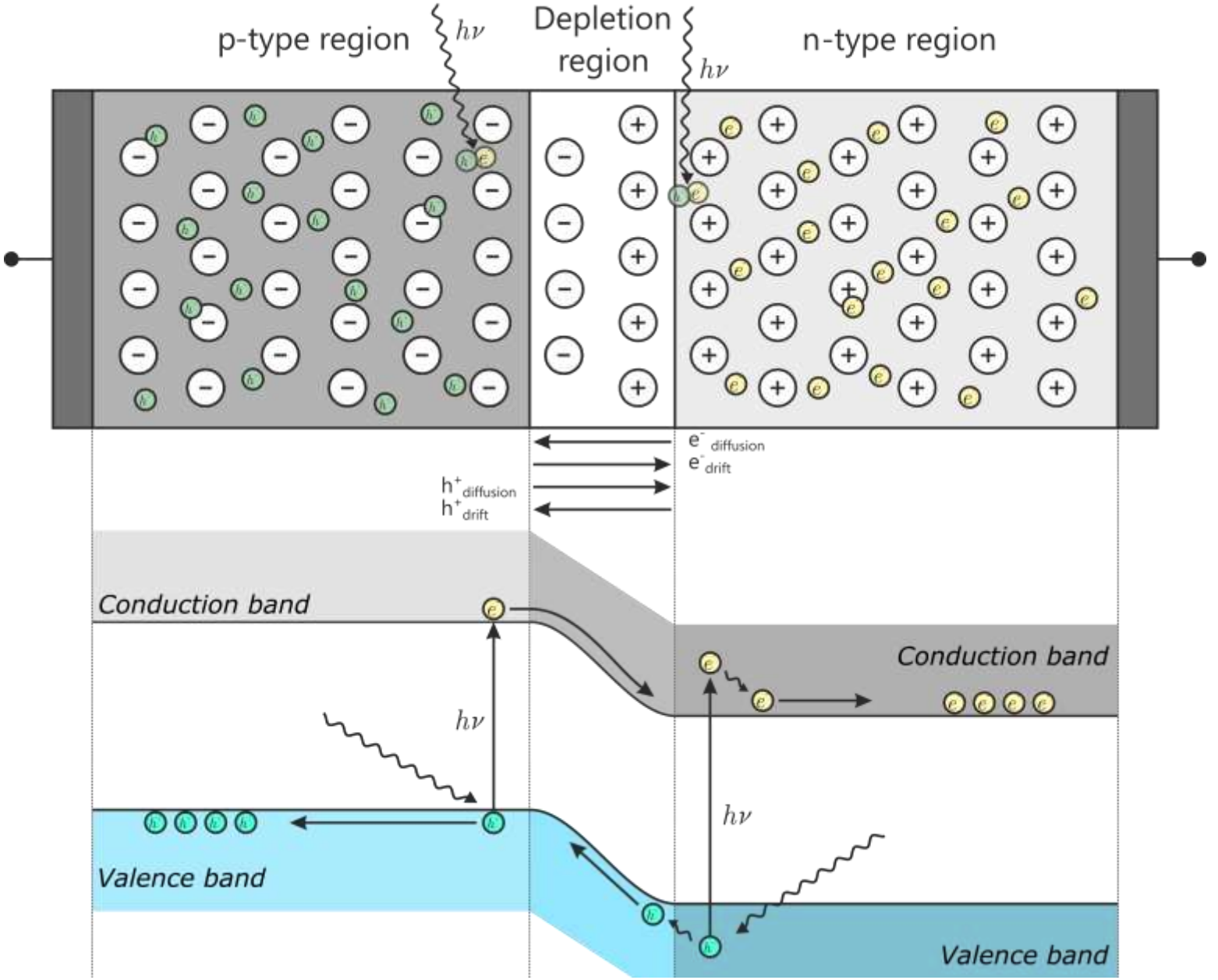


Photovoltaics – basic mechanism



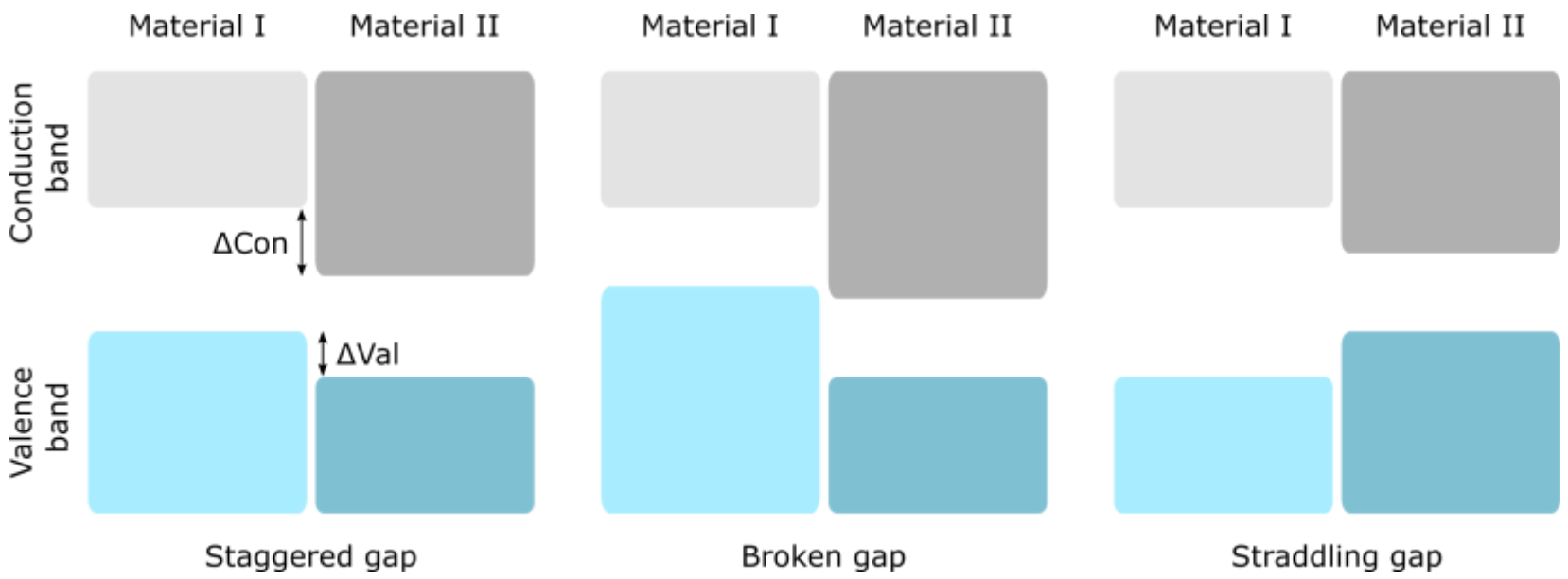
pn - junction

- Exploitation of the photovoltaic effect
- Interface (junction) between two materials (usually semiconductors)
- Diodes, transistors, solar cells, LEDs, integrator circuits, etc.



Alignment types

- The behaviour of a junction depends crucially on the alignment of the energy bands at the interface
  - Band bending, band offsets
- Search for suitable materials

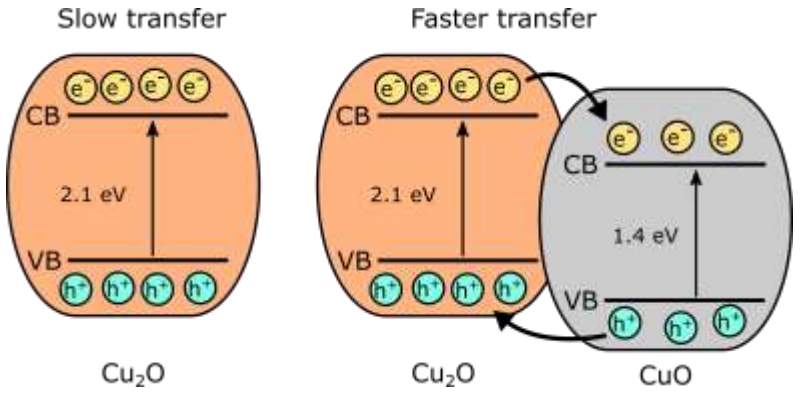


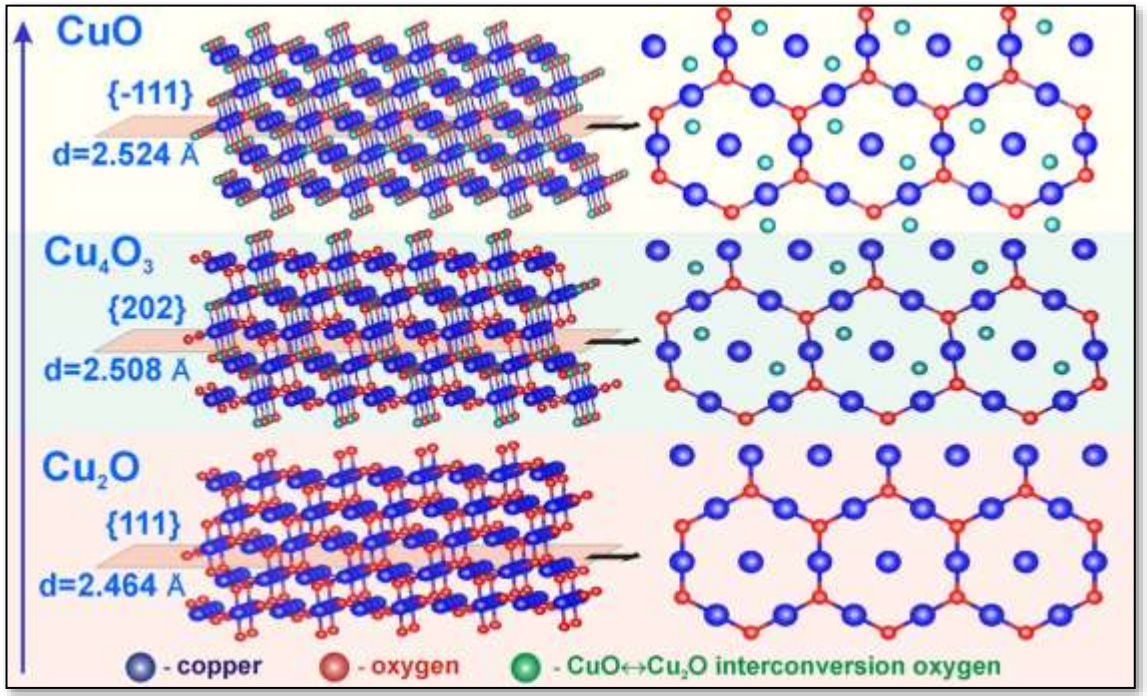
Project itself

- *Heterojunction of copper oxides: assessing the role of band alignment and vacancy diffusion across the interface from studies based on density functional theory*

Cuprite
Cu_2O

Tenorite
CuO





D. A. Svintsitskiy et al, Phys. Chem. C **117**, 14588 (2013)

Alternative (pseudo)view…

- Cuprite

"…minimises conflict between genders at work in professions where women are discourages from promotion…encourages harmony if men find it difficult to work for a female employer."

- Tenorite

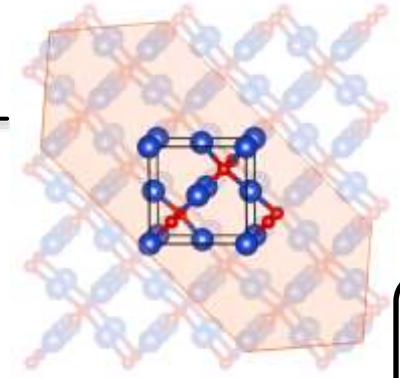
"…stimulate the healing energies of the earth. It is a very calming stone. And as such is very useful in group endeavours."

Toolkit

pymatgen

CRYSTAL

- Analyse surfaces
- Epitaxial matching
- Coherent interfaces



Bulk (substrate)

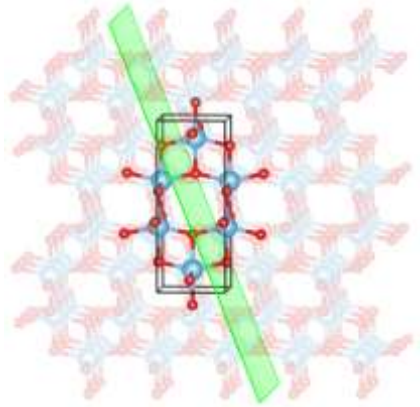
Add oxidation states and spin (substrate)

Cleave surface (polarity, symmetry)

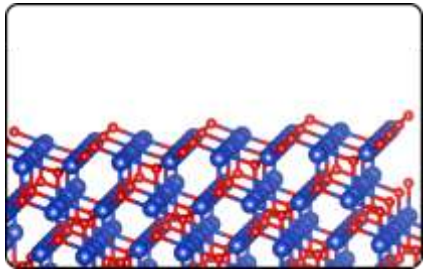
Bulk (film)

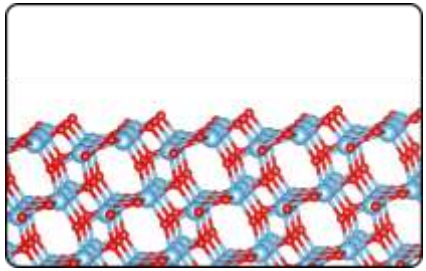
Add oxidation states and spin (film)

Cleave surface (polarity, symmetry)

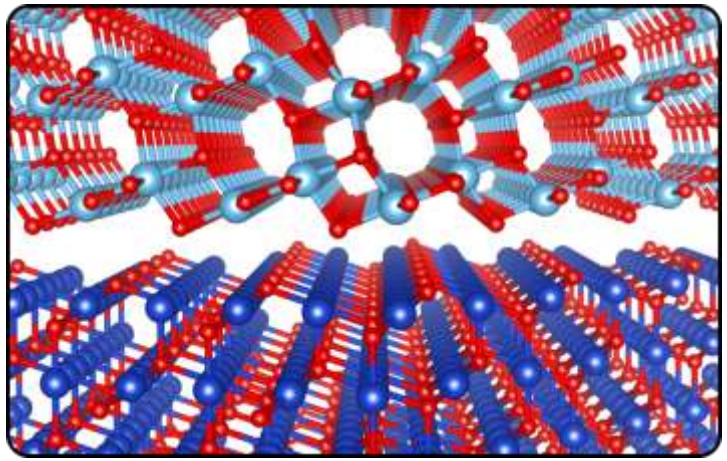


Substrate – film termination pair
Substrate and film thickness





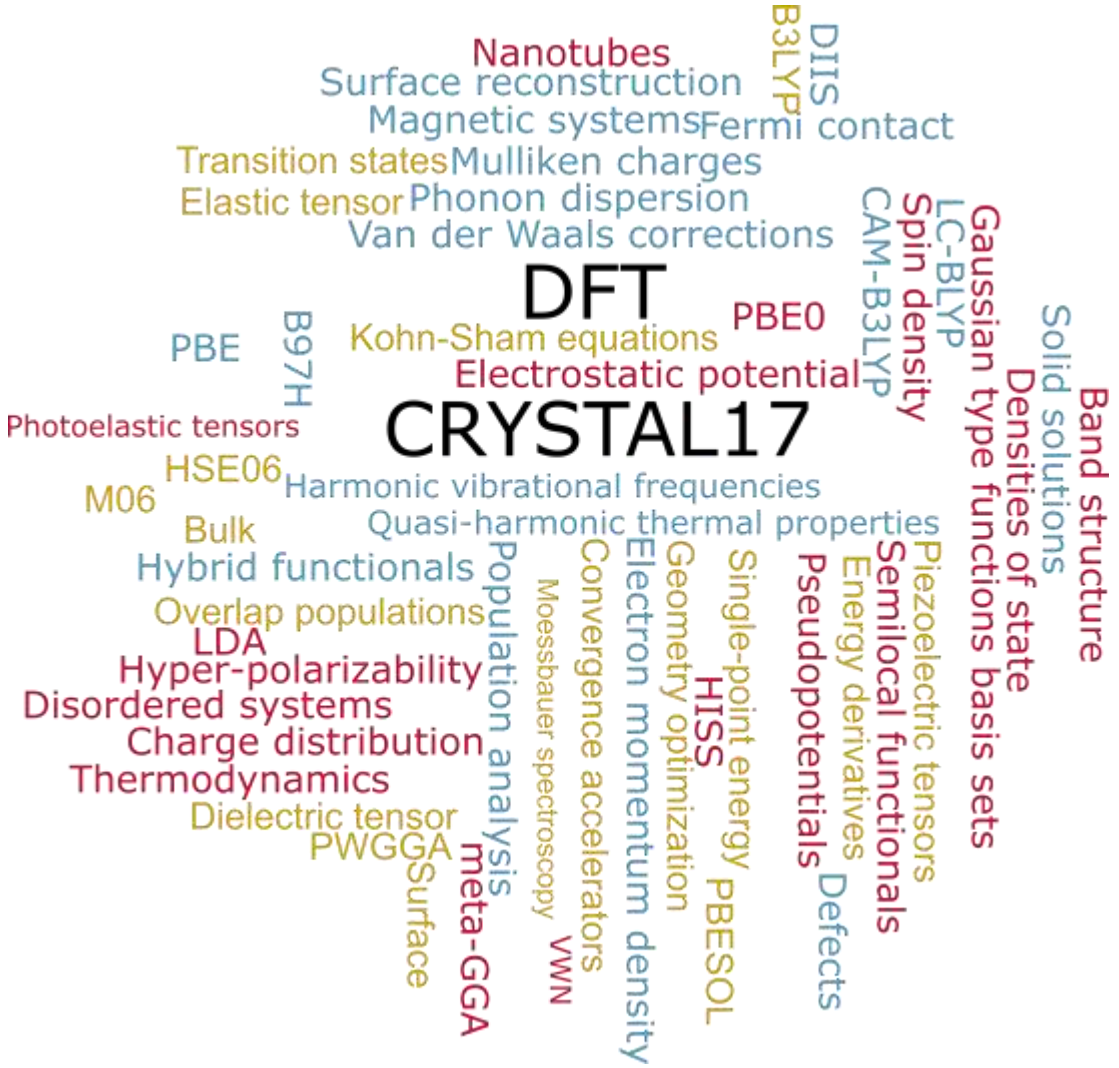
Interface structures



TiO_2(101)

Cu_2O(111)

Why DFT? Why Imperial? Why ARCHER2?



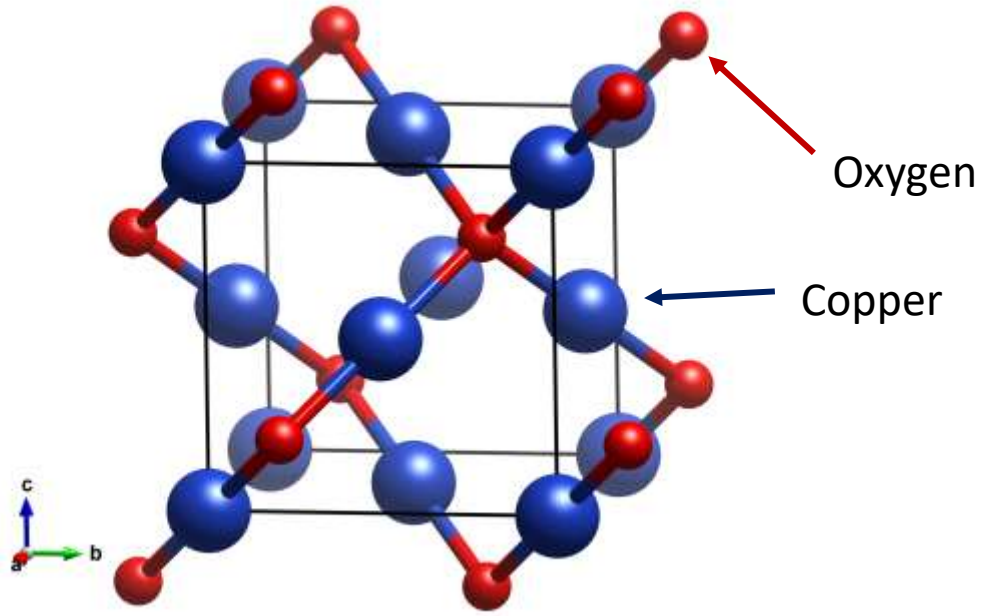
@**HPC-Europa3** – excellent platform to collaborate on short term project (test "wacky ideas")

@**Imperial** – expertise with the usage and coding of CRYSTAL17

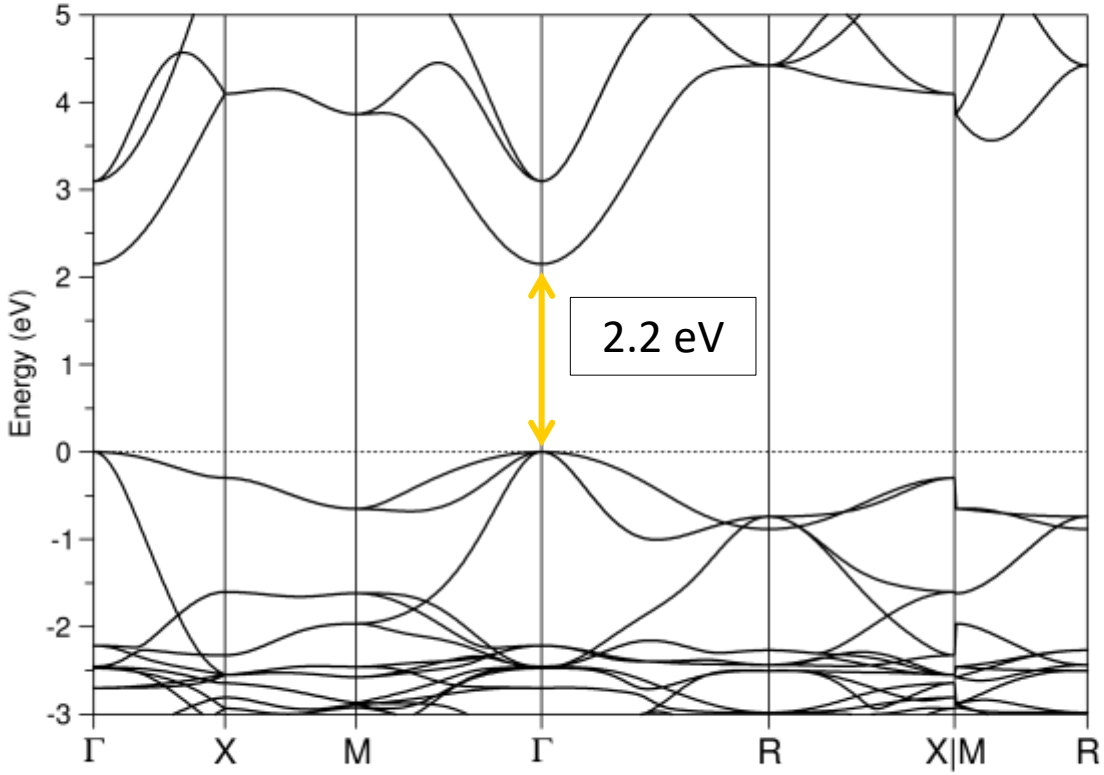
@**ARCHER2** – ideal hardware for system size and complexity + support (Catherine and William – BIG thanks!)

Results – Cu_2O

- First transition dipole forbidden; quadrupole allowed
- Fundamental gap around 2.17 eV

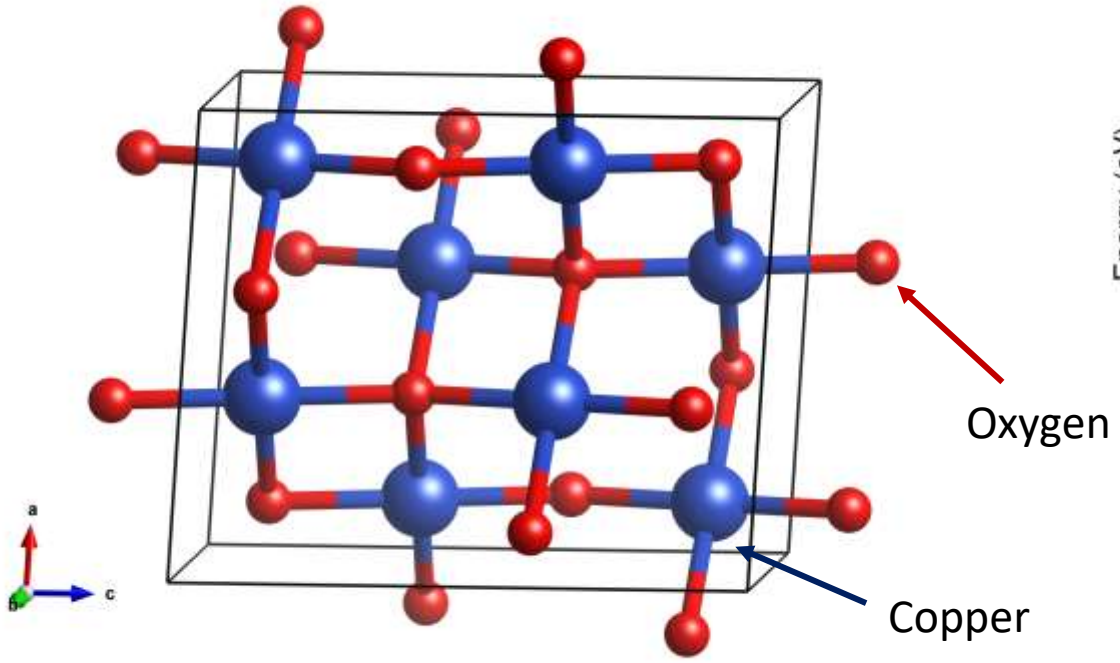


- Band diagram

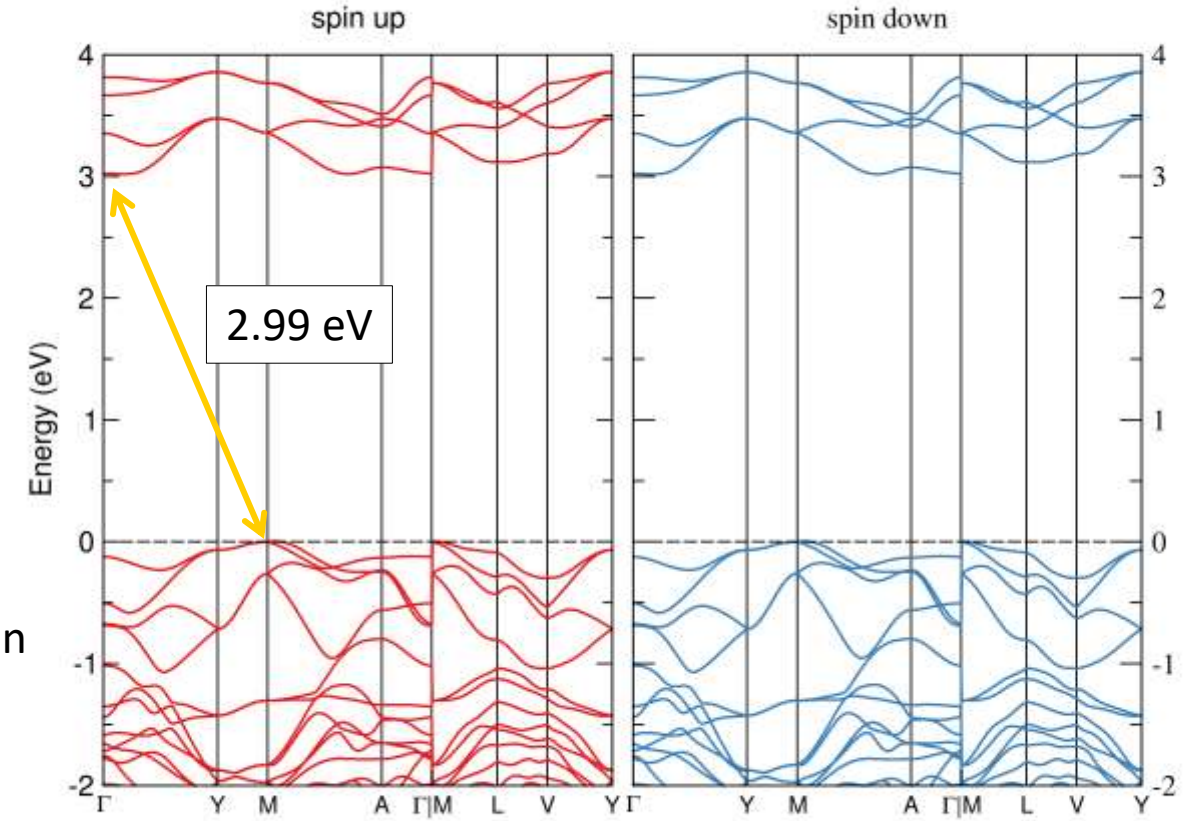


Results – CuO

- Monoclinic, strongly-correlated nature
- Intrinsic magnetism (AFM),
  E_g = 1.4 - 1.7 eV

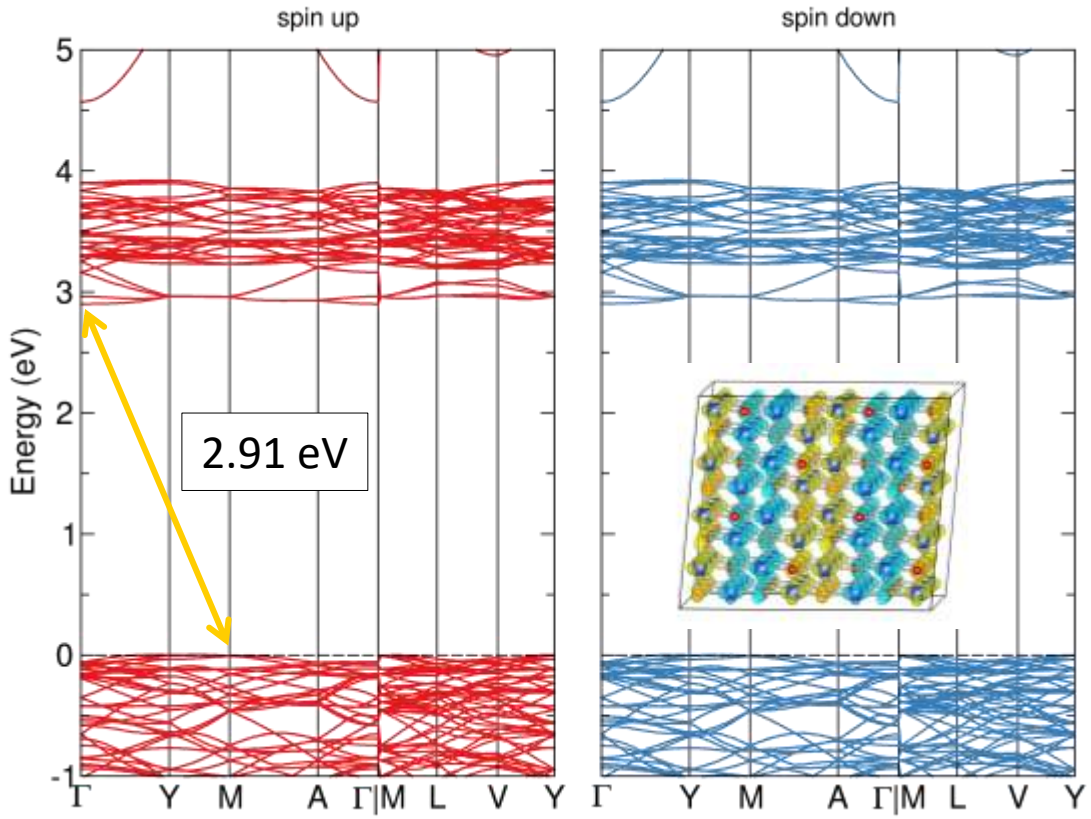


- Band diagram

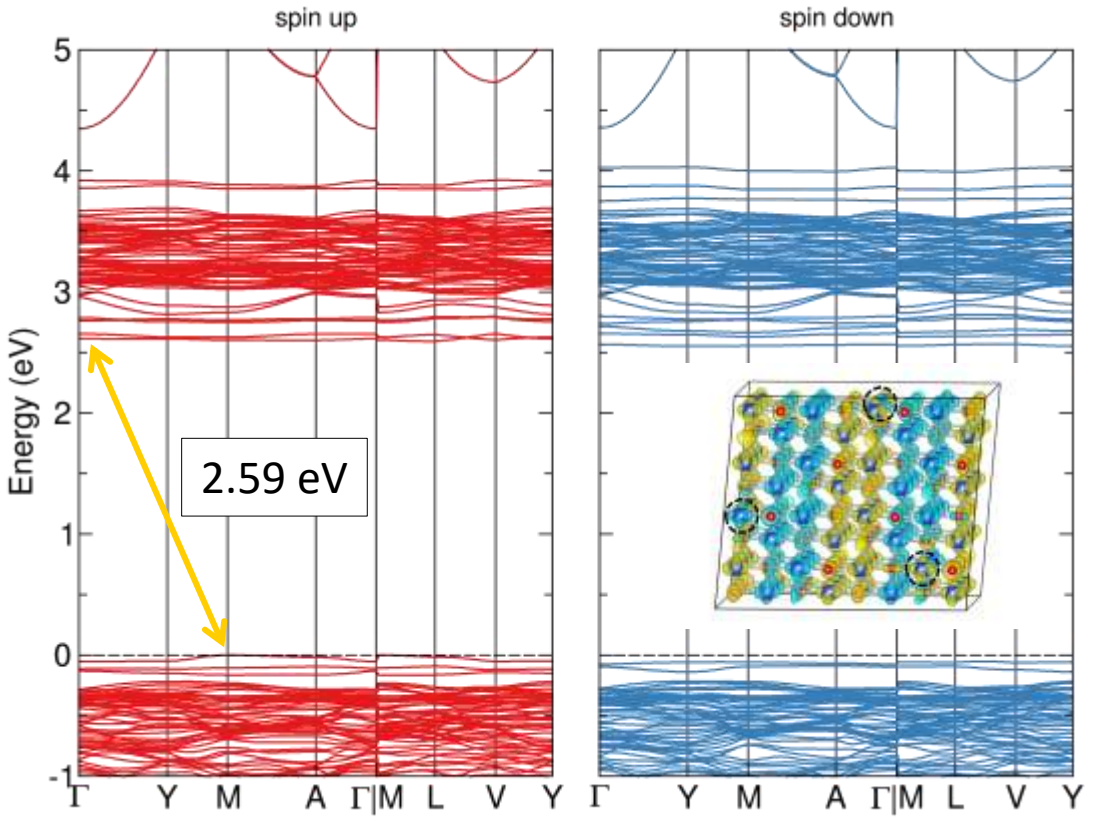


Results – CuO

- 2x3x2 supercell, perfect (ground state) spin arrangement

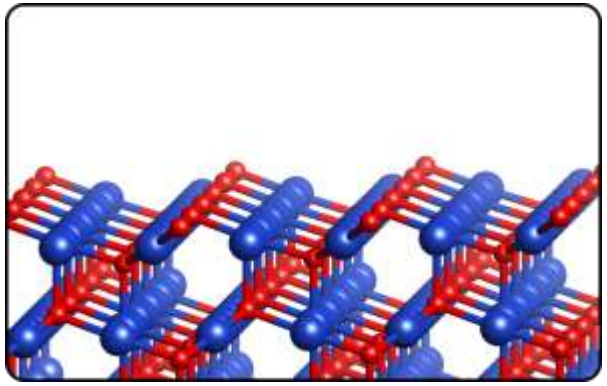


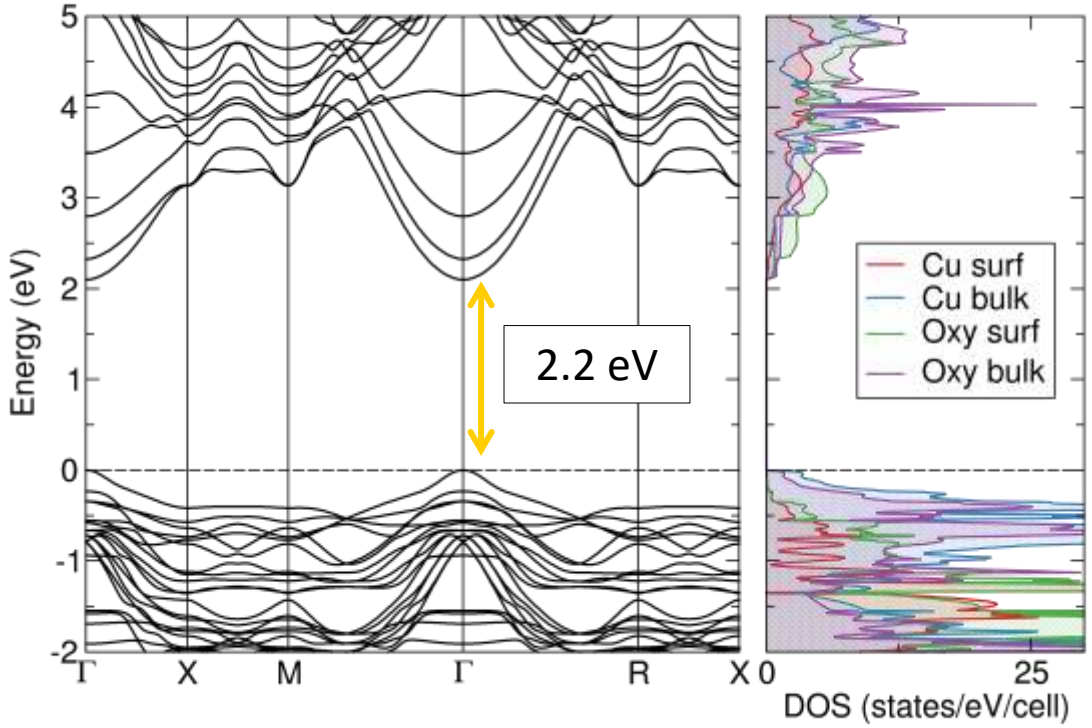
- 2x3x2 supercell, with ~ 5% spin alteration → ΔE = 0.1eV/spin

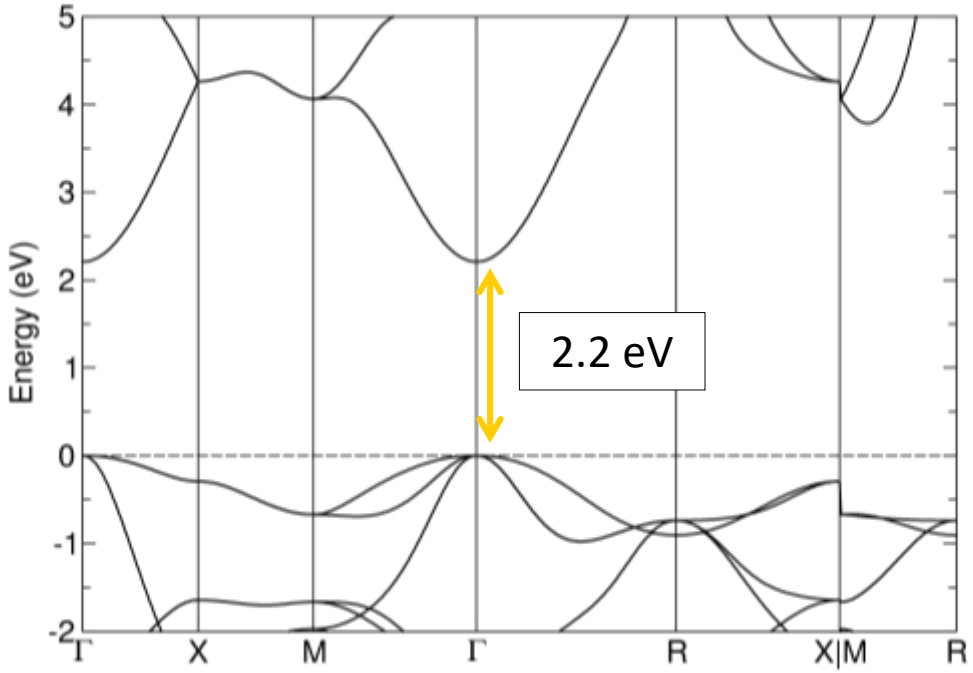


Results – surfaces

- Cu_2O (111), 15.6 Å thick
- γ = 1.136 J/m^2



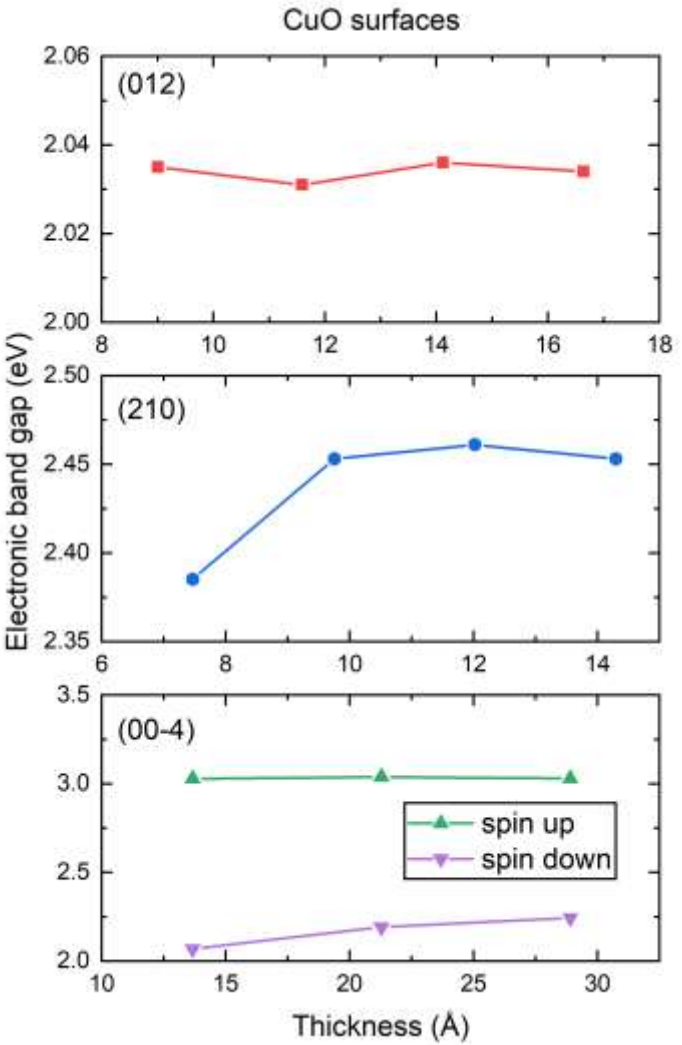




Results – CuO surface

Miller index	Surface energy (J/m2)	Band gap (eV)
(1 1 1)	0.863	2.461
(-1 1 1)	0.935	2.036
(0 1 1)	0.890	2.651
(2 0 -2)	1.329	2.067

The absorption spectra [Fig. 1(a)] show a systematic blueshift in the absorption edge for CuO nanostructures, with the increase in the concentration of $KMnO_4$. The indirect bandgap of the nanostructures corresponding to the lower $KMnO_4$ concentration was estimated to be ~1 eV, and indirect transitions were found to be dominant in comparison with direct transitions. The direct bandgap was calculated using the Tauc plot [Fig. 1(b)]. As the concentration of $KMnO_4$ increased from 0.2 to 50 mM, the direct bandgap was enhanced from 3.27 to 4 eV. Such a

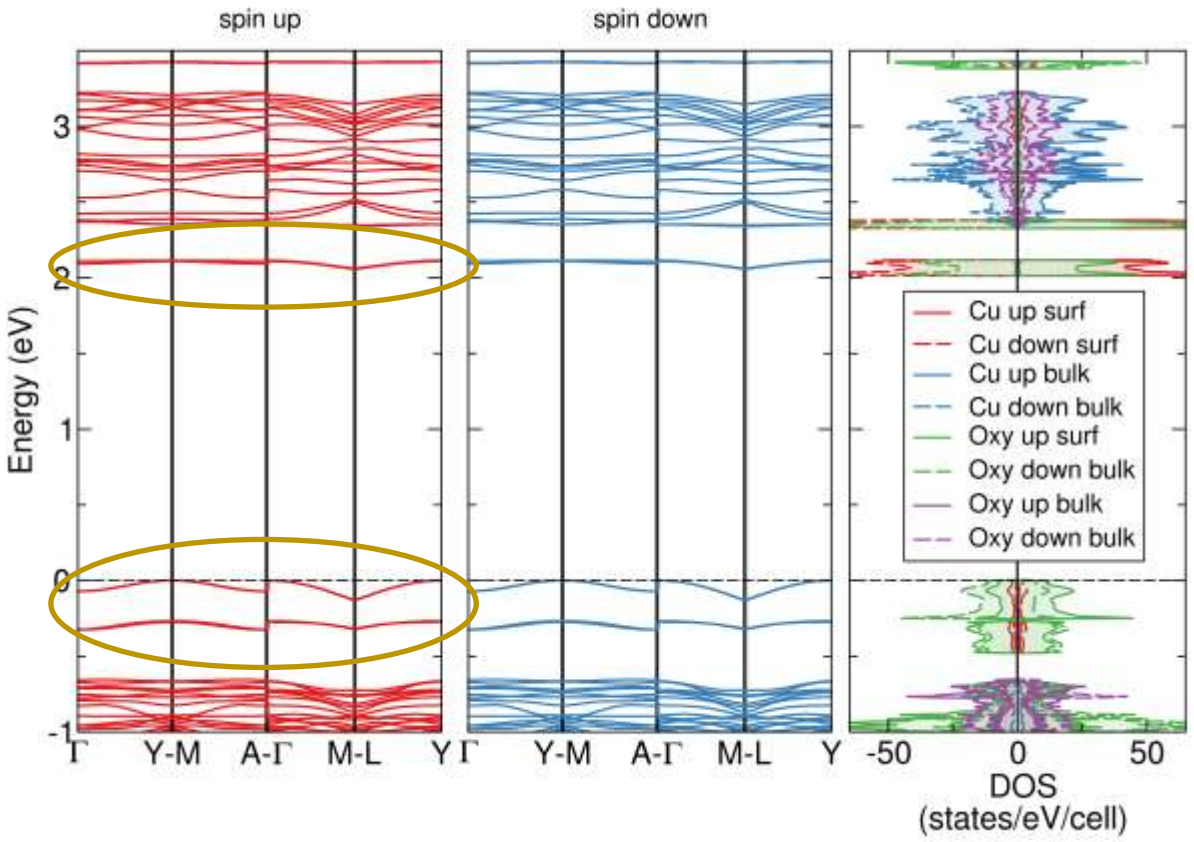


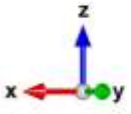
Appl. Phys. Lett. 116, 111102 (2020)

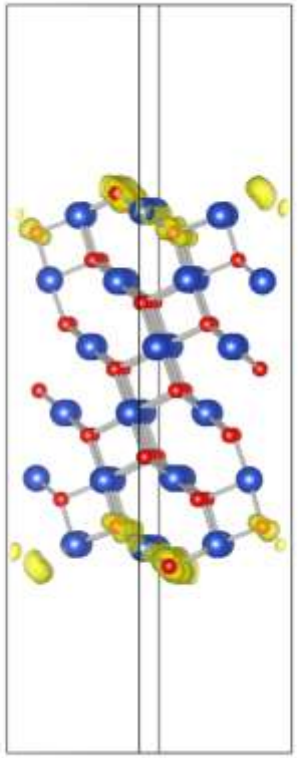
Results – CuO surface

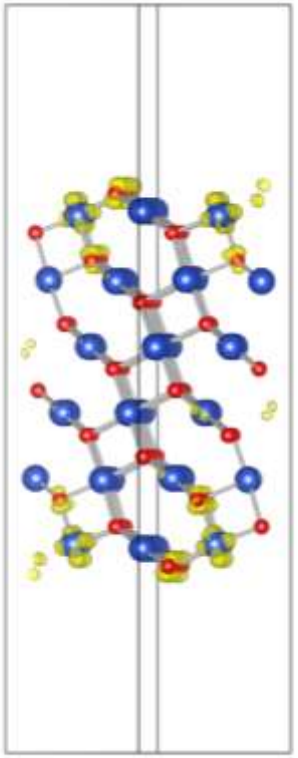
(-111) conventional, E_g = 2.05 eV

- Partial electron density





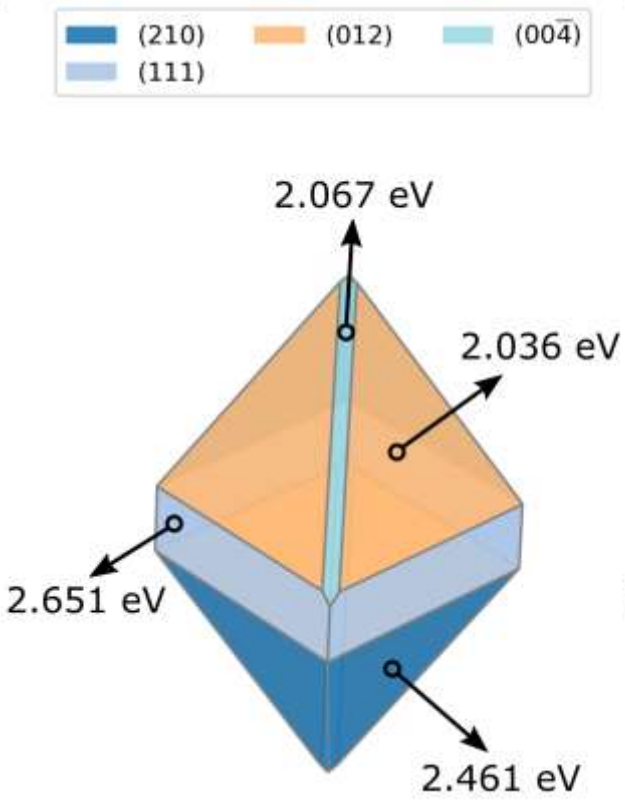




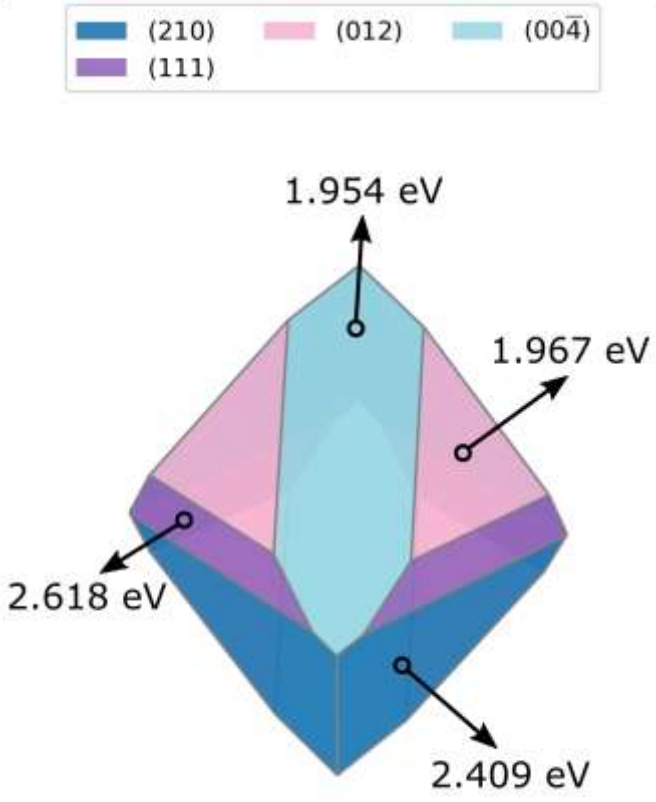
Živković *et al*, submitted

CuO morphology

B3LYP



HSE06

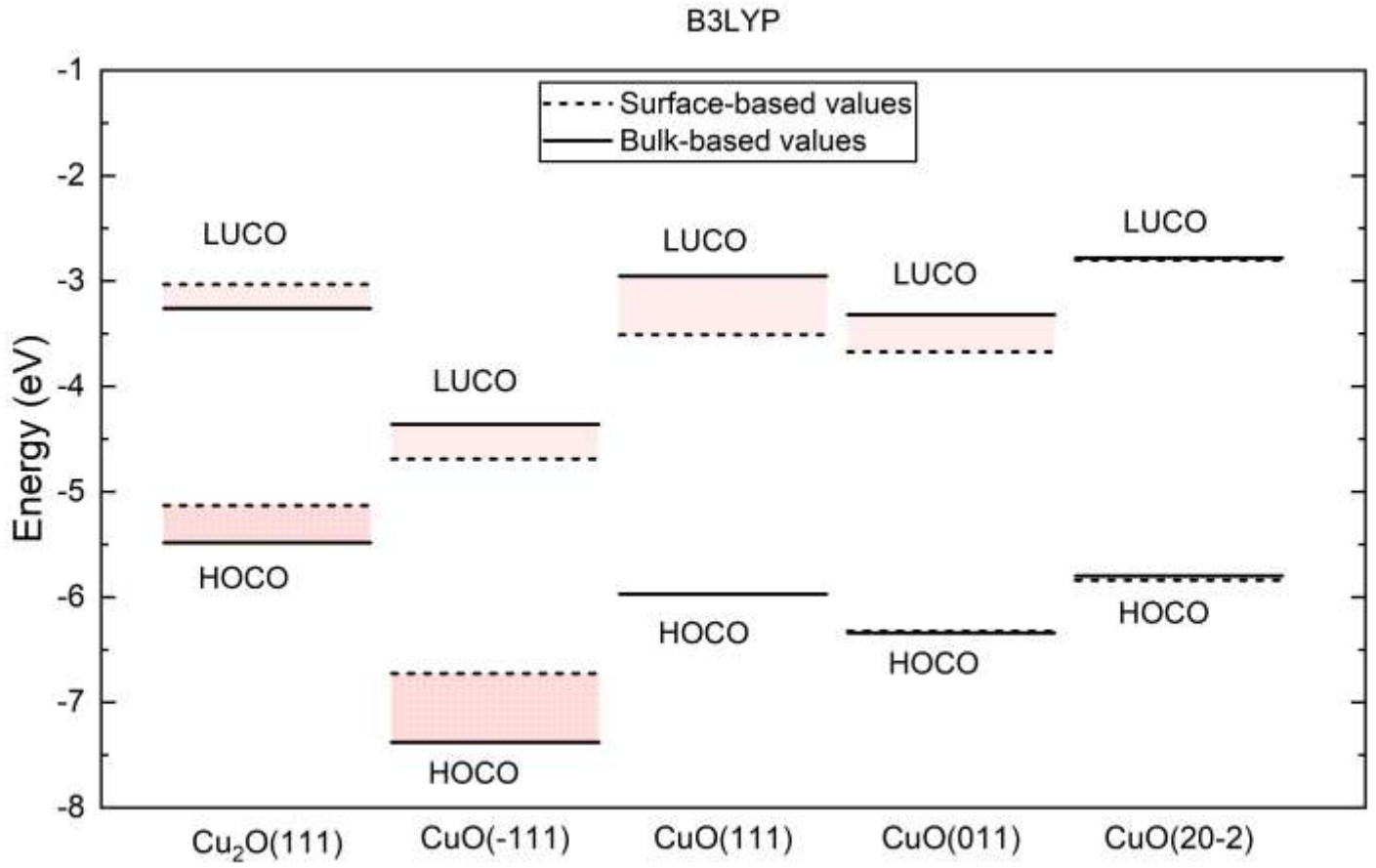


Conventional	Magnetic
(1 1 1)	(2 1 0)
(-1 1 1)	(0 1 2)
(0 1 1)	(1 1 1)
(2 0 -2)	(0 0 -4)

Miller index	Polarizability tensor, Alpha(Bohr^3)		
	XX	YY	ZZ
(1 1 1)	3395.52	2365.65	409.17
(-1 1 1)	2709.04	2716.87	436.37
(0 1 1)	2467.05	3030.10	431.39
(2 0 -2)	747.07	924.44	144.15

Živković *et al*, submitted

Band alignment (independent compounds)

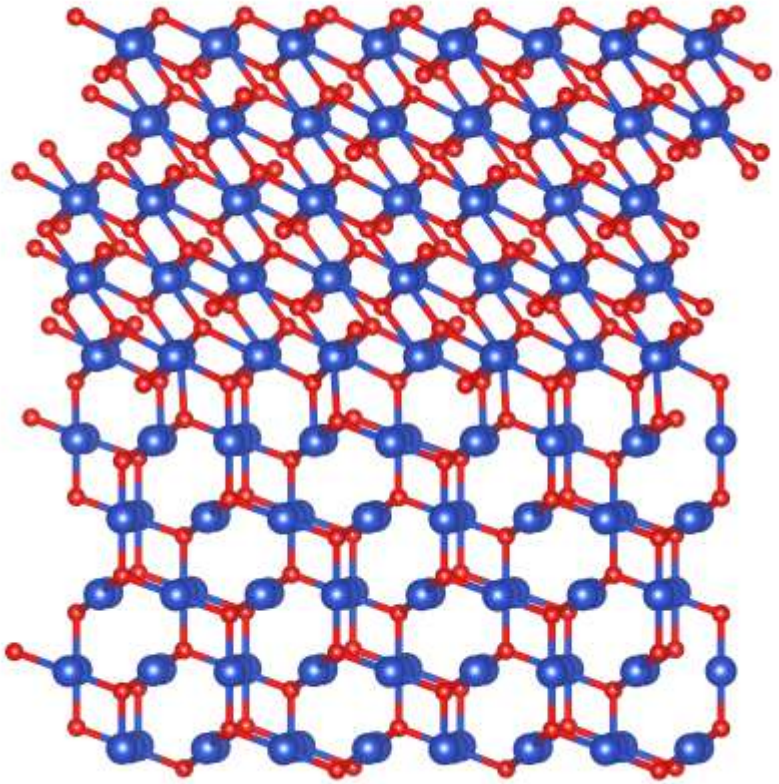


- Tunability depending on growth direction (?)

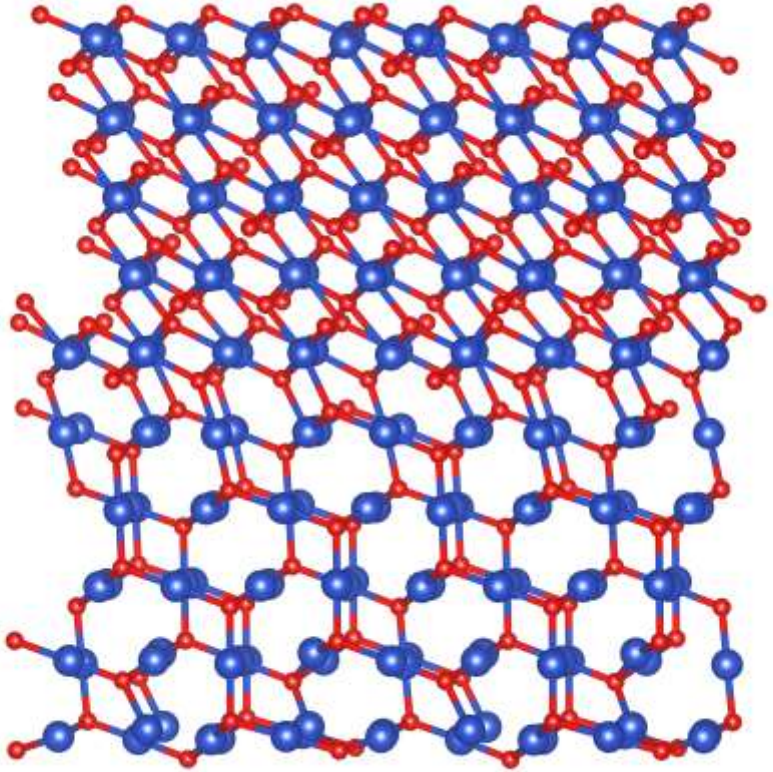
Živković *et al*, submitted

Explicit interface: CuO(-111) on Cu_2O(111)

- Initial structure



- Relaxed structure



Živković *et al*, submitted

Explicit interface: CuO(-111) on Cu_2O(111)

- Initial structure
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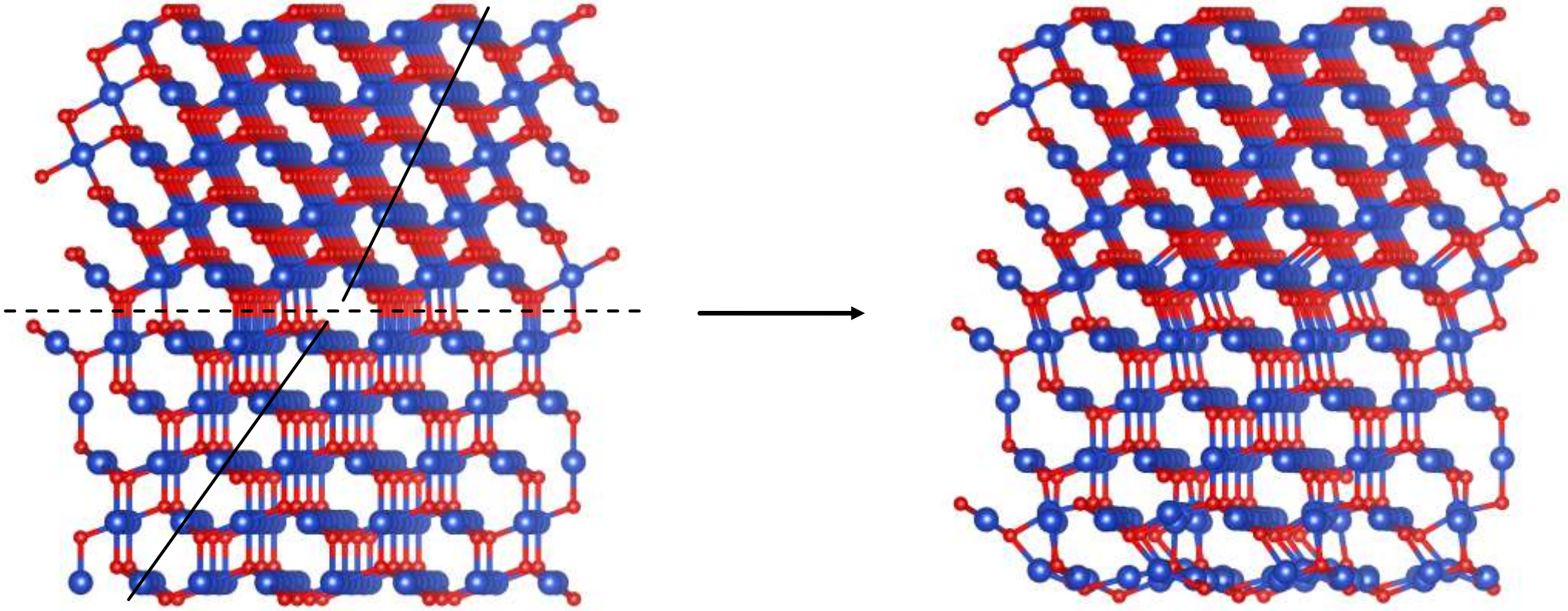
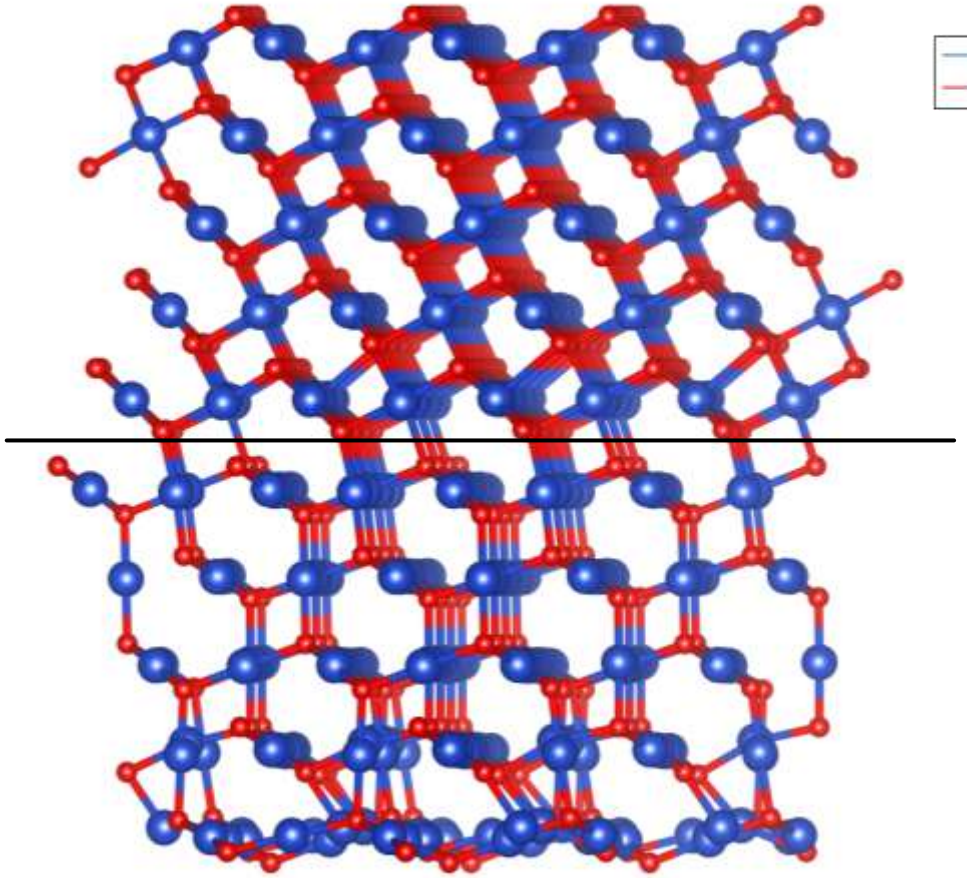
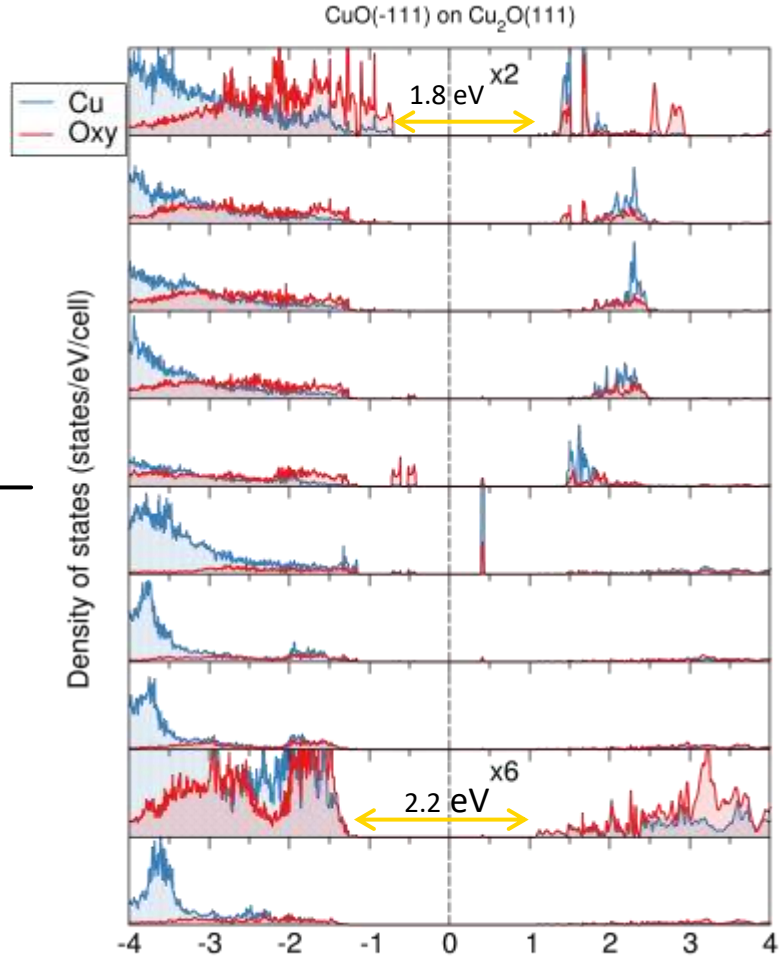


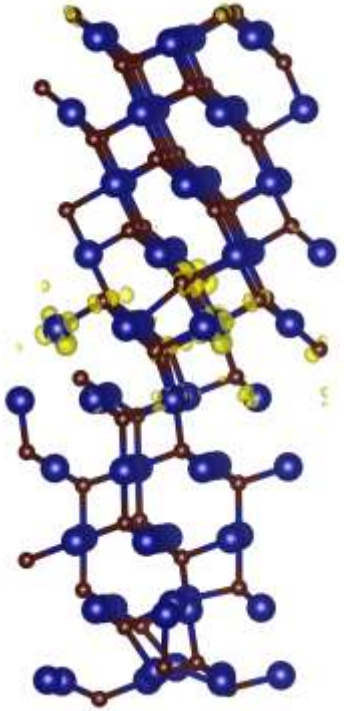
Živković *et al*, submitted

CuO(-111) on Cu_2O(111): Electronic layer-projected DOS

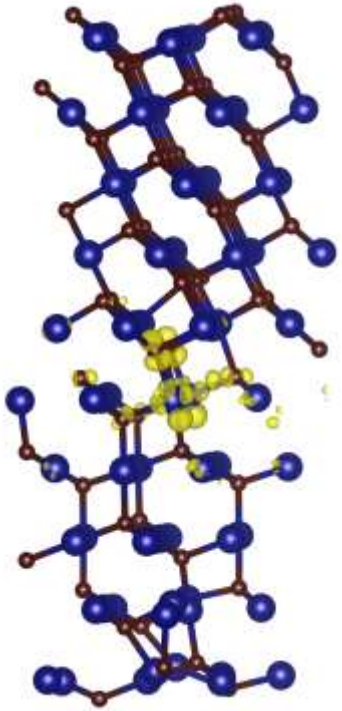




E_f - 0.5eV

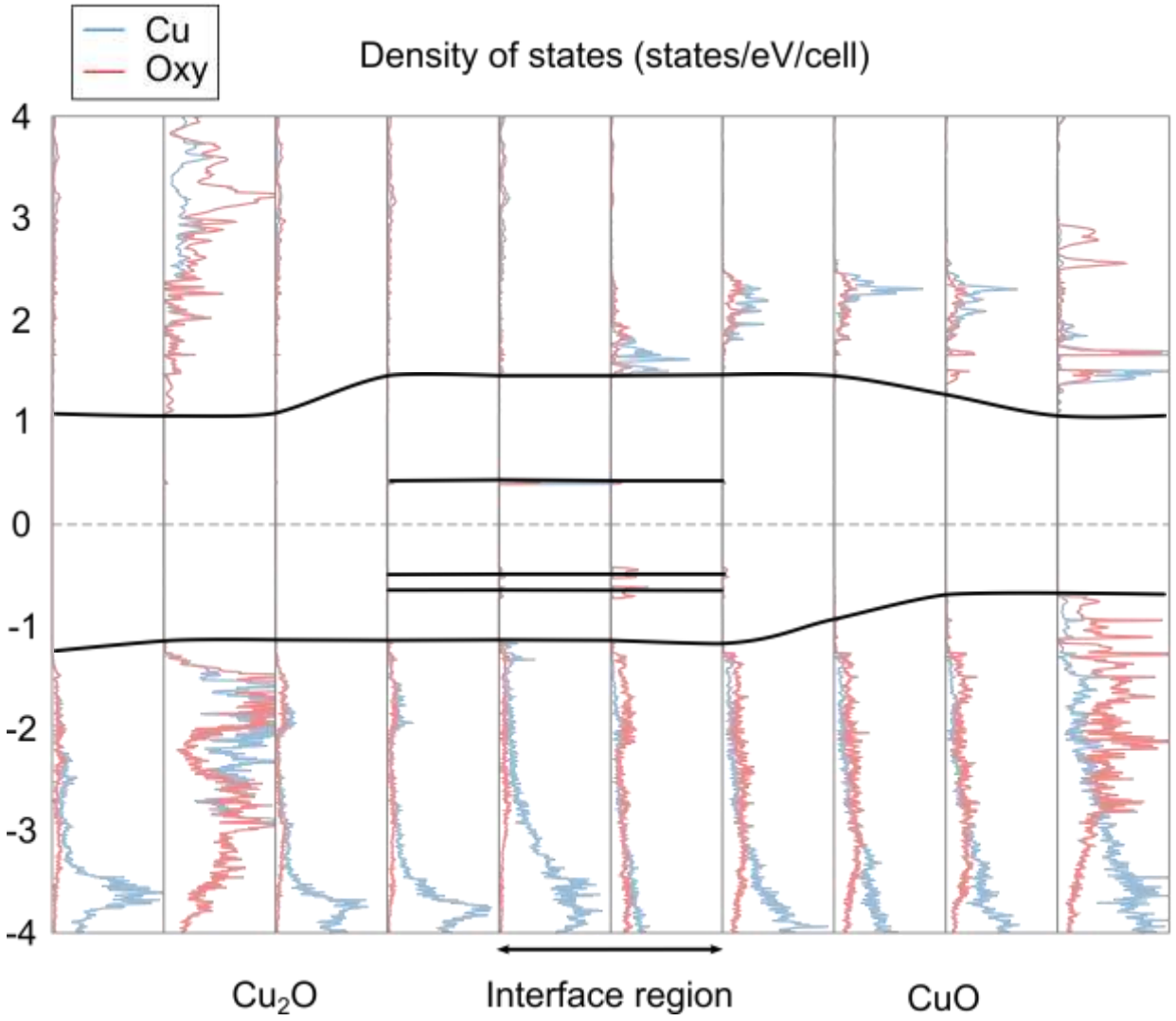


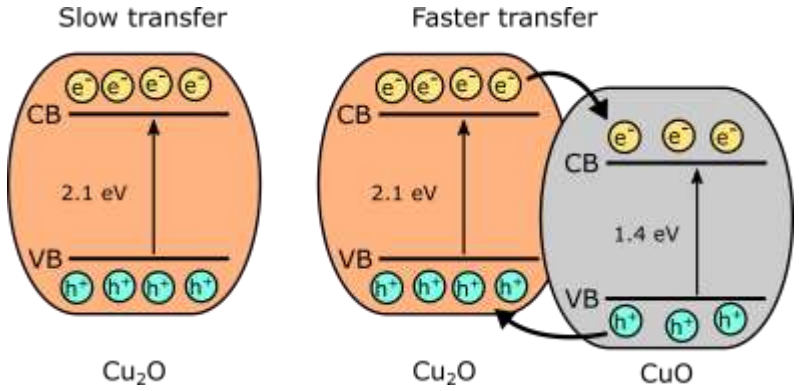
E_f + 0.5eV

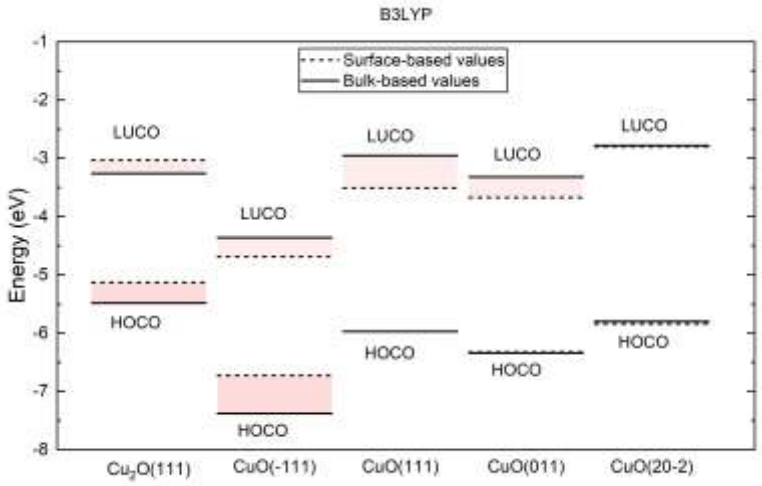


Živković *et al*, submitted

CuO(-111) on Cu_2O(111): Electronic layer-projected DOS





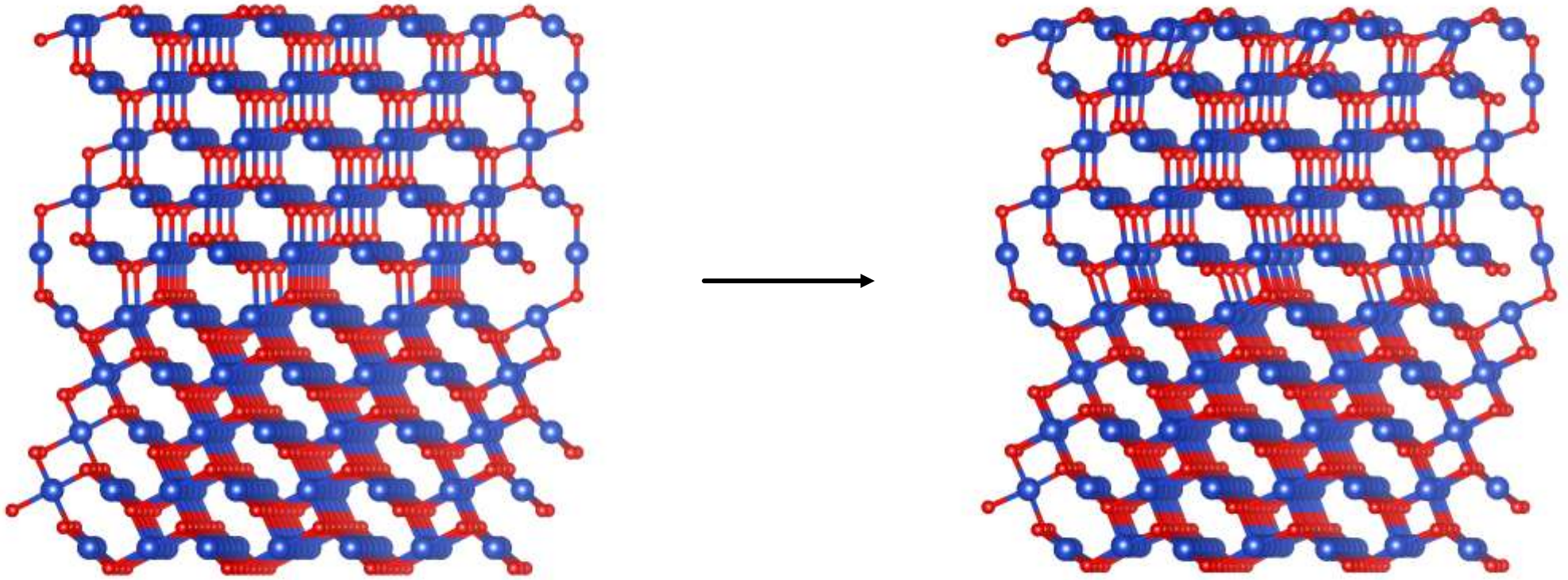


Utrecht University

Živković *et al*, submitted

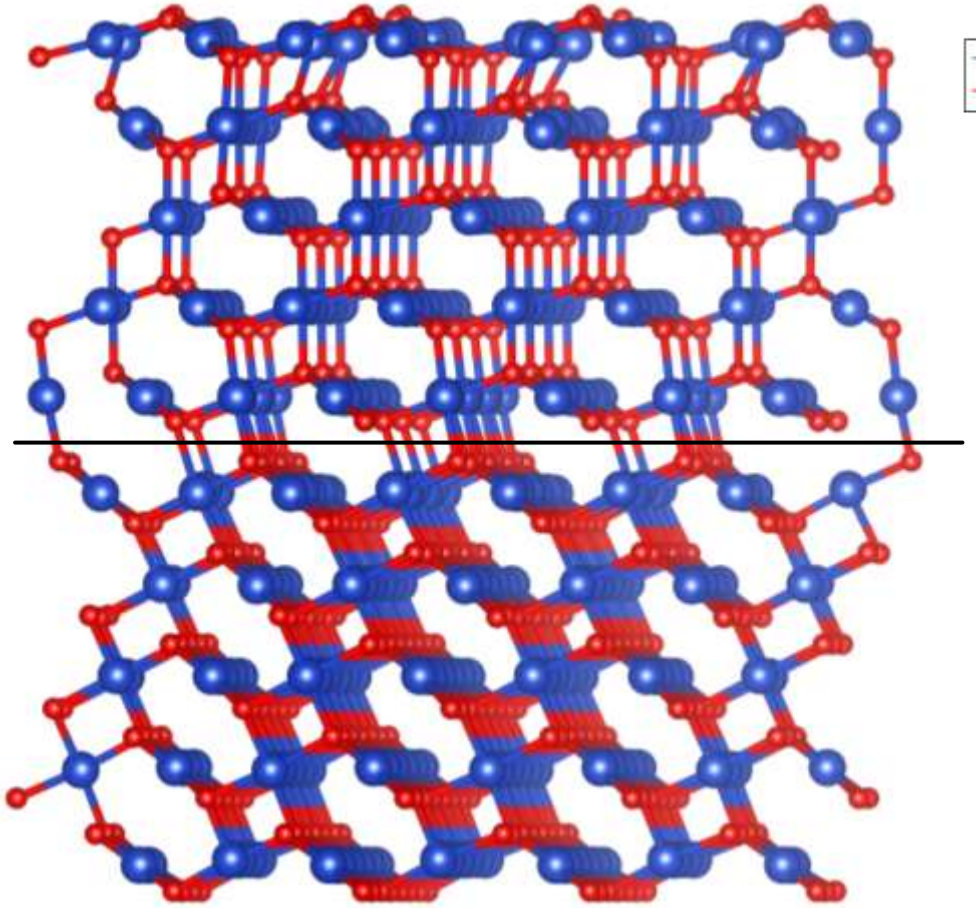
Explicit interface: $Cu_2O(111)$ on $CuO(-111)$

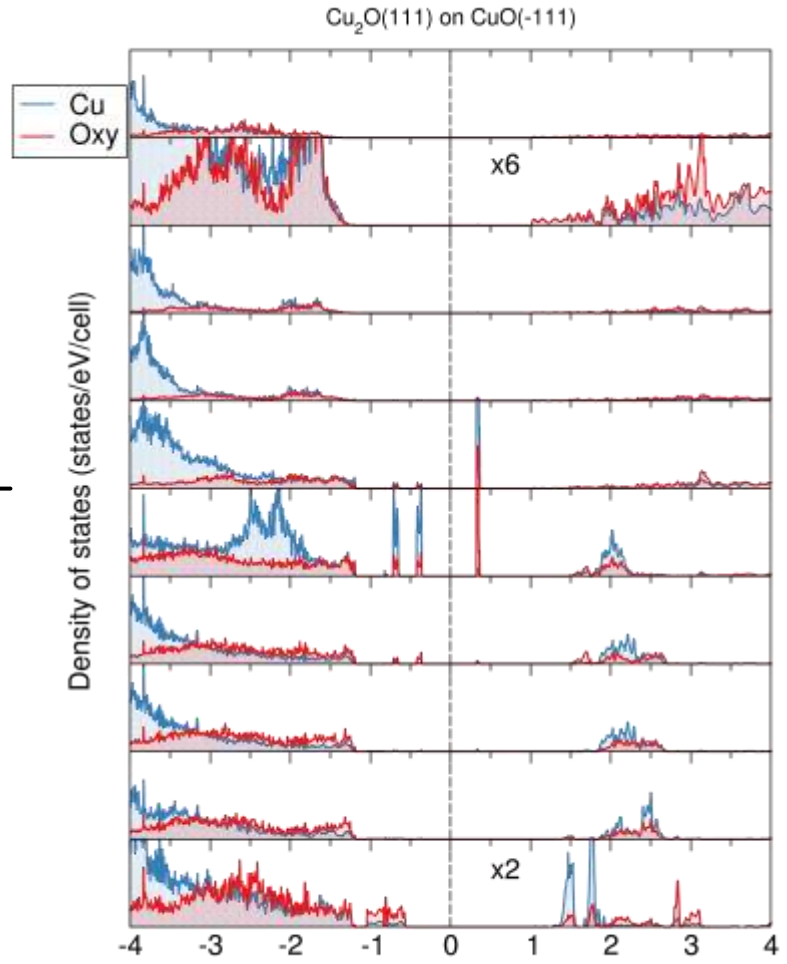
- Initial structure
- Relaxed structure



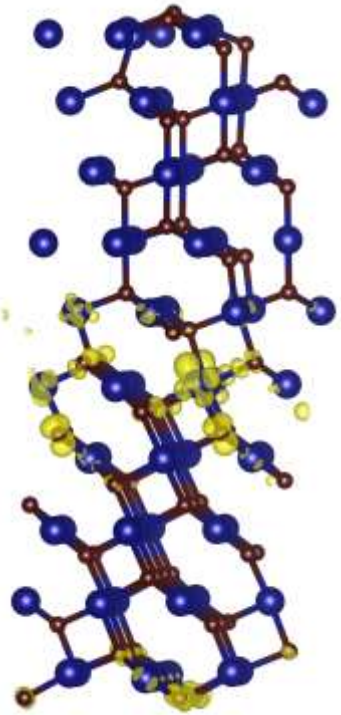
Živković *et al*, submitted

$Cu_2O(111)$ on CuO(-111)

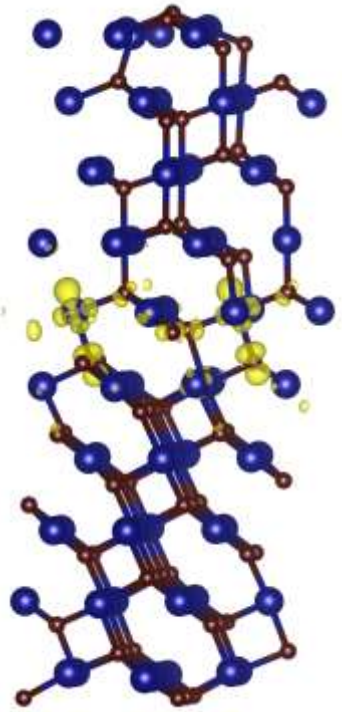




E_f - 0.5eV



E_f + 0.5eV



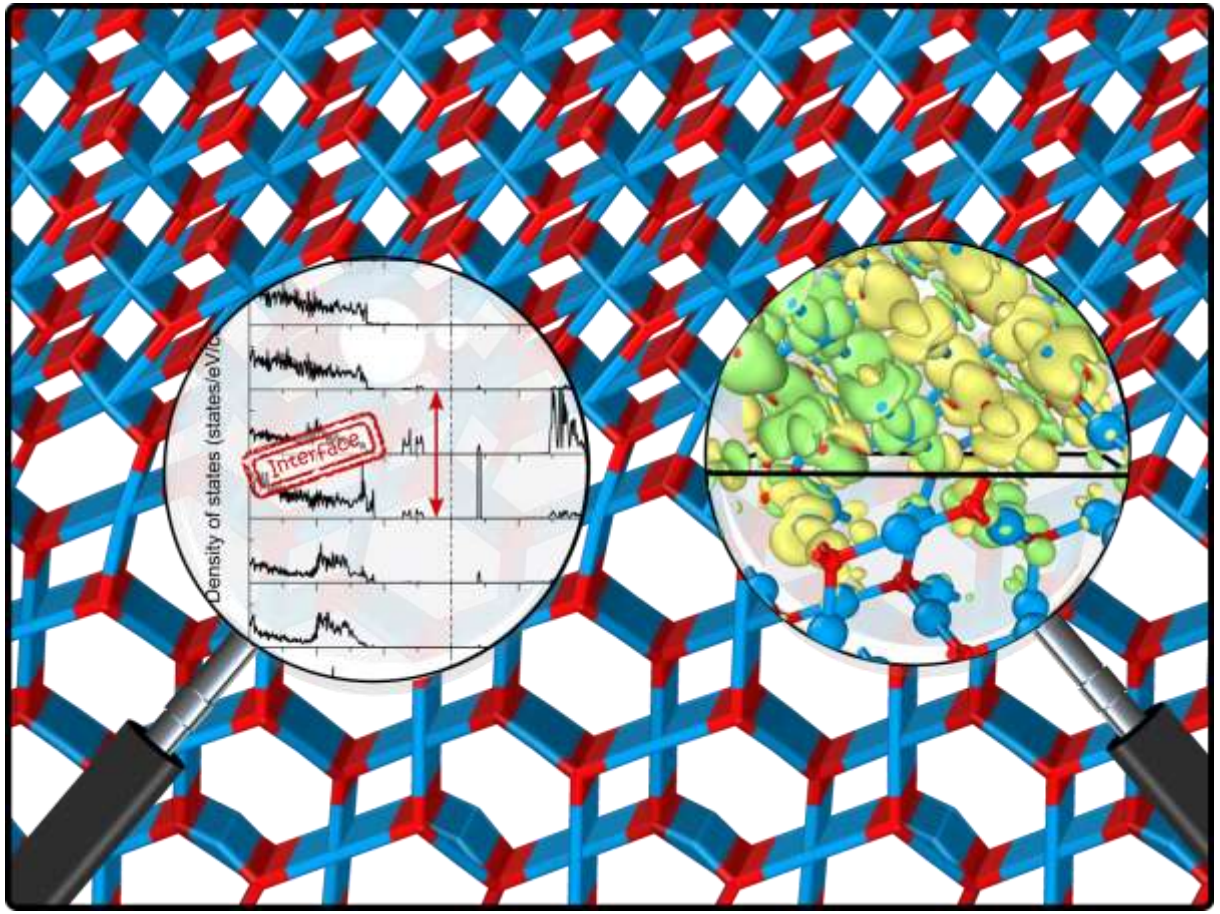
Last slide

So far:

- Independent alignment misleading
- States present at the CuO/Cu_2O interface

What's next?

- CuO/Cu_2O interface with different surfaces
- $CuO/Cu_4O_3/Cu_2O$ interface



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Thank You all for Your attention

Questions? Comments? Critique? Ideas?

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“ ... and may your God go with you.“

Dave Allen