

Theoretical insights into oxygen defects on transition metal and rare earth oxide surfaces

M. Verónica Ganduglia–Pirovano

Institute of Catalysis and Petrochemistry, CSIC, Madrid, Spain

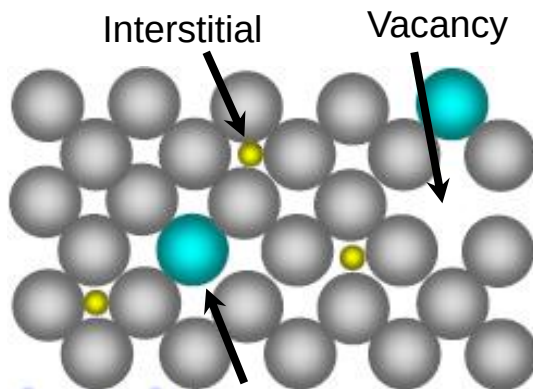
Defects in bulk crystals

No crystal of significance size is perfect !

Types of Imperfections

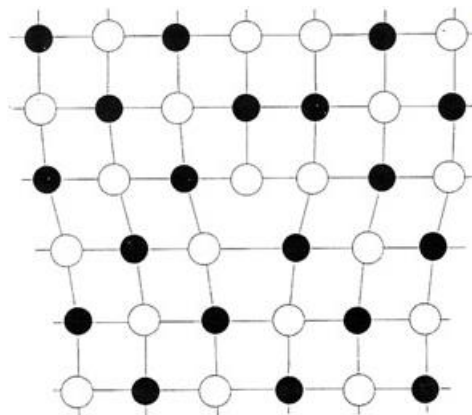
- | | | |
|------|---------------|---|
| ▪ 0D | Point Defect | Vacancies; Interstitials; Substitution |
| ▪ 1D | Line Defect | Dislocation |
| ▪ 2D | Planar Defect | Surface; Grain Boundary; Stacking Fault |

Point Defect

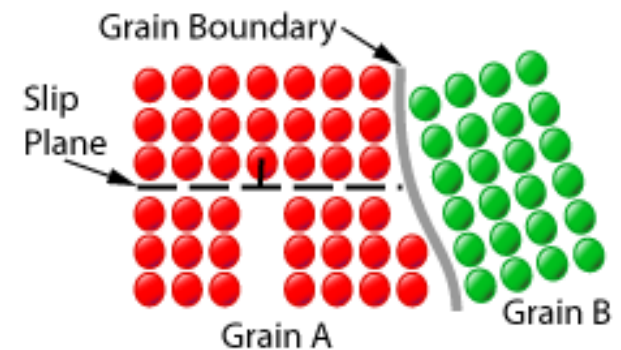


Substitution

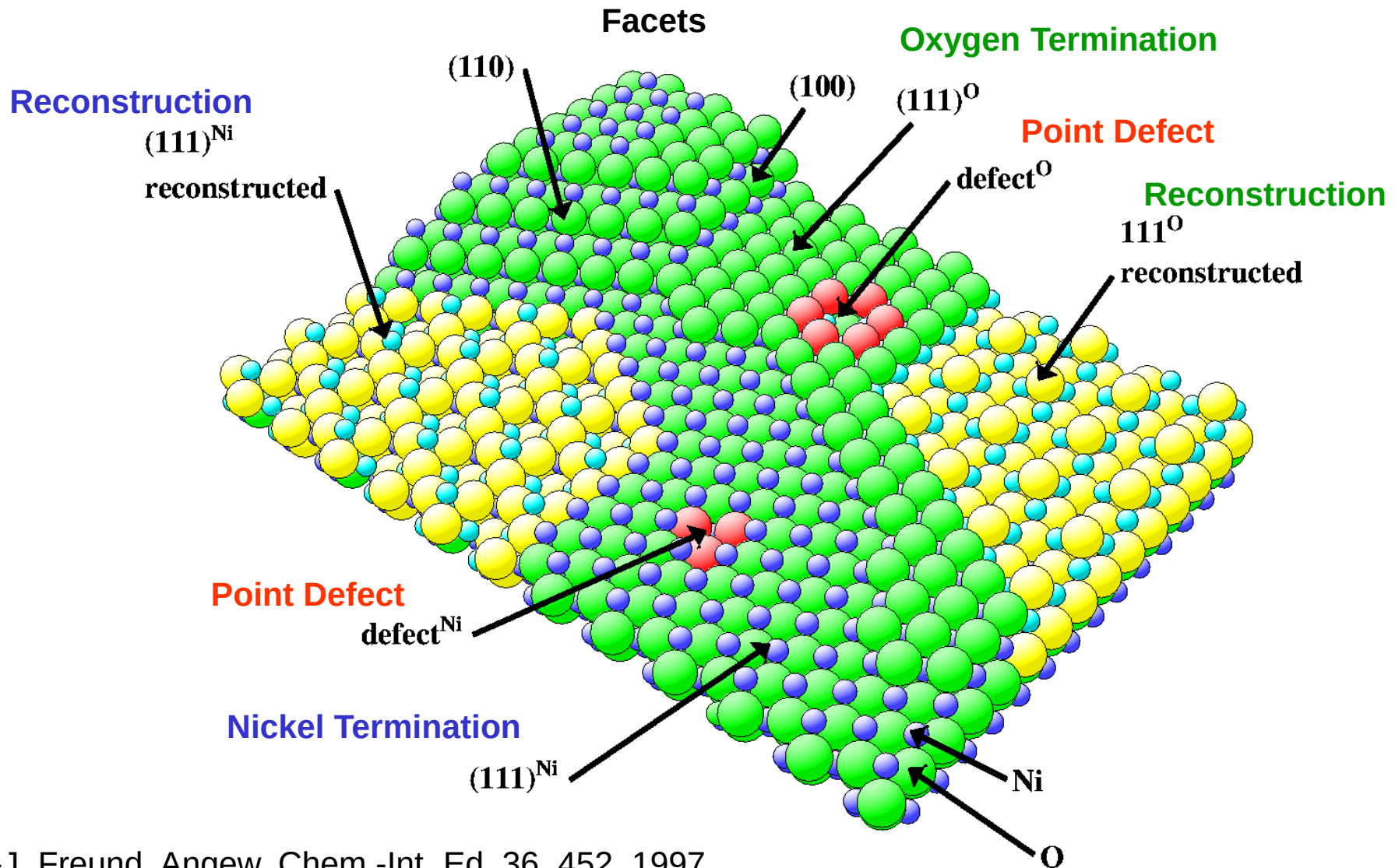
Line Defect



Planar Defect

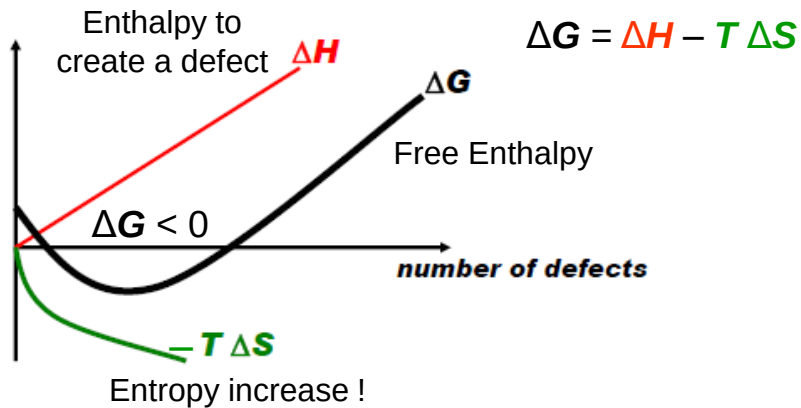


Defects on surfaces: The example of NiO(111)



Defects in bulk and on surfaces of transition metal and rare earth oxides

Defects are always present in a real crystals due to thermodynamic reasons!



Non-stoichiometry is common amongst transition metal and rare-earth compounds
e.g., Fe_xO where $0.957 > x > 0.833$

Oxygen vacancies can be produced by

- irradiation of the sample
- thermal annealing

The « beauty » of imperfection

Adding atoms to a semiconductor can improve its electronic properties. In an **oxide**, taking atoms away can have a similar electronic effect — one that could, it seems, be exploited in **device applications**.

Jochen Mannhart and Darrell G. Schlom, Nature **430**, 620 (2004)

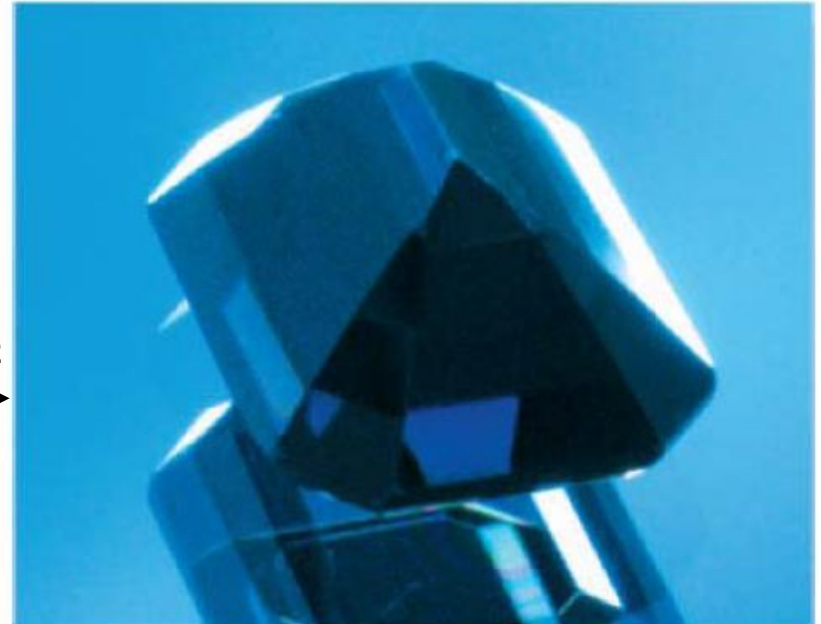
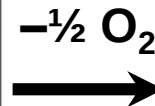
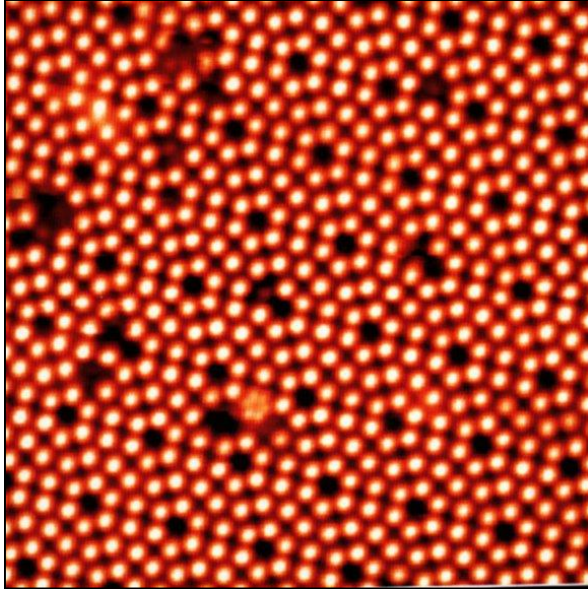


Figure 1 Now you see it, now you don't. These micrographs of a SrTiO₃ crystal show the effect of removing oxygen atoms, leaving vacancies in

the crystal lattice: the glistening oxidized gem is transformed into a dull blue, conductive crystal .

Scanning Tunneling Microscopy/Spectroscopy (STM/STS)



clean Si(111) surface in ultra high vacuum conditions
(otherwise the surface would immediately oxidize and
we would see amorphous SiO₂)

**What are seeing?
Atoms?**

Scanning Tunneling Microscopy/Spectroscopy (STM/STS)

- Tunneling current between tip and sample

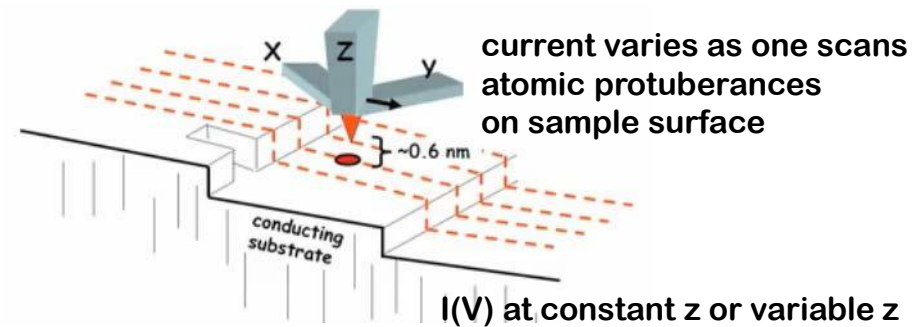
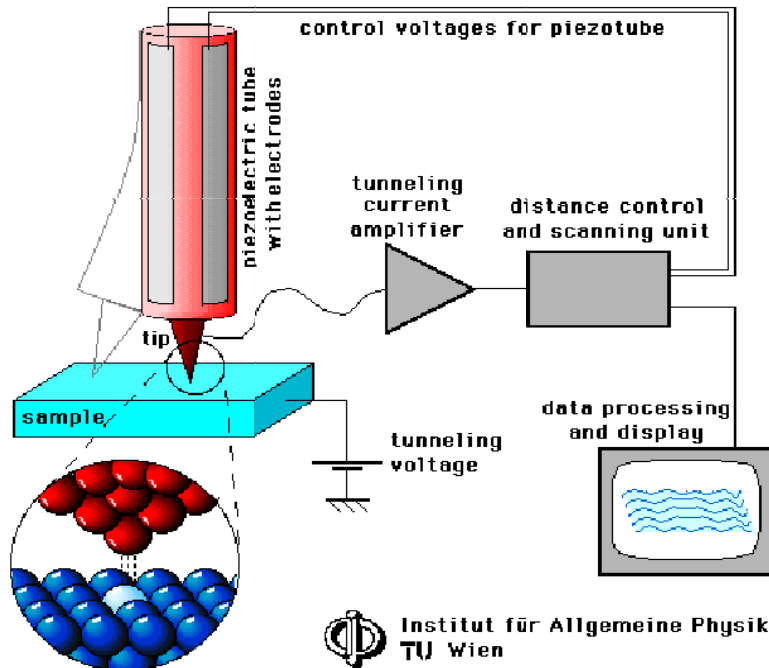
Gerd Binnig and Heinrich Rohrer, Nobel Prize ,86

$$I \sim (V/z) \exp(-A\sqrt{\phi} z)$$

ϕ ... Workfunction, typically 3-5 eV

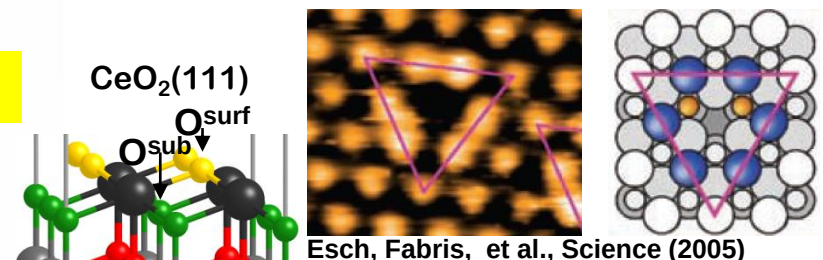
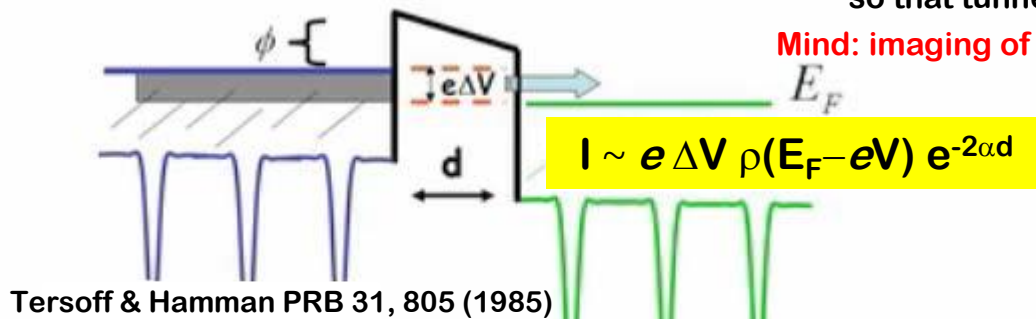
z ... Tip-sample separation, 4-10 Å

Scanning mode → 2D atomic resolution images



In constant current mode uses feedback loop to control a voltage applied to piezo-scanner in order to continuously adjust the tip height, so that tunneling current is maintained → „topographic“ image

Mind: imaging of local electron density of states with atomic resolution

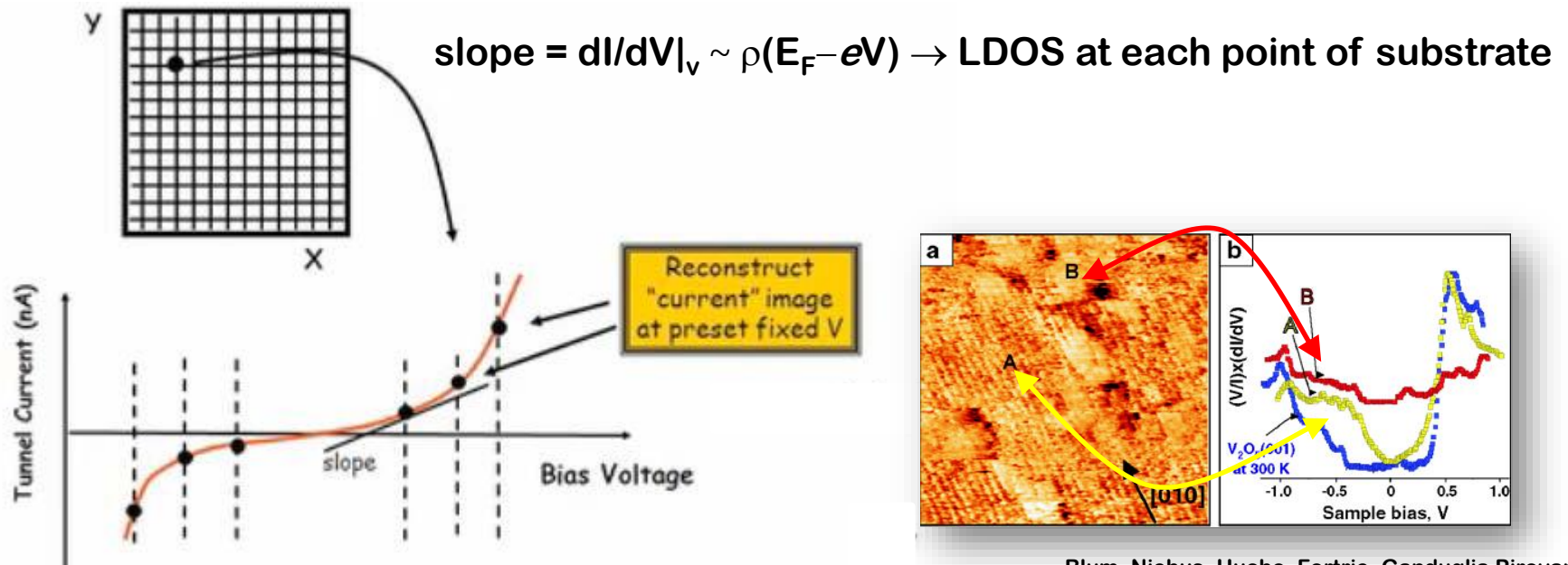


Scanning Tunneling Microscopy/Spectroscopy (STM/STS)

Spectroscopy mode → I-V profiling at specific sites (LDOS)

$$I \sim e V \rho(E_F - eV) e^{-2\alpha d}$$

probe V-dependent filled and empty states at each (x,y) point



Blum, Niehus, Hucho, Fortrie, Ganduglia Pirovano, Sauer, Shaikhutdinov, Freund, PRL99, 226103 (2007)

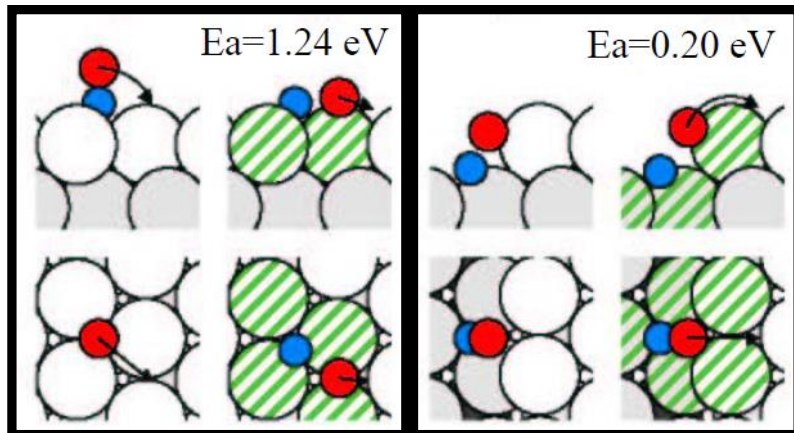
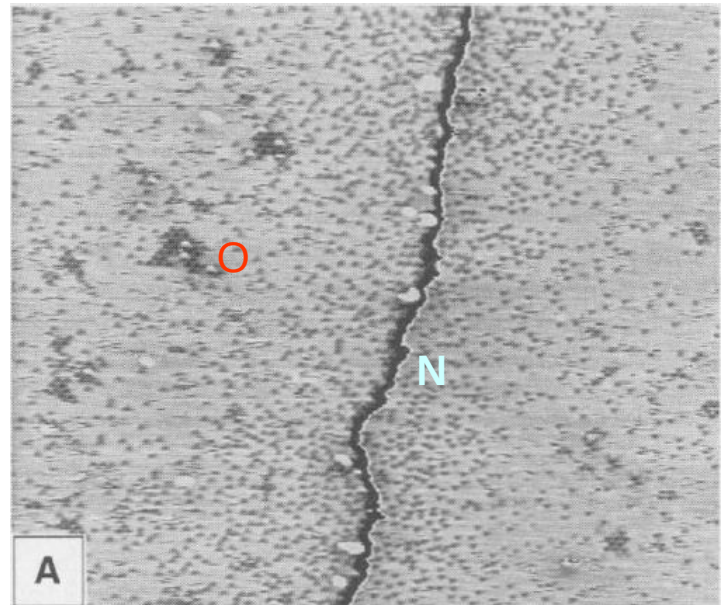
The « beauty » of imperfection at surfaces

Defects at surfaces such as **steps**, **kinks**, and **edges**, as well as **point defects** usually have much **higher reactivity** toward adsorbates relative to flat terraces due to reduced coordination.

NO dissociation at Ru steps

STM 0.5 hour after exposure to 0.3 L of NO

T.Zambelli, J. Winterlin, J. Trost, G. Ertl,
Science 273273, 1688 (1996)

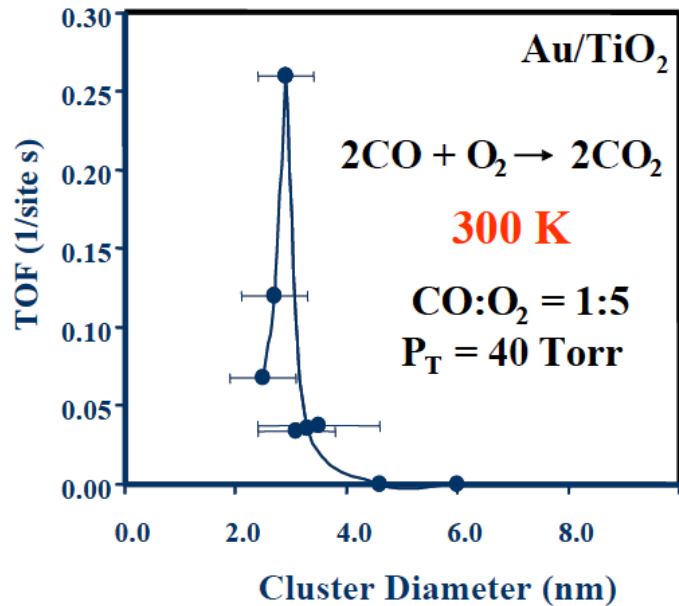


N–O bond activation at Ru steps

B. Hammer, Phys. Rev. Lett. 83, 3681 (1999)

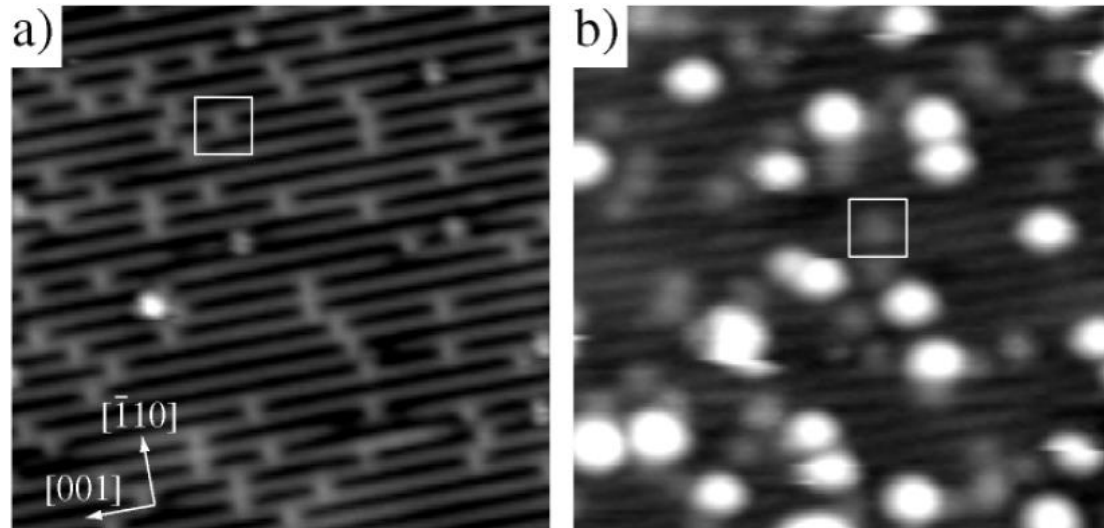
Reducible oxides in catalysis: Titania

TiO₂ supported Au clusters: Defects as anchors



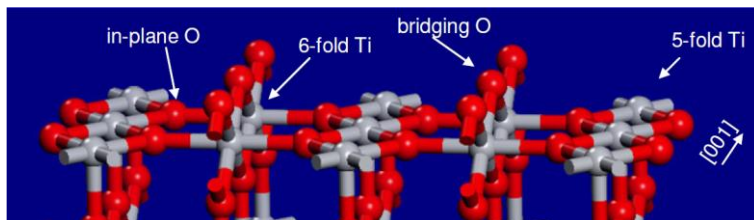
Important factors in promoting the activation of adsorbed species:

- cluster perimeter
- cluster size
- charge of the Au cluster
- **special site (defect) on the oxide support**



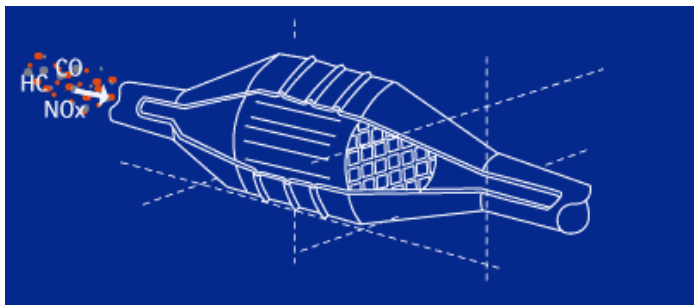
E. Wahlström et al., Phys. Rev. Lett., 90, 026101 (2003)

TiO₂(110)



M. Haruta, Catal. Today. 36, 153 (1997)

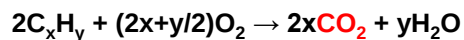
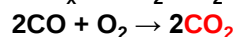
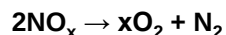
Reducible oxides in catalysis: Ceria



http://www.rhodia-ec.com/site_ec_us/catalysis/index_automotive.htm

Catalytic converter

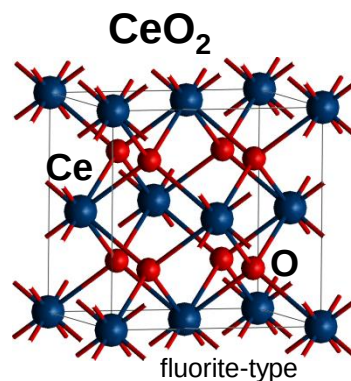
transforms the primary pollutants in the exhaust gas into non-toxic less harmful compounds



CO₂ is a pollutant as a greenhouse gas

Catalyst formulation

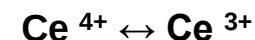
- precious metals Pt, Rh, Pd → active phase
- alumina → support
- Zr-doped ceria → oxygen storage capacity (OSC)
- ZrO₂ → enhances OSC, thermal stability



Oxygen Storage Capacity

an 'oxygen-sponge'

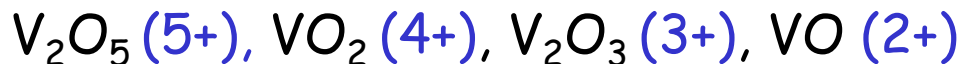
releasing and absorbing oxygen according to the catalytic reaction required (oxidation or reduction)



CeO₂ supported metal and oxide catalysts are singled out as very promising for various reactions; ceria can stabilize reduced states

Reducible oxides in catalysis: Vanadia

- large variety of oxidation states:



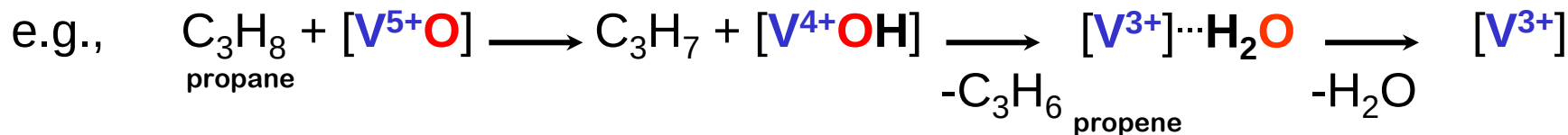
V^{2+} V^{3+} V^{4+} V^{5+}

- active and selective in oxidation reactions:

- SO_2 to SO_3 in the production of sulfuric acid
- benzene to maleic anhydride (polyester resins)
- Selective oxidative dehydrogenation alkanes to alkenes



Mars-van Krevelen redox mechanism

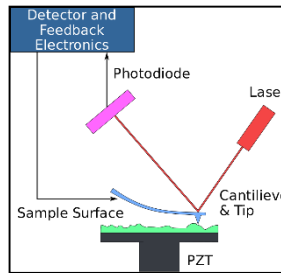


isotopic labelling → **lattice oxygen** participation

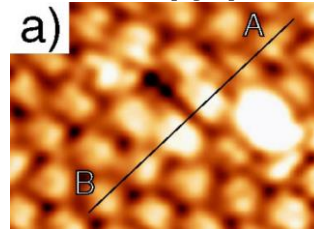
The surface reducibility is key to the function

Oxygen defects on transition metal and rare earth oxide surfaces: Questions

- Defect structure?
Structure relaxation?

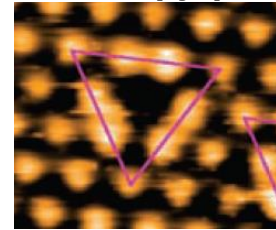


Atomic Force
Microscopy (AFM)



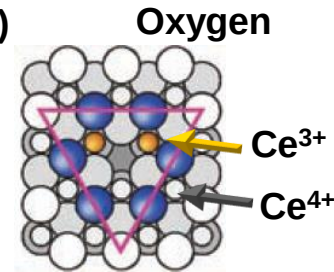
Torbrügge et al., PRL (2007)

Scanning Tunneling
Microscopy (STM)



Esch, Fabris, et al., Science (2005)

$\text{CeO}_2(111)$: surface O defect

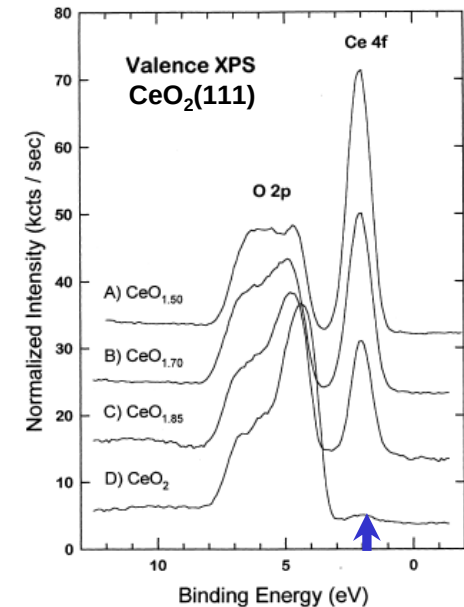
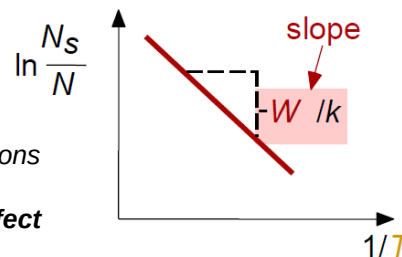


- Electronic structure?
Which states do the „left“ electrons populate?

Interplay between defects, localization,
and structure relaxation

- Energy cost? $\frac{N_s}{N} = \exp\left(\frac{-W}{kT}\right)$

N_s : defect number under equilibrium conditions
 N : number of lattice positions
 W : energy difference of defect vs. no defect
 k : Boltzmann constant; T : temperature



D. R. Mullins et al.,
Surf. Sci. (1999)

Oxygen defects on transition metal and rare earth oxide surfaces: Questions

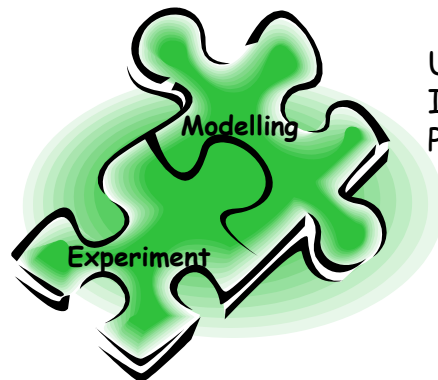
Notwithstanding the experimental progress, a full picture which includes

- the effect on the electronic structure,
- the fate of the left electrons,
- the defect induced structure relaxation
- the defect formation energy

would still remain, in most cases, an elusive goal without the support from theory



Computer modelling

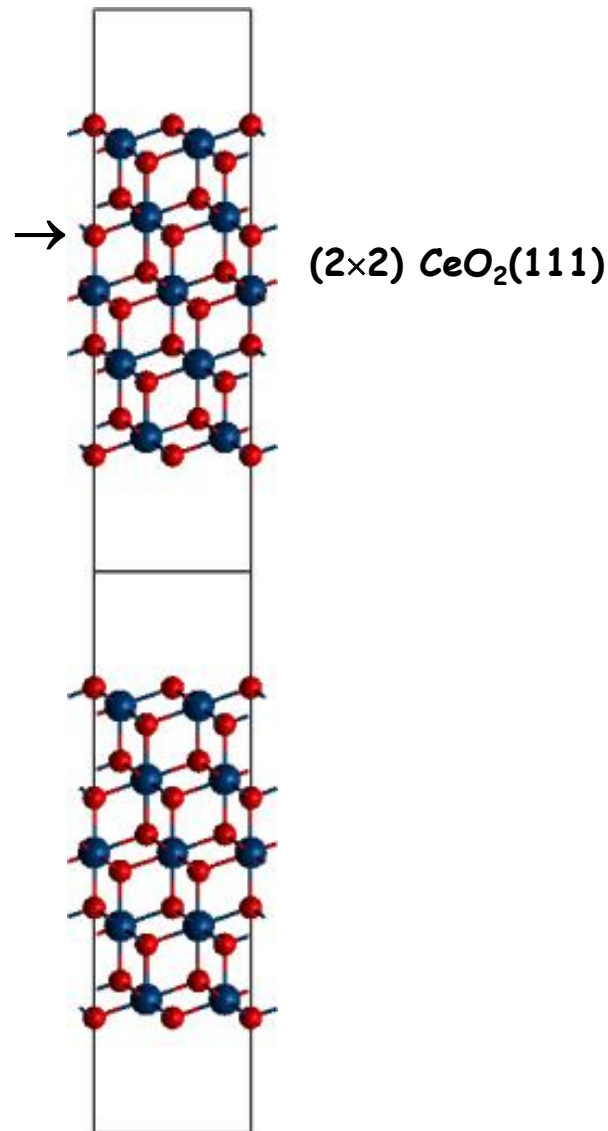


Understanding
Insight
Prediction

Theoretical Modelling

Surface models

Periodic approach: supercell or slab geometry



Methods

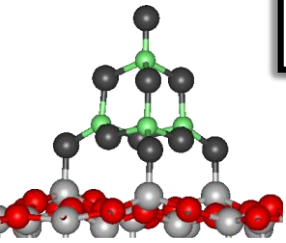
Density Functional Theory DFT



W. Kohn

Chemistry Nobel Prize 1998

The 3 minutes Density Functional Theory gist



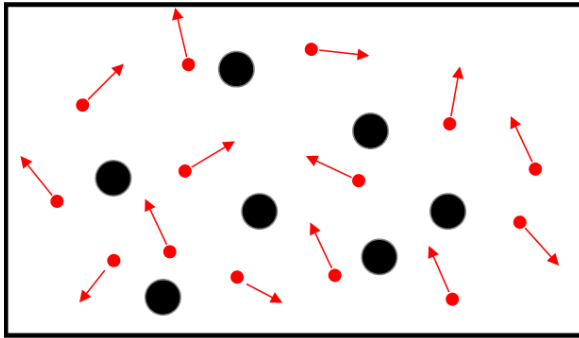
$$H = \sum_{i=1}^{N_e} \left[-\frac{\hbar}{2m_e} \nabla_i^2 + V_N(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_N \leftrightarrow n_0$$

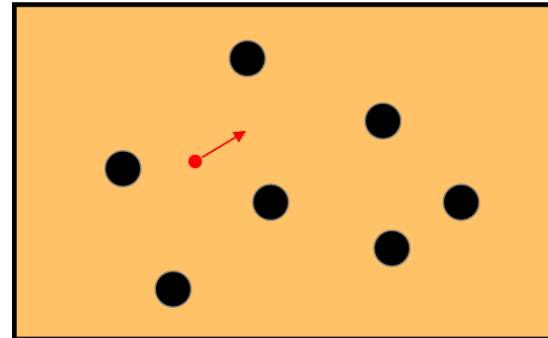
$$E_0[n_0] = \min_{\Psi \rightarrow n_0} \langle \Psi | H | \Psi \rangle$$

Kohn-Sham DFT '65

Hohenberg-Kohn '64



Interacting particles in real potential



Non-interacting fictitious particles in effective potential

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow |\varphi_1(\mathbf{r}_1) \varphi_2(\mathbf{r}_2) \dots \varphi_N(\mathbf{r}_N)|$$

Variational
Principle

$$n(\mathbf{r}) \equiv n_s(\mathbf{r}) = \sum_{i=1}^{N_e} |\varphi_i(\mathbf{r})|^2$$

$$V_H(\mathbf{r}) = \int d^3\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Hartree

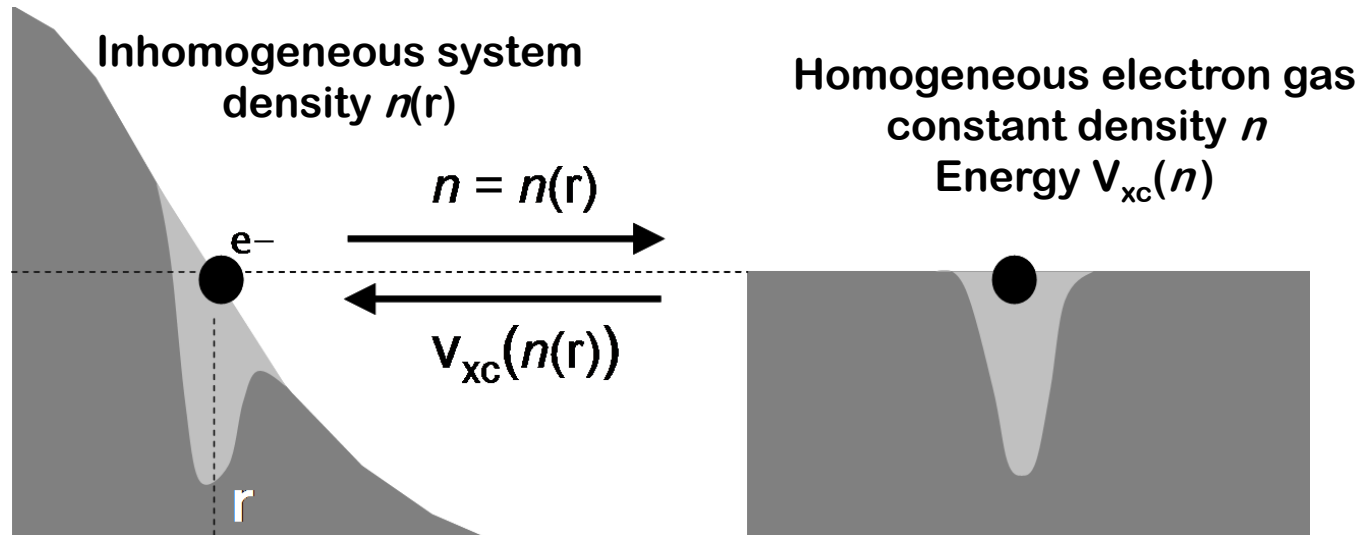
KS equations

DFT-KS is exact!!

$$\left[-\frac{\hbar}{2m_e} \nabla_i^2 + V_N(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

DFT: The approximated $E_{xc}[n]$ functional

The Local Density Approximation (LDA): The „mother“ of all approximations

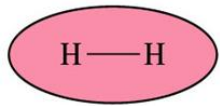


Generalized Gradient Approximation (GGA): $V_{xc}(n(r), \nabla n(r))$

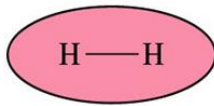
- ❑ Many many flavours: PW91, PBE, revPBE, BP86, BLYP, ...
- ❑ Include (at least partially) correlation effects where overlap is appreciable
- ❑ Dispersion interactions (vdW) NOT included
- ❑ Self-interaction **NOT** fully canceled

Deficiencies { **Overestimation:** Electron delocalization, metallic character, atomization energies
Underestimation: Band gaps, energy barriers

vdW interactions: London forces

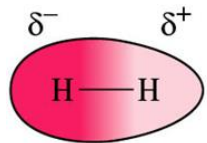


Molecule A

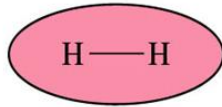


Molecule B

No polarization



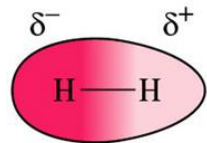
Molecule A



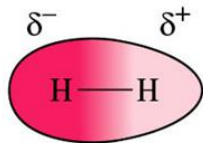
Molecule B

electrons are constantly moving!
instantaneous dipole

Depends on the electronic *response* of the system;
stronger between easily polarizable molecules



Molecule A



Molecule B

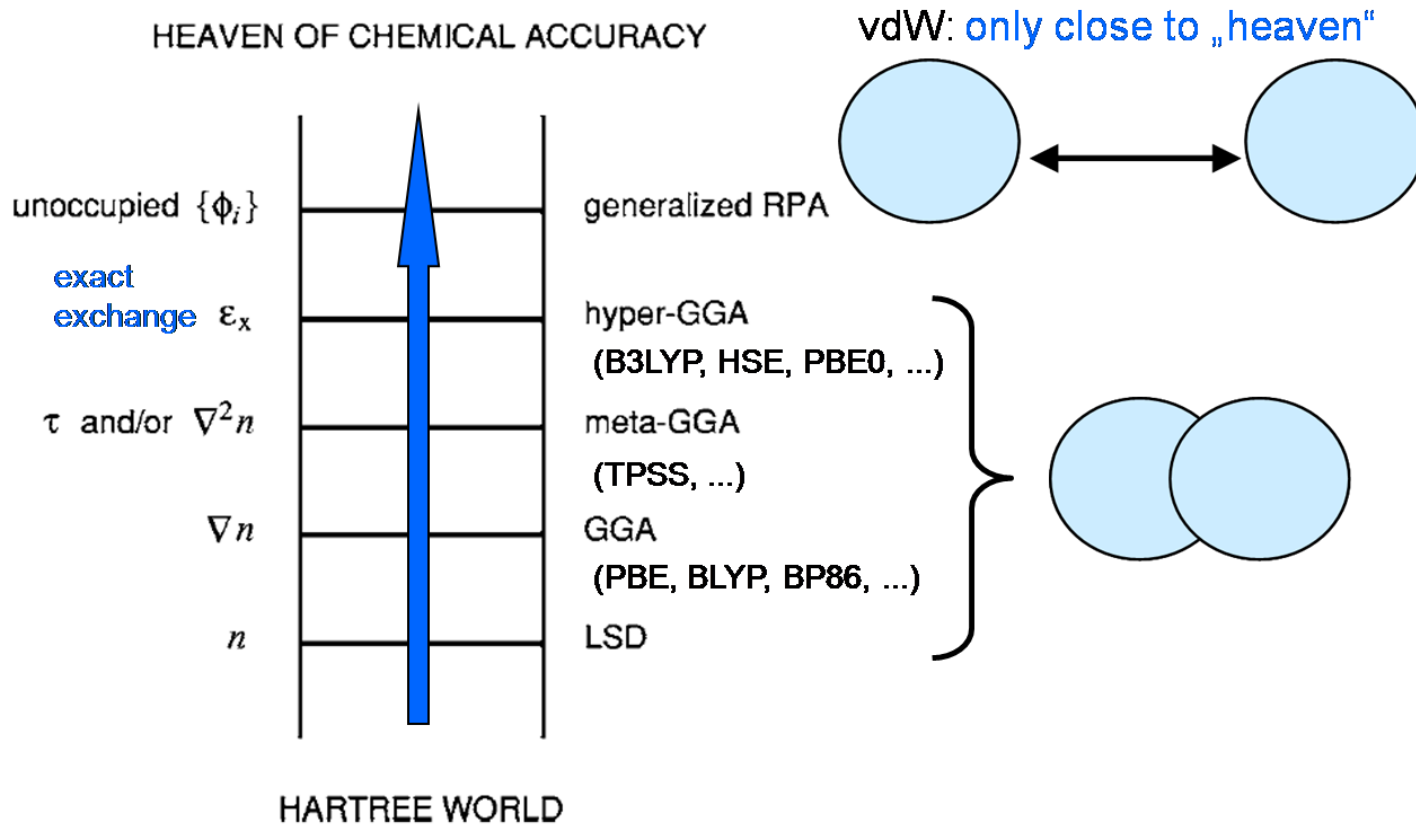
Correlated
spontaneous & induced charge-density fluctuations
give net attractive Coulomb interaction

instantaneous dipole on A
induces dipole on B

A true quantum-mechanical effect !!

DFT: The Jacob's ladder

J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov,
G. Scuseria, G. I. Csonka, JCP 123, 062201 (2005)



DFT: Basis sets and pseudopotentials

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \underbrace{v_{\text{ext}}(\mathbf{r}) + v_{\text{coul}}^e(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})}_{\text{Full-potential / pseudopotential}} \right) \underbrace{\psi_{n\mathbf{k}}(\mathbf{r})}_{\text{Planewave : VASP, ABINIT ; LAPW : FLAPW, WIEN2K ; Numerical : SIESTA}} = \epsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r})$$

no preconceptions regarding the form of the solution, the absence of basis set superposition error, and the ability to efficiently calculate the forces on atoms

Pseudopotential

Replace strong ionic potential with weaker pseudopotential which gives identical valence electron wavefunctions outside core region, $r > r_c$.

Ab-initio pseudopotentials are calculated from all-electron DFT calculations on a single atom.

Pseudo-wavefunction has no nodes for $r < r_c$ unlike true wavefunction.

Smooth pseudo can be represented with few plane waves.

Planewaves

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) |\phi_{\mathbf{k}}(\mathbf{G})\rangle$$

n band; $\mathbf{k}$ in BZ

Planewave

$$\langle \mathbf{r} | \phi_{\mathbf{k}}(\mathbf{G}) \rangle = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$

Maximum kinetic energy of a plane wave

$$\langle \phi_{\mathbf{k}}(\mathbf{G}) | -\frac{\hbar^2}{2m} \nabla^2 | \phi_{\mathbf{k}}(\mathbf{G}) \rangle = \frac{\hbar^2 (\mathbf{k} + \mathbf{G})^2}{2m} \leq E_{\text{cut}}$$



Periodic Table

Periodic table of the elements

period	group	1*	2											13	14	15	16	17	18
		1*	IIa											IIIa	IVa	Va	VIa	VIIa	0
1		H																	He
2		Li	Be											B	C	N	O	F	Ne
3		Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
4		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7		Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112	113	114	115	116		
													(Uub)	(Uut)	(Uuq)	(Uup)	(Uuh)		
lanthanide series				58	59	60	61	62	63	64	65	66	67	68	69	70	71		
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
actinide series				90	91	92	93	94	95	96	97	98	99	100	101	102	103		
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

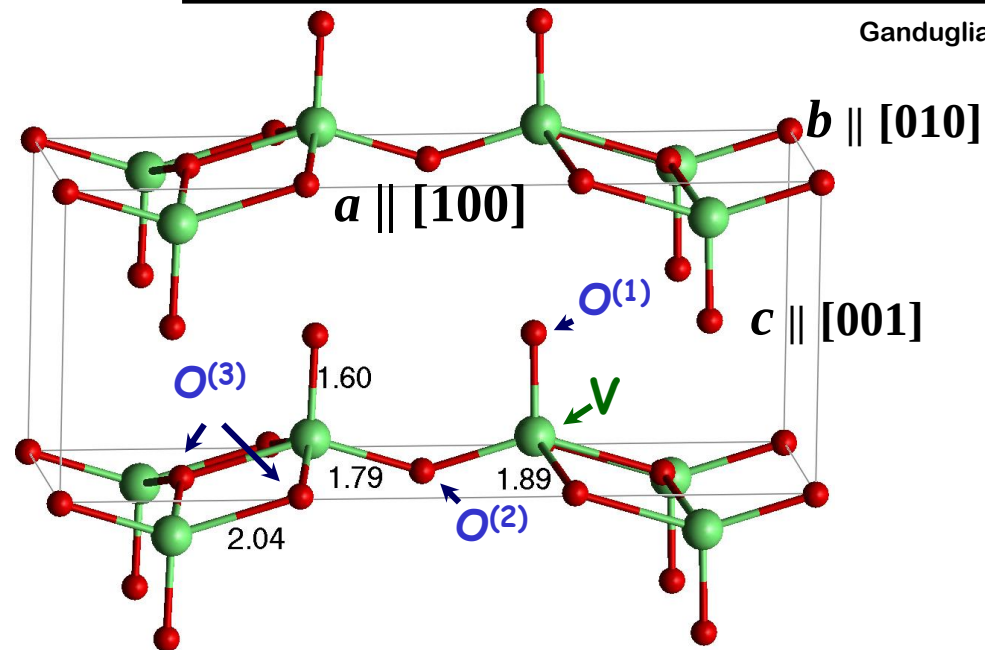
* Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

** Numbering system widely used, especially in the U.S., from the mid-20th century.

*** Discoveries of elements 112–116 are claimed but not confirmed. Element names and symbols in parentheses are temporarily assigned by IUPAC.

V_2O_5 bulk and the V_2O_5 (001) surface

Ganduglia-Pirovano, Sauer, Phys. Rev. B 70, 45422 (2004)



Å PW91 Exp.

a	11.55	11.51	$\Delta a/a = 2\%$
b	3.58	3.56	$\Delta b/b = 1\%$
c	4.84	4.37	$\Delta c/c = 11\%$

 weak interacting layers

Vienna Ab initio Simulation Package VASP

DFT+D: The 2nd generation

S. Grimme, J. Comp. Chem. 25, 1463 (2004); ibid 27, 1787 (2006)

$$E_{DFT+D} = E_{KS} + E_{disp}$$

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f(R_{ij})$$

global scaling factor s_6

empirical coefficients (related to polarisability) C_6^{ij}

atom-atom distance R_{ij}

damping factor (avoid singularity $R \sim 0$) $f(R_{ij})$

2nd generation:

- C_6 and damping function are independent of the underlying functional
- s_6 E_{xc} dependent scaling parameter:

0.75 PBE	1.05 BP86
1.20 BLYP	1.0 TPSS
1.05 B3LYP	

Long-range interactions are „adjusted“ to the different behavior of E_{xc} at intermediate distances

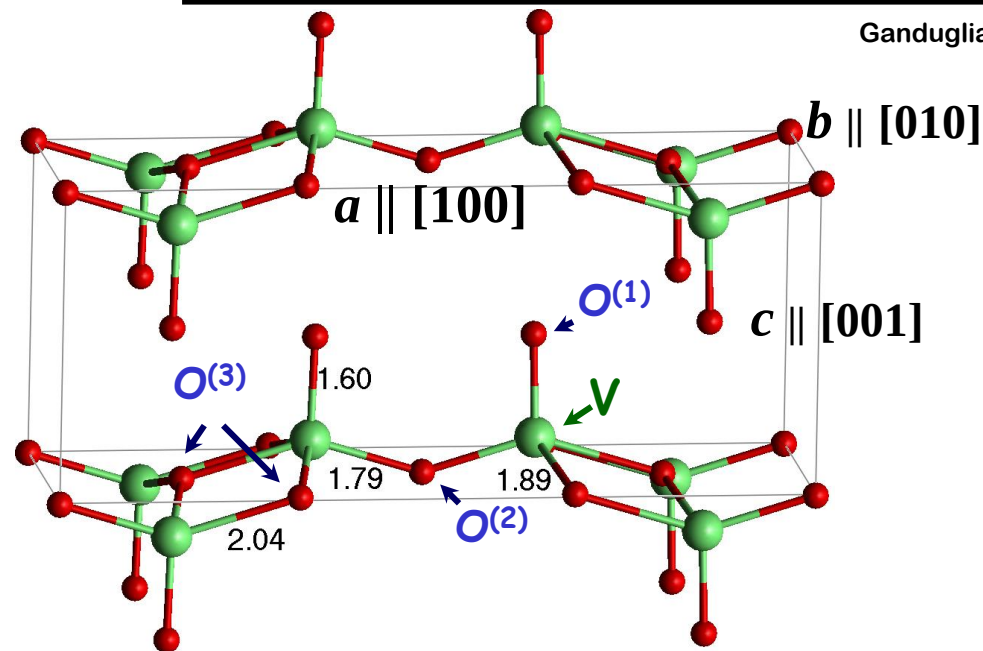
Bulk V_2O_5

c 4.86 PBE 4.50 PBE+D 4.37 Exp

Kerber, Sierka, and Sauer J Comp Chem 29, 2088-2097 (2008)

V₂O₅ bulk and the V₂O₅ (001) surface

Ganduglia-Pirovano, Sauer, Phys. Rev. B 70, 45422 (2004)



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<i>a</i>	11.55	11.51	$\Delta a/a = 2\%$
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<i>c</i>	4.84	4.37	$\Delta c/c = 11\%$

weak interacting layers

Vienna Ab initio Simulation Package VASP

M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, PRL 92, 246401 (2004)

vdW-DF new parametrization of E_{xc}

$$E_{xc}^{\text{vdW-DF}}[n] = E_x^{\text{GGA}}[n] + E_c^{\text{LDA}}[n] + E_c^{\text{nl}}$$

exchange

shorter range

LDA

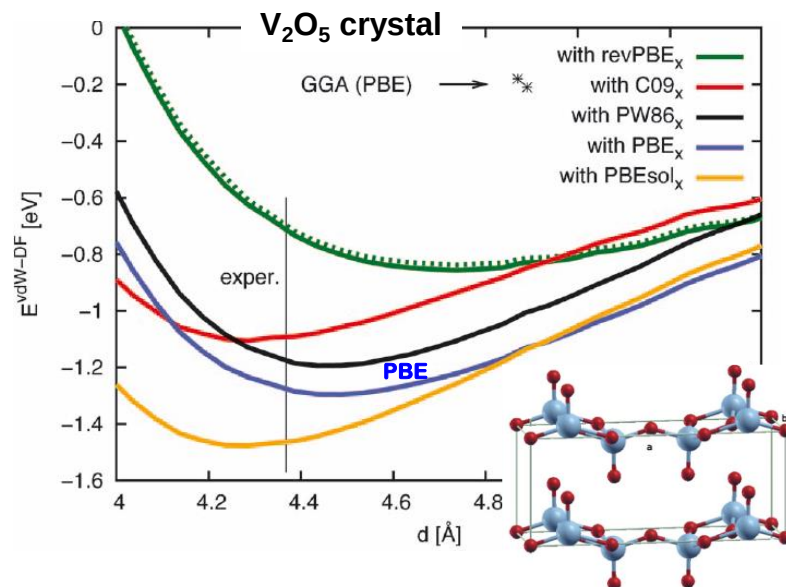
non-local
long range

$$E_c^{\text{nl}} = \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

kernel

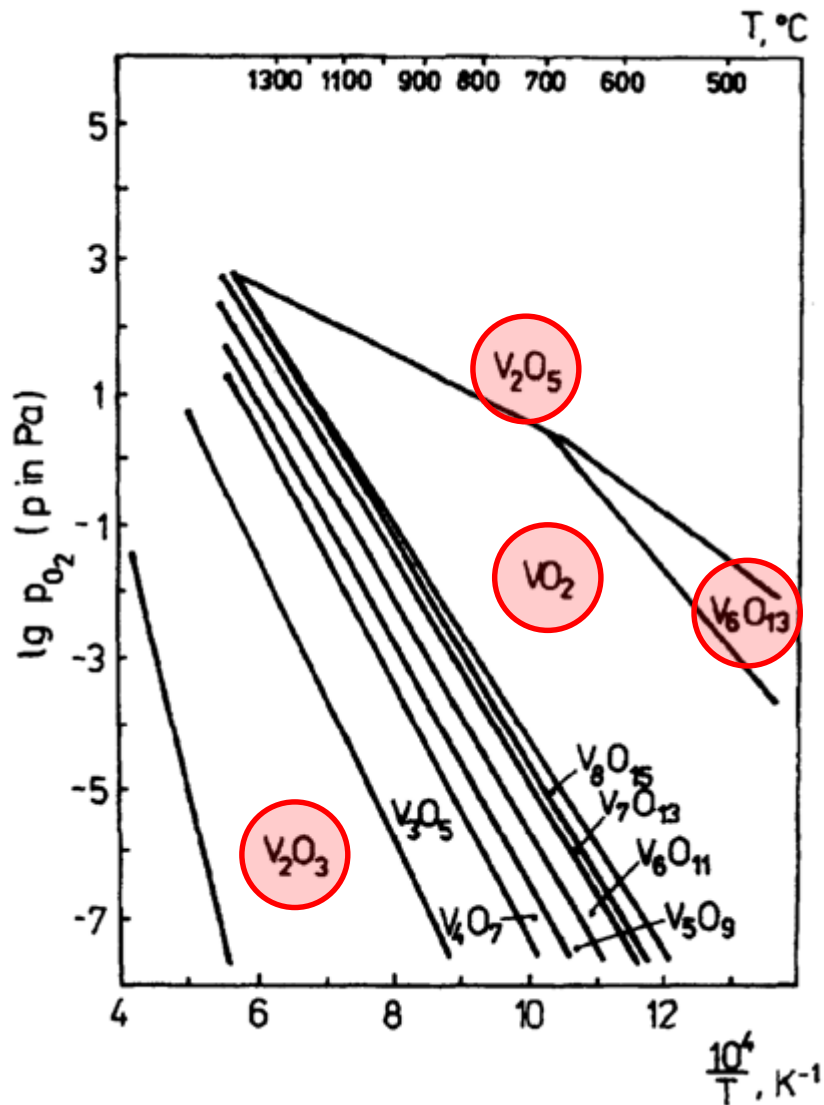
New non-local functional

$$\phi(\mathbf{r}, \mathbf{r}') = \phi(q_0(\mathbf{r}), q_0(\mathbf{r}')) \text{ with } q_0 = q_0(n(\mathbf{r}), \nabla n(\mathbf{r}))$$



Londero, Schröder, PRB 82, 054116 (2010)

Vanadium oxide bulk phases



Most vanadium oxide bulk phases exhibit a metal-insulator transition

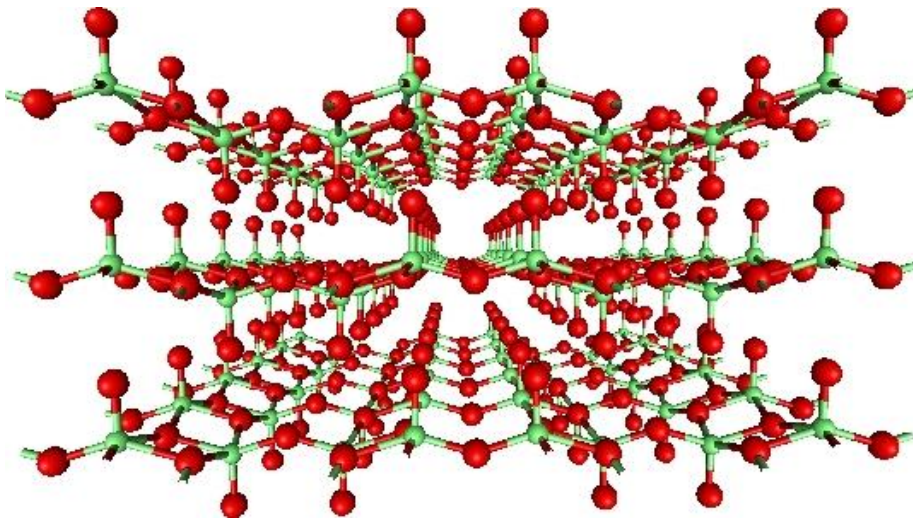
V_6O_{13} : V^{4+}, V^{5+}
MIT @ 150 K

V_2O_3 : V^{3+}
MIT @ 168 K

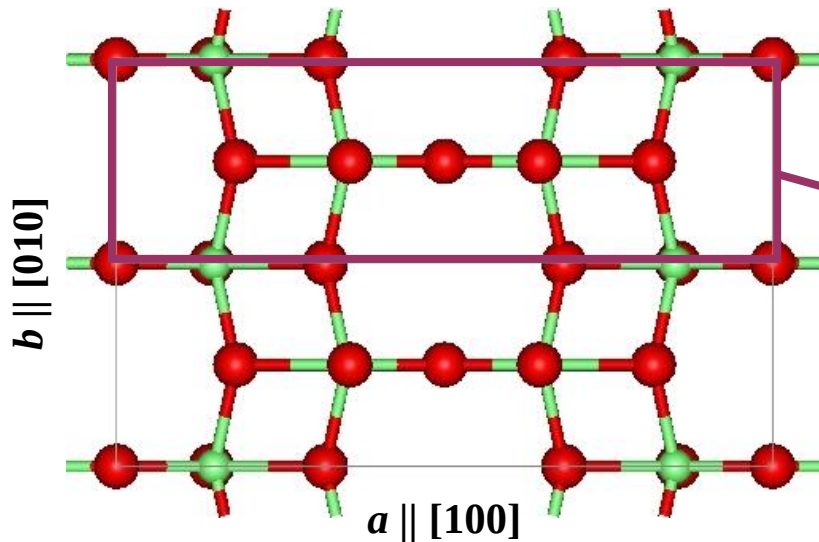
VO_2 : V^{4+}
MIT @ 340 K

V_2O_5 : V^{5+}
no MIT

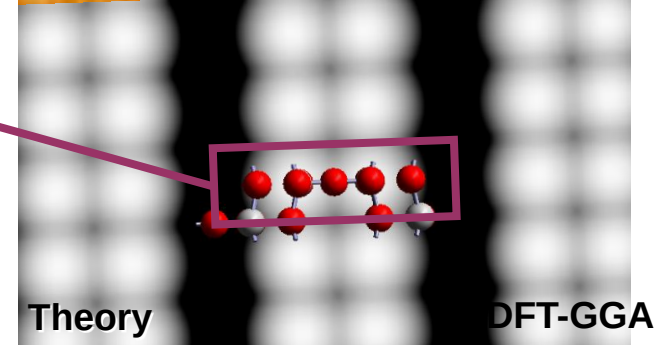
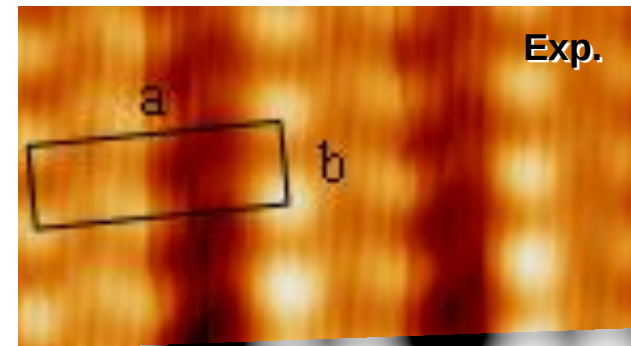
The V_2O_5 (001) surface



Weak
interaction

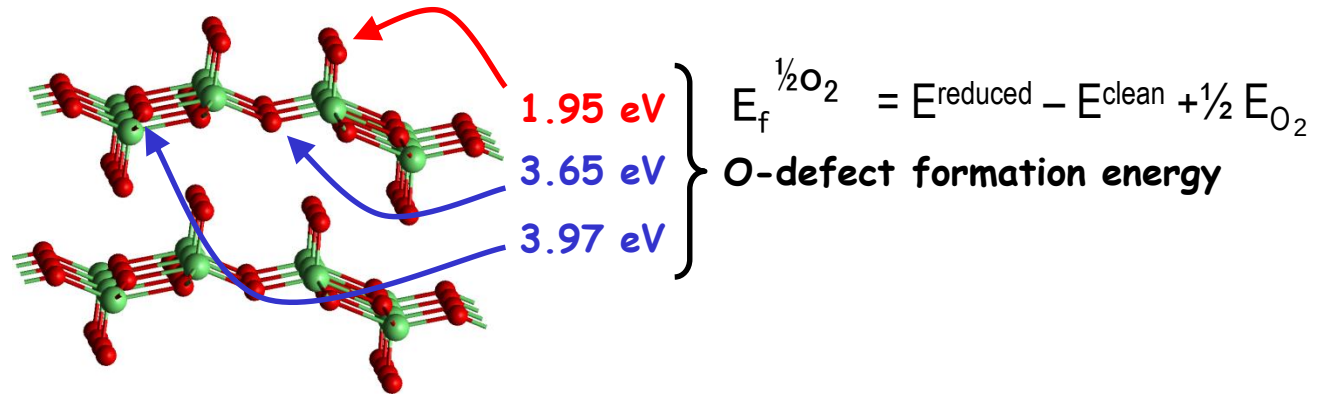


STM @ 300 K (occup. states)



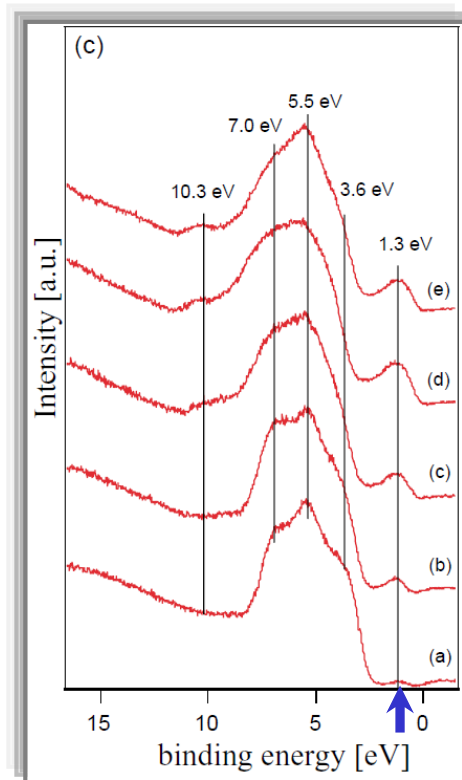
4×2 nm², -1.1 V, 0.45 nA

V_2O_5 bulk and the V_2O_5 (001) surface



$V_2O_5(001)$: Formation of neutral oxygen defects

Q.-H. Wu et al., Applied Surface Science 236, 473 (2004)



ultraviolet photoelectron spectroscopy

Reduction by
thermal annealing

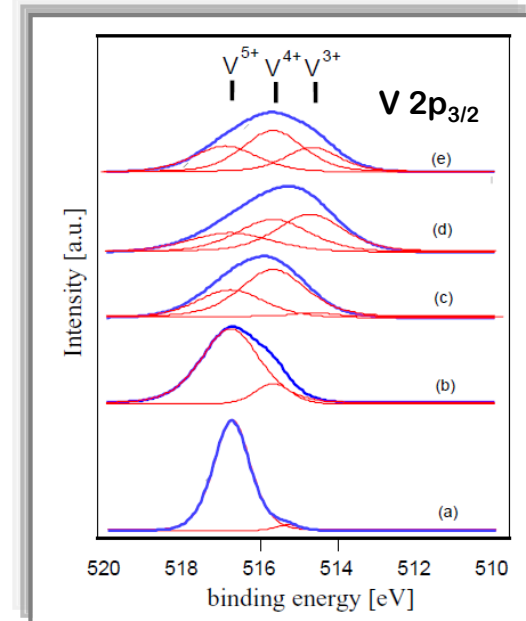


Fig. 4. Fitted data of V $2p_{3/2}$ lines after removal of background for different treatments in UHV chamber: (a) RT, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 400 °C in 10^{-6} mbar oxygen.

- **UPS:** Defect state in the $O_{2p}-V_{3d}$ gap (2.3 eV),
~1 eV below E_F ; V_{3d} nature

- **XPS:** $V^{5+} \rightarrow V^{4+} \rightarrow V^{3+}$

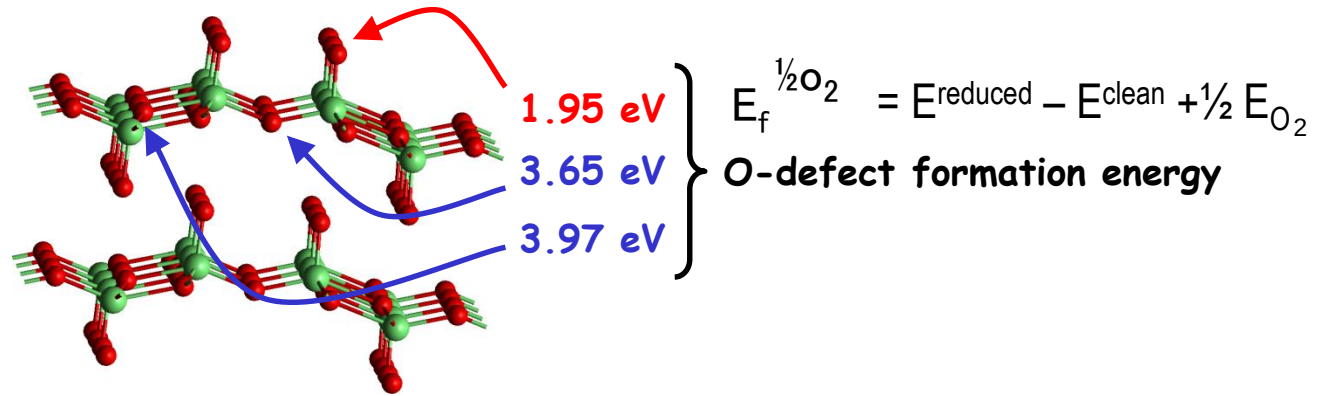
V^{4+} ?

Where is the excess charge?

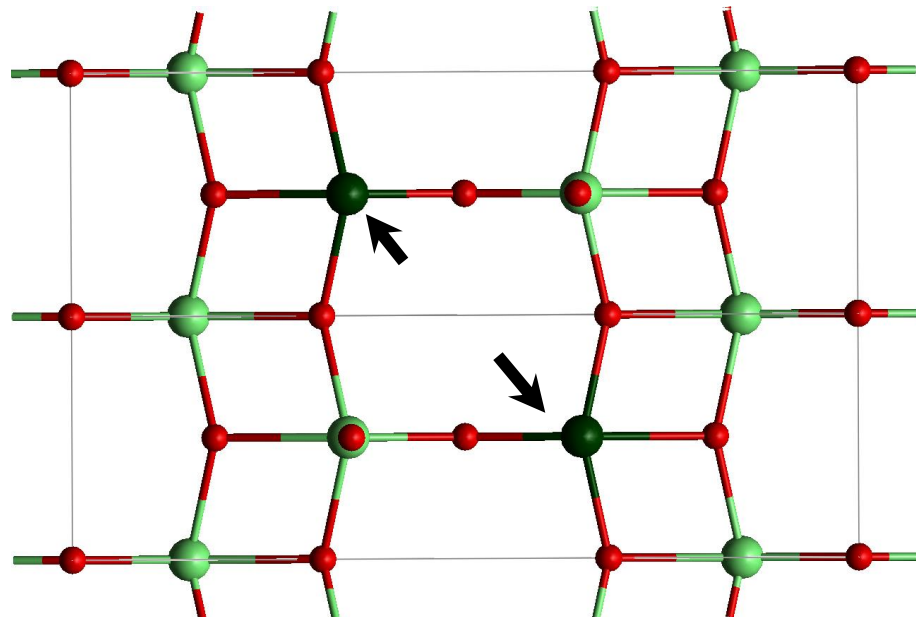
- **STM:** surface oxygen defects with non-random structure

Blum et al, Phys. Rev. Lett. 99, 226103 (2007)

V_2O_5 bulk and the V_2O_5 (001) surface

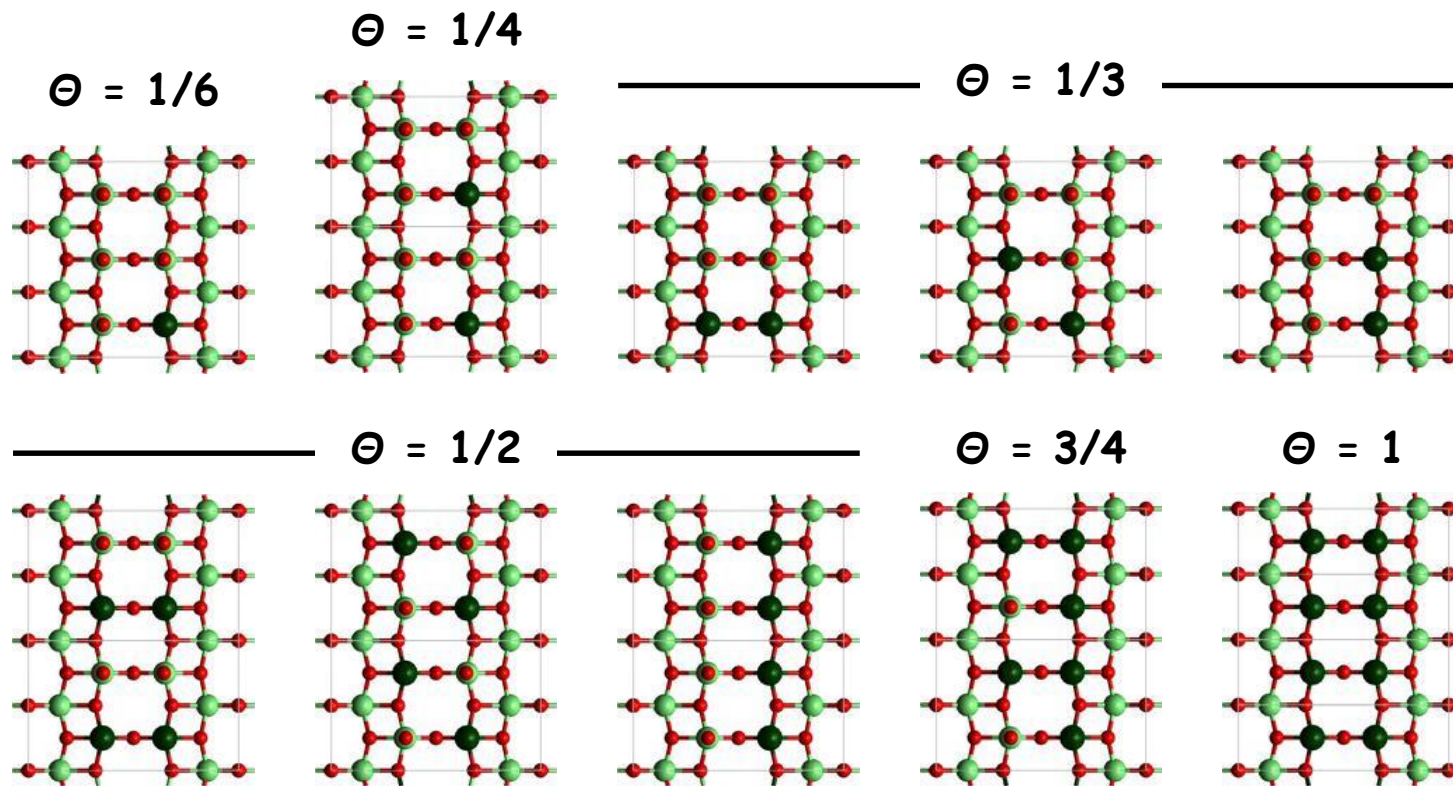
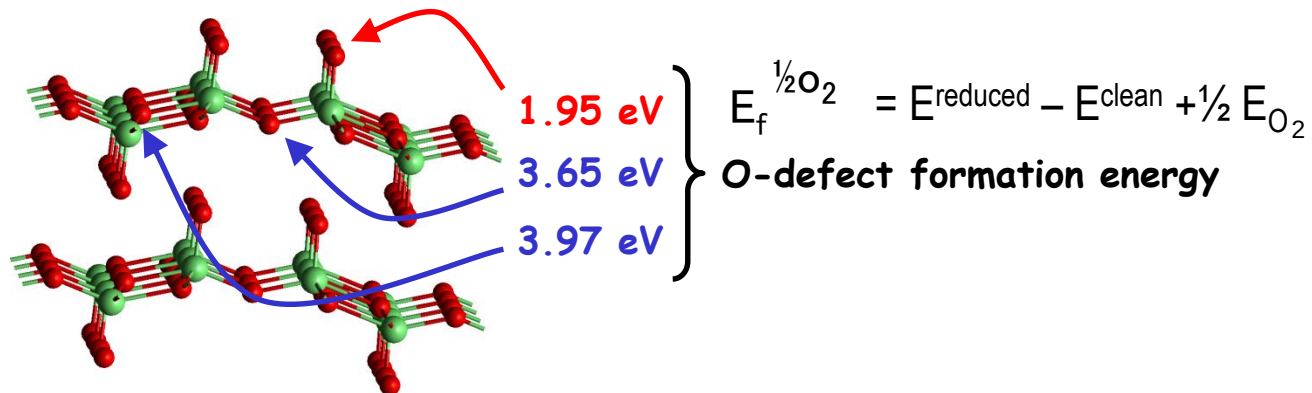


V_2O_5 (001)



$b \parallel [010]$

Simulation of reduced V_2O_5 (001)



Θ = Vanadyl defect concentration

Stability of reduced $V_2O_5(001)$



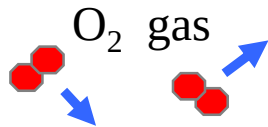
$$\Delta\gamma_{\text{surf}}(T,p) = [G_{\text{slab}}^{\text{reduced}}(T,p,N_{\text{def}}) - G_{\text{slab}}^{\text{clean}}(T,p) + N_{\text{def}} \frac{1}{2} \mu_{O_2}(T,p)] / A$$

$$G = E - TS + pV$$

$$G(p, T) = E(0\text{ K}) + E^{\text{vib}}(T) - T [S^{\text{vib}}(T) + S^{\text{config}}] + pV$$

$$G(p, T) = \underbrace{E(0\text{ K})}_{\text{Total Energy}} + \underbrace{F^{\text{vib}}(T)}_{\text{Helmholtz Energy}} - T \underbrace{S^{\text{config}}}_{\text{Entropy}} + pV$$

$$\Delta\gamma_{\text{surf}}(T,p) \approx [E_{\text{slab}}^{\text{reduced}}(N_{\text{def}}) - E_{\text{slab}}^{\text{clean}} + N_{\text{def}} \frac{1}{2} \mu_{O_2}(T,p)] / A$$



surface layer

V_2O_5 crystal

Stability of reduced $V_2O_5(001)$



$$\Delta\gamma_{\text{surf}}(T,p) = [G_{\text{slab}}^{\text{reduced}}(T,p,N_{\text{def}}) - G_{\text{slab}}^{\text{clean}}(T,p) + N_{\text{def}} \frac{1}{2} \mu_{O_2}(T,p)] / A$$

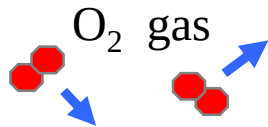
$$\Delta\gamma_{\text{surf}}(T,p) \approx [E_{\text{slab}}^{\text{reduced}}(N_{\text{def}}) - E_{\text{slab}}^{\text{clean}} + N_{\text{def}} \frac{1}{2} \mu_{O_2}(T,p)] / A$$

$$\Delta\gamma_{\text{surf}}(T,p) \approx N_{\text{def}} [E_f^{\frac{1}{2}O_2}(\Theta) + \frac{1}{2} \Delta\mu_{O_2}(T,p)] / A$$

$$\frac{1}{2} \Delta\mu_{O_2} = \frac{1}{2} \mu_{O_2} - \frac{1}{2} E_{O_2}$$

Oxygen chemical potential

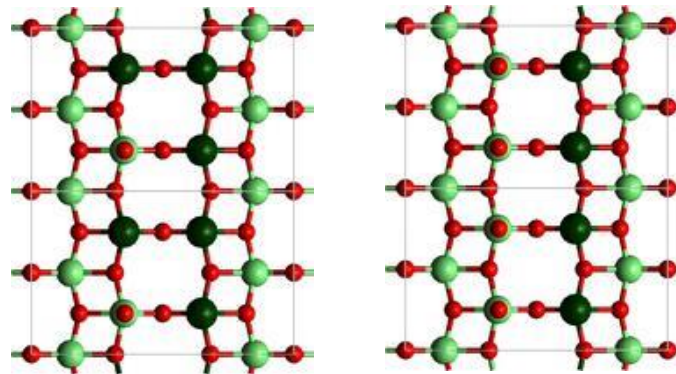
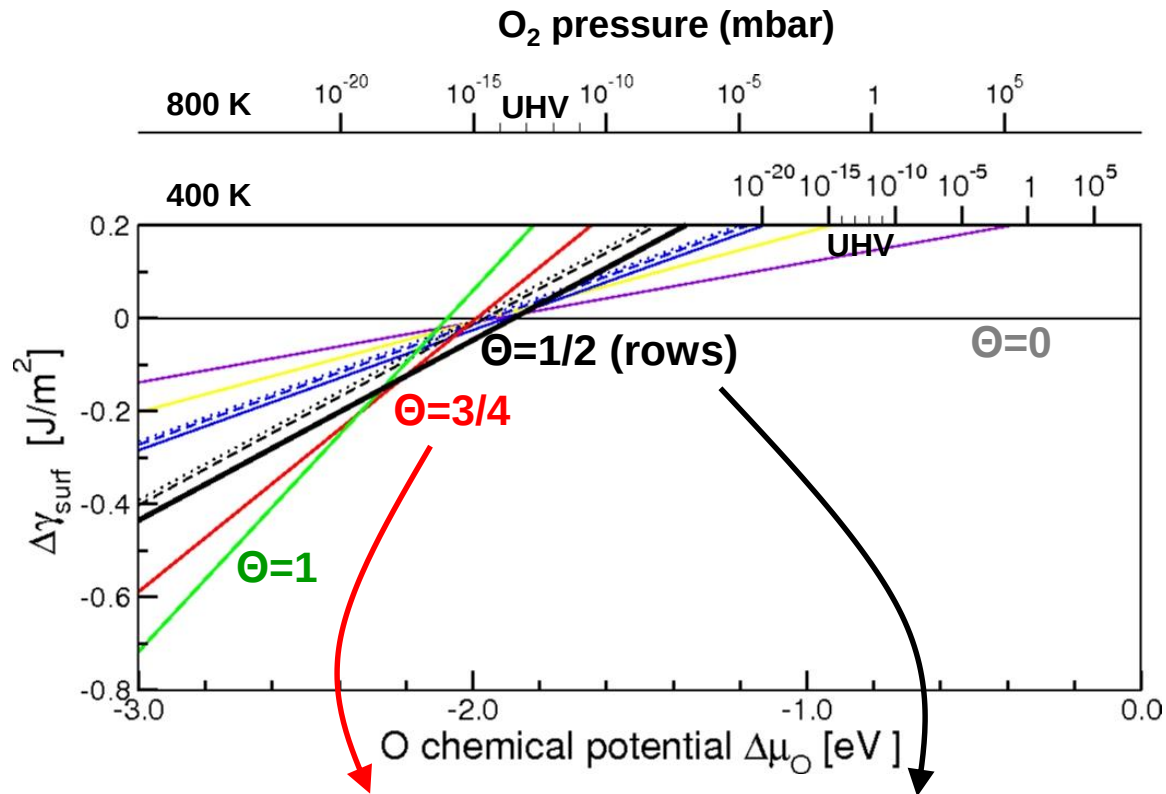
$$\mu_{O_2}(T,p) = \mu_{O_2}(T,p^\circ) + RT \ln(p/p^\circ)$$



surface layer

V_2O_5 crystal

Stability of reduced $V_2O_5(001)$

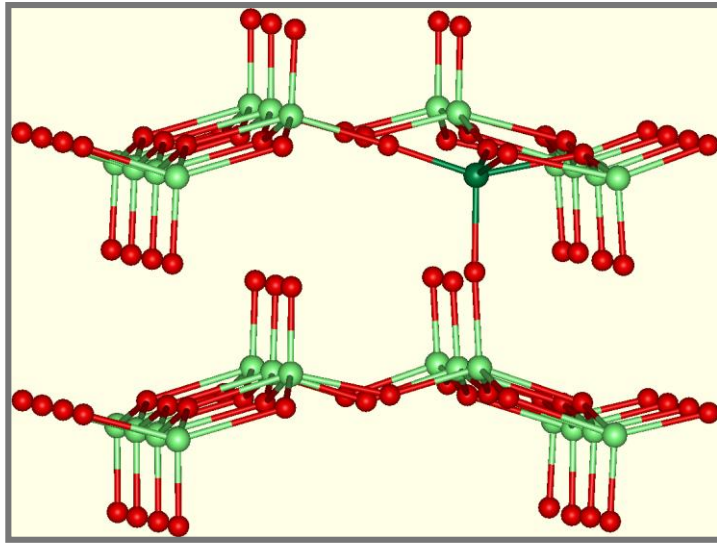


Θ	$1/6 \rightarrow 1/3 \rightarrow 1/2$
$E_f^{\frac{1}{2}O_2}$	$1.93 \rightarrow 1.87 \rightarrow 1.83 \text{ eV}$

Defect induced relaxations

$$\Theta = 1/6 \rightarrow 1/3$$

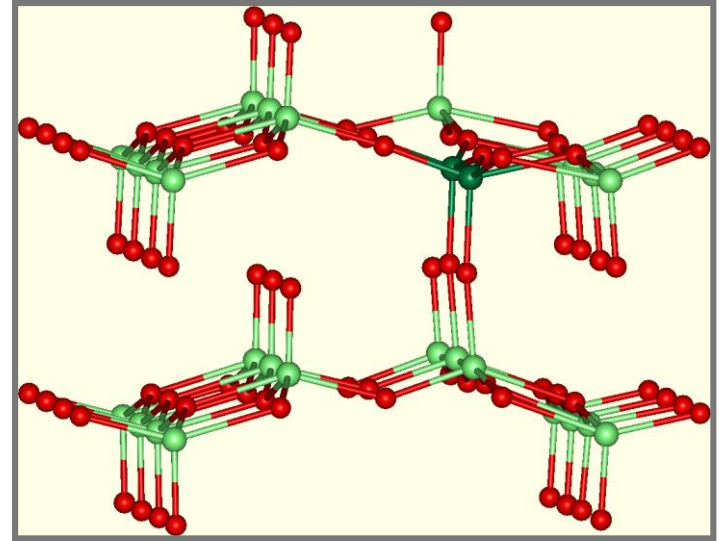
Induced relaxations
take place in a
concerted way



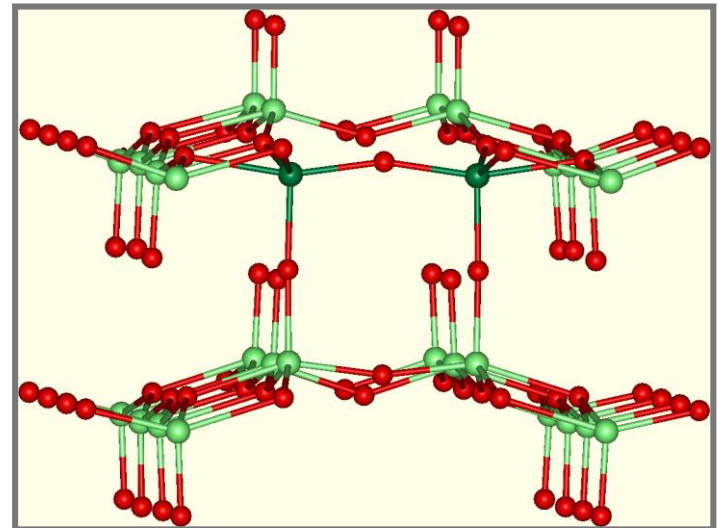
Isolated defect



Pairs || [010]



Pairs || [100]

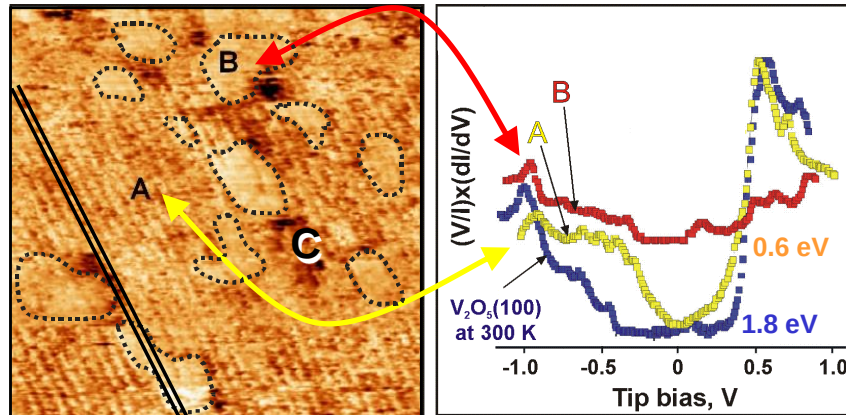


Induced relaxations
do **not** take place
cooperatively

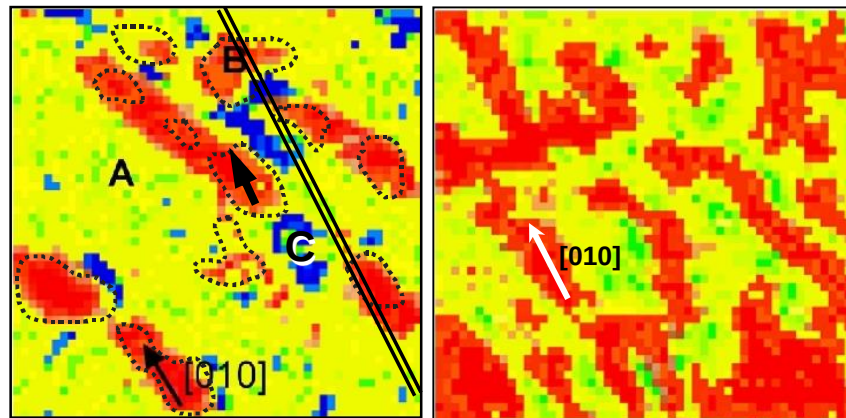
$V_2O_5(001)$ reduction

STM @350K

STS @350K



@400K



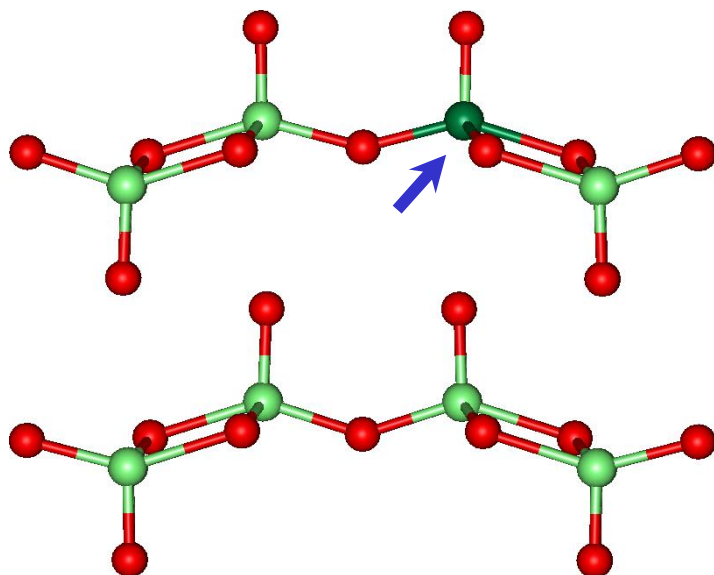
surface **insulator-metal** transition

350-400 K

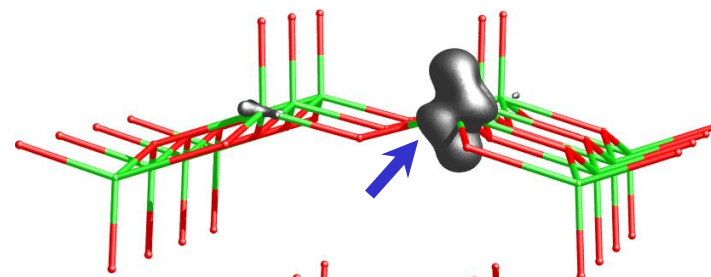
Bandgap map

O-defect induced structural and electronic effects

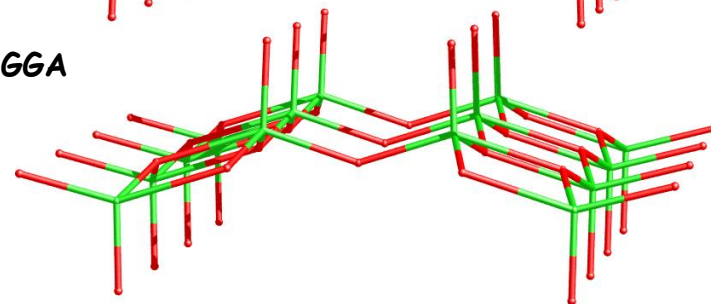
Isolated defect $\Theta = 1/6$



Spin density

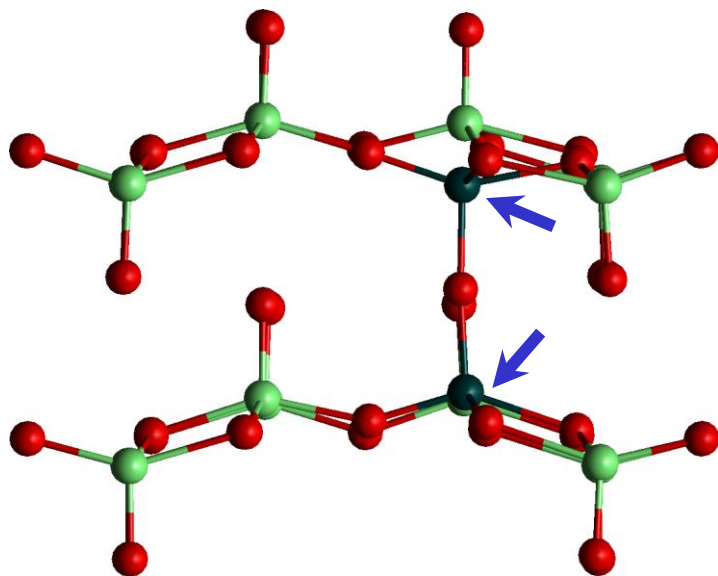


DFT-GGA

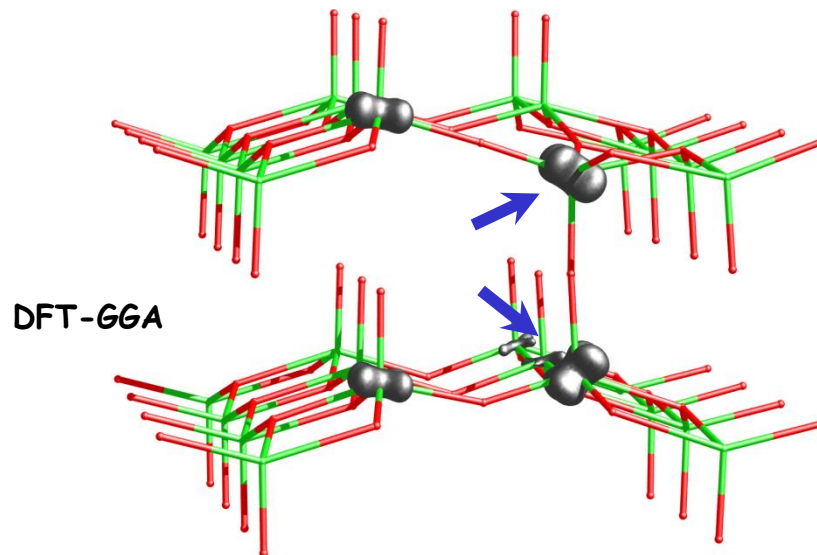


O-defect induced structural and electronic effects

Isolated defect $\Theta = 1/6$

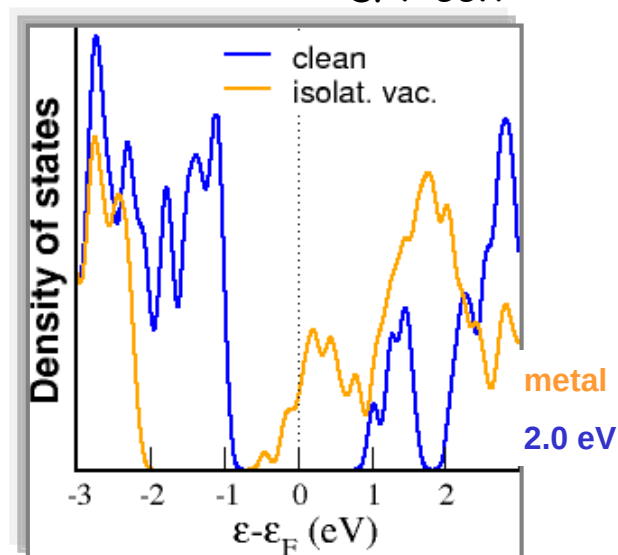


Spin density



DFT-GGA

DFT-GGA



The choice of the computational method

DFT: GGA? 

GGA+U? 

Hybrid? 

Problems: electron delocalization
metallic character

Solutions:

„expensive“ solution: **Hybrid-DFT**

„cheap“ solution: **DFT (LDA/GGA)+U**

Da Silva, Ganduglia-Pirovano,
Sauer, Bayer, Kresse, PRB 75 (2007)

Ganduglia-Pirovano, Hofmann,
Sauer, Surf. Sci. Rep. 62 (2007)

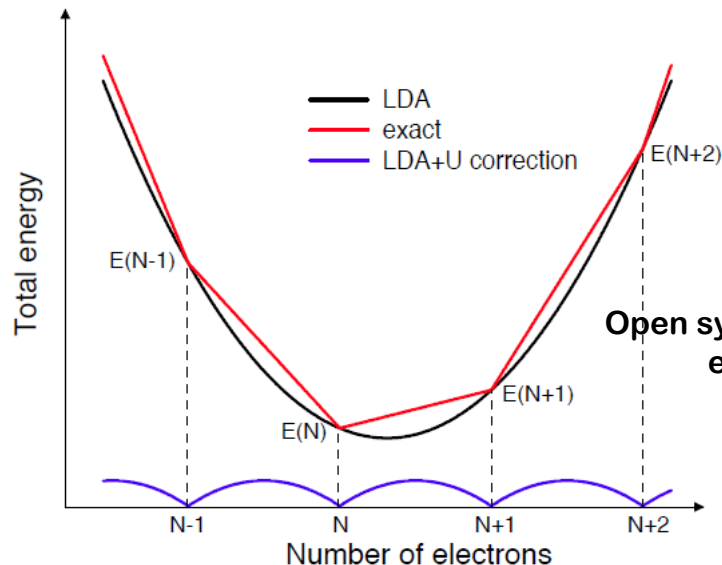
exact-exchange

on-site Coulomb repulsion

Dudarev et al., PRB 57 (1998)

$$E_U = \frac{U}{2} \sum_{I,\sigma} Tr[n^{I\sigma}(1 - n^{I\sigma})]$$

U fitted to experiment



Correction associated to the curvature of E(N)

Open system in contact with an
electron reservoir

M. Cococcioni et al PRB 71, 035105 (2005)

The choice of the computational method

DFT: GGA? 

GGA+U? 

Hybrid? 

Problems: electron delocalization
metallic character

Solutions:

„expensive“ solution: **Hybrid-DFT**

„cheap“ solution: **DFT (LDA/GGA)+U**

Da Silva, Ganduglia-Pirovano,
Sauer, Bayer, Kresse, PRB 75 (2007)

Ganduglia-Pirovano, Hofmann,
Sauer, Surf. Sci. Rep. 62 (2007)

exact-exchange

on-site Coulomb repulsion

Dudarev et al., PRB 57 (1998)

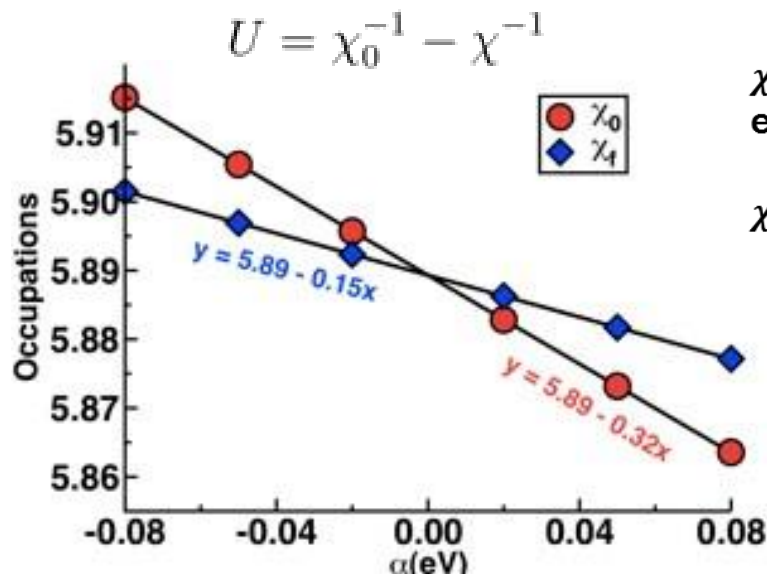
U fitted to experiment

calculated by linear response

$$E(\alpha^I) = \min_{\gamma} \{ E_{DFT}[\gamma] + \alpha^I n^I \}$$

$$\chi = \partial^2 E / \partial \alpha_I \partial \alpha_J = \partial n_I / \partial \alpha_J$$

M. Cococcioni et al PRB 71, 035105 (2005)



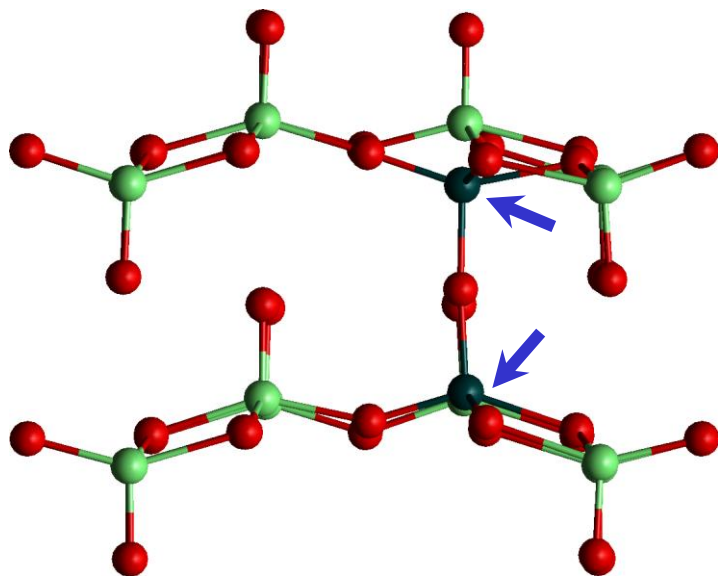
χ_0 bare response due to rehybridization of the
electronic states upon perturbation

χ response due to electron-electron interactions

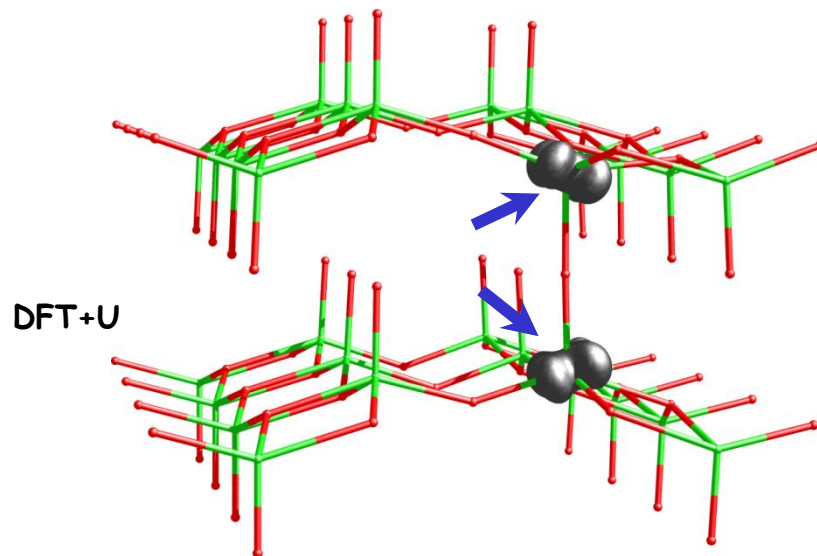
For MnO, the bare and self-consistent
slopes are -0.32 and -0.15, respectively,
giving $U = 3.47$ eV

O-defect induced structural and electronic effects

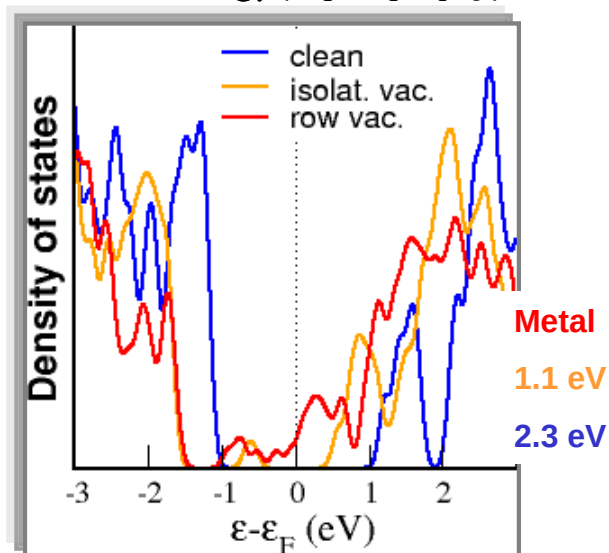
Isolated defect $\Theta = 1/6$



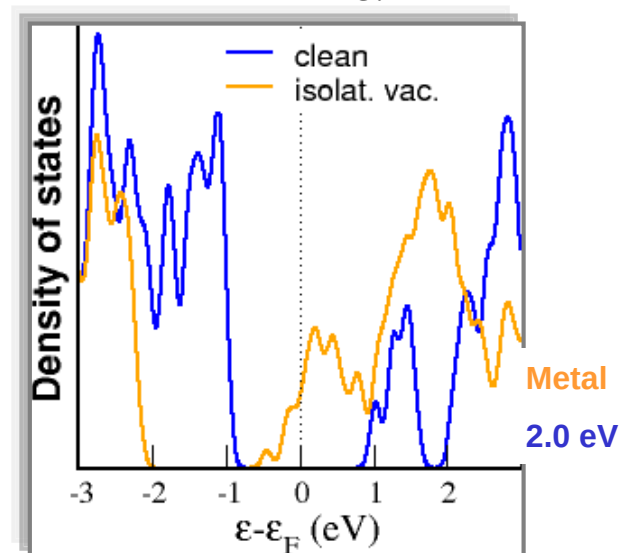
Spin density



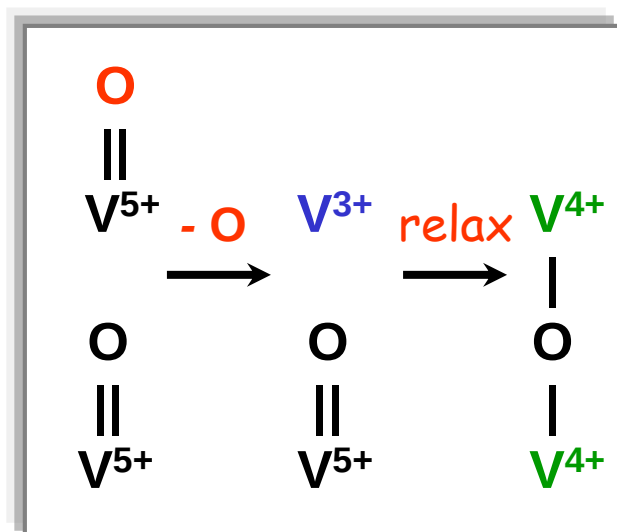
DFT+U $U'=3$ eV



DFT-GGA



O-defect induced structural and electronic effects



The existence
of V⁴⁺ is
explained !

$$E_f^{\frac{1}{2}\text{O}_2} [\text{eV}] = E_{\text{reduced}} - E_{\text{clean}} + \frac{1}{2} E_{\text{O}_2}$$

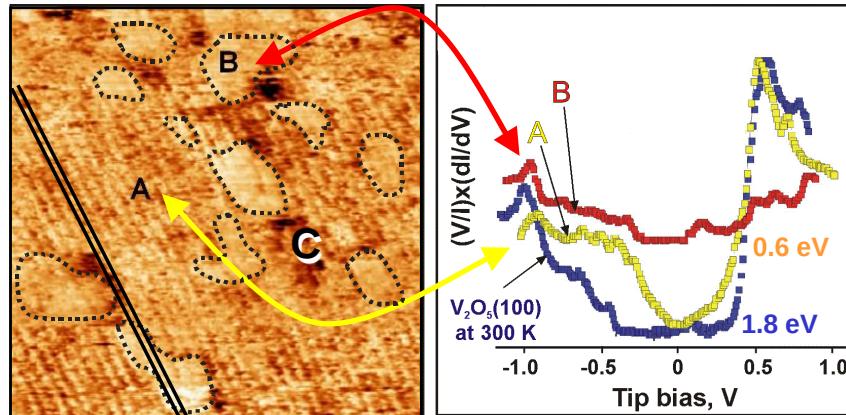
$$\begin{array}{c} 3.76 \\ \downarrow \text{relax} \\ 1.93 \end{array}$$

Defect formation energy	$E_f^{\frac{1}{2}\text{O}_2}$ [eV]	O ₂ dissociation energy [eV per atom]
PW91:	1.93 slab	PW91: 3.10
PW91+U:	1.41 slab	$\rightarrow \sim 0.5 \text{ eV}$
B3LYP:	1.17 cluster	B3LYP: 2.60
exp:	1.3 bulk (molten)	exp: 2.62

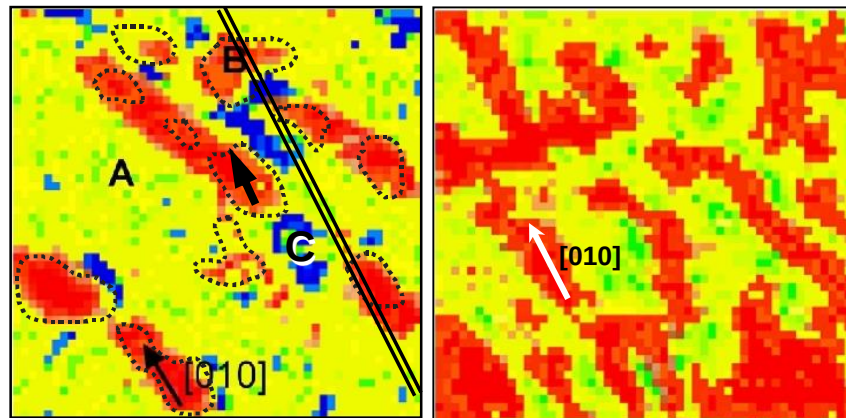
$V_2O_5(001)$ reduction

STM @350K

STS @350K



@400K

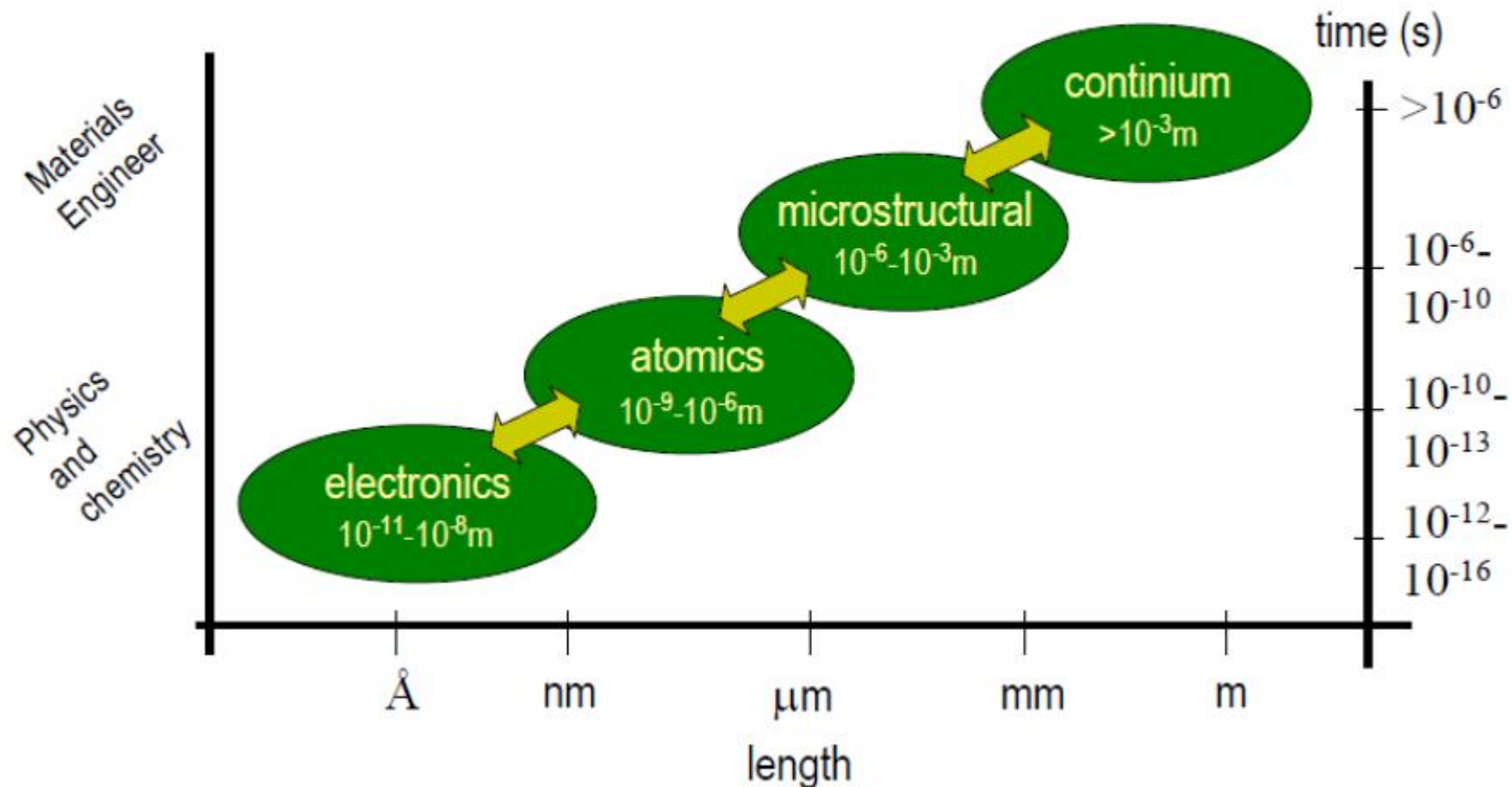


surface **insulator-metal** transition

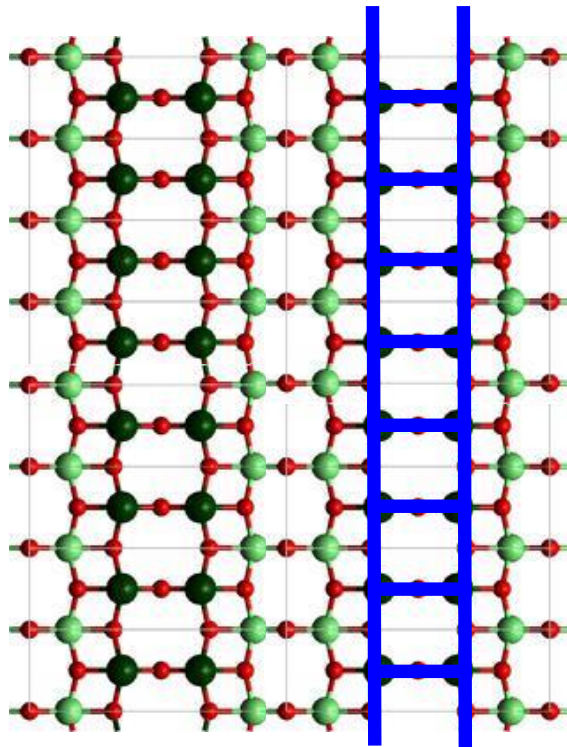
350-400 K

Bandgap map

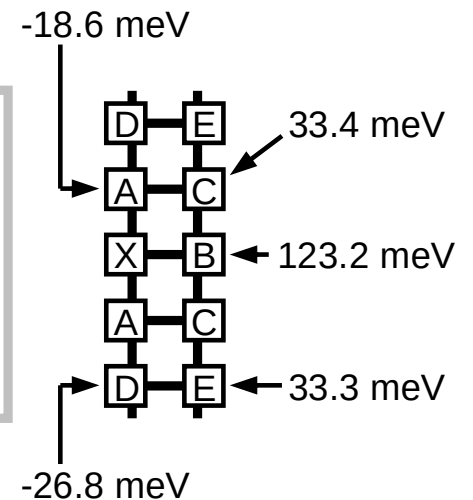
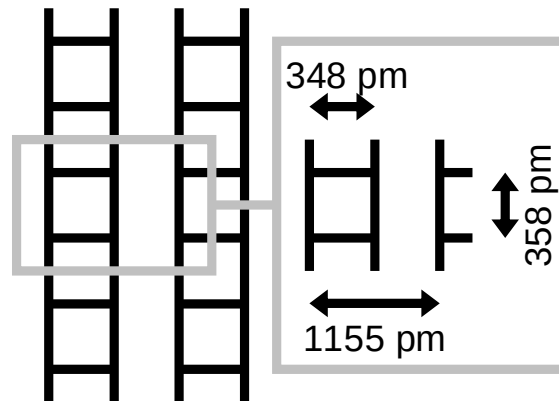
Space and time in materials



Monte Carlo Simulations

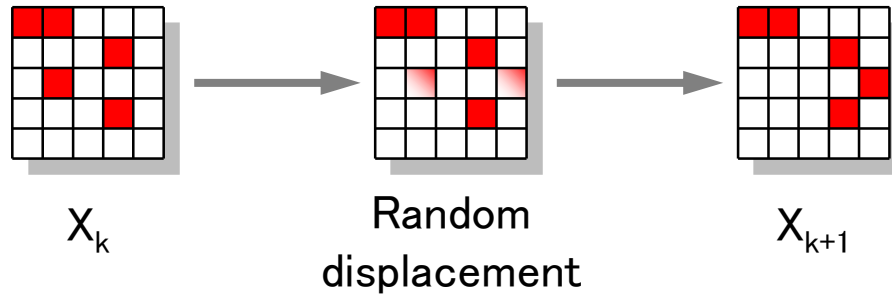


50 double rows
150 sites / row
15,000 sites



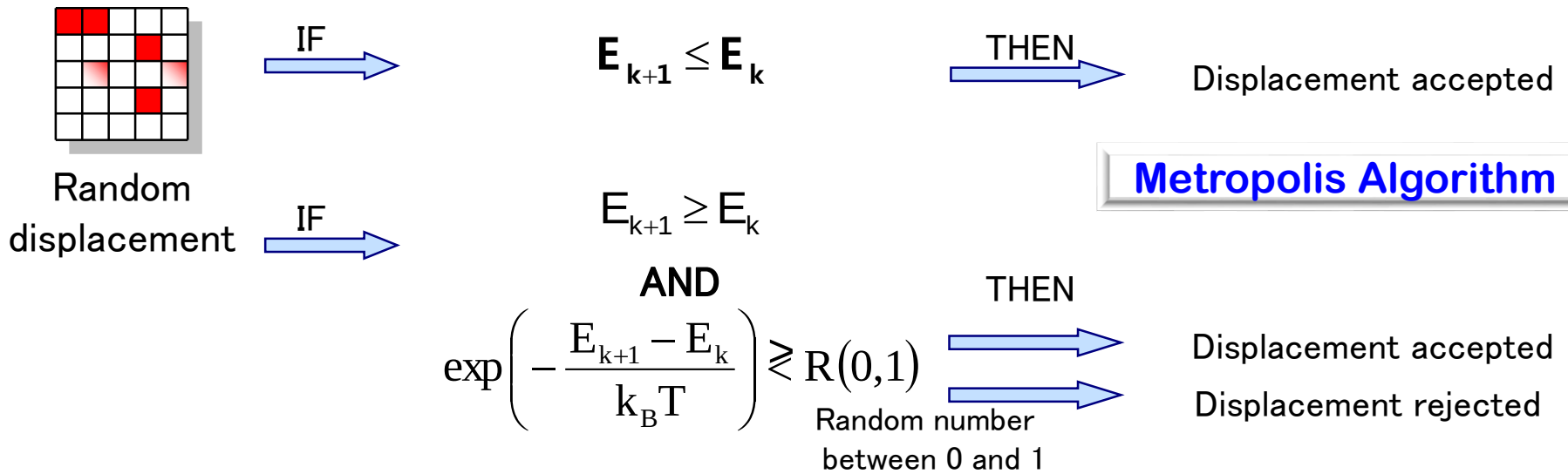
Principles of Monte Carlo simulations

Phase-space sampling

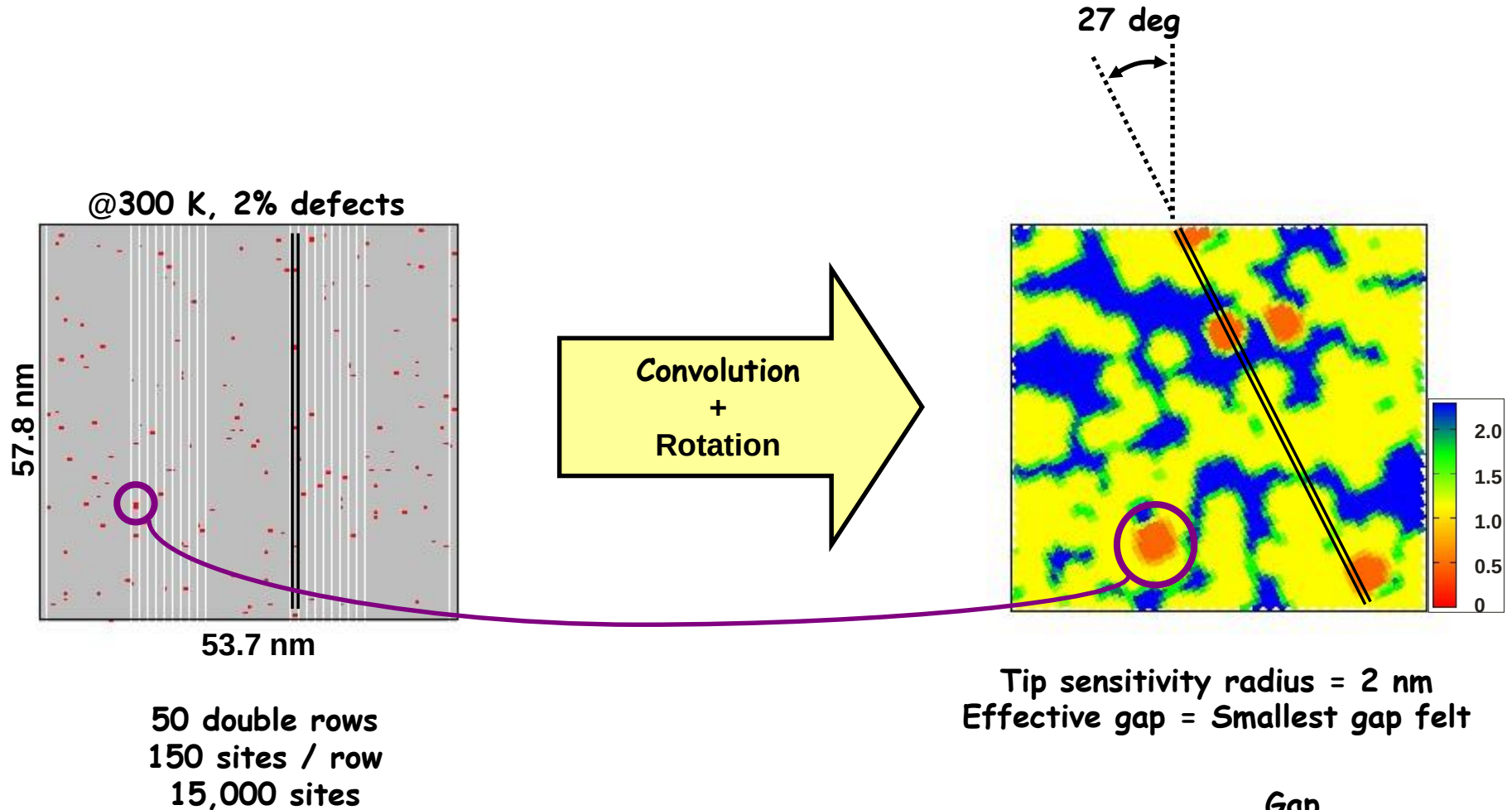


$$\langle X \rangle = \lim_{N \rightarrow +\infty} \frac{1}{N} \sum_{k=1}^N X_k$$

For a Boltzmann distribution



Simulated band gap maps



DFT+U		Gap
{	No defect	2.28 eV
	Isolated defects	1.12 eV
	Pair defects	0.46 eV
	Others	0.00 eV

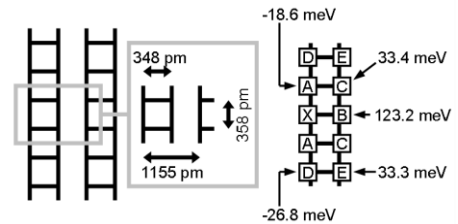
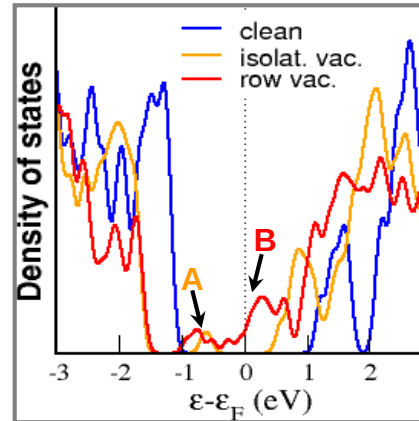
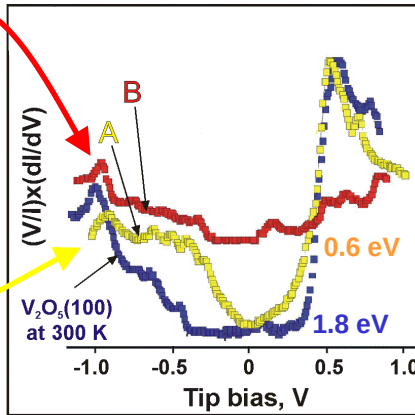
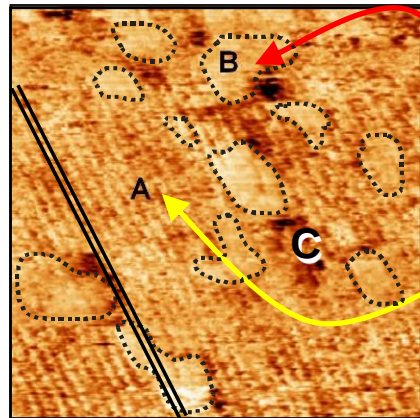
$V_2O_5(001)$ reduction

STM @350K

STS @350K

DFT+U U=3 eV

Monte Carlo network

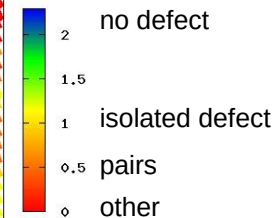
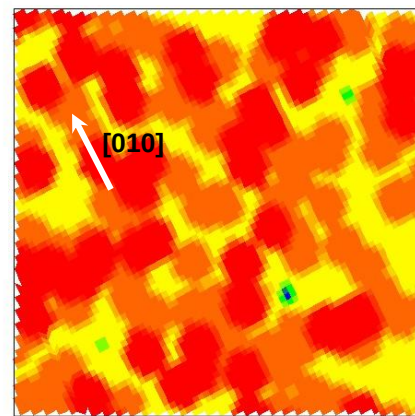
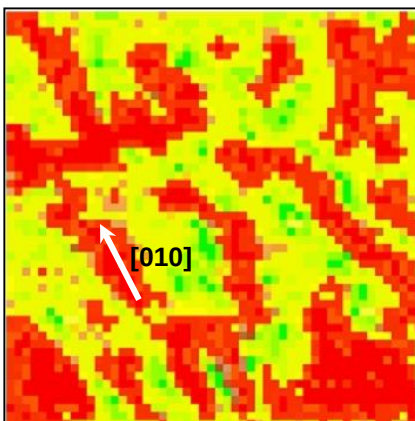
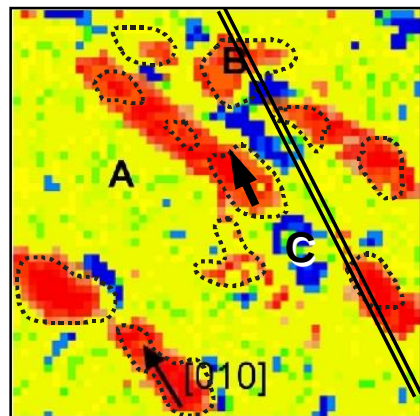


50x50 nm² -1.3 V 0.24 nA
@350K

@400K

7% reduced sites @300 K

50 double rows
150 sites/row
15,000 sites



surface **insulator-metal** transition

350-400 K

Bandgap map

Monte Carlo simulated
Bandgap map

The facile
reduction along
[010] constitutes
a prediction!!

$V_2O_5(001)$ defects: Summary

- **Relaxation:** V–O–V bond formation (GGA & GGA+U & Hybrid)

- substantial (~ 1 Å); reduction of $E_f^{1/2O_2}$ (~ 2 eV)

- essential role in the resulting electronic structure ($2\times V^{4+}$); too delocalized (GGA)

- **Defect formation energy:**

Method	PW91	PW91+U	B3LYP
$E_f^{1/2O_2}$	1.93	1.41	1.17

quantitative differences exist

We recognize the merit of PW91 in predicting the alignment of vanadyl defects along the [010] direction

Ganduglia-Pirovano, Sauer, Phys. Rev. B 70, 45422 (2004)

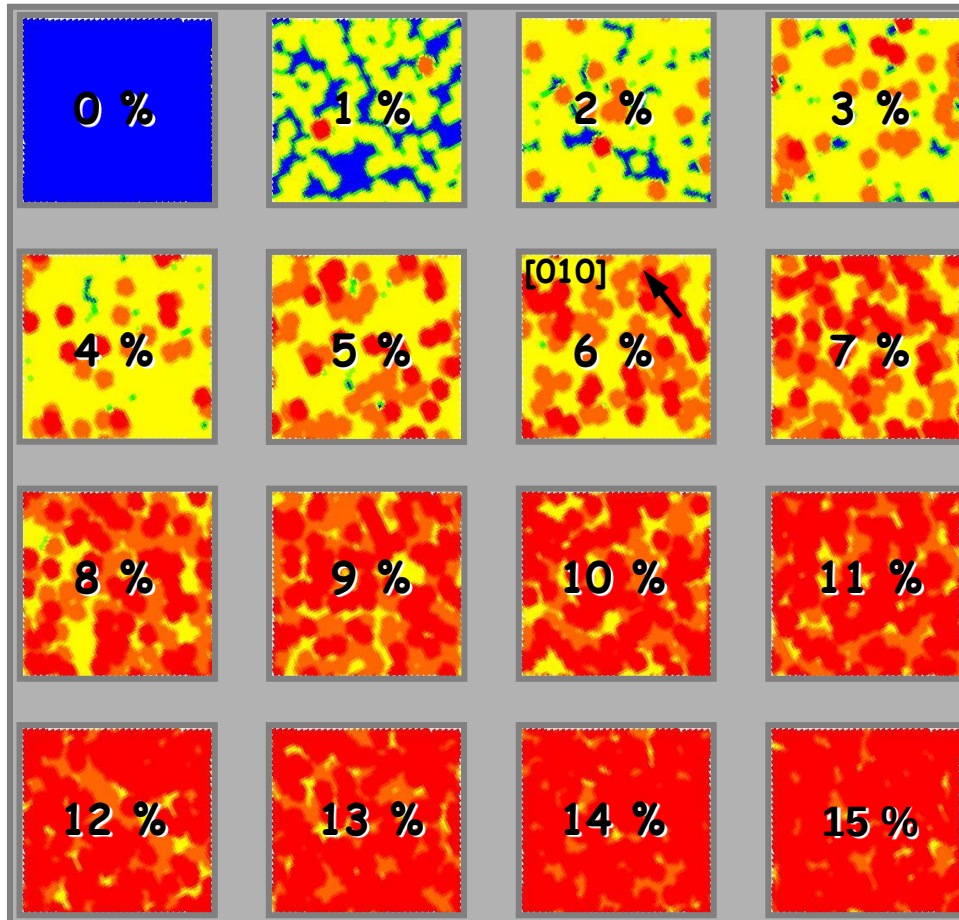
Blum, Niehus, Hucho, Fortrie, Ganduglia Pirovano, Sauer, Shaikhutdinov, Freund, Phys. Rev. Lett. 99, 226103 (2007)

Ganduglia-Pirovano, Hofmann, Sauer, Surf. Sci. Rep. 62 (2007)

Oxygen Defects at Reducible Oxide Surfaces: The Example of Ceria and Vanadia, M. V. Ganduglia-Pirovano in *Defects on Oxide Surfaces*, edited by G. Thornton and J. Jupille (Springer, 2015), pp. 149-190.

Monte Carlo Simulations

Effect of the defect concentration @300K

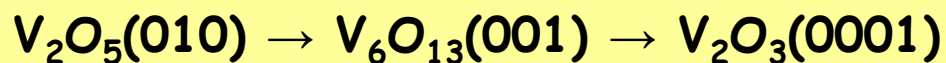
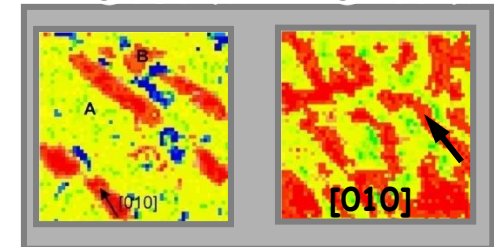


~10% fully metallic surface

Experiment

@350 K

@400 K



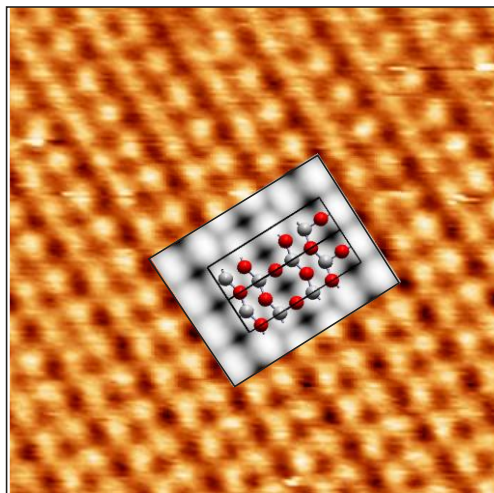
@800 K

Heating the V_2O_5 (001) surface up to 800 K



$V_6O_{13}(001)$

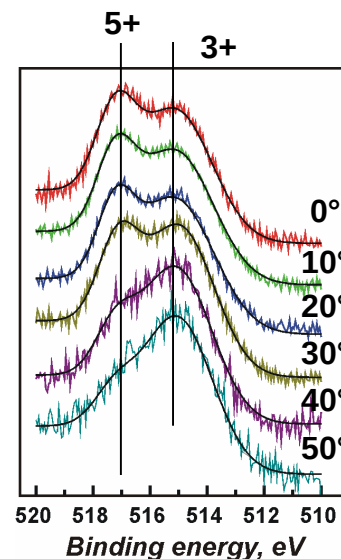
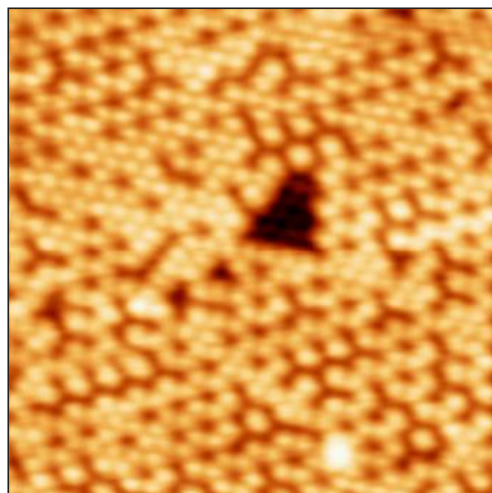
metal



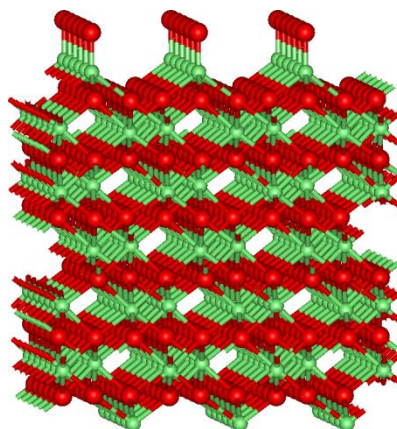
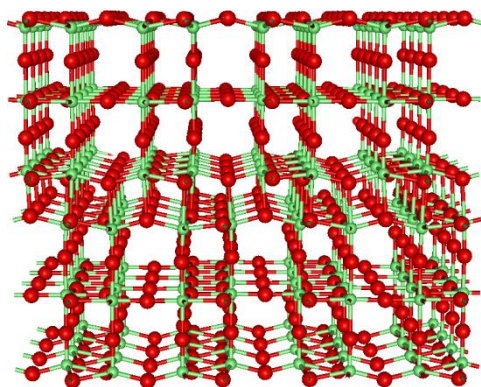
$5 \times 5 \text{ nm}^2$, +0.18 V, 0.3 nA
Unoccupied states

$V_2O_3(0001)$

metal



reconstruction
involves **only**
the **outermost**
layers

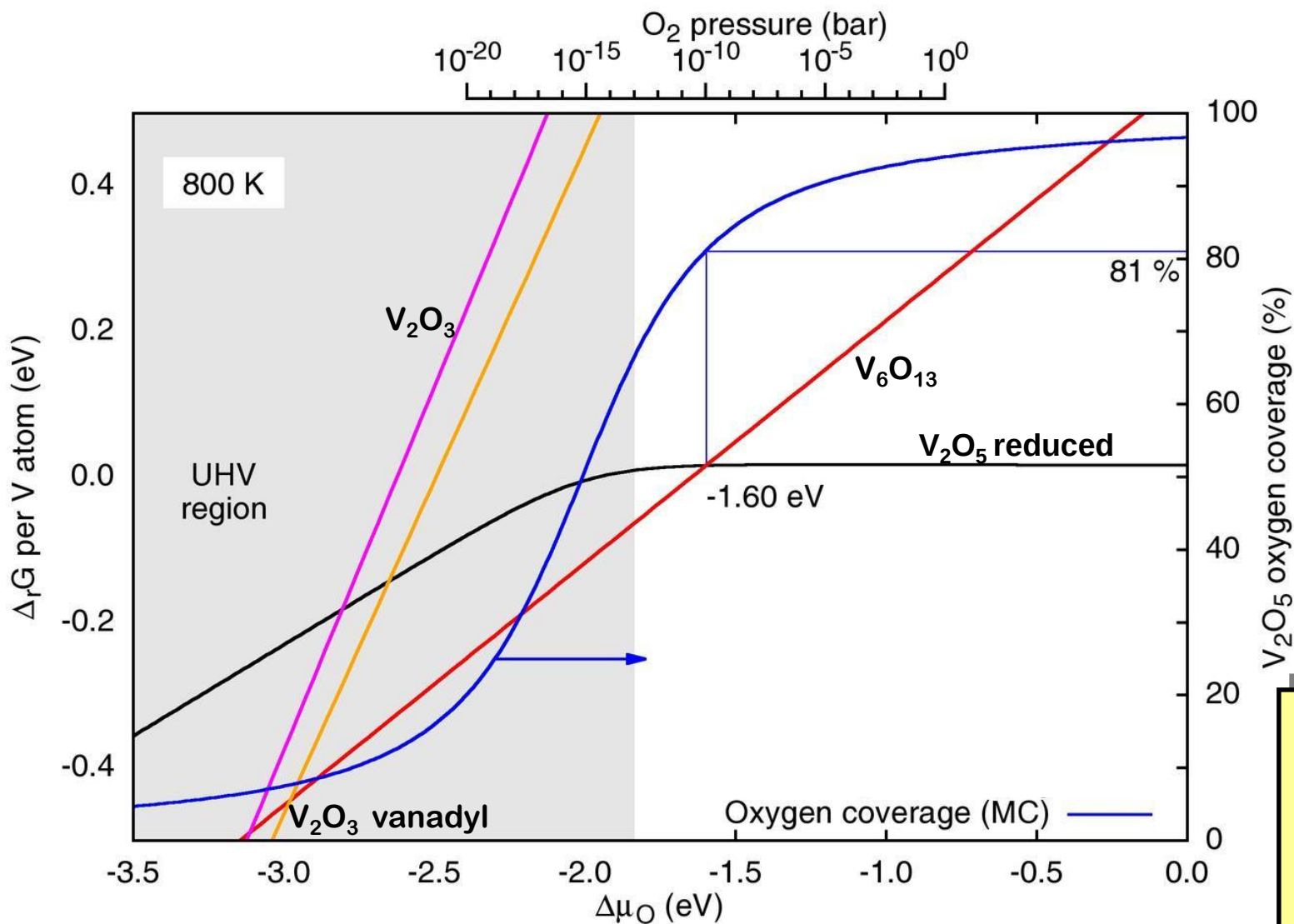


vanadyl terminated
up to 1000 K

Dupuis, Abu Haija, Richter, Kuhlbeck,
Freund, Surf. Sci. 233, 75 (2003)

Schoiswohl, Sock, Surnev, Ramsey, Netzer,
Kresse, Andersen, Surf. Sci. 555, 101 (2004)

Revised stability of reduced $V_2O_5(001)$



350 K: 2.6%

400 K: 3.4%

800 K: V_6O_{13}

Final remarks

Theoretical results concur with recent experimental findings

@300-400 K

$V_2O_5(001)$ surface MIT due to oxygen loss

- Vanadyl defects grow along the [010] direction forming trenches (up to 10 sites)

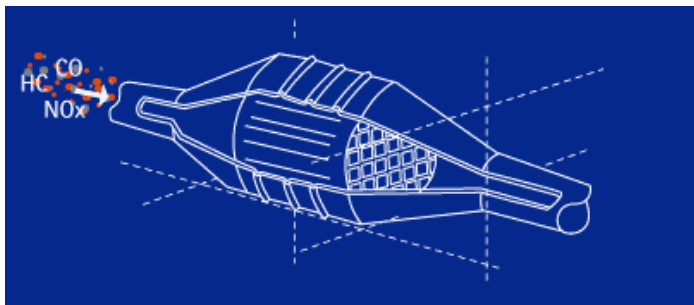
@800 K

$V_2O_5(001) \rightarrow V_6O_{13}(001) \rightarrow V_2O_3(0001)$

- Transition to metallic $V_6O_{13}(001)$ occurs for ~20 % of defects

DFT, DFT+U, and Monte Carlo simulations helped us rationalize experiments

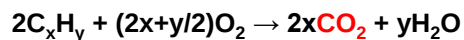
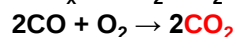
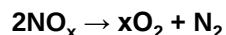
Reducible oxides in catalysis: Ceria



http://www.rhodia-ec.com/site_ec_us/catalysis/index_automotive.htm

Catalytic converter

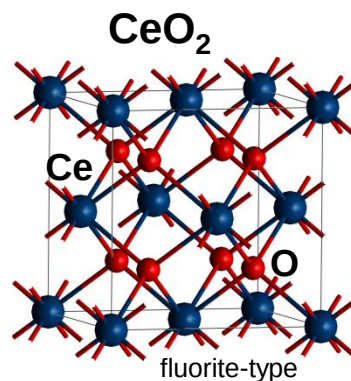
transforms the primary pollutants in the exhaust gas into non-toxic less harmful compounds



CO₂ is a pollutant as a greenhouse gas

Catalyst formulation

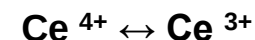
- precious metals Pt, Rh, Pd → active phase
- alumina → support
- Zr-doped ceria → oxygen storage capacity (OSC)
- ZrO₂ → enhances OSC, thermal stability



Oxygen Storage Capacity

an 'oxygen-sponge'

releasing and absorbing oxygen according to the catalytic reaction required (oxidation or reduction)



CeO₂ supported metal and oxide catalysts are singled out as very promising for various reactions; ceria can stabilize reduced states

CeO₂(111): Formation of neutral oxygen defects

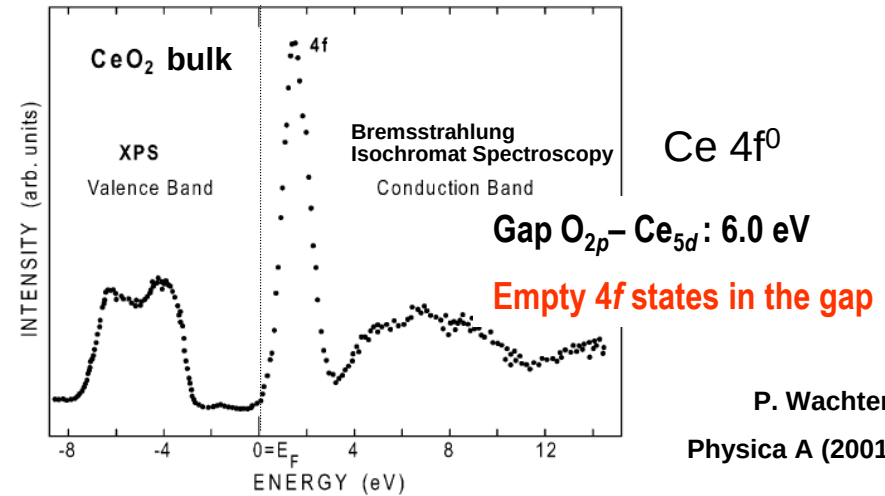
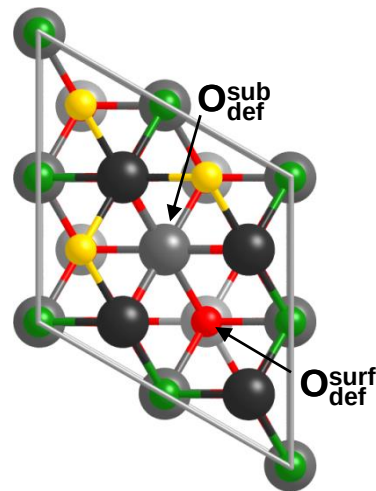
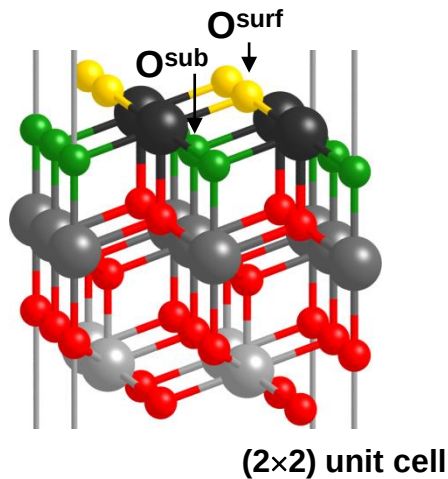
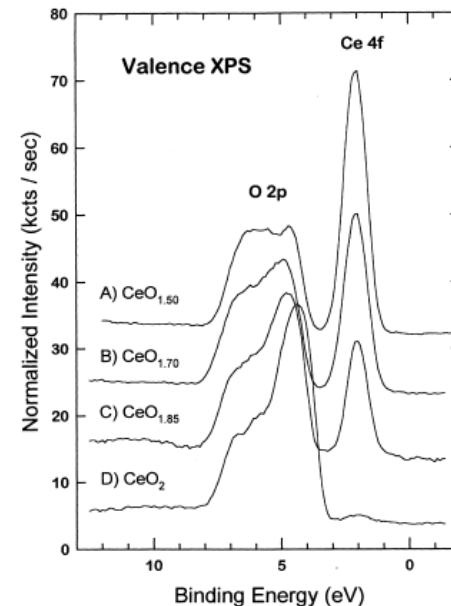
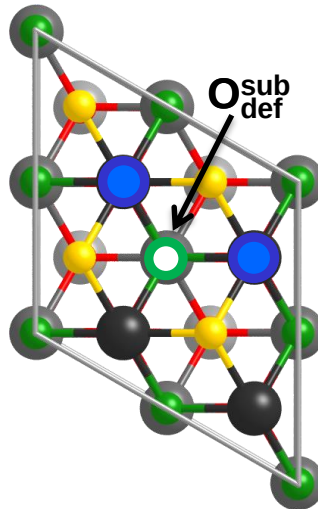


Fig. 3. XPS and BIS spectra of CeO₂.

- **UPS/XPS:** Defect state in the O_{2p}–Ce_{4f} gap,
~1.2 eV above top valence band; Ce_{4f} nature
Ce⁴⁺ → Ce³⁺

Generally accepted view:
Ce³⁺ in nearest neighbor
positions



D. R. Mullins et al.,
Surf. Sci. (1999)

The choice of the computational method

DFT: GGA? 

GGA+U? 

Hybrid? 

Problems: electron delocalization
metallic character

Solutions:

„expensive“ solution: **Hybrid-DFT**

„cheap“ solution: **DFT (LDA/GGA)+U**

exact-exchange

on-site Coulomb repulsion

Dudarev et al., PRB 57 (1998)

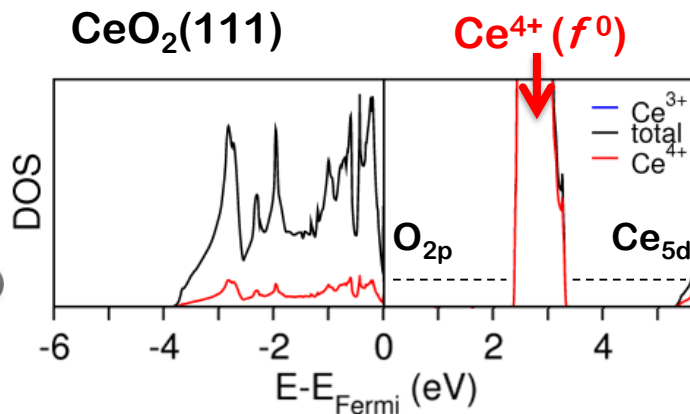
$U_{\text{GGA}} = 4.5 \text{ eV}$ Cococcioni, de Gironcoli, PRB 71 (2005)

Da Silva, Ganduglia-Pirovano,
Sauer, Bayer, Kresse, PRB 75 (2007)

Ganduglia-Pirovano, Hofmann,
Sauer, Surf. Sci. Rep. 62 (2007)



□ Creation of a neutral O vacancy $2 \times \text{Ce}^{4+} \rightarrow 2 \times \text{Ce}^{3+}$



insulator $\text{Ce}^{4+} (f^0)$

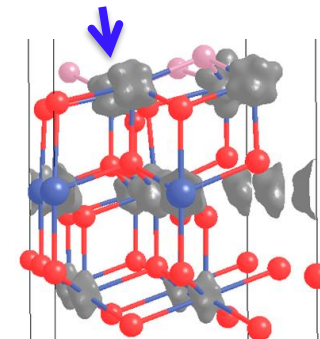
$\text{CeO}_{2-x}(111)$

$\Theta = 1/4$

all Ce ions
partially
reduced !

$\text{Ce}^{(4-\delta)+}$

 **PBE**



metal $\text{Ce}^{(4-\delta)+}$

The choice of the computational method

DFT: GGA? 

GGA+U? 

Hybrid? 

Problems: electron delocalization
metallic character

Solutions:

„expensive“ solution: **Hybrid-DFT**

exact-exchange

„cheap“ solution:

DFT (LDA/GGA)+U

on-site Coulomb repulsion

Dudarev et al., PRB 57 (1998)

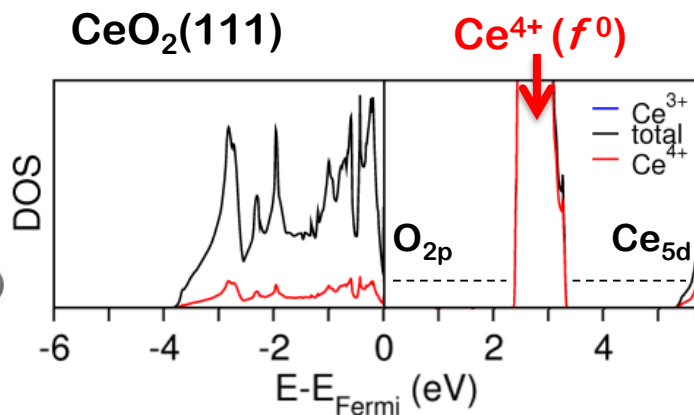
$U_{\text{GGA}} = 4.5 \text{ eV}$ Cococcioni, de Gironcoli, PRB 71 (2005)

Da Silva, Ganduglia-Pirovano,
Sauer, Bayer, Kresse, PRB 75 (2007)

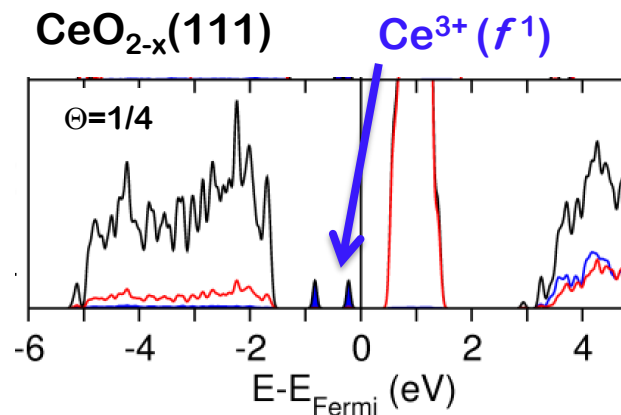
Ganduglia-Pirovano, Hofmann,
Sauer, Surf. Sci. Rep. 62 (2007)



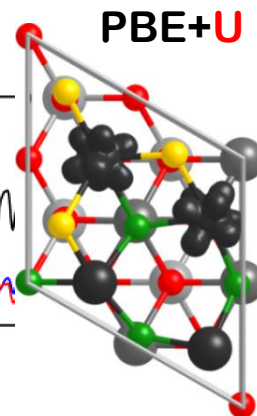
□ Creation of a neutral O vacancy $2 \times \text{Ce}^{4+} \rightarrow 2 \times \text{Ce}^{3+}$



insulator $\text{Ce}^{4+} (f^0)$



insulator $\text{Ce}^{3+} (f^1)$



Reduced ceria: The method of choice

Hybrid functionals

admix a certain amount of Fock exchange to (a part of) a semi-local density functional

$$\text{PBE0} \quad E_{xc}^{\text{PBE0}} = \frac{1}{4} E_x^{\text{HF}} + \frac{3}{4} E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

Perdew, Ernzerhof, Burke, J. Chem. Phys. 105, 9982 (1996)

$$\text{HSE06} \quad E_{xc}^{\text{HSE06}} = \frac{1}{4} E_x^{\text{HF,SR},\omega} + \frac{3}{4} E_x^{\text{PBE,SR},\omega} + E_x^{\text{PBE,LR},\omega} + E_c^{\text{PBE}}$$

Heyd, Scuseria, Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

Krukau, Vydrov, Izmaylov, Scuseria, J. Chem. Phys. 125, 224106 (2006)

$$\text{Coulomb kernel} \quad \frac{1}{r} = S_{\omega}(r) + L_{\omega}(r) = \frac{1 - \text{erf}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r}$$

$$\text{range separation} \quad \omega = 0.207 \text{ \AA}^{-1} \quad \text{no long-range HF exchange}$$
$$\omega = 0 \text{ \AA}^{-1} \rightarrow \text{PBE0}$$

DFT+U

Hubbard $U_{\text{eff}} = (U - J)$ term added to the LDA and PBE functionals for Ce f electrons

Dudarev et al., Phys. Rev. B 57, 1505 (1998)

$$\text{LDA+U} \quad U_{\text{LDA}} = 5.3 \text{ eV}$$

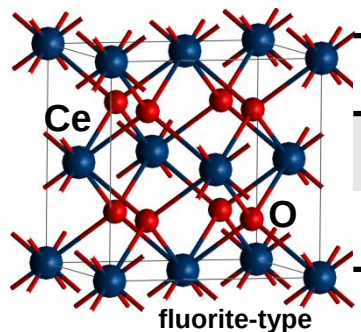
$$\text{PBE+U} \quad U_{\text{PBE}} = 4.5 \text{ eV}$$

Fabris, de Gironcoli, Baroni, Vicario, Balducci, Phys. Rev. B 72, 237102 (2005)

Cococcioni, de Gironcoli, Phys. Rev. B 71, 035105 (2005)

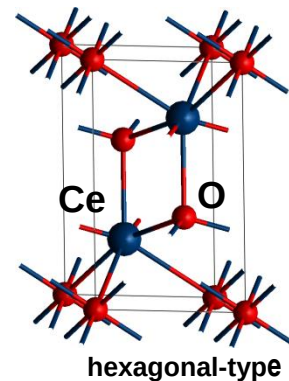
Ceria bulk: Structure and electronic properties

Da Silva, Ganduglia-Pirovano, Sauer, Bayer, Kresse, PRB 75, 045121 (2007)



CeO_2	HSE*	exp.
a_0 (Å)	5.40	5.41
$\text{O}_{2p}\text{-Ce}_{5d}$ gap (eV)	7.0	6.0

Ce_2O_3 -AF	HSE*	exp.
a_0 (Å)	3.87	3.89
c_0 (Å)	6.08	6.06
$\text{Ce}_{4f}\text{-Ce}_{5d+4f}$ gap (eV)	2.5	2.4



Equilibrium volume

□ Hybrid: -1% underestimation

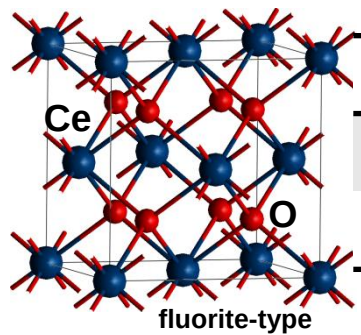
Band gap

□ Hybrid: ~1 eV larger than exp CeO_2

* In agreement with P.J. Hay, R.L. Martin, J. Uddin, G. Scuseria, J. Chem. Phys. 125, 034712 (2006)

Ceria bulk: Structure and electronic properties

Da Silva, Ganduglia-Pirovano, Sauer, Bayer, Kresse, PRB 75, 045121 (2007)

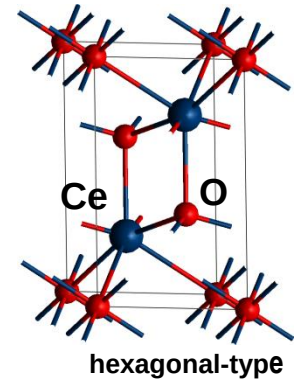


CeO_2	HSE*	LDA+U	PBE+U	exp.
a_0 (Å)	5.40	5.40	5.49	5.41
$\text{O}_{2p}\text{-Ce}_{5d}$ gap (eV)	7.0	5.3	5.3	6.0

$$U_{\text{LDA}} = 5.3 \text{ eV}$$

$$U_{\text{GGA}} = 4.5 \text{ eV}$$

Ce_2O_3 –AF	HSE*	LDA+U	PBE+U	exp.
a_0 (Å)	3.87	3.86	3.92	3.89
c_0 (Å)	6.08	5.96	6.18	6.06
$\text{Ce}_{4f}\text{-Ce}_{5d+4f}$ gap (eV)	2.5	2.4	2.6	2.4



Equilibrium volume

❑ **Hybrid:** –1% underestimation

❑ **LDA+U:** –0.6% (CeO_2); –3.2% (Ce_2O_3)

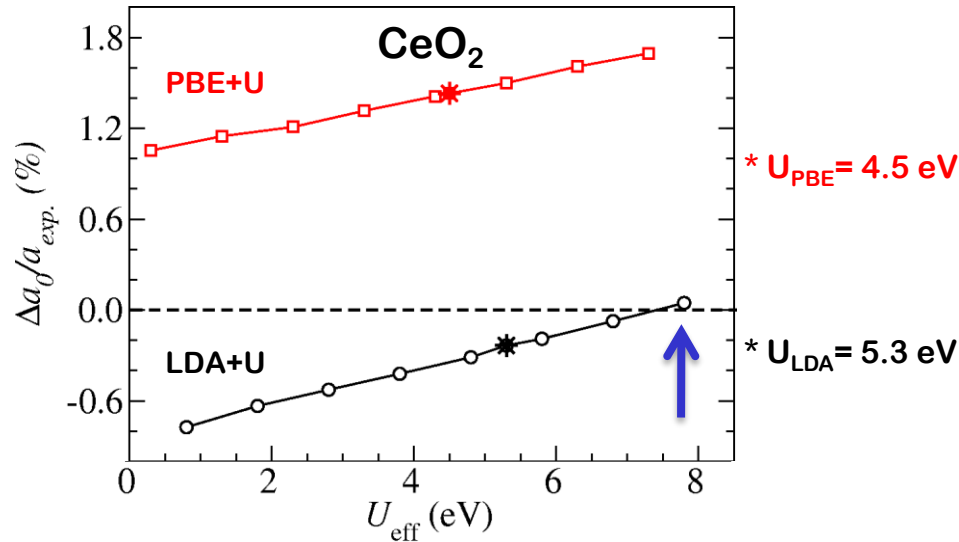
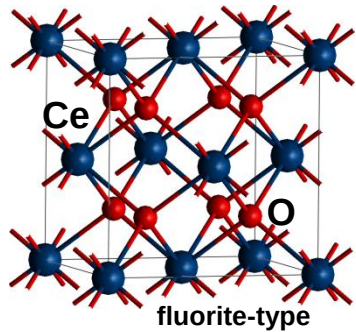
❑ **PBE+U:** +4.5% (CeO_2); +3.6% (Ce_2O_3)

Band gap

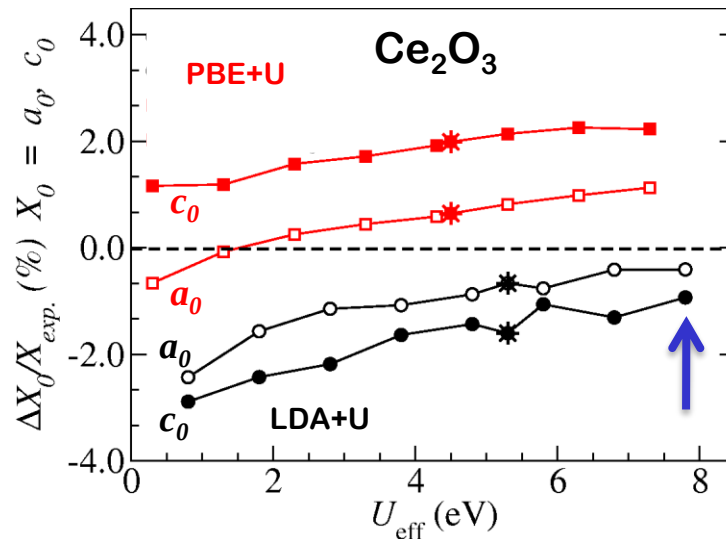
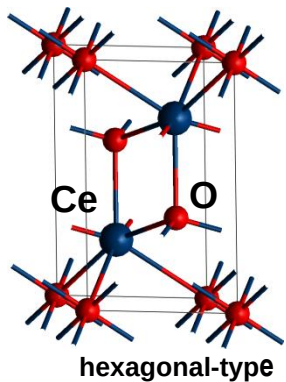
❑ **Hybrid:** ~1 eV larger than exp. gap CeO_2

❑ **DFT+U:** ~1 eV smaller than exp. gap (CeO_2)
U shifts f -states in the gap

The dependence on the U parameter: Structure

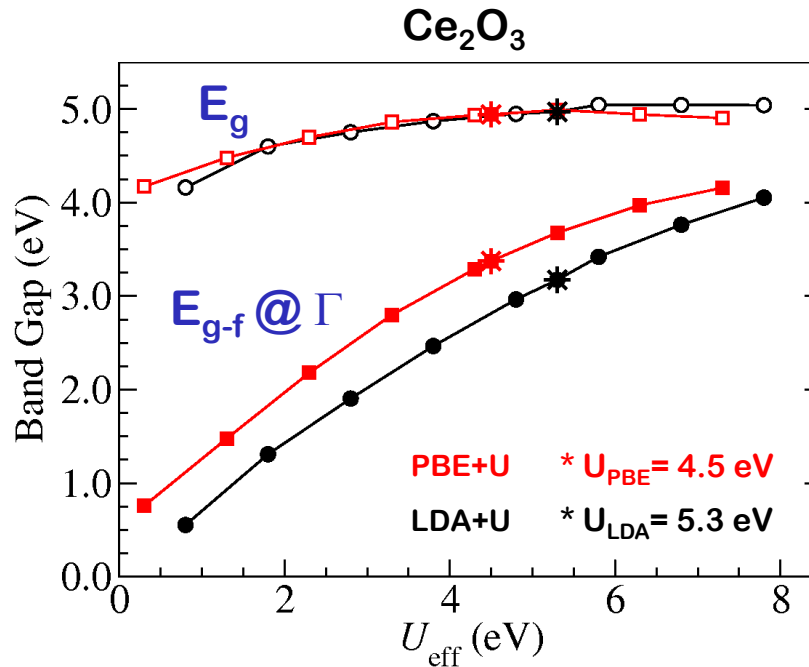
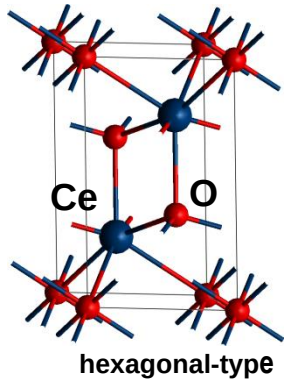


□ linear increase with U



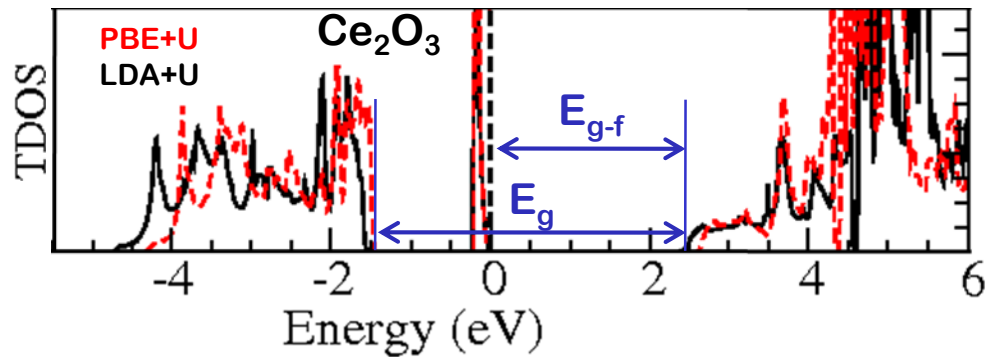
□ LDA+U(~8 eV) close to exp.

The dependence on the U parameter: Band gap



□ E_g roughly constant

□ U shifts f-states



smaller U:

- occupied f-states toward CB (Ce₂O₃); smaller E_{g-f} gap

Ceria bulk: Thermodynamic properties

Da Silva, Ganduglia-Pirovano, Sauer, Bayer, Kresse, PRB 75, 045121 (2007)



	HSE	LDA+U	PBE+U	exp.
$\Delta H(\text{eV})$	3.16	3.04	2.29	3.57/4.03

Reduction energy

❑ Hybrid: 0.4 – 0.9 eV underestimation

❑ LDA+U: 0.5 – 1.0 eV

❑ PBE+U: 1.3 – 1.7 eV

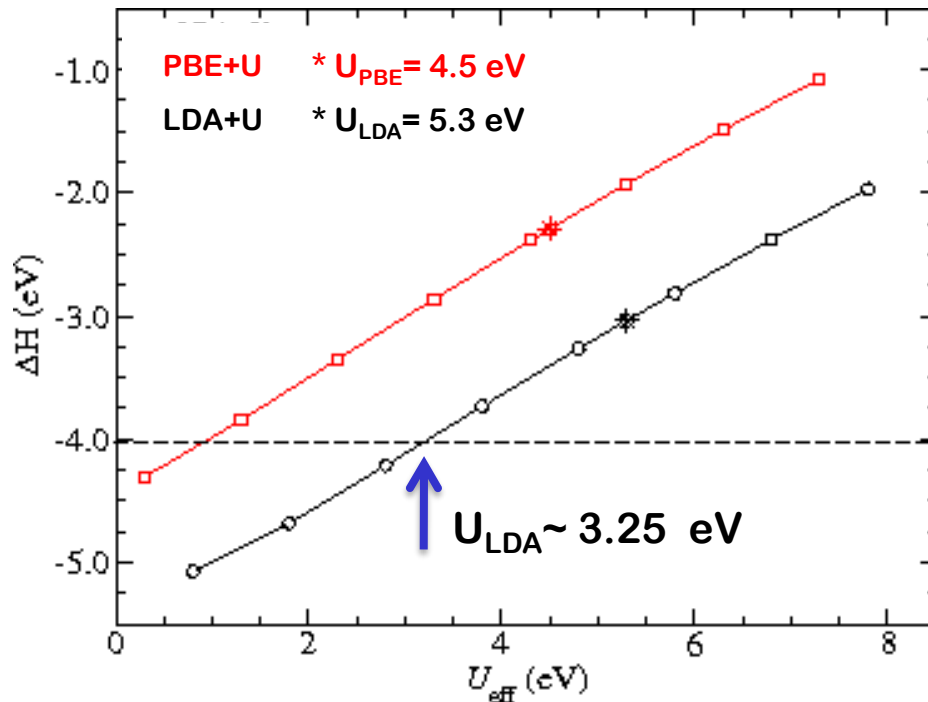
Not fully satisfactory



The dependence on the U: Thermodynamic properties



	PBE0	HSE	LDA+U	PBE+U	exp.
$\Delta H(\text{eV})$	3.14	3.16	3.04	2.29	3.57/4.03



□ linear dependence with U

smaller U:

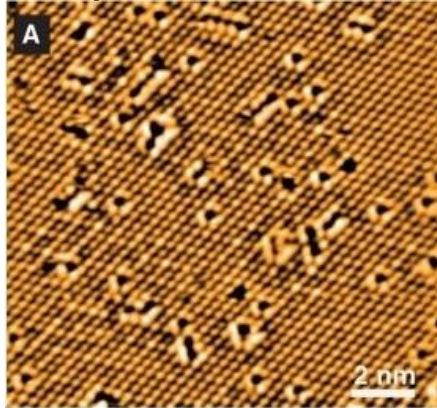
- corrects reduction energy ☺
- yields a smaller $E_{\text{g-f}}$ Ce_2O_3 gap ☹
- yields a smaller Ce_2O_3 volume ☹

No unique U for best description of all properties

CeO₂(111): Structure of near-surface oxygen defects

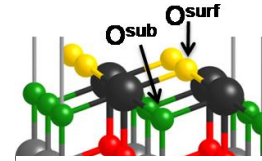
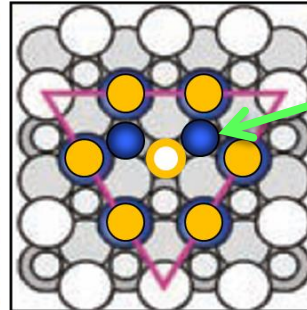
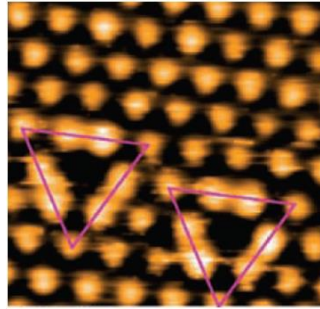
STM

occupied states—O lattice

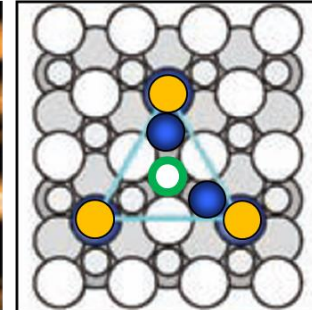
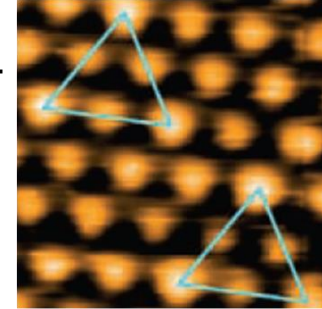


1 min 900°C + cooling 300°C

surface defect



subsurface defect



Esch, Fabris, et al., Science 309, 752 (2005)

LDA+U

Theory: Excess charge on N.N.

Defect formation energy [eV]

$$\Delta E_{\text{def}}^{\text{surf-sub}}$$

$$\Delta E \begin{cases} + \text{sub} \\ - \text{surf} \end{cases}$$

Ce³⁺ LDA+U

NN-NN -0.03

U_{LDA} = 5.3 eV

50%-50% surf-sub

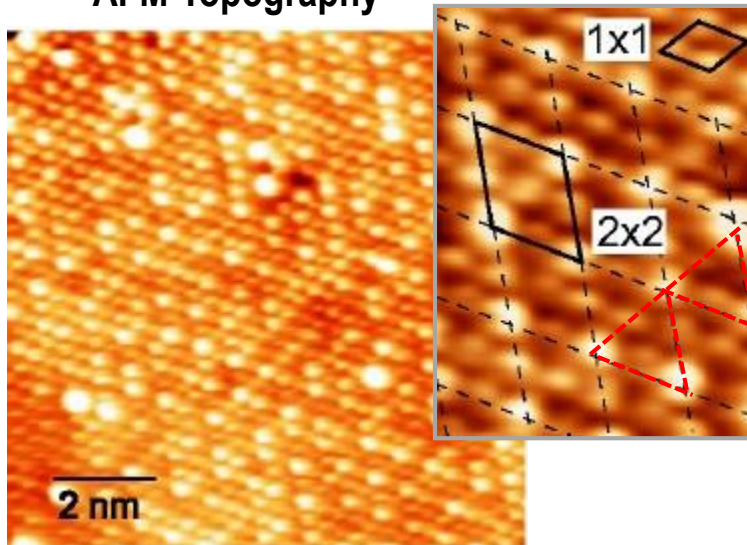
Defect formation energy [eV]

Ce ³⁺	surface		subsurface		$\Delta E_{\text{def}}^{\text{surf-sub}}$	
	PBE+U	LDA+U	PBE+U	LDA+U	PBE+U	LDA+U
NN-NN ¹	2.15	2.92	1.89	2.95	+0.26	-0.03

[1] Fabris et al., J. Phys. Chem. B 109, 22860 (2005)

$\text{CeO}_2(111)$: Structure of near-surface oxygen defects

AFM-Topography



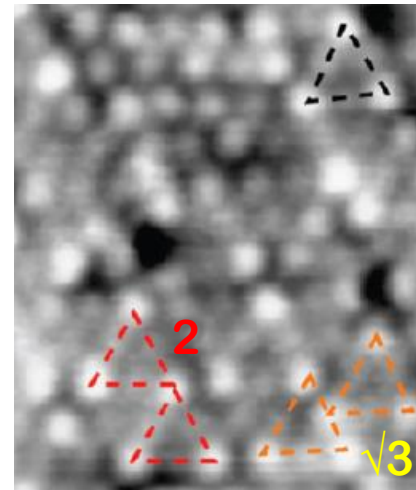
2 min 900°C + cooling 80 K

Torbrügge et al., PRL 99, 056101 (2007)

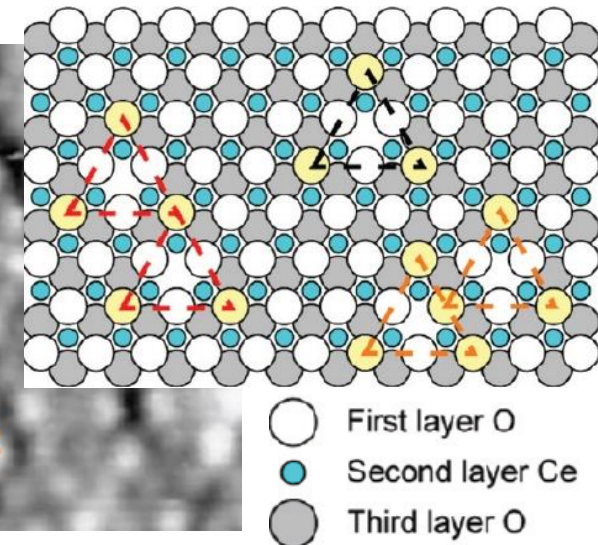
subsurface defects

2 lattice spacings separation

STM



Ceria film grown on Pt(111)



Grinter et al., J. Phys. Chem. C 114, 17036 (2010)

subsurface defects pairs

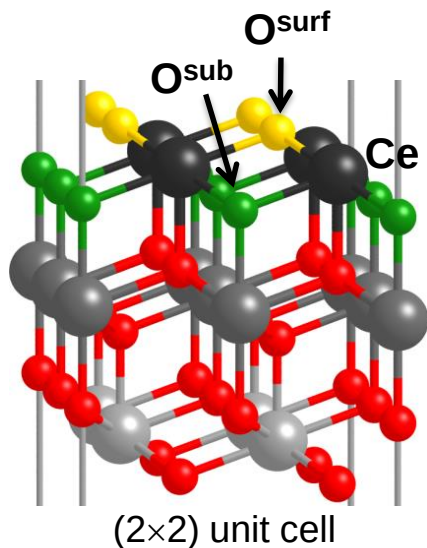
$\sqrt{3}$ and 2 lattice spacings separation

□ Nature of the **repulsive interaction** underlying the **vacancy ordering**?

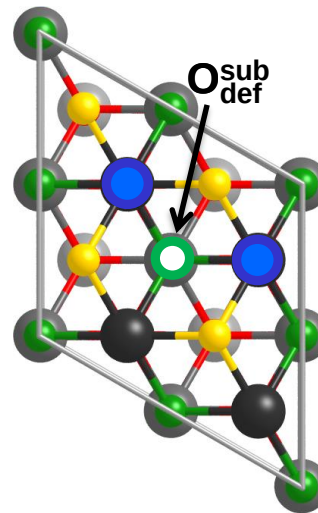
$\text{CeO}_2(111)$ and its oxygen defect structure

❑ isolated defects and electron localization

Surface or subsurface?



Where are the Ce^{3+} ?



Accepted view:
 $\text{Ce}^{3+} \rightarrow$ nearest neighbor

❑ higher defect concentration

- Thermodynamically stable phase for reducing conditions?
- Surface, subsurface, mixed?
- Repulsive or attractive interaction? Origin of interaction?

CeO₂(111) subsurface and surface defects: Unrelaxed structures

PBE+U spin density

surface

subsurface

$$\Delta E \begin{cases} + \text{sub} \\ - \text{surf} \end{cases}$$

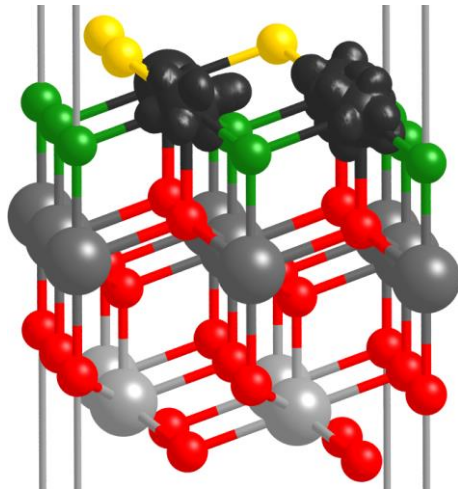
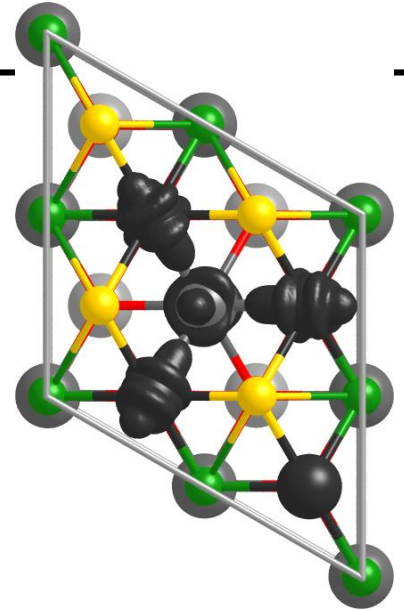
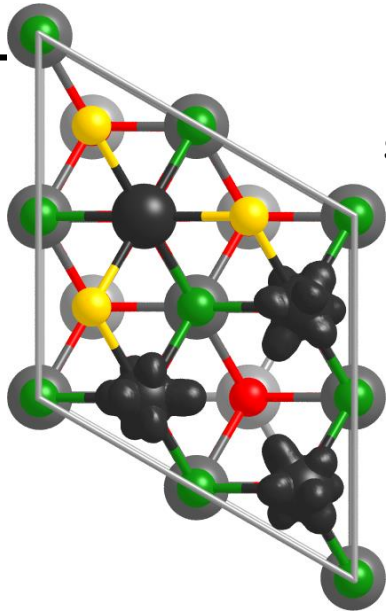
Defect Formation Energy E_{def} [eV]

$$\Delta E_{\text{def}}^{\text{surf-sub}}$$

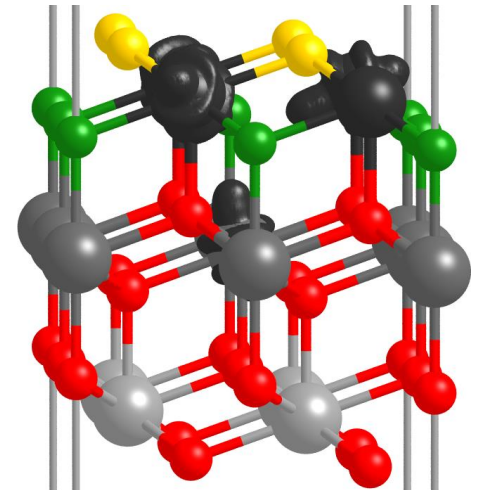
−0.18 (PBE+U)

−0.27 (LDA+U)

unrelaxed structures:
preference for surface defects



localization on the 3
nearest neighbors



localization on the 4
nearest neighbors

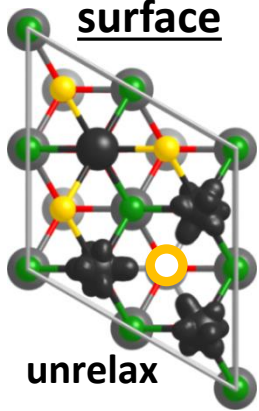
$\text{CeO}_2(111)$ defects: The excess charge localization

Ganduglia-Pirovano, Da Silva, Sauer, PRL 102, 026101 (2009)

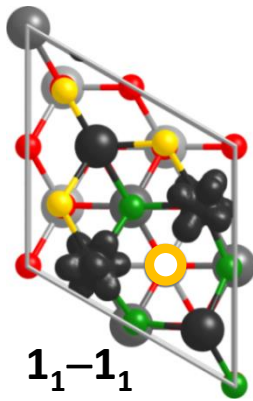
HSE spin density-FM

□ DFT predicts multiple local minima

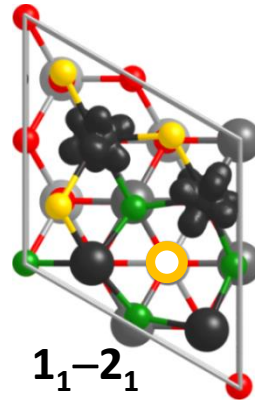
surface



unrelax

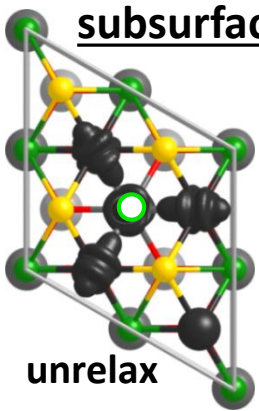


1_1-1_1

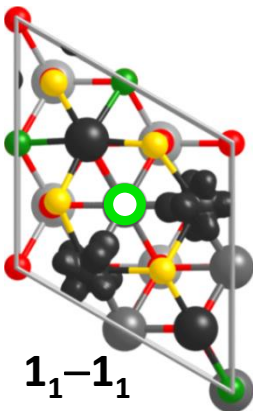


1_1-2_1

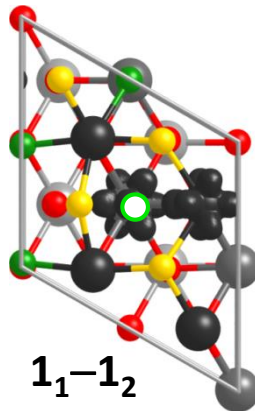
subsurface



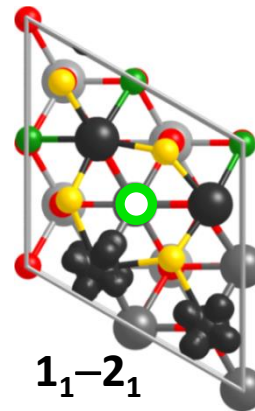
unrelax



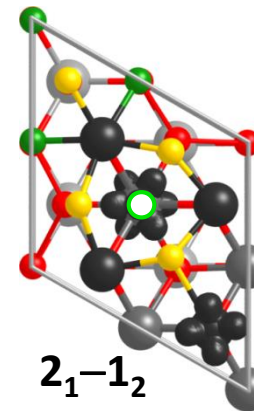
1_1-1_1



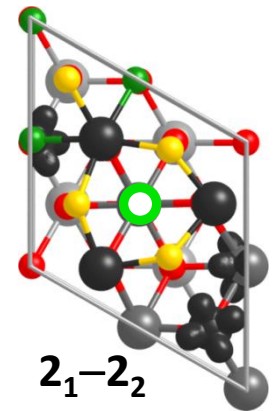
1_1-1_2



1_1-2_1



2_1-1_2

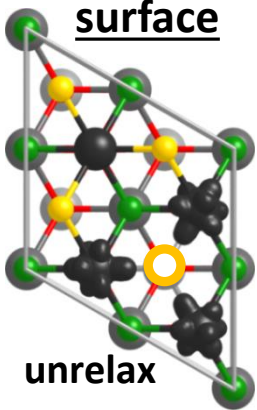


2_1-2_2

The defect formation energy wrt. $\frac{1}{2} \text{O}_2$ [eV]

Ganduglia-Pirovano, Da Silva, Sauer, PRL 102, 026101 (2009)

surface

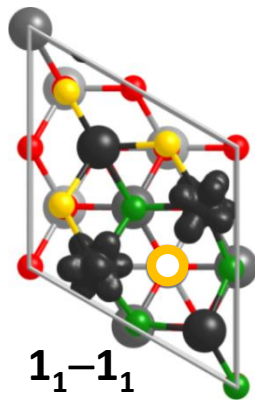


unrelax

HSE

LDA+U

PBE+U

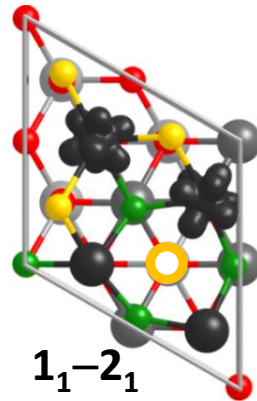


1_1-1_1

3.30

3.31

2.50



1_1-2_1

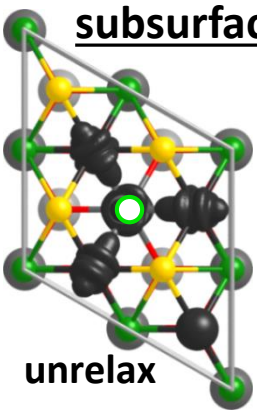
3.10

3.21

2.34

Defects are prone to be bound to Ce^{4+} !!

subsurface

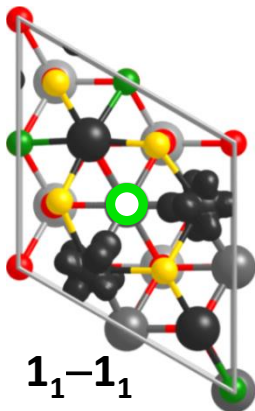


unrelax

HSE

LDA+U

PBE+U

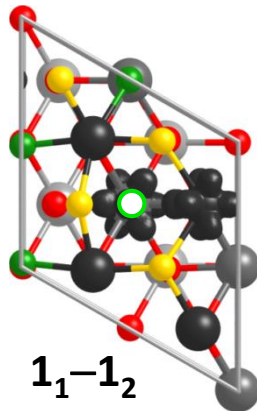


1_1-1_1

3.21

3.39

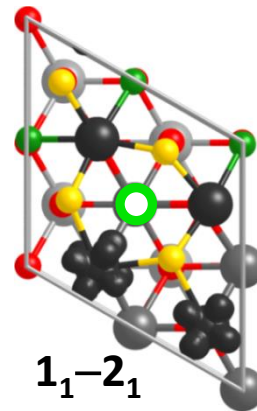
2.38



1_1-1_2

3.40

2.40

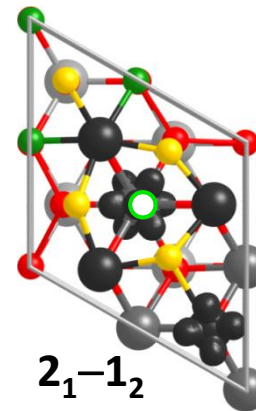


1_1-2_1

2.79

3.08

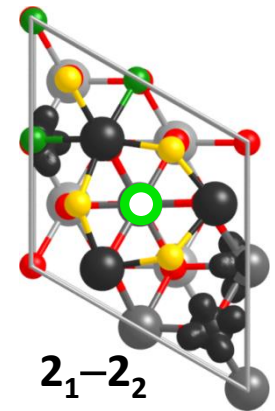
2.00



2_1-1_2

3.17

2.08



2_1-2_2

2.65

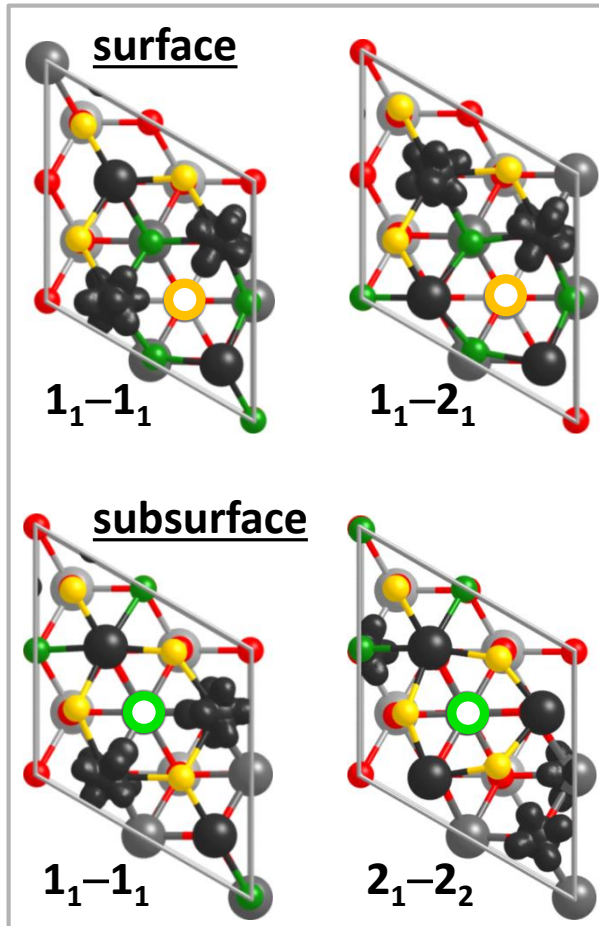
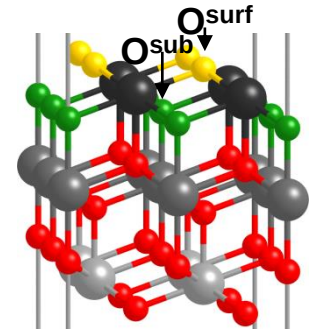
2.99

1.87

CeO₂(111) defects: Surface vs. subsurface

STM & LDA+U: Esch et al., Science 309,752 (2005) → **50%–50%**

AFM: Torbrügge et al., PRL 99, 056101(2007) → **subsurface**



Defect formation energy [eV]

	$\Delta E_{\text{def}}^{\text{surf-sub}}$		
Ce ³⁺	HSE	LDA+U	PBE+U
NN ^[1]		-0.03	+0.26
NN	+0.09	-0.08	+0.12
NNN	+0.45	+0.22	+0.47

$\Delta E \begin{cases} + \text{sub} \\ - \text{surf} \end{cases}$

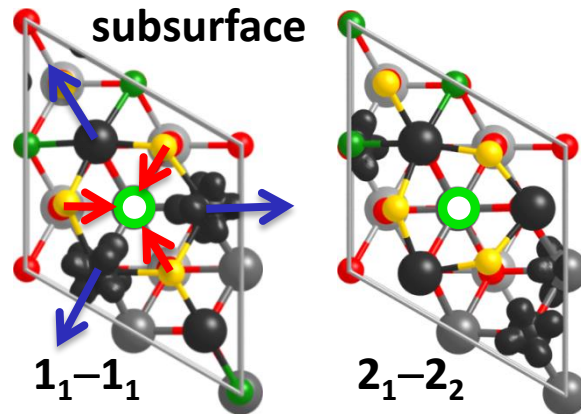
[1] Fabris et al., JPCB 109, 22860 (2005)

The subsurface position is considerable more stable than the surface one

The lattice relaxation effects

Ganduglia-Pirovano, Da Silva, Sauer, PRL 102, 026101 (2009)

- Ce move away and O towards the vacant site → **tension-compression regions**



Compressed Ce^{3+}
in NN sites

subsurface defect		
Ce^{3+}	$E_{\text{def}}(\text{eV})$	$\text{Ce}^{3+}-\text{O} (\text{\AA})$
NN	3.10	2.39; 2.39
NNN	2.65	2.47; 2.44

HSE-structures

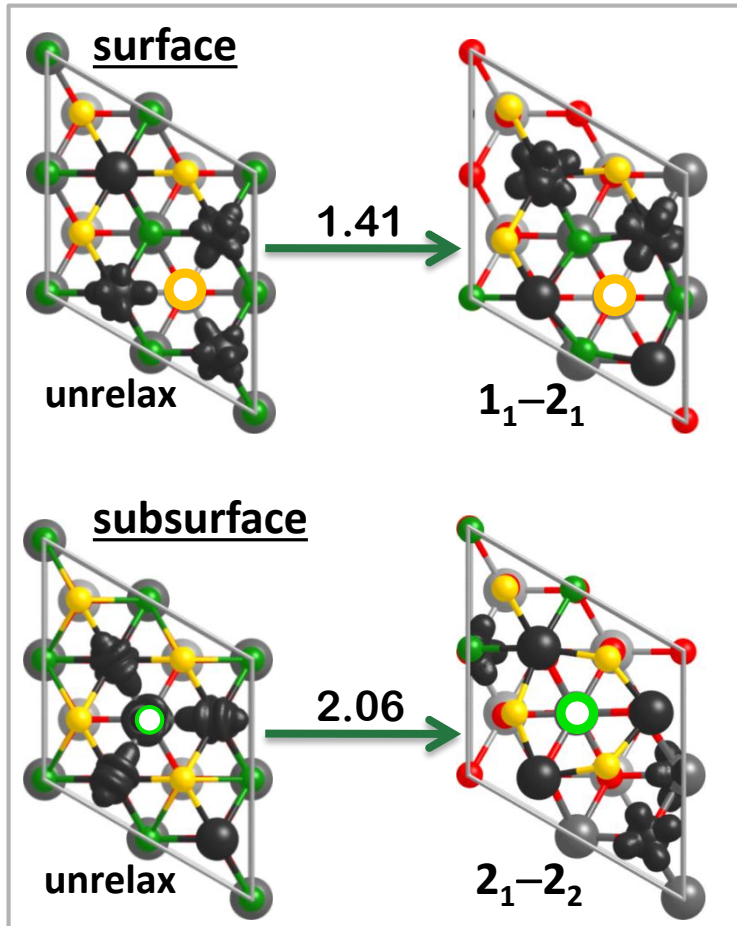
Ce_2O_3 : 2.50 Å

Lattice relaxation effects are crucial

- localization phenomenon
- proneness of defects to be bound by Ce^{4+}

Lattice relaxation effects and the subsurface preference

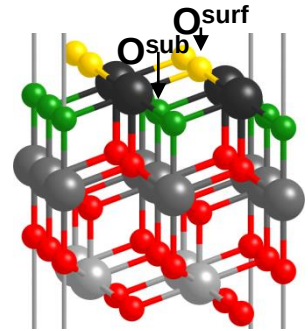
Energy gain due to relaxation [eV]



Defect formation energy [eV]

$$\Delta E \begin{cases} + \text{sub} \\ - \text{surf} \end{cases}$$

	ΔE_{def} PBE+U
unrelax	-0.18
NNN	+0.47



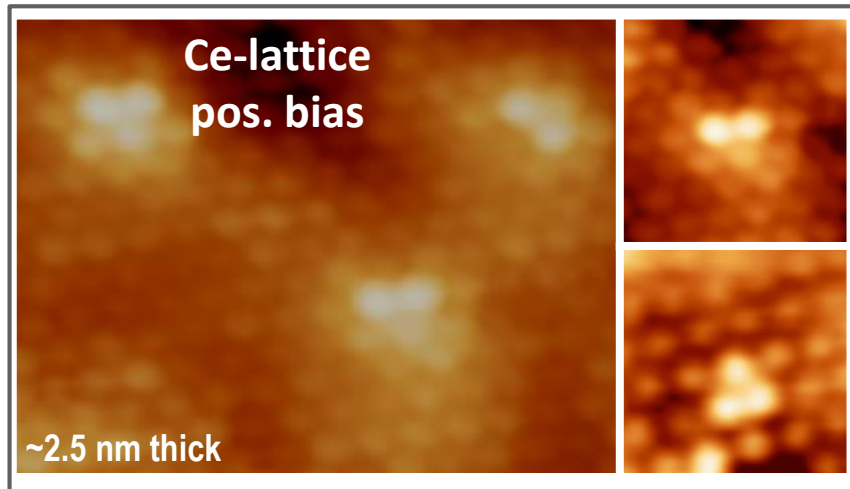
Lattice relaxation effects are crucial to the subsurface preference

Electron localization in defective $\text{CeO}_2(111)$ films

Jerratsch, Shao, Nilius, Freund, Popa, Ganduglia-Pirovano, Sauer, PRL 106, 246801 (2011)

Ceria film grown on Ru(0001)

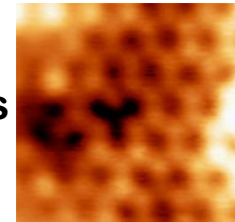
STM



$U_s = 1.1 \text{ V}$, $5.5 \times 5.5 \text{ nm}^2$

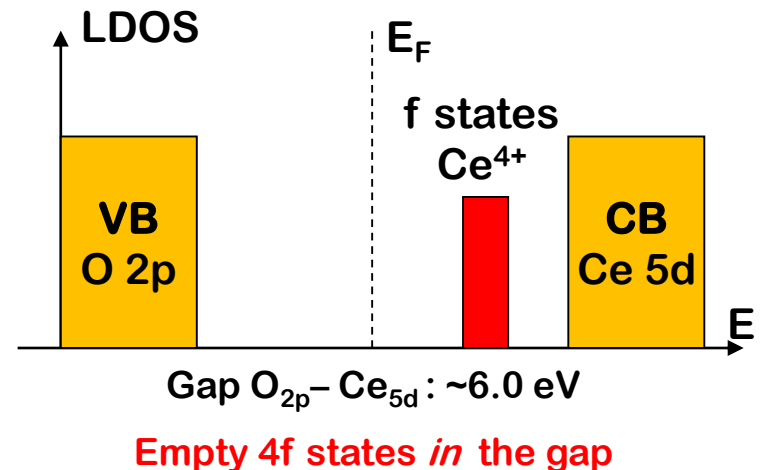
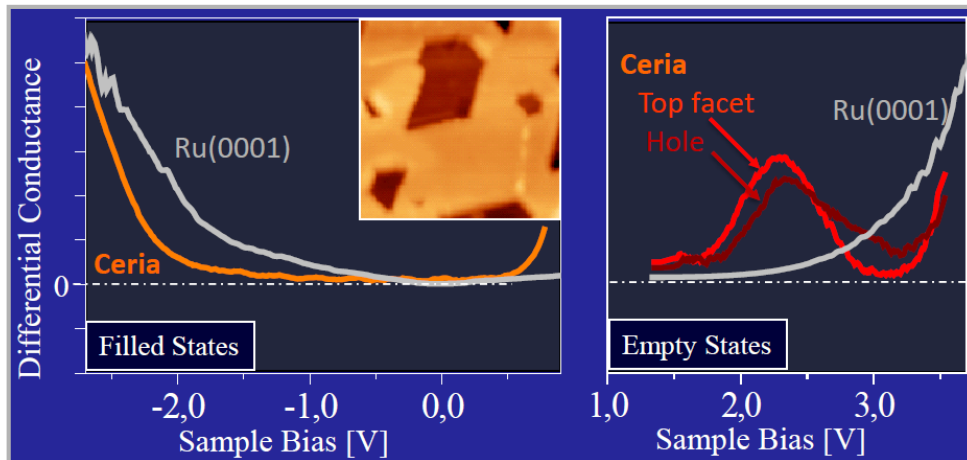
$1.8 \times 1.8 \text{ nm}^2$

- irradiation with 50 eV electrons
→ **surface defects**
- **double/triple protrusions** at positive bias
- O-lattice at negative bias



STS

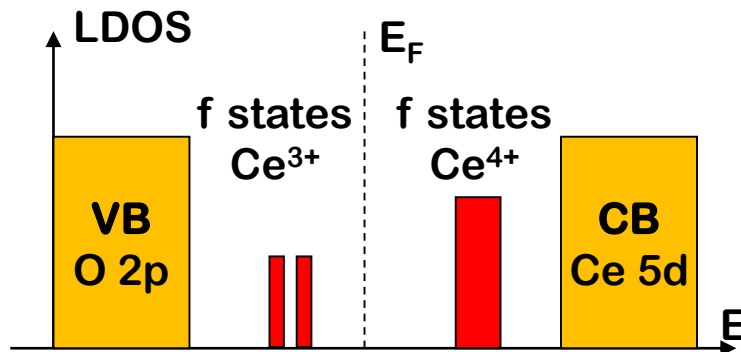
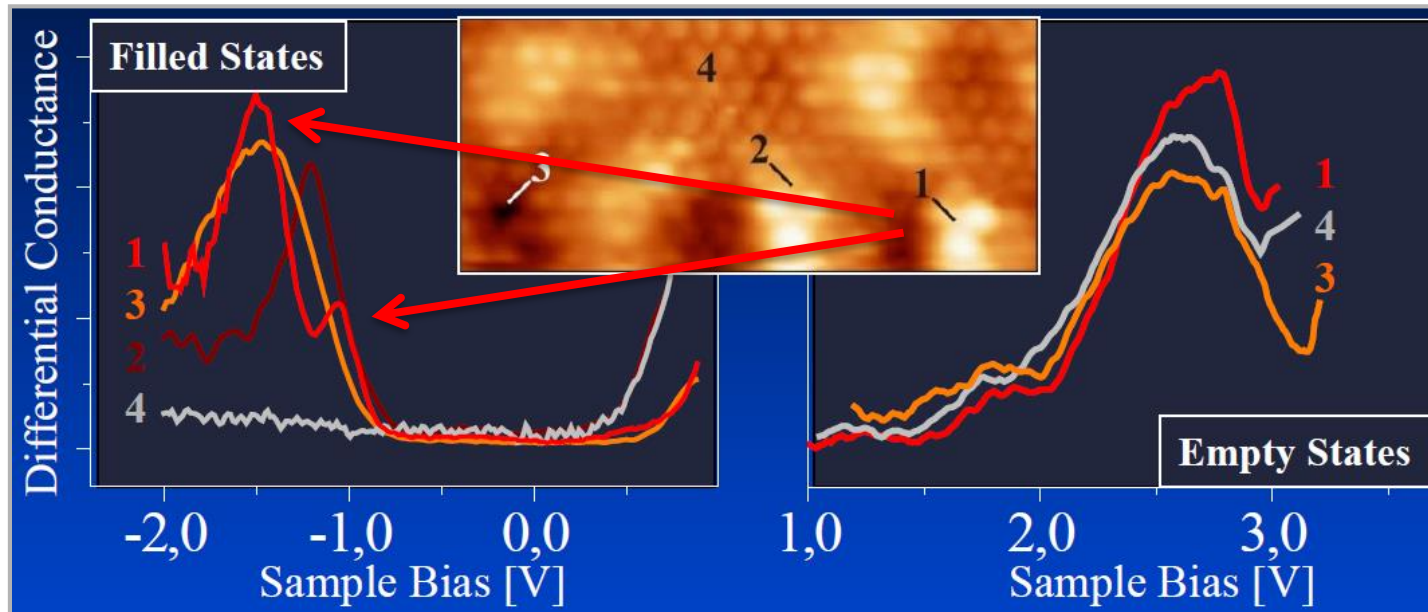
unreduced ceria



Reduced $\text{CeO}_2(111)$: STS-Experiment

Jerratsch, Shao, Nilius, Freund, Popa, Ganduglia-Pirovano, Sauer, PRL 106, 246801 (2011)

reduced ceria

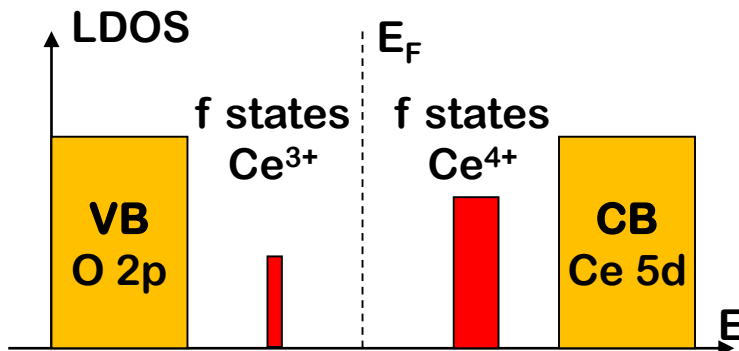
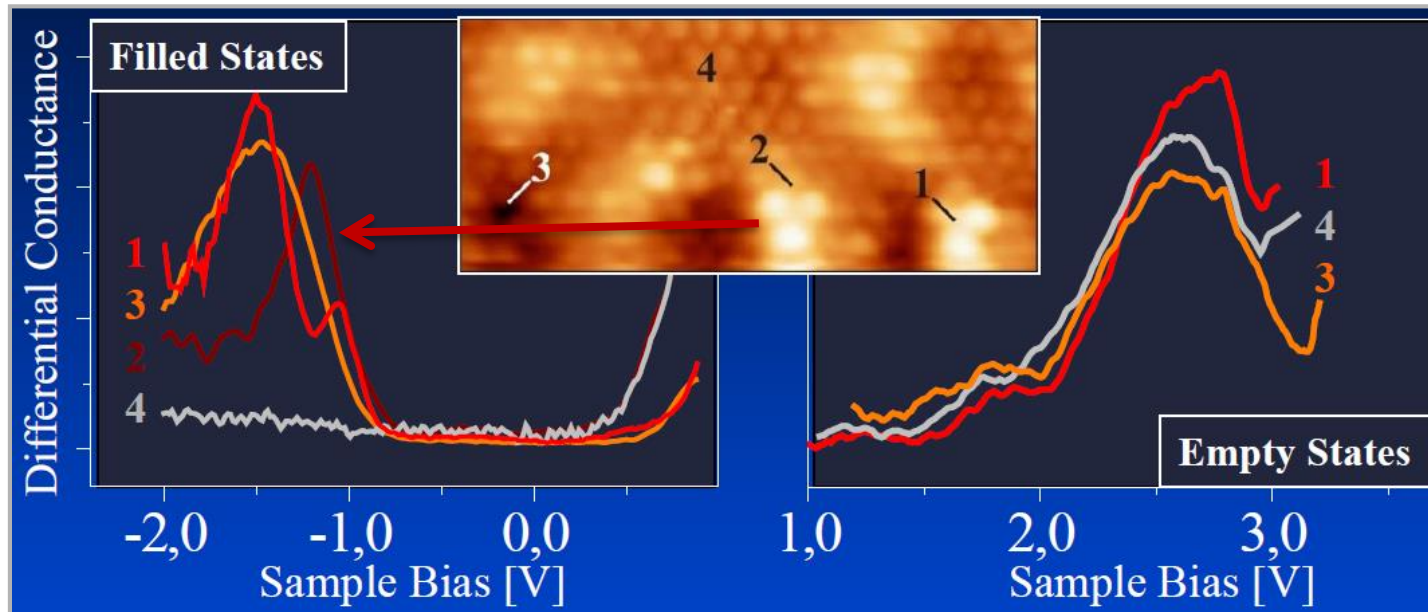


- ☒ Filled 4f states in reduced CeO_2 films
- ☒ Splitting of 4f states for pair protusion

Reduced $\text{CeO}_2(111)$: STS-Experiment

Jerratsch, Shao, Nilius, Freund, Popa, Ganduglia-Pirovano, Sauer, PRL 106, 246801 (2011)

reduced ceria



Where are the Ce^{3+} ions?

- ☐ Filled 4f states in reduced CeO_2 films
- ☐ **No splitting** of 4f states for **triple** protusion

STM-theory

DFT prediction: defects are prone to be bound to Ce^{4+}

Empty state
image

Ce^{3+}



Ce^{4+}



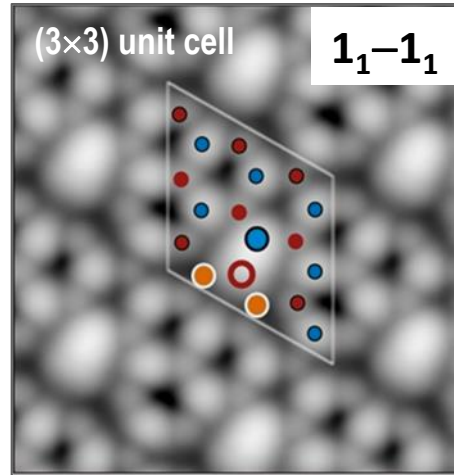
O^{2-}



O_{def}



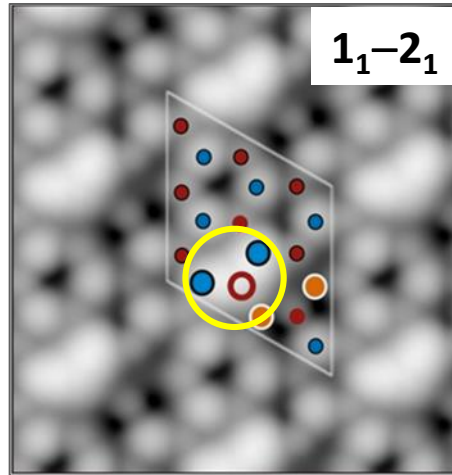
NN-NN



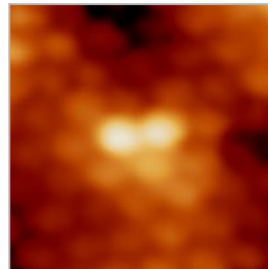
one Ce^{4+}

Not observed
in the
Experiment

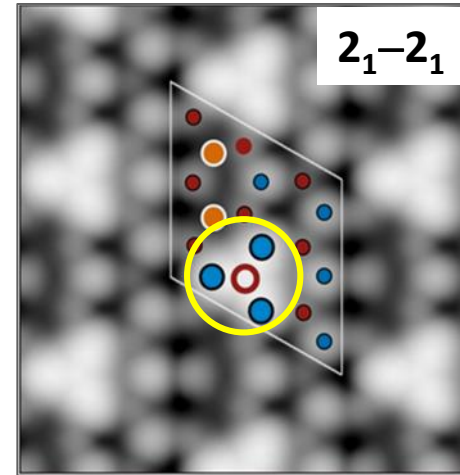
NN-NNN



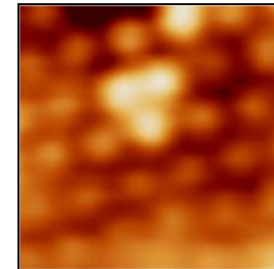
two Ce^{4+}



NNN-NNN



three Ce^{4+}



- Characteristic defect patterns induced by Ce^{4+} ions next to the defect
(2_1-2_1 ; 3_1-2_1 ; $4_1-2_1 \rightarrow$ triple protusion)

- Tendency of Ce^{3+} ions to be away from the defect; Ce^{3+} are not visible

The DFT prediction
is confirmed !

STM-theory

Jerratsch, Shao, Nilius, Freund, Popa, Ganduglia-Pirovano, Sauer, PRL 106, 246801 (2011)

LUMO

Empty state
image

NNN—NNN

Ce^{3+}

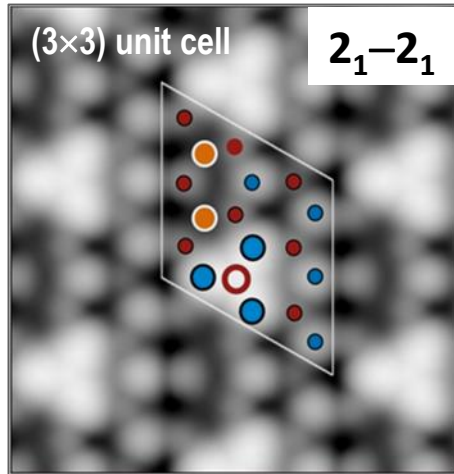
Ce^{4+}

O^{2-}

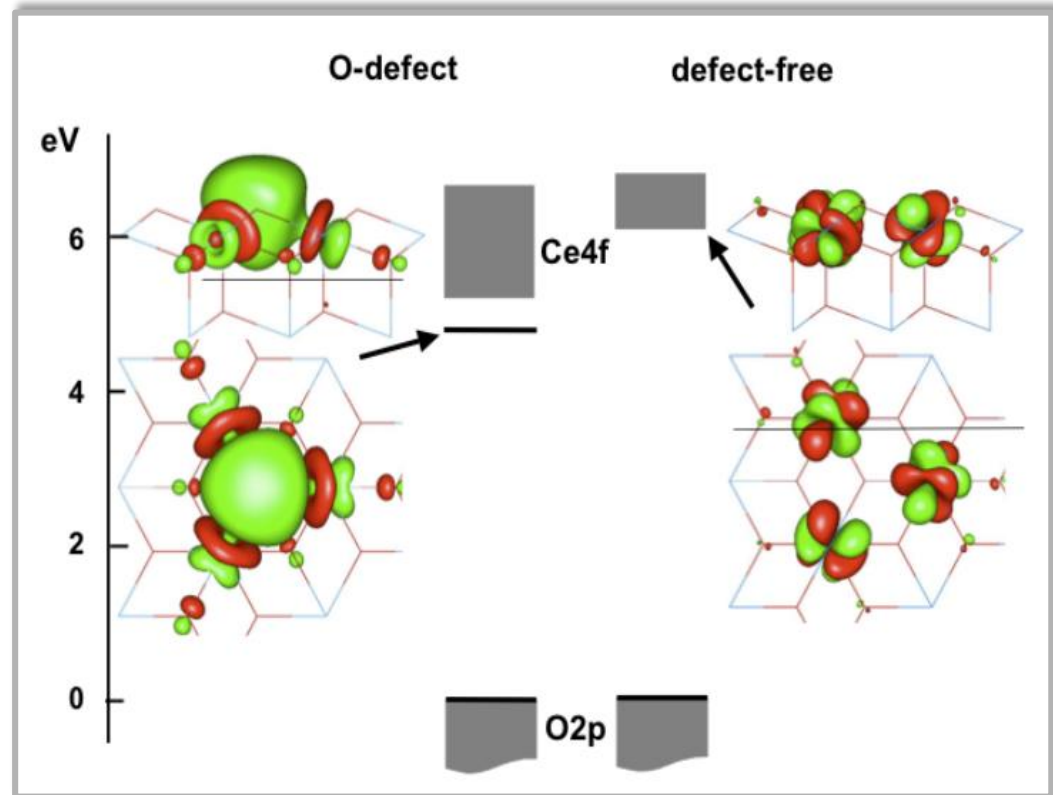
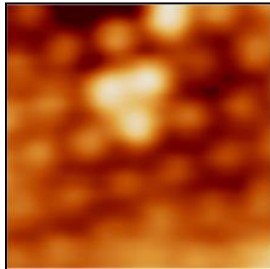
O_{def}

(3×3) unit cell

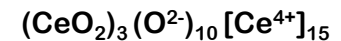
2_1-2_1



three Ce^{4+}

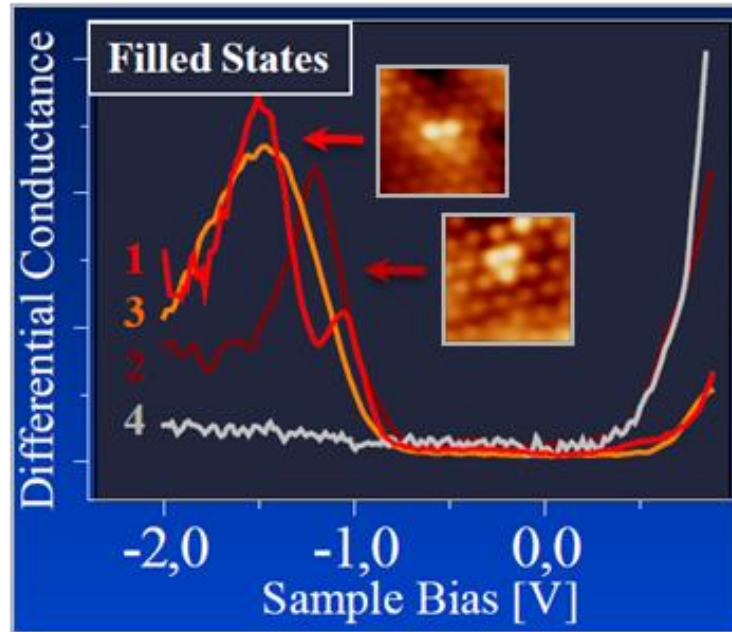


PBE0 embedded cluster

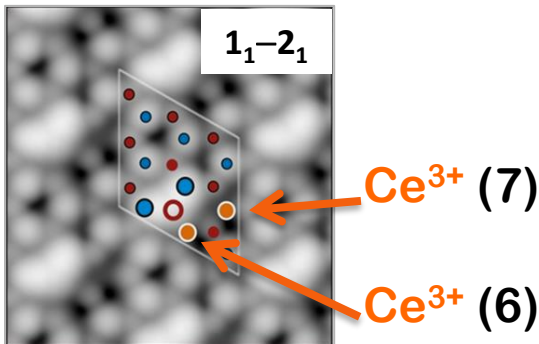


- Bright appearance due to 'delocalized' 4f orbitals with respect to regular Ce^{4+}

STS-theory

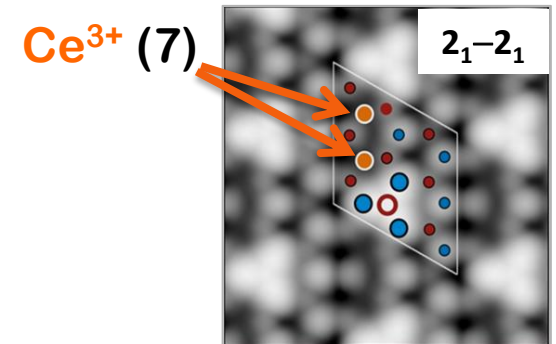


pair protusion:
splitting of 4f states



- different coordination number
~0.1 eV splitting

triple protusion:
no splitting of 4f states



- same coordination number
0 eV splitting

O-vacancy structures at varying concentration

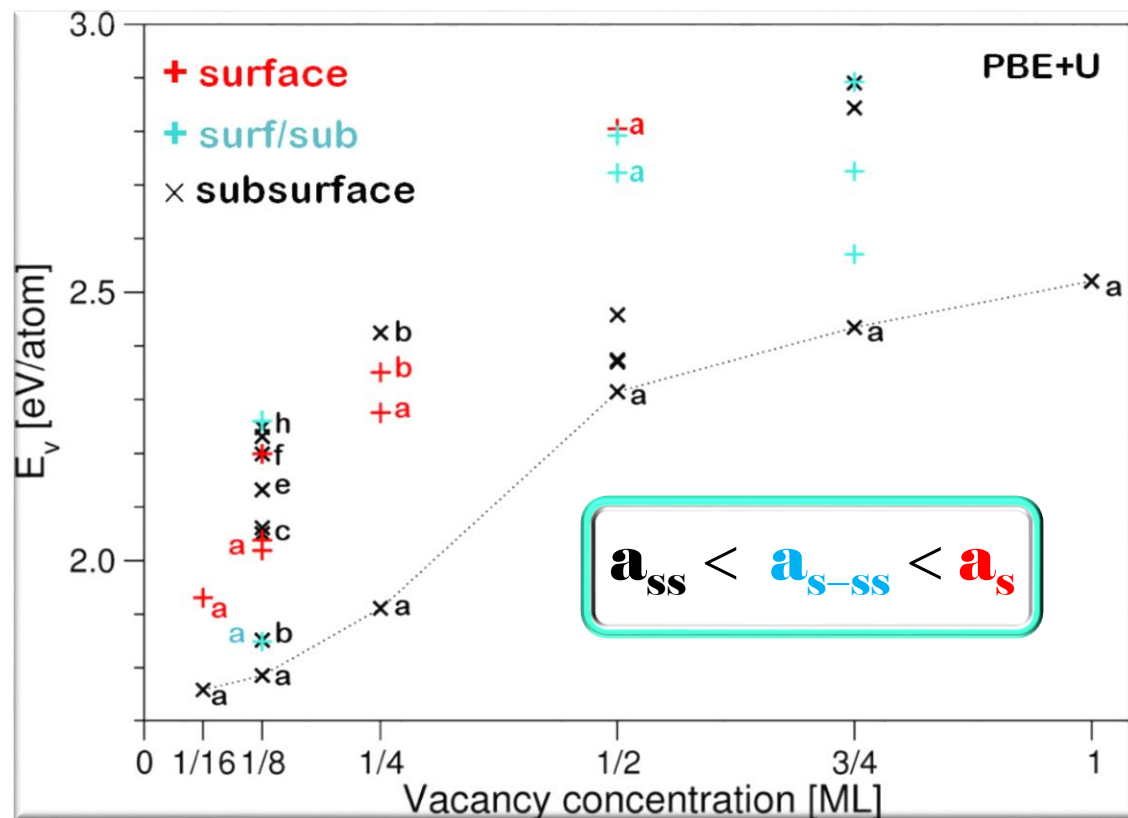
G. E. Murgida and M.V. Ganduglia-Pirovano,
PRL 110, 246101 (2013)

□ Θ ($1/16 \leq \Theta \leq 1$): 1/16, 1/8, 1/4, 1/2, 3/4, 1

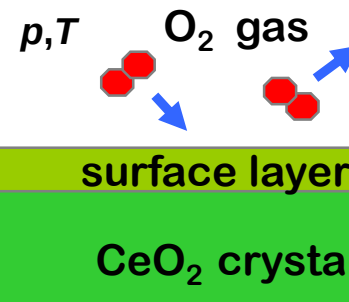
□ subsurface $a_{ss} < b_{ss} < c_{ss} < \dots$
 □ surface/subsurface $a_{s-ss} < b_{s-ss} < c_{s-ss} < \dots$
 surface $a_s < b_s < c_s < \dots$

33 structures!!

□ Ce^{3+} preference for NNN positions & outermost Ce-layer; max. Ce^{3+} – Ce^{3+} distance



Most stable structures
subsurface vacancies only !



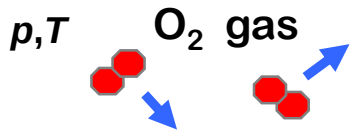
Stability of reduced $\text{CeO}_2(111)$



$$\Delta\gamma_{\text{surf}}(T,p) = [G_{\text{slab}}^{\text{reduced}}(T,p,N_{\text{def}}) - G_{\text{slab}}^{\text{clean}}(T,p) + N_{\text{vac}}^{1/2} \mu_{\text{O}_2}(T,p)] / A$$

$$\Delta\gamma_{\text{surf}}(T,p) \approx [E_{\text{slab}}^{\text{reduced}}(N_{\text{def}}) - E_{\text{slab}}^{\text{clean}} + N_{\text{def}}^{1/2} \mu_{\text{O}_2}(T,p)] / A$$

$$\Delta\gamma_{\text{surf}}(T,p) \approx N_{\text{def}} [E_{\text{v}}(\ominus) + \frac{1}{2} \Delta\mu_{\text{O}_2}(T,p)] / A$$



surface layer

CeO_2 crystal

$$\frac{1}{2} \Delta\mu_{\text{O}_2} = \frac{1}{2} \mu_{\text{O}_2} - \frac{1}{2} E_{\text{O}_2}$$

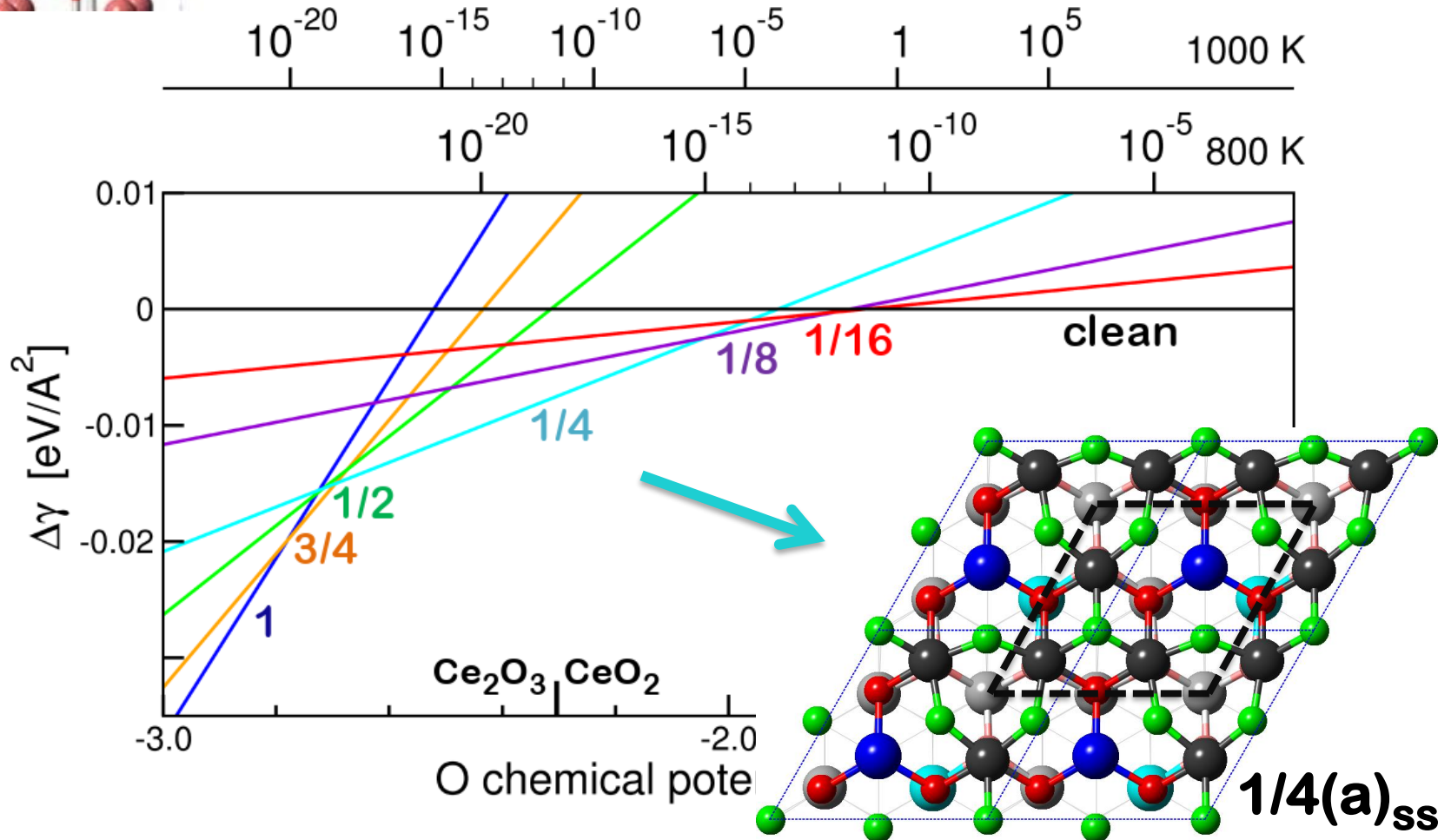
Oxygen chemical potential

$$\mu_{\text{O}_2}(T,p) = \mu_{\text{O}_2}(T,p^\circ) + RT \ln(p/p^\circ)$$



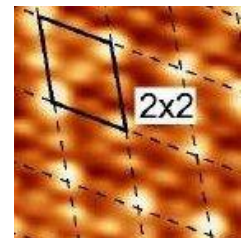
Stability of reduced $\text{CeO}_2(111)$

G. E. Murgida and M.V. Ganduglia-Pirovano, PRL 110, 246101 (2013)

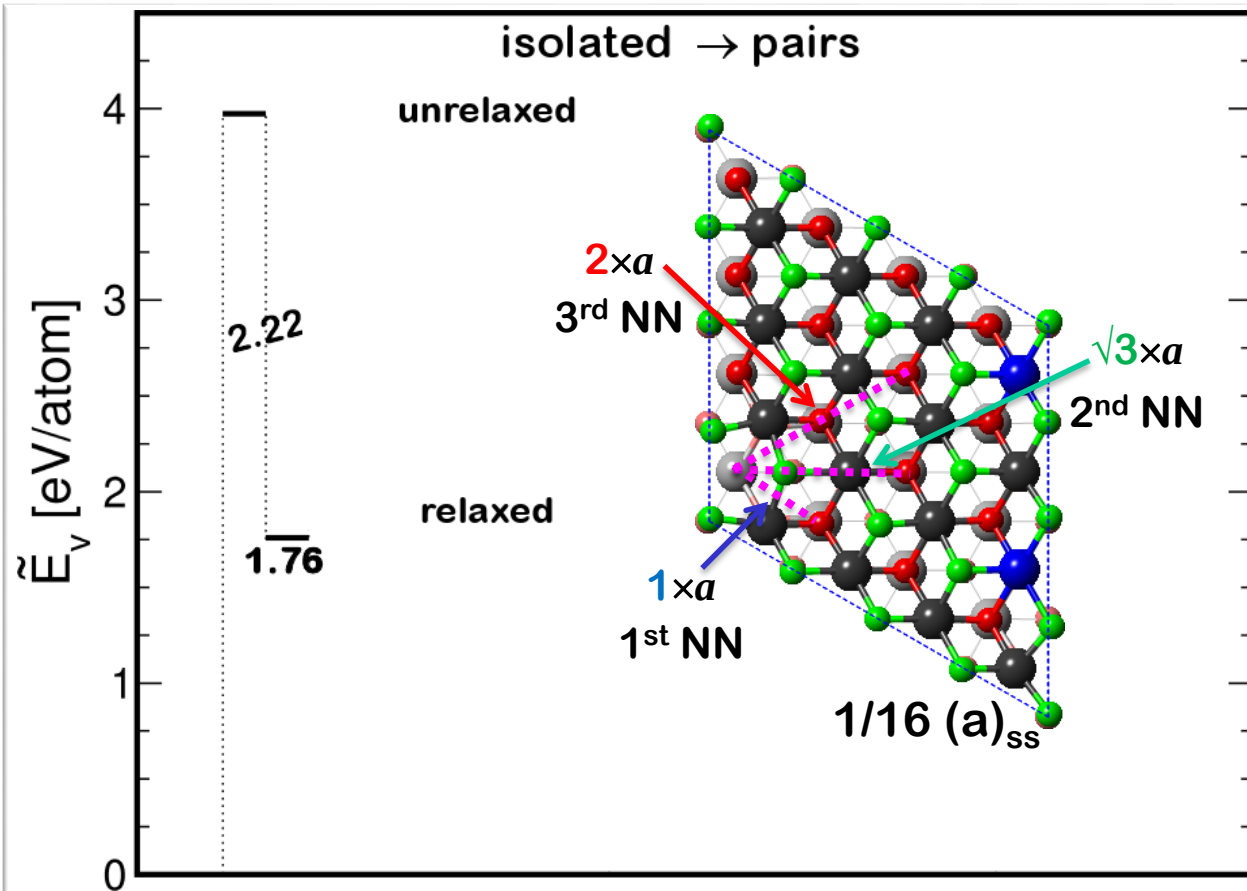


□ (2×2) pattern of subsurface vacancies → third neighbors

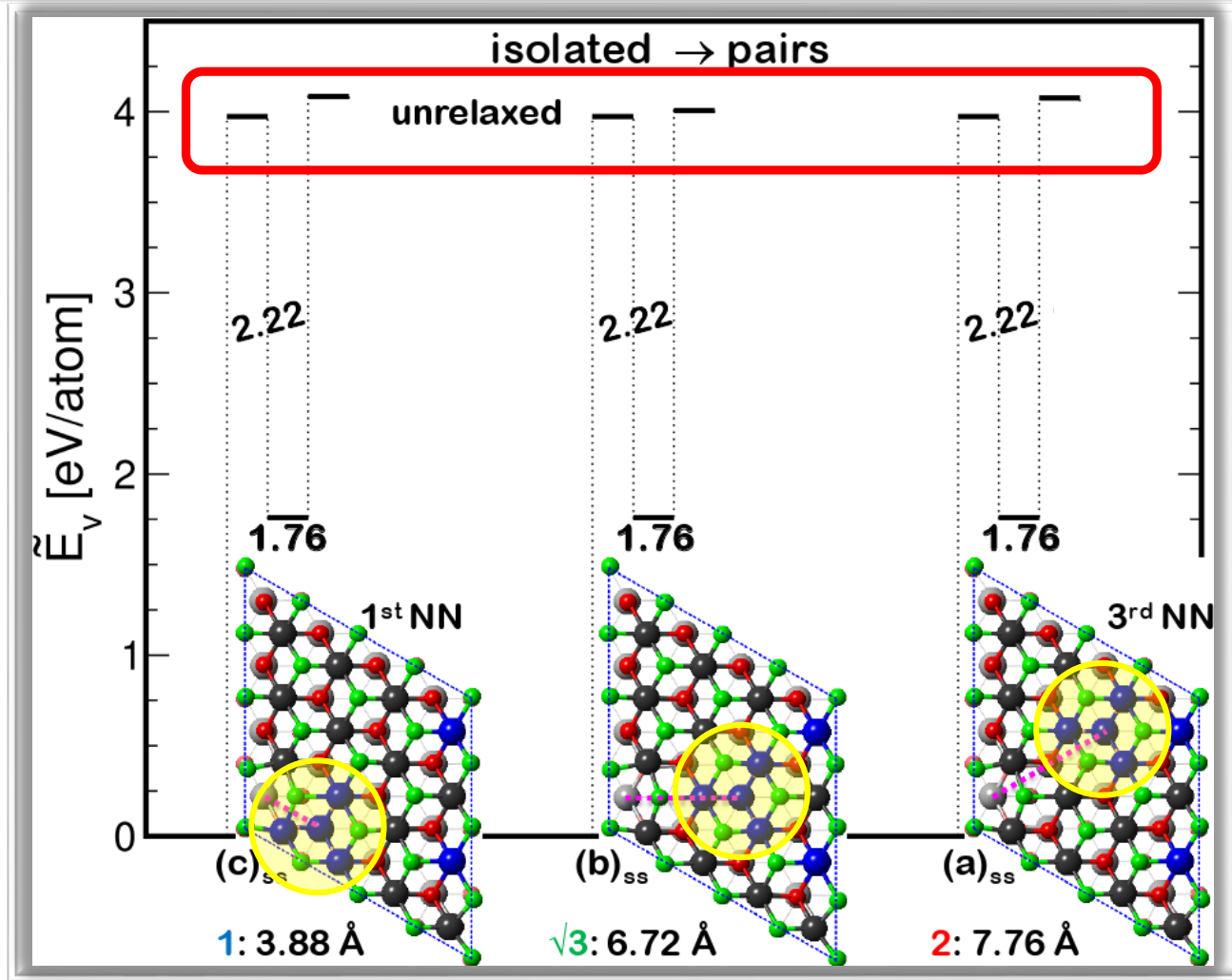
Agreement with experiment!



Why subsurface vacancies do NOT agglomerate?

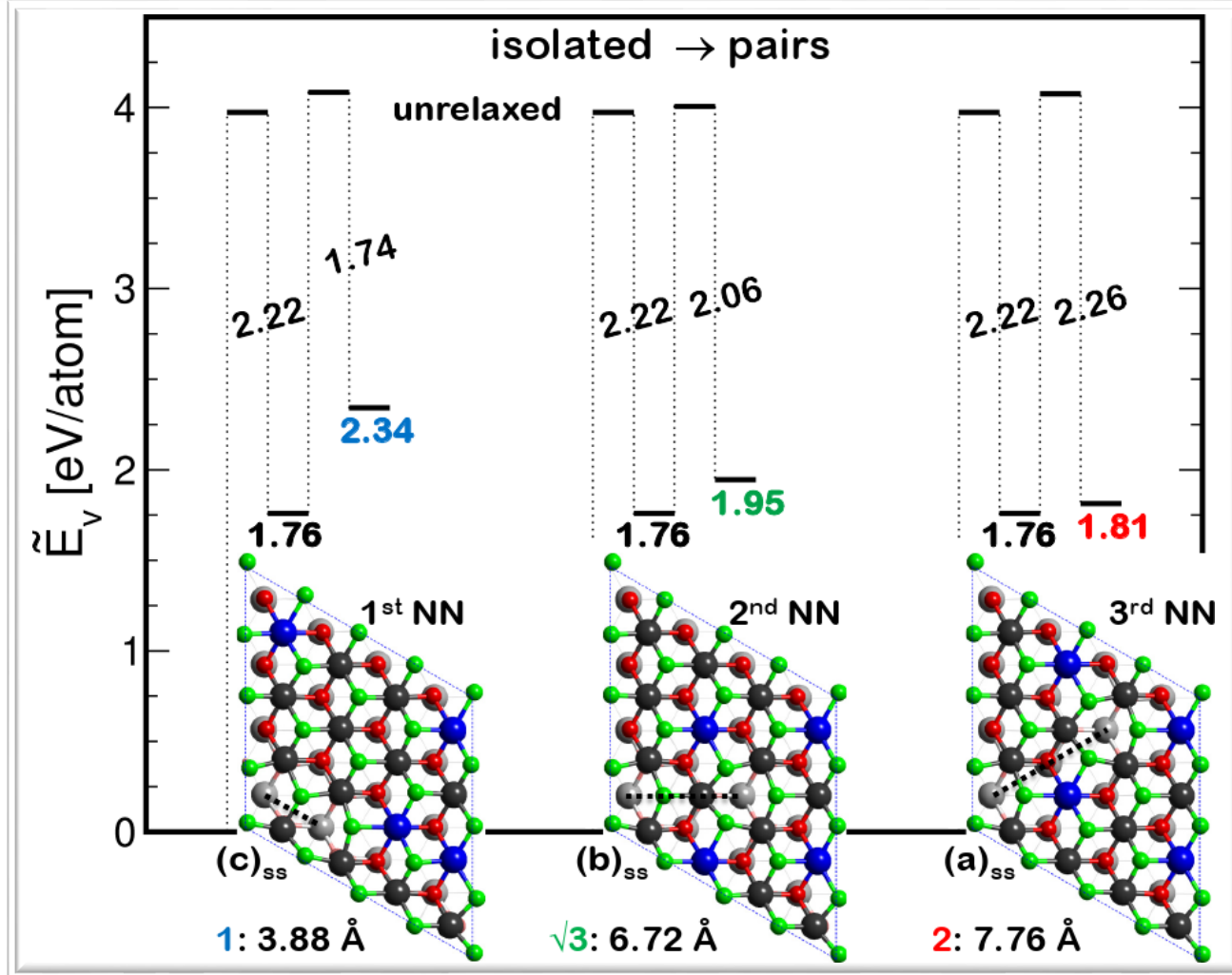


Why subsurface vacancies do NOT agglomerate?



- energy for additional unrelaxed vacancy $\sim$ constant;
slightly larger than first vacancy (by up to ~ 0.1 eV)
- two additional electrons shared by the 4 Ce neighbors $\rightarrow 4 \times \text{Ce}^{3.5+}$

Why subsurface vacancies do NOT agglomerate?



❑ relaxation energy gain depends on distance !!

❑ atomic displacements of first vacancy counteracted by second vacancy
→ net increase in the formation energy

The repulsive interaction

$2 \times \text{isolated} \rightarrow \text{pair} + \text{CeO}_2(111)$

$$\Delta E = + 0.58 \text{ eV}$$

1st NN

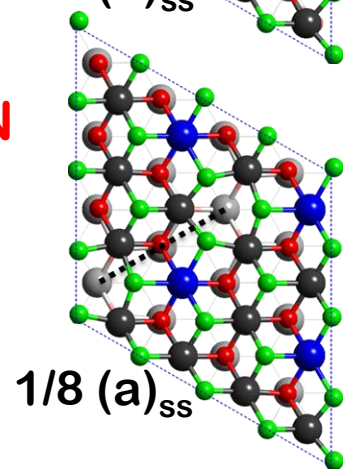
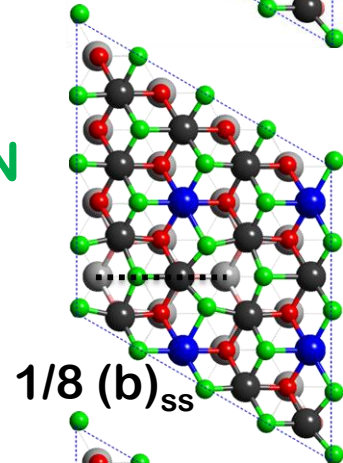
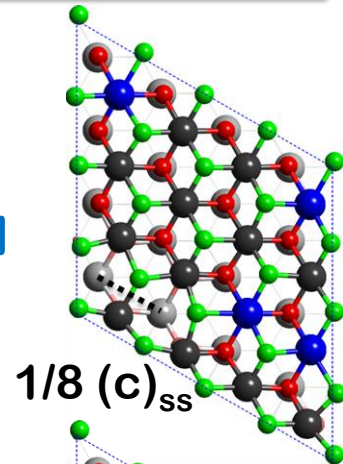
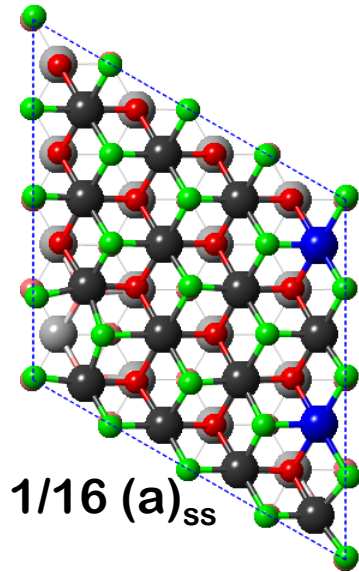
atomic displacements of first vacancy
counteracted by second vacancy
→ net increase in the formation energy

$$\Delta E = + 0.19 \text{ eV}$$

2nd NN

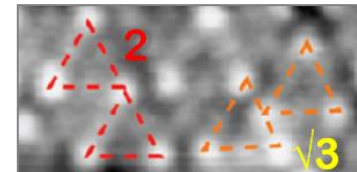
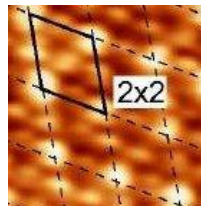
$$\Delta E = + 0.05 \text{ eV}$$

3rd NN



□ a vacancy repels others from its immediate vicinity!!

□ (2×2) structure → all 3rd NN !!



Grinter et al., JPC C 114, 17036 (2010)

Torbrügge et al., PRL 99, 056101 (2007)

Reduced CeO₂(111): Conclusions

- ❑ DFT **predicts** a tendency of Ce³⁺ ions to be away from the defect
- ❑ STM/STS +DFT **confirm** the tendency of defects to bind to Ce⁴⁺ ions
- ❑ DFT **predicts** a preference for subsurface O defects ($1/16 \leq \Theta \leq 1\text{ML}$)
- ❑ DFT + statistical thermodynamics **predict** a (2×2) subsurface vacancy structure → consistent with experiments

Explanations in terms of defect-induced lattice relaxation effects

- localization phenomenon
- proneness of defects to be bound by Ce⁴⁺
- subsurface preference
- repulsive interactions between subsurface vacancies

We recognize the merit of DFT+U and hybrid approaches in predicting the subsurface preference and the NNN localization

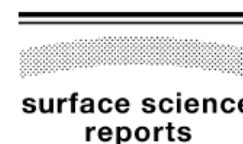
What have we learned and remaining challenges



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Surface Science Reports 62 (2007) 219–270



www.elsevier.com/locate/surfrep

Oxygen vacancies in transition metal and rare earth oxides: Current state of understanding and remaining challenges

M. Verónica Ganduglia-Pirovano*, Alexander Hofmann, Joachim Sauer

Humboldt-Universität zu Berlin, Institut für Chemie, Unter den Linden 6, D-10099 Berlin, Germany

Accepted 26 March 2007

Abstract

Defects at transition metal (TM) and rare earth (RE) oxide surfaces, neutral oxygen vacancies in particular, play a major role in a variety of technological applications. This is the motivation of numerous studies of partially reduced oxide surfaces. We review, discuss, and compare theoretical data for structural and electronic properties and energetic quantities related to the formation of oxygen defects at TM and RE oxide surfaces using TiO_2 , ZrO_2 , V_2O_5 , and CeO_2 as examples. Bulk defects, as far as relevant for comparison with the properties of reduced surfaces, are briefly reviewed. Special attention is given to the fate of the electrons left in the system upon vacancy formation and the ability of state-of-the-art quantum-mechanical methods to provide reliable energies and an accurate description of the electronic structure of the partially reduced oxide systems.

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What have we learned and remaining challenges

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Defects at Oxide Surfaces

Editors: Jupille, Jacques, Thornton, Geoff (Eds.)

Chapter 5 Oxygen Defects at Reducible Oxide Surfaces: The Example of Ceria and Vanadia

María Verónica Ganduglia-Pirovano

Abstract Cerium and vanadium oxide-based systems play a major role in a variety of technological applications, with the reducibility of the systems being crucial to their functionality in the applications. The in-depth understanding and control of the type, density, and distribution of oxygen vacancies provide a means to influence the electronic structure and to tailor the systems' functionality. Hence, a great deal of experimental and theoretical work has been devoted to the study of partially reduced ceria and vanadia, both surfaces and bulk. Here, theoretical data for structural and electronic properties and energetic quantities related to the formation and interaction of neutral oxygen vacancies at the $\text{CeO}_2(111)$ and $\text{V}_2\text{O}_5(001)$ surfaces are reviewed, discussed and compared. Experimental findings on oxygen defects in ceria and vanadia are briefly reported. Special attention is given to the fate of the electrons left in the system upon vacancy formation, the vacancy-induced lattice relaxation, whether vacancies agglomerate or repel each other, and the ability of state-of-the-art quantum-mechanical methods to provide an accurate description of the geometric and electronic structures of the partially reduced oxide systems as well as reliable oxygen defect formation energies.

