An “order N” method for the atomistic simulation of nano-oxides: Metal-supported MgO(100) islands

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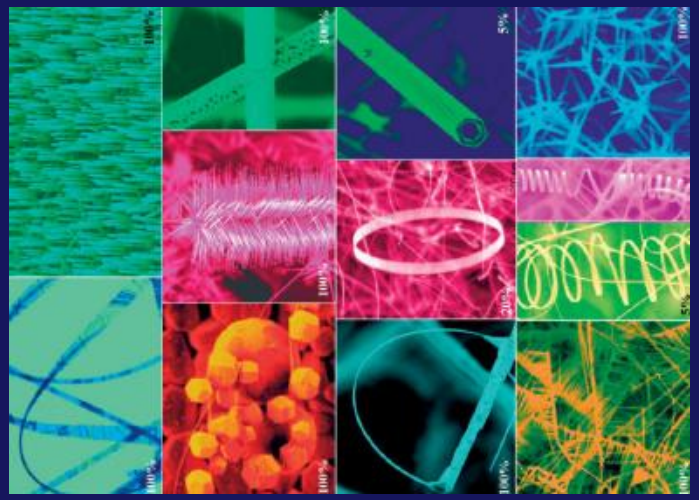
*PRB **81**, 155409(2010)*

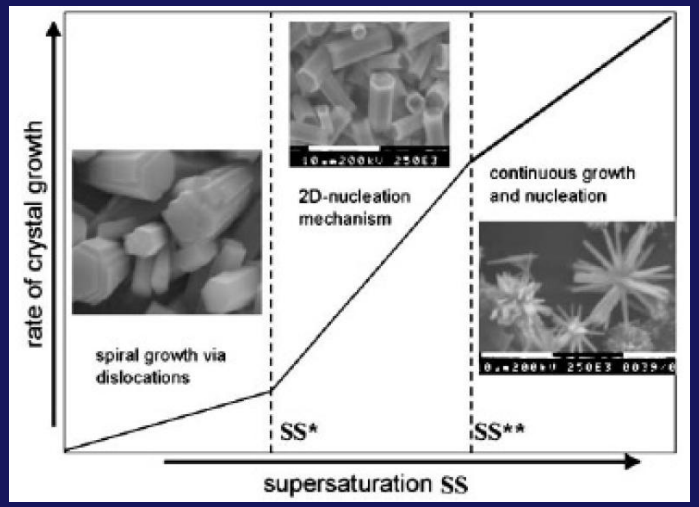
Oxide nano-objects: structure and properties

Structural complexity driven by the environment & growth conditions

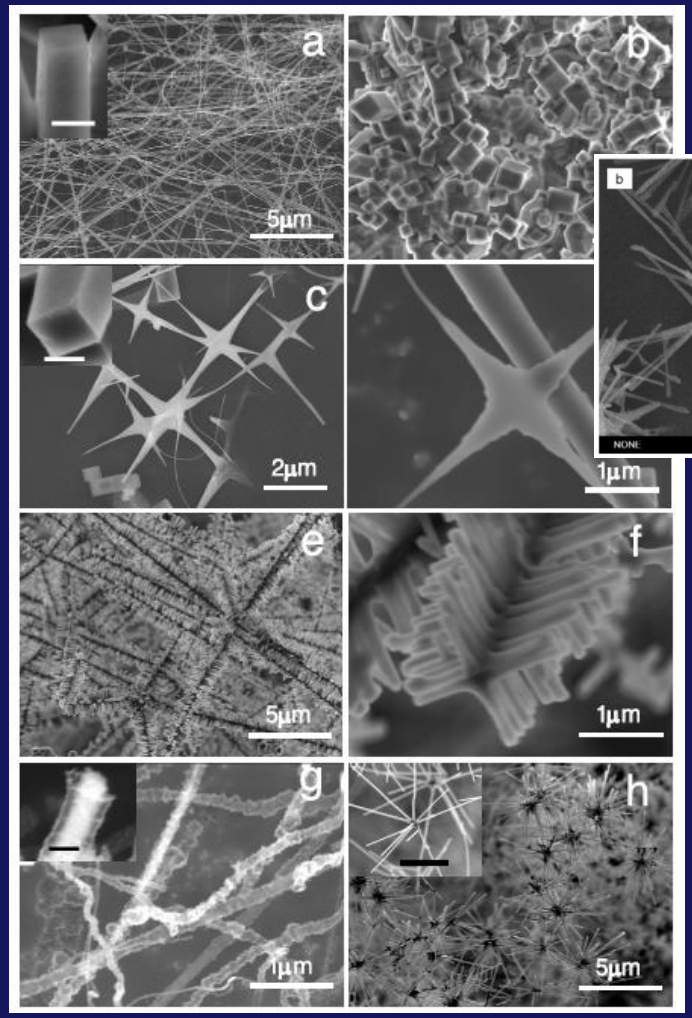


ZnO

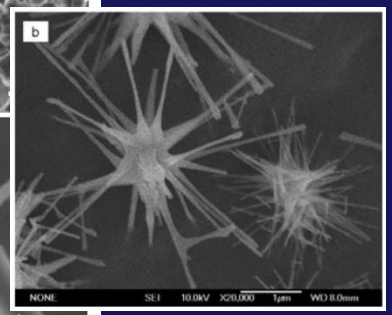
Z.L. Wang et al. (2004)



Govender et al. (2004)



MgO



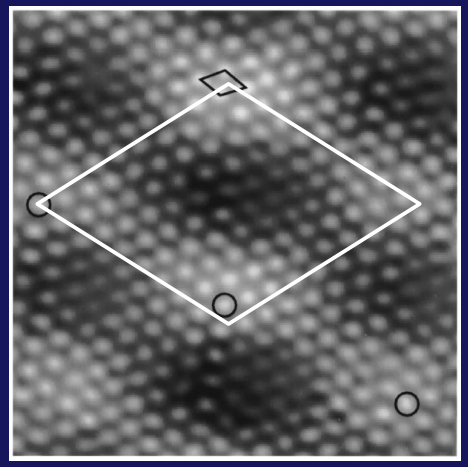
X.-S. Fang et al. (2005)

Y. Hao et al. (2006)

A large number of complex structures cannot be treated directly by ab initio simulations.

Metal-supported oxide 1ML

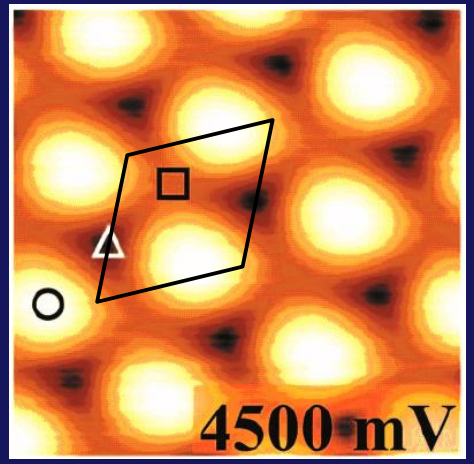
FeO(111)/Pt(111)



Moiré structure due to the lattice mismatch (periodicity ~ **25 Å).**

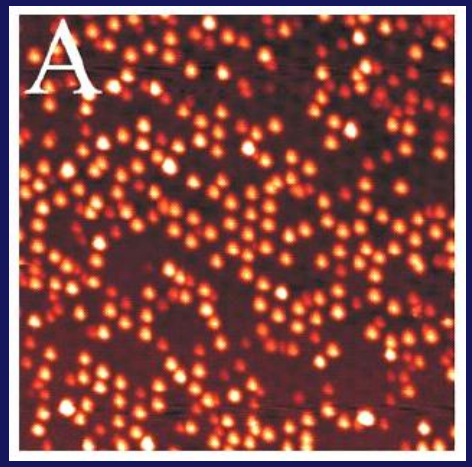
Strong rumpling of the oxide layer due to interface charge transfer.

M. Ritter et al.,
*PRB **57**, 7240 (1998).*
JG, C. Noguera,
PRB 79, 155433 (2009).



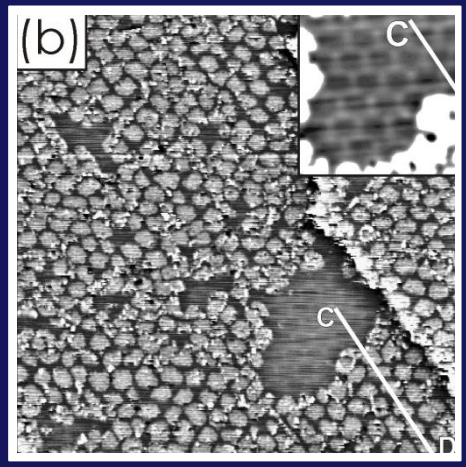
Modulation of the surface potential driven by the structure of the metal/oxide interface.

E. Rienks et al.,
*PRB **71**, 241404 (2005).*
L. Giordano et al.,
*PRB **76**, 075416 (2007).*



Spontaneous charging and self-organization of adsorbates (Au monomers).

Nilius et al.,
*PRL **95**, 066101 (2005).*
L. Giordano et al.,
*PRL **101**, 026102 (2008).*



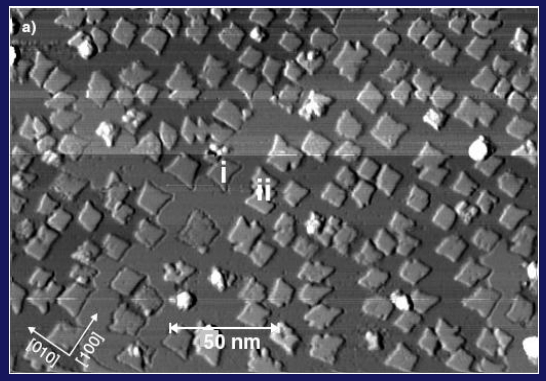
Registry-dependent oxidation of oxide film.

Low temperature catalytic activity!

Y.-N. Sun et al.,
J. Catal. 266, 359 (2009).
L. Giordano et al.
JPC C 114, 21504 (2010).

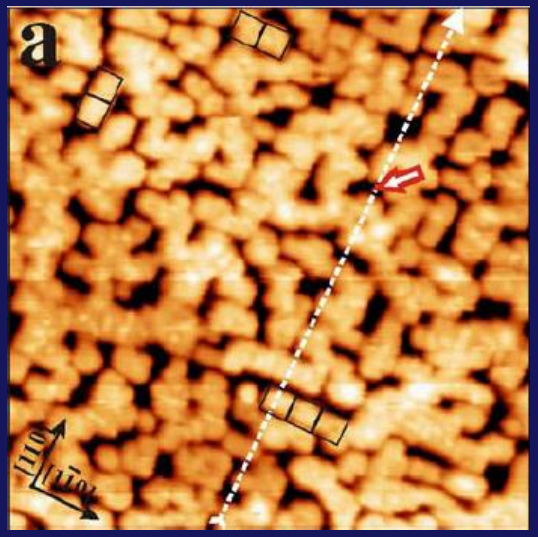
MgO islands and films on transition/noble metal substrates

MgO(100)/Ag(100)



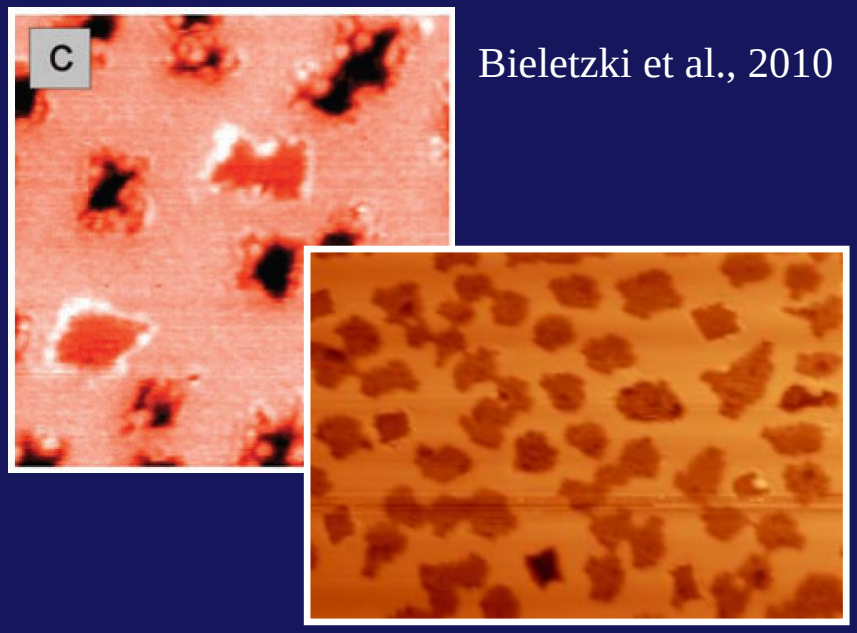
Schintke et al., 2004

MgO(100)/Mo(100)



Benia et al., 2010

MgO(100)/Ag(100)

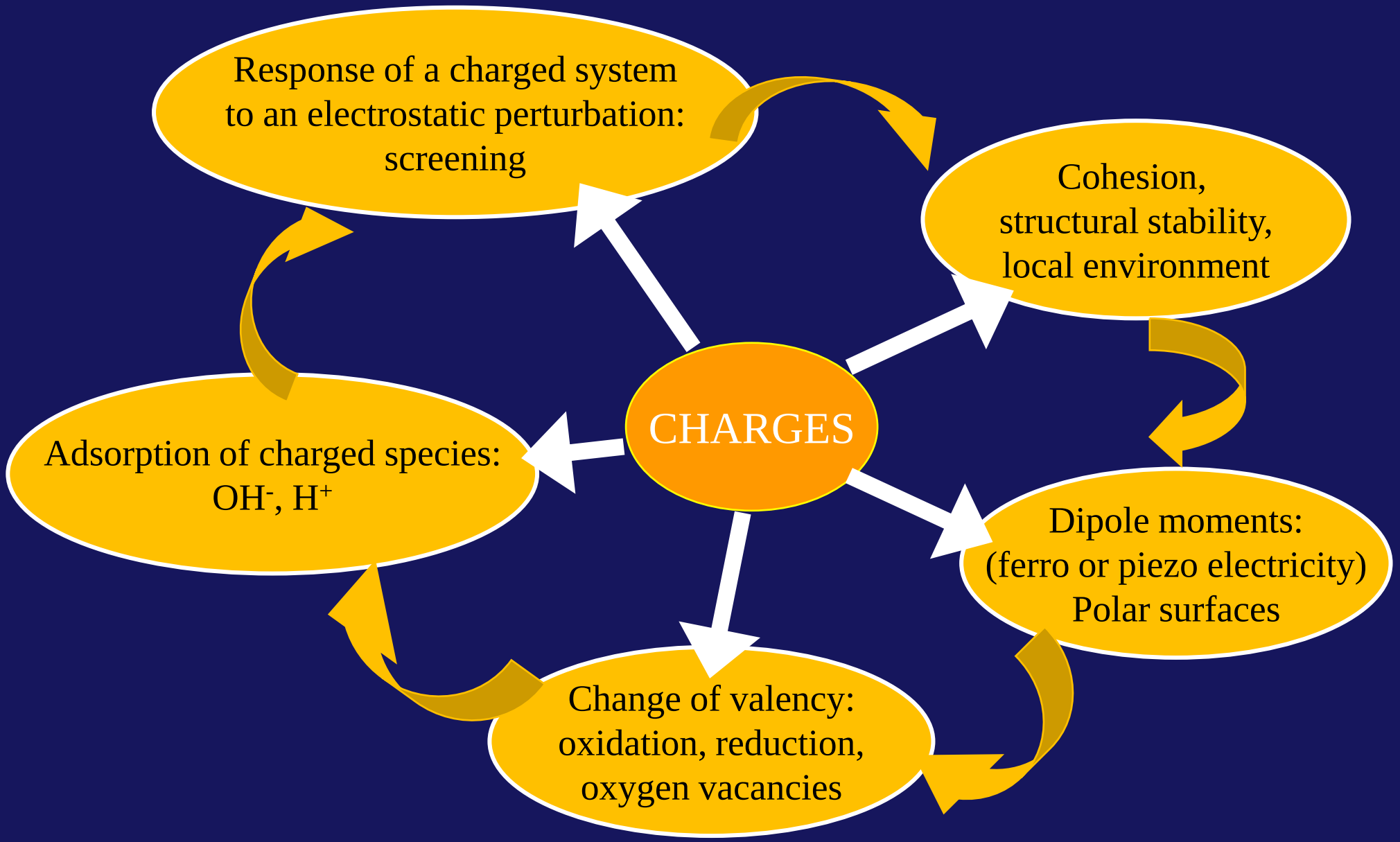


Bieletzki et al., 2010

Cabailh et al., 2011

- interfacial strain due to lattice mismatch?
- formation of Moiré pattern & interface dislocation?
- magic sizes and shapes?

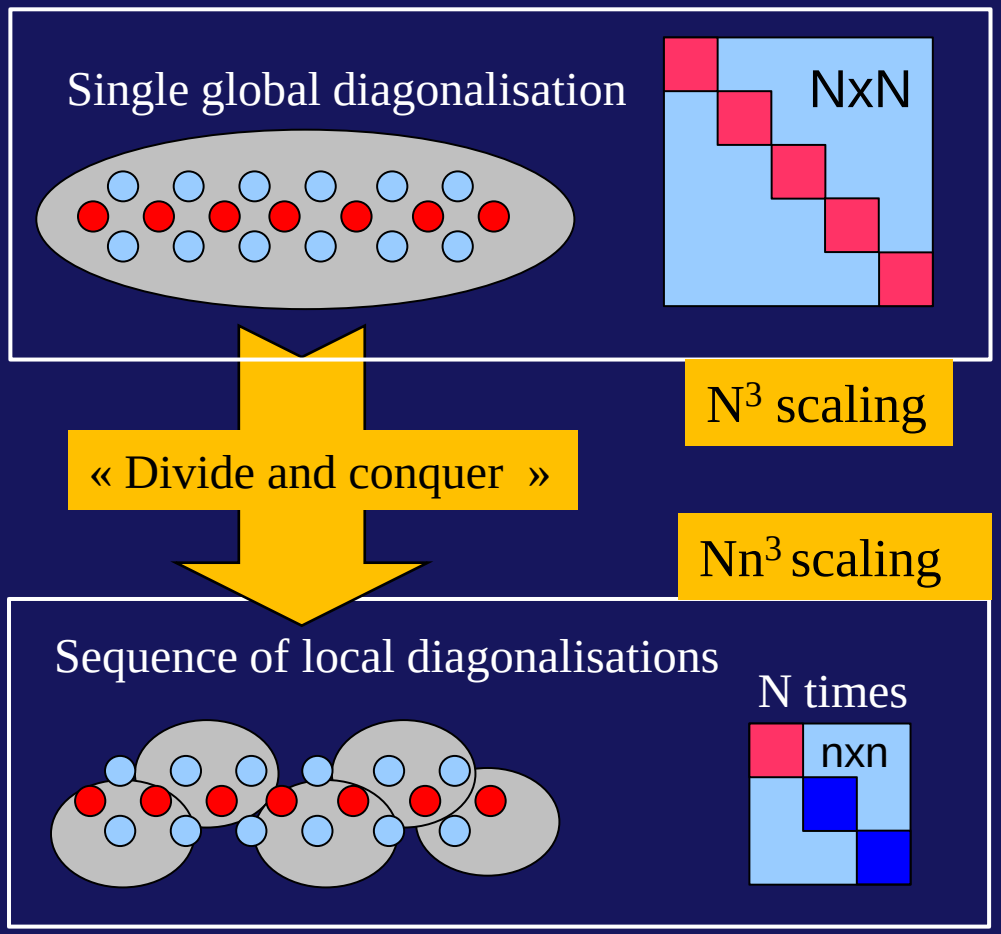
Coupling between electronic and structural degrees of freedom

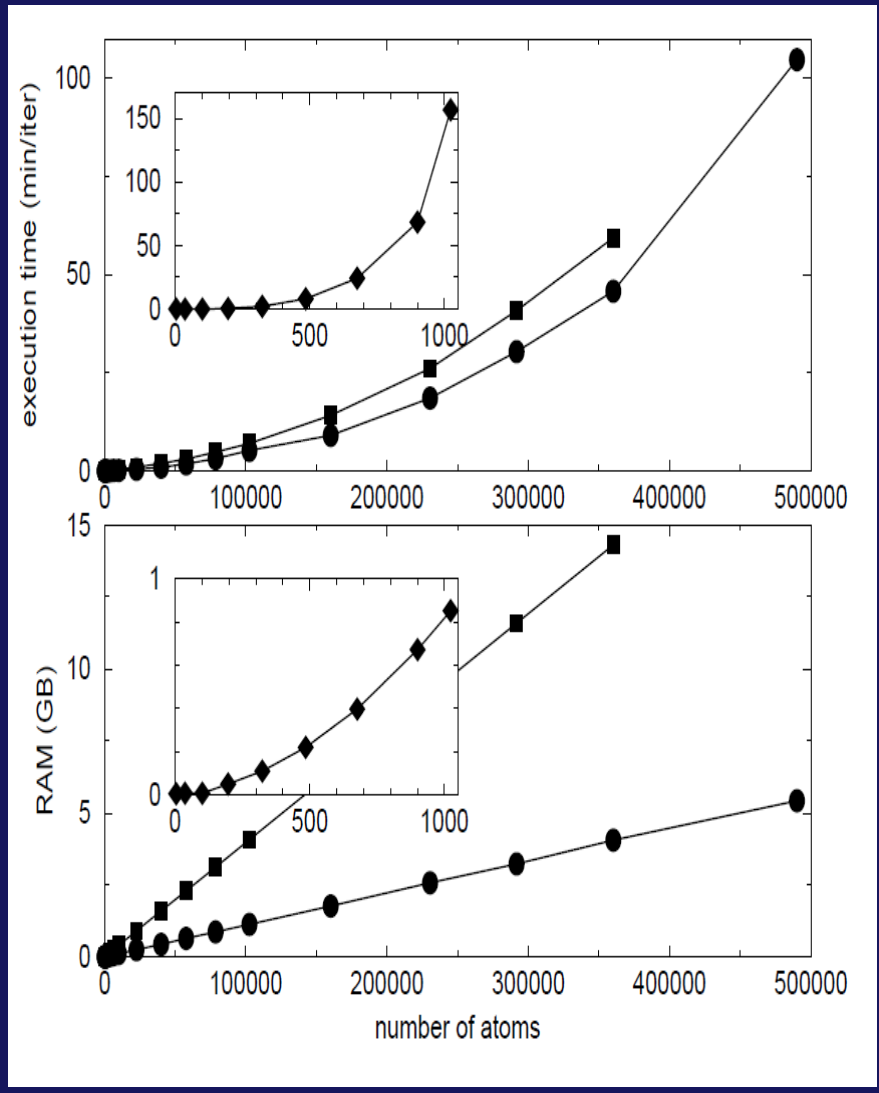


Self-consistent treatment of the electronic structure may be necessary

“Order N” method: background and performances

Semi-empirical Hartree-Fock quantum approach (INDO)



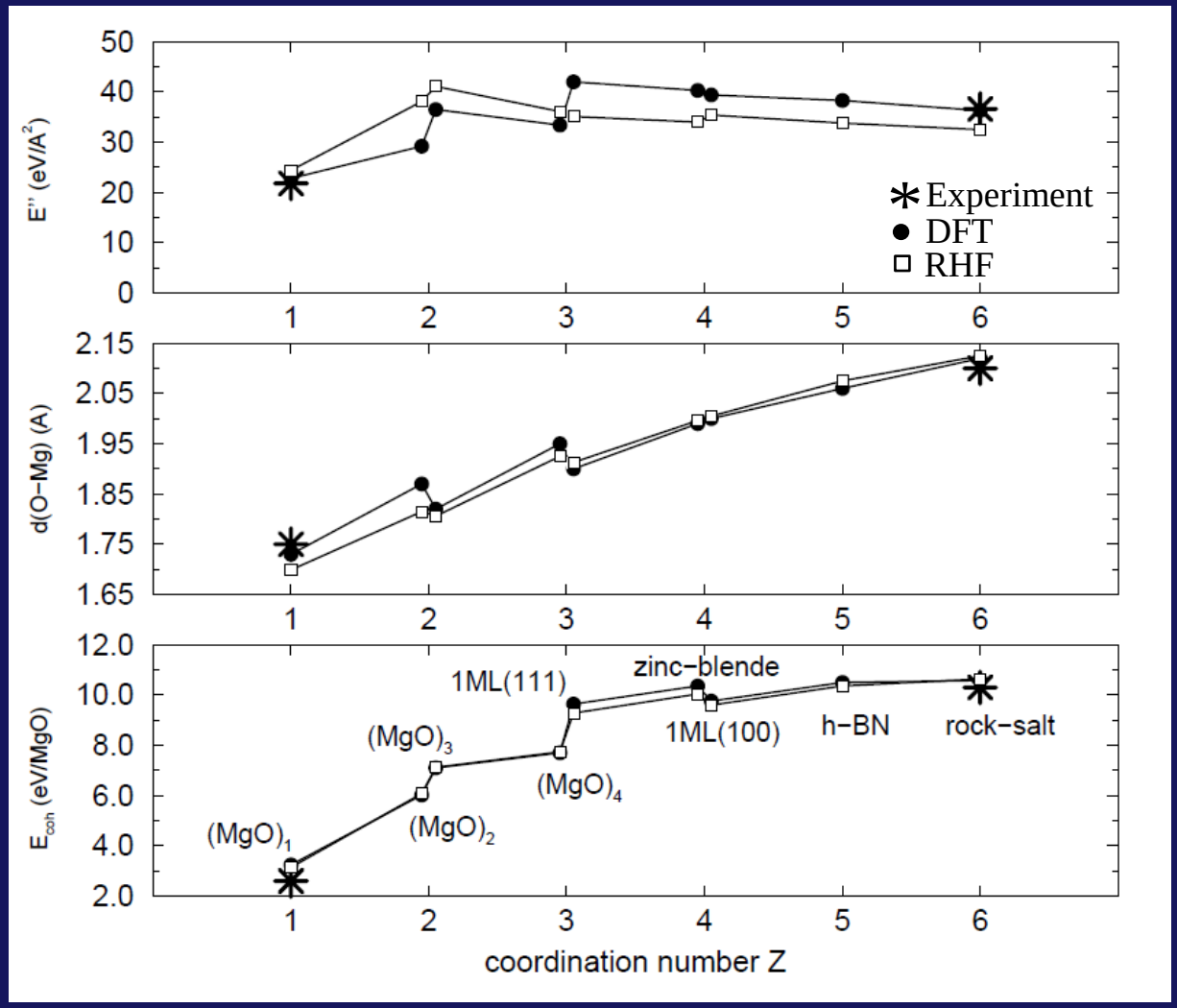


Eg., for 100 000 atoms:

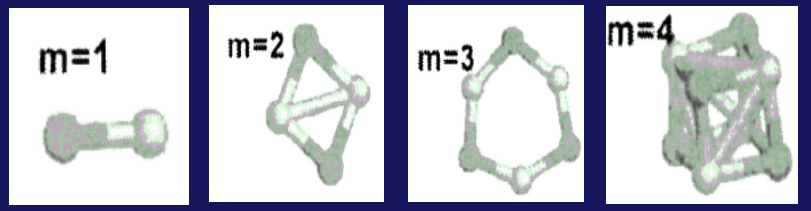
* 5-10 min/iteration ⟷ 100 000 years/iter.
* 8 GB RAM ⟷ 7 TB RAM

Adjustment of parameters

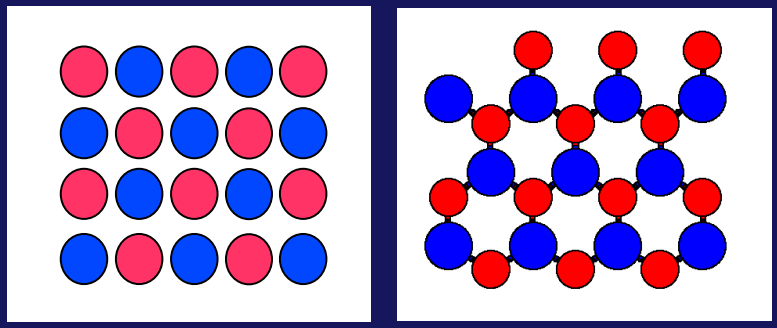
Case of MgO: adjustment to experimental and DFT results



Clusters (0D)

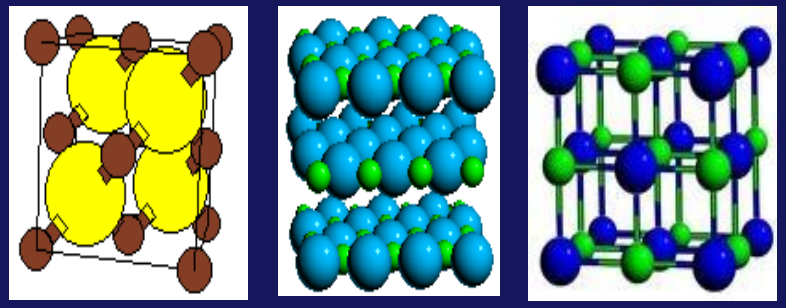


2D layers



1ML (100) 1ML (111)

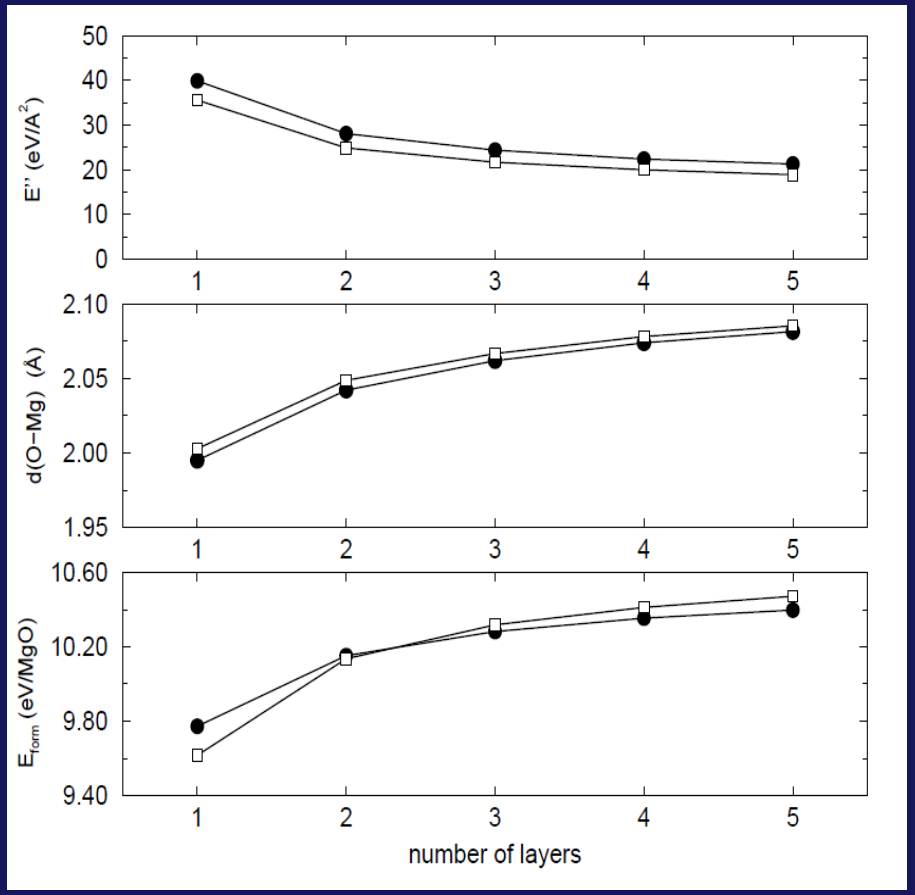
3D periodic structures



ZnS (B3) h-BN (Bk) Rocksalt (B1)

Transferability of the parameterization

Test of accuracy for unsupported MgO(001): films of increasing thickness

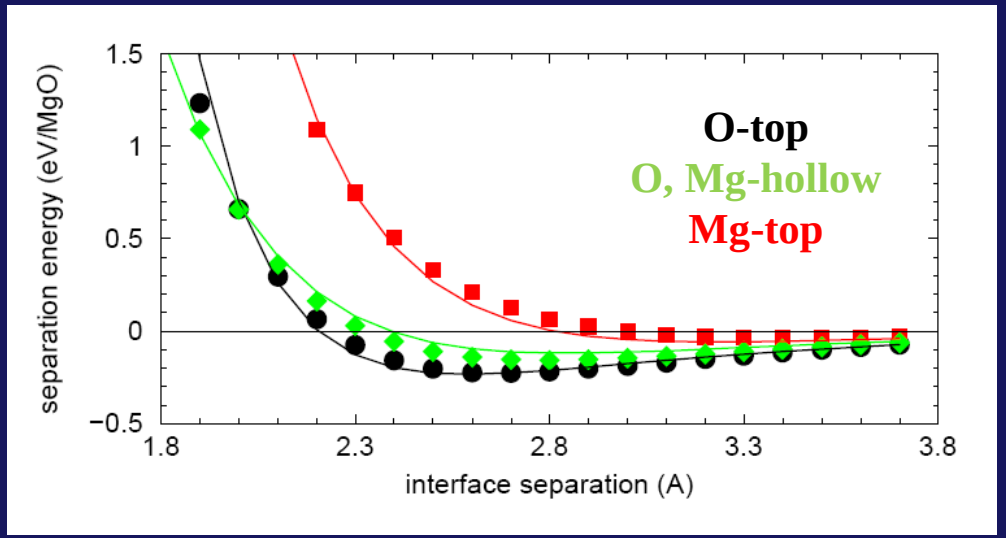


Metal substrate: Potential energy surface

Case of weak metal-oxide interaction (eg., MgO/Ag(100)):

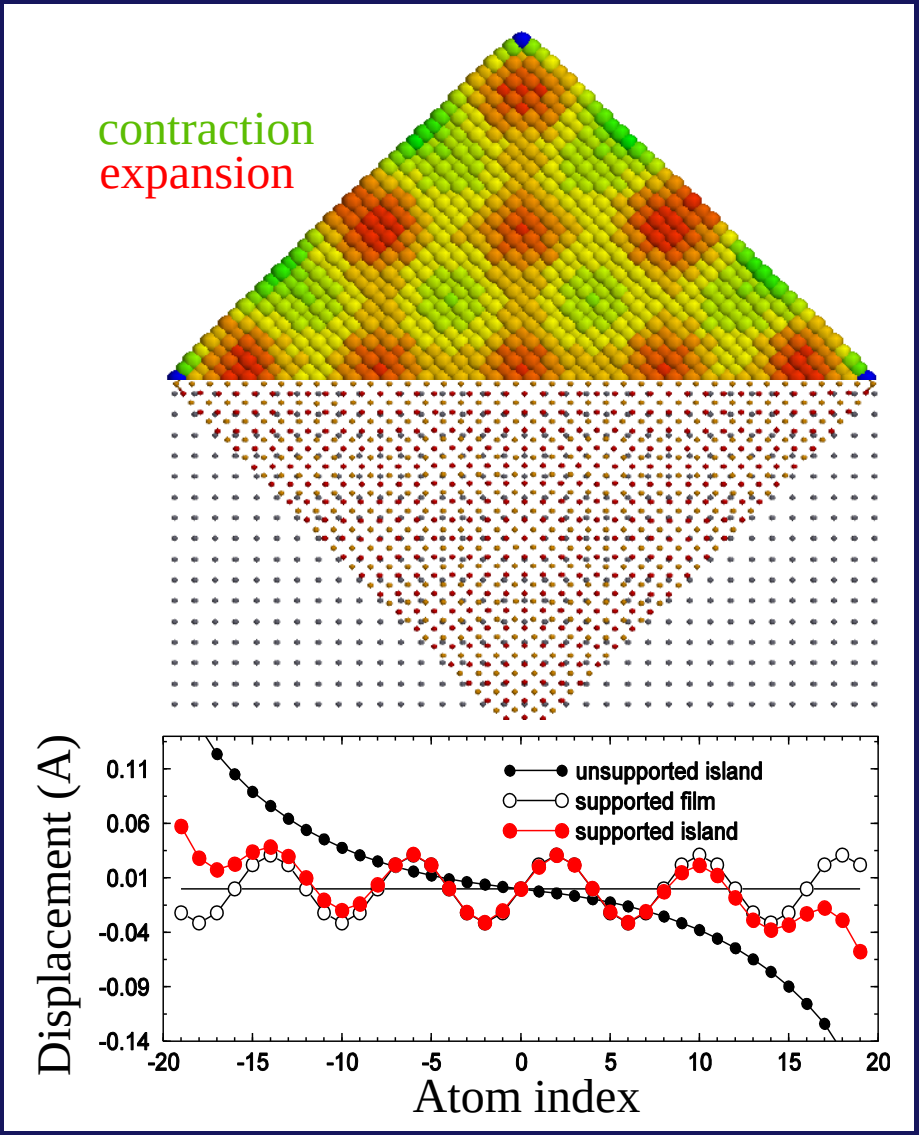
$$E^{sub} = \sum_{i=1}^{N} E_{\text{int}}^{at_i}(x_i, y_i, z_i)$$

$$E_{\text{int}}^{at}(x,y,z) = a(z) + b(z)[\cos(\frac{2\pi x}{a}) + \cos(\frac{2\pi y}{a})] + c(z)[\cos(\frac{2\pi(x+y)}{a}) + \cos(\frac{2\pi(x-y)}{a})]$$



MgO(100) islands on a metal (100) substrate

Effect of the substrate on the island's structure



- Moiré pattern due to lattice mismatch;
- local lattice distortion (Mg-O distances):
  coincidence zones: bond expansion
  interfacial dislocations: bond contraction

Displacement of ions along x axis:

$$x_n = n\gamma a + \alpha a \sin 2\pi n(1-\gamma) + \delta x_n$$

γa = mean lattice parameter
γ=7/8: 8 oxygen rows for 7 metal rows
δx_n= edge effects

Dislocation network lattice parameter:

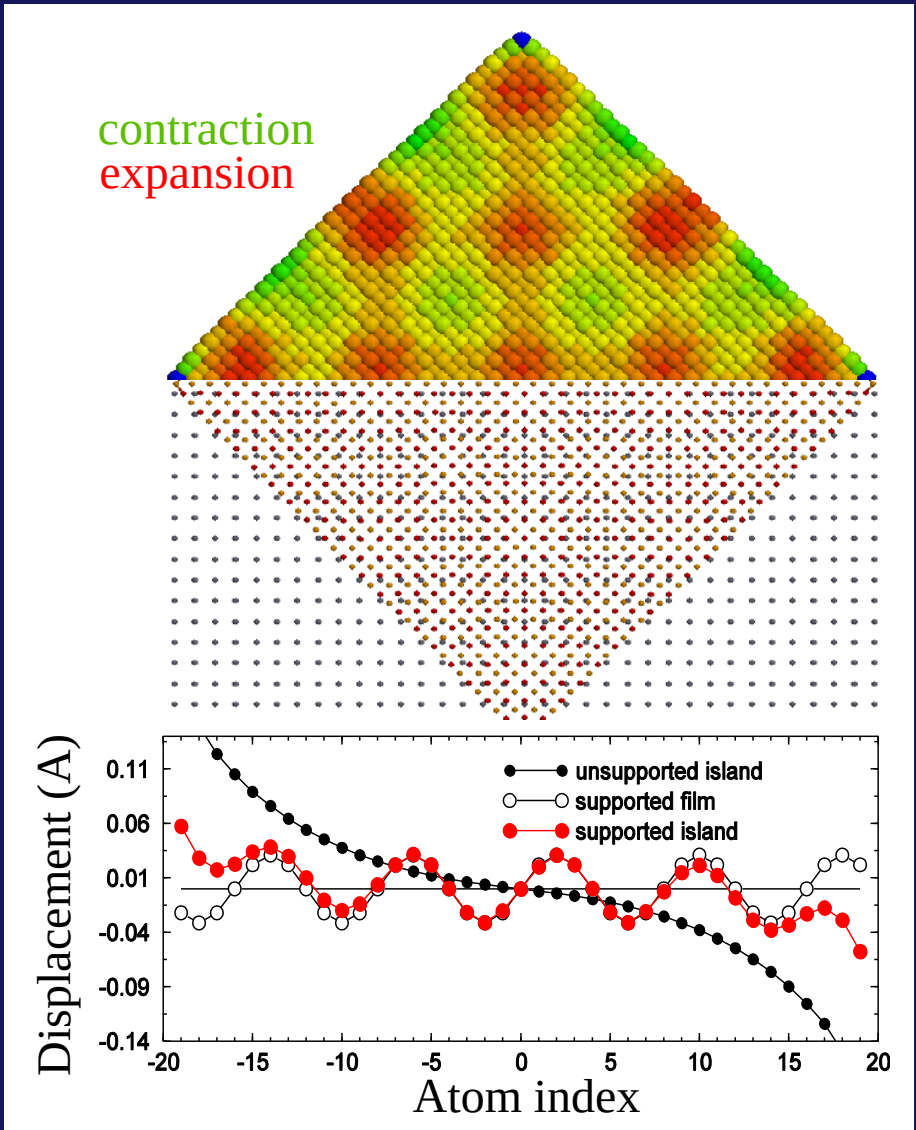
$$A = \frac{\gamma a}{1-\gamma}$$

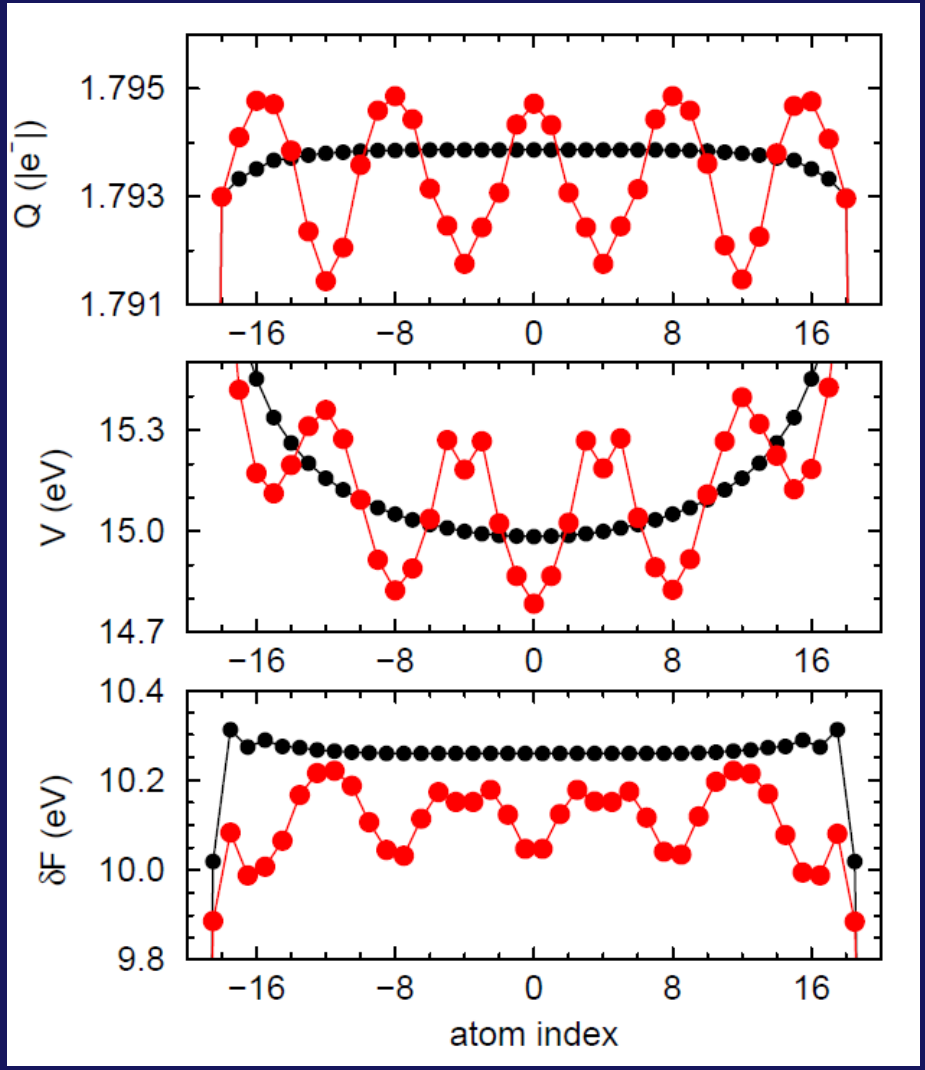
In the present case (a=3.2 A, F=2): $\gamma a \sim a_{MgO\ unsupported}$

Periodicity determined by the lattice misfit at the interface.

MgO(100) islands on a metal (100) substrate

Effect of the substrate on the island's electronic characteristics





Coincidence zones: expanded bonds, lower electrostatic potential, smaller gap

MgO(100) islands on a metal (100) substrate

STM observation of Moiré pattern MgO/Mo(001)

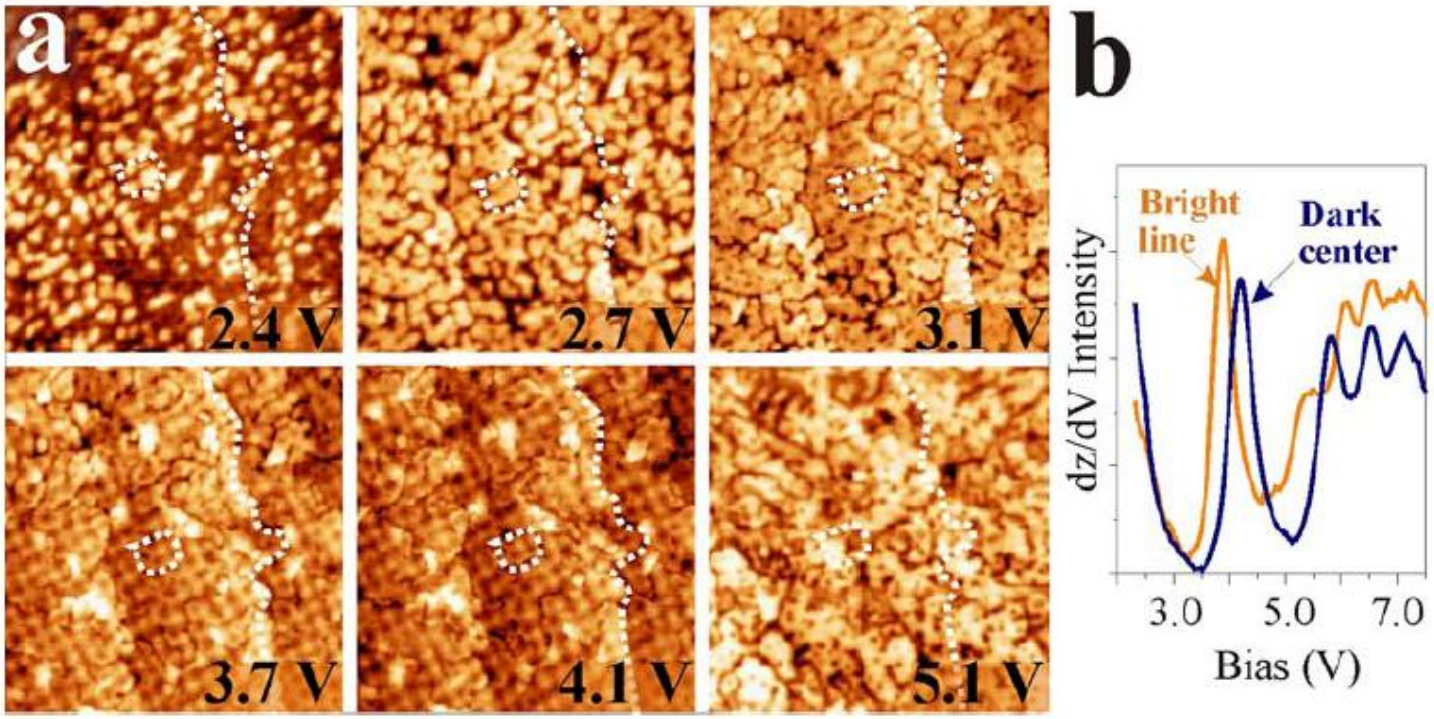
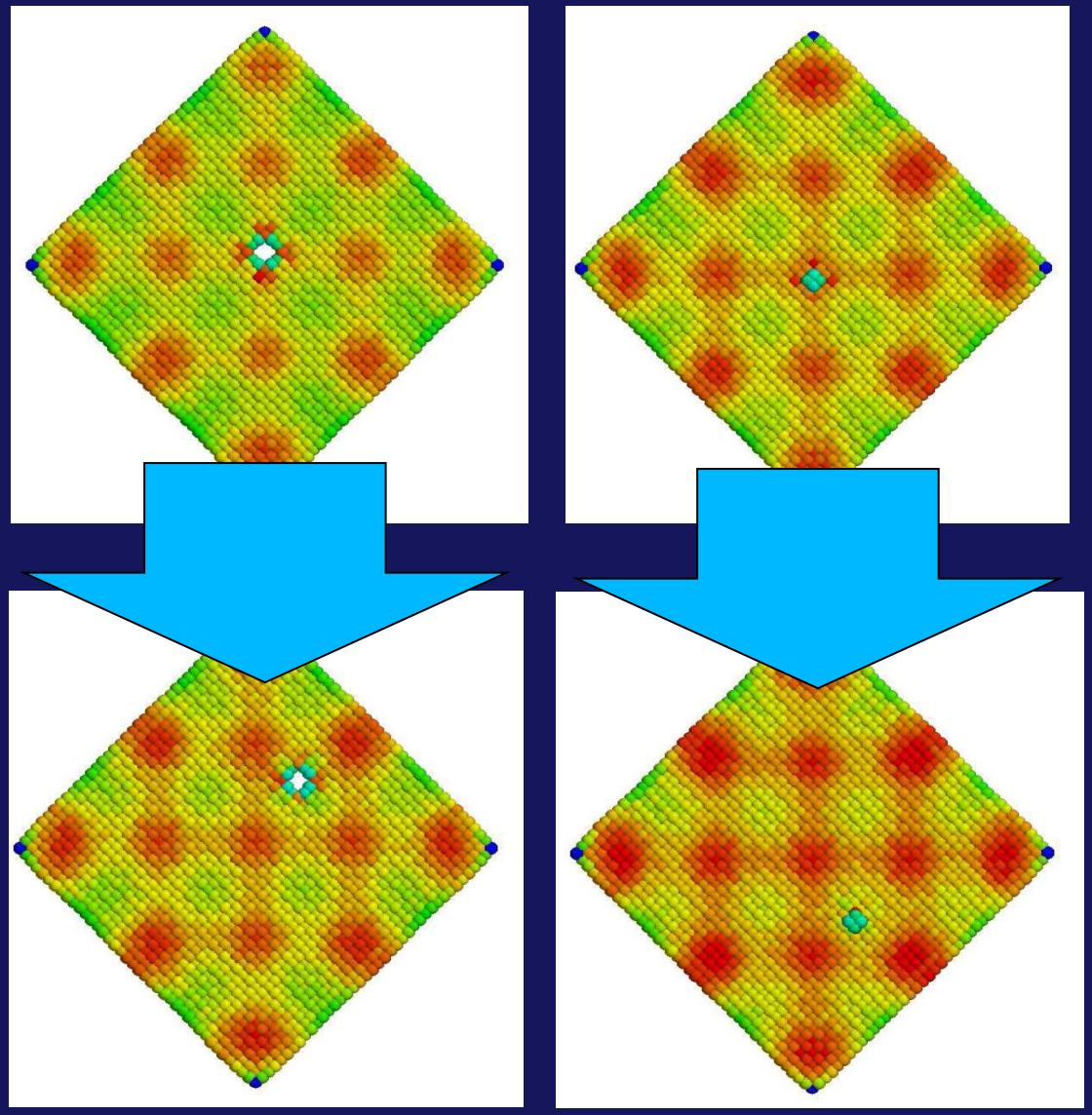


Fig. 5: (a): STM bias series of an identical MgO/Mo(001) region (100 × 100 nm^2). The dashed lines mark selected domain boundaries and should serves as guides to the eye. The characteristic square pattern is only visible in a small bias range around 4.0 V. **(b)** dz/dV spectra taken above a bright and a dark region of the coincidence pattern. The first FER is clearly down-shifted above the bright lines compared to the center of the coincidence cell.

H.M. Benia, P. Myrach, N. Nilius, H.-J. Freund , Surf. Sci. 604, 435 (2010)

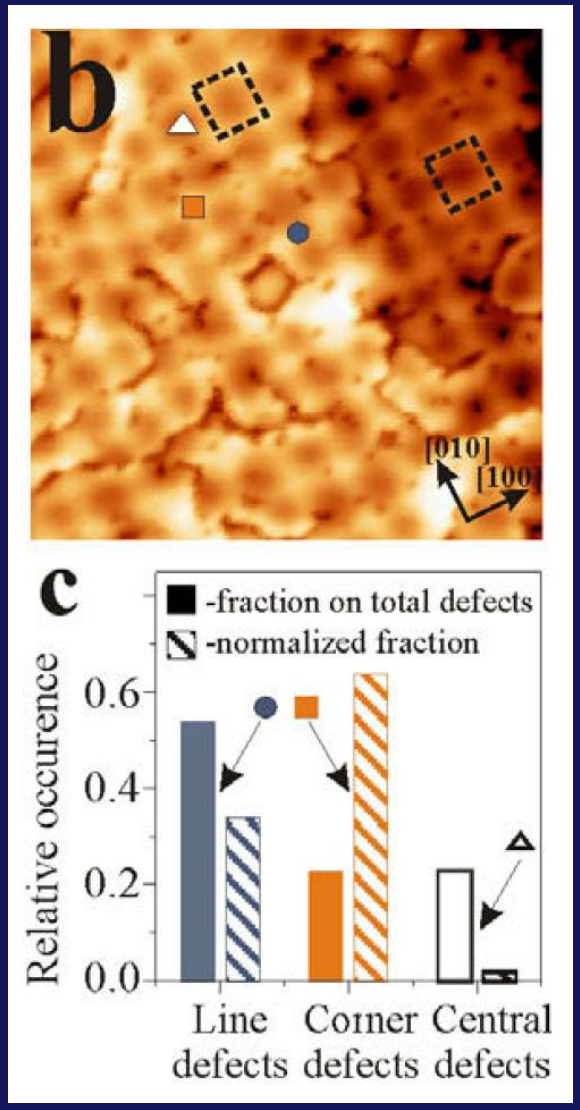
MgO(100) islands on a metal (100) substrate

Effect of the substrate induced constrain on the preferential position of point defects



$(MgO)_2$ vacancy

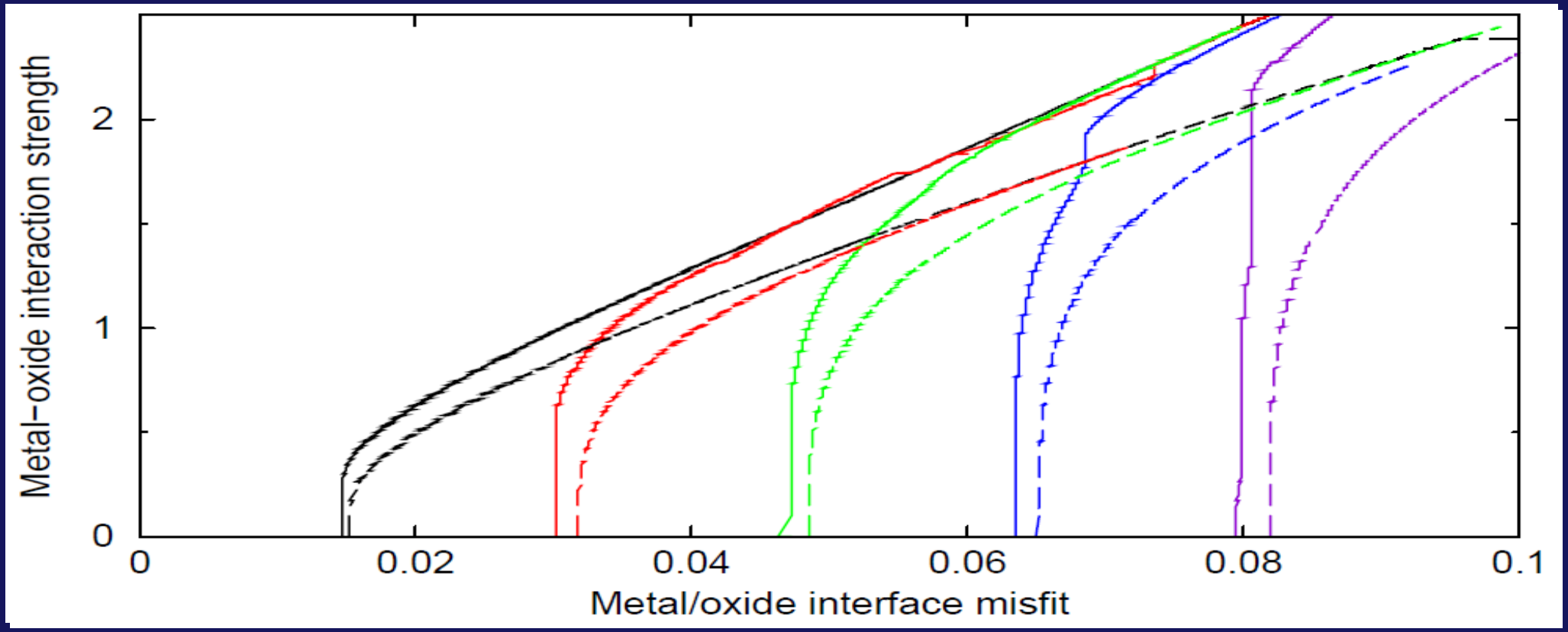
adsorbed $(MgO)_2$



Benia et al. 2010

Exploring phase diagram (misfit, interaction strength): 1D chains

Numerical solution for a linear $(MgO)_{60}$ chain

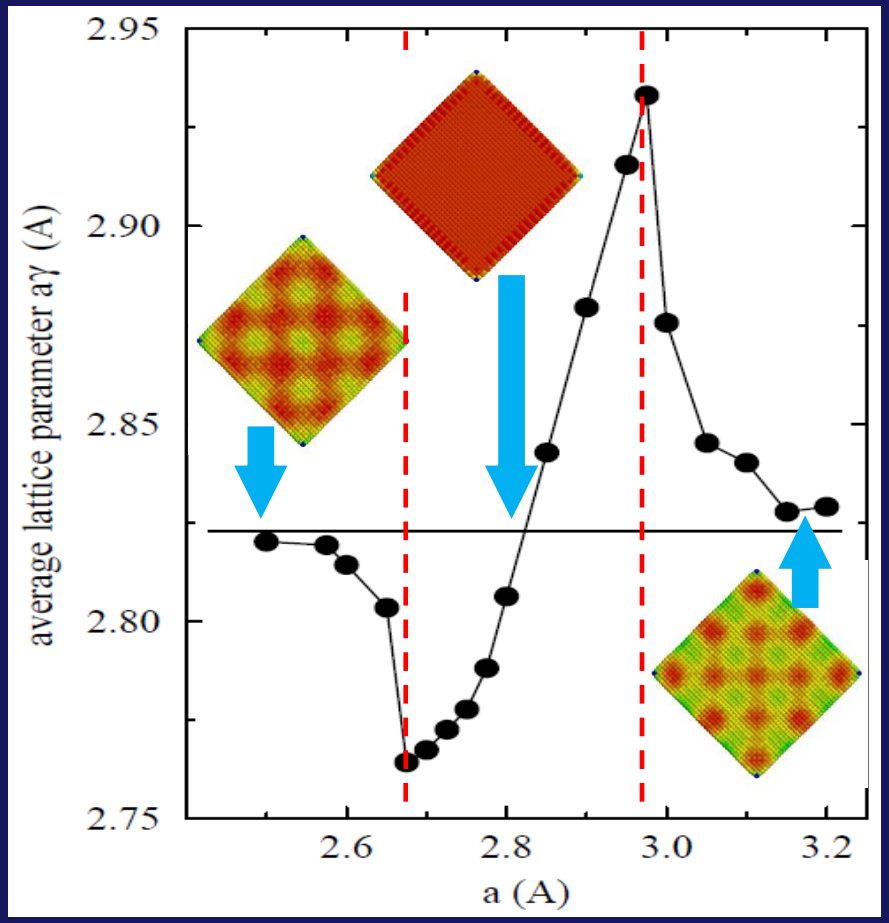


- di-atomic periodic unit,
- vertical relaxation of all atoms,
- “realistic” border effects.

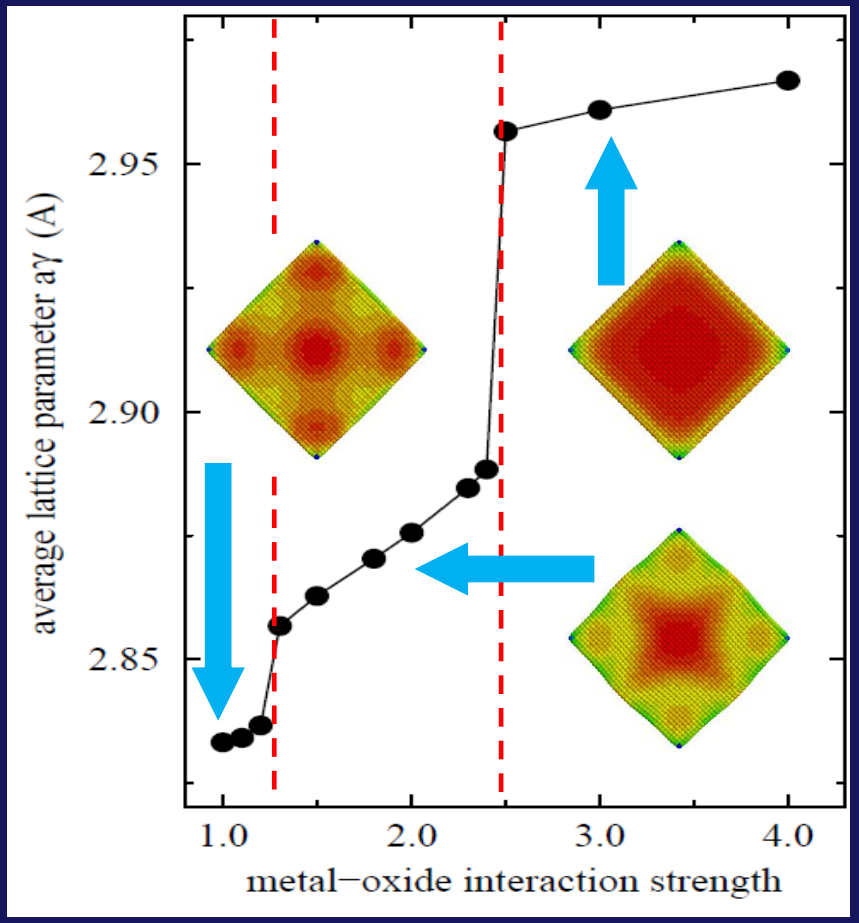
R. Niedermayer Thin Films 1 (1968) 25

Exploring phase diagram (misfit, interaction strength): 2D islands

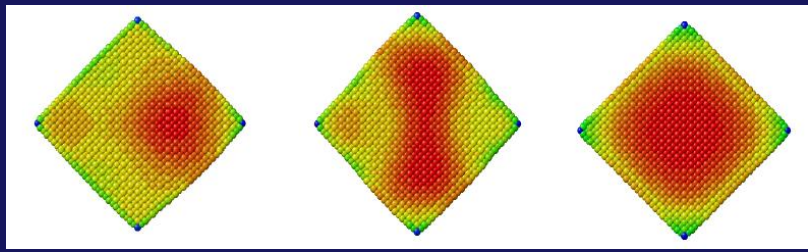
Oxide/substrate misfit



Oxide-substrate interaction strength



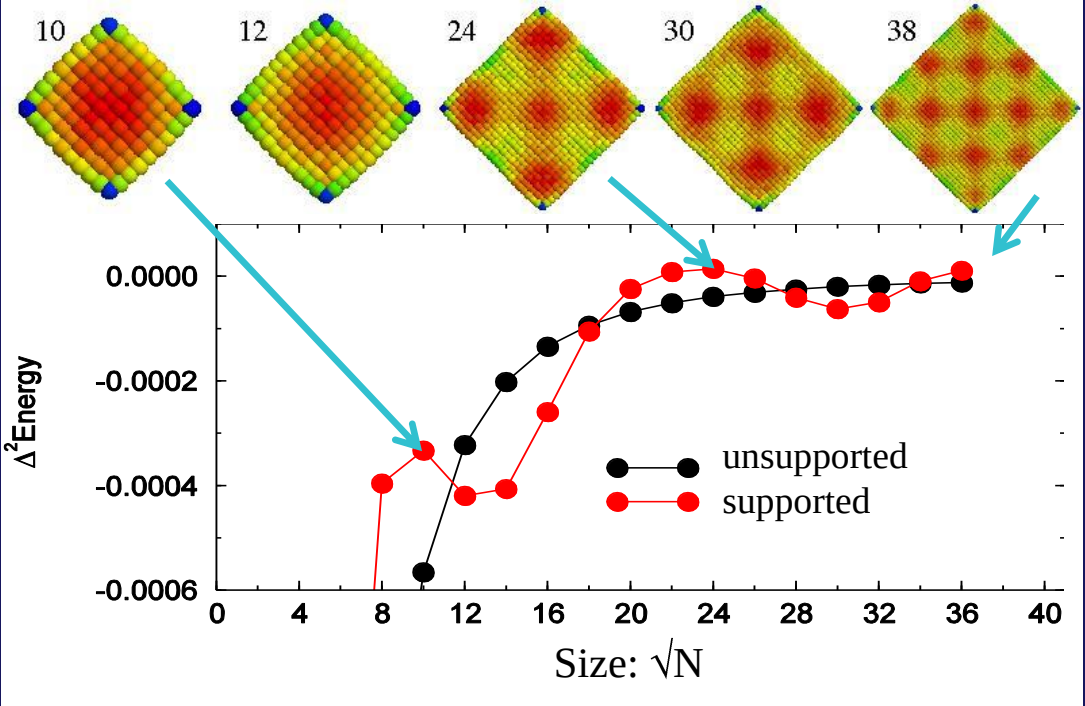
BUT: Spontaneous tetragonal distortion at small size (N=900)



MgO(100) islands on a metal (100) substrate

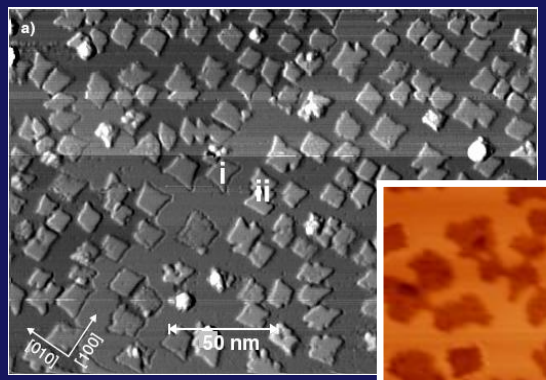
Stability as a function of size: magic islands

$$\Delta^2 E(N) = E(N+1) + E(N-1) - 2E(N) > 0$$



$$L = \frac{1}{\sqrt{2}} \frac{\gamma a}{1-\gamma} = \frac{A}{\sqrt{2}}$$

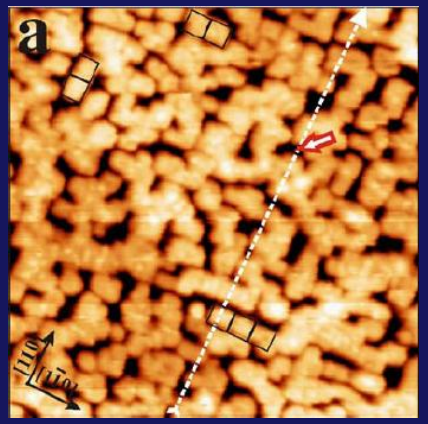
MgO/Ag(100)



Schintke et al. 2004
Average island size 70Å

Cabailh et al. 2011
Average island size: 80±10Å

Ag: a=2.832 Å
MgO: a_I=2.824 Å
Consistent with γa ~ a_I

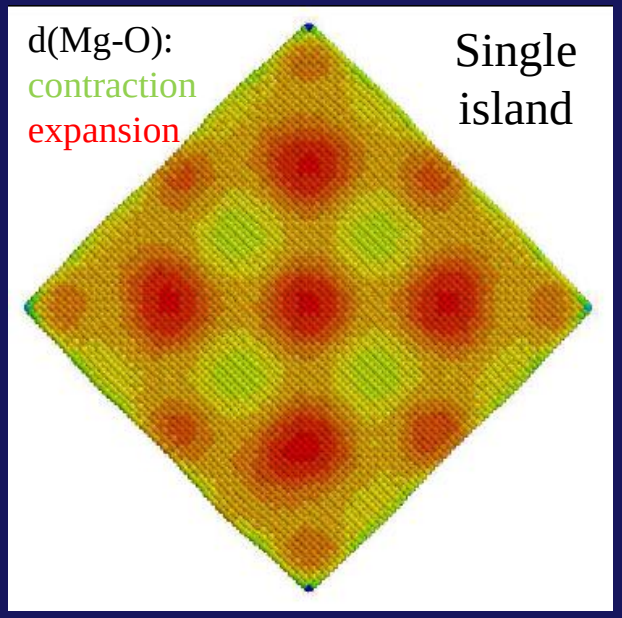


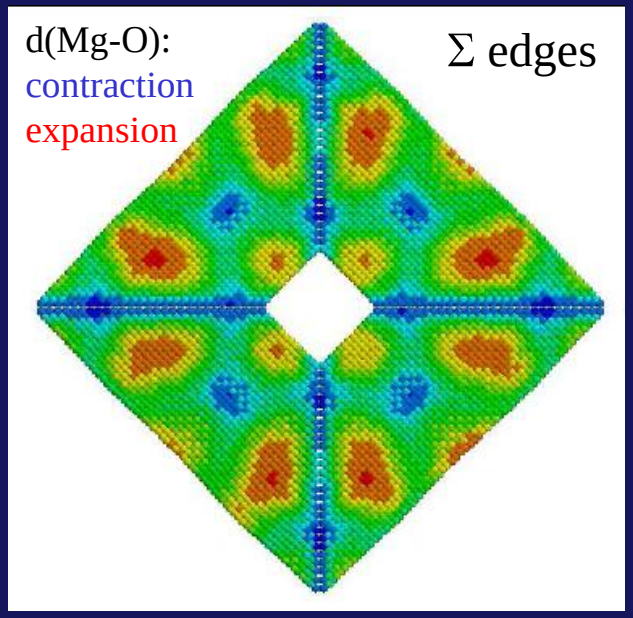
MgO/Mo(100)

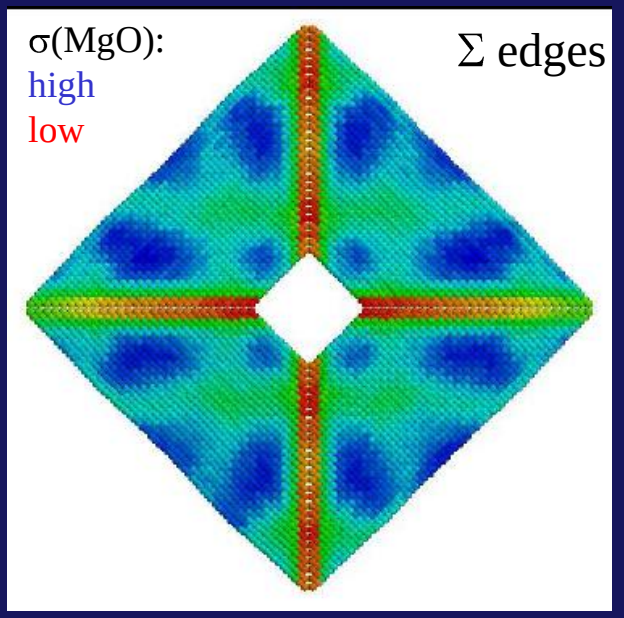
Benia et al. 2010
Average island size: 45-55 Å

Mo: a=3.147 Å
MgO: a_I=2.824 Å
Consistent with γa >a_I

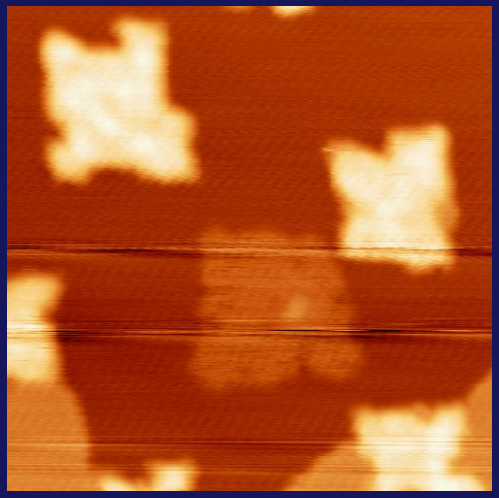
Substrate-induced patterning of island edges

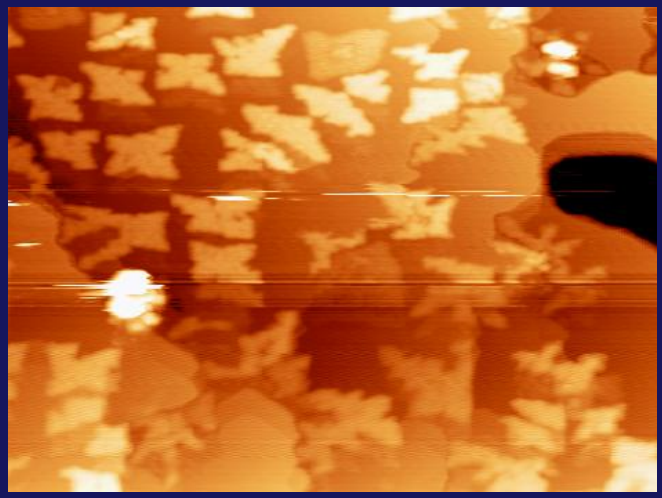






Growth shapes:
MgO/Ag(100)





Cabailh et al. 2011

Summary

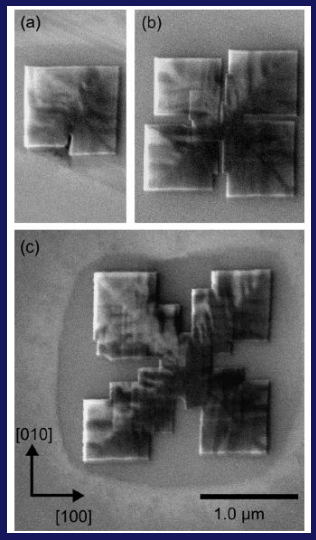
* Semi-empirical atomistic “order N” approach for large scale calculations.

* Application to (medium size) MgO(100) islands on a metal substrate:

  - Potential Energy Surface method
  - structure of the islands (Moiré, interfacial dislocations, commensurability locking, edge effects)
  - electronic structure (inhomogenity inside the islands, edge effects)
  - size effects:
    - smallest sizes, mainly driven by edge effects
    - larger sizes: oscillatory behavior related to introduction of dislocations
    - magic islands
  - phase diagram (interaction, misfit)

* Perspectives

  - beyond PES approximation
  - equilibrium/growth shapes
  - adsorption properties



Shape transition
Anatase TiO_2(001)/$SrTiO_3$(001)
Marshall and Castell 2009