Elementary mechanisms of homoepitaxial growth in MgO(001) : from the isolated adsorbates to the complete monolayer

Second ABINIT WORKSHOP, 10-12 May 2004

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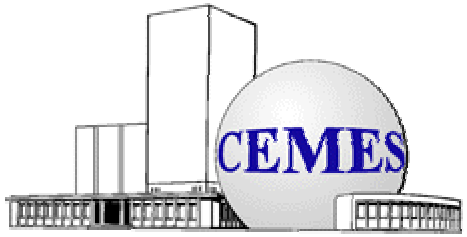


Elementary mechanisms of crystal growth

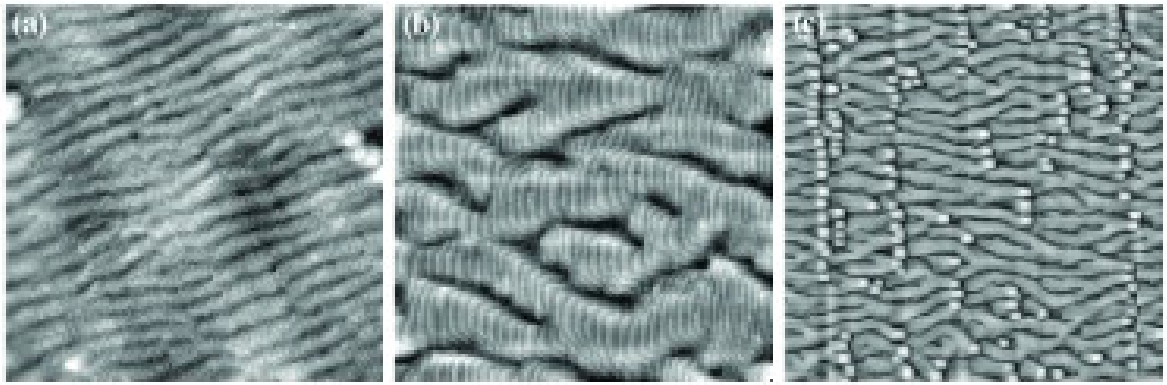
Crystal growth

Growth of metal oxides : unknown mechanisms
(compared to simple metals and semi-conductors)

Why studying the growth of oxides ?

Better control => Good quality surfaces/interfaces

Can growth instabilities in oxides lead to a spontaneous nanostructuration ?



« Step-flow » growth mode

Cu(100)
J. Neel et al,
J. Phys. Cond. Matter.
15 (2003), S3227-S3240

System and method

The system

MgO(001) : prototypical case

Method

a) DFT calculations : ABINIT
GGA-PBE
Troullier-Martins pseudopotentials
Slab geometry (4 layers) / Cut-off = 28 Hartrees
System size = 60-100 atoms

b) Classical Molecular Dynamics (« semi-empiric » potentials)
in the case of stoichiometric ionic systems

Overview

MgO growth : 3 phases

1 – Isolated species : Mg, O, O_2

2 – Surface redox reactions

3 – Nucleation phenomena

Isolated species : ***Mg atom***, O atom, O_2 molecule

Atomic Mg

Adsorption (physisorption)

Diffusion

Small clusters

Dissociation

Steps

Desorption

[010]

[100]

Mg neutral

E_{ads} = 0.45 eV

Diffusion : 0.3 eV

Mg

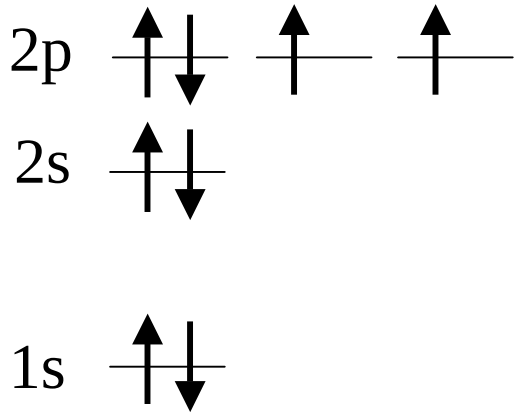
Mg

... either they bind to a step edge

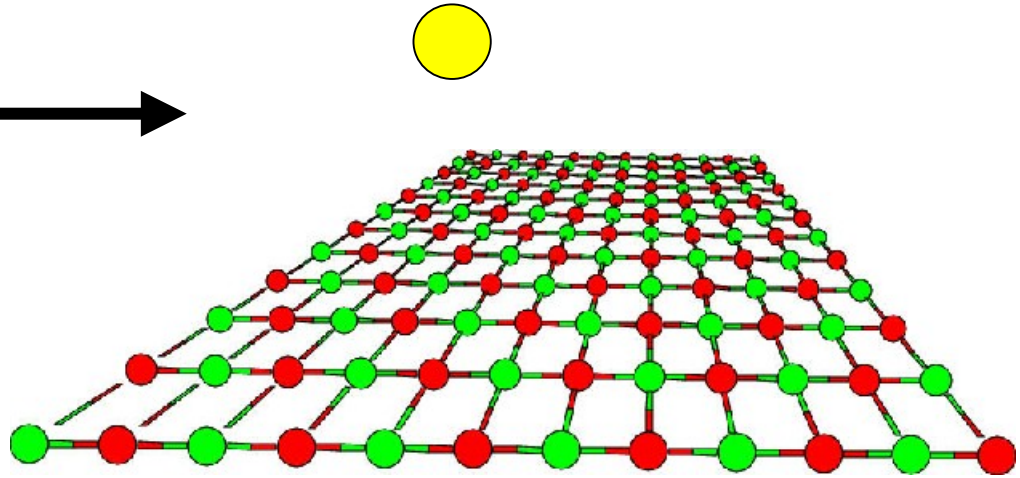
Attraction / $E_{binding}$ = 1 eV

Isolated species : Mg atom, ***O atom***, O_2 molecule

The free oxygen atom :



Adsorption on MgO(001):



Ground state : S = 1

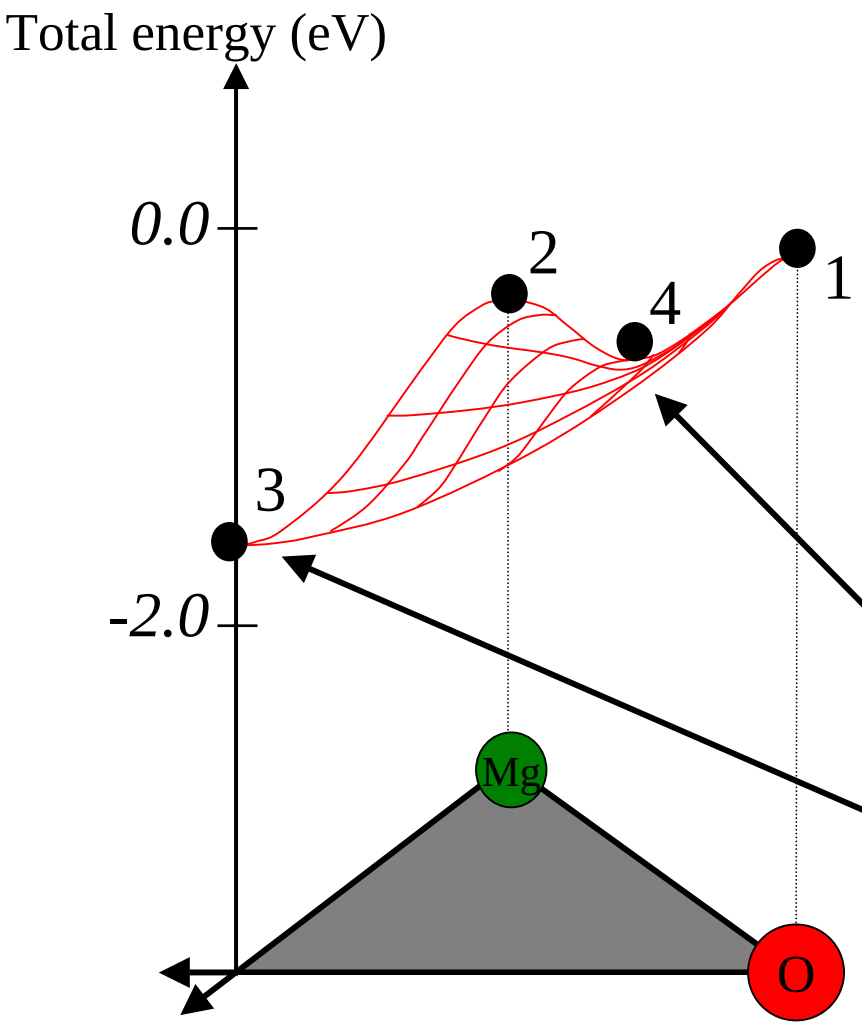
Ground state : S = ?

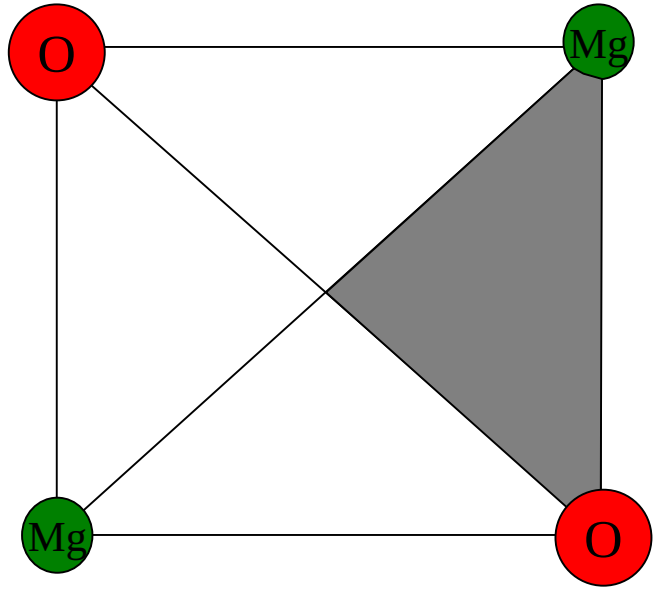
→ *Depends on the adsorption site on the surface !*

→ *We computed TWO Born-Oppenheimer surfaces.*

Isolated species : Mg atom, ***O atom***, O_2 molecule

The Spin-polarized B.O. surface :





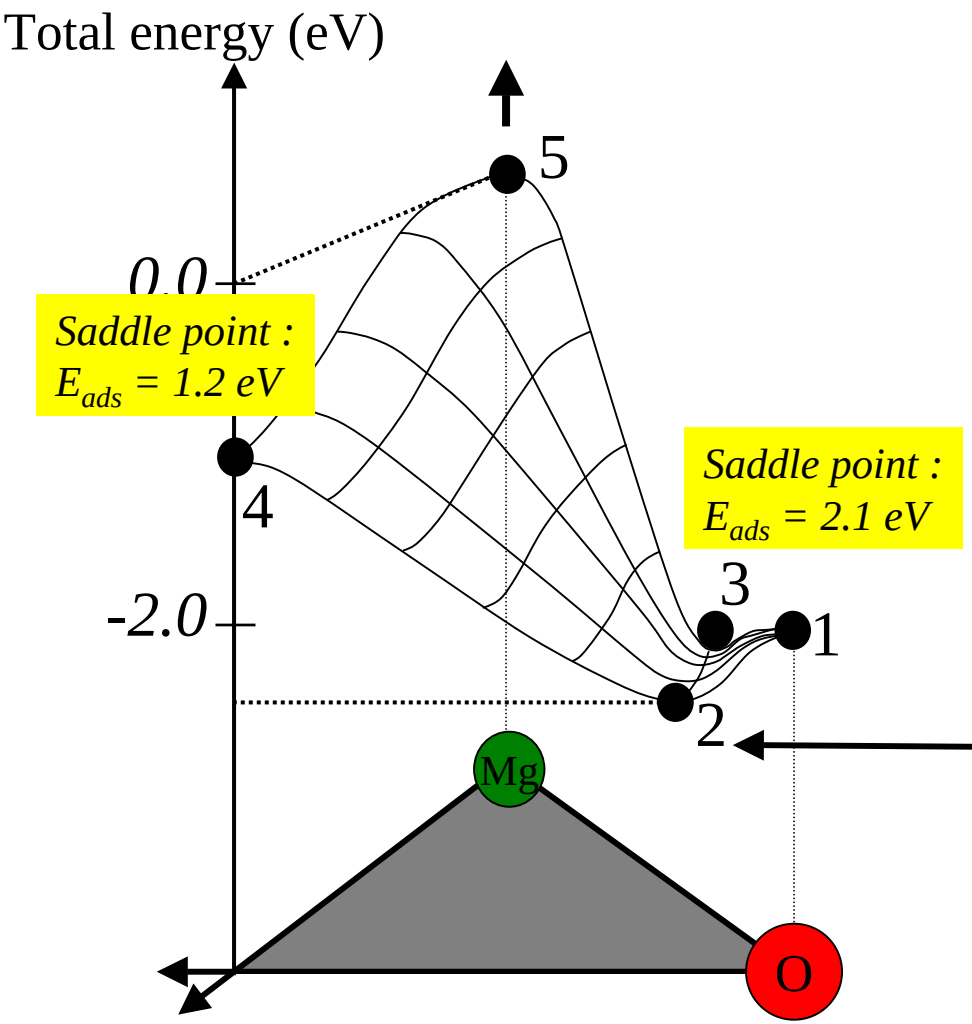
Surface unit cell : irreducible part

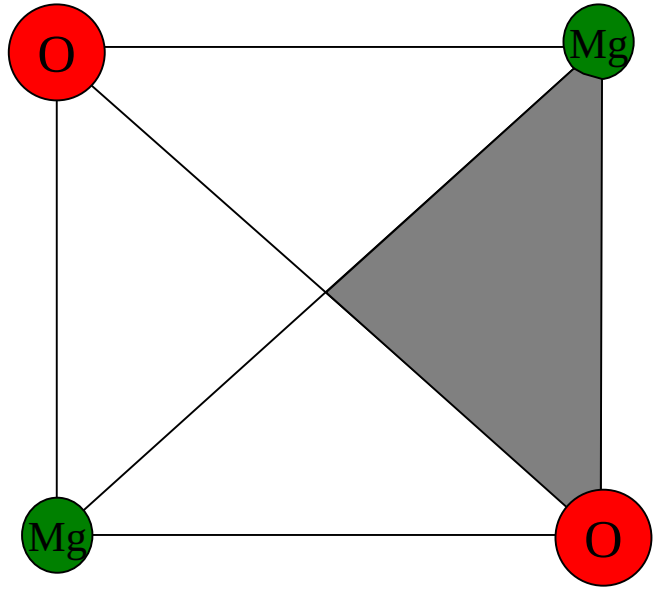
Saddle point : E_{ads} = 1.1 eV

Minimum : E_{ads} = 1.5 eV

Isolated species : Mg atom, ***O atom***, O_2 molecule

The non spin-polarized B.O. surface :





Surface unit cell : irreducible part

Minimum : E_{ads} = 2.3 eV

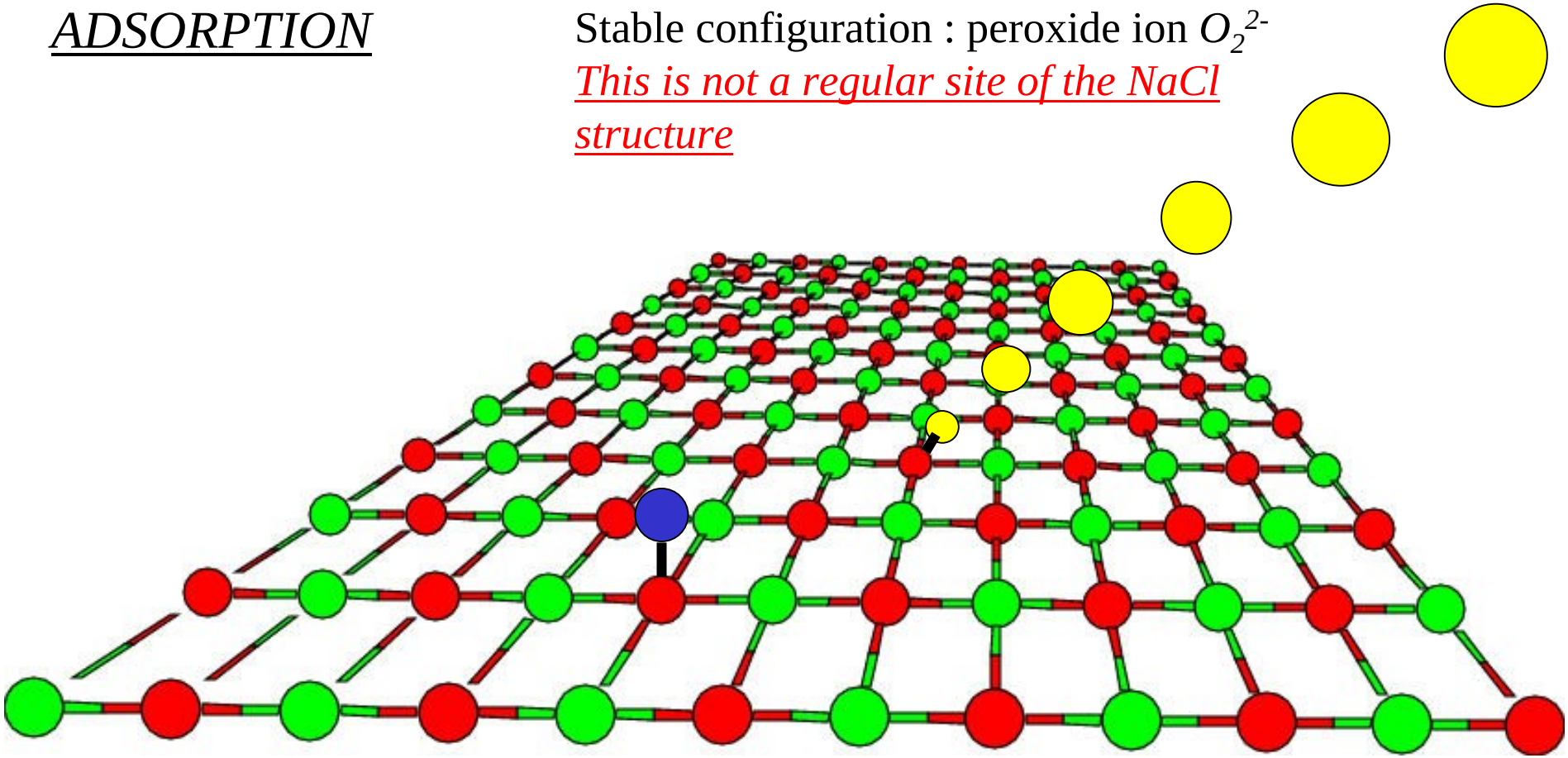
The most stable configuration
Is not spin-polarized.
What is it ?

Isolated species : Mg atom, ***O atom***, O_2 molecule

ADSORPTION

Stable configuration : peroxide ion O_2^{2-}

This is not a regular site of the NaCl structure



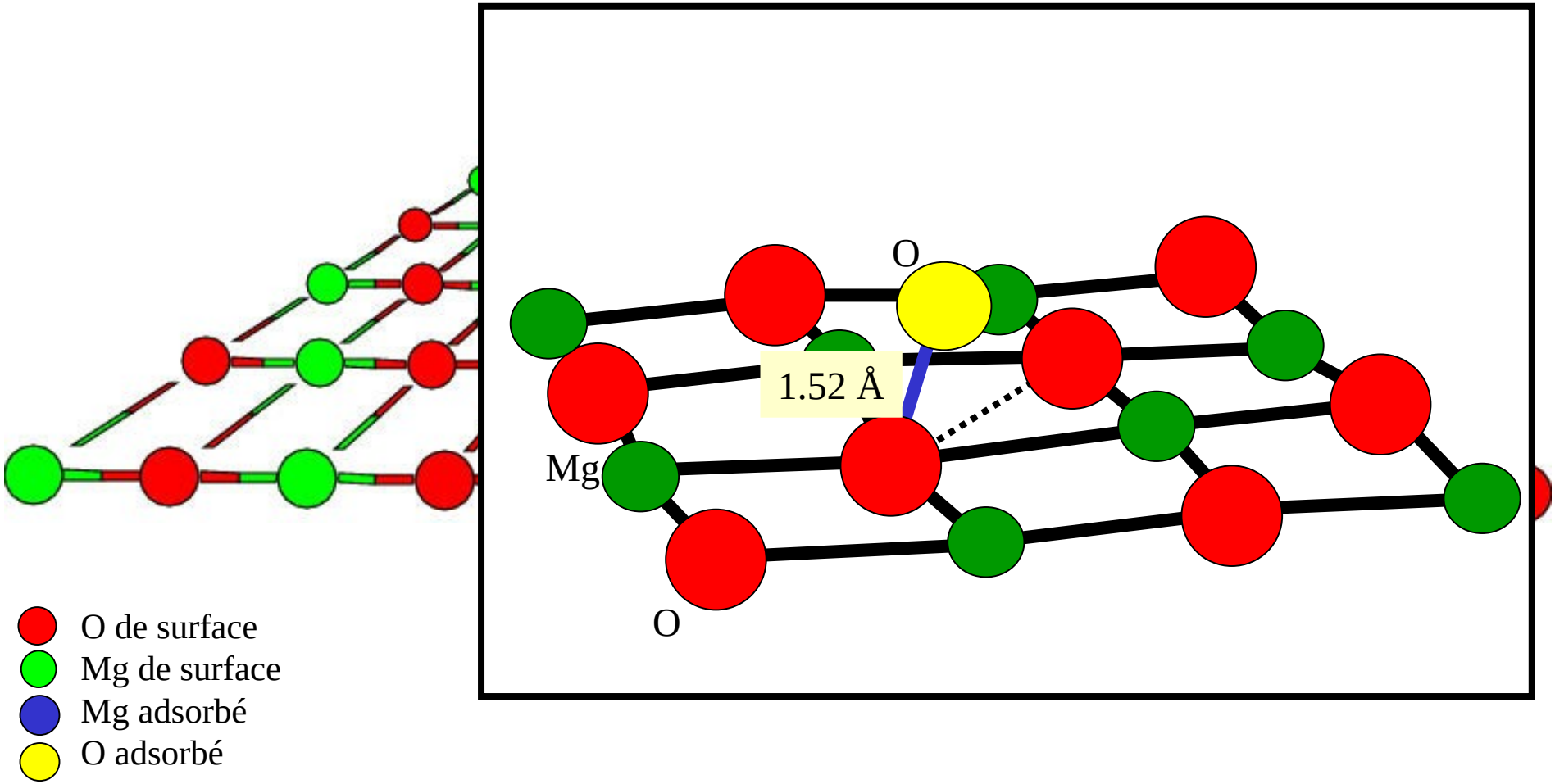
- O de surface
- Mg de surface
- Mg adsorbé
- O adsorbé

Isolated species : Mg atom, ***O atom***, O_2 molecule

ADSORPTION

Stable configuration : peroxide ion O_2^{2-}

This is not a regular site of the NaCl structure



Isolated species : Mg atom, ***O atom***, O_2 molecule

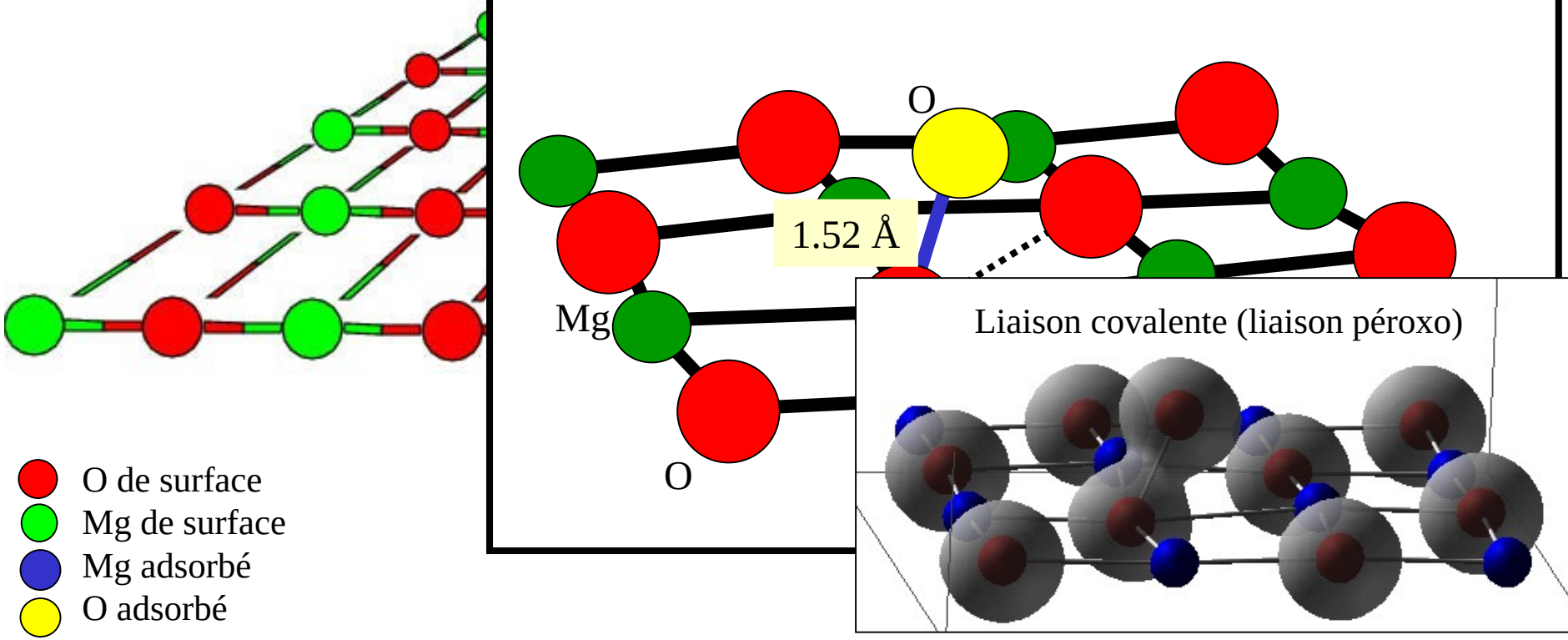
ADSORPTION

Stable configuration : peroxide ion O_2^{2-}

This is not a regular site of the NaCl structure

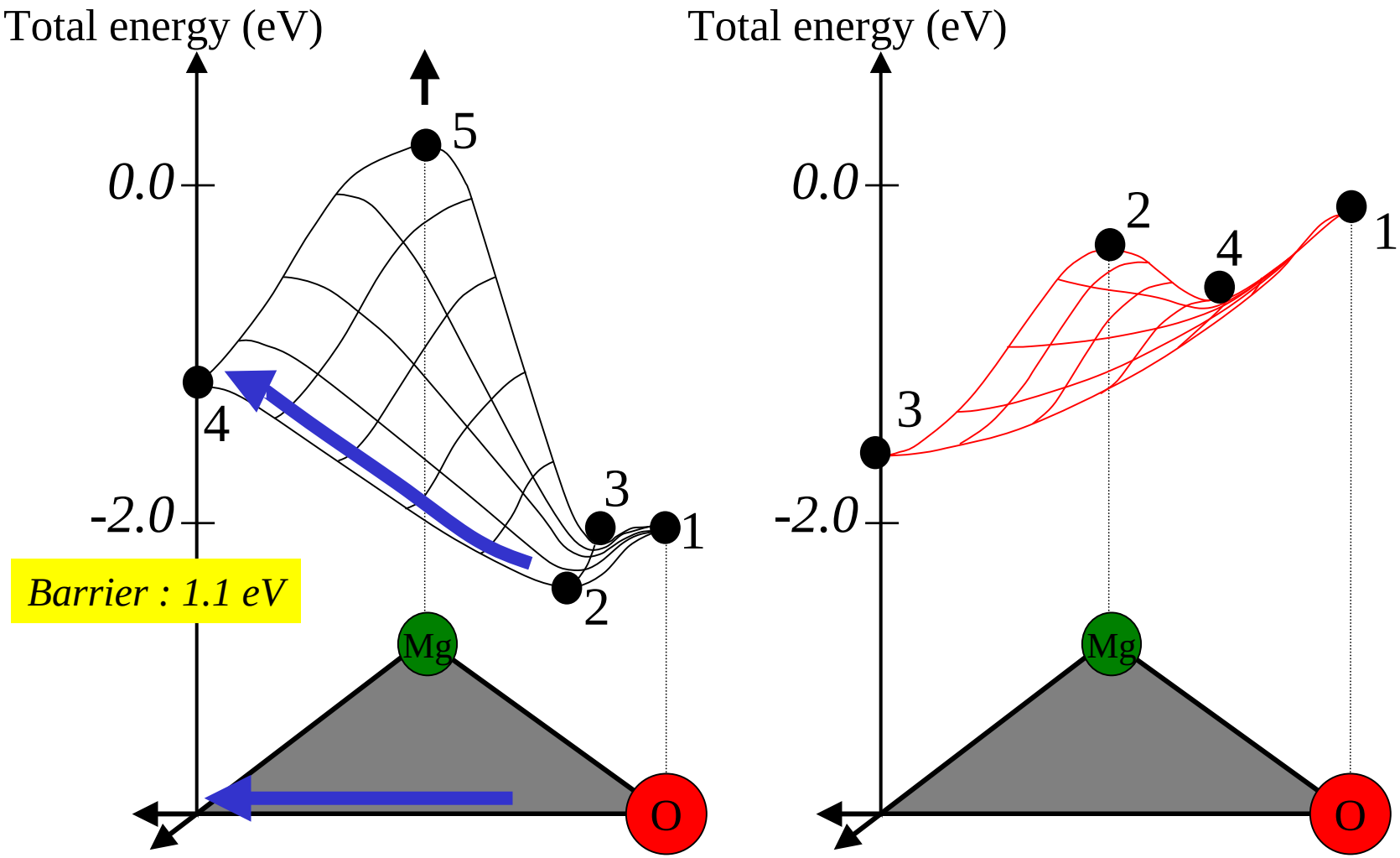
Strong interaction with charge transfer

E_{ads} ~ 2.3 eV



Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION ? *3 saddle points => 3 possible movements*

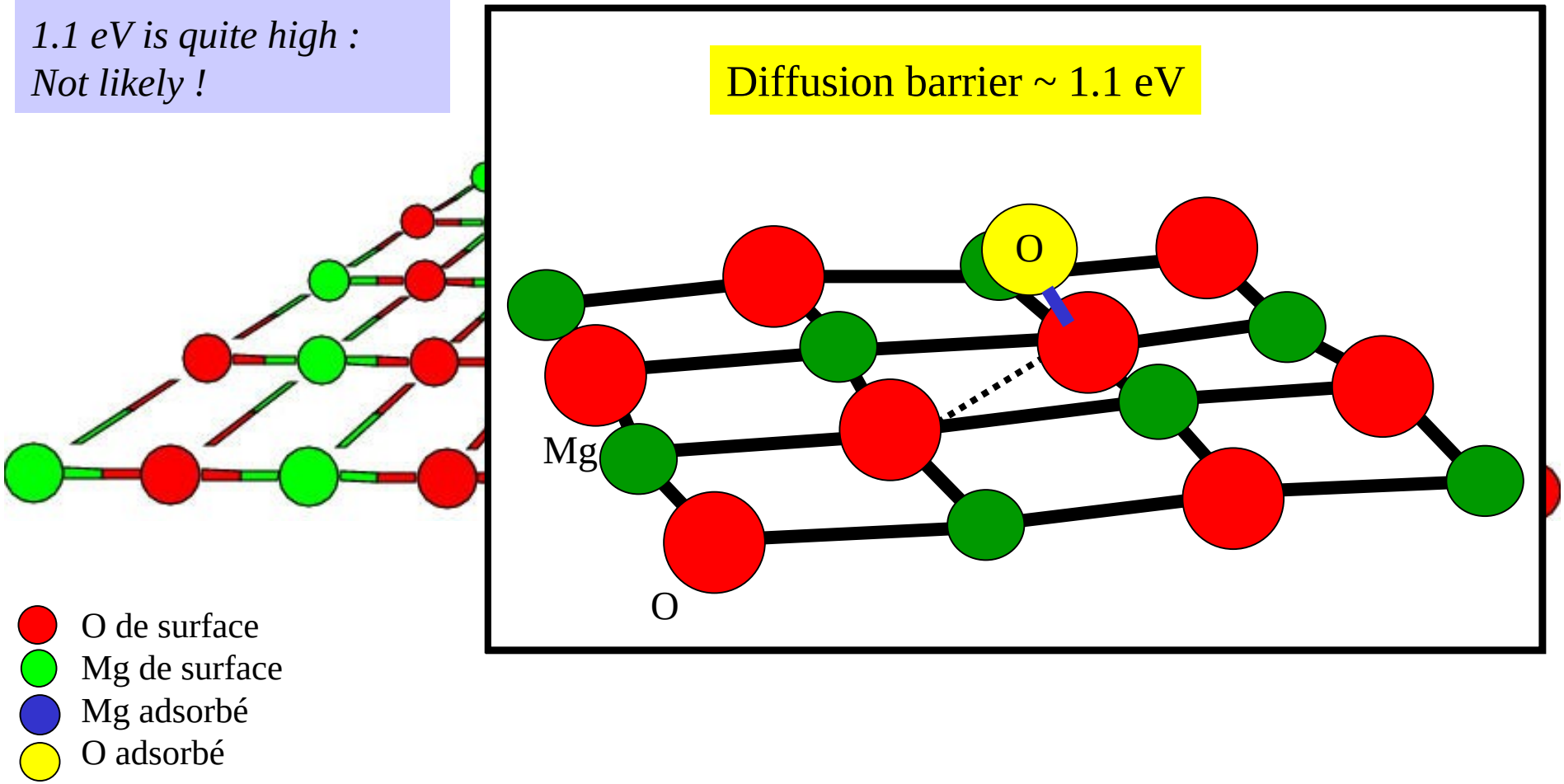


Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION

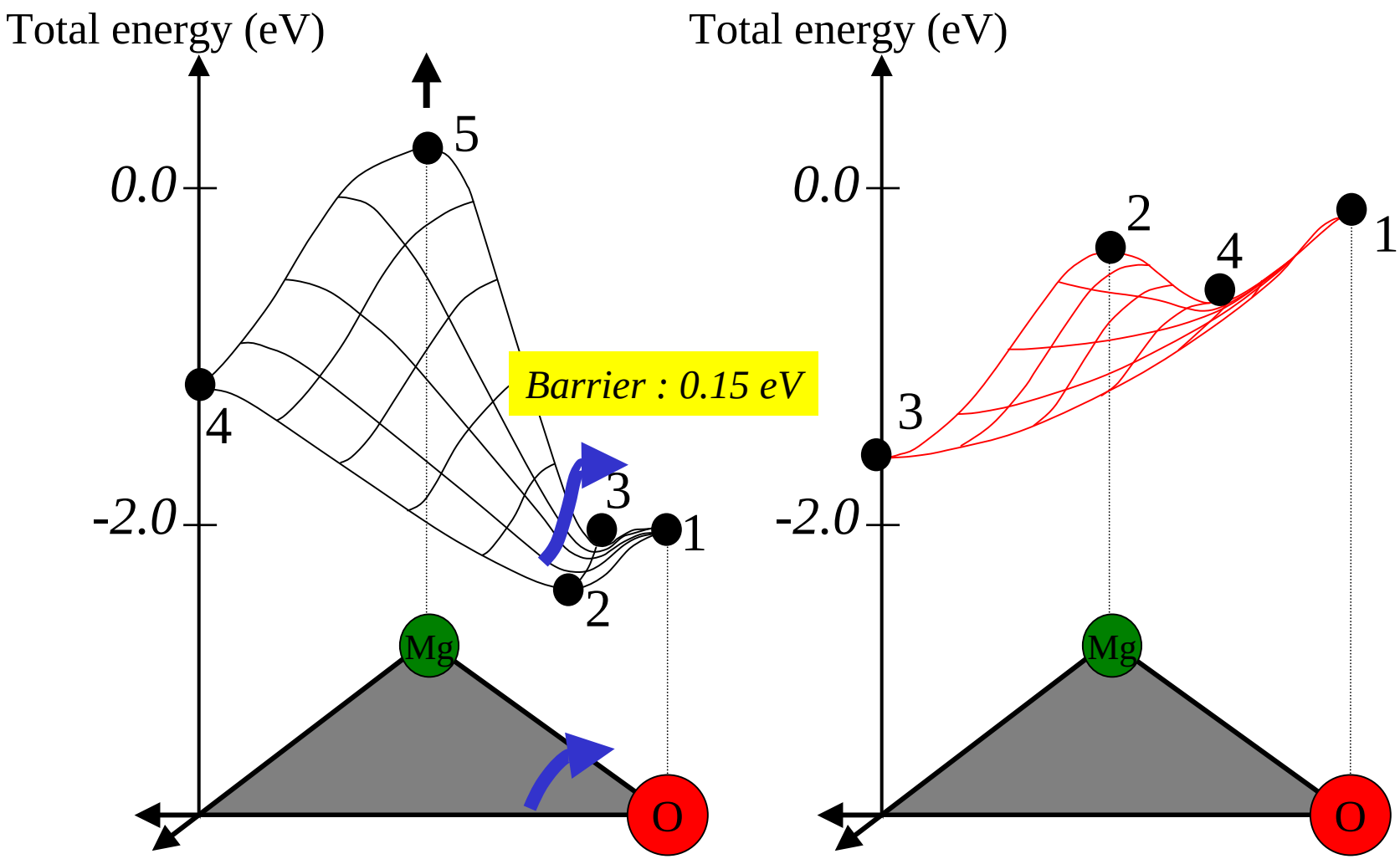
This movement implies to ***break the peroxo*** *bond.*

1.1 eV is quite high :
Not likely !



Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION ? *3 saddle points => 3 possible movements*



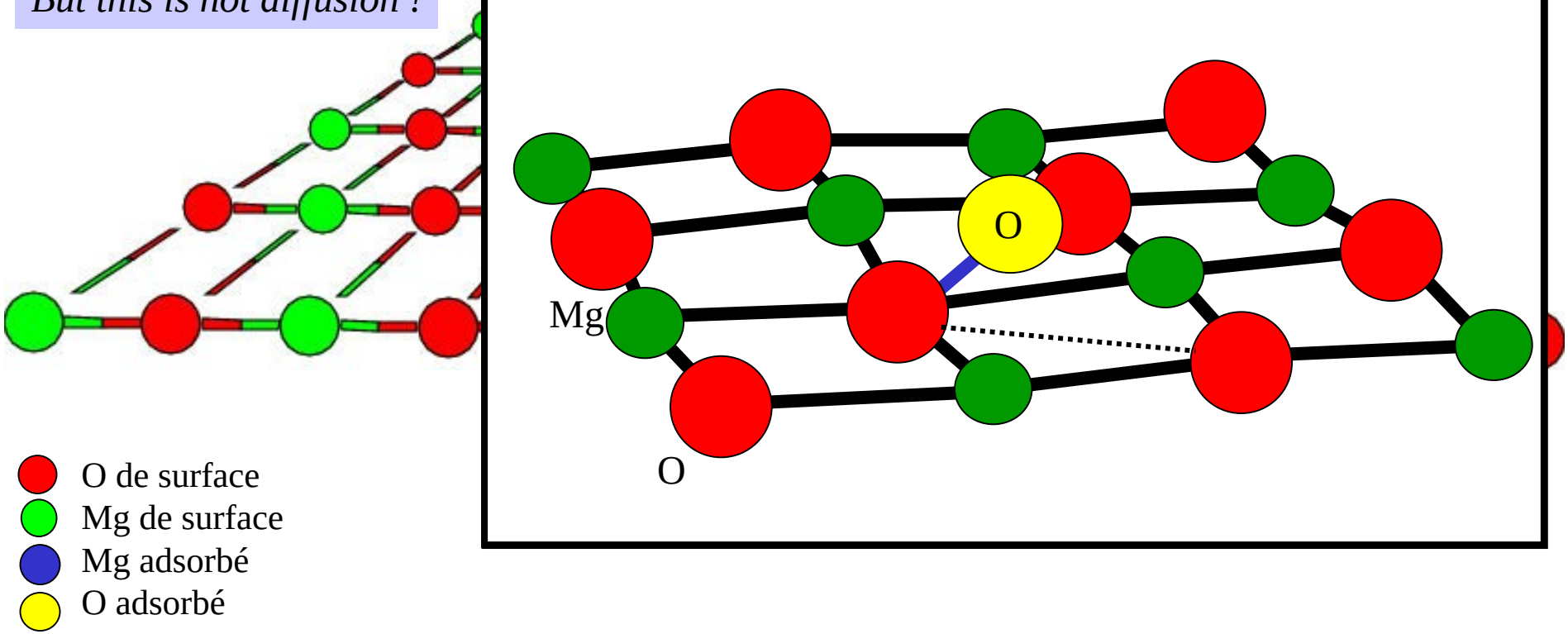
Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION

Rotation of the peroxide ion around its surface oxygen atom
Barrier ~ 0.15 eV

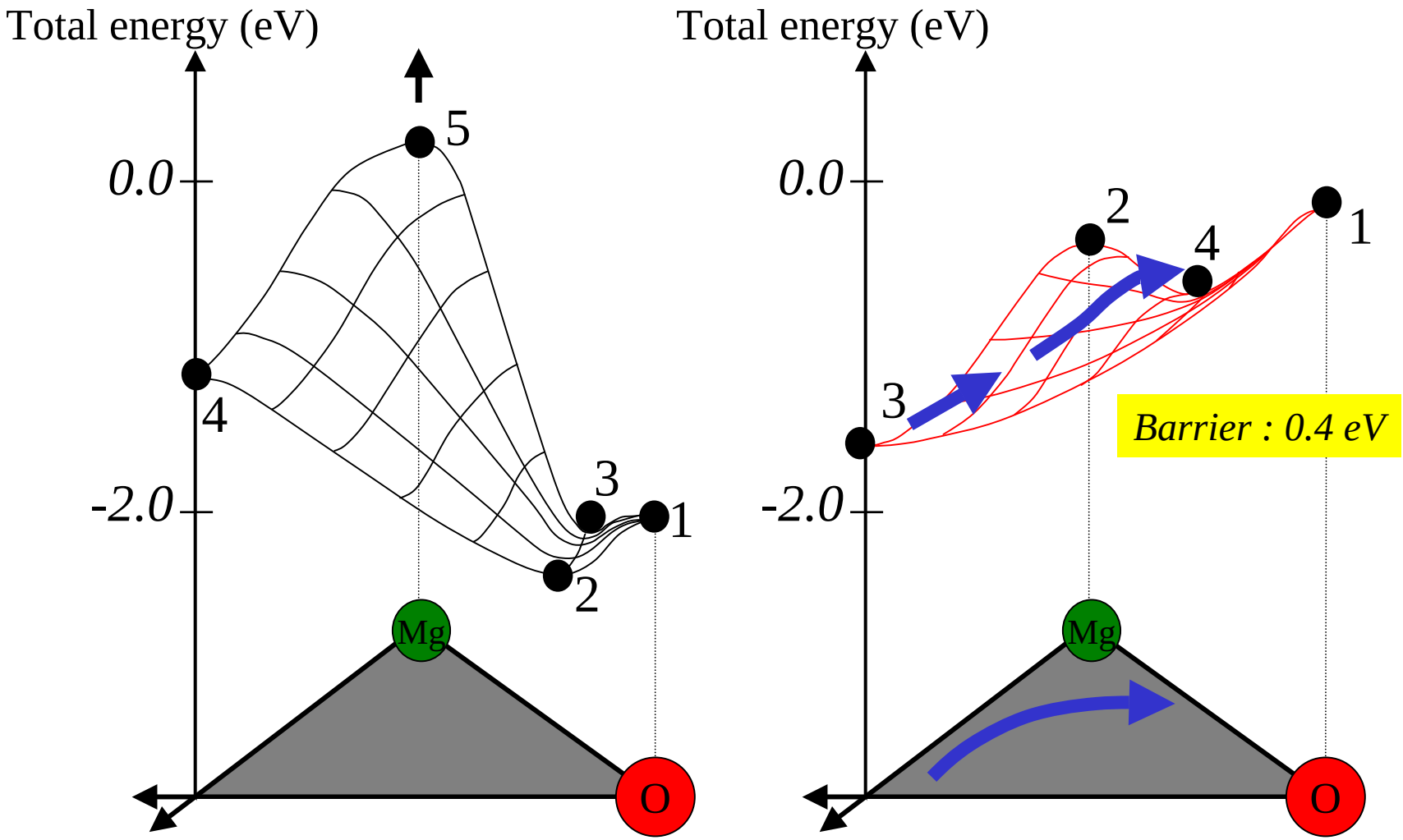
*No need to **break the peroxo** bond.*

Very likely !
But this is not diffusion !



Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION ? *3 saddle points => 3 possible movements*



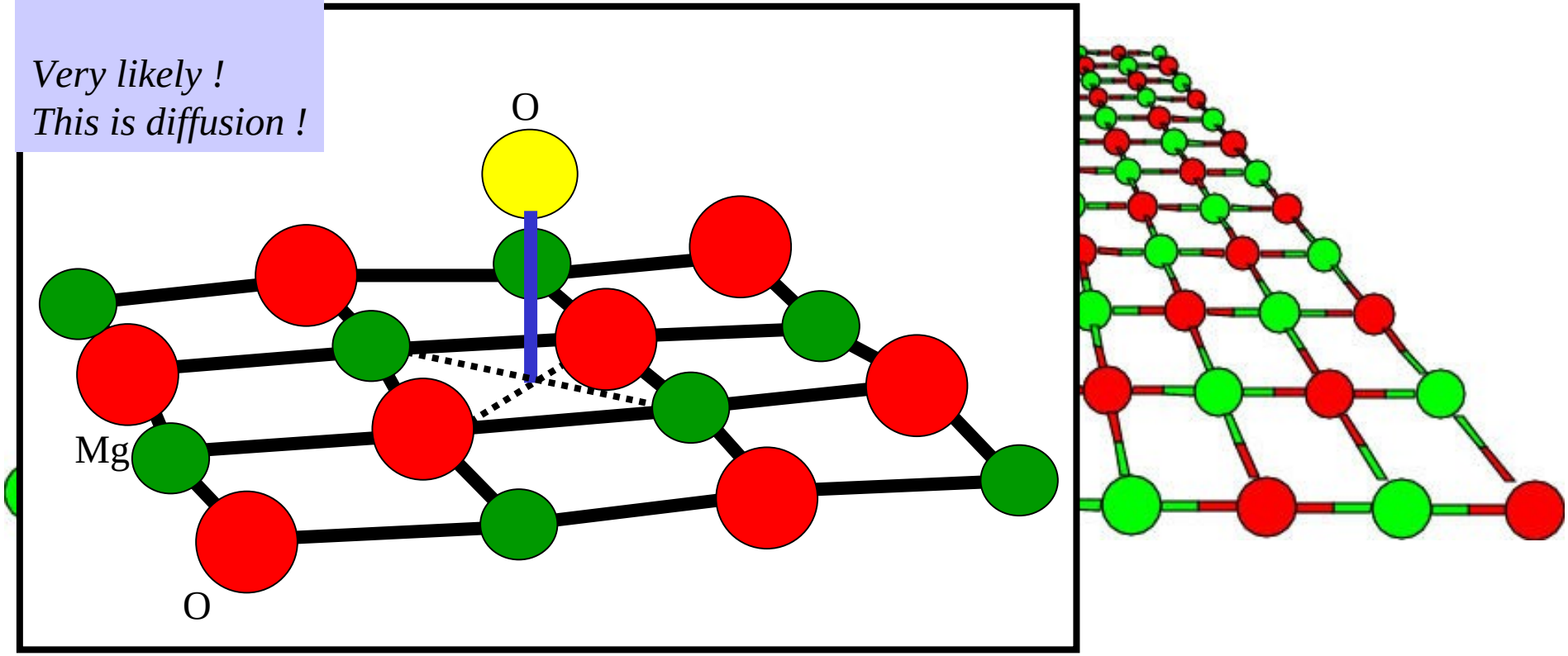
Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION

configuration / spin-polarized

Barrier : 0.4 eV

Very likely !
This is diffusion !

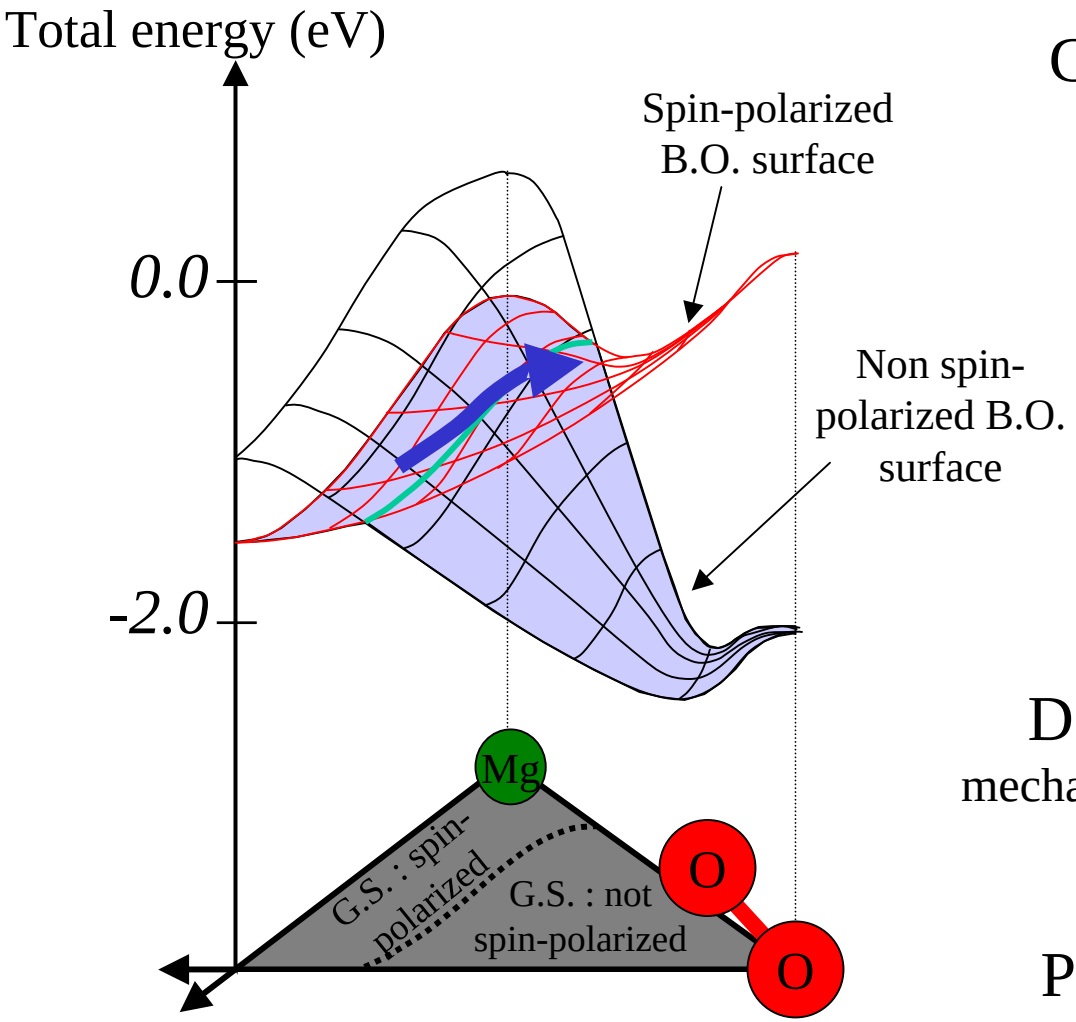


Isolated species : Mg atom, ***O atom***, O_2 molecule

DIFFUSION

Spin-polarized oxygen diffuses

Non spin-polarized oxygen is fixed (peroxide ion O_2^{2-})



Gazeous phase : O(S=1)

↓

Adsorption

(spin-polarized surface)

↓

Diffusion

(Barrier = 0.4 eV)

↙

Desexcitation

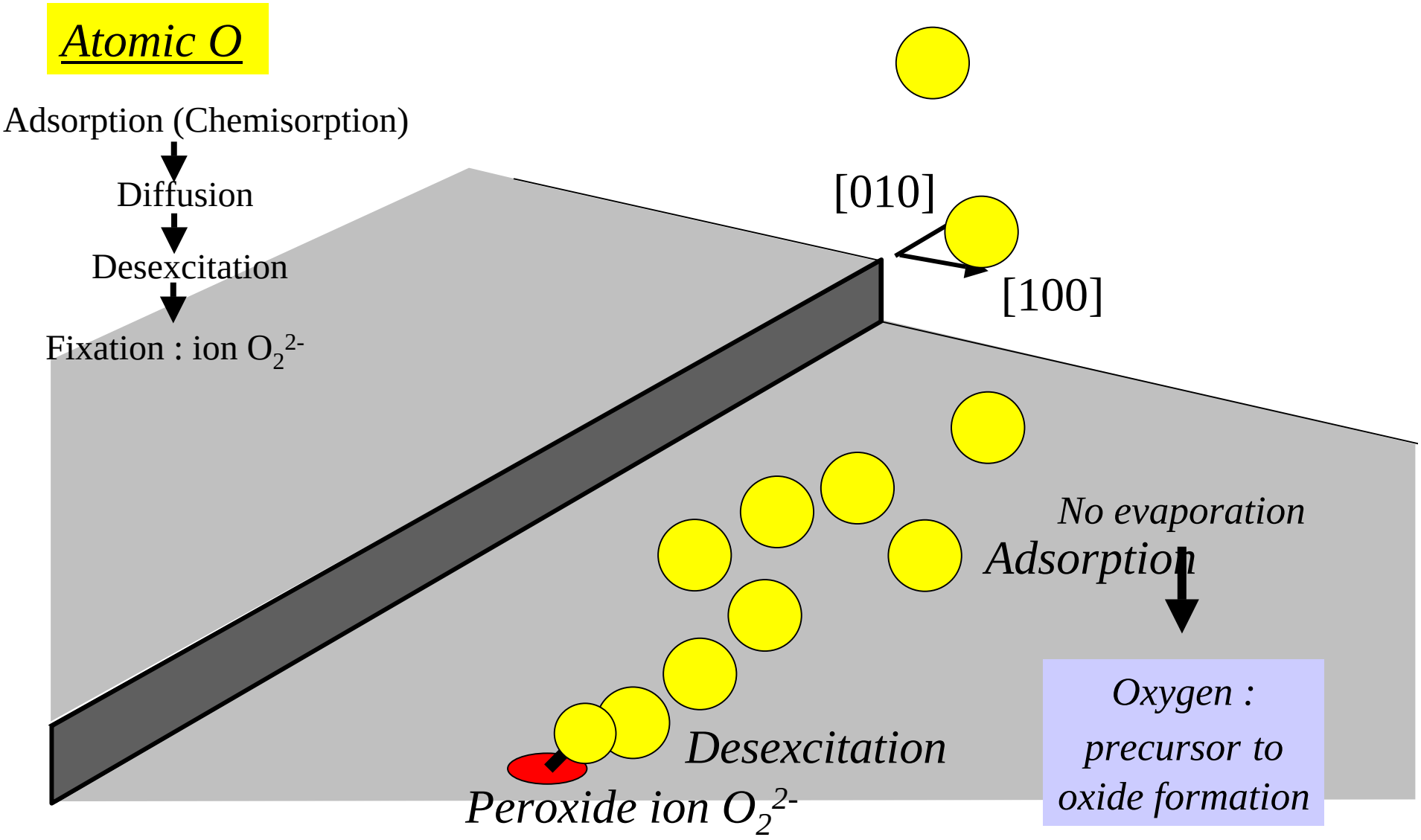
mechanism? probability?

↓

Peroxide ion

No more diffusion !

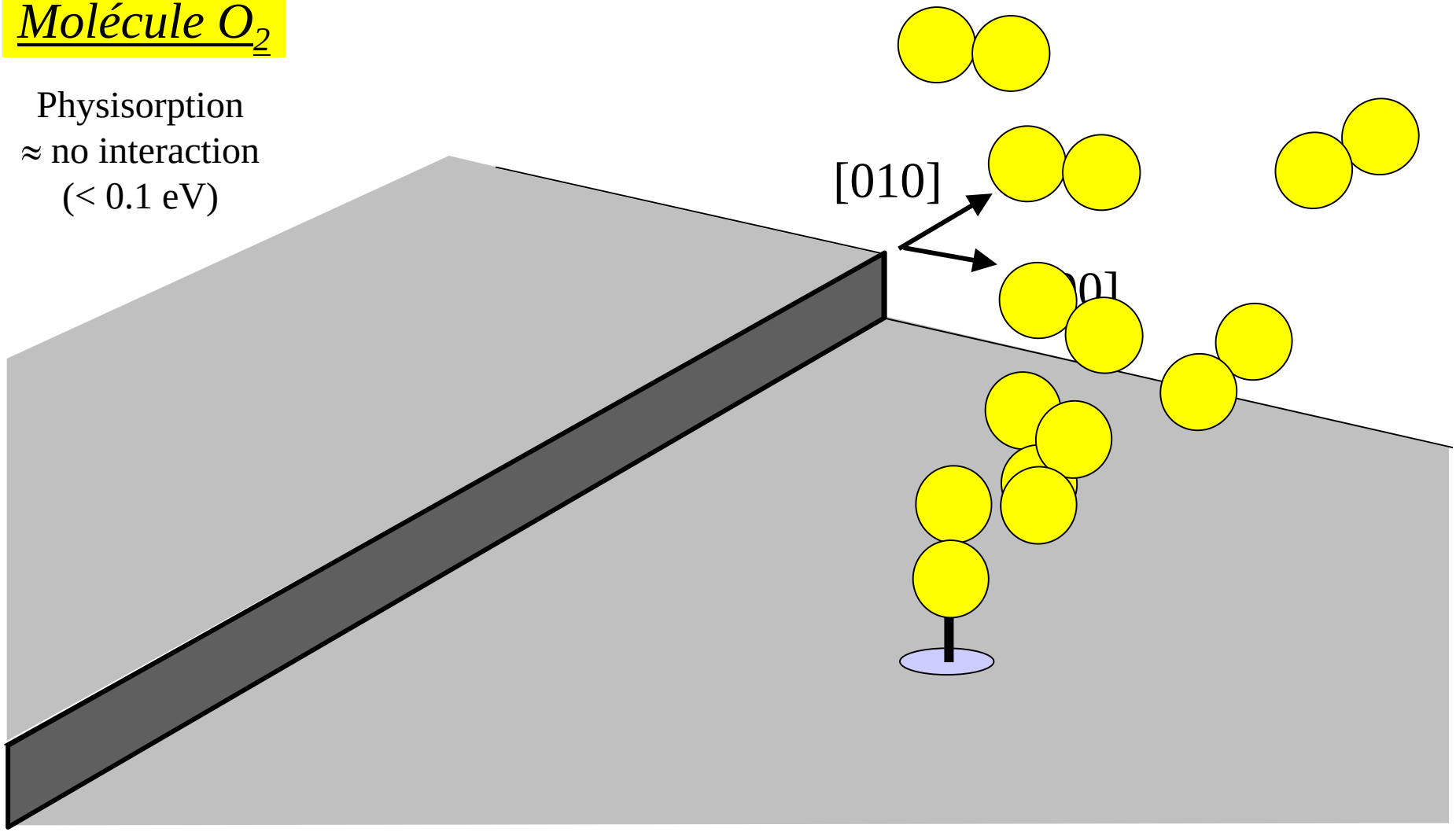
Isolated species : Mg atom, ***O atom***, O_2 molecule



Isolated species : Mg atom, O atom, ***O_2 molecule***

Molécule O_2

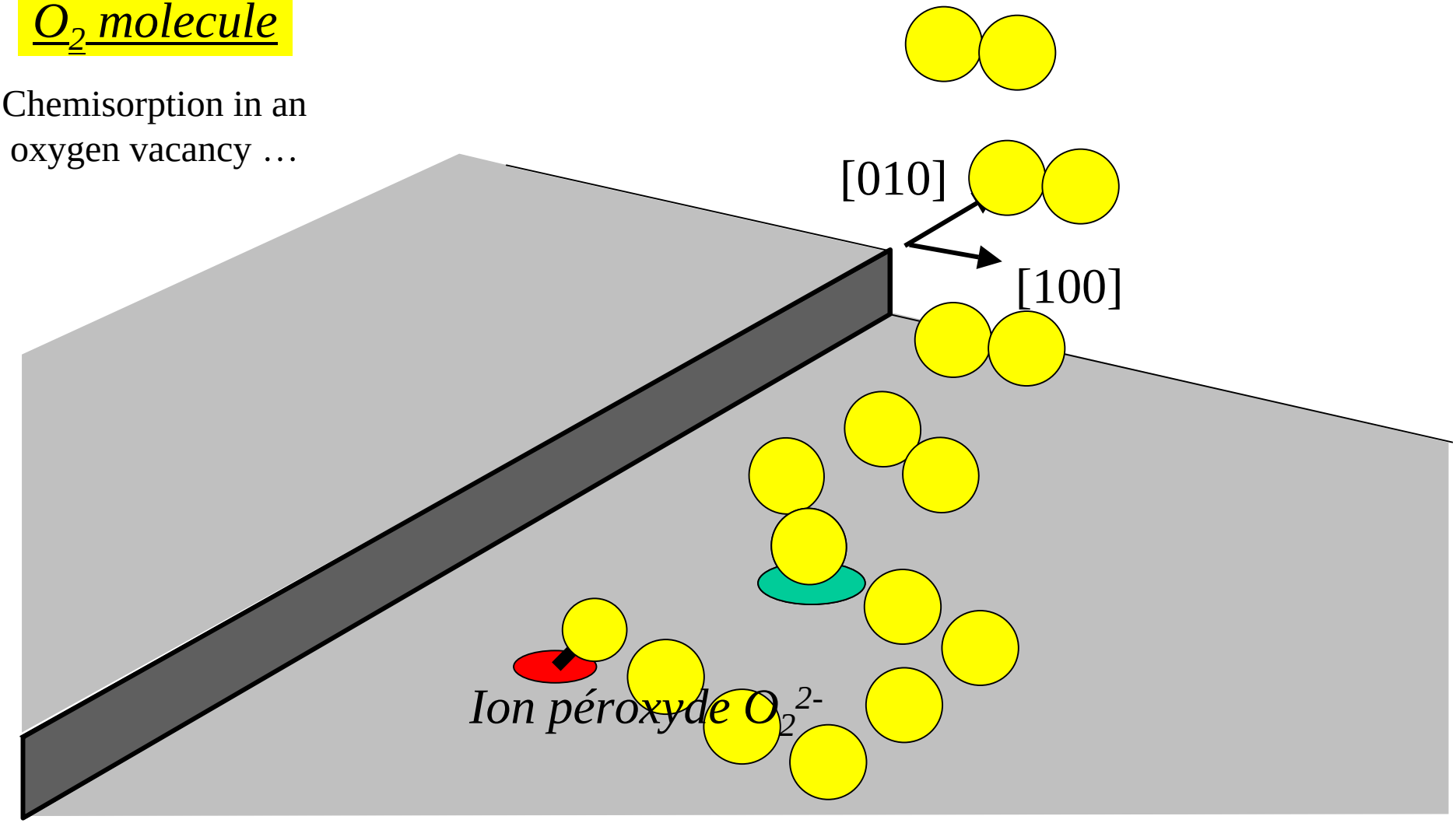
Physisorption
≈ no interaction
(< 0.1 eV)



Isolated species : Mg atom, O atom, ***O_2 molecule***

O_2 molecule

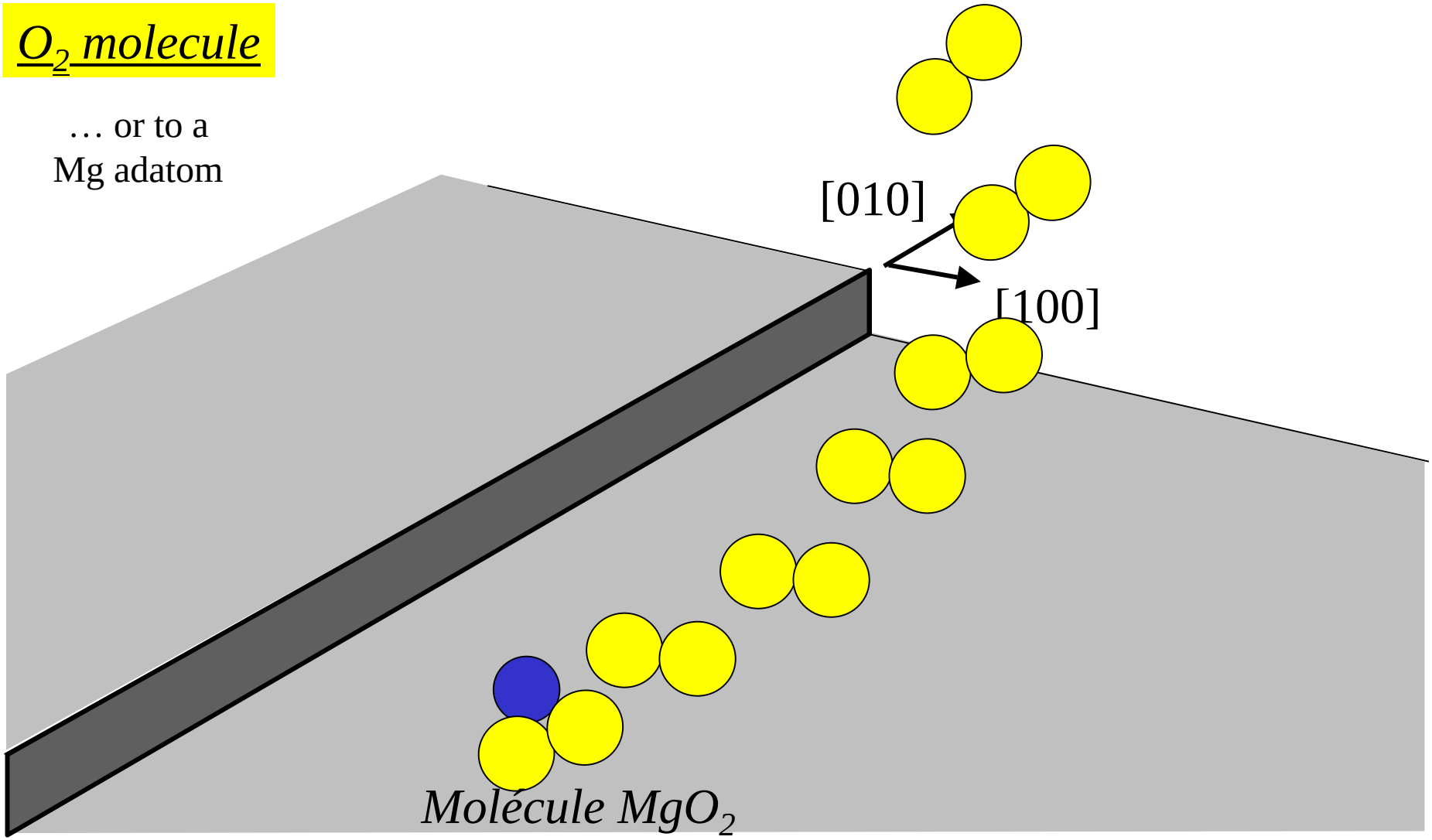
Chemisorption in an oxygen vacancy …



Isolated species : Mg atom, O atom, ***O_2 molecule***

$\underline{O_2}$ molecule

… or to a
Mg adatom



Isolated species : Mg atom, O atom, O_2 molecule

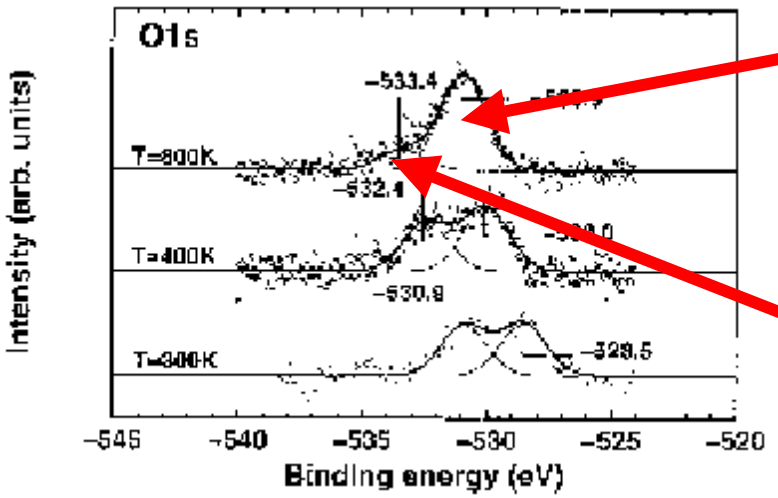
CONCLUSION

Gazeous oxygen (O, O_2)
+
MgO(001) surface, perfect
or with defects

→ Peroxide ions O_2^{2-}

O_2^{2-} & O^{2-} : different oxidation degrees → XPS measurements ?

Expérimental results : pic O 1s

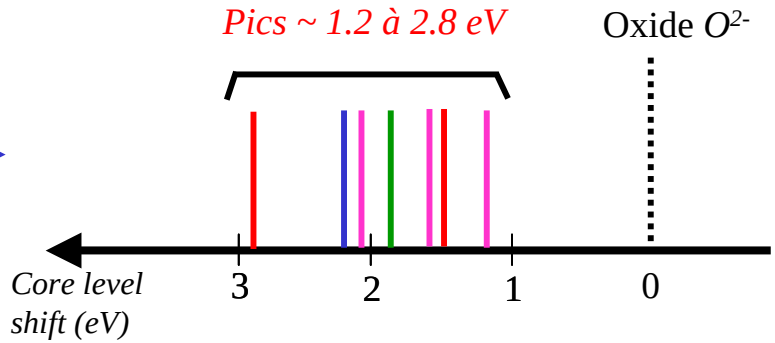


D. Peterka et al., Surf. Sci. ***431*** *(1999), 146*

Oxide O^{2-}

Less reduced oxygen
ΔE ~ 2 à 3 eV
$\Rightarrow O_2^{2-}$

DFT simulation of XPS spectra :



$\Rightarrow$ the ***peroxide ions*** may be responsible for the observed shift

Overview

MgO growth : 3 phases

1 – Isolated species : Mg, O, O_2

2 – Surface redox reactions

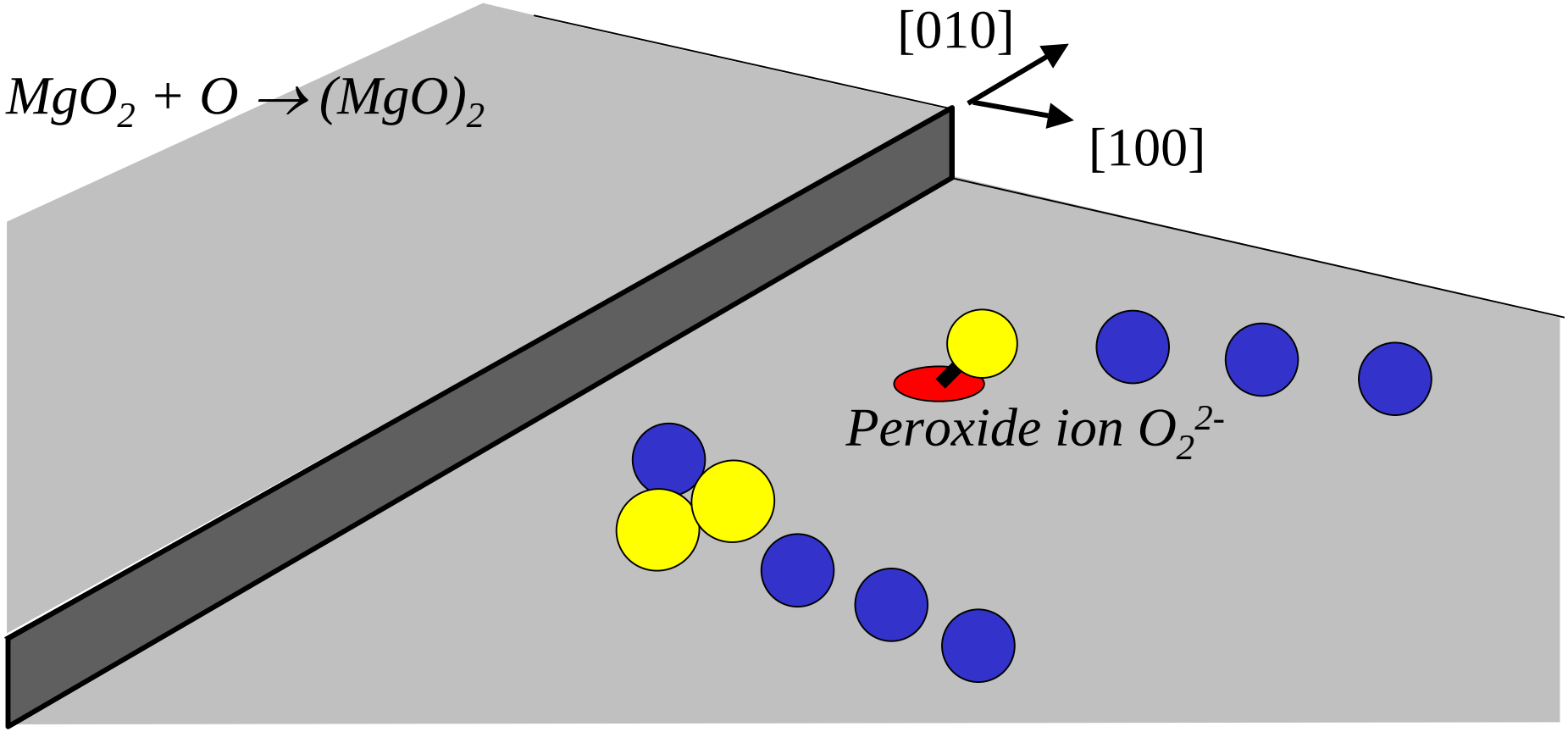
3 – Nucleation phenomena

Surface redox reactions

Oxide formation : surface redox reaction

$Mg + O \rightarrow MgO$

$MgO_2 + O \rightarrow (MgO)_2$



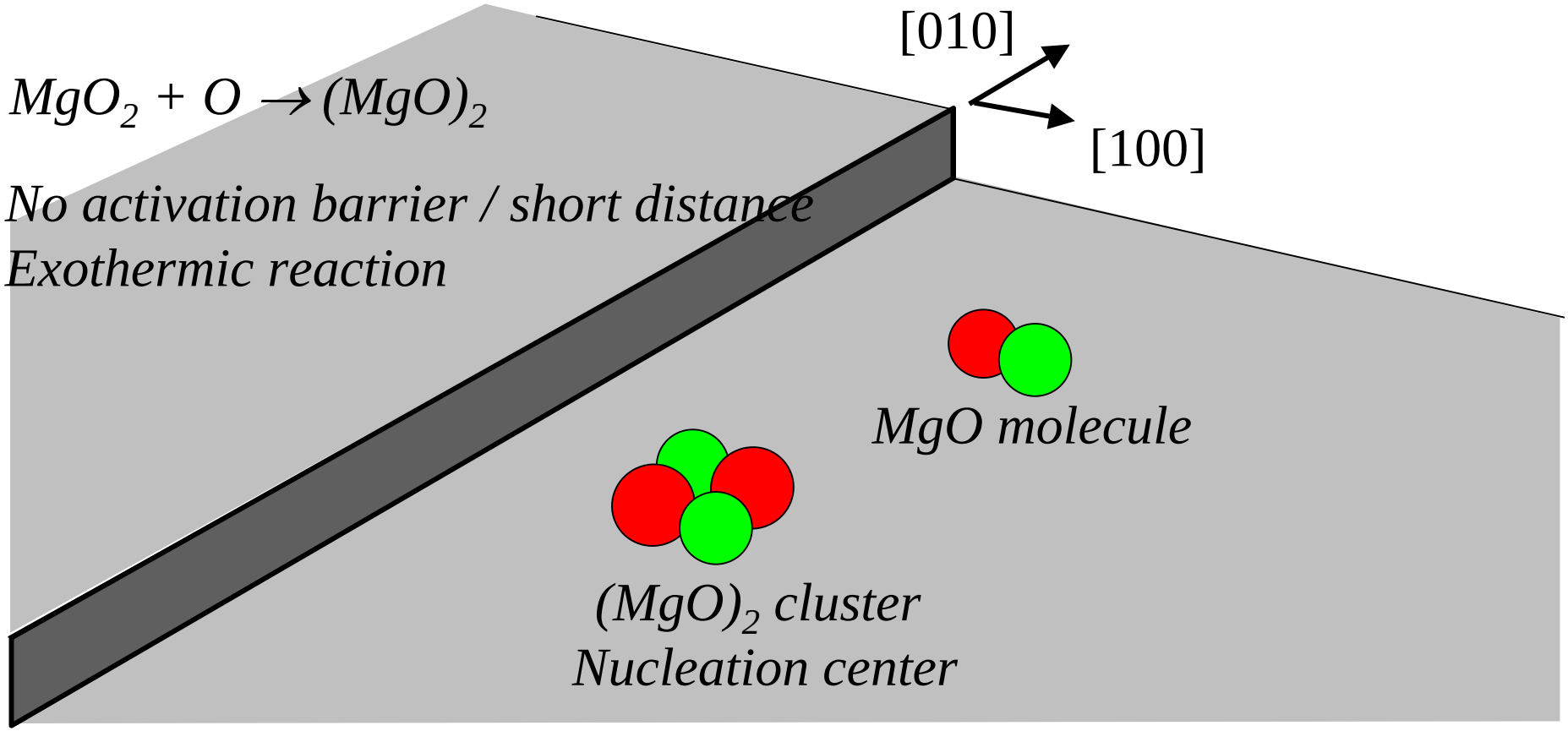
Surface redox reactions

Oxide formation : surface redox reaction

$Mg + O \rightarrow MgO$

$MgO_2 + O \rightarrow (MgO)_2$

No activation barrier / short distance
Exothermic reaction

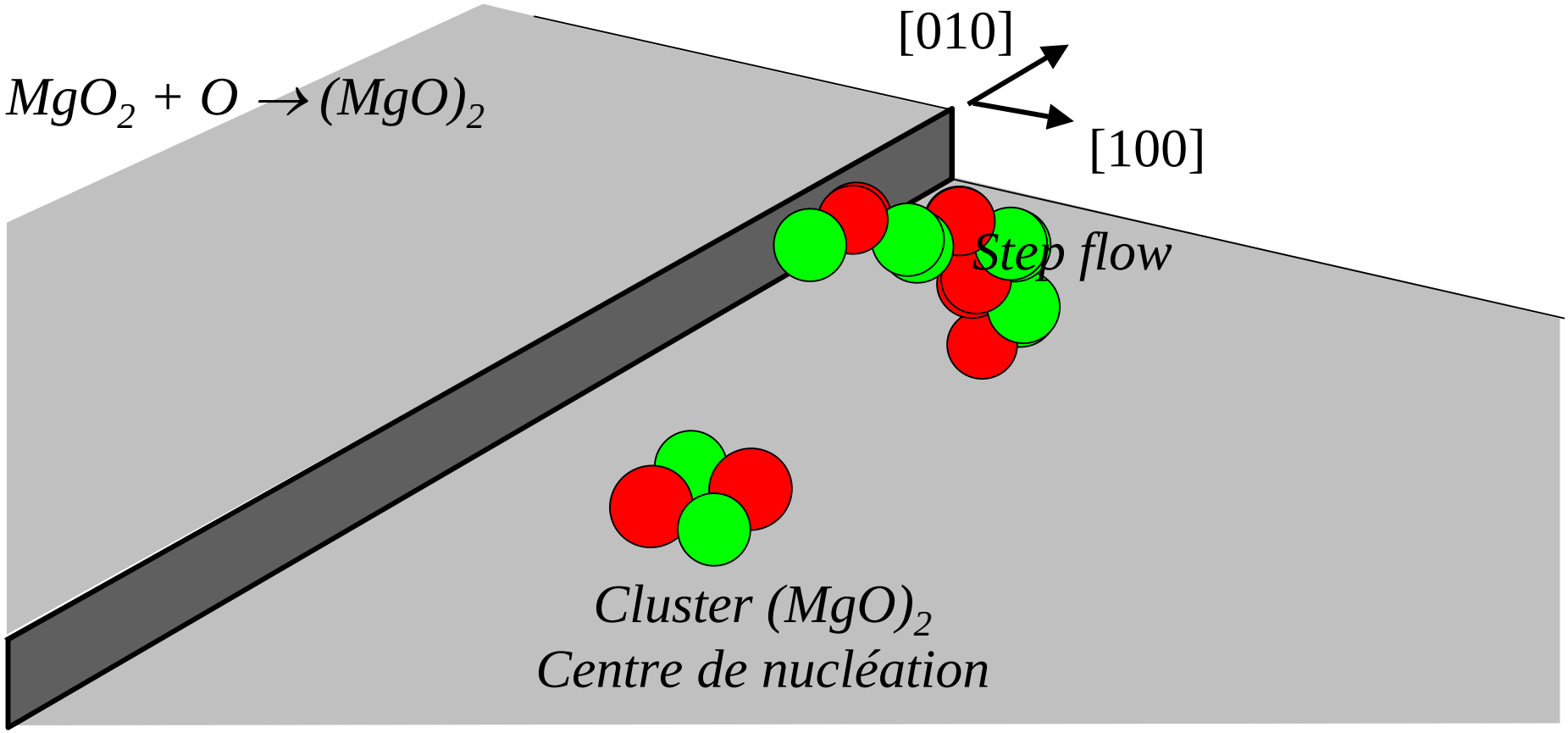


Surface redox reactions

Oxide formation : the MgO molecule

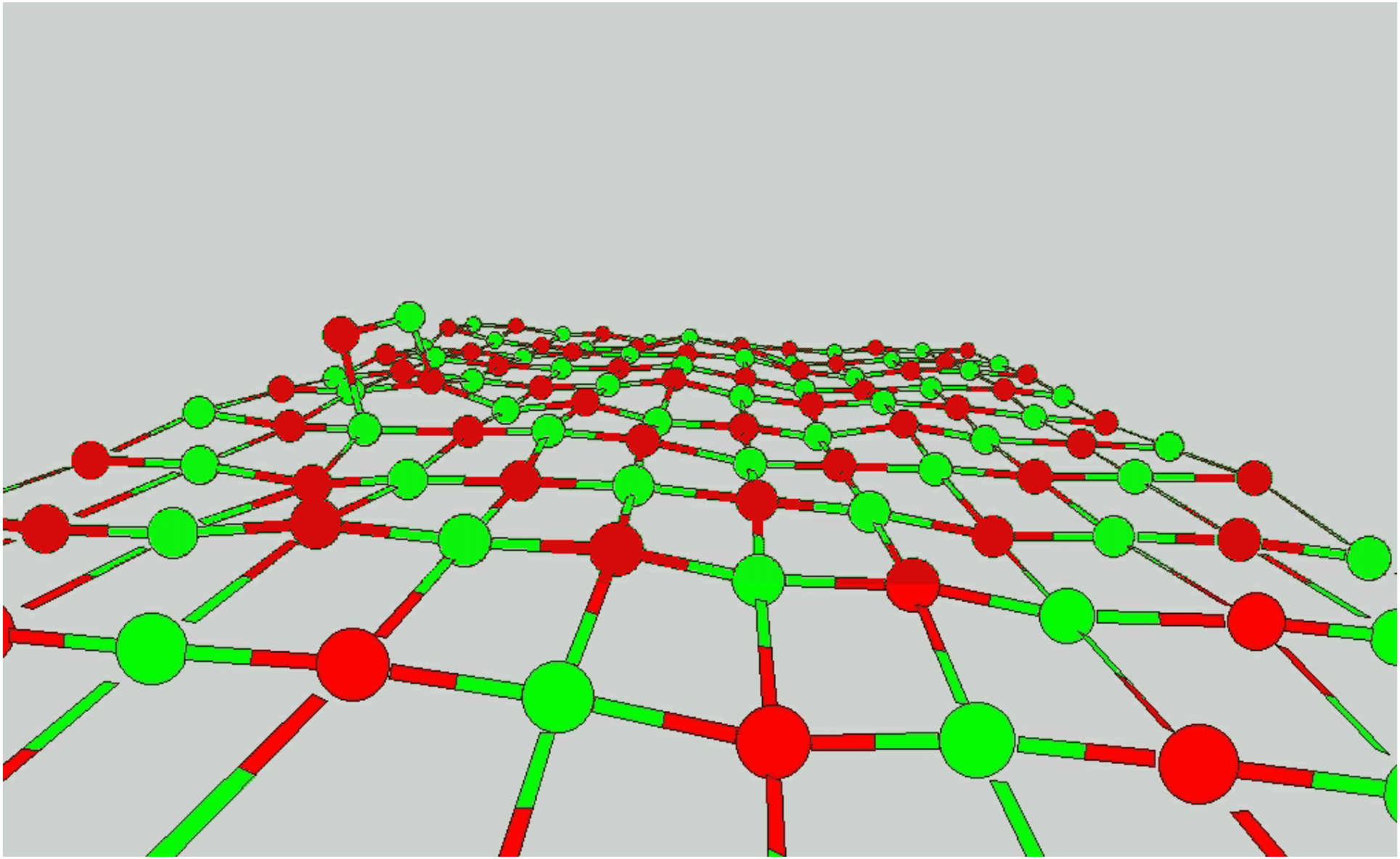
$Mg + O \rightarrow MgO$

$MgO_2 + O \rightarrow (MgO)_2$



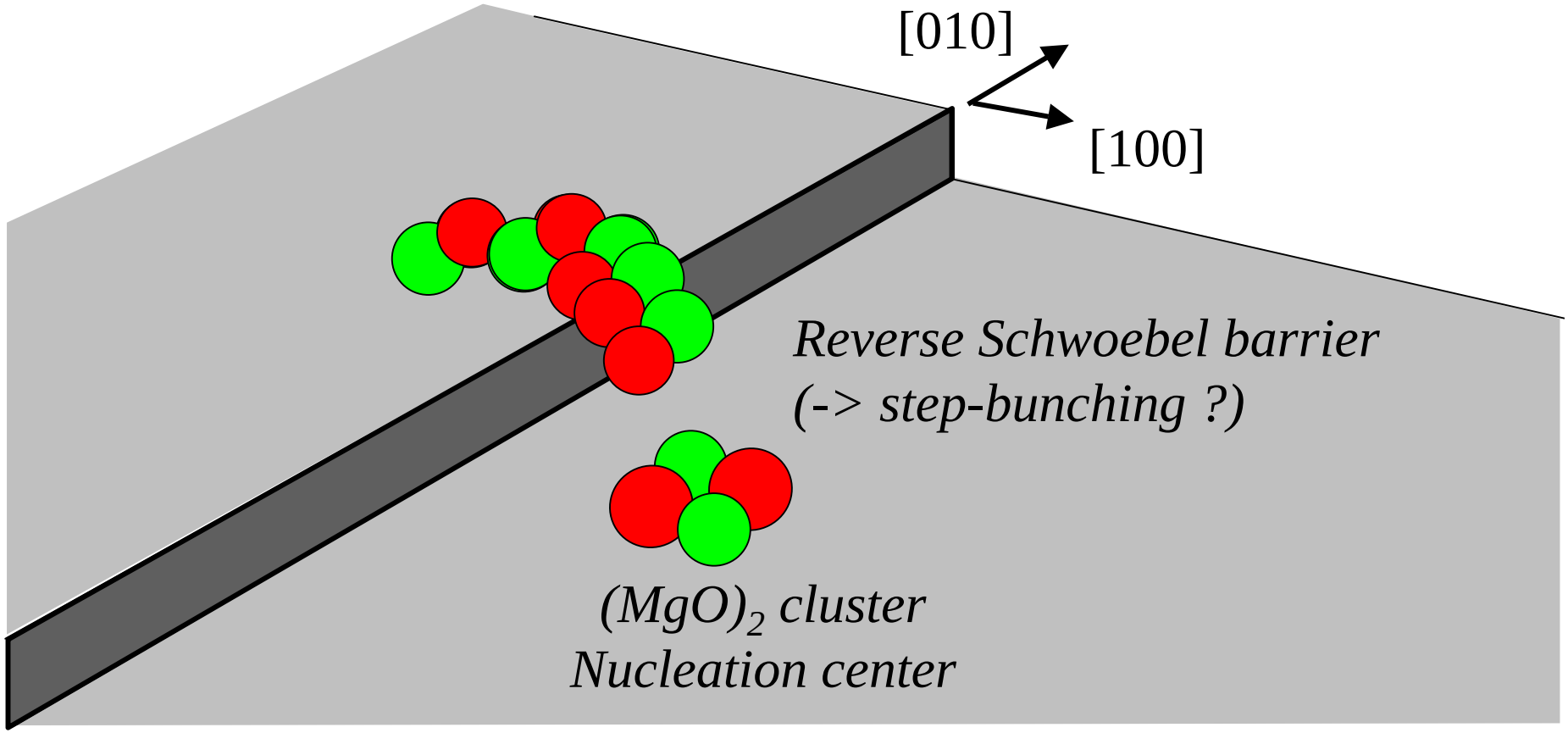
Surface redox reactions

Diffusion of the MgO molecule : Molecular Dynamics / T = 1000 K



Surface redox reactions

Oxide formation : the MgO molecule



Overview

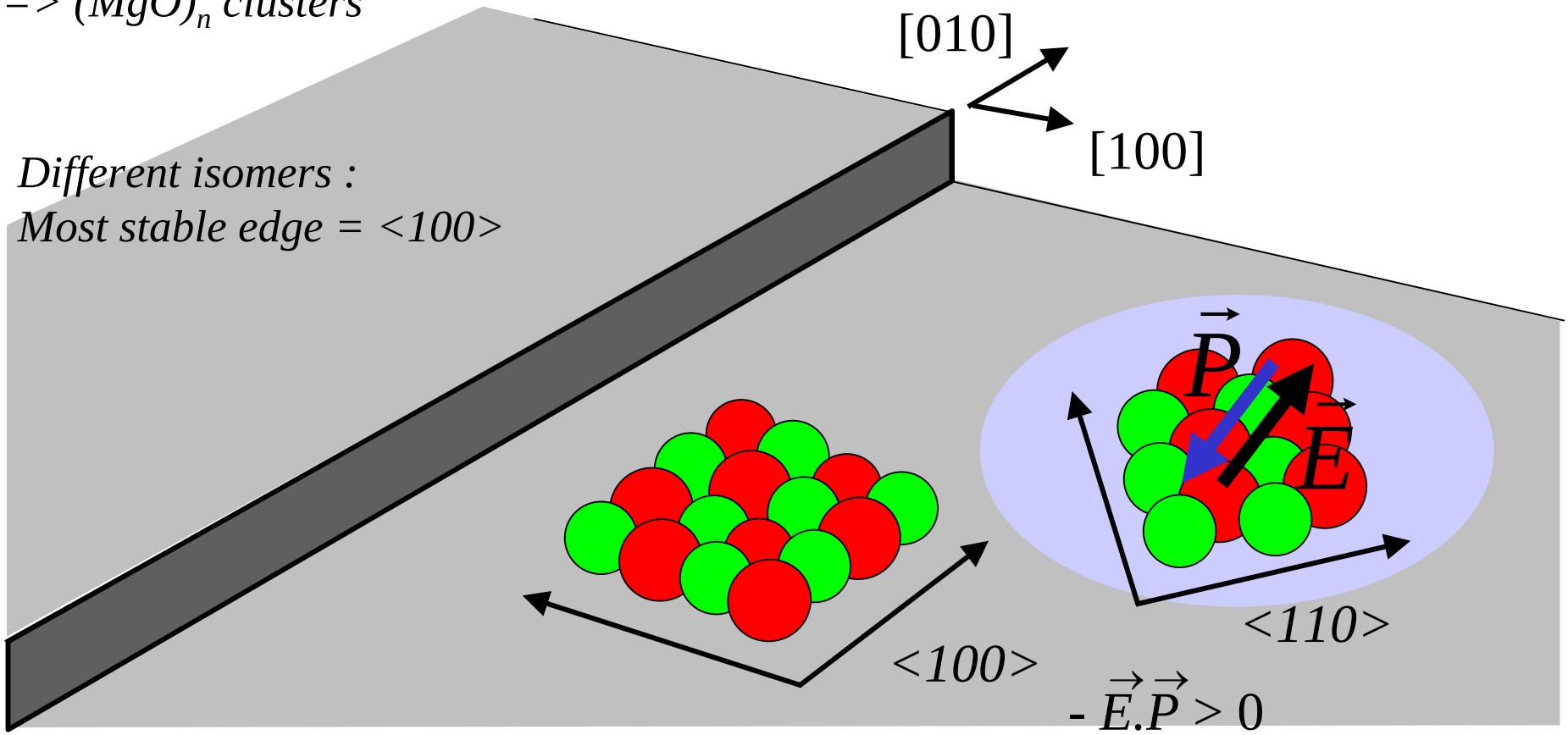
MgO growth : 3 phases

1 – Isolated species : Mg, O, O_2
2 – Surface redox reactions
3 – Nucleation phenomena

Oxide nucleation

Stoichiometric clusters

Encounter of several MgO molecules
=> $(MgO)_n$ clusters

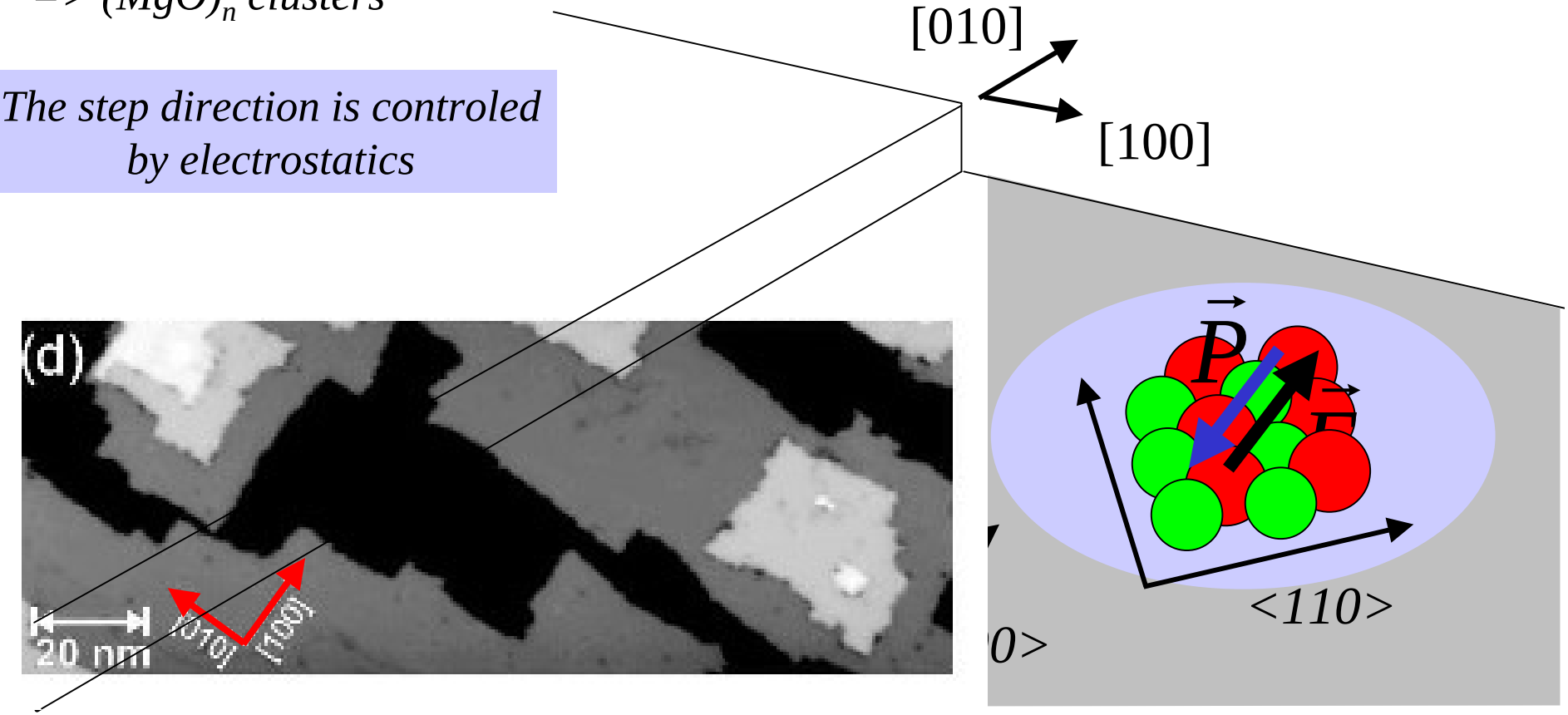


Oxide nucleation

Stoichiometric clusters / steps

Encounter of several MgO molecules
=> $(MgO)_n$ clusters

The step direction is controled by electrostatics



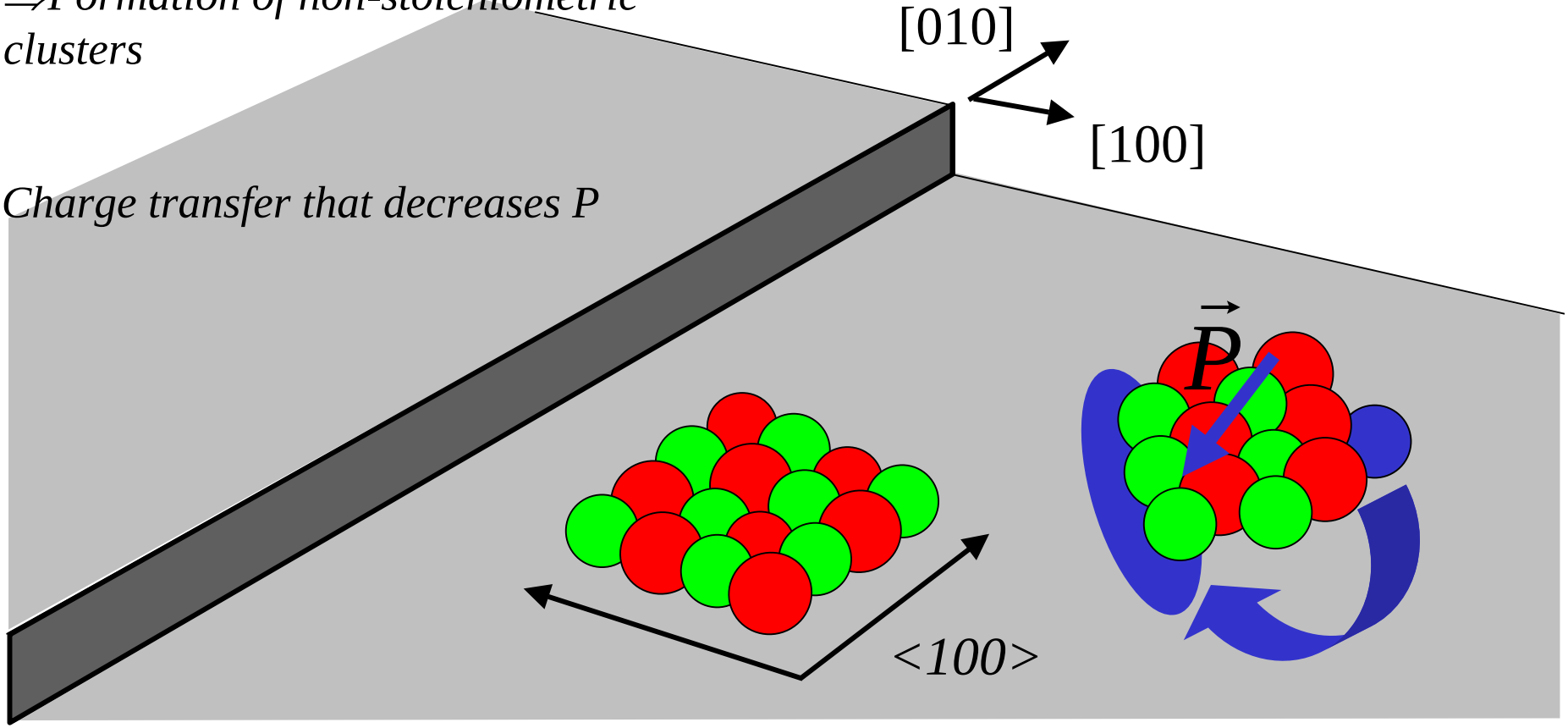
W. D. Schneider, Surf. Sci. ***514*** *(2002), 74*

Oxide nucleation

« Polar » clusters :

Adsorption of Mg diffusing adatoms
⇒Formation of non-stoichiometric clusters

Charge transfer that decreases P



Oxide nucleation

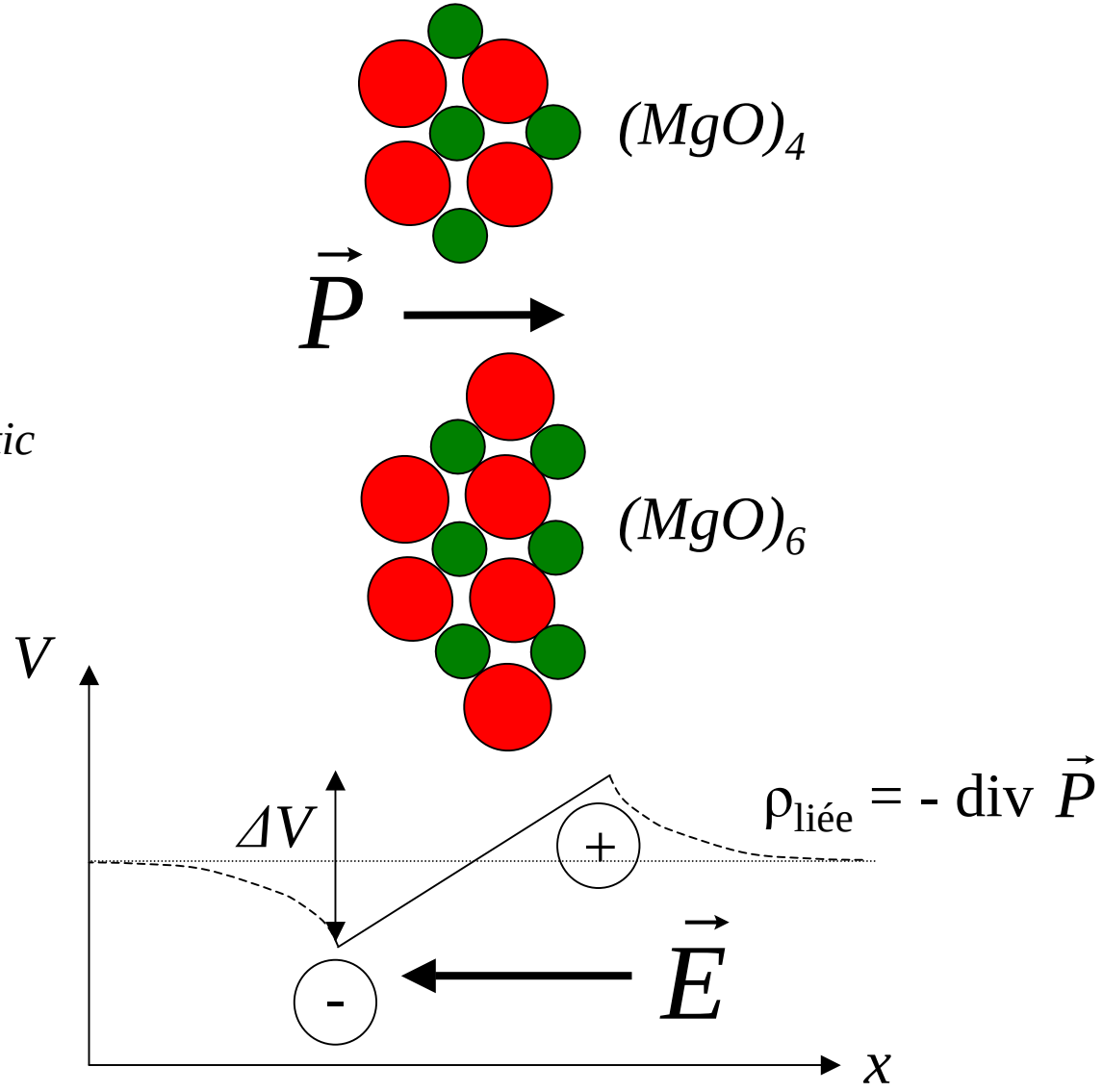
Mg adsorption at steps : the role of macroscopic fields

P =>

- Surface density of charge

- Macroscopic electric field

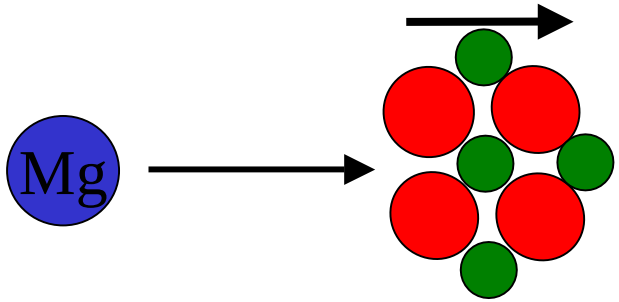
- ΔV : difference of electrostatic potential

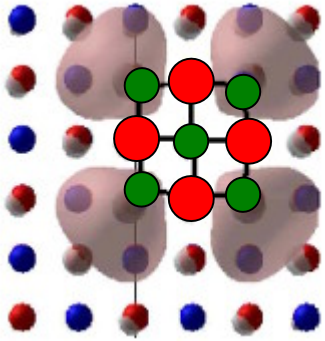


Oxide nucleation

Mg adsorption at steps : the role of macroscopic fields

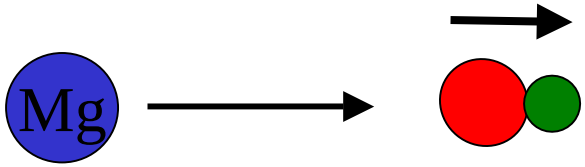
Adsorption in the low V region : Strong decrease in the dipole
Very strong Mg-cluster binding energy

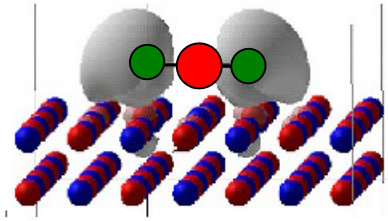




homo

P = 0 (symmetry center)
E = 2.64 eV





P = 0 (symmetry center)
E = 1.94 eV

Conclusion

1) At the atomic scale : first idea of what can be the growth of an oxide

Dynamics
- Important surface diffusion : Mg, MgO, O (balistic)
-Schwoebel barriers : direct (Mg) and reverse (MgO)

Equilibrium :
- Role of electrostatics (step directions)

=> Possibility of a « step-flow » growth mode

2) Microscopic parameters for a KMC simulation

3) Cf GaAs(110) vicinal surfaces : does an oxide surface spontaneously produce instabilities and nanostructures ?

Conclusion

GaAs(110)

Ga → *Chemisorption : Precursor* → *Diffuses*

As → *Physisorption* → *Diffuses*

GaAs molecule → *Diffuses* → *Direct Schwoebel barrier*

Growth instabilities :
- *Step-bunching (low T)*
- *Step-meandering (High T)*

MgO(100)

O → *Chemisorption : Precursor* → *Does not diffuse*

Mg → *Physisorption* → *Diffuses*

MgO molecule → *Diffuses* → *Reverse Schwoebel barrier*

? … KMC !

Conclusion

1) At the atomic scale : first idea of what can be the growth of an oxide

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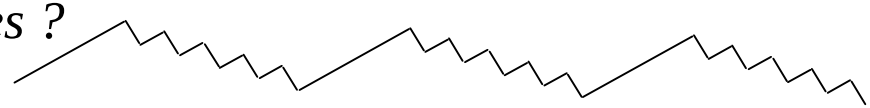

Reverse Schwoebel barrier => STEP-BUNCHING instability

... complex ! (different species, redox reactions, electrostatics)