Polar surfaces in a nutshell

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OUTLINE

- The polar catastrophe
- Electrostatics: micro/macro
- Compensated polar surfaces
- ZnO(0001): Zn-vacancy ordering
- MgO(111): the (2x2) reconstruction
- Ultra-thin MgO(111) films: exotic phases?

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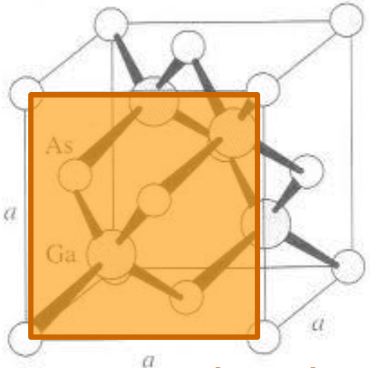
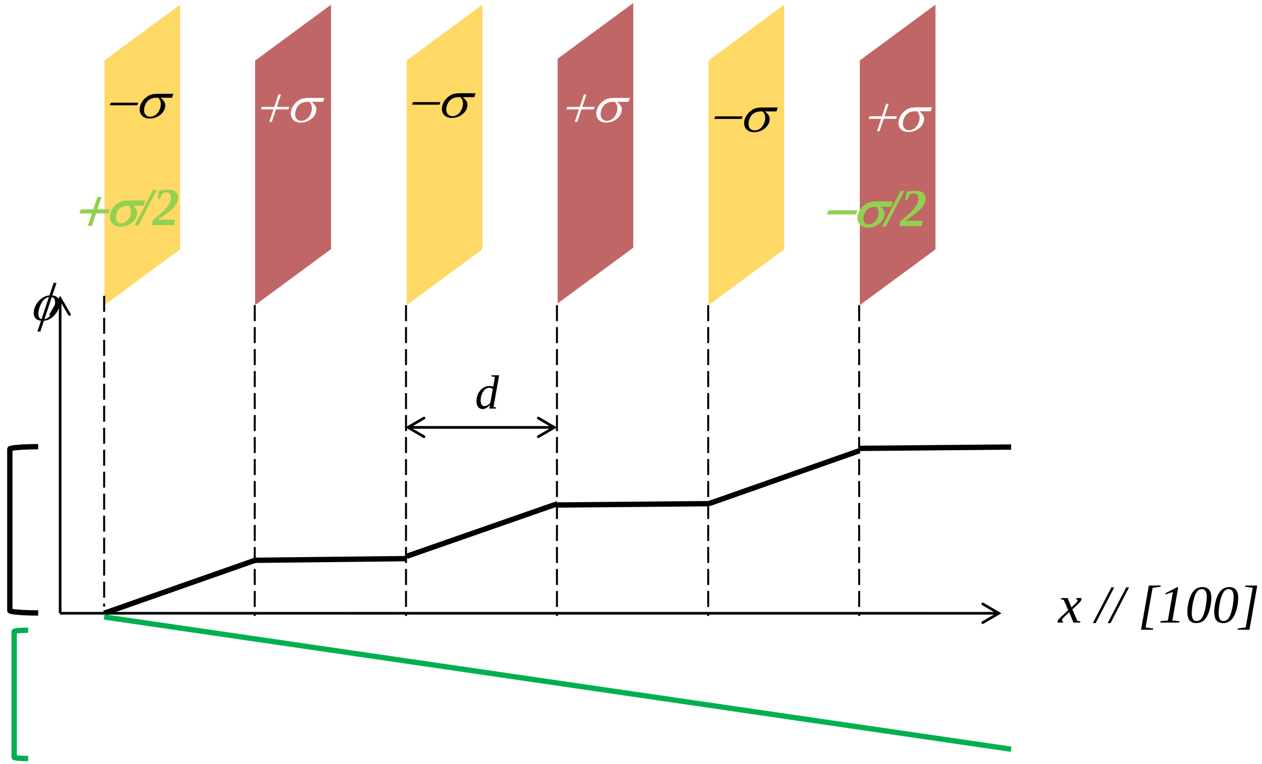
Polar surfaces: basic electrostatics

Polar orientations: charged ideal atomic planes ➔ Model of planar capacitors



GaAs(100)



$$\Delta\phi = N\frac{\sigma\, d}{2\varepsilon_0}$$

$$\boxed{\Delta\phi' = -(N-\frac{1}{2})\frac{\sigma\, d}{2\varepsilon_0}}$$

$$\Delta\phi^{(1)} = \frac{\sigma\, d}{2\varepsilon_0} = \frac{q}{\varepsilon_0 a} \approx \frac{0.1}{8.9\times 5.6}\times 10^{-19+12+10} V \approx 2V$$

The potential drop of a double layer is even bigger than the fundamental gap (note ε_r~10.9)

$$\boxed{\Delta\phi + \Delta\phi' = -\frac{\Delta\phi^{(1)}}{2}}$$

Electrostatic stability calls for a « compensating » surface charge $\sigma/2$

The « polar catastrophe »

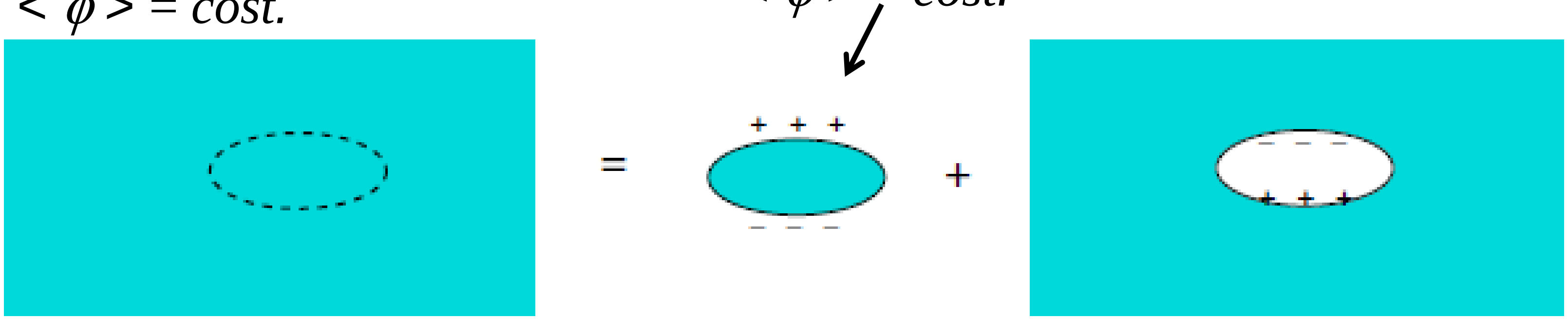
A crystal cannot sustain a macroscopic polarization $\vec{P}$
in absence of an external electric field

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$

In textbooks: polarization= dipole/unit volume … Uhm...
Nothing is said about the <u>surface charge</u>

Virtually infinite crystal in electrostatic equilibrium
$< \phi > = cost.$

Finite (real) crystal at the same electrostatic potential
$< \phi > = cost.$



Surface charges at the surface of an insulator must be specified
in order to set the potential inside a finite sample

$$< \vec{P}(\vec{r}) > = \frac{1}{\Omega}\int_{\Omega} d^3r\, \vec{P}(\vec{r}) = \frac{1}{\Omega}\int_{\Omega} d^3r\, \vec{r}\rho(\vec{r}) + \frac{1}{\Omega}\int_{S} ds\, \vec{r}\left(\vec{P}\cdot\hat{n}\right)$$

RM. Martin, PRB 9 (1974) 1998:

Bulk contribution:

Flux through the surface:

- The polar catastrophe
- Electrostatics: micro/macro
- Compensated polar surfaces
- ZnO(0001): Zn-vacancy ordering
- MgO(111): the (2x2) reconstruction
- Ultra-thin MgO(111) films: exotic phases?

A step backward: microscopic/macroscopic

Classical electrostatics
Consider fields and other quantities as macroscopic (e.g the « test charge »).

Solid state physics
deals with microscopic quantities, at the atomic scale.

- **Is there any connection ?**
- **Are Maxwell's equations valid at any scale ?**

YES! (to both questions) This can be done through « macroscopic averages »

Microscopic operator	(ex. charge density operator)	$\hat{f} = \sum_i q_i \, \delta(\vec{r} - \vec{r}_i)$
Microscopic quantity	(ex. charge density)	$f(\vec{r}) = \langle \Psi \vert \hat{f} \vert \Psi \rangle$
Macroscopic average	(convolution with a weight function w)	$< f(\vec{r}) > = \frac{1}{\Omega_0} \int_{\Omega_0} d^3r' \, w(\vec{r}') \, f(\vec{r} - \vec{r}')$

➔ Macroscopic averages commute with spatial differentiation

➔ Maxwell's equations are OK

$$\boxed{\frac{\partial < f(\vec{r}) >}{\partial x_\alpha} = < \frac{\partial f(\vec{r})}{\partial x_\alpha} >}$$

Macroscopic averages: an example

$(AlAs)_3(GaAs)_3$
(100) superlattice

M.Peressi et al, J.Phys.D 31 (1998)

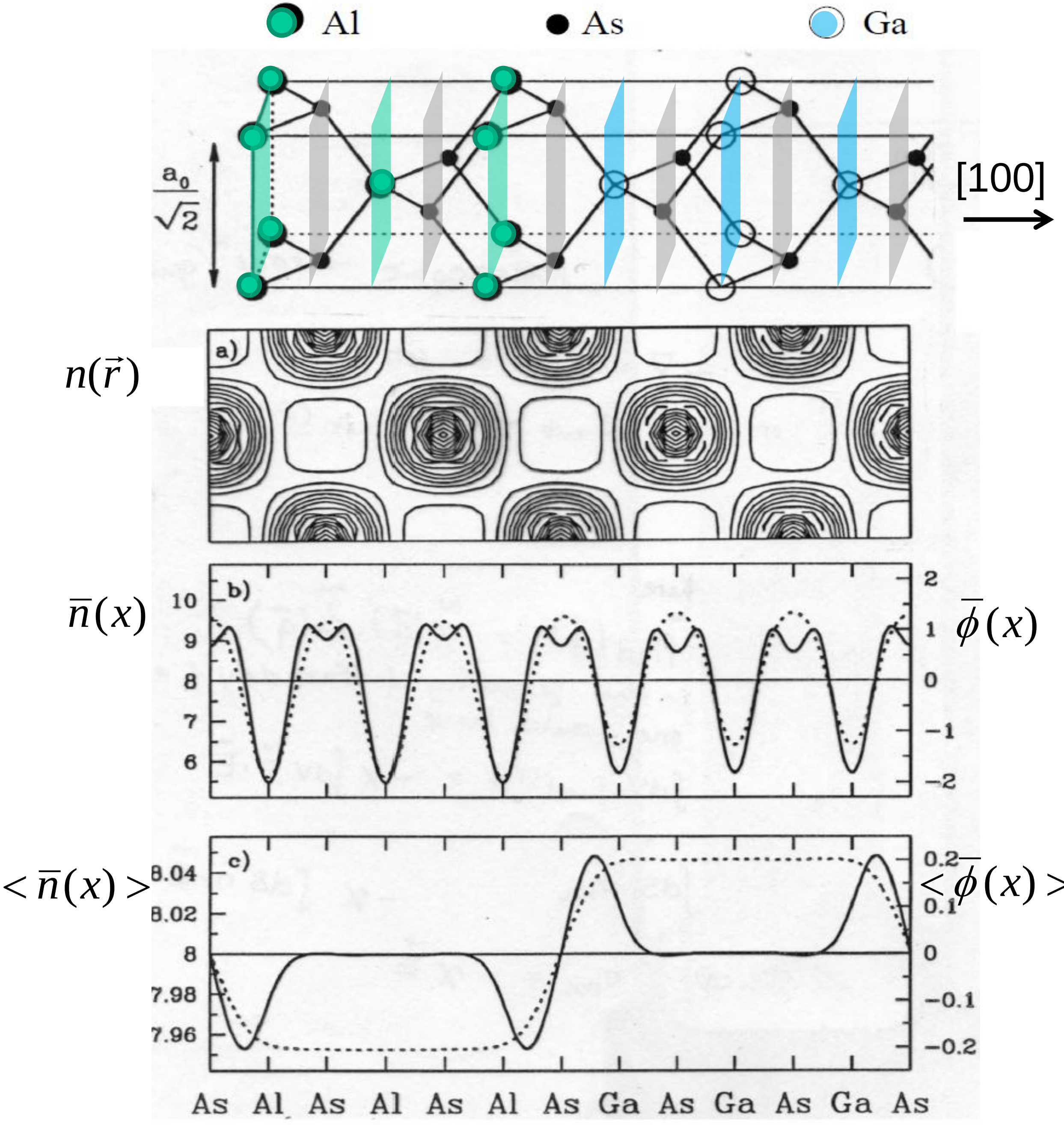
Electron density contour

Lateral average

$$\bar{f}(x) = \frac{1}{A}\int dy \int dz \; f(x,y,z)$$

Macroscopic average

$$< \bar{f}(x) > = \frac{1}{a}\int_{x-\frac{a}{2}}^{x+\frac{a}{2}} dx' \;\; \bar{f}(x')$$



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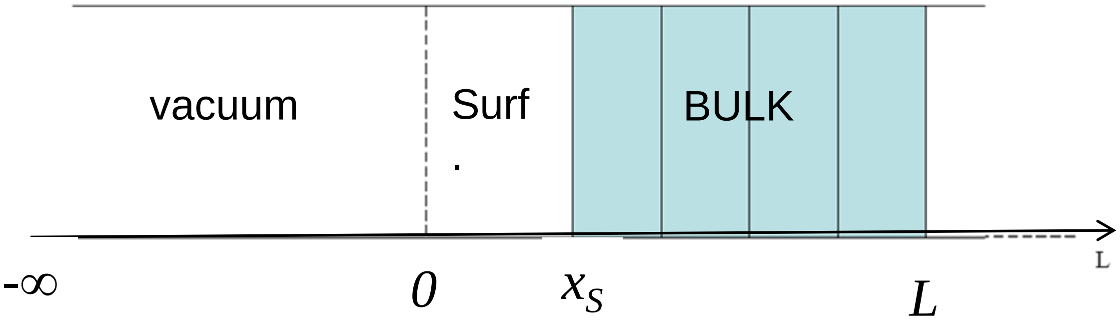
1D Polarization (along the surface normal)

$$\bar{P}(x) = \frac{1}{A}\int dy \int dz\, P(x,y,z)$$

Lateral average of
normal polarization



$$<\bar{P}(x)> = \frac{1}{L}\int_0^L dx\, \bar{P}(x) = \frac{1}{L}\left[x\bar{P}(x)\right]_0^L - \frac{1}{L}\int_0^L dx\, x\frac{d\bar{P}(x)}{dx} = \bar{P}(L) + \frac{1}{L}\cancel{\int_0^{x_S} dx\, x\bar{\rho}(x)} + \frac{1}{L}\int_{x_S}^{L} dx\, x\bar{\rho}(x)$$

$$\xrightarrow[L\to\infty]{} \bar{P}(x_S) + \frac{1}{L}\int_{x_S}^{L} dx\, x\, \bar{\rho}(x) = -\int_{-\infty}^{x_S} dx\, \bar{\rho}(x) + \int_{x_S}^{x_S+a} dx\, x\, \bar{\rho}(x) = -\sigma_S(x_S) + \frac{\bar{\mu}_B(x_S)}{aS}$$

Planar density, integrated in the surface region

First moment of the charge distribution (« bulk dipole » with origin at x_S)

Condition for electrostatic stability

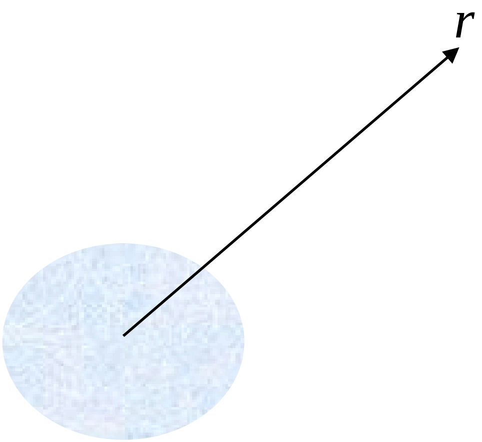
(no macroscopic polarization)

$$\boxed{Q_S(x_S) = \frac{\mu_B(x_S)}{a}}$$

The surface charge at the surface/bulk border is related to the bulk dipole moment computed by choosing this border as the origin of the unit cell

Electrostatics: multipole expansion

Let's consider the electrostatic potential in a point r far from a **localized** charge distribution



$$\phi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} q_{lm} \frac{1}{r^{l+1}} Y_{lm}(\theta,\varphi)$$

$$q_{00} = \sqrt{\frac{1}{4\pi}} \int d^3x\, \rho(\vec{x})$$

Total charge $Q \equiv \sqrt{4\pi}\, q_{00}$

$$q_{10} = \sqrt{\frac{3}{4\pi}} \int d^3x\, z\rho(\vec{x})$$

Dipole moment $\vec{p} = \int d^3x\, \vec{x}\rho(\vec{x})$

$$\phi(\vec{r}) = \frac{Q}{r} + \frac{\vec{p}\cdot\vec{r}}{r^3} + \dots$$

What about crystals ?

They are macroscopic, periodic and virtually infinite systems!

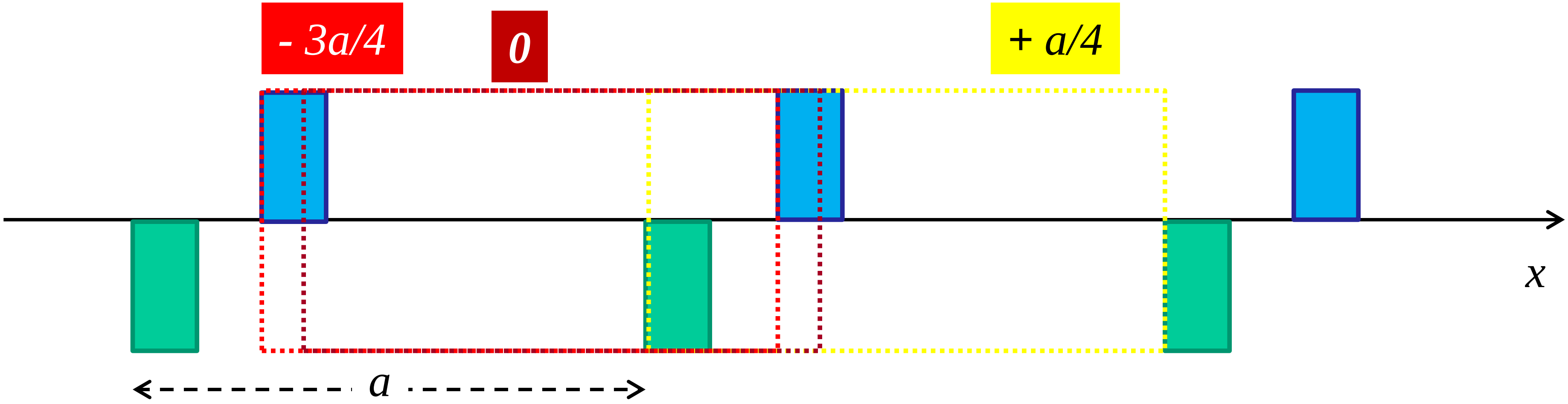
Dipole moment and periodic distributions

$$\bar{\mu}_B(x_S) = \frac{1}{a}\int_{x_S}^{x_S+a} dx\, x\, \bar{\rho}(x)$$

function of x_S (the origin of the unit cell)

➔ ILL DEFINED !

➔ Can take arbitrary values



Theorem:

For a PERIODIC charge distribution, it is ALWAYS possible to choose the origin of the unit cell in order to have a NULL DIPOLE MOMENT

The theorem is independent of the specific form of $\rho(x)$

proof cannot be found in textbooks, but in Goniakowski, Finocchi, Noguera, Rep.Progr.Phys. 71 (2008) 016501 :

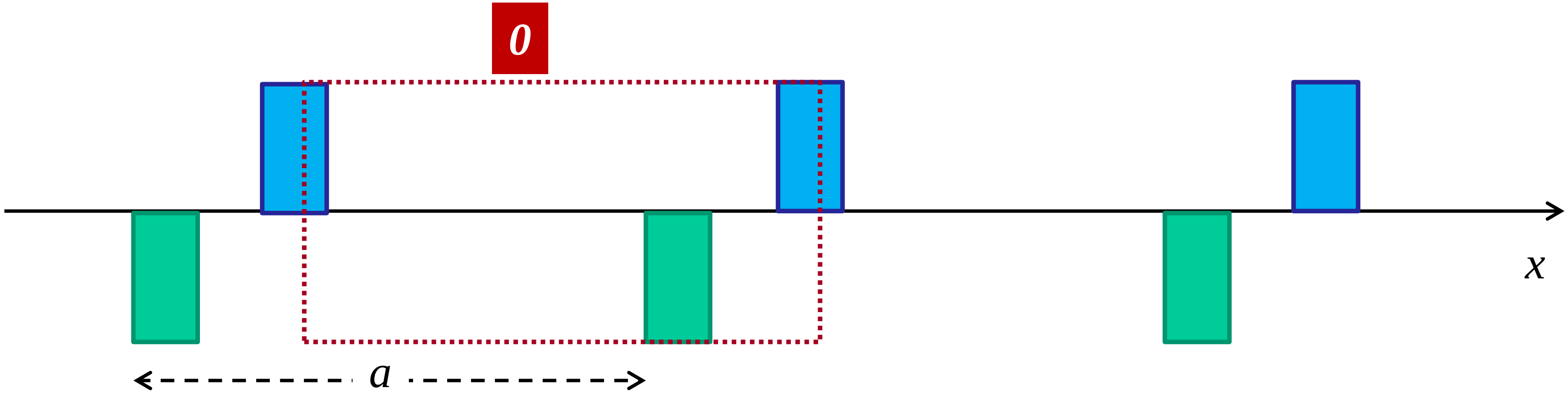
How to avoid the polar catastrophe

Condition for null macroscopic polarization

$$Q_S(x_S) = \frac{\mu_B(x_S)}{a}$$

A simple recipe (there are others):

1. Consider formal charges for ions
2. Find the origin for zero-dipole unit cell: $\mu_B=0$
3. If the origin passes through atomic planes (polar surfaces), eliminate the residual surface charge Q_s (take away some ions or put extra charges)



Take away ¾ surface ions (left) and ¼ surface ions (right)
→ (2x2) or (4x1) reconstructions, etc.

➔ COMPENSATED POLAR SURFACES

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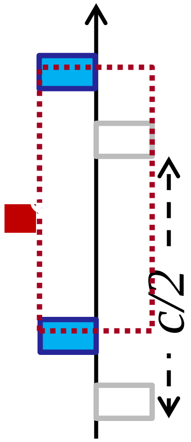
ZnO(0001)



Compensated surface:

-¼ Zn atoms at the surface

(or reduce by ~¼ the surface charge)

ZnO(0001)

Clean and stoichiometric (1x1) surface is metallic and not very stable

Wander et al, PRL (2001)

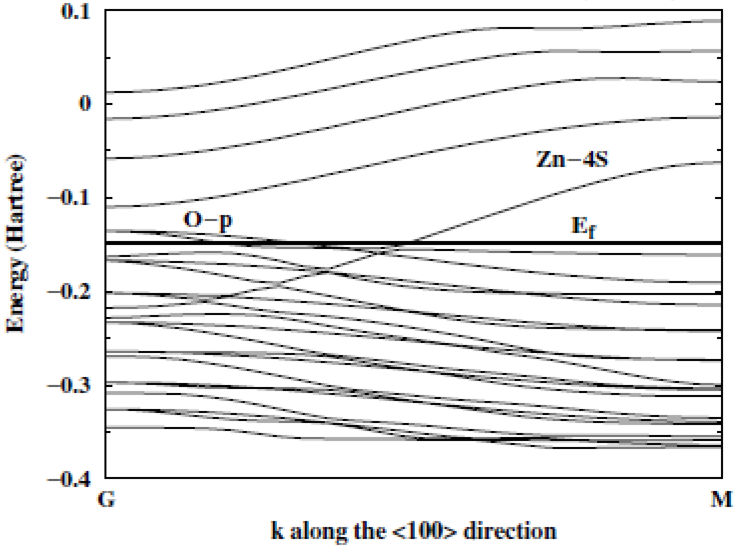


FIG. 3. The band structure of the S7 slab. The energy scale is in hartrees (H). The partially occupied Zn-4s band and the unoccupied O-p band are labeled. E_f denotes the Fermi level of the system.

(1x1) is stabilized in Zn-rich conditions and presence of Hydrogen:

➔ Adsorption of (coverage ~1/2):

- OH$^-$ /Zn surface
- H$^+$ /O surface

Meyer, PRB 69 (2004)

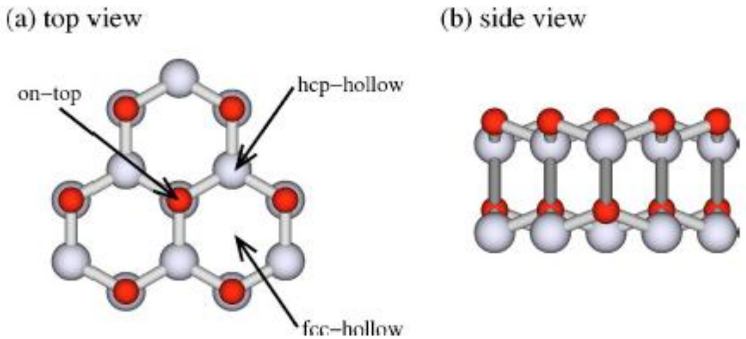
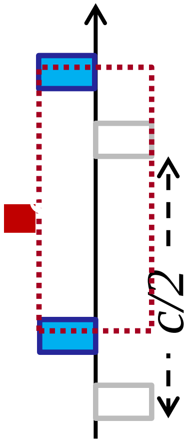


FIG. 4. Schematic diagram of the high-symmetry adsorption sites for OH groups on the Zn-terminated polar ZnO surface. Small/dark spheres represent Zn, large/gray spheres O atoms.

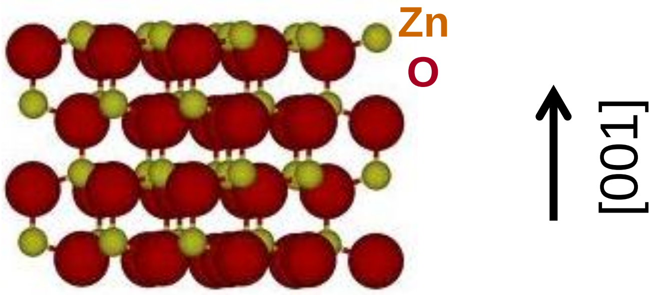
ZnO(0001)



Compensated surface:

-¼ Zn atoms at the surface

(or reduce by ~¼ the surface charge)



ZnO(0001)

Clean surface in UHV: Zn vacancies rearrange

→ « triangular reconstructions »

Dulub et al, PRL 90 (2003)

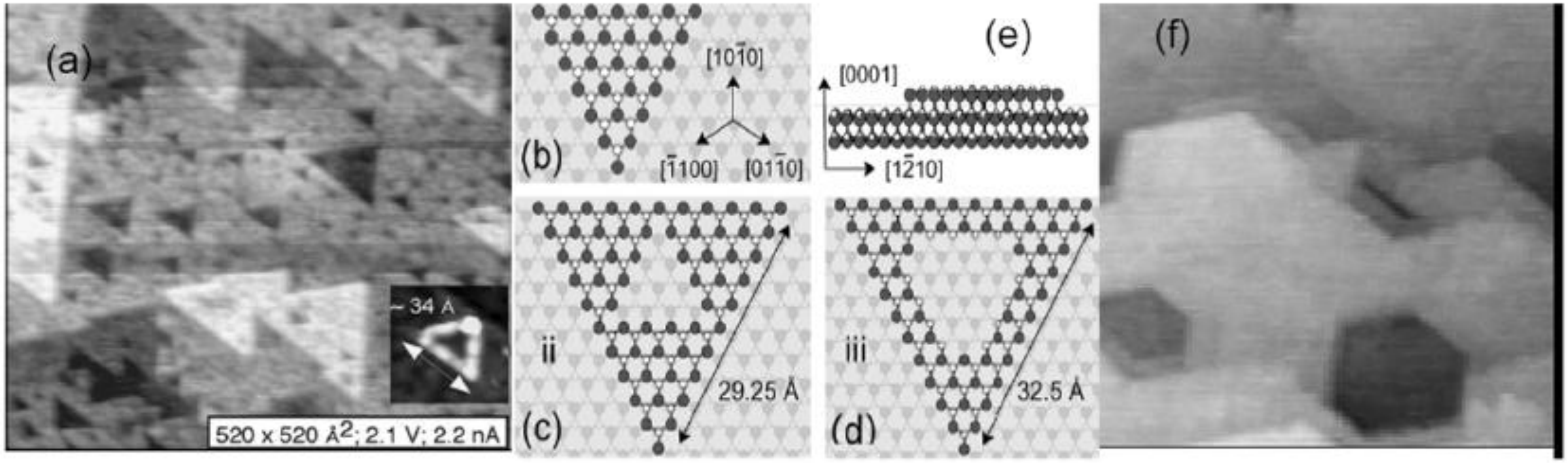


Figure 25. (*a*) STM image of magic triangles on the Zn-termination; (*b*), (*c*) and (*d*) different atomic models for magic triangles fulfilling the compensation criterion (small white balls: Zn; large dark balls: O); (*e*) side view of the Zn-terminated surface; (*f*) STM image of hexagonal holes on the O-termination. Reprinted from [360] with permission from Elsevier, copyright 2002 and from [361] with permission from the American Physical Society, copyright 2003.

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Compensated polar surfaces: prototypes

1. Dissociative water adsorption on MgO(111) *[Noguera ('93); Refson('95)]*

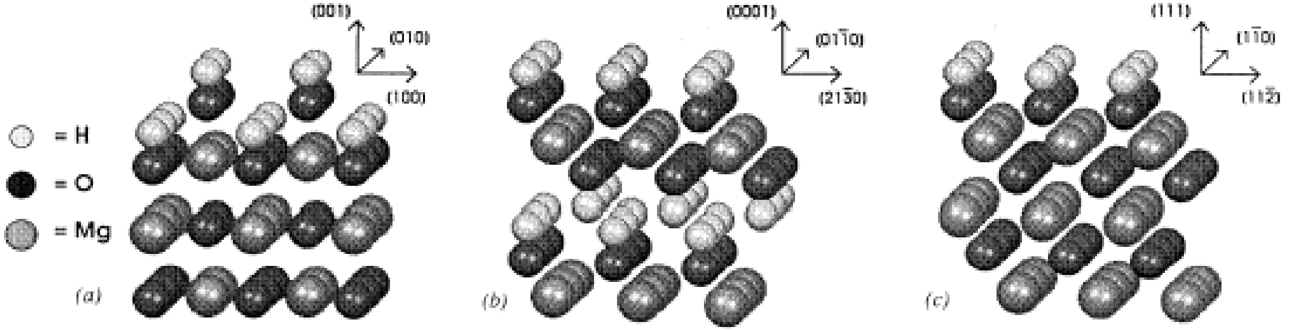


FIG. 1. (a) Hypothetical hydroxylated (001) surface of MgO, (b) (0001) surface of $Mg(OH)_2$, (c) our postulated (111) hydroxyl surface of MgO. The top three O-Mg-O layers of an oxygen-terminated MgO (111) surface have the same structure as $Mg(OH)_2$ (0001). The (111) hydroxyl surface may be equivalently constructed by protonation of an oxygen-terminated surface or by hydroxylation of a magnesium-terminated surface.

2. The octopole reconstruction of rocksalt(111) *[Lacmann('65); Wolf('93)]*

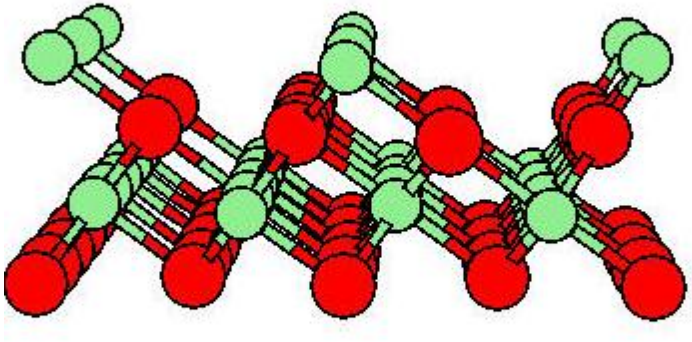
Any structure built from a simple cubic cell with 4 anions + 4 cations - " the octopole " - is free from dipole moments.

3-fold coordinated surface atoms on top of triangular pyramids with {100} {010} {001} facets ➔ (2x2) pattern

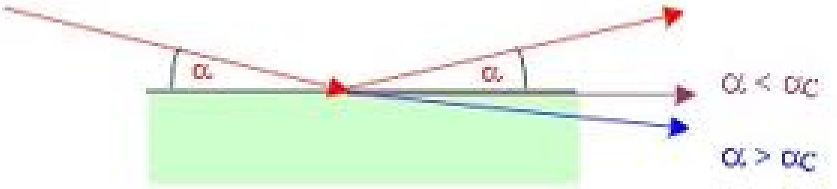
Non stoichiometric surface

Electrostatic condition for stability is fulfilled

N_{at}	Q
1	+2
3	-6
4	+8
……	

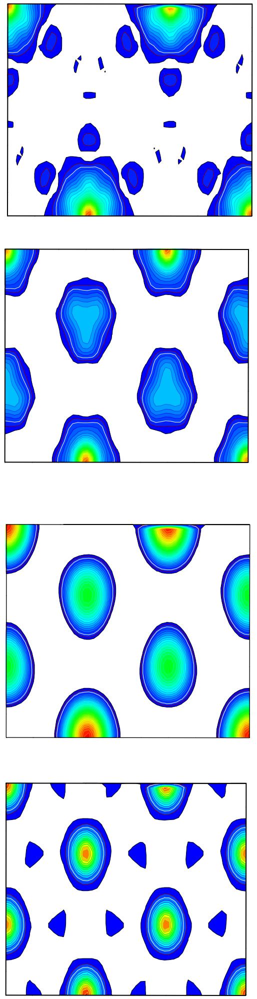


Pattersson maps of MO(111) surfaces from GIXS



Grazing Incidence
X-ray Diffraction

NiO(111)



RT
100%
$\chi^2=1.3$

210°C
82%
$\chi^2=0.7$

430°C
62%
$\chi^2=0.6$

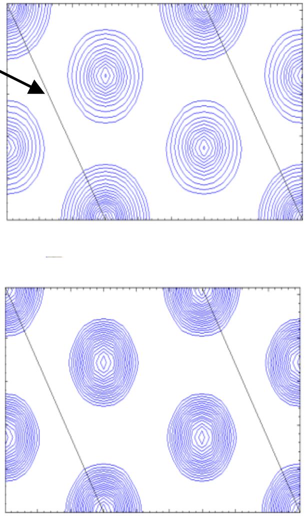
700°C
7%
$\chi^2=1.3$

● **O** ● **Ni**

Any Mg-oct + O-oct combination fails to reproduce the GIXS data

MgO(111)

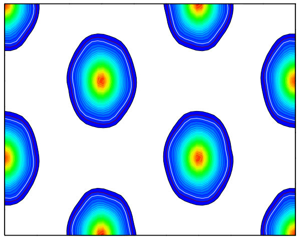
Mixture ?



RT

254°C

CoO(111)
∀ *T*

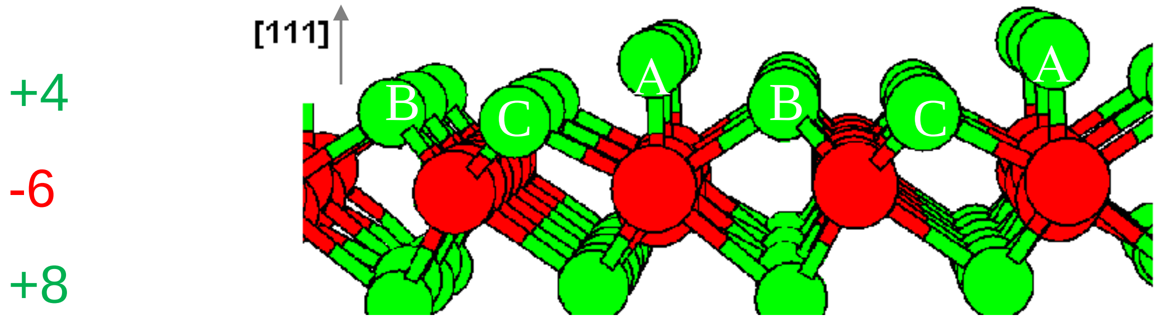


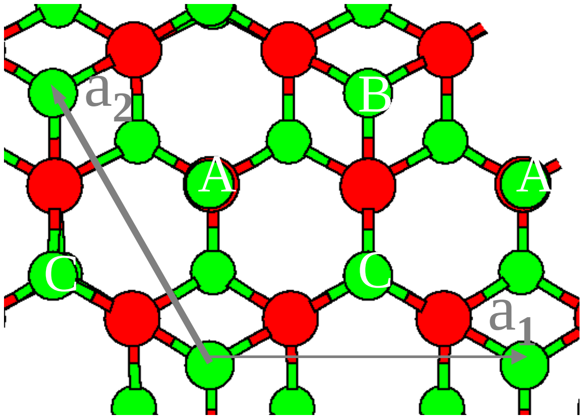
A.Barbier et al
PRB 62 (2000) 16056

C. Mocuta et al, Appl. Surf. Sci. 162-163 (2000)

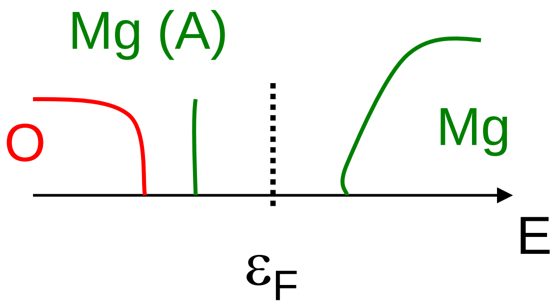
Finocchi et al, PRL 92 (2004) 136101

MgO(111) (2x2) : hex-Mg / MgO





- Can be thought either as a Mg over-layer on the ideal MgO(111) or as a O-spi without the apical O.
- The three surface Mg (A,B,C) are markedly inequivalent
- From the topological (Bader) charges : Mg$^{(A)}$ almost neutral

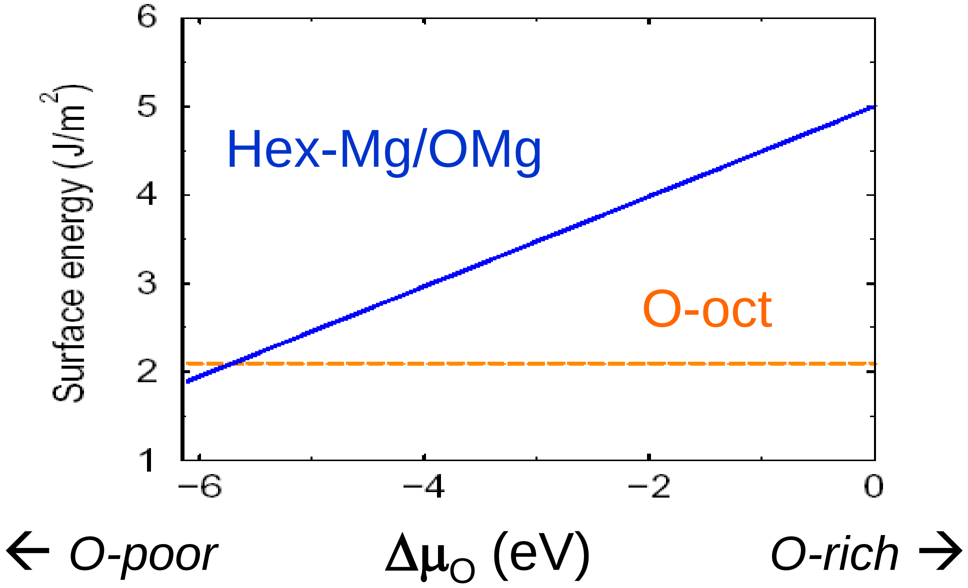


Compensated through anomalous filling : Mg$^{(A)}$ almost neutral

Nevertheless, insulating surface -- because of the weak V_{Mad} on Mg(A)

MgO(111) (2x2) : hex-Mg + O-oct (theory)

Hex-Mg/OMg favored in very O-poor environments, O-oct in more O-rich



➔ Minimal (two-phase) model :

hex-Mg for very low p_O,

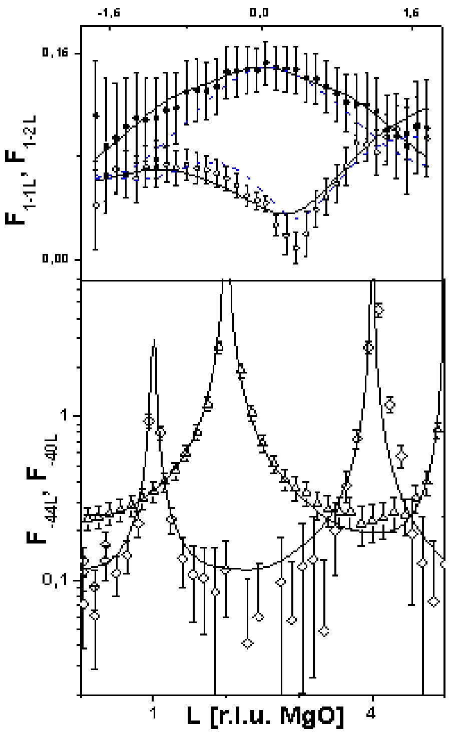
O-oct in more O-rich environments

Also assume they can coexist in variable proportions on the surface

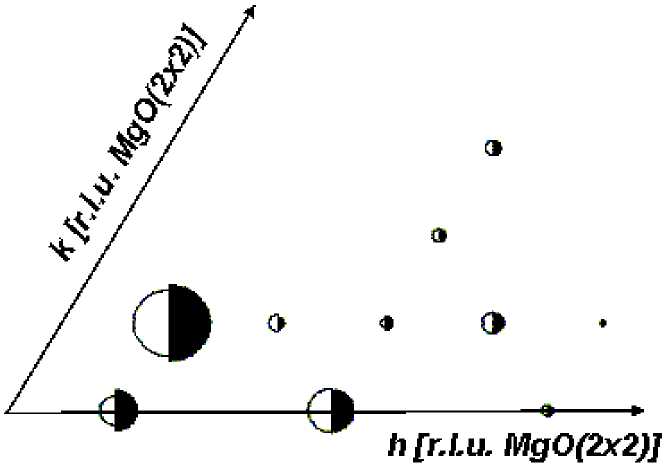
MgO(111) (2x2) : hex-Mg + O-oct (experience)

☺ Good fit of the GIXS data with : λ O-oct + $(1-\lambda)$ hex-Mg

(atomic positions and charges taken from the theory - no fitting parameters but λ)



➔ Evolution of the surface structure as a function of temperature and O pressure: $\lambda = \lambda\,(T, p_O)$



- Minimal (two-phase) model : hex-Mg + O-oct (so far, the best solution)
- Neither theory nor experiments (taken separately) could explain the (2x2) reconstruction in terms of a comprehensive structural model

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“Uncompensated” polarity in ultra-thin dielectric films grown along a polar direction

Finite number N of atomic layers

- ➔ No « bulk » polarization
- ➔ Sustainable layer dipole ?

$$\Delta\phi \cong N\Delta\phi^{(1)} < E_G$$

- ➔ Existence of a critical size N_C beyond which the film is no more insulator
- ➔ Size-sensitive electronic properties

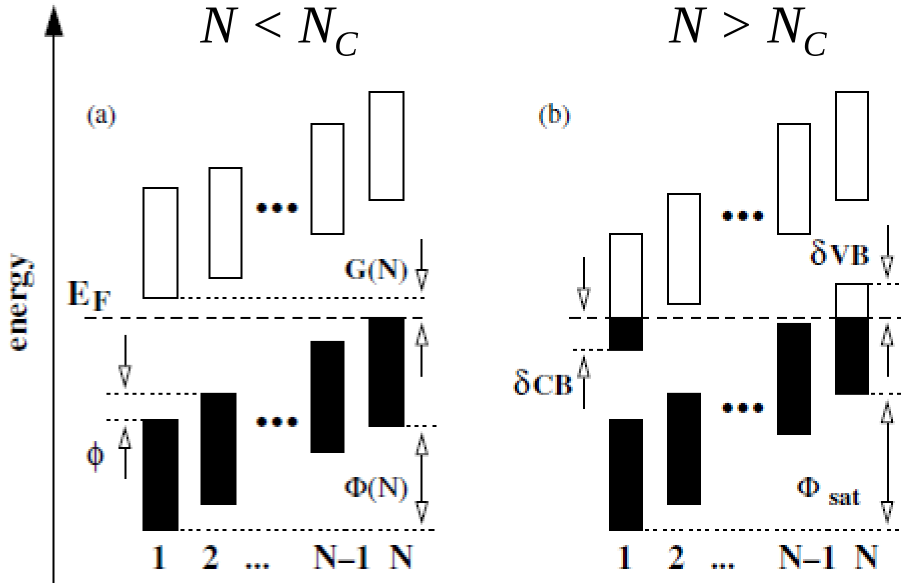
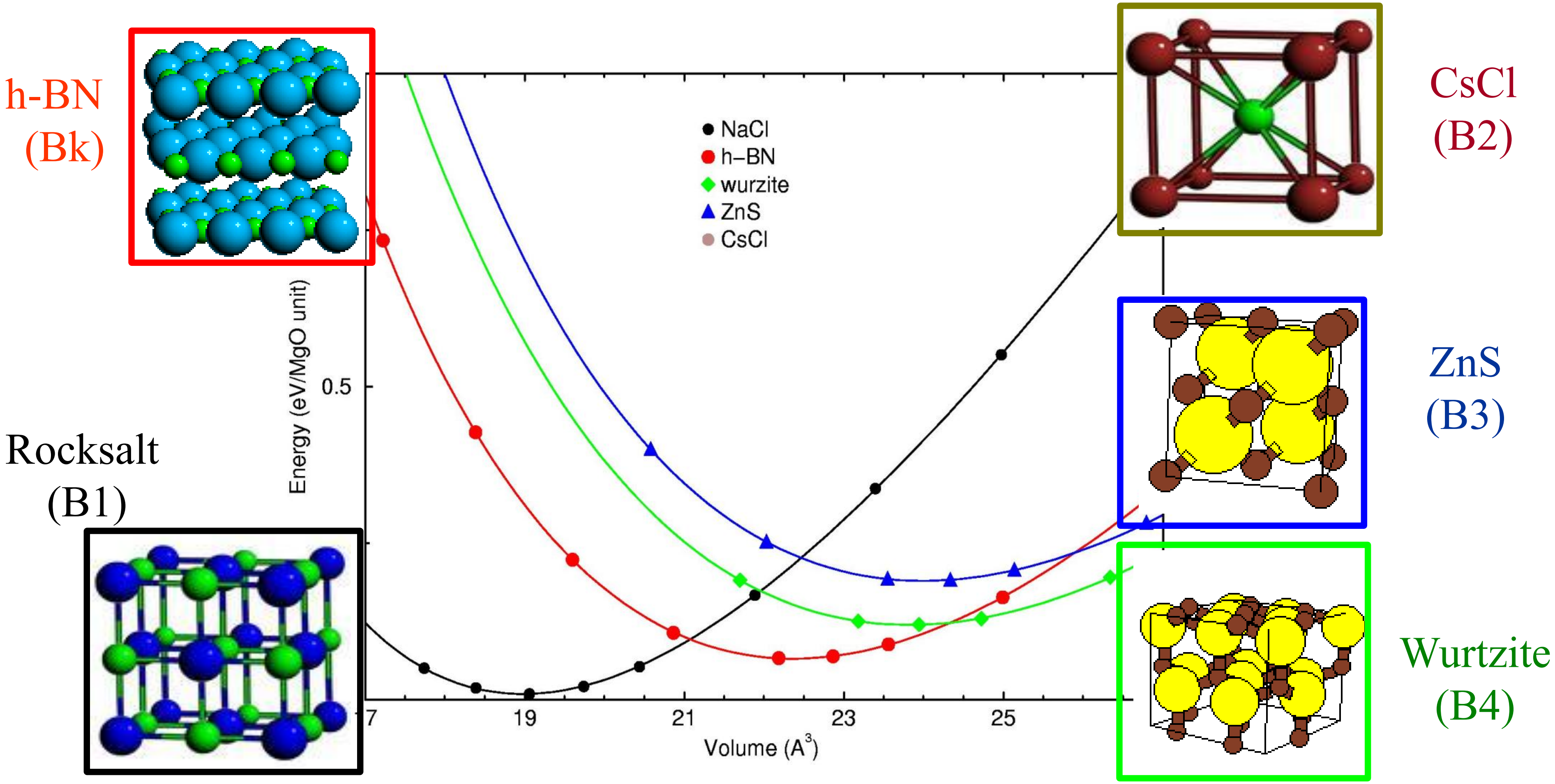


Figure 30. Sketch of the electronic structure of ultra-thin films in their low and high thickness regimes. 1st and Nth bilayer correspond, respectively, to cation- and anion-terminated film surfaces. Filled and empty electronic states are represented in black and white, respectively. E_F denotes the Fermi level. Reprinted

MgO: phase diagram (bulk)



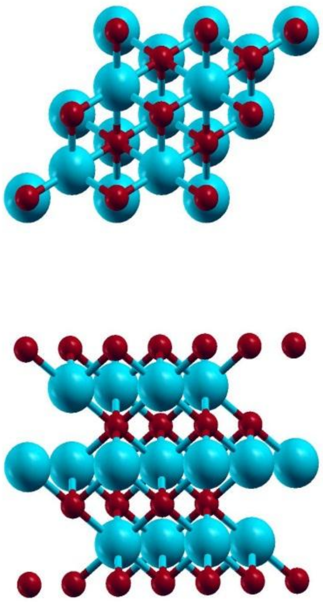
Bulk: B_1(rocksalt) more stable than Bk (hex)

However, the (111) surface is polar for B_1 while (0001) non polar in Bk

MgO: polarity of different structures

NaCl (111)

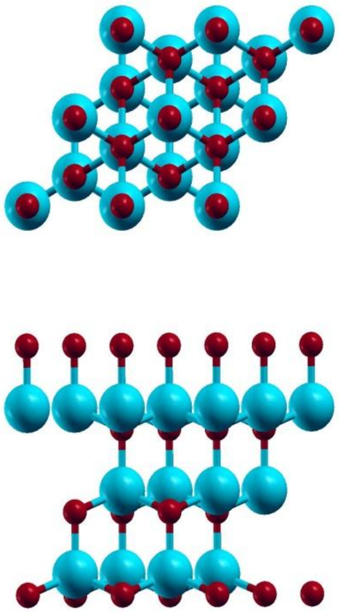
$R_1/(R_1+R_2) = 0.50$



fcc

ZnS (111)

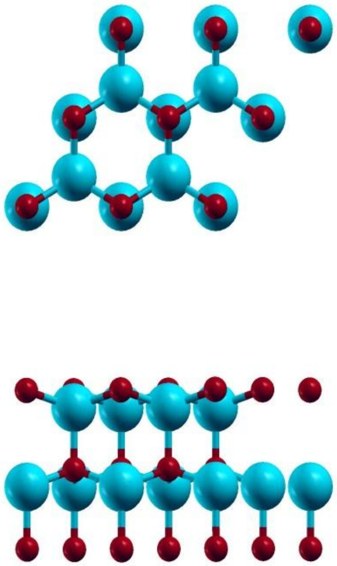
$R_1/(R_1+R_2) = 0.25$



fcc

wurzite (0001)

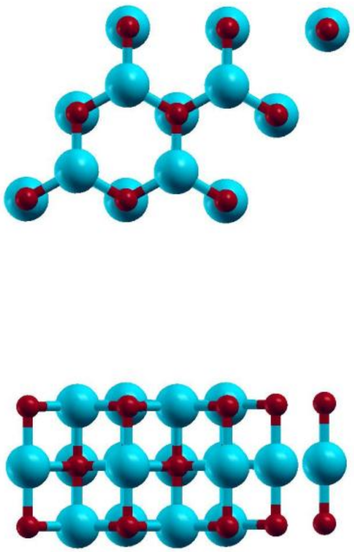
$R_1/(R_1+R_2) = 0.21$



hex

h-BN (0001)

$R_1/(R_1+R_2) = 0.00$

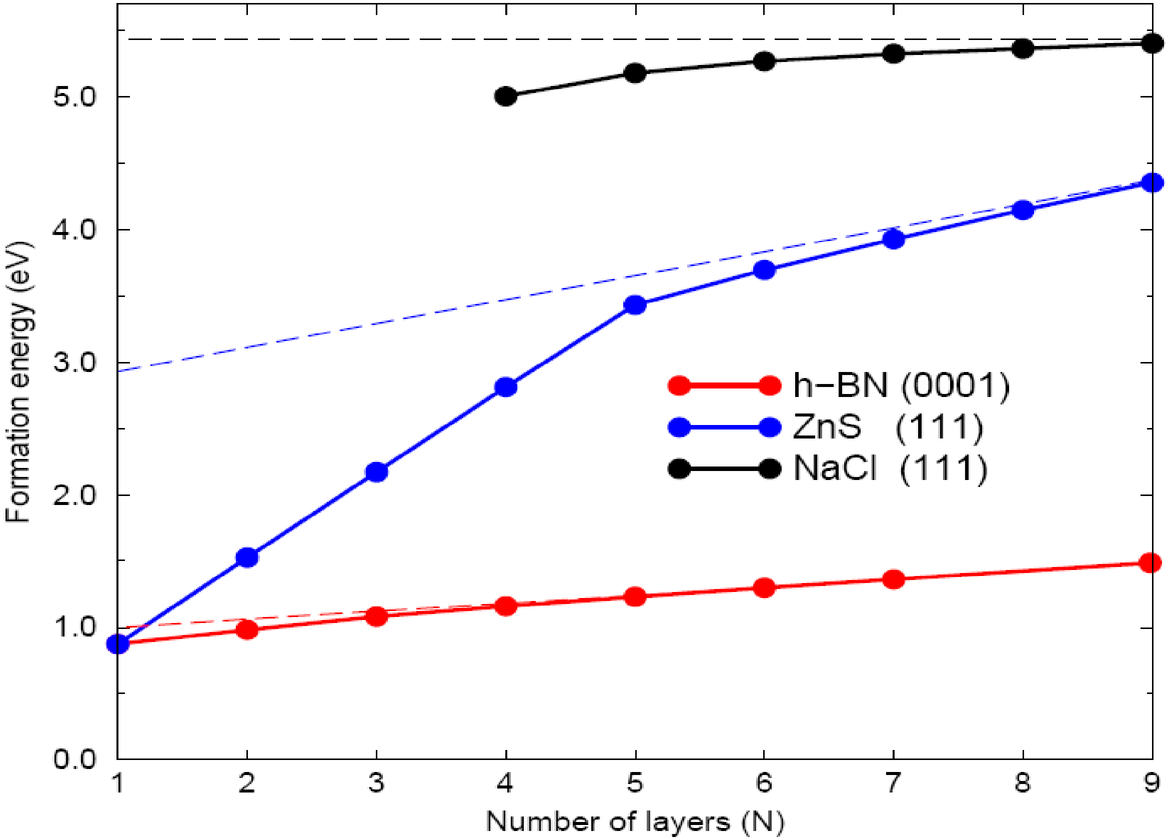


hex

MgO: phase diagram of free-standing films

Hexagonal B_k (0001)
more stable for N<30

B1 (2x2) octopole
more stable for N>30



➔ By keeping the planar hexagonal symmetry, there might be structural changes as a function of the slab thickness

MgO(111) / Ag(111) thin films

Models of the interface registry:

Goniakowski et al, PRL 2004

(1x1) interface:

MgOB1-Ag: lattice mismatch = 3.6%

MgOB3-Ag: lattice mismatch =10.8%

$MgOB_k$-Ag lattice mismatch = 20.2%

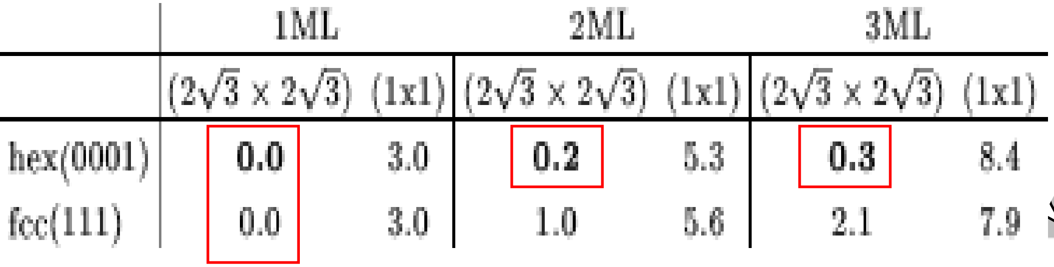
(2√3 x 2√3) R30° interface:

MgOB1-Ag: lattice mismatch = 10.8%

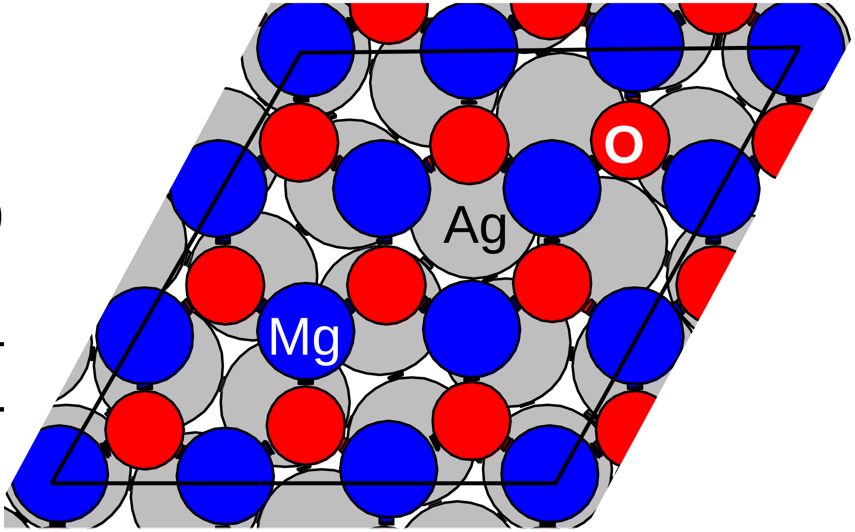
MgOB3-Ag: lattice mismatch = 2.6%

$MgOB_k$-Ag lattice mismatch = 4.9%

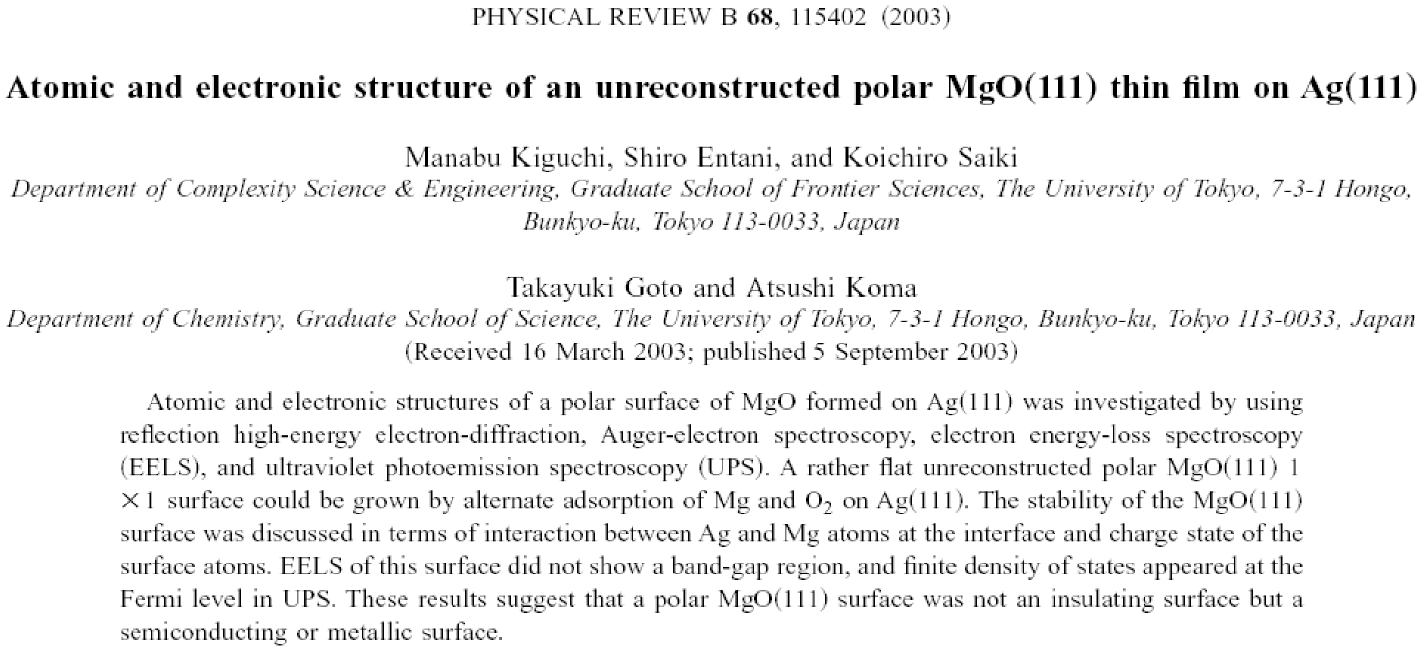
No means to simulate a fully relaxed interface. (2√3 x 2√3) R30° interface is nevertheless much more stable than (1x1)



	1ML		2ML		3ML	
	$(2\sqrt{3} \times 2\sqrt{3})$	(1x1)	$(2\sqrt{3} \times 2\sqrt{3})$	(1x1)	$(2\sqrt{3} \times 2\sqrt{3})$	(1x1)
hex(0001)	0.0	3.0	0.2	5.3	0.3	8.4
fcc(111)	0.0	3.0	1.0	5.6	2.1	7.9



MgO(111) thin films / Ag(111) : experiments



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Atomic and electronic structure of an unreconstructed polar MgO(111) thin film on Ag(111)

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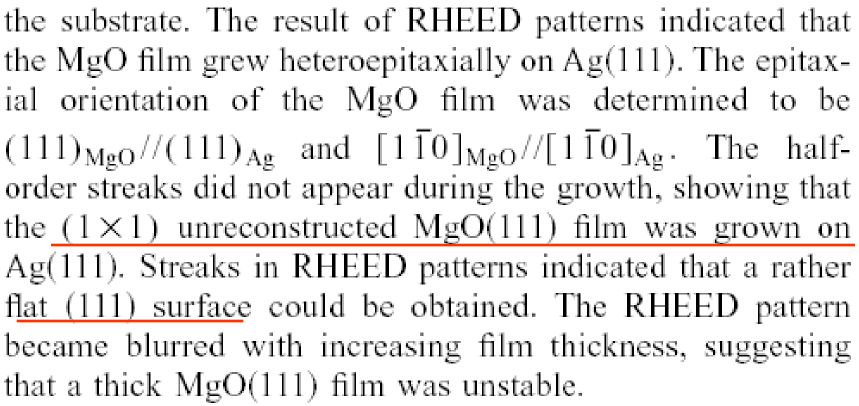
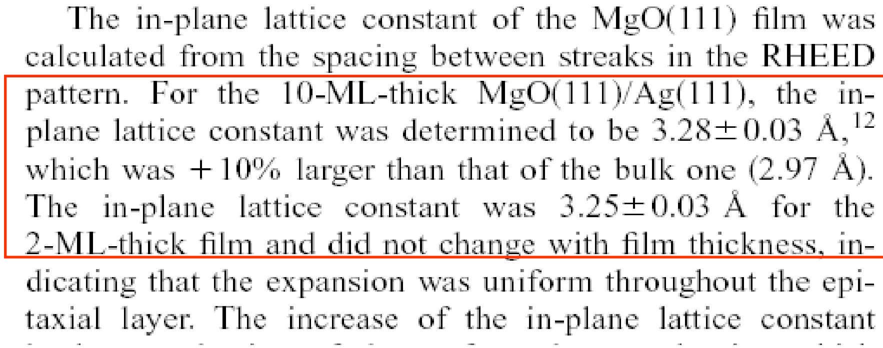
Atomic and electronic structures of a polar surface of MgO formed on Ag(111) was investigated by using reflection high-energy electron-diffraction, Auger-electron spectroscopy, electron energy-loss spectroscopy (EELS), and ultraviolet photoemission spectroscopy (UPS). A rather flat unreconstructed polar MgO(111) 1 ×1 surface could be grown by alternate adsorption of Mg and O_2 on Ag(111). The stability of the MgO(111) surface was discussed in terms of interaction between Ag and Mg atoms at the interface and charge state of the surface atoms. EELS of this surface did not show a band-gap region, and finite density of states appeared at the Fermi level in UPS. These results suggest that a polar MgO(111) surface was not an insulating surface but a semiconducting or metallic surface.



the substrate. The result of RHEED patterns indicated that the MgO film grew heteroepitaxially on Ag(111). The epitaxial orientation of the MgO film was determined to be $(111)_{MgO}//(111)_{Ag}$ and $[1\bar{1}0]_{MgO}//[1\bar{1}0]_{Ag}$. The half-order streaks did not appear during the growth, showing that the (1×1) unreconstructed MgO(111) film was grown on Ag(111). Streaks in RHEED patterns indicated that a rather flat (111) surface could be obtained. The RHEED pattern became blurred with increasing film thickness, suggesting that a thick MgO(111) film was unstable.



The in-plane lattice constant of the MgO(111) film was calculated from the spacing between streaks in the RHEED pattern. For the 10-ML-thick MgO(111)/Ag(111), the in-plane lattice constant was determined to be 3.28±0.03 Å,[12] which was +10% larger than that of the bulk one (2.97 Å). The in-plane lattice constant was 3.25±0.03 Å for the 2-ML-thick film and did not change with film thickness, indicating that the expansion was uniform throughout the epitaxial layer. The increase of the in-plane lattice constant

CONCLUSIONS

- The polar catastrophe never happens: polar surfaces are always compensated (no macroscopic polarization through the sample)

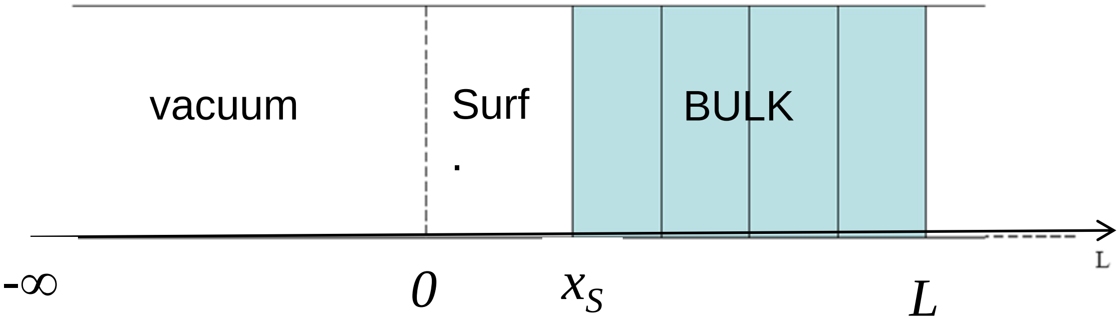
- Simple recipe to build up structural models of compensated polar surfaces (but reality is often beyond human imagination!)

- Polar surfaces of oxides are extremely sensitive to external conditions (chemical environment, temperature, annealing, etc.)
- ZnO(0001): Zn-vacancy ordering or H adsorption, as a function of environment
- MgO(111): the (2x2) reconstruction is a mixture of two (or more) structure
- Ultra-thin MgO(111) films: exotic phases?

1D Polarization (along the surface normal)

$$\bar{P}(x) = \frac{1}{A}\int dy \int dz\, P(x,y,z)$$

Lateral average of normal polarization



$$<\bar{P}(x)> = \frac{1}{L}\int_0^L dx\,\bar{P}(x) = \frac{1}{L}\left[x\bar{P}(x)\right]_0^L - \frac{1}{L}\int_0^L dx\, x\frac{d\bar{P}(x)}{dx} = \bar{P}(L) + \frac{1}{L}\cancel{\int_0^{x_S} dx\, x\bar{\rho}(x)} + \frac{1}{L}\int_{x_S}^L dx\, x\bar{\rho}(x)$$

$$\xrightarrow[L\to\infty]{} \bar{P}(x_S) + \frac{1}{L}\int_{x_S}^{L} dx\, x\,\bar{\rho}(x) = -\int_{-\infty}^{x_S} dx\,\bar{\rho}(x) + \int_{x_S}^{x_S+a} dx\, x\,\bar{\rho}(x) = -\sigma_S(x_S) + \frac{\bar{\mu}_B(x_S)}{aS}$$

Planar density, integrated in the surface region

First moment of the charge distribution (« bulk dipole » with origin at x_S)

Condition for electrostatic stability

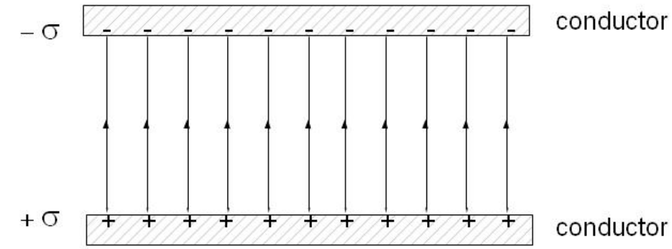
(no macroscopic polarization)

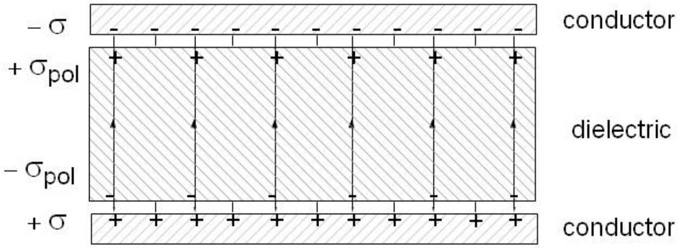
$$\boxed{Q_S(x_S) = \frac{\mu_B(x_S)}{a}}$$

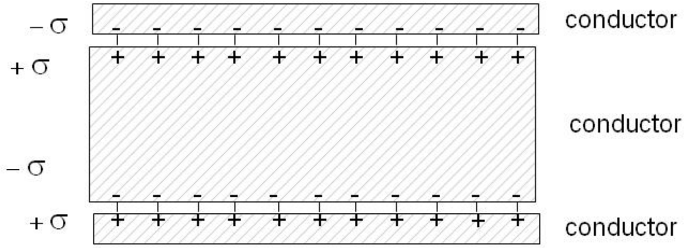
The surface charge at the surface/bulk border is related to the bulk dipole moment computed by choosing this border as the origin of the unit cell

Polarization in dielectrics (insulators)

From the very beginning:
Faraday's experience







Electric field between plates and dielectric

$$\sigma_{POL} = \vec{P}\cdot\hat{n} \;\Rightarrow\; E = \frac{\sigma - \sigma_{POL}}{\varepsilon_0}$$

Amount of polarization charge that is displaced out of the insulator (Ω is a volume including the dielectric, S the corresponding surface)

$$\int_\Omega d\Omega\, \rho_{POL} = \Delta Q_{POL} = -\int_S ds\, \vec{P}\cdot\hat{n} = -\int_\Omega d\Omega\, \vec{\nabla}\cdot\vec{P}$$

$$\Rightarrow \quad \rho_{POL} = -\vec{\nabla}\cdot\vec{P}$$

Macroscopic polarization:

$$<\vec{P}(\vec{r})> = \frac{1}{\Omega}\int_\Omega d^3r\, \vec{P}(\vec{r}) =$$

$$= \frac{1}{\Omega}\int_S ds\, \vec{r}\left(\vec{P}\cdot\hat{n}\right) + \frac{1}{\Omega}\int_\Omega d^3r\, \vec{r}\rho(\vec{r})$$

Surface contribution:

Bulk contribution:

The MgO(111) (2x2) reconstruction : the oct-O + hex-Mg model

Minimal (two-phase) model : hex-Mg + O-oct

So far, the best solution

- **Consistent with the observed surface decomposition at very low p_O**
- **The hex-Mg to O-oct transformation does not need big matter displacement (add a surface O and relax locally)**
- **Excellent fit of the GIXS data in a wide (p_O T) range**

CONCLUSION

Neither theory nor experience (taken separately) could explain the (2x2) reconstruction in terms of a comprehensive structural model

Only the conjunction of the two methods solved the issue, even for a “simple” system like MgO !

Finocchi et al, PRL 2004