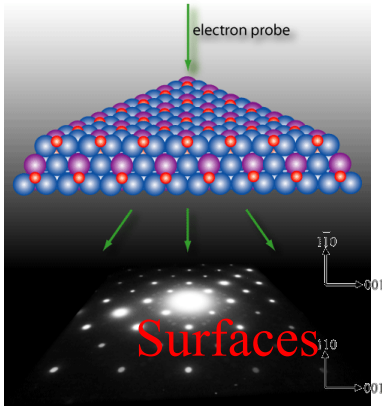
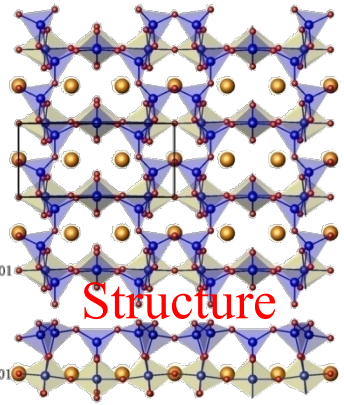
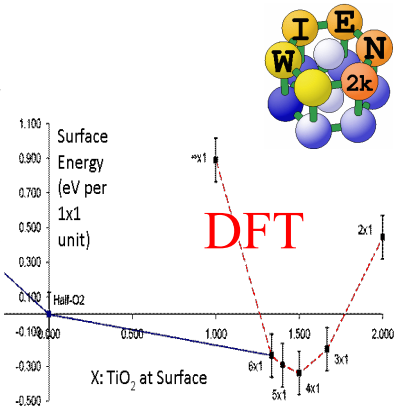
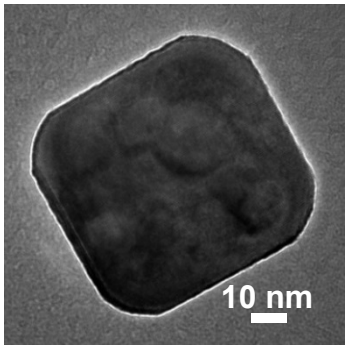
Pauling's Rules for Oxide Surfaces

L. D. Marks

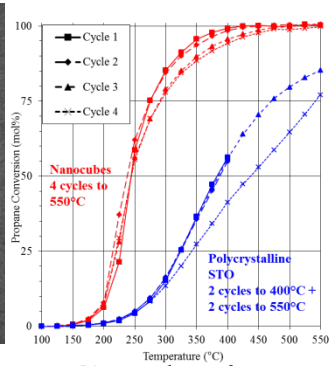








NanoCatalysts



Catalysis

Acknowledgements

TEM: N. Erdman (FEI), A. Subramanian (Intel), A. Chiaramonti (NIST), A. Becerra (Dow), A. Loon (Intel), J. Enterkin (Philips 66), D. Keinzle (Premier International), Y. Lin (W. Digital), L. Crosby, P. Koirala, Z Mansley (BNL)

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DEPARTMENT OF THE NAVY ONR Science & Technology

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Motivation

- Oxide surfaces are everywhere:
  - Everything in this room
  - Active catalysts
  - Catalytic supports
  - Multiferroic Oxides
  - Solid Oxide Fuel Cells
  - Corrosion products
  - Metal implants
  - Buildings (cement)

Baha'i Temple, Wilmette, IL

Looking to the future

Need to better understand oxide surfaces:

Reduce corrosion, ~3% of GDP

Reduce friction, ~ 5% of GDP

Understand why implants fail

Quality control for low-power oxide electronics

Deliberate design of better catalysts

Image Source:
John Stringer
Electric Power Research Institute

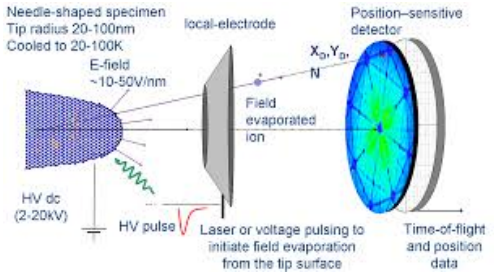
Corrosion Costs ~ 500 Billion EU/Yr in Europe

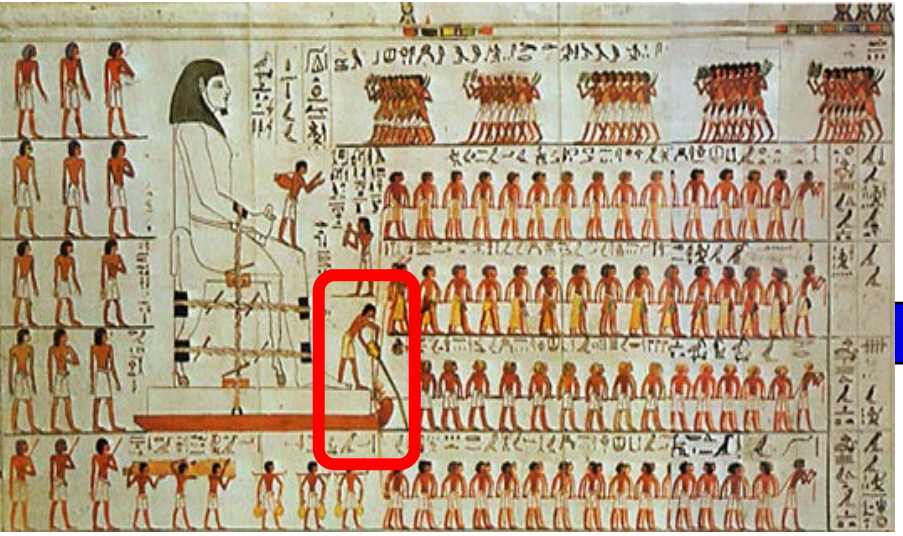
Rusted Deck and Ventilation Equipment
Source: www.corrdefense.org

Much of the science of corrosion was developed in the 1980's or earlier

What is really going on at the atomic scale, and near surface with potentials of ~ 10^9 Vm^{-1}?

What can 21st Century tools tell us about ways to minimize corrosion?





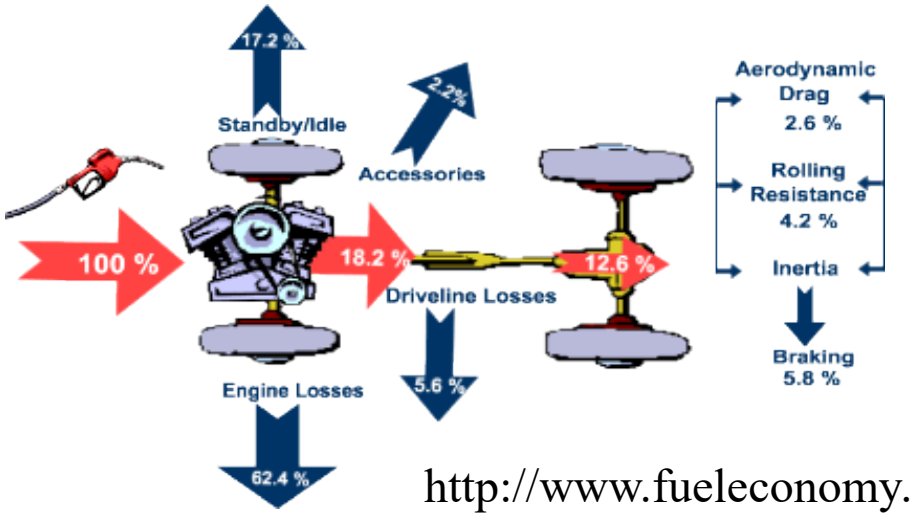
Friction

~5% of GDP

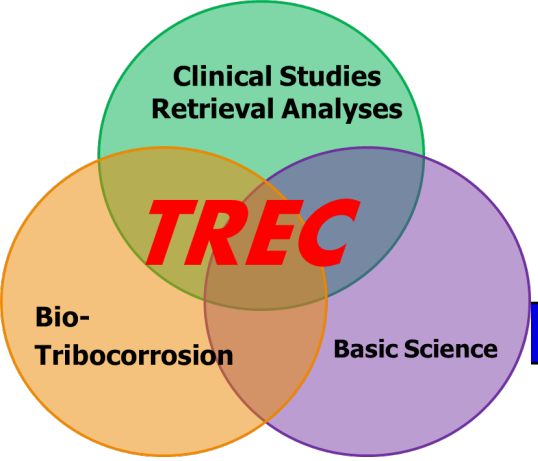
30% of power in a new auto engine

"…the greatest source of new energy is the energy we waste today."

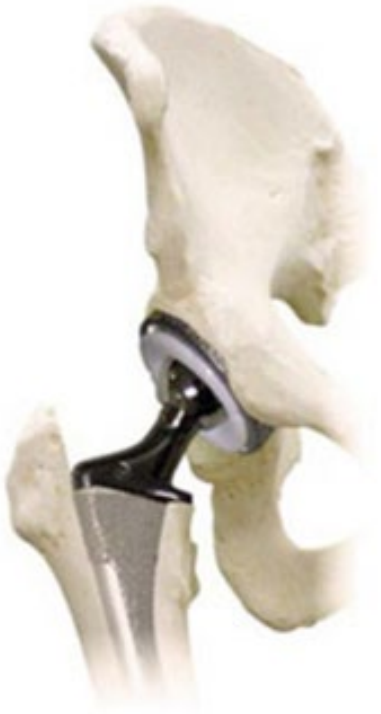
Samuel Bodman, U.S. Secretary of Energy, 2008



http://www.fueleconomy.gov



~1/2 Million/Yr in US



In 20 years implants will be grown (and/or printed)

That is not soon enough

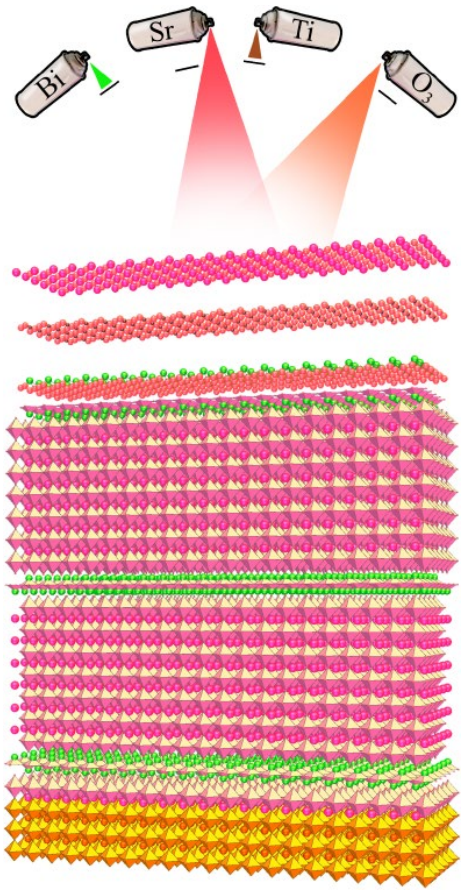
Metallic biomedical implants corrode in the human body leading to severe problems

What is going on? How do we improve them? Do different surface oxides matter?

UNIVERSITÄT DUISBURG ESSEN

RUSH UNIVERSITY MEDICAL CENTER

Oxide Electronics



For oxide electronics to be commercial five-sigma reproducibility will be required

What are the real details, atom-by-atom of oxide MBE growth?

How do we control it, precisely?

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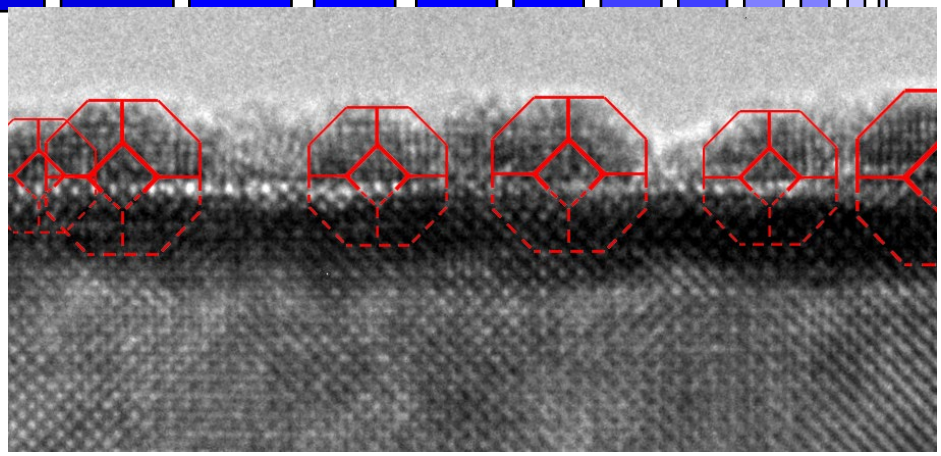
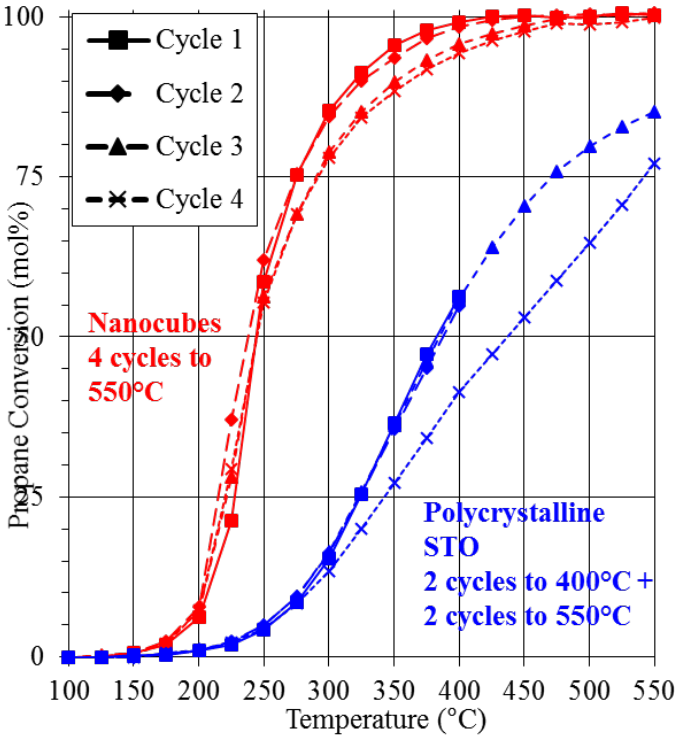
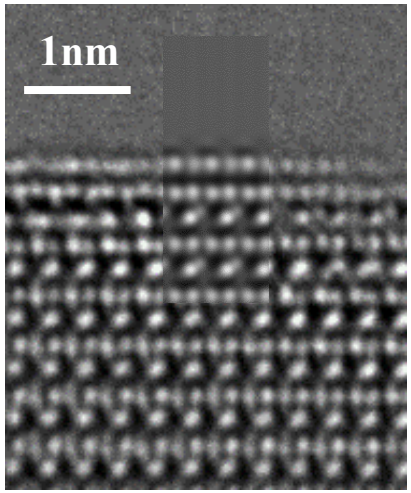
Better Catalysts, *by Design*







TiO_2 DL

Control the nanoparticles by epitaxy on oxides

J. A. Enterkin, K. R. Poeppelmeier, L. D. Marks, Nano Lett. 11, 993 **(2011)**

ICEP

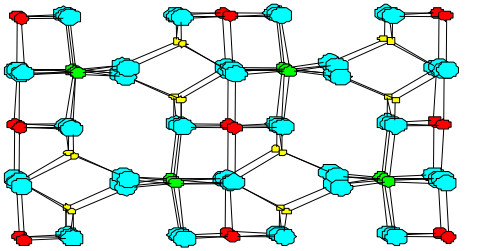
….at an oxide surface

Typical cartoons/visuals used in the literature

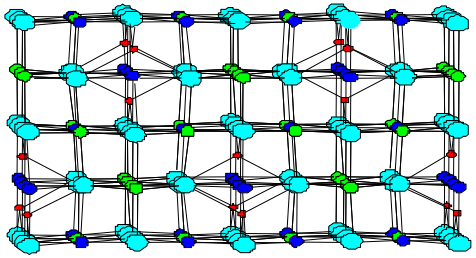
$Mg_3V_2O_8$

H_2 / propane

$Mg_3V_2O_6$

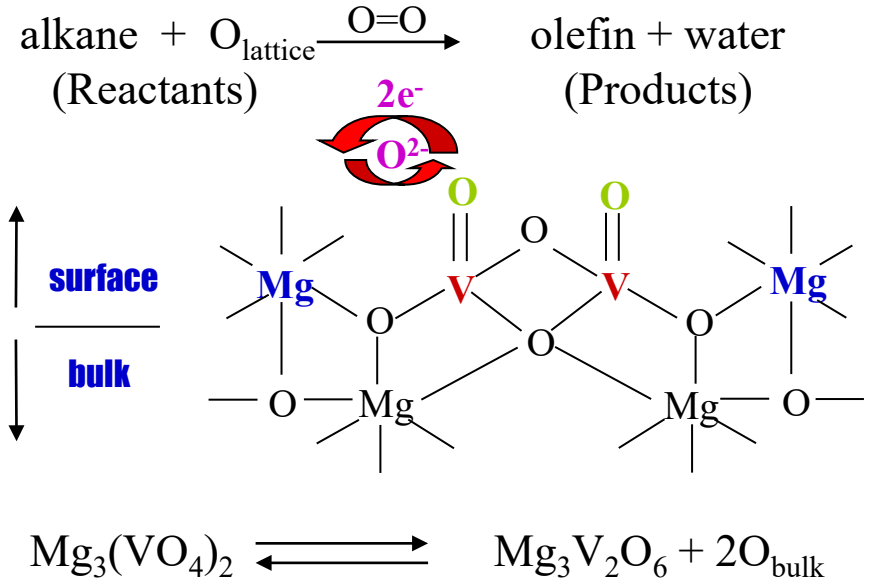


[100]



[011]

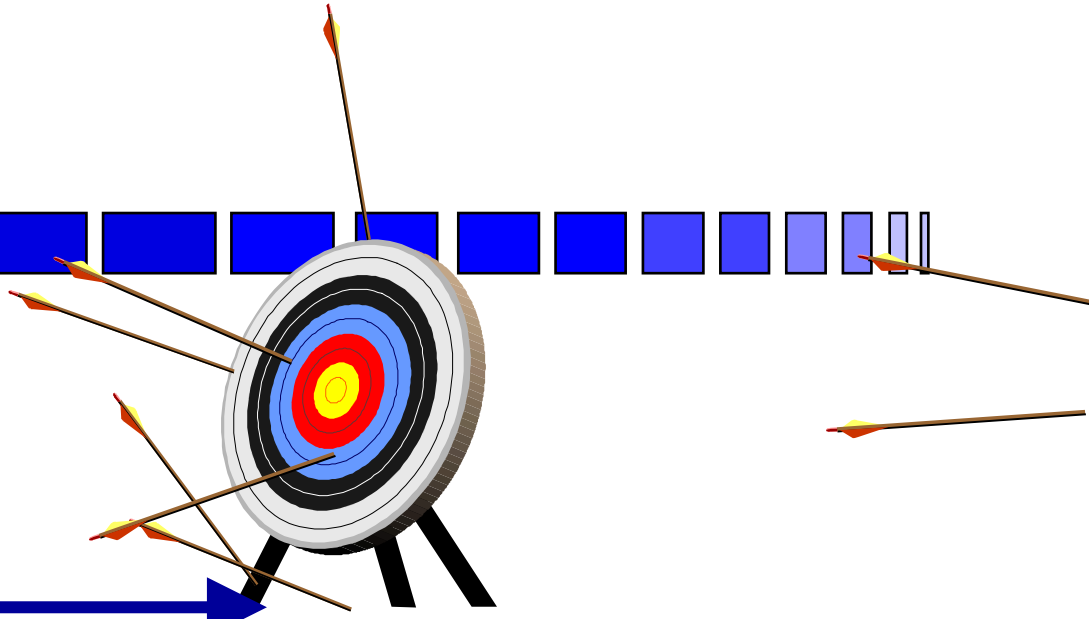
The activity and selectivity are closely related to the structures of the catalyst used.



This cartoon is almost certainly far from reality about the surface structure

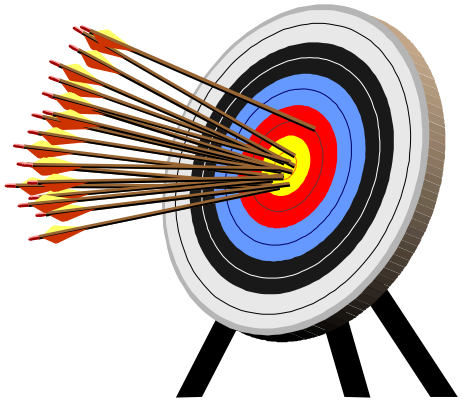
Broad Vision

Discovery-based



Time

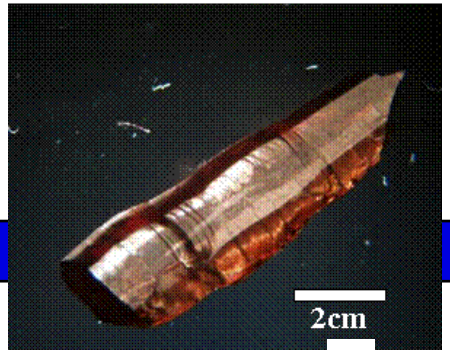
Oxide Surfaces
By Design



Time

Adapted From: Paget Donnelly, Nanomaterials By Design, Chemical Industry R&D Roadmap, www.chemicalvision2020.org/downloads/nanochemroadmap_presentation_1-5-04.ppt

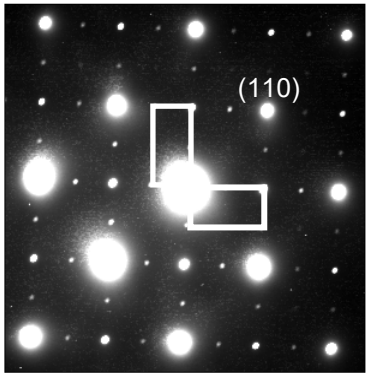
Single Crystal Growth



Corrosion

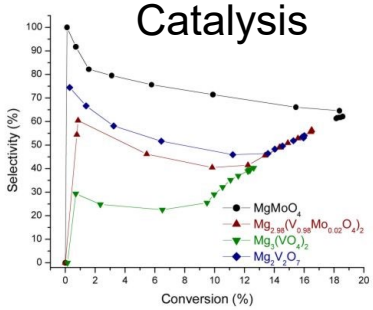
Tribology

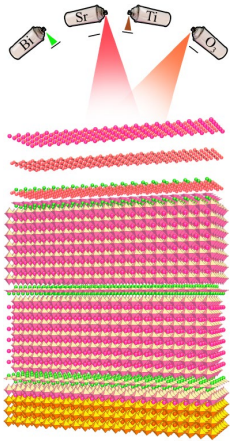
Crystallography



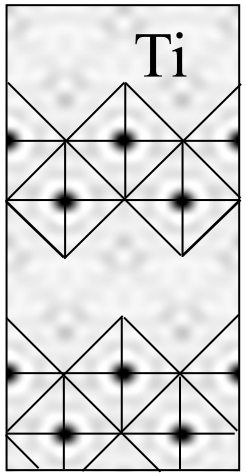
Bridge the Materials Gap

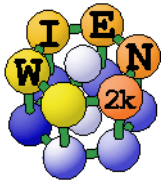
Catalysis

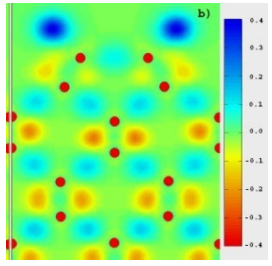




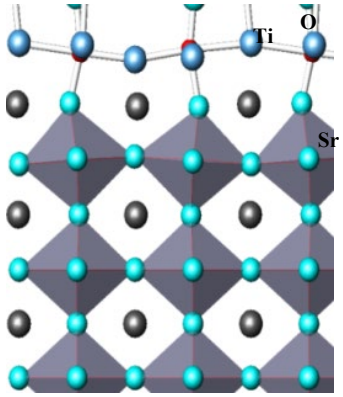
Growth



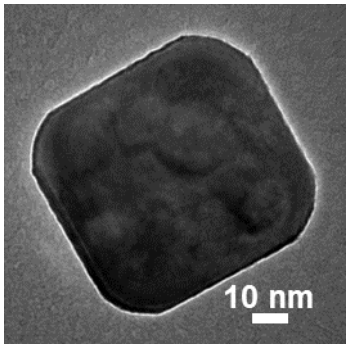




Direct Methods & DFT

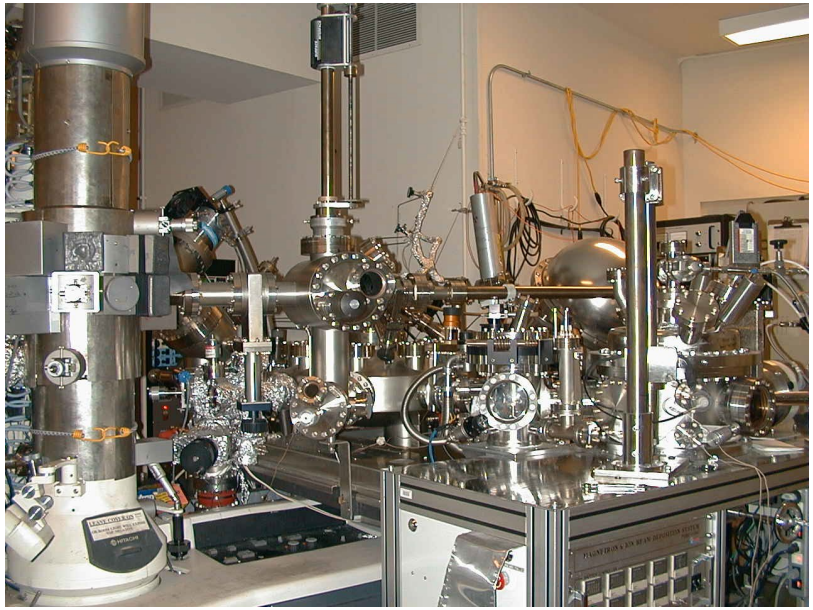


Surface Structure



Shape Control

Key experimental tools

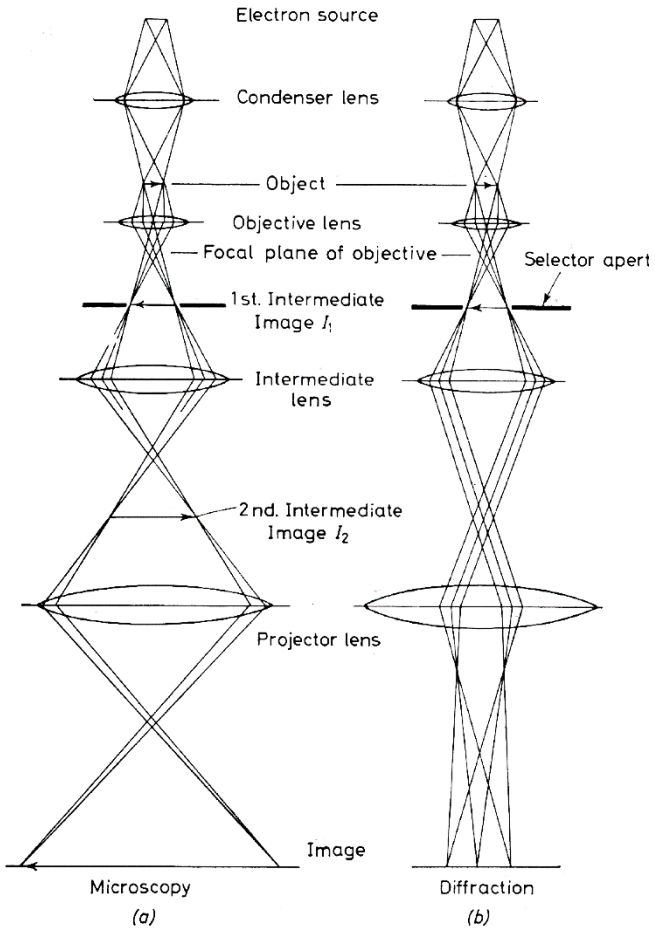


100-300 keV

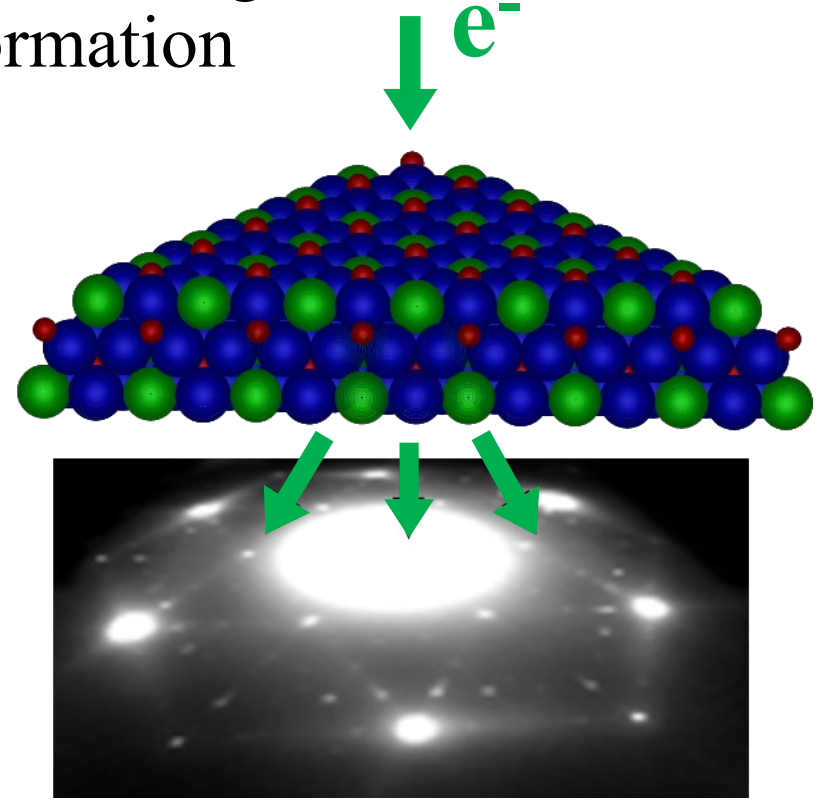
7 GeV

Both give approximately kinematical data for surfaces
Weak Signals
Electron scattering is substantially stronger than x-ray, better S/N

First Core Method



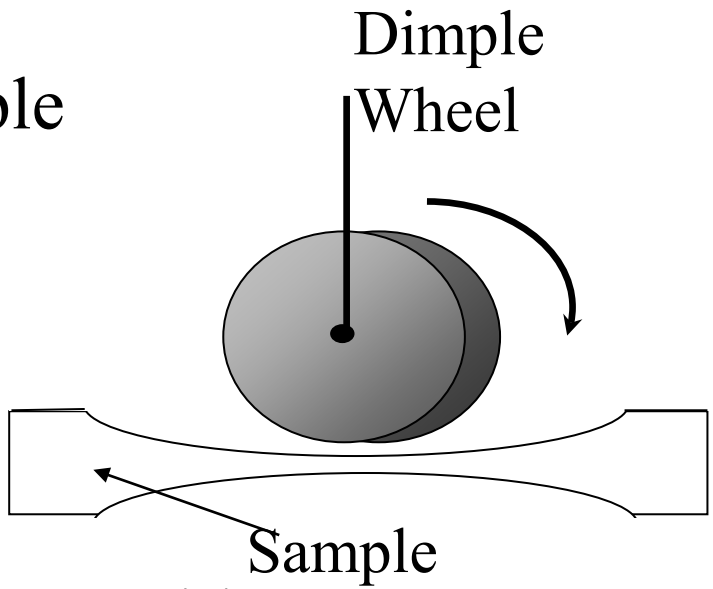
- Incident 100-300 kV electrons
- Collect images or diffraction information

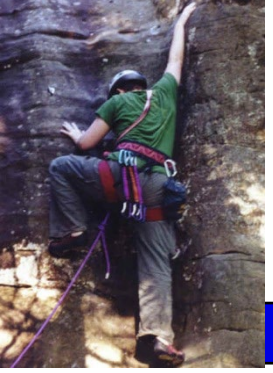


+SXRD, STM, XPS, UPS, DFT….

Sample preparation (an art)

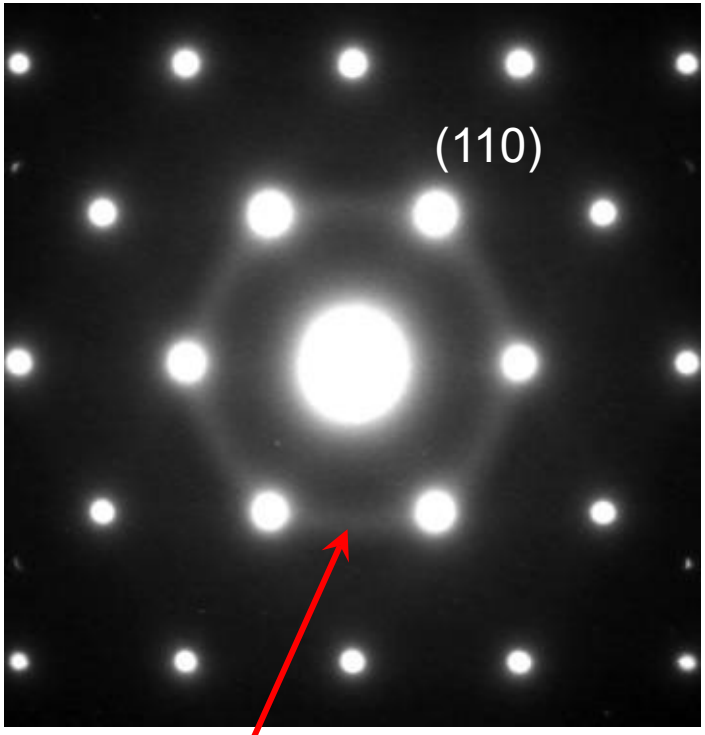
- Cut 3mm disc or mount sample
- Dimple thin to 10 μm
- Thin to < 0.1 μm
  - Ion beam (damage)
  - Chemical (?)
- Anneal damage (*carefully!)*
- Last step similar to making new oxides
  - Try a time/temperature: if it works, celebrate
  - If it does not, try again…..
  - All you need are enough grads/undergrads

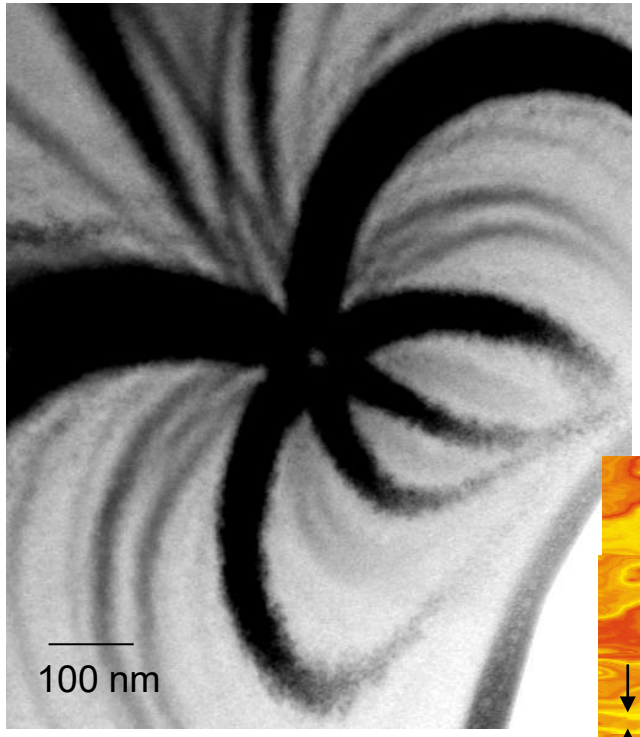


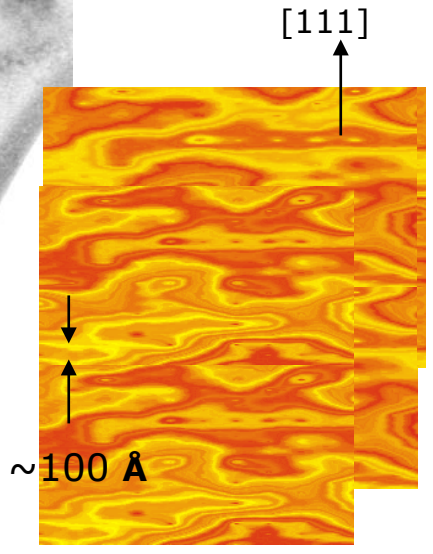


$SrTiO_3$ (111): Pre-annealing

Sample is under stress, disordered, and non-stoichiometric

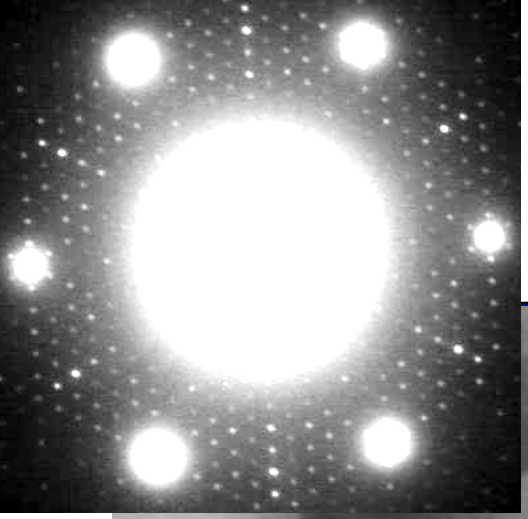


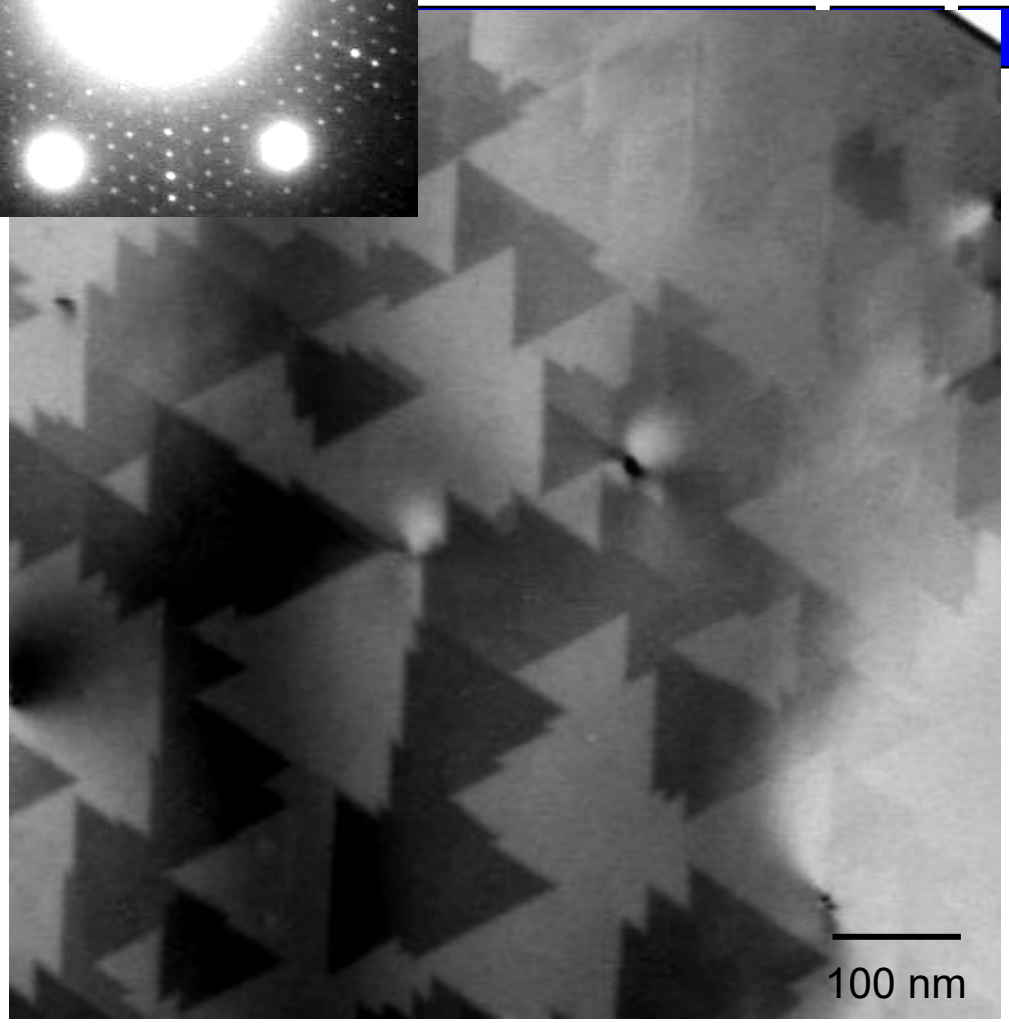




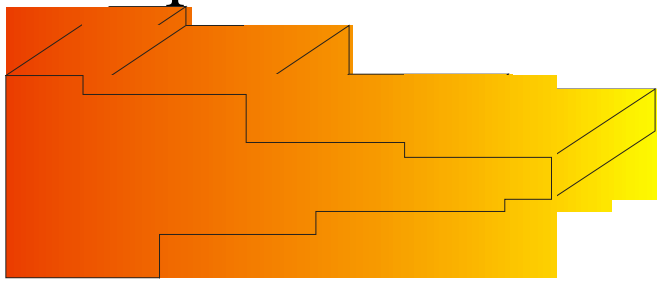
A. N. Chiaramonti *et al.*, Surf. Sci. **602**, 3018 (2008).

$SrTiO_3$ (111): Annealed





- Surfaces are:
  - ordered, flat
  - covered in large often triangular terraces and step bunches
- Reconstructed
- Air stable (months)
- Reproducible

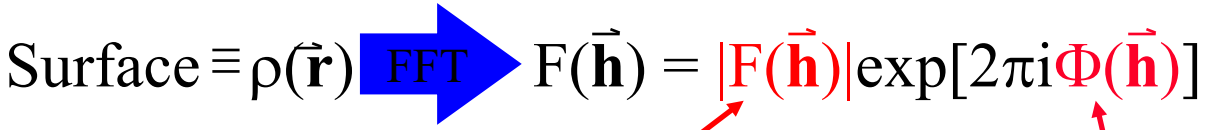


A. N. Chiaramonti *et al.*, Surf. Sci. **602**, 3018 (2008).

How to solve a structure?

- Guess, then refine
  - Will always give something, but if the guess is wrong GIGO
- Use Patterson function
  - Difficult for complicated structures
- Get an image
  - STM is hard to interpret
  - HREM is difficult for surfaces (and not always possible)
- Use DFT
  - If the original guess is wrong, GIGO
  - Functionals can be (very) inaccurate for oxides
- Try something else?

Diffraction Phase Problem



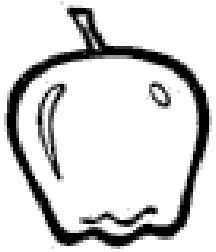
Measured diffraction intensities

$|F(\vec{h})| = [I(\vec{h})]^{1/2}$

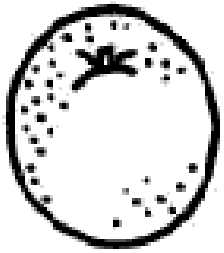
Unmeasured

An equal opportunity problem – true for x-ray and electron diffraction

Phase: Apples & Oranges



FT ➡ $A_a \exp(-i \phi_a)$



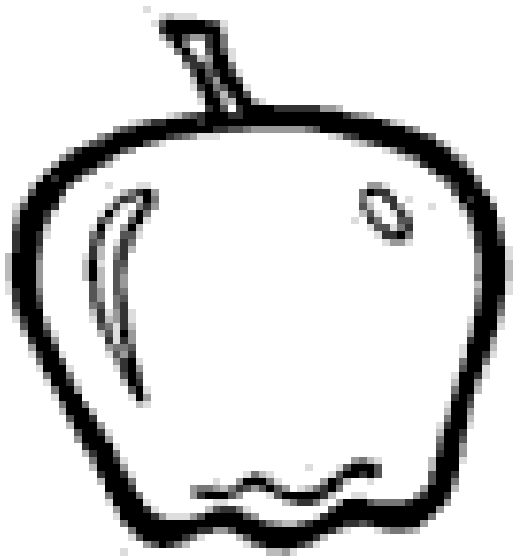
FT ➡ $A_o \exp(-i \phi_o)$

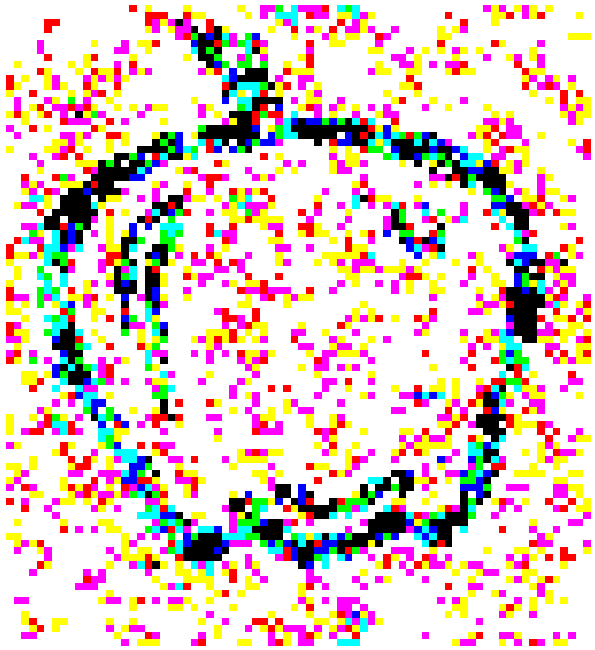
\+

$A_o \exp(-i \phi_a)$ ➡ IFT ➡ { Oranle ? Appge ?

Phase of Apple + Amplitude of Orange = ?

Phase of Apple = Apple





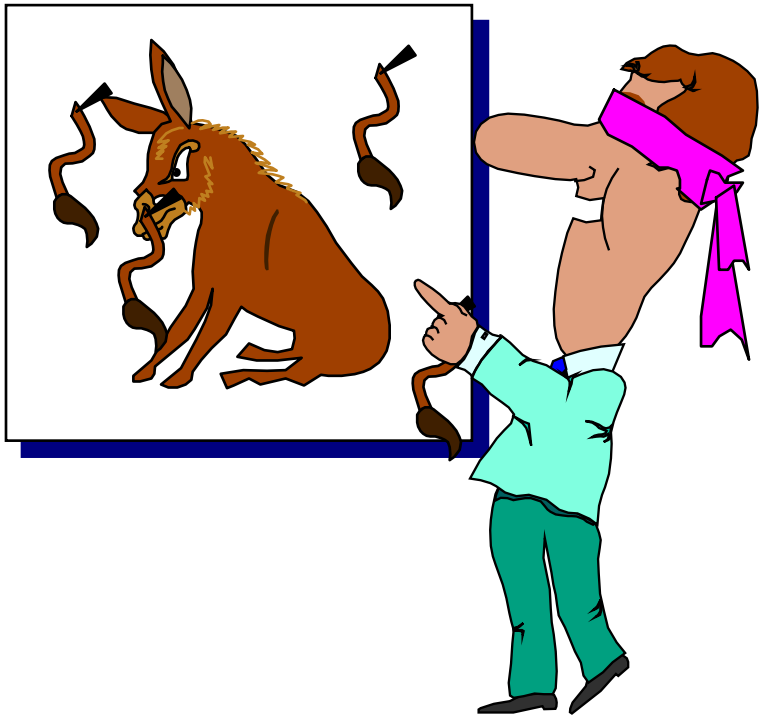
$FT^{-1}\ \{A_o \exp(-i\ \phi_a)\}$ ➡ Apple

Phase is more important than amplitude

Second Core: Solve Structures

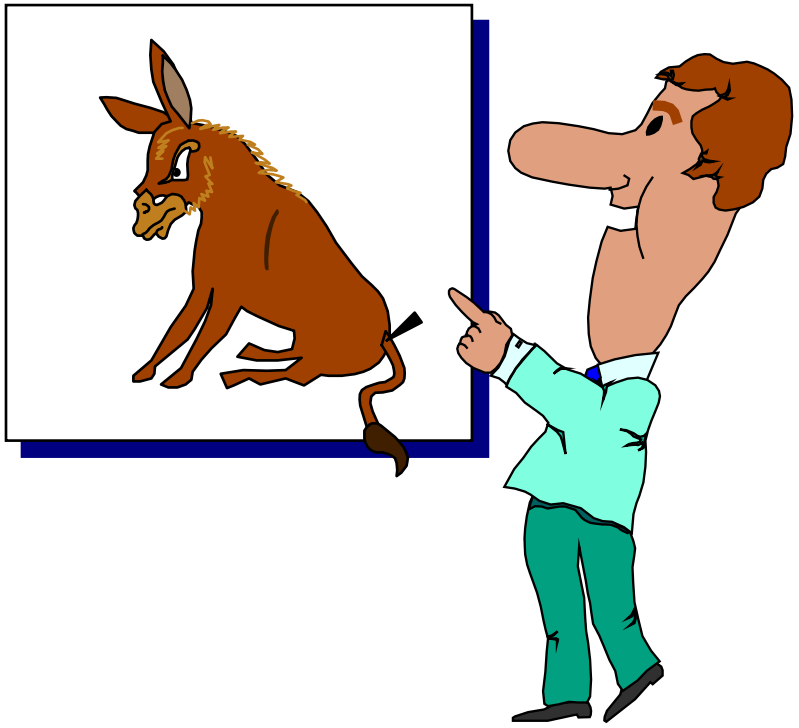
Indirect Methods:

"Trial and Error"



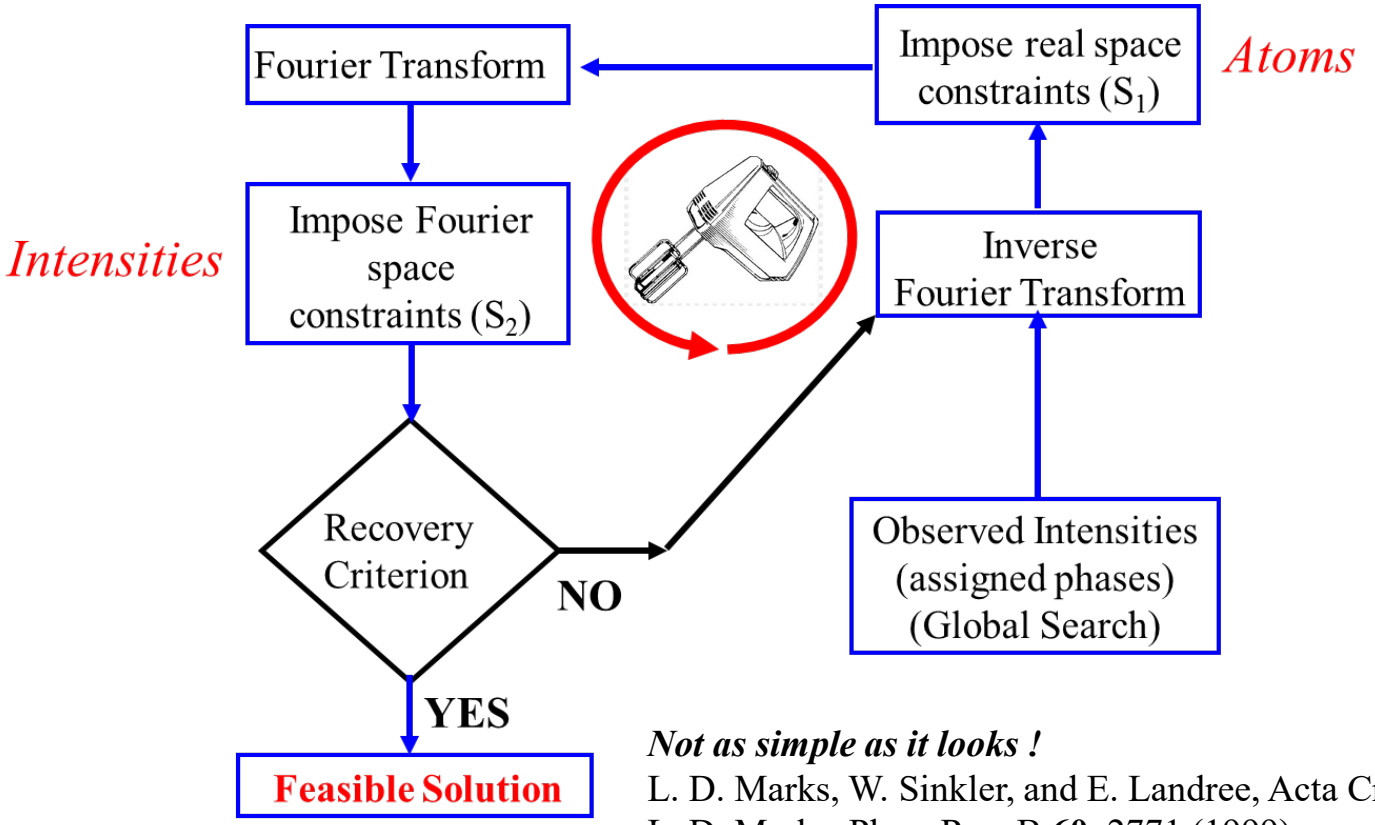
Direct Methods:

Using available information to find solutions



Second Core: Direct Methods

R. Gerchberg and W. O. Saxton, Optik 35, 237 (1972)



Not as simple as it looks !

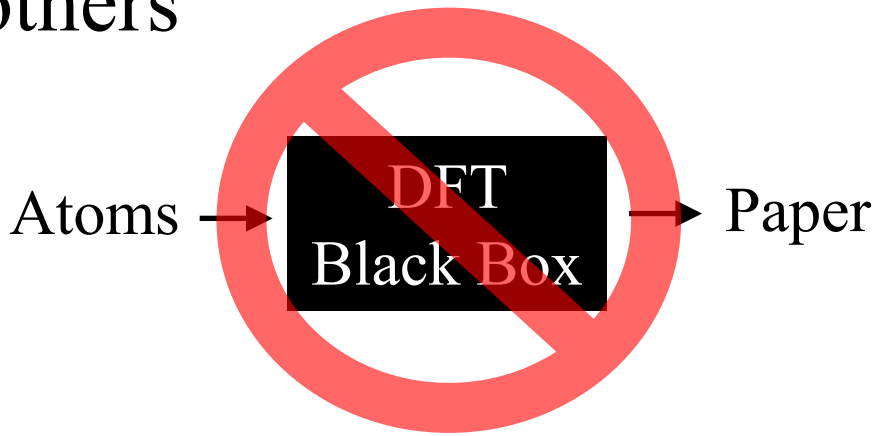
L. D. Marks, W. Sinkler, and E. Landree, Acta Cryst A**55**, 601 (1999)

L. D. Marks, Phys. Rev. B **60**, 2771 (1999)

L. D. Marks *et al.*, Surf. Rev. Lett. **5**, 1087 (1998).

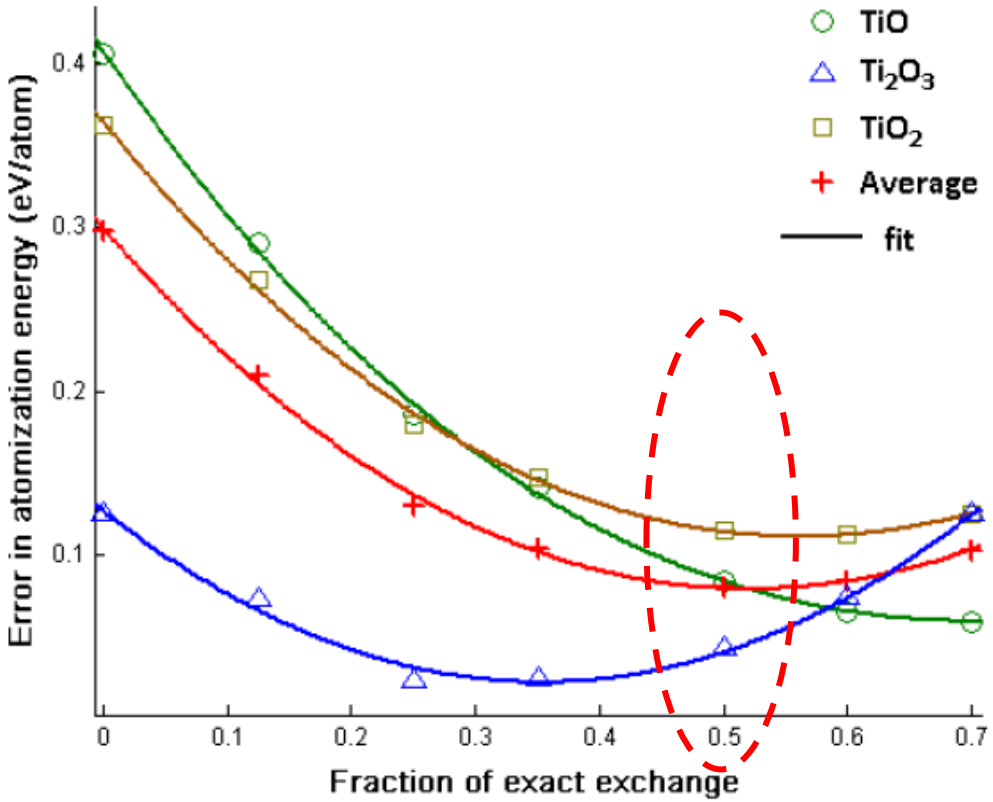
Third Tool: DFT

- GIGO – DFT only refines, it is not a search method
- DFT energies can have serious errors for oxides
- All DFTs are equal, but some DFTs are ***much*** more equal than others



Apologies to George Orwell

Example of error estimation

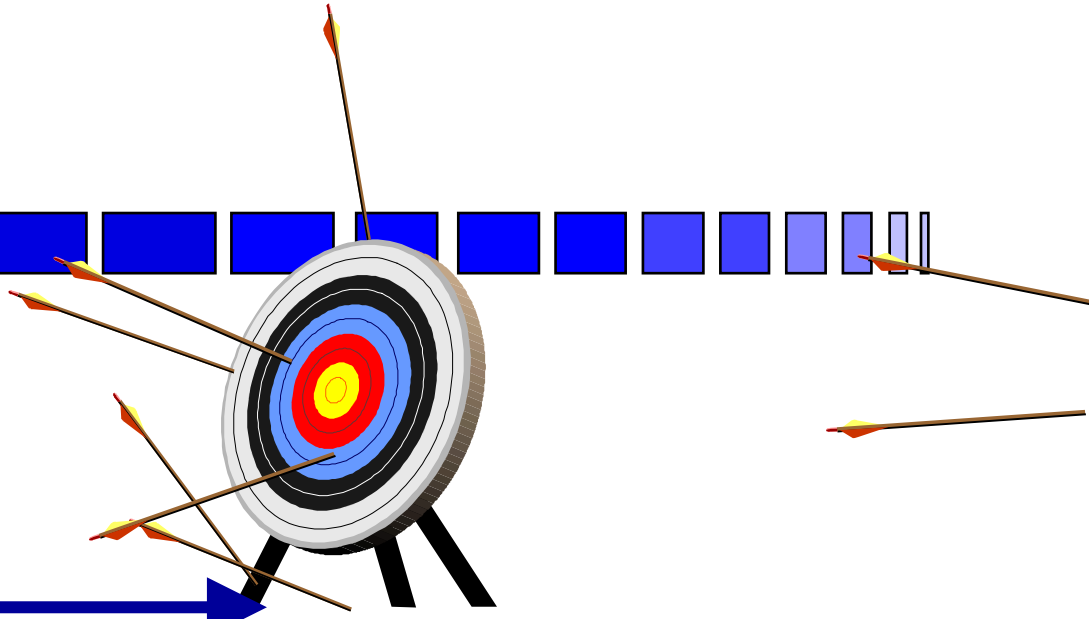


Calculate the atomisation energy for various TiO_x clusters as a function of on-site exact exchange in TPSSh

e.g. Surf. Sci. 2009, 603 (14), 2179 (2009); Surf. Sci. 604 (2), 155 (2010)

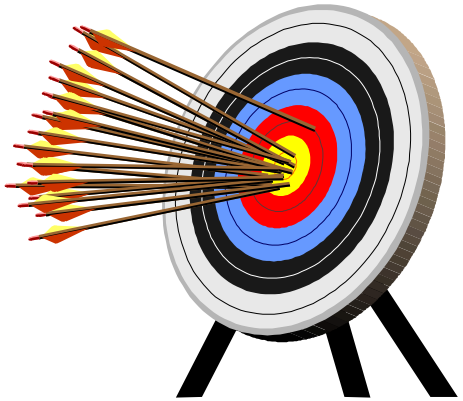
Broad Vision

Discovery-based



Time

Oxide Surfaces
By Design



Time

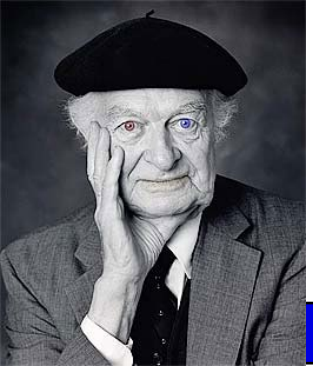
Adapted From: Paget Donnelly, Nanomaterials By Design, Chemical Industry R&D Roadmap, www.chemicalvision2020.org/downloads/nanochemroadmap_presentation_1-5-04.ppt

Broad Vision

- Solving surface structures is good
  - Predicting the structure without analysis is better
- A good inorganic chemist can predict the structure of a bulk oxide….without calculation
  - Success rate is not 100%, but is close
- What about oxide surfaces?

Oxide Surfaces from the Bulk

- Bulk oxide structure is a chemical problem
- Requires consideration of local bonding – tight-binding approximation, not delocalized electrons
- Why not apply the same thinking to oxide surfaces?
- ***Need "why", not just "what" for design***



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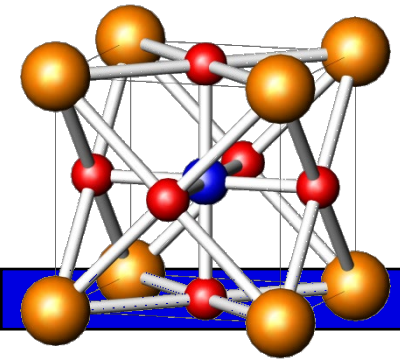
L. Pauling, The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* **51**, 1010 (1929).

Now for some Science



Perovskite Surfaces (2002)

- ~43,000 articles on perovskites
  - ~21,000 on strontium titanate
- 637 articles on perovskite surface structures
  - 571 articles say what reconstruction is present
- None provided crystallographic solutions

.....

- 2019 Update (Google Scholar)
  - Perovskite Surface Structure ~ 366,000
  - Perovskite Surface Atomic Structure ~ 147,000

$SrTiO_3$ reconstructions (2019)

(001)	(110)	(111)
2x1	3x1	2x2
√2x√2	4x1	3x3
2x2	5x1	4x4
c4x2	6x1	√7x√7
c6x2	2x4a,b	√13x√13
Dilines	2x5a,b	5x5
Trilines		6x6
√5x√5		9x9
√13x√13		

Published
Today (Published)

- About 40 different reconstructions reported
- 20 have been solved
- Reduced surfaces unclear
- The most complex surfaces of *any* known material

Three examples

- Connect TED, DFT, STM (and chemistry); the $SrTiO_3$ (110) surface
- What lies beyond order: glass-like tilings (constrained Ising model) on $SrTiO_3$, the $\sqrt{13}x\sqrt{13}$ (001) reconstruction
- Entropy and disorder, more complex Pott's model for $SrTiO_3$ (111)

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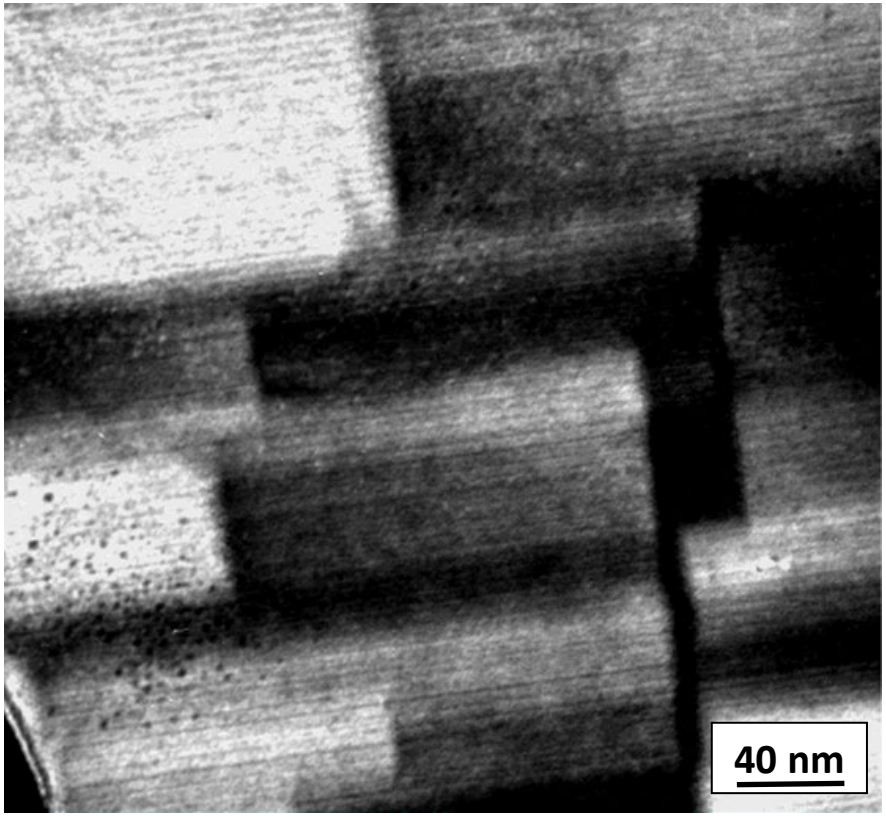
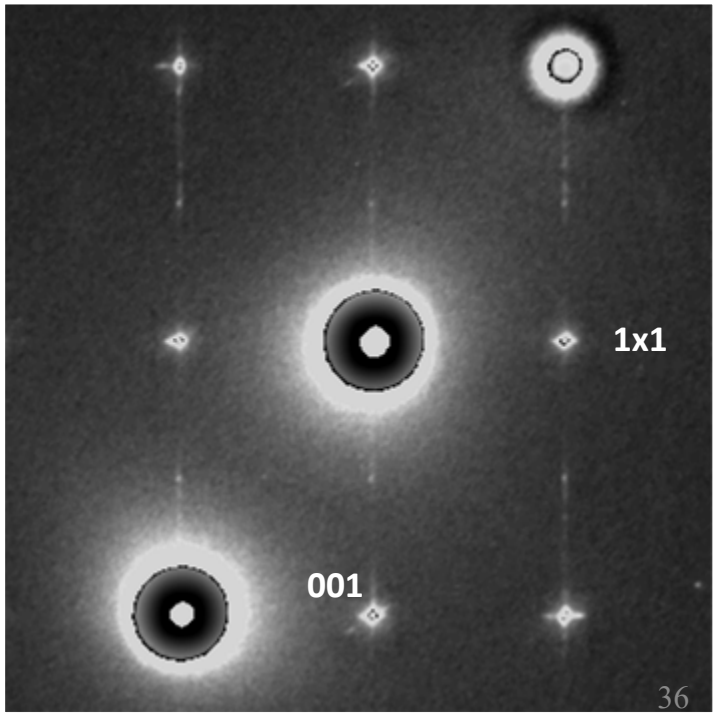
$SrTiO_3$ (110): 900C in O_2

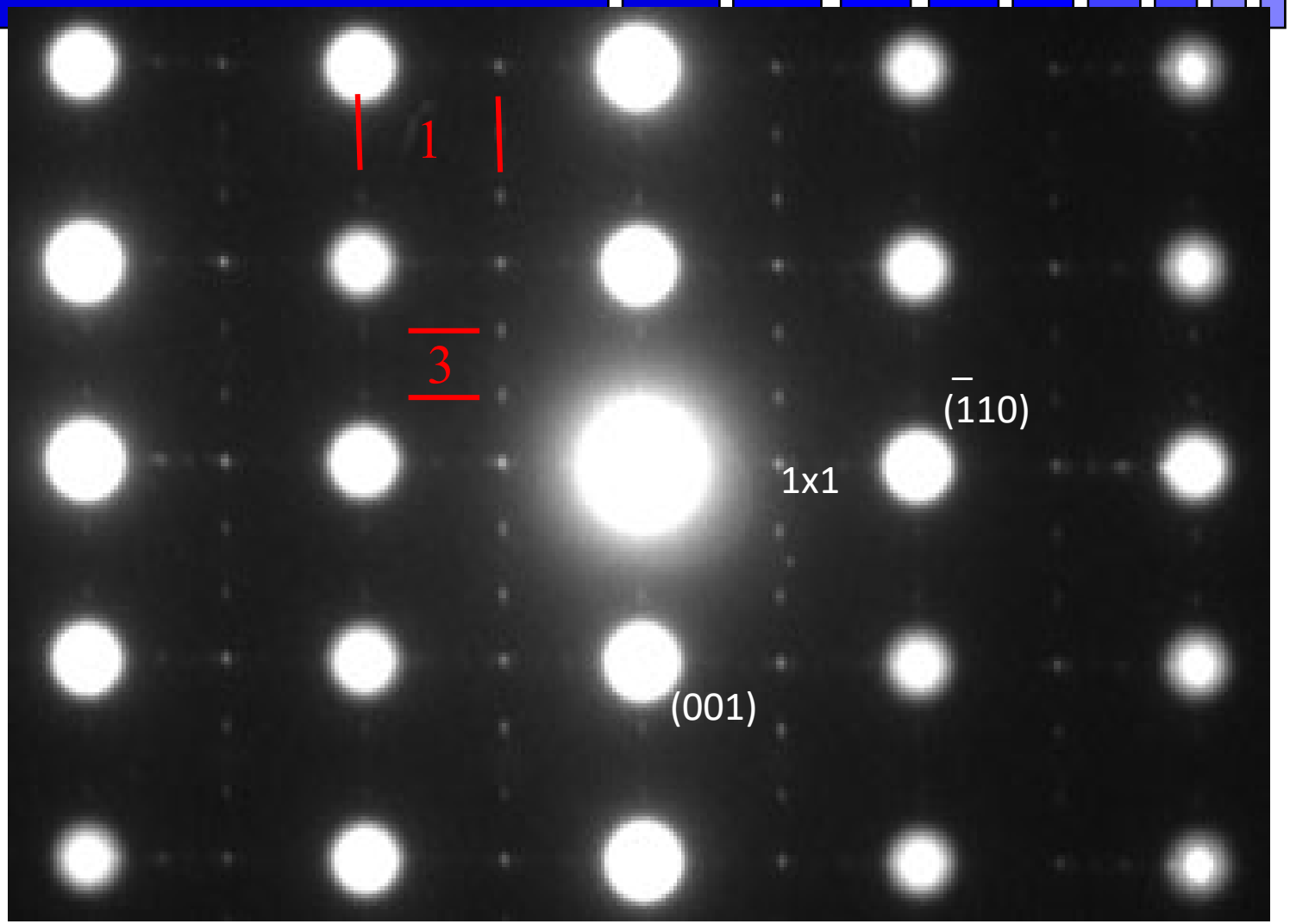
Dark Field



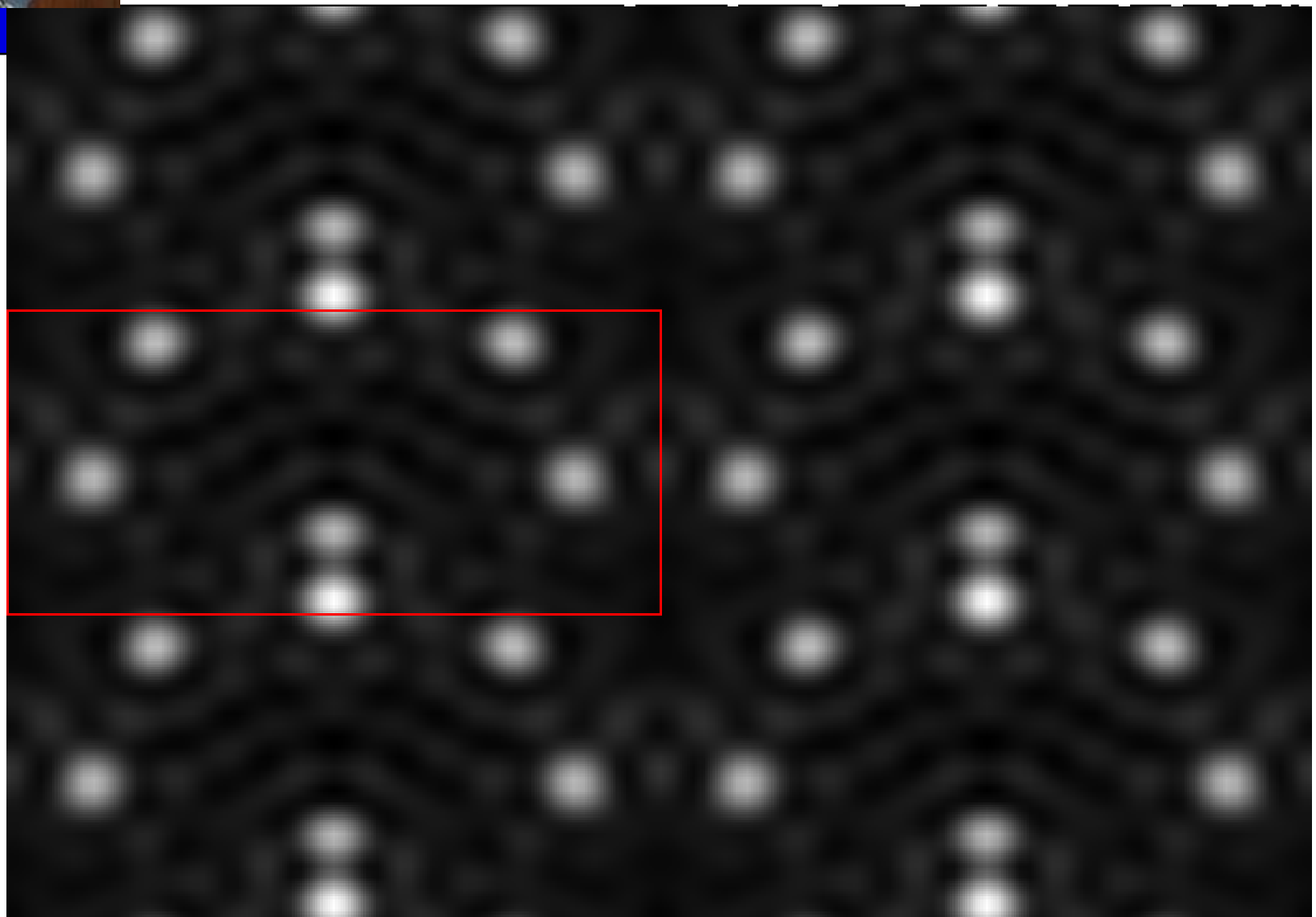


N. Erdman, PhD Thesis, 2002

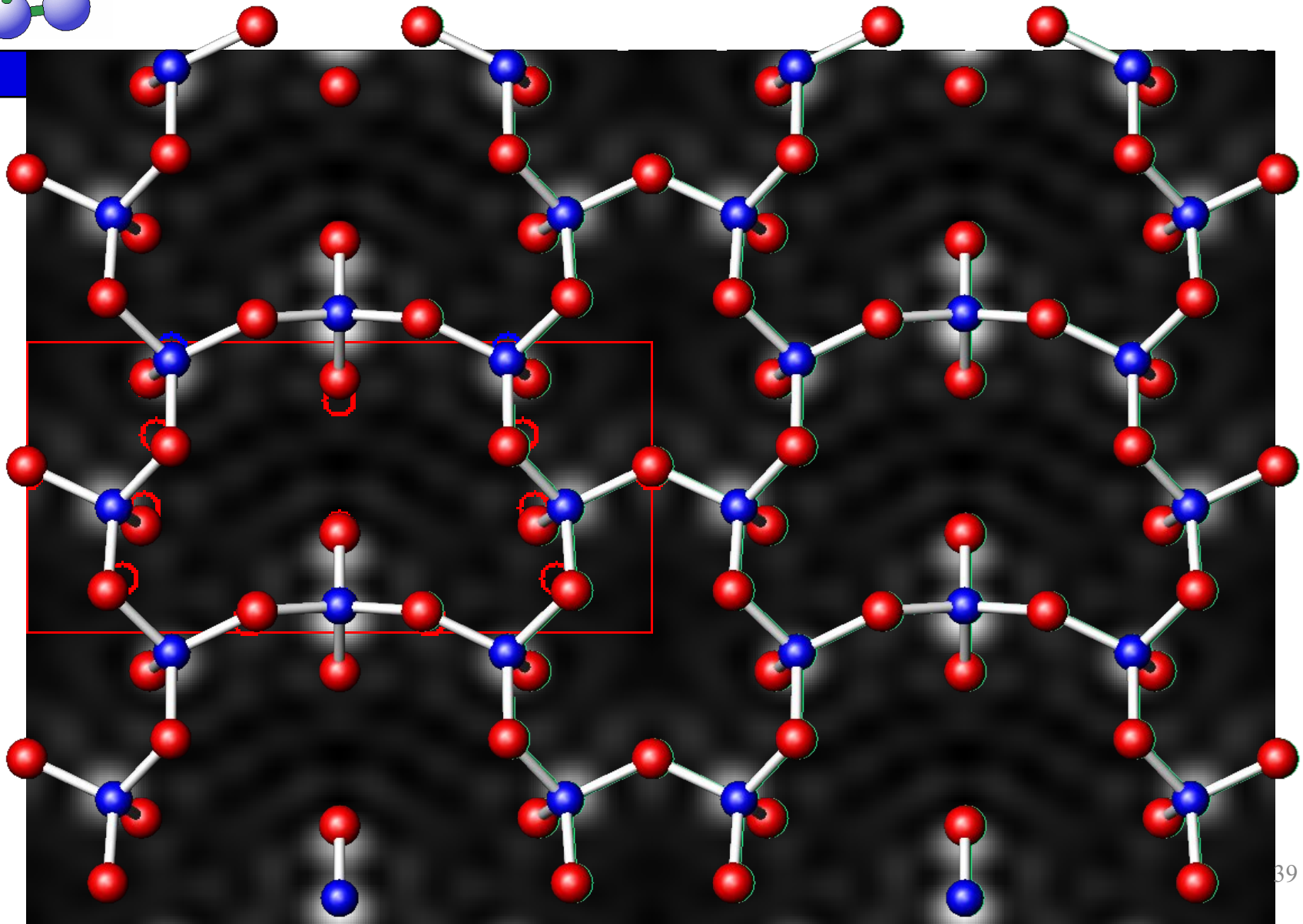
1000 °C in flowing O_2



Direct Methods Solution

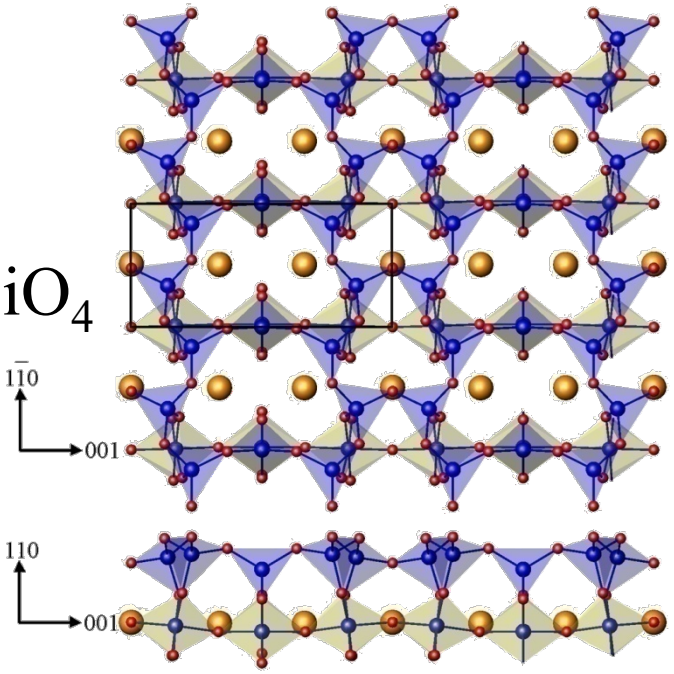


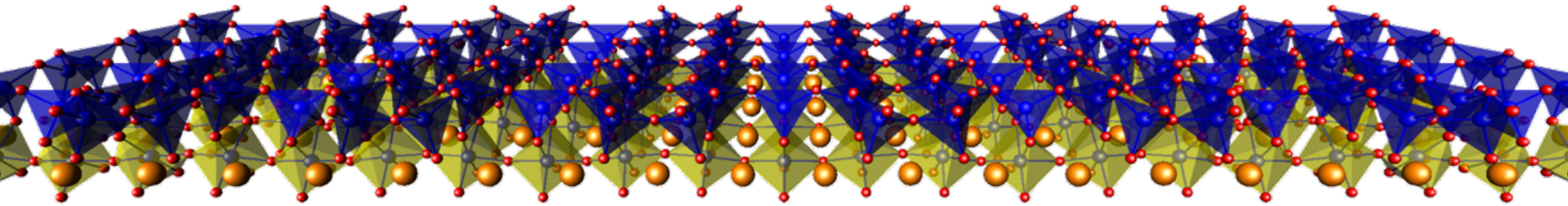
Atomic Positions Refined



$SrTiO_3$ (110) 3x1

- TiO_2 overall surface stoichiometry
  - Ti_5O_7 atop O_2 termination
  - Ti_5O_{13} atop SrTiO termination
- Surface composed of corner sharing TiO_4 tetrahedra
  - Arranged in rings of 6 or 8 tetrahedra
  - 4 corner share with bulk octahedra
  - 1 edge shares with bulk octahedron



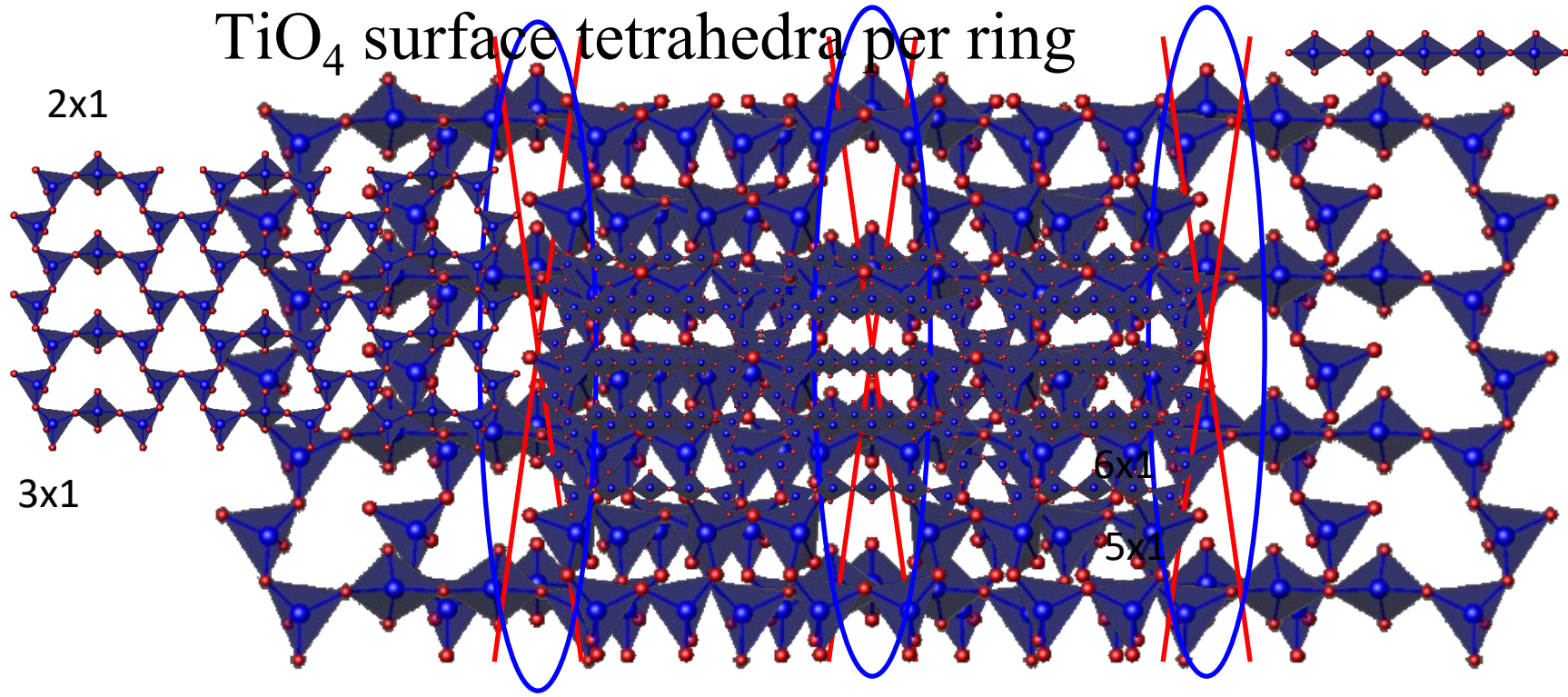


Blue polyhedra are surface polyhedra, gold are bulk octahedra, orange spheres Sr, blue spheres Ti, red spheres O

Enterkin et. al., Nature Materials, 2010

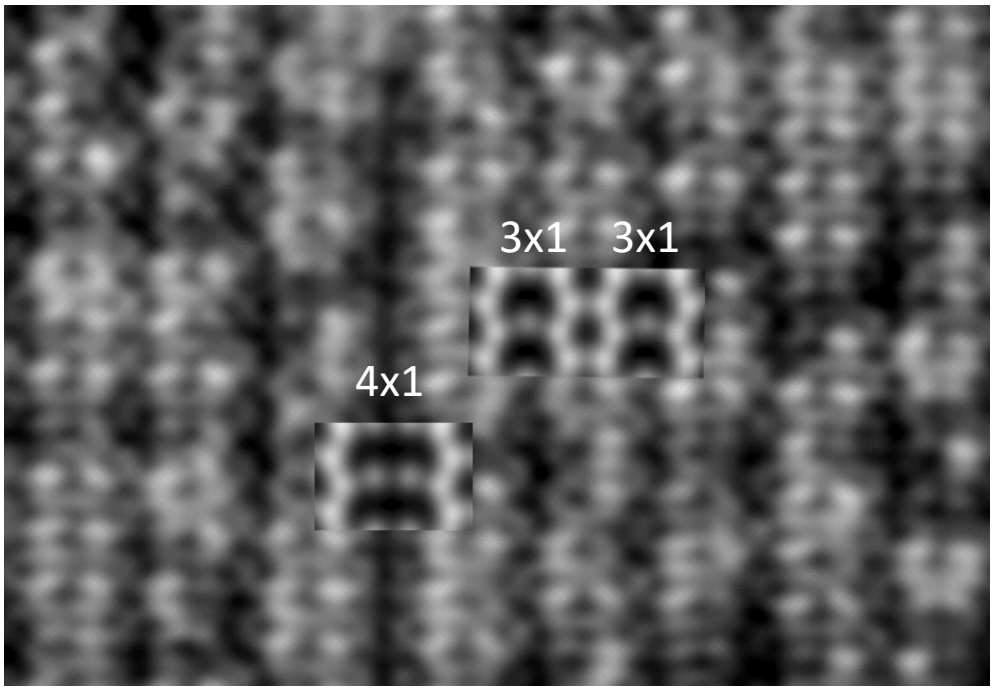
$SrTiO_3$ (110) nx1

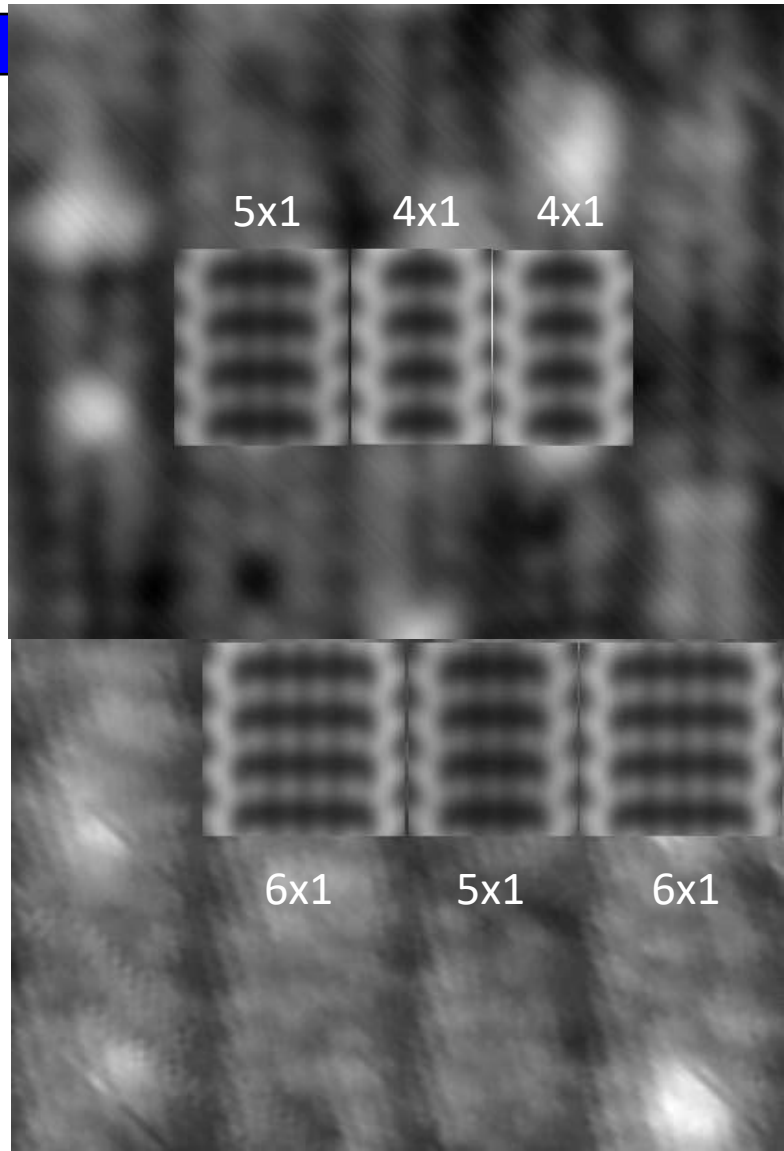
- Expansion to other nx1 by changing the number of TiO_4 surface tetrahedra per ring



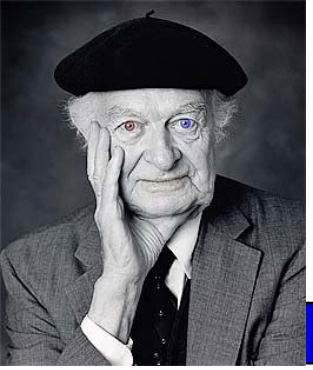
Intergrowths

STM with simulations (DFT)





Enterkin et. al., Nature Materials, 2010



Pauling's Rules: SrTiO3 (110)

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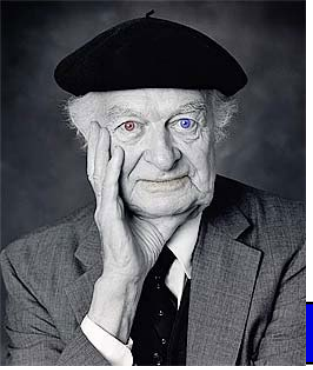
L. Pauling, The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* **51**, 1010 (1929).



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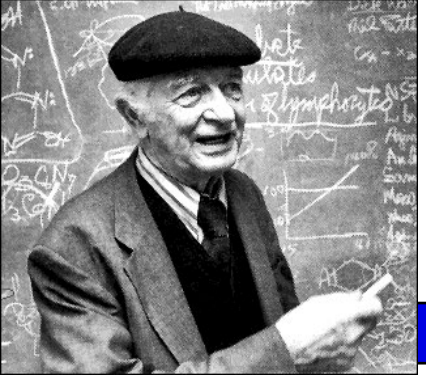
Pauling Bond Strength

- $S_p = V_c/N_c$
  - V_c is the valence of the cation and
  - N_c is its coordination number
- The sum of the bond strengths received by each anion tends to compensate the valence of the anion.
- This rule implies that the cations and anions arrange themselves in such a way as to provide local valence neutrality.



Bond Valence Sums (BVS)

- Development of electronegativity/positivity concepts from work of Pauling and others
- Idea is that the valence of an atom is the sum of the individual bond valences surrounding the atom
- If BVS is “right”, energy is low; if BVS not right often problems with structure
- This is a *Bulk* concept, used in surface science all the time (e.g. XPS is calibrated against BVS)

BVS & DFT are consistent, as they have to be

Bond Valence Sums

$S_{MO} = \exp((R_0^{MO} - R)/b_{MO})$

R_0^{MO}, b_{MO} constants for a given metal/oxygen combination (b_{MO}=0.37)

$V_M = \Sigma\, S_{MO}$ (over nearby oxygens)

$V_O = \Sigma\, S_{MO}$ (over nearby metals)

Brese, N. E. & O'Keeffe, M.; Acta Cryst. B47 (1991) 192-197; Brown, I. D. & Altermatt, D.; Acta Cryst. B41 (1985) 244-247; Brown, I. D.; in Structure and Bonding in Crystals, edited by M. O'Keeffe & A. Navrotsky, Vol. II, pp. 1-30. New York; Academic Press (1981).

Valence is *not* charge

- A source of endless confusion!
- 4+ is the *Valence*
- +4 is a *Charge*
- $SrTiO_3$ is:
  - $Sr^{2.1+}\ Ti^{4.1+}\ O_3^{2.1-}$ ($Sr^{2+}Ti^{4+}O_3^{2-}$)
  - $Sr^{+1.6}\ Ti^{+2.2}\ O_3^{-1.2}$ (Bader method)
- Note: "grep Bond *.tnn" in Wien2k

Instability Index

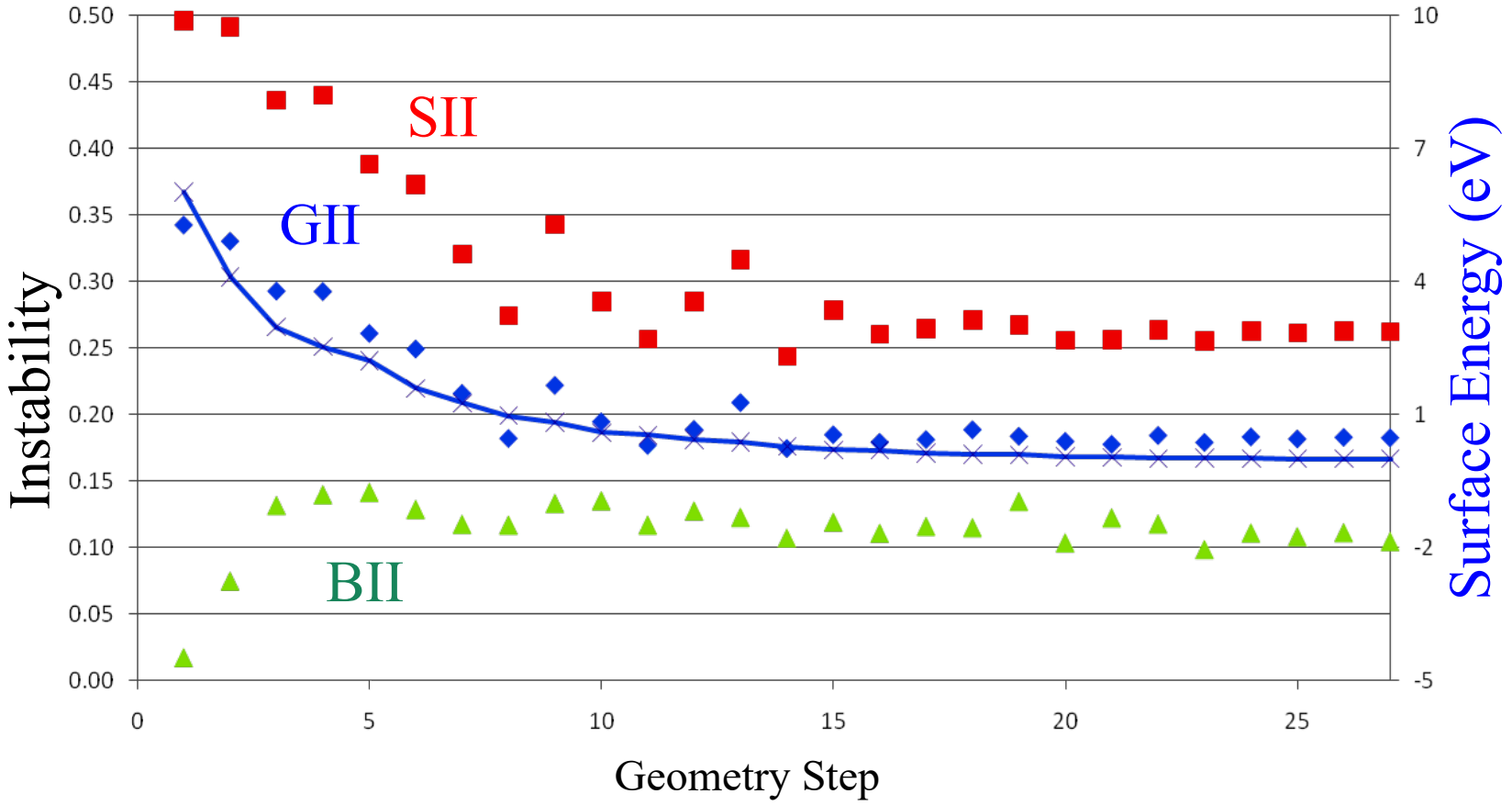
- Global Instability Index (GII)

$$GII = \sqrt{\frac{\sum(BVS - BVS_0)^2}{N}}$$

  - BVS is actual bond valence sum
  - BVS_0 is expected whole number value
  - N is the number of atoms
- Surface Instability Index (SII)
  - Same as global instability index, but for surface atoms only

Enterkin et al, Surf. Sci. 606 (3-4), 344 (2012)

DFT & BVS



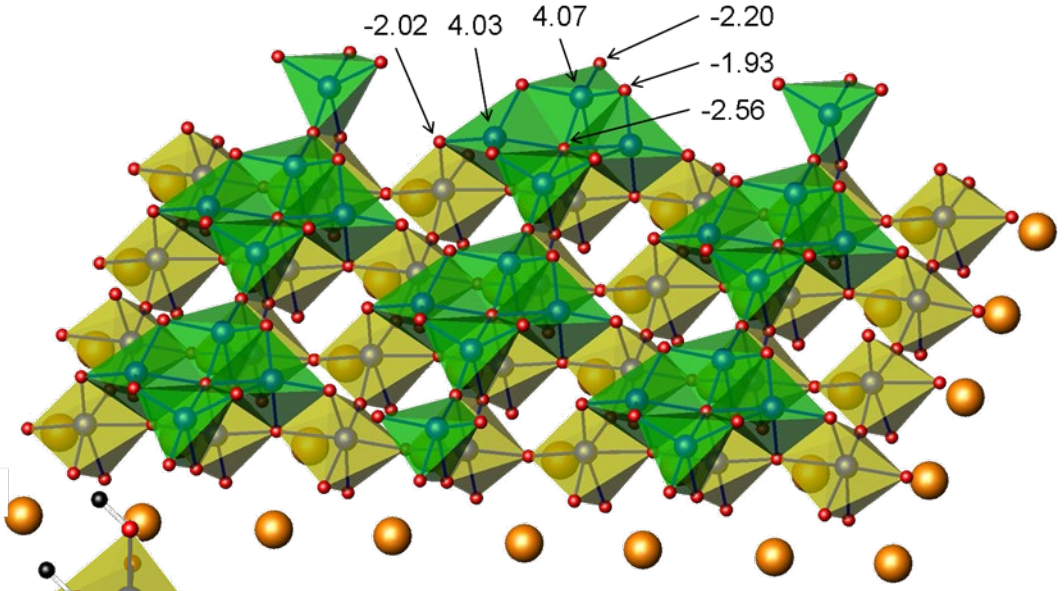
$MgO\ (111) + H_2O$

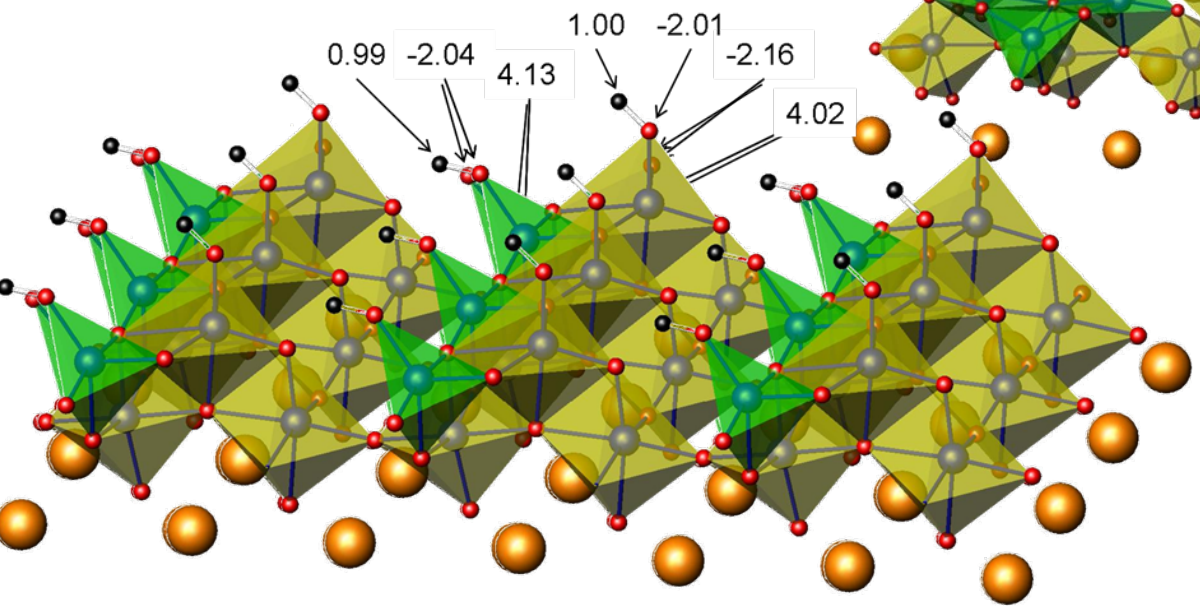
J. Enterkin, A. Becerra-Toledo, K. R. Poeppelmeier, L. D. Marks. Surf. Sci. 606, 344 (2012)

BVS and adsorption

c4x2 SII 0.17

H_2O desorbs easily (in-situ XPS)



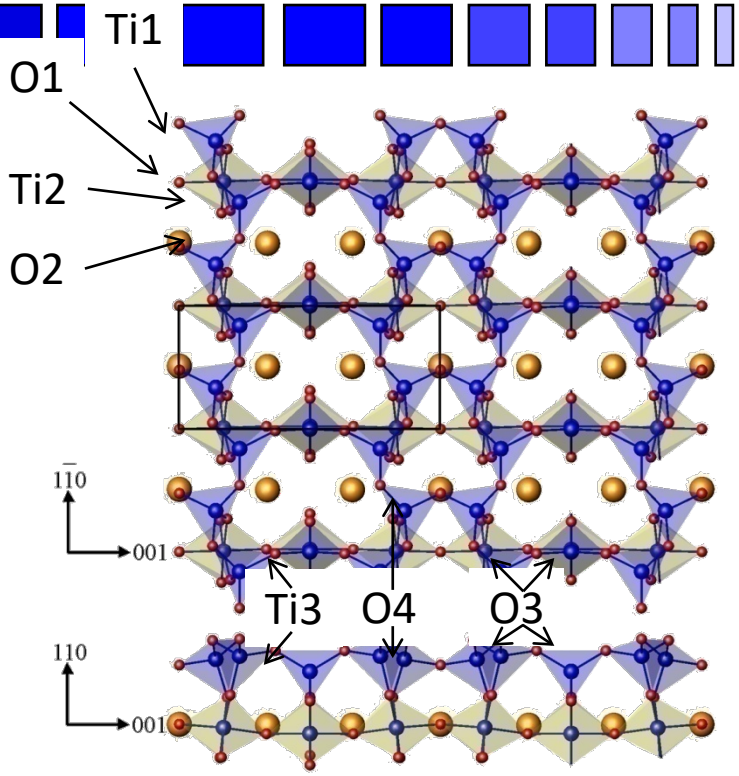


c2x1 SII 0.12
H_2O desorption sluggish (in-situ XPS)

A. E. Becerra-Toledo, D. M. Kienzle, J. Enterkin, L. D. Marks, *Surf. Sci.* 606, 791 (2012).

$SrTiO_3$ (110) 3x1

- Bond valence sums
  - Ti1 = 4.04
  - Ti2 = 4.08
  - Ti3 = 4.04
  - O1 = 2.03-
  - O2 = 2.02-
  - O3 = 2.04-
  - O4 = 2.19-



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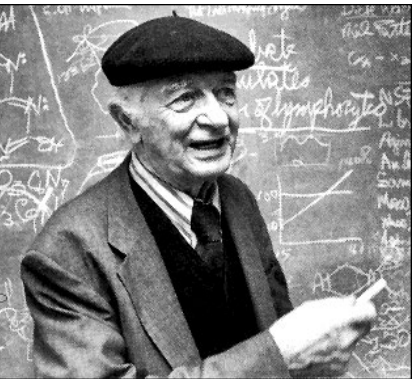
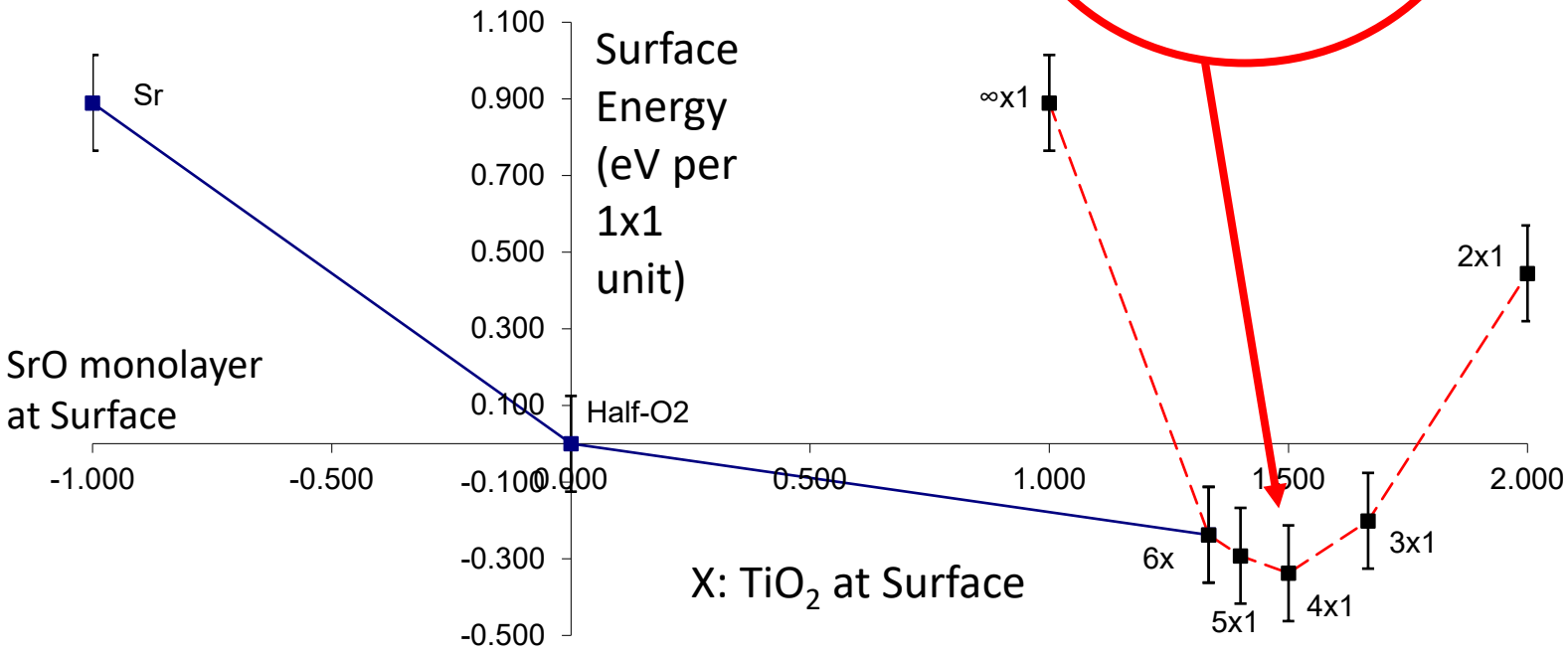


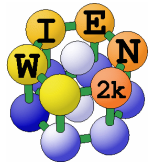
Enterkin et. al., Nature Materials, 2010

The principles determining the structure of complex ionic crystals. J. Am. Chem. Soc. 51 (4): 1010 1929.

$SrTiO_3$ (110) Bond Valence Sums

Bond Valence		Sr	Half-O_2	∞x1	6x1	5x1	4x1	3x1	2x1
Surf	Ti(Sr)	1.88	3.83	3.41	3.87	3.93	3.99	4.06	4.02
Surf	O	1.49-	1.94-	1.21-	1.88-	1.95-	1.99-	2.05-	2.07-
Sub-surf	O	2.61-	1.88-	2.07-	2.02-	2.04-	2.05-	2.05-	1.94-





TPSSh

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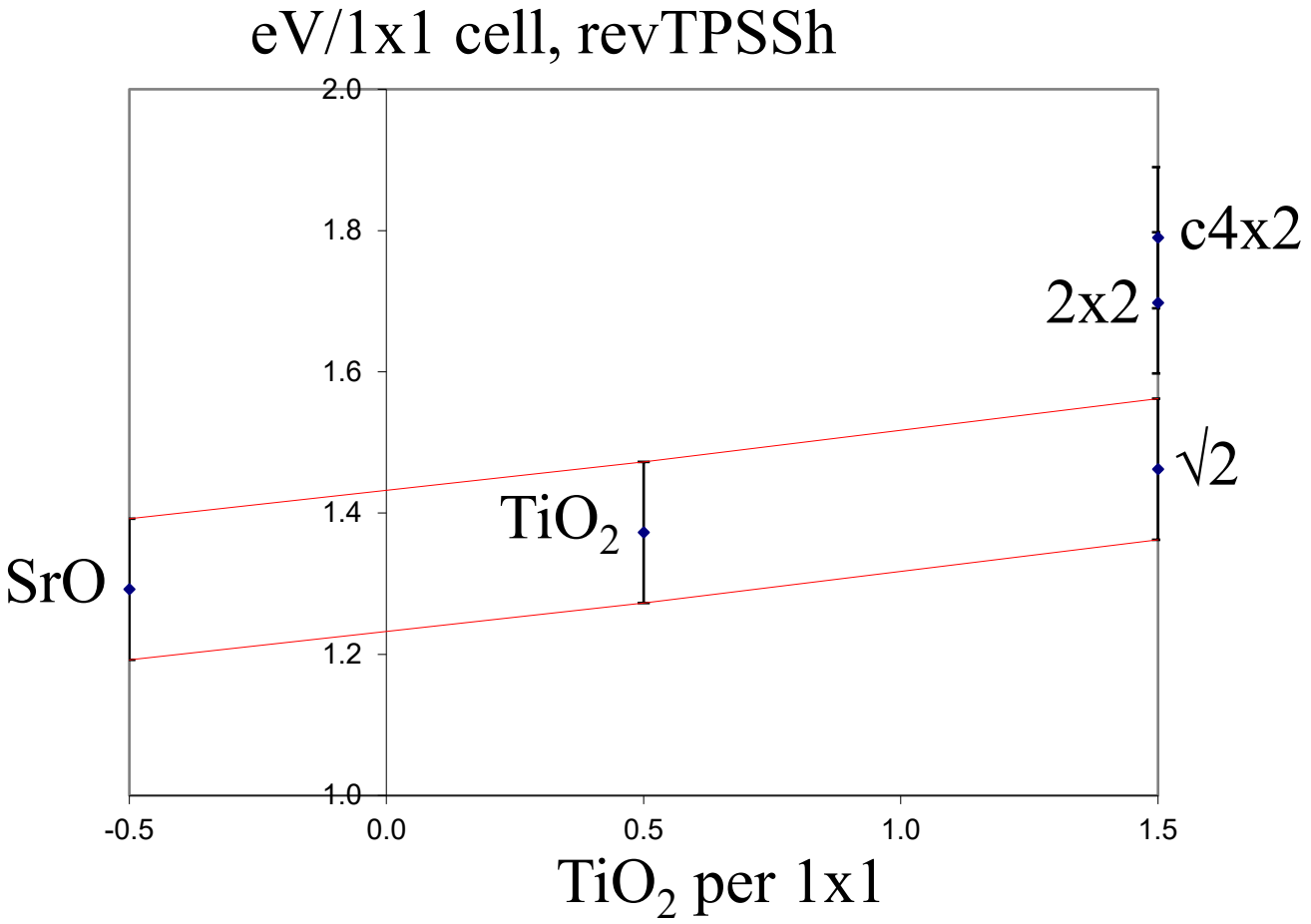
- Entropy and disorder, more complex Pott's model for $SrTiO_3$ (111)

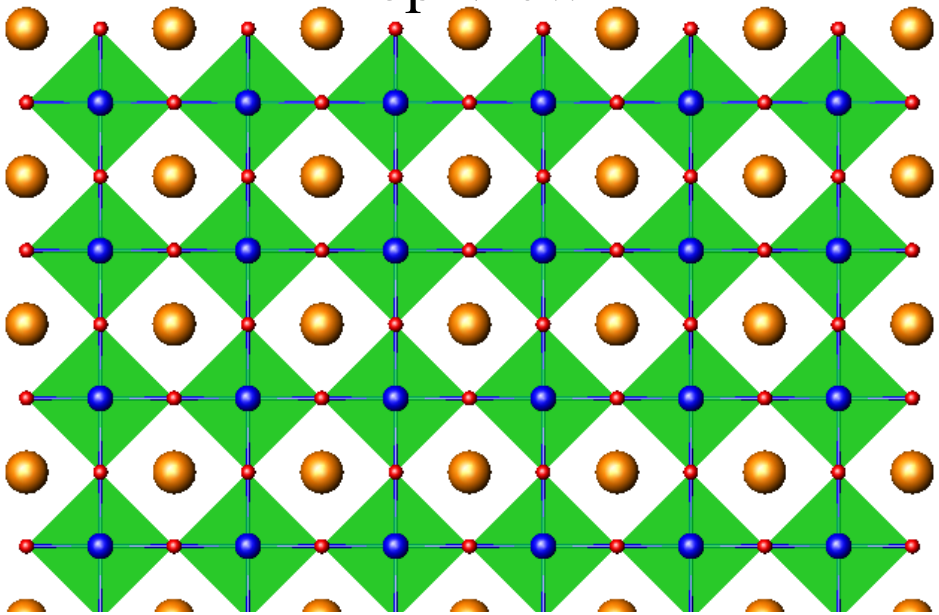
$STiO_3$ (001) Energies



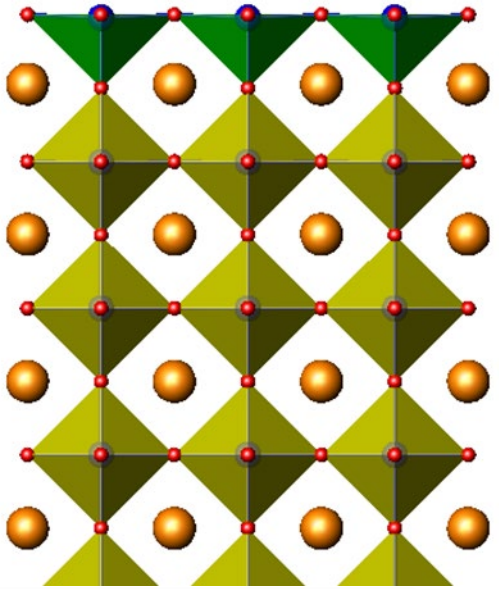
For errors, see L. D. Marks *et al.*, Surf. Sci. **603**, 2179 (2009)
For revTSPP J.P. Perdew, PRL **103**, 026403 (2009)

Common features: 1x1 Base

Top View

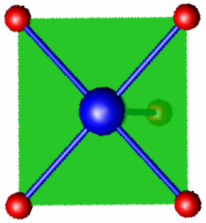


Side View

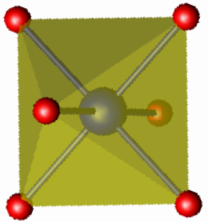


Building Blocks:

Sr (not critical)



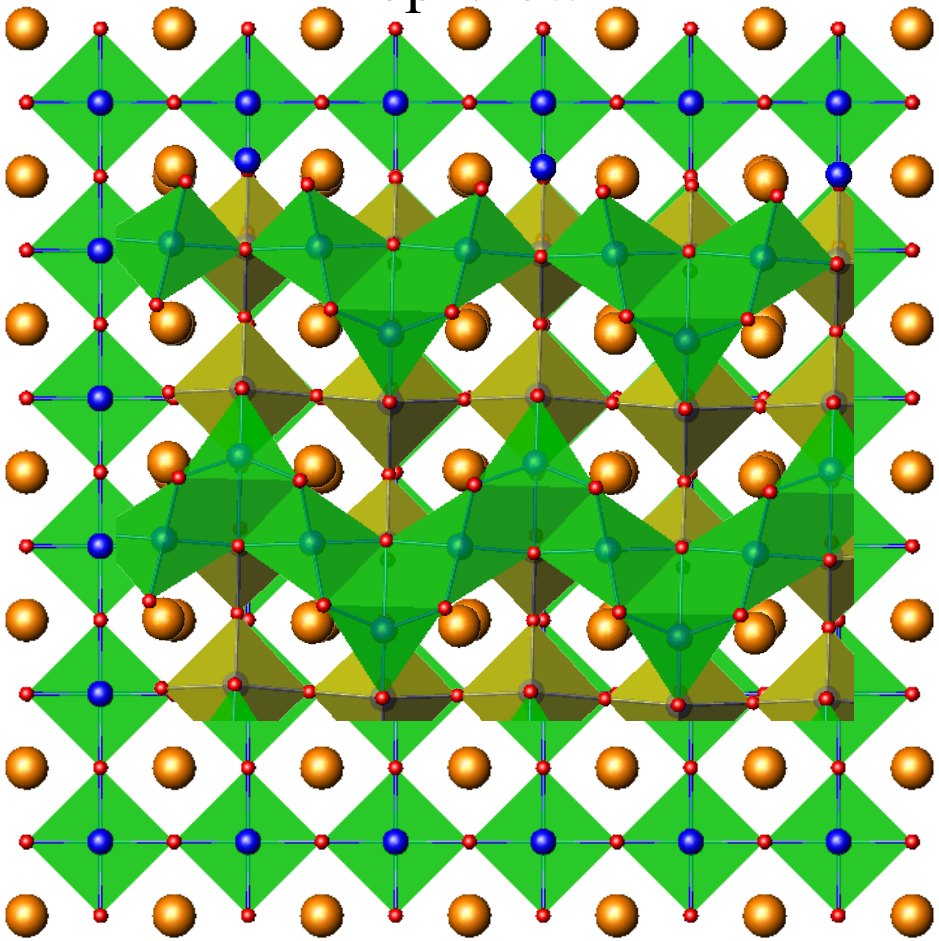
5-fold Ti



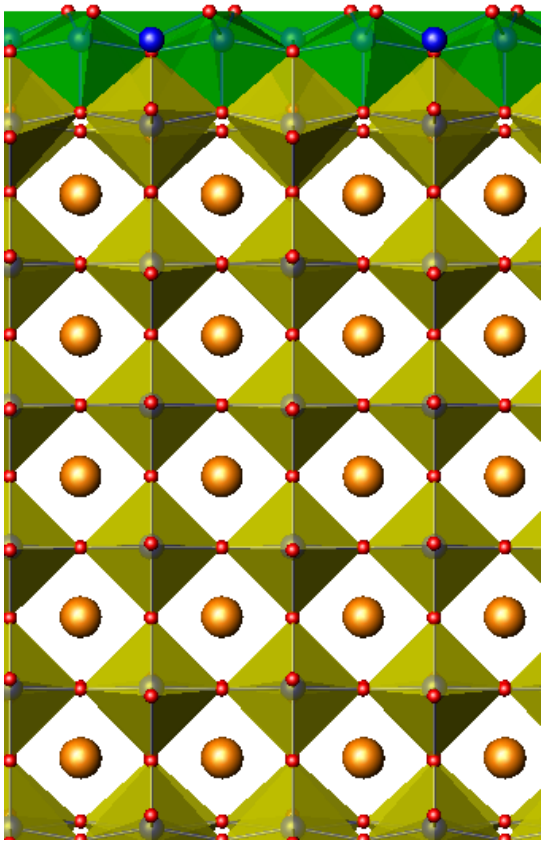
6-fold Ti

2x2 Structure

Top View



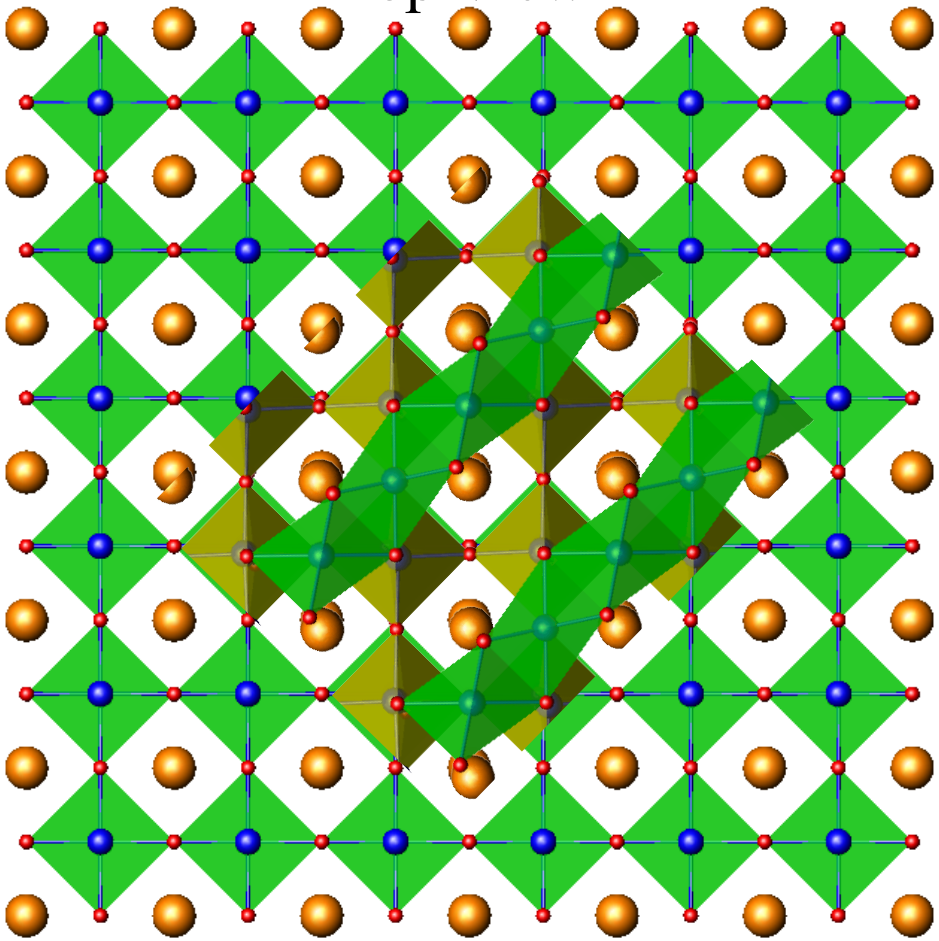
Side View



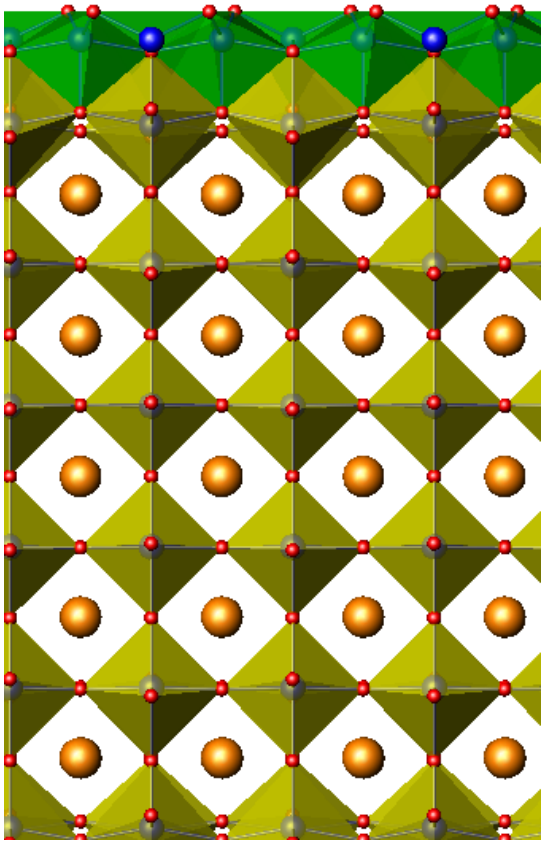
O. Warschkow *et al.*, Surf. Sci. **573**, 446 (2004).

√2x√2 R45

Top View



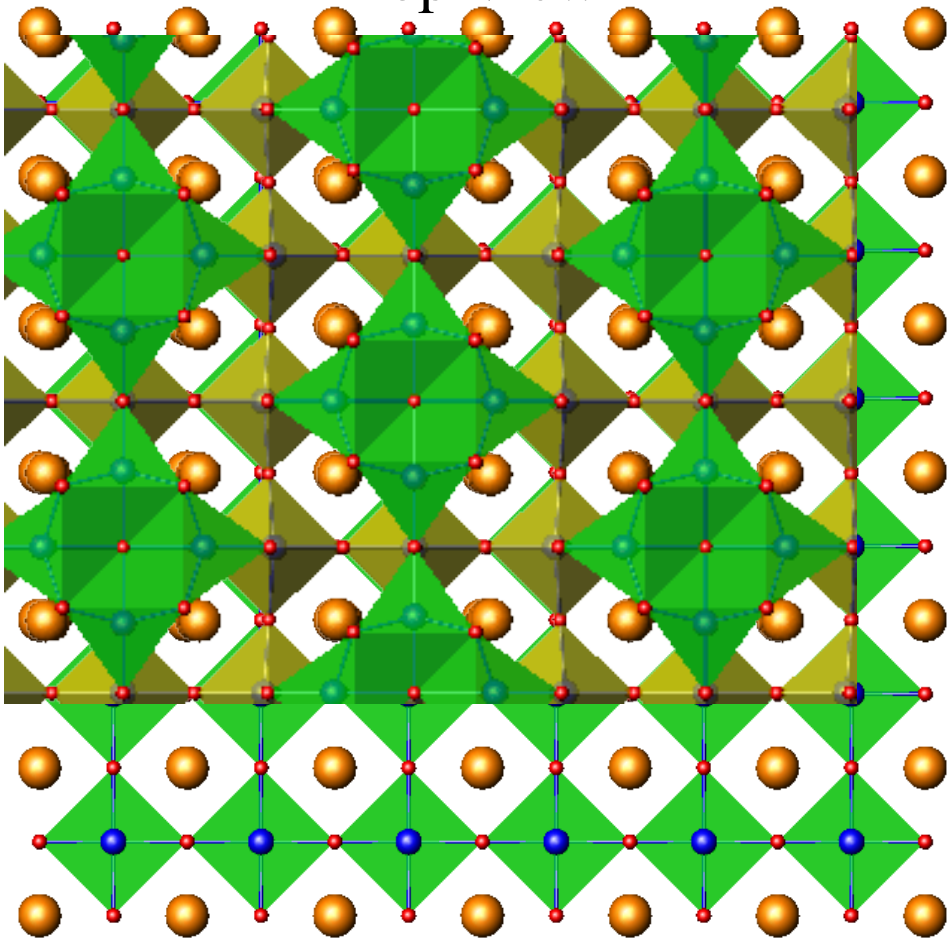
Side View



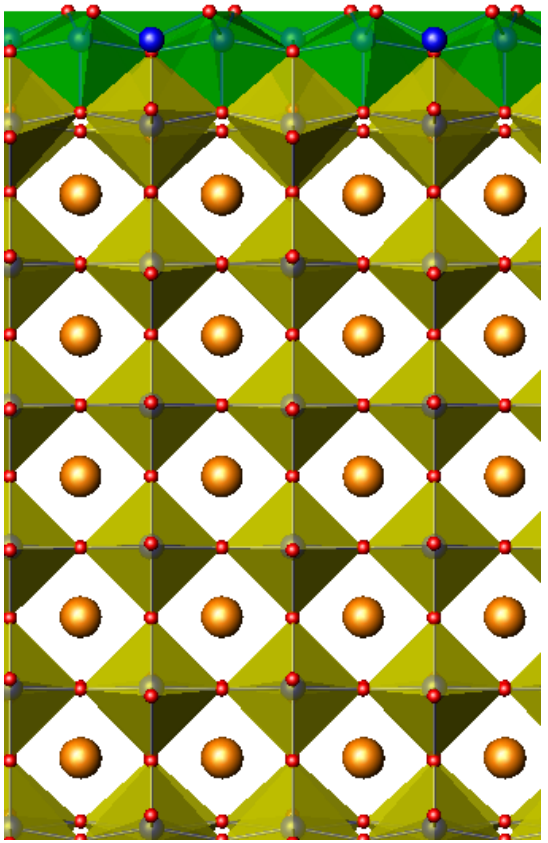
O. Warschkow *et al.*, Surf. Sci. **573**, 446 (2004).

c(4x2)

Top View

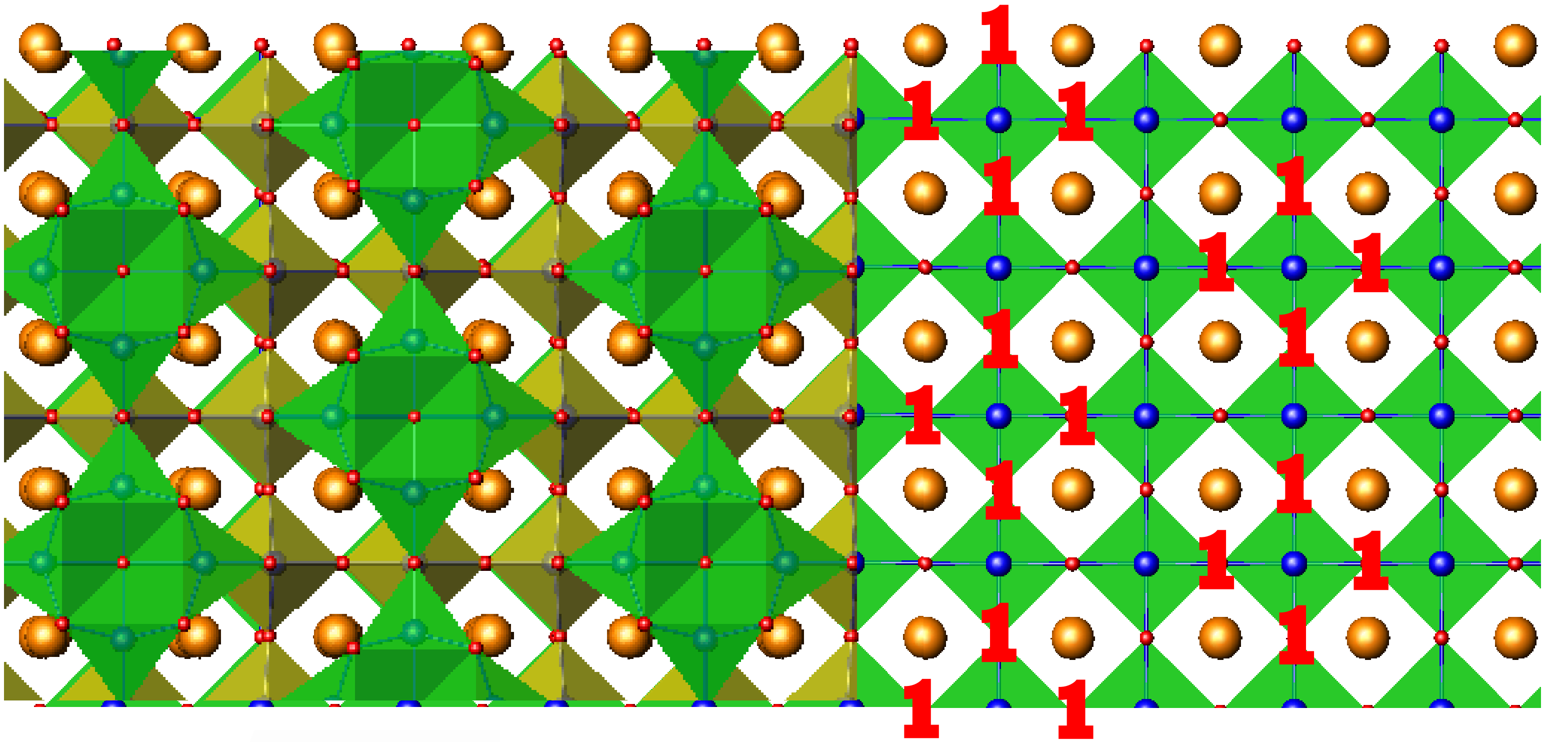


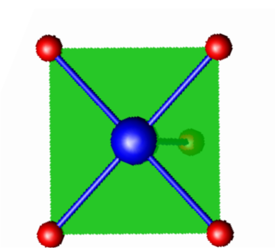
Side View



N. Erdman *et al.*, J. Am. Chem. Soc. **125**, 10050 (2003).

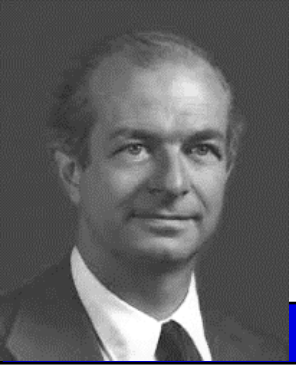
Constrained Ising Model





= 1

S. Cook et al, in preparation



Pauling's Rules: SrTiO3 (001)

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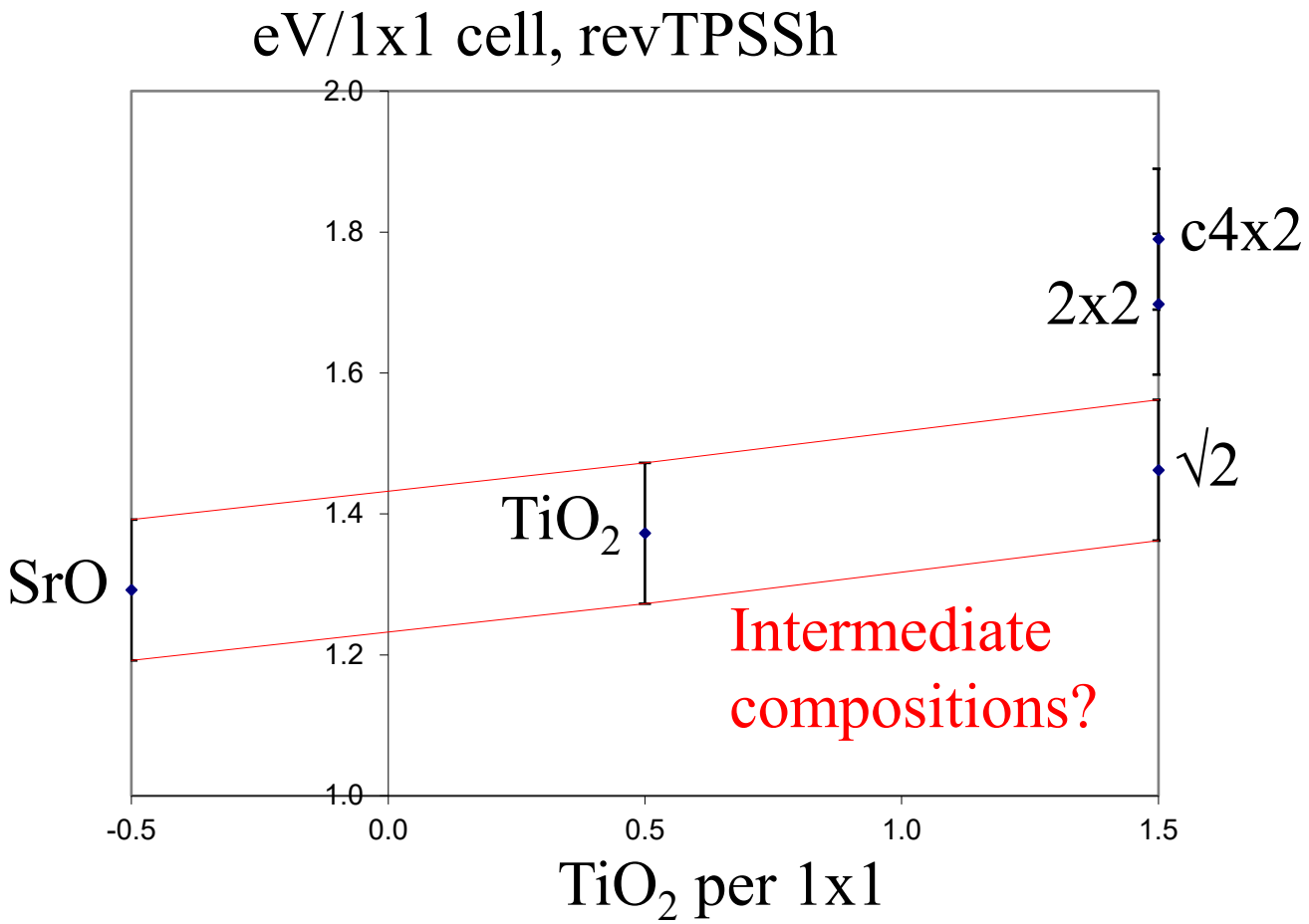
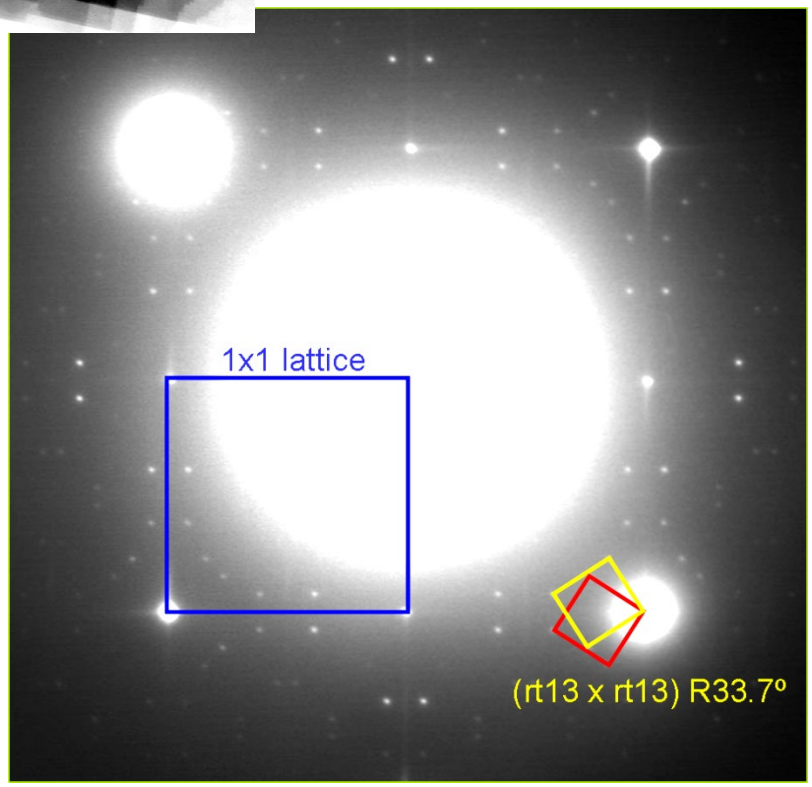
L. Pauling, The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* **51**, 1010 (1929).

$STiO_3$ (001) Energies

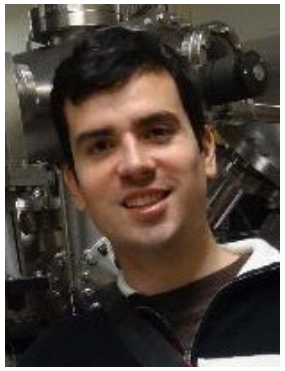


For errors, see L. D. Marks *et al.*, Surf. Sci. **603**, 2179 (2009)
For revTSPP J.P. Perdew, PRL **103**, 026403 (2009)

√13x√13 R33.7 $SrTiO_3$ (100)

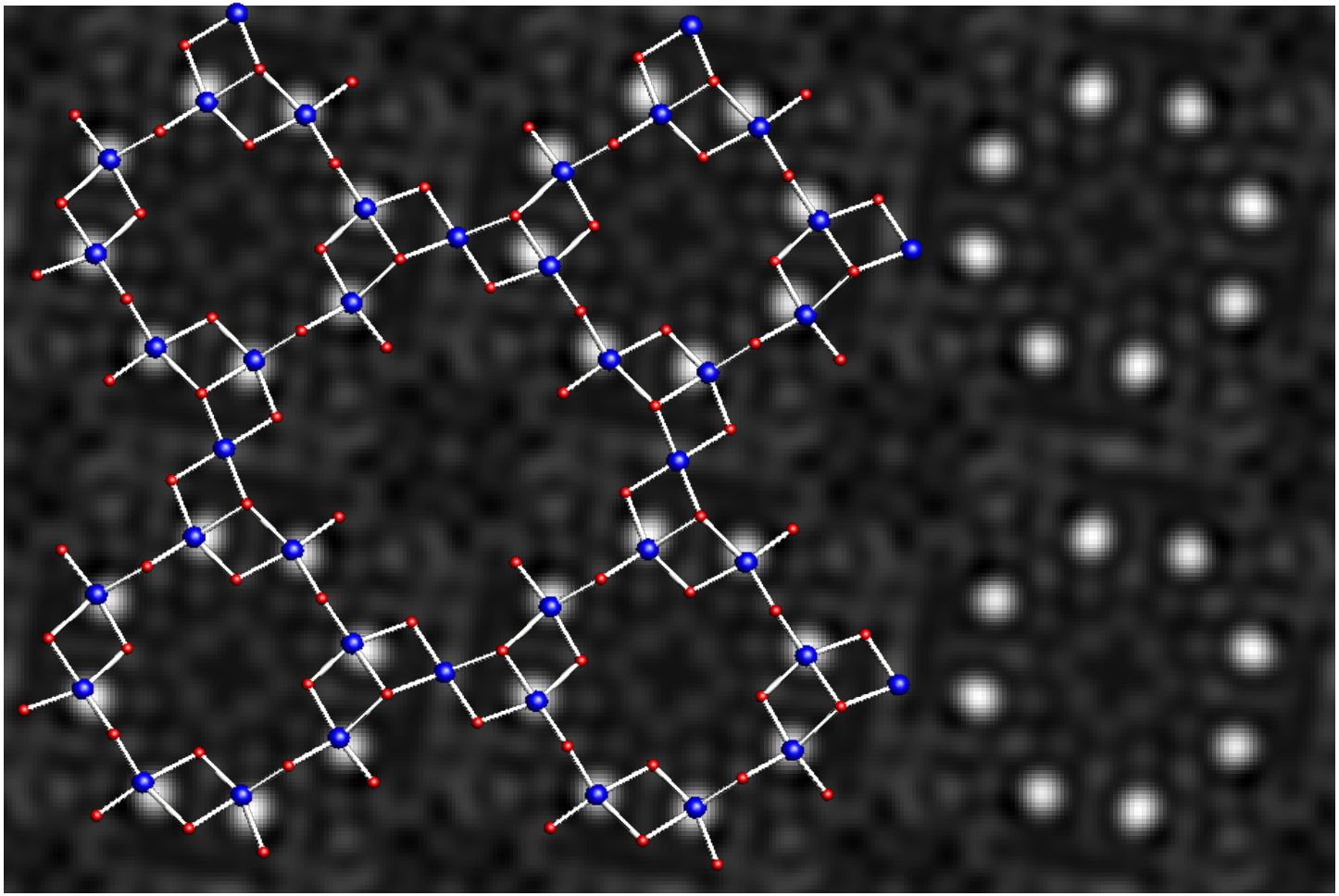


- Make a "normal" sample
- Buffer-etched *then* annealed
- Changes surface TiO_2 excess

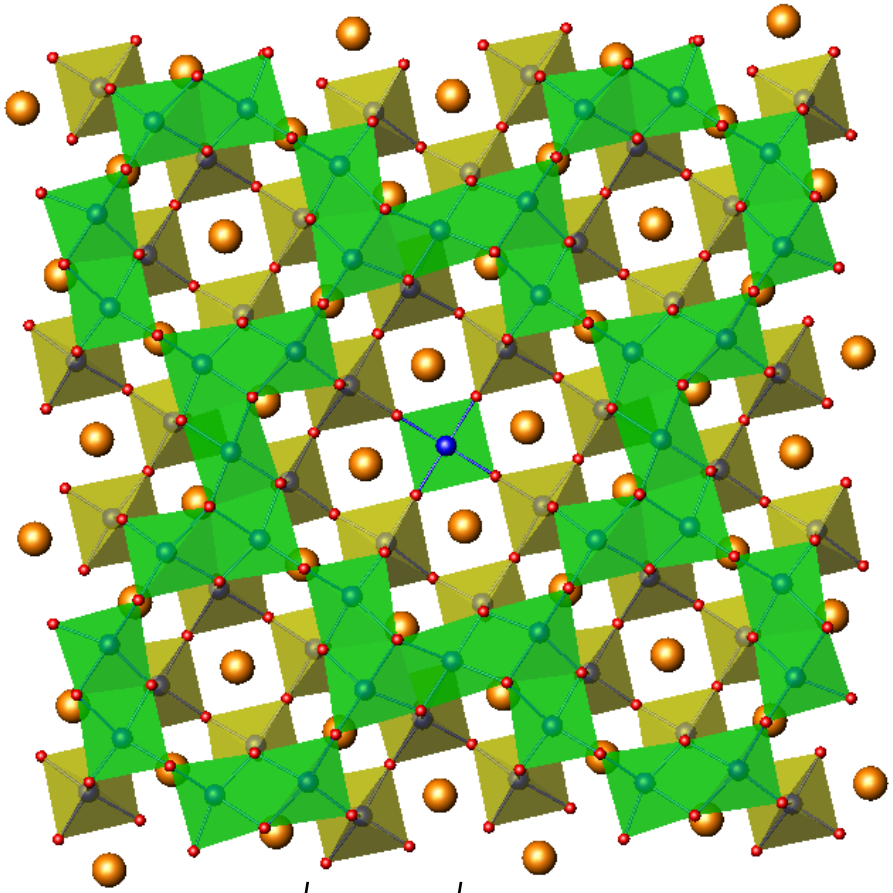


D. M. Kienzle, A. E. Becerra-Toledo, and L. D. Marks, Phys. Rev. Lett. 106, 176102 (2011)

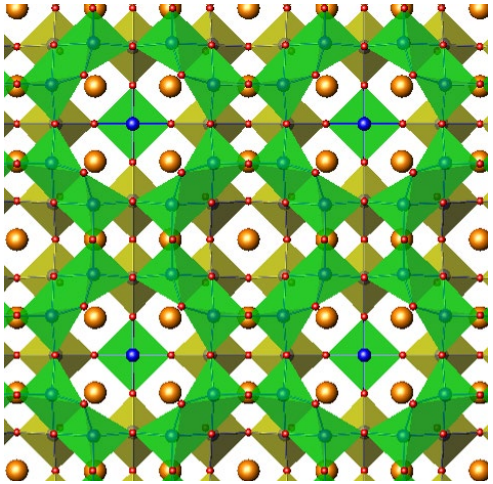
(001) √13x√13 Initial Map



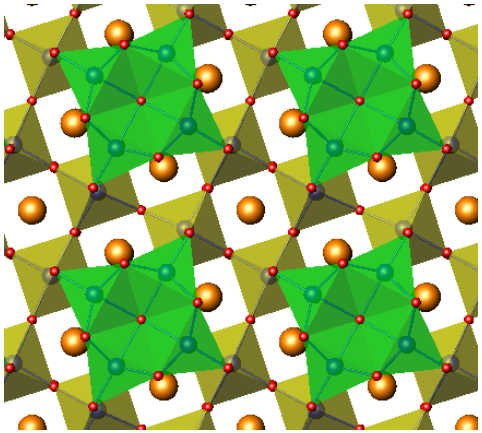
Larger tilings (Ising Model)



√13x√13

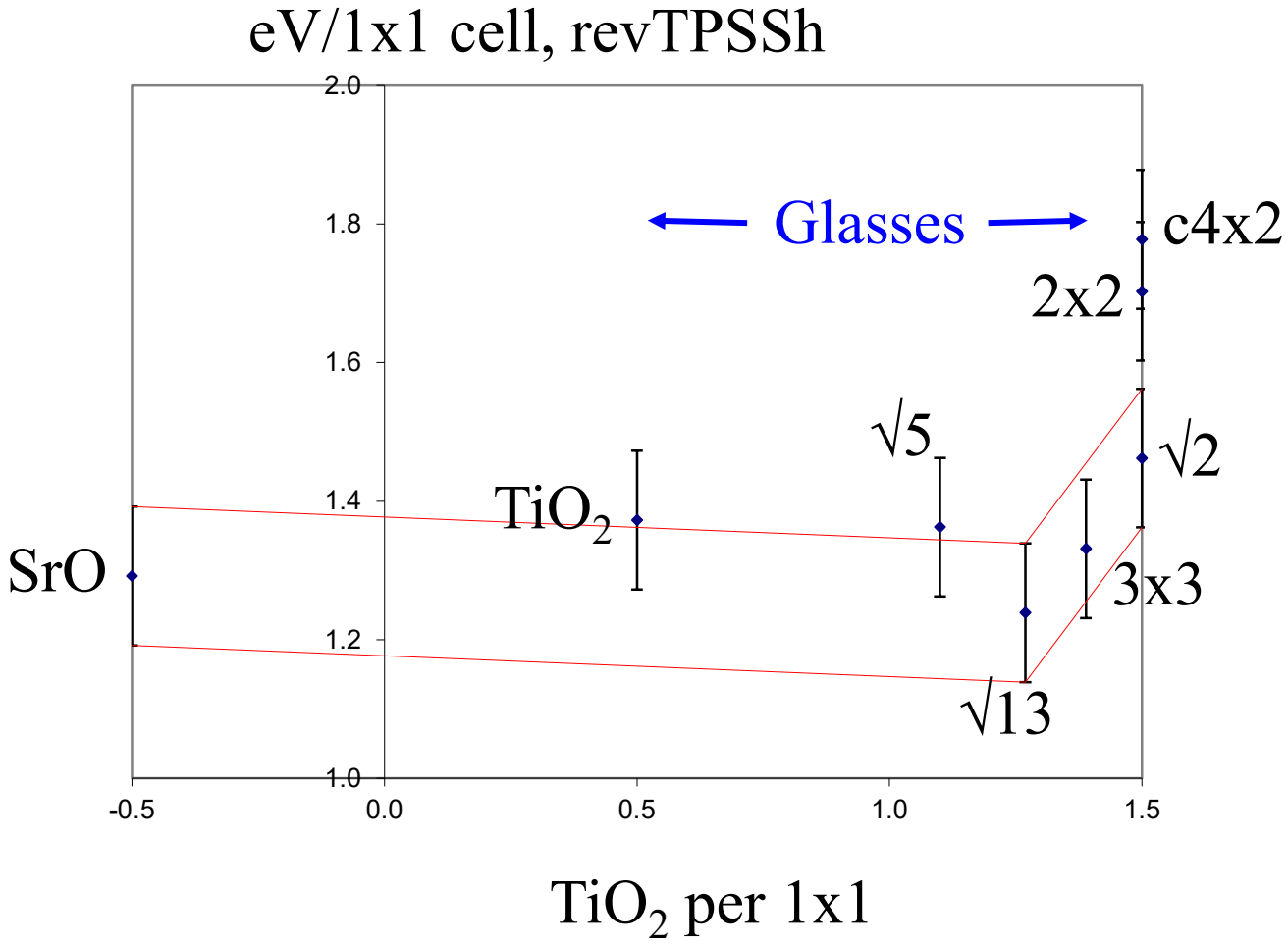


3x3



√5x√5

Stable according to DFT



D. M. Kienzle, A. E. Becerra-Toledo, and L. D. Marks, PRL. 106, 176102 (2011)

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L. Pauling, The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* **51**, 1010 (1929).

Three examples

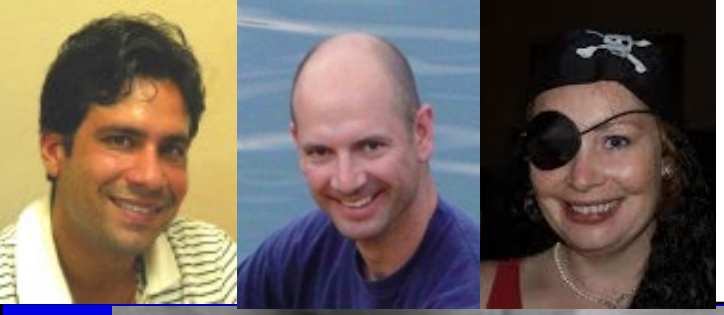
- Connect TED, DFT, STM (and chemistry); the $SrTiO_3$ (110) surface
- What lies beyond order: glass-like tilings (constrained Ising model) on $SrTiO_3$, the $\sqrt{13}x\sqrt{13}$ (001) reconstruction
- Entropy and disorder, more complex Pott's model for $SrTiO_3$ (111)

In This House We Obey The Laws of Thermodynamics

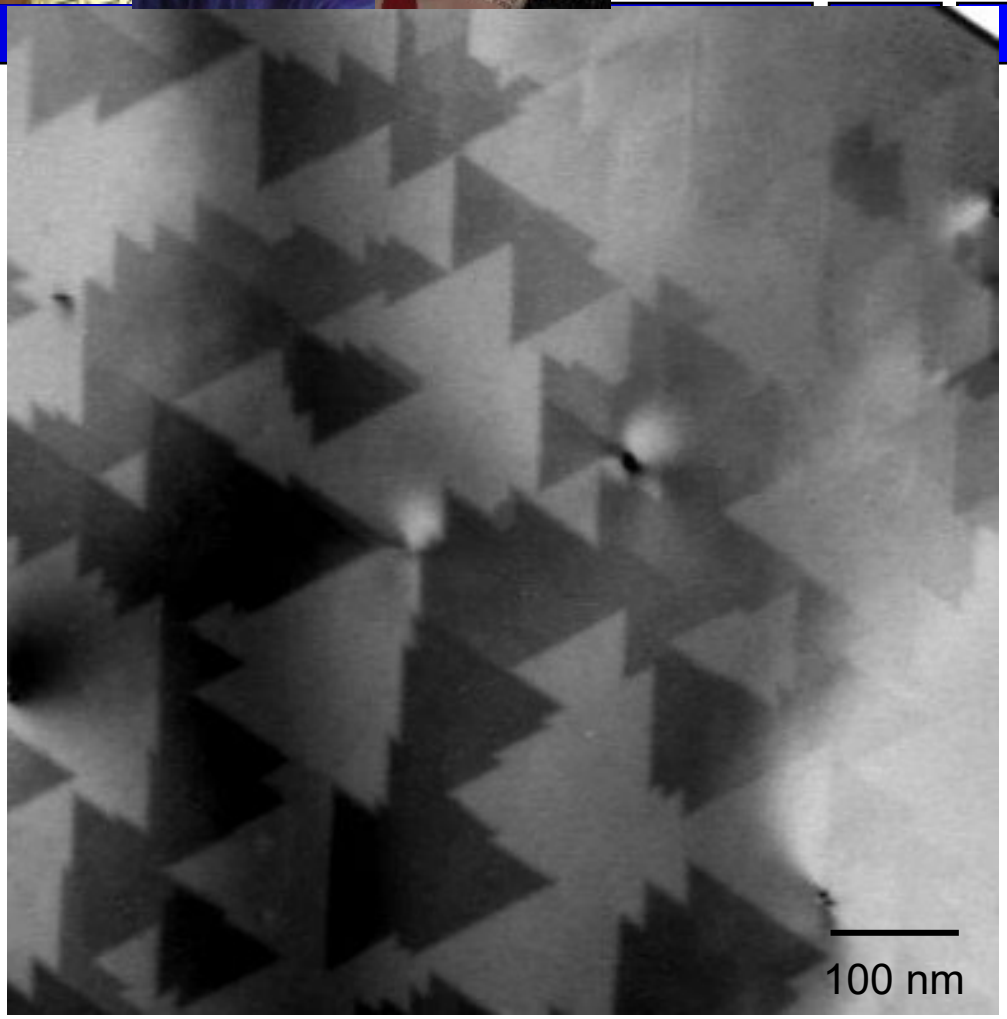
Homer Simpson

aka Free Energy

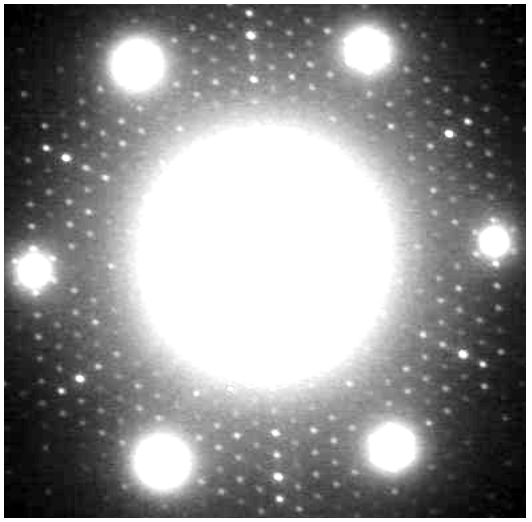
Enthalpy and Entropy



$SrTiO_3$ (111)



- Complex series of nxn reconstructions, 2<n<6
- Similar to other surfaces or not?



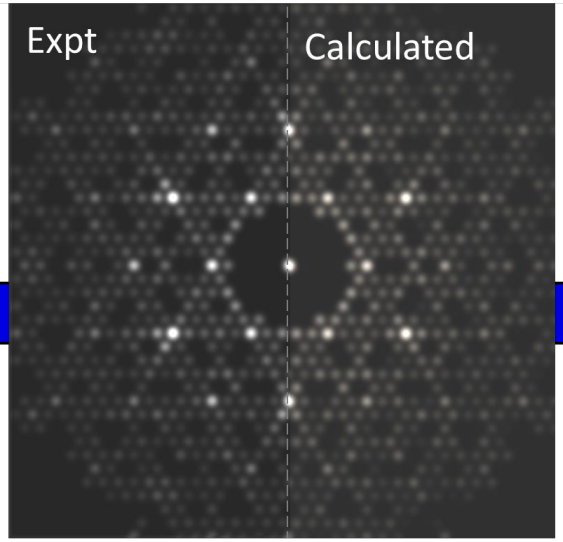
L. D. Marks, A. N. Chiaramonti1, S. U. Rahman and M. R. Castell, PRL, **114**, 226101 (2015)

Is it just enthalpy that matters?

- At elevated temperatures configurational entropy can dominate for Potts/Ising models
- In an ideal solution model with variable TiO_2 excess at the surface,

$$c_i = \frac{\exp(-n_i\{G_i - \mu f_i\}/kT)}{\sum \exp(-n_i\{G_i - \mu f_i\}/kT)},$$

- c_i is the fraction of each surface phase, G_i the free energy per 1×1 unit cell, n_i the number of cells in the surface unit cell, fi the TiO_2 excess per 1×1 unit cell and μ the TiO_2 surface chemical potential.

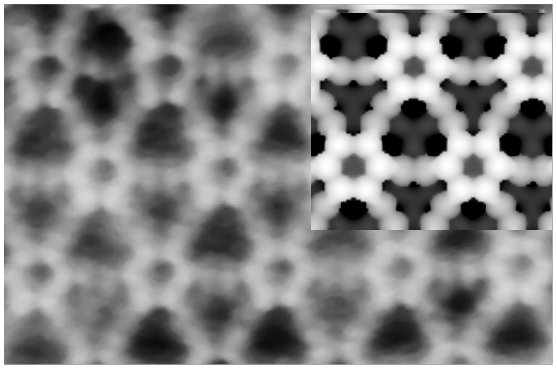


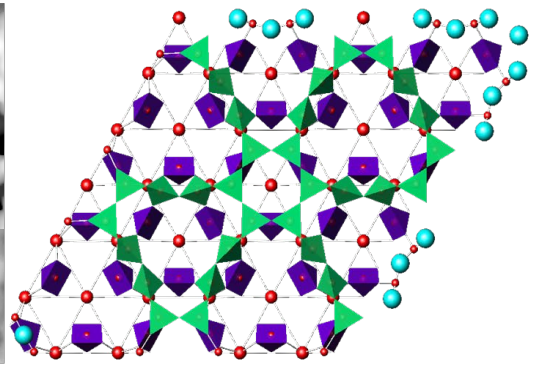
TED

3x3 & 4x4 ordered

Similarities to both (110) & (001)

3x3

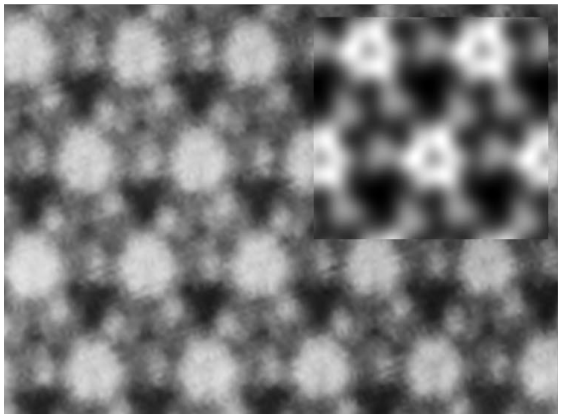


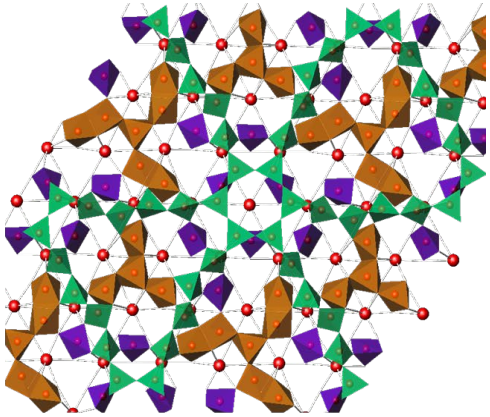


Green TiO_4, similar to (110)

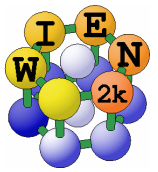
Purple, TiO_5, similar to (001)

4x4

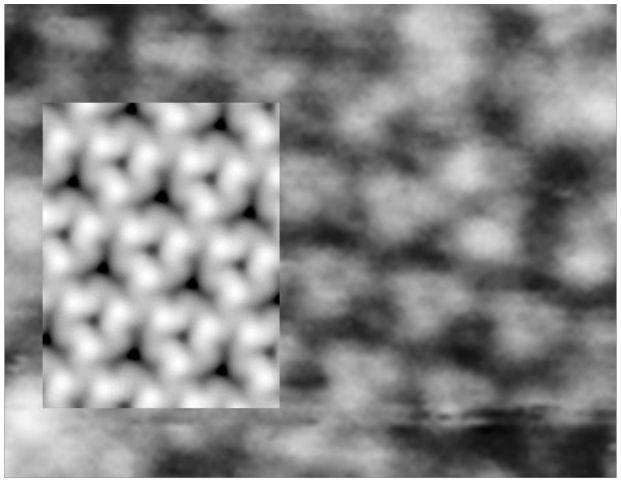


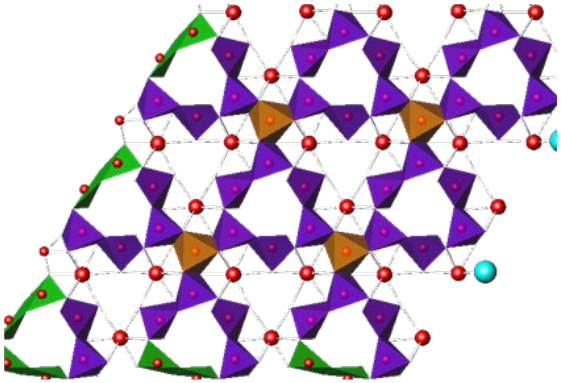


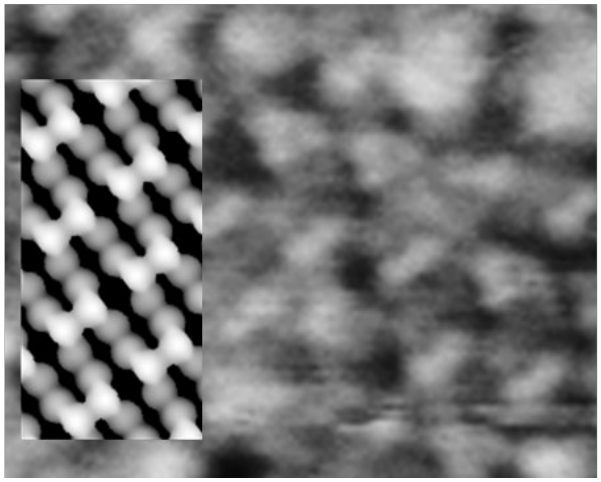
Brown TiO_6

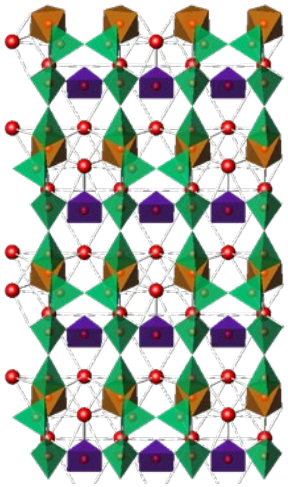


2x2 more complex



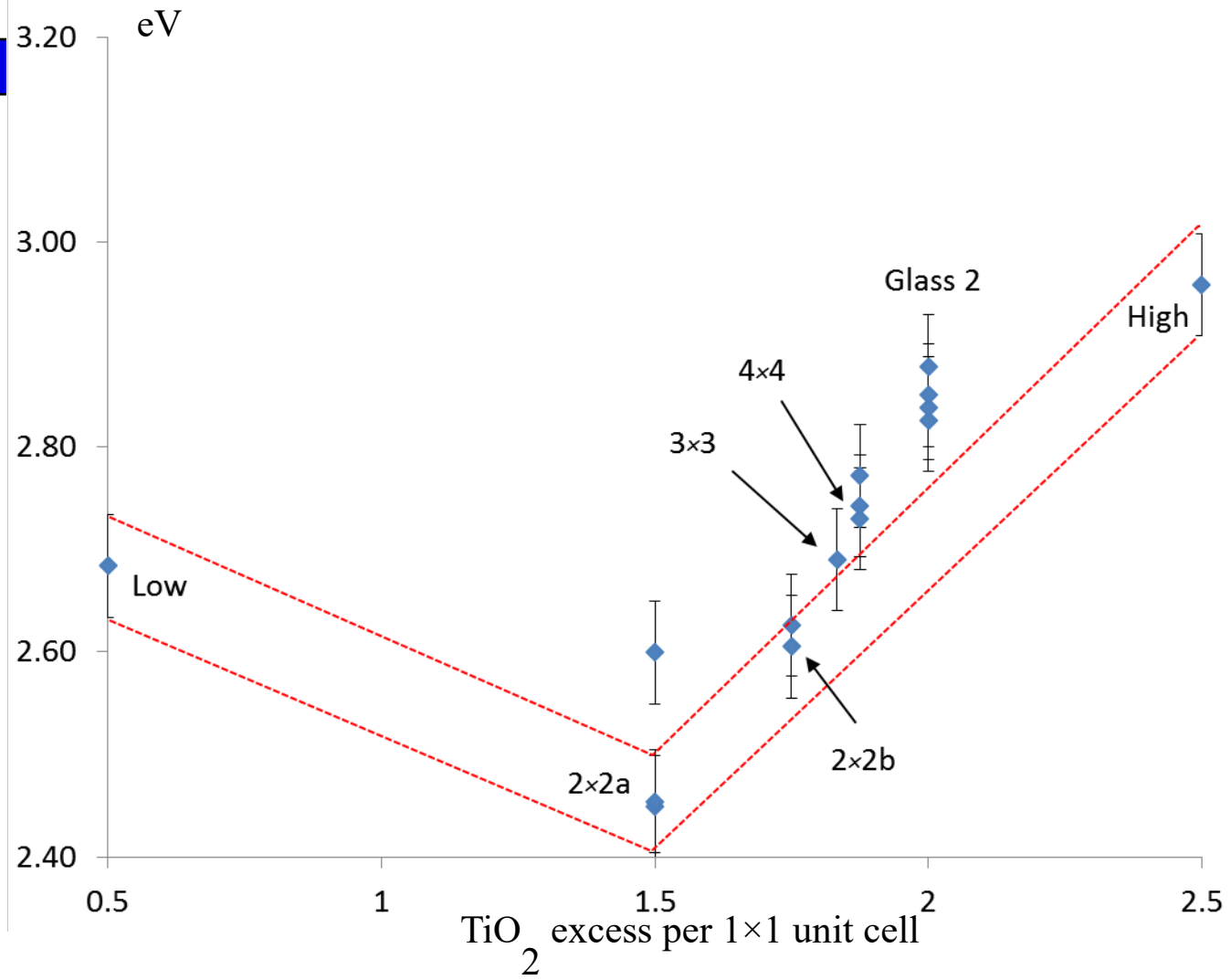




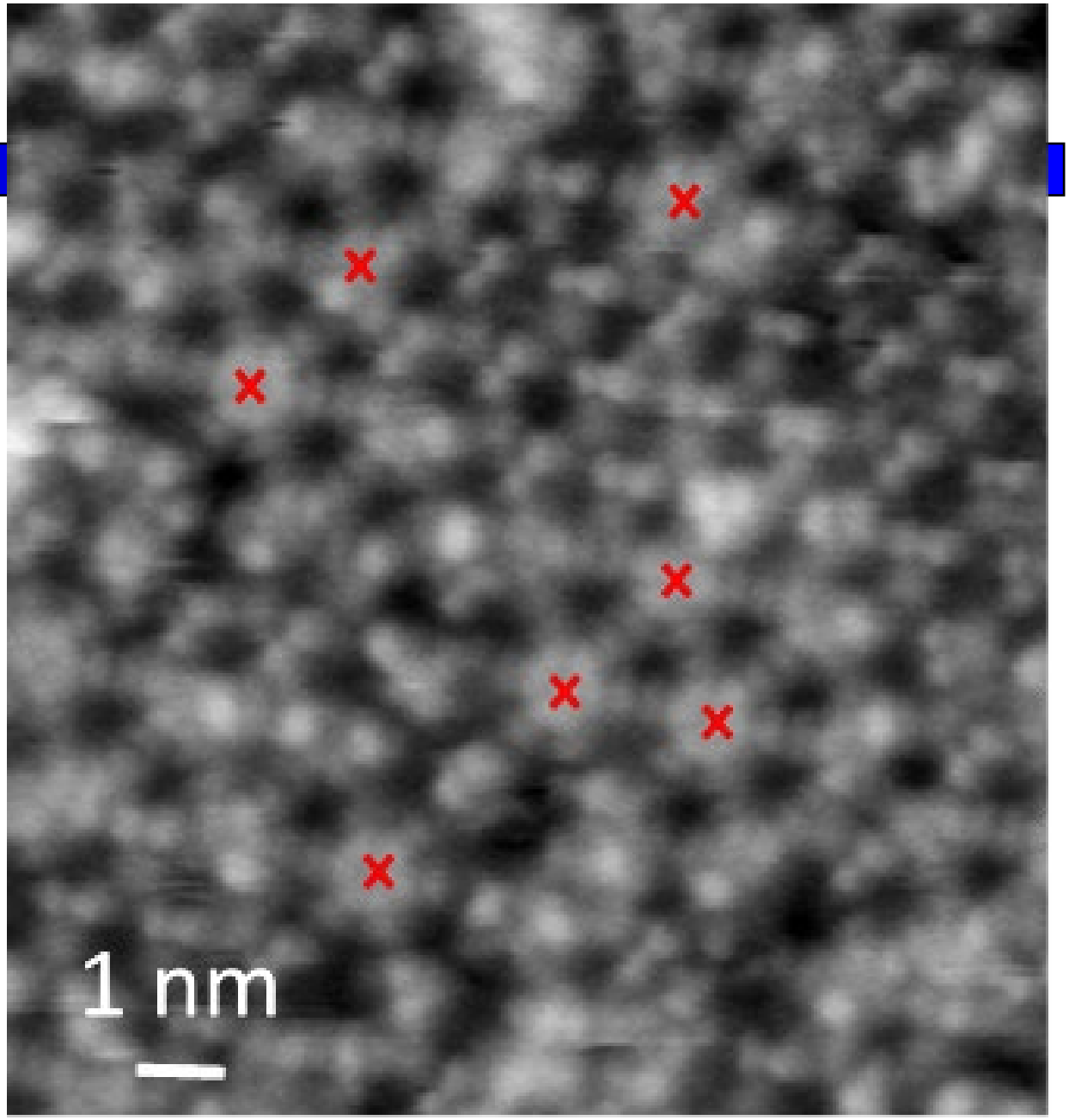


More than one 2x2 structure

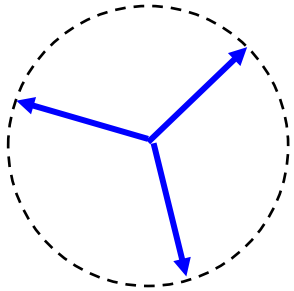
Convex Hull


eV
3.20
3.00
2.80
2.60
2.40
0.5
1
1.5
2
2.5
Low
2×2a
3×3
4×4
Glass 2
High
2×2b
TiO2 excess per 1×1 unit cell

Configurational disorder, Potts prediction

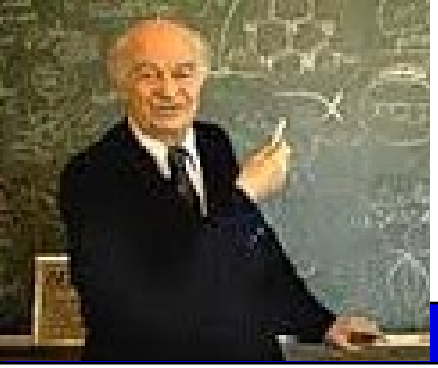


3 dimer orientations of 2x2, rotational glass



3x3 (crosses) embedded

Result is general



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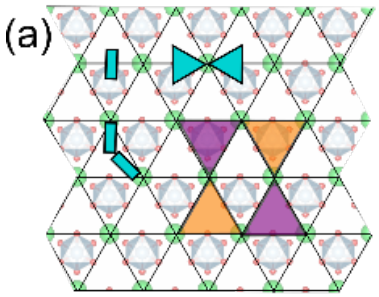
(111) Rules (Double Layer)

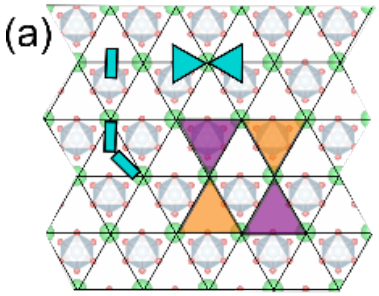


Turquoise- face and edge tetra. In double layer reconstructions (layer closest to vacuum, above purple and gold Ti atoms)

1. Topmost Ti's are all 4-coordinated tetrahedral (tet.)
2. Tet. are either face or edge-displaying
3. Face tet. occur at the type of sites shown (one corner is directly above Sr site, the other two are always near the center of the triangular grid such that the tet. spans two triangles)
4. Edge tetra. can have either 1 topmost O directly over an Sr with the other O in the center of a triangle grid or (much less common) both topmost O's over the center of two grid triangles- spanning (as shown)
5. Ti in the layer below follow the same rules to the single Ti-layer reconstructions but now rely on the Ti in the topmost layer to provide sufficient bonding for O's
6. Stoichiometry is maintained (Sr can be added/removed to ensure this)
7. Must be at least p-3 in symmetry

T. Andersen et al, Surface Science Reports. 2018.73.213.

(111) Rules (Single Layer)



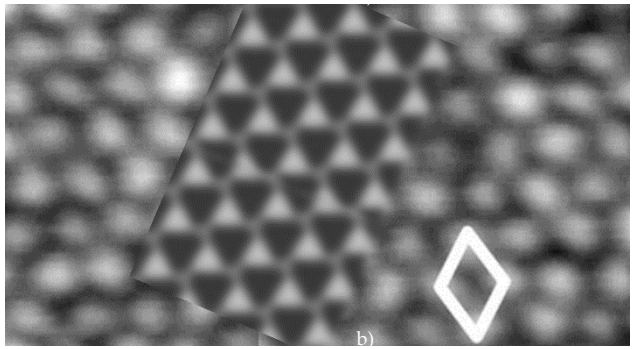
Purple/gold- 5-fold and 6-fold Ti in both single and double-layered reconstructions (occur directly above bulk termination)

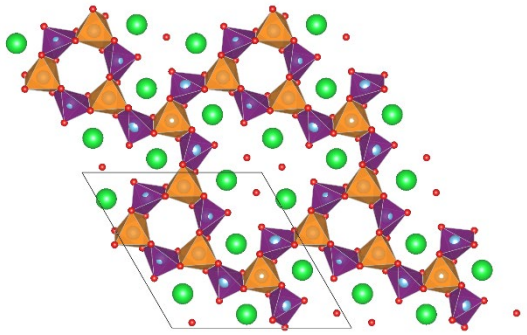
1. Fill in the grid triangles- Ti are all either 5 (purple) or 6-fold (gold)
2. Ti on “natural Ti sites” (empty triangles) are lower energy than the other triangle sites- reconstruction will maximize the number of “natural Ti sites” filled
3. Stoichiometry is maintained (Sr can be removed to ensure this)
4. Topmost O’s are only ever shared by 2 Ti
5. Must be at least p-3 in symmetry

(111) New Structures

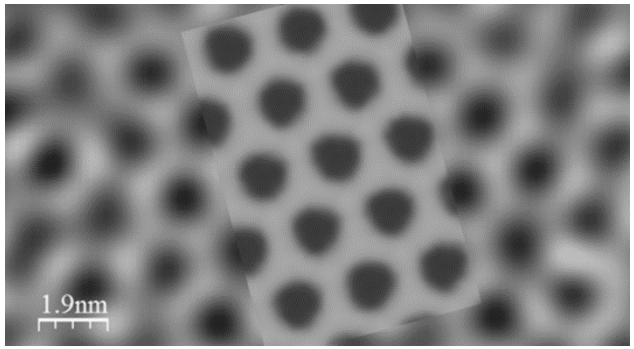
Single-layer reconstructions generated using rules:

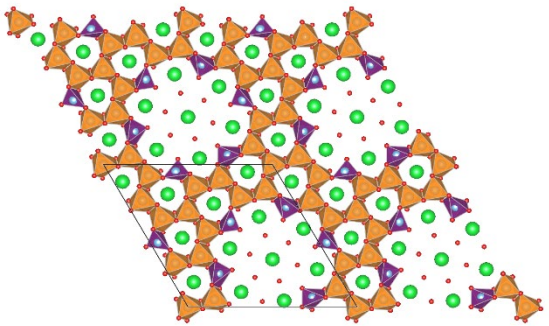
$(\sqrt{7} \times \sqrt{7})R19.1°$



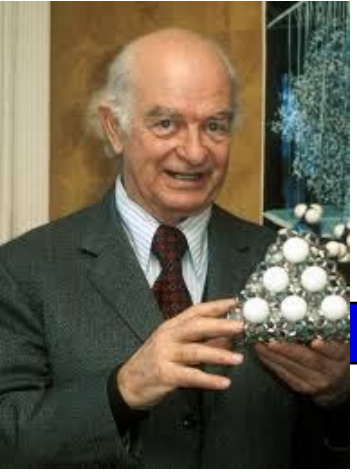


$(\sqrt{13} \times \sqrt{13})R13.9°$





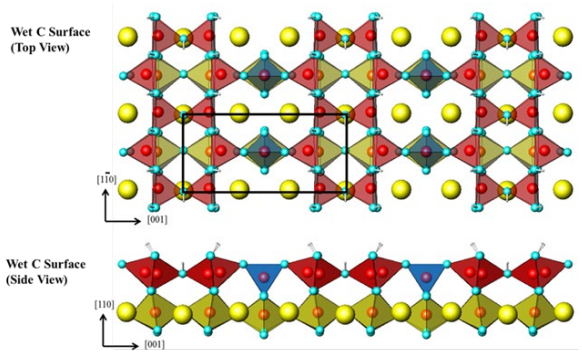
T. Andersen et al, Surf Sci. 2018;675:41.

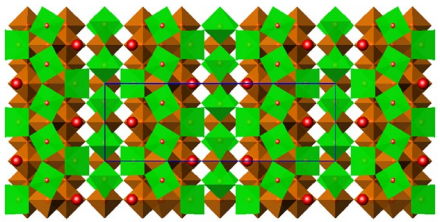


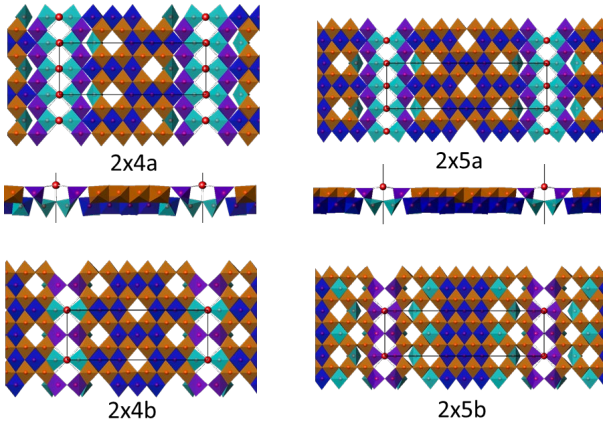
The analysis is general

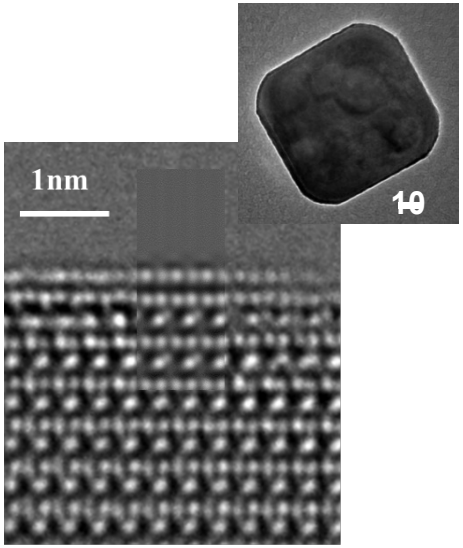
There are many more kinetic/thermodynamic reconstructions

But…they all follow the same rules

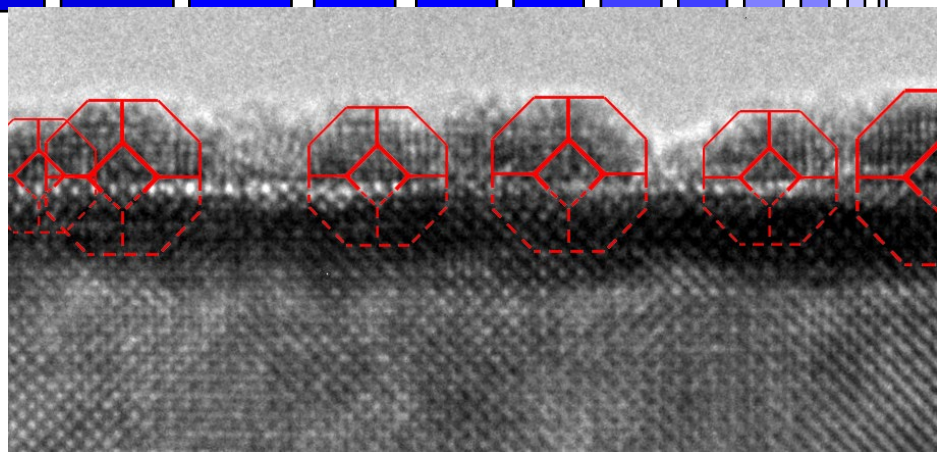


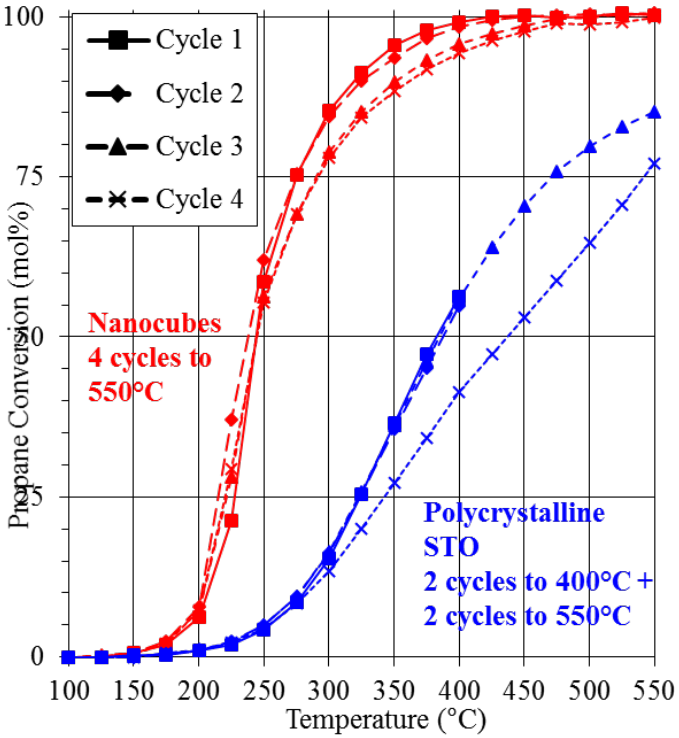


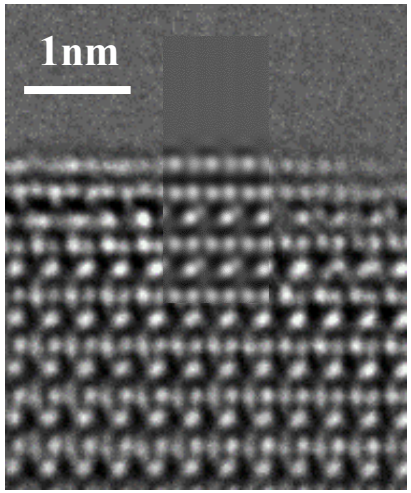




Better Catalysts, *by Design*







TiO_2 DL

Control the nanoparticles by epitaxy on oxides

J. A. Enterkin, K. R. Poeppelmeier, L. D. Marks, Nano Lett. 11, 993 **(2011)**

ICEP

Can we exploit the surfaces?

- In catalysis the underlying oxide is often ignored
- What about different surface structures and chemistry?
- Can we design catalysts by designing the oxide?

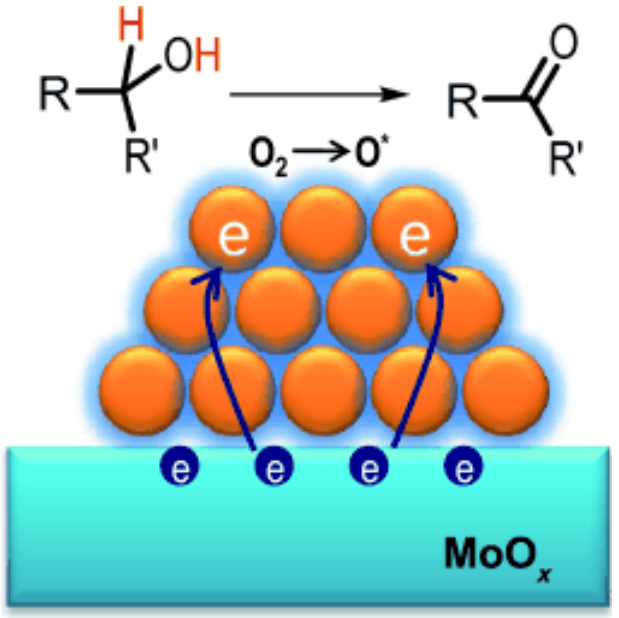
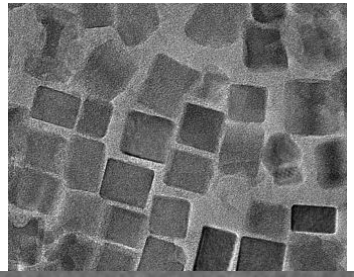


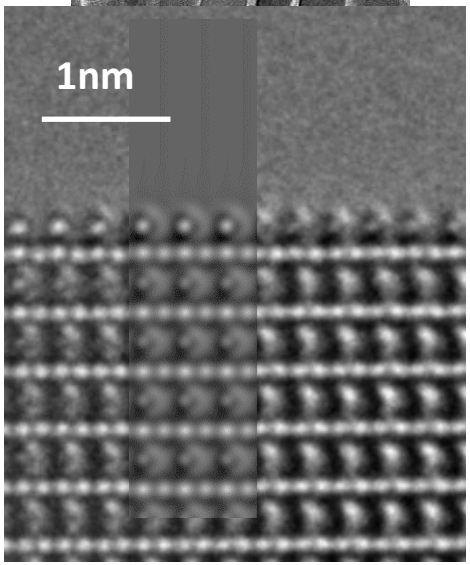
Image from Wang et al, Angewandte Chemie, 51, 3883, 2012

PRL **111, 156101 (2013)**

Nanoparticle surfaces?

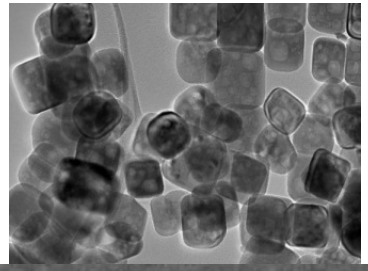
Oleic Acid

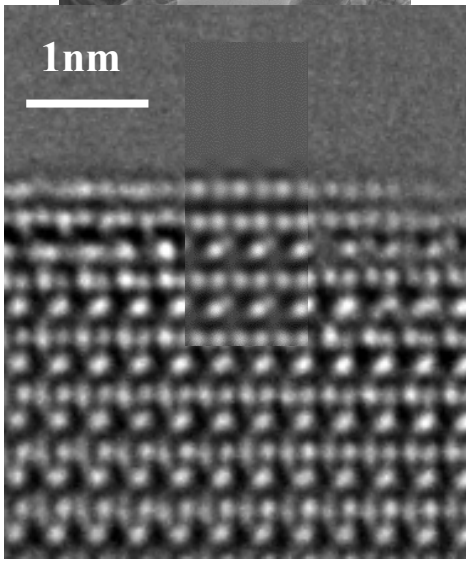




SrO surface

Acetic Acid



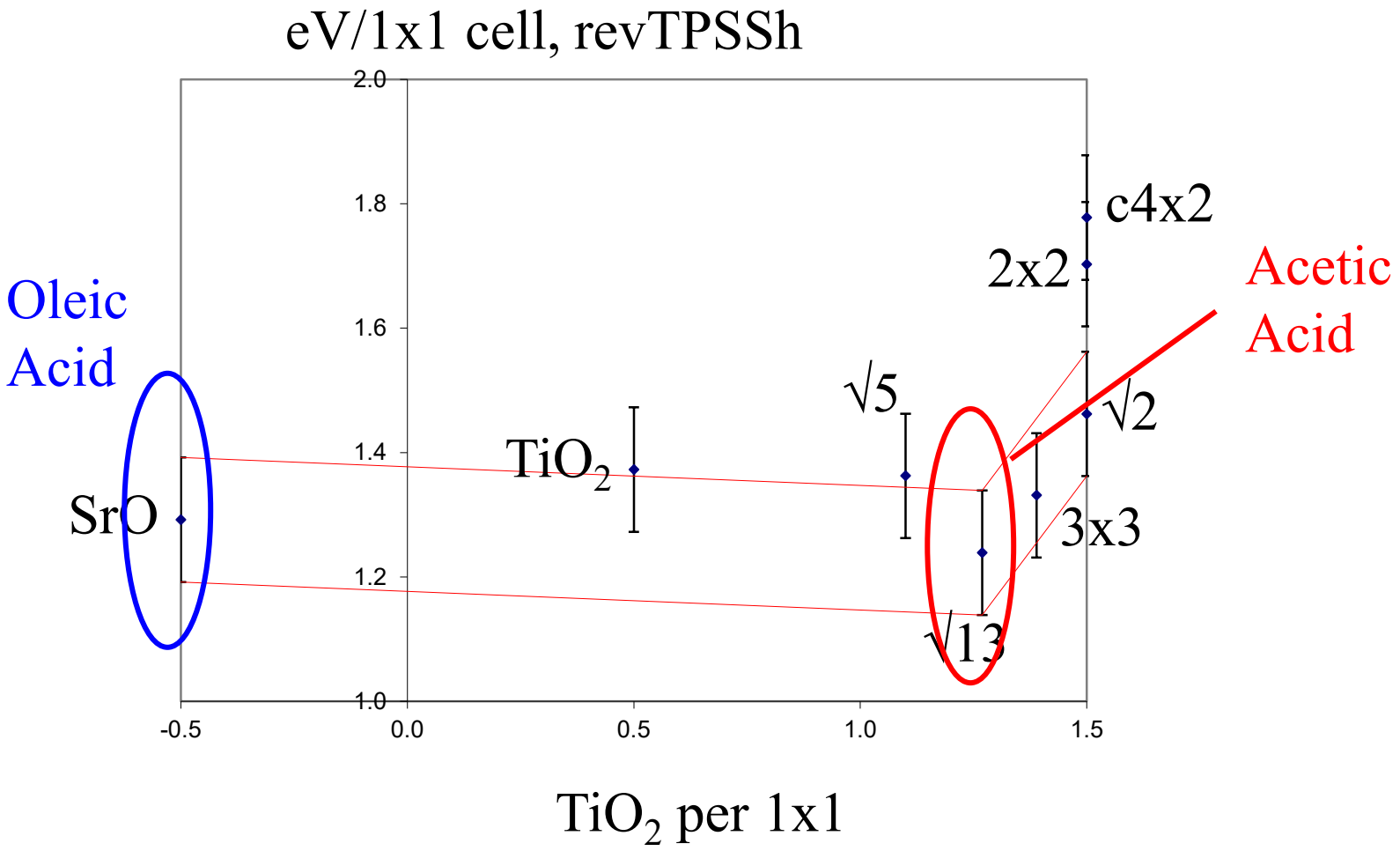


TiO_2 DL

ANL
ACAT

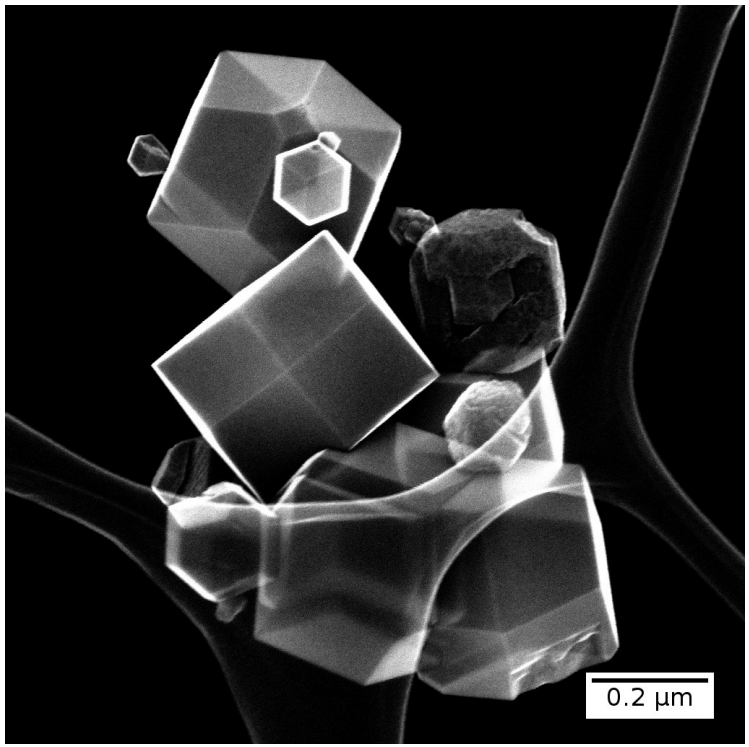
Profile imaging: L. D. Marks & D. J. Smith, Nature, 1983. **303** 316

Stable according to DFT

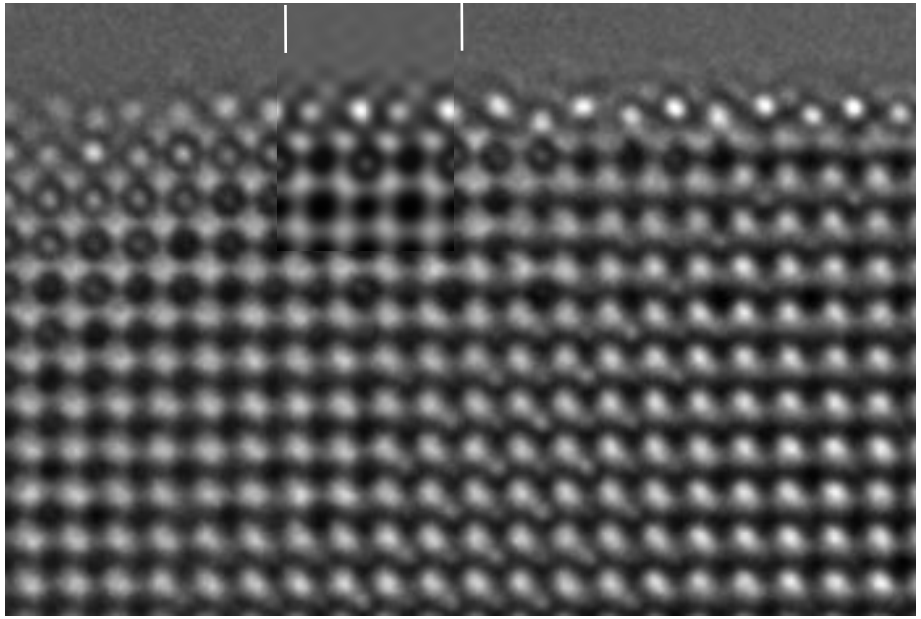


D. M. Kienzle, A. E. Becerra-Toledo, and L. D. Marks, PRL. 106, 176102 (2011)

Glycerol Synthesis



SEM

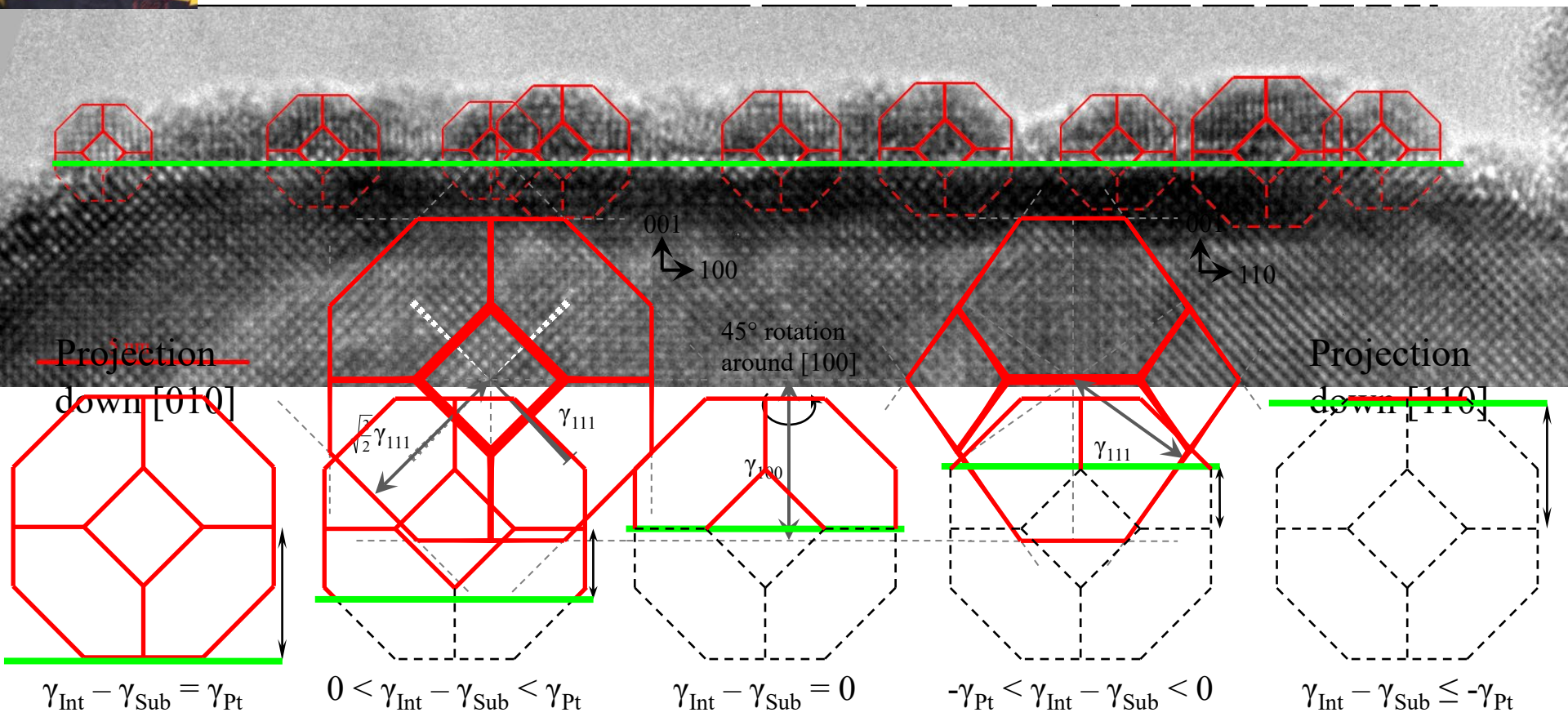


HREM

4x1 Reconstruction on
$SrTiO_3$ {110} facets

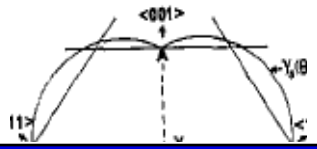
Crosby et al, Nanoscale **8**, 16606 (2016).

Wulff & Winterbottom



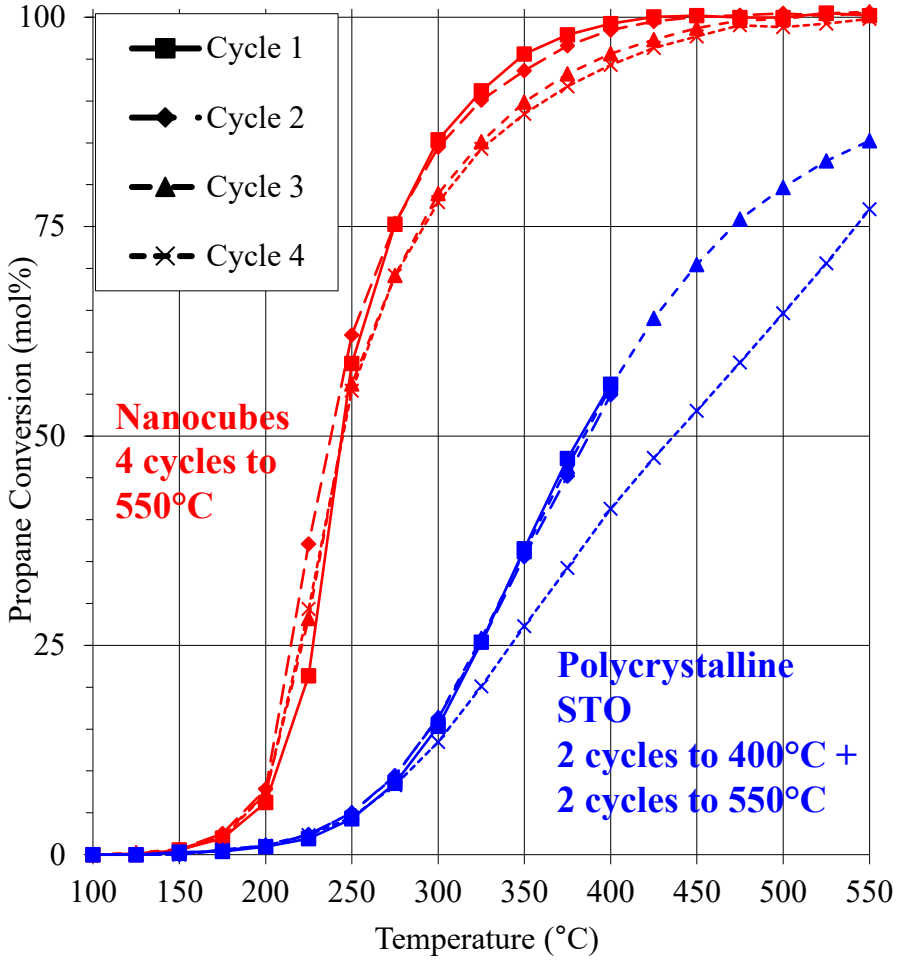
J. A. Enterkin, K. R. Poeppelmeier, L. D. Marks, Nano Lett. 11, 993 **(2011)**; G. Z. Wulff, Kristallogr. Mineral. 34, 4490 **(1901)**; W. L. Winterbottom, Acta Metallurgica 15, 303 **(1967)**

Propane Oxidation

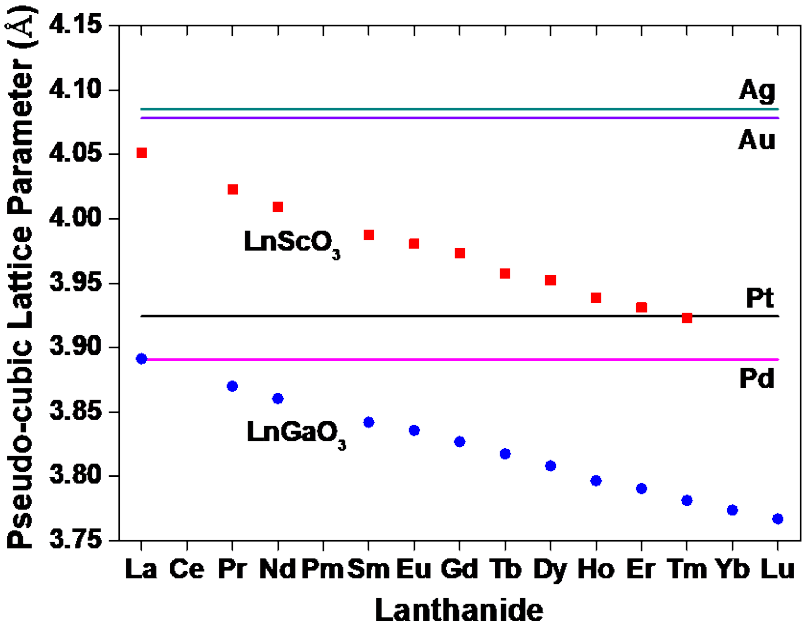


$Pt/SrTiO_3$ epitaxy stabilizes metallic Pt

- For particle of radius R
  $\Delta G=\Delta G_{Ox}+3\Delta\gamma_{Int}/2R$
- More reactive Pt/PtO_x core/shell structure in oxidizing conditions
- Flux of reactants also different for different surfaces

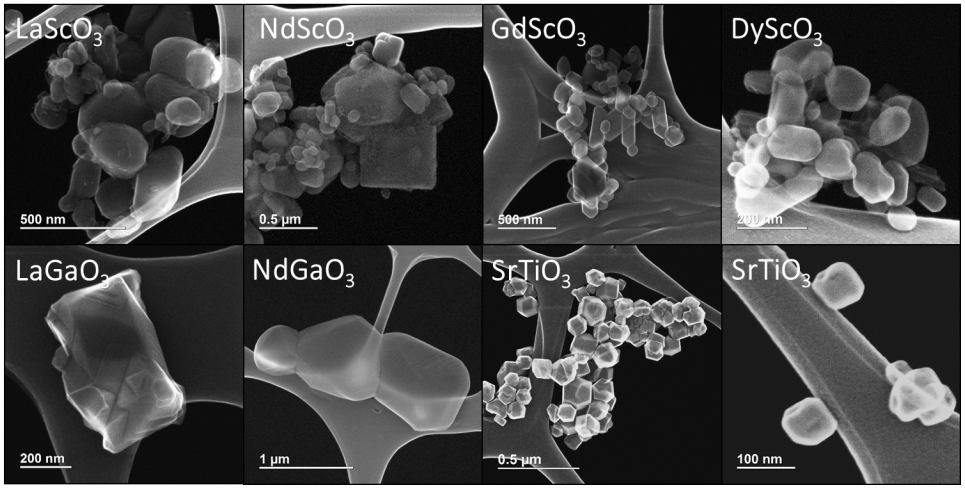


J. A. Enterkin et al,, ACS Catalysis 1, 629 **(2011)**

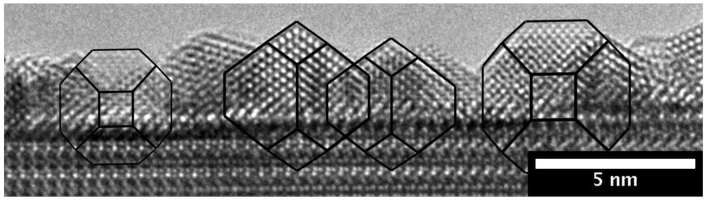


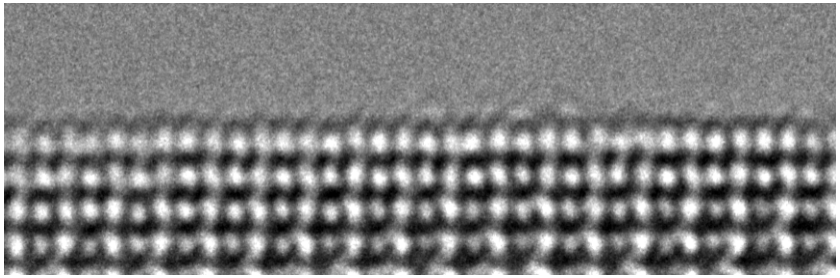
More systematic

Synthesized Support Materials

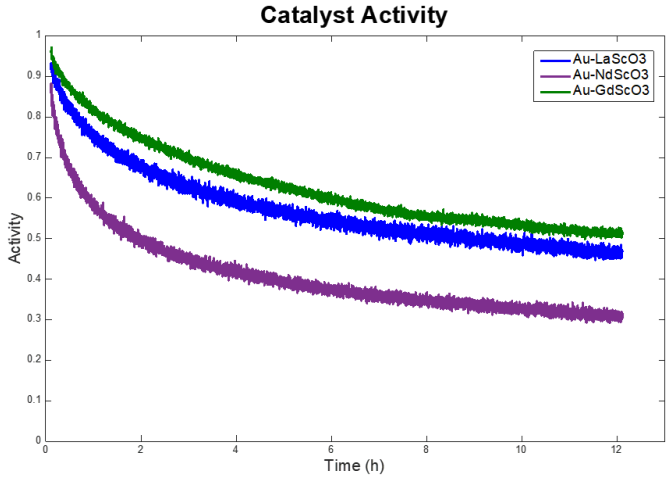


(110) and (111) Au on $NdScO_3$

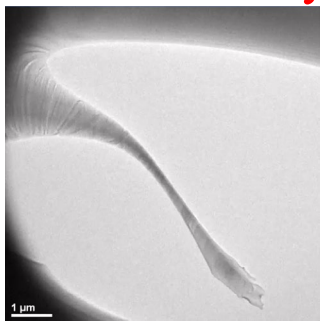




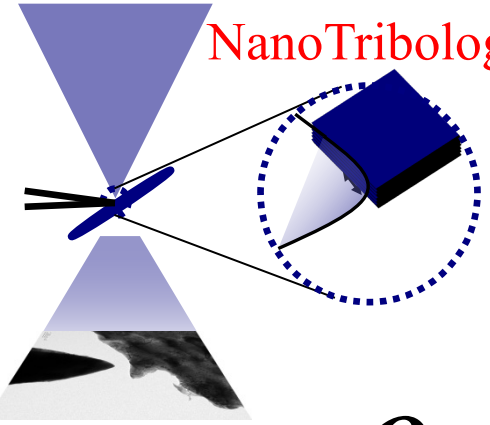
Double-layer Sc_2O_3 terminations

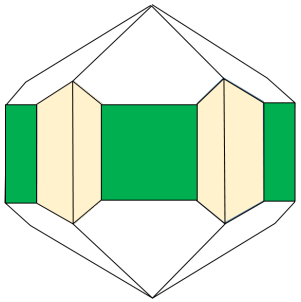


Flexoelectricity



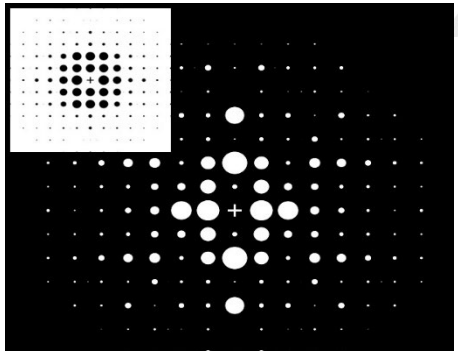
NanoTribology





Nanparticles

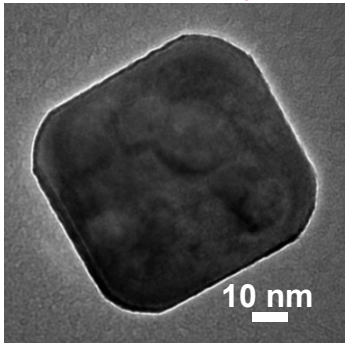
Corrosion



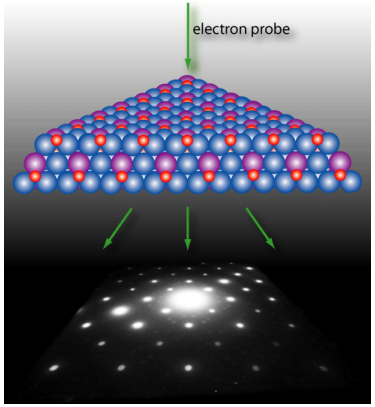
Questions?

Research is to see what everybody else has seen, and to think what nobody else has thought
Albert Szent-Györgi

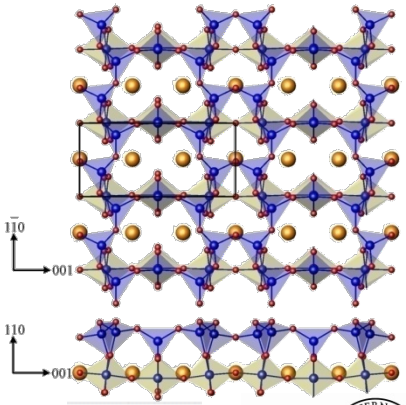
NanoCatalysts



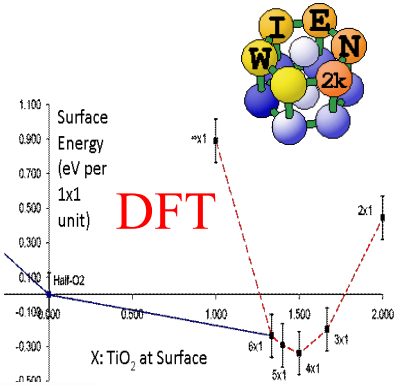
Advanced TEM

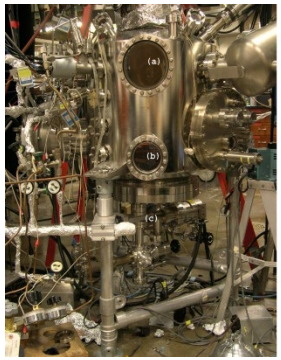


Structure



DFT





Catalysis

Surfaces

National Science Foundation
WHERE DISCOVERIES BEGIN

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