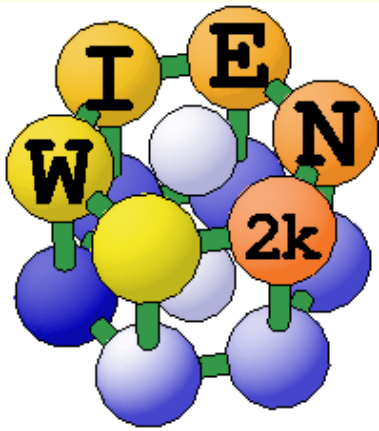
Electronic and geometric structure of the h-BN/Rh(111) Nanomesh

Peter Blaha

Institute of Materials Chemistry, TU Wien

Austria



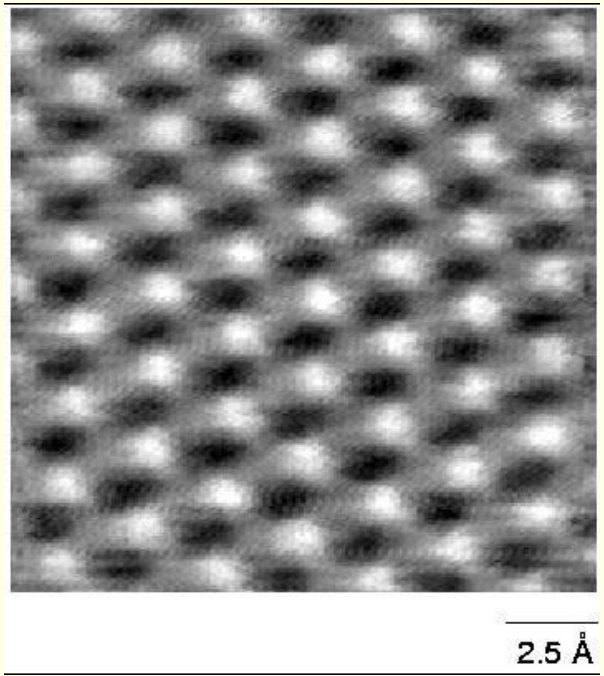
within an EU-projoct lead by J.Osterwalder (Univ.Zürich)
and a joint DFG/FWF project H.Over/P.Blaha

h-BN on transition metal-surfaces

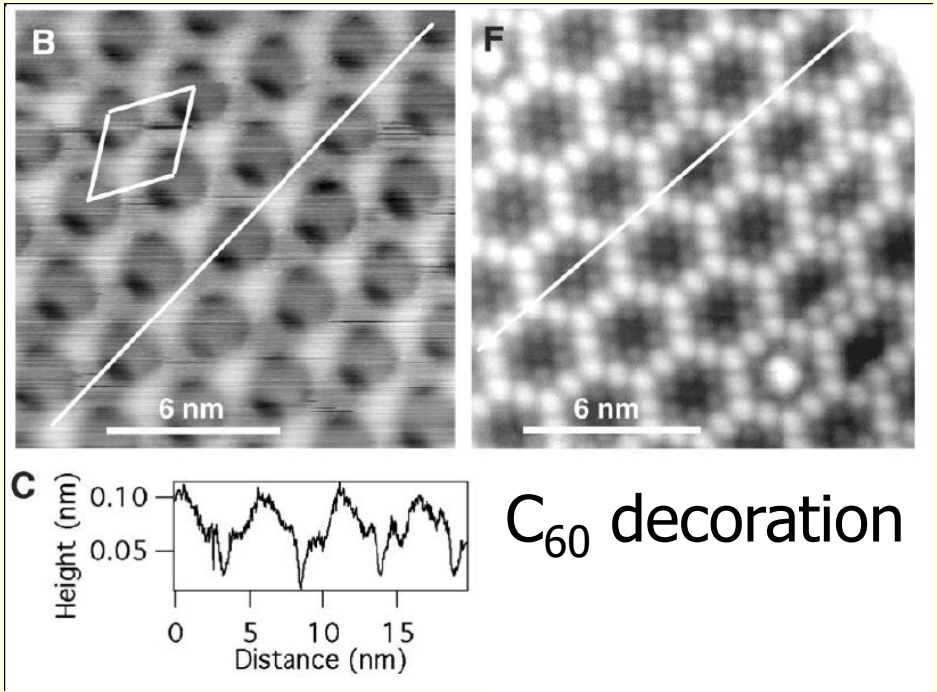
- thermal decomposition of borazine $(HBNH)_3$ on hot TM metal surfaces (~1000K)

- forms simple (1x1) or very complex structures as seen by STM

- h-BN/Ni(111); Cu(111)



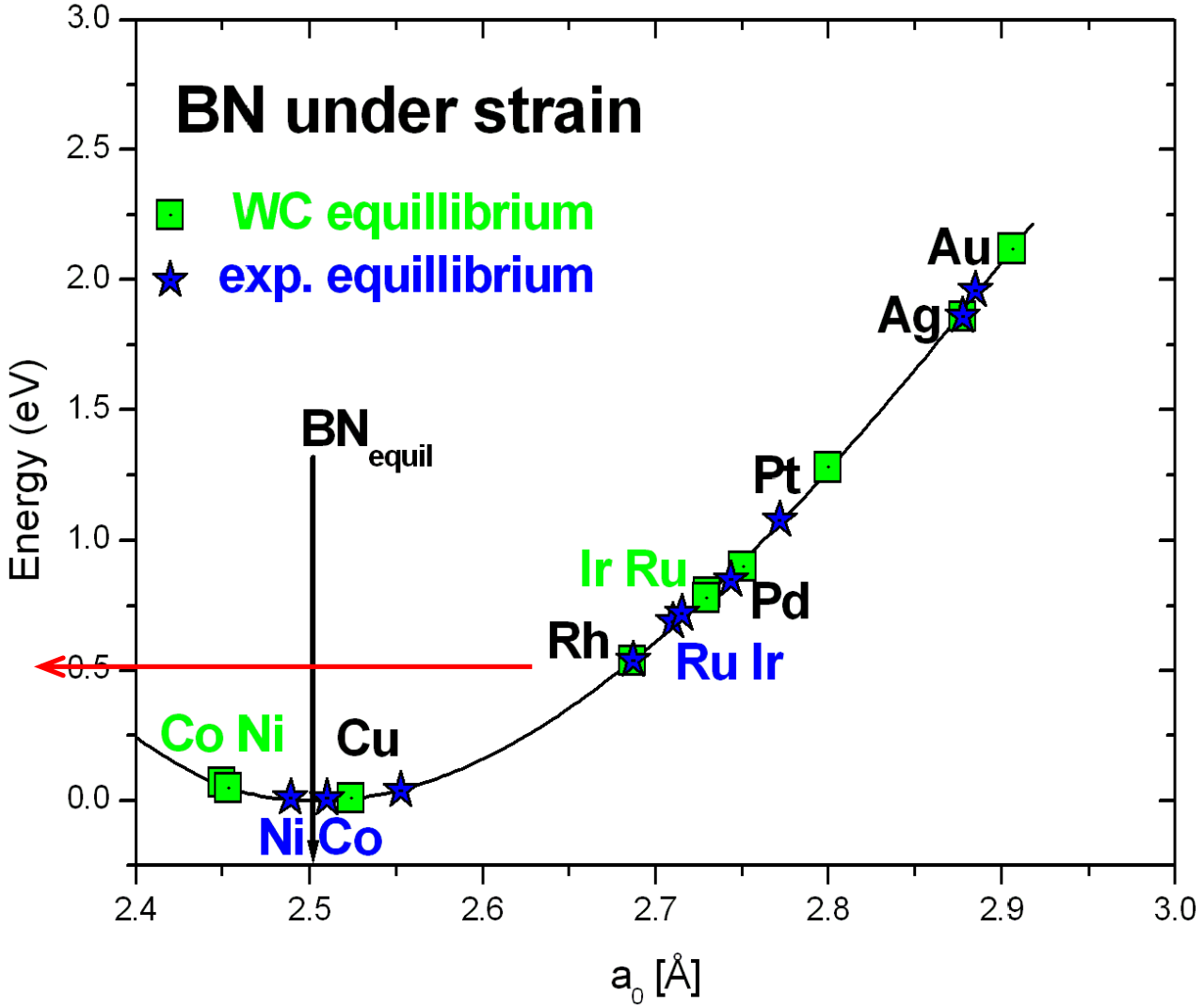
h-BN/Rh(111); Ru(001); Pt(111)



C_{60} decoration

Strain energy of BN on TM(111)

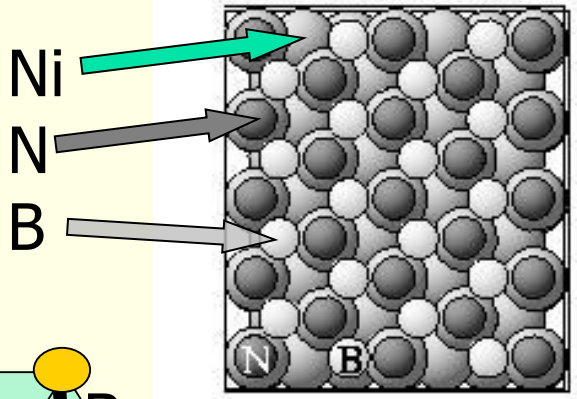
Lattice missmatch

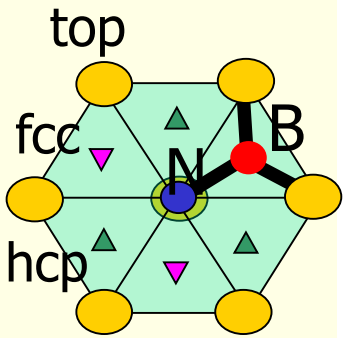


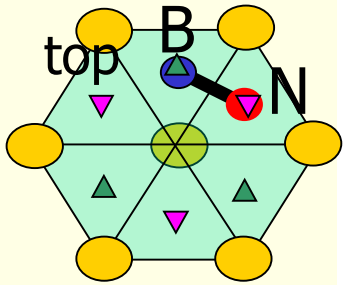
0.5eV/BN

Possible positions of B and N on Ni(111):

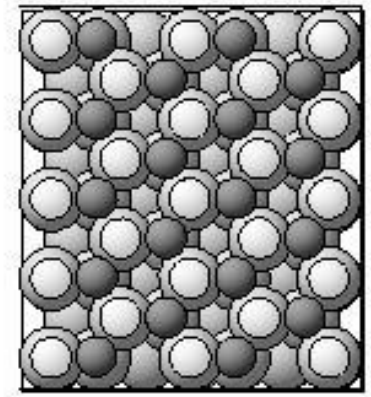
- Only N on „top" of Ni gives stable structures
- (top,fcc) by only 9 meV/BN more stable than (top,hcp)



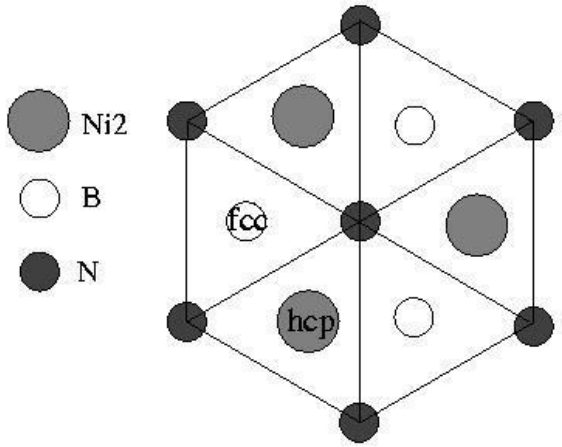


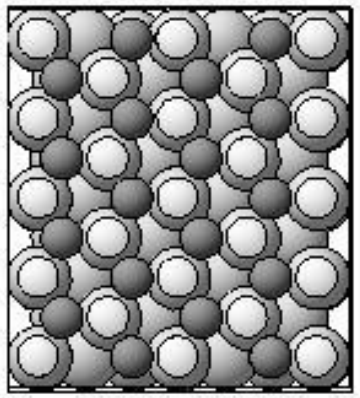


(N,B)=(top,fcc)

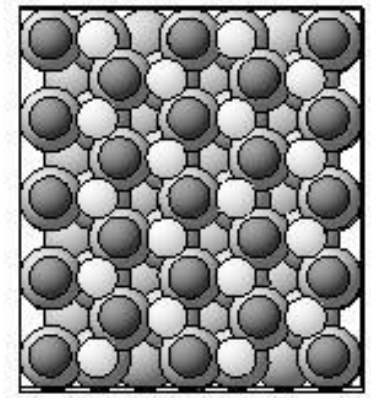


(N,B)=(hcp,top)

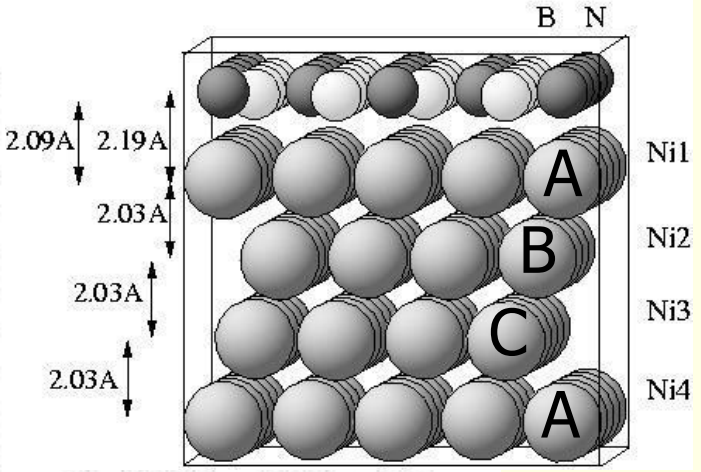




(N,B)=(fcc,top)



(N,B)=(top,hcp)

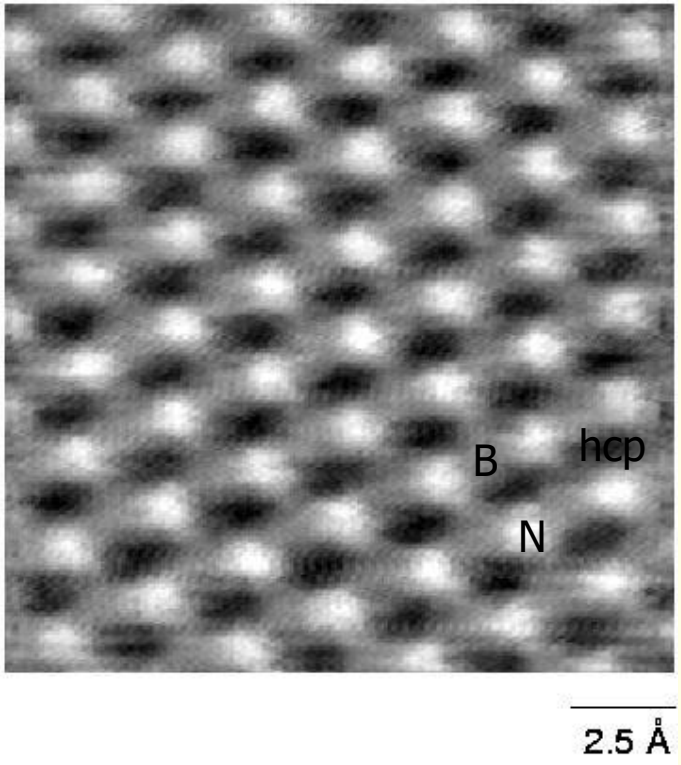


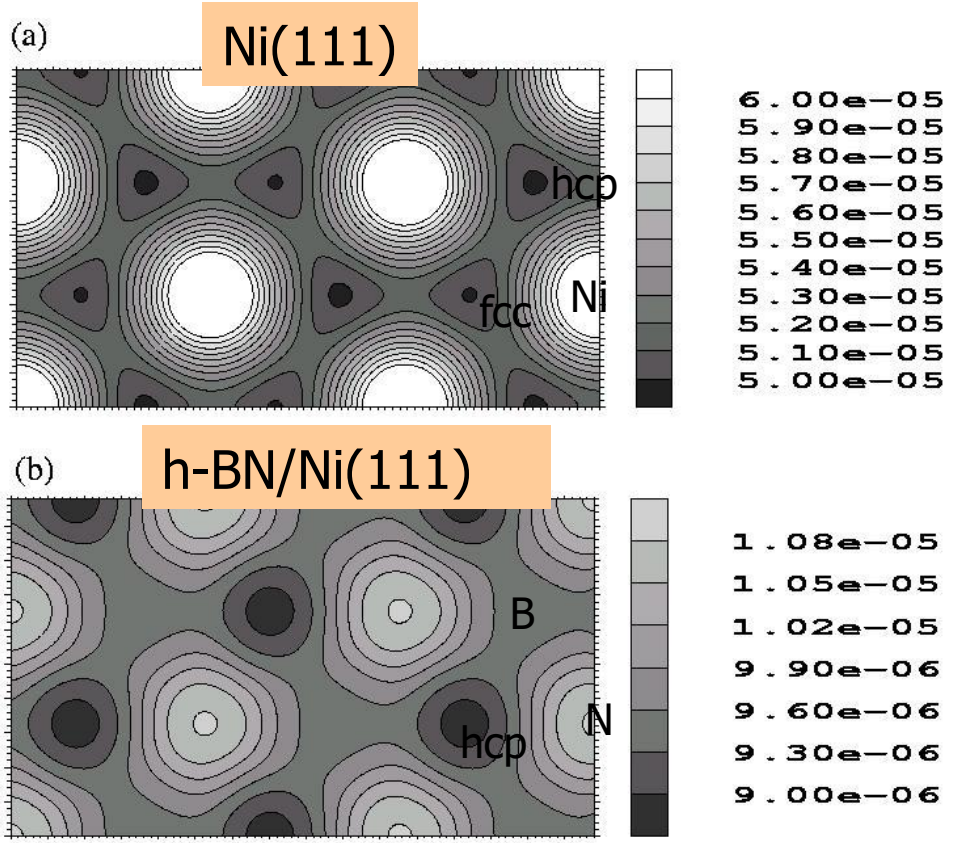
STM-data of h-BN/Ni(111)

$$I_t \propto \sum_v |\Psi_v(r_0)|^2 \delta(E_v - E_F)$$

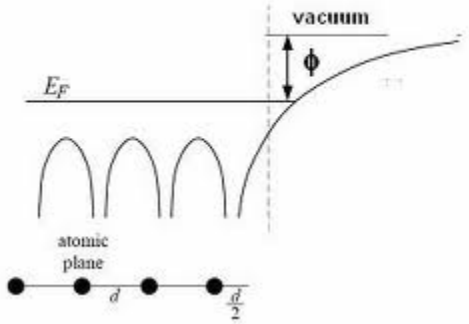
Electron densities at
E_F +/- 0.08eV
r_0: 2.5A from surface

- Exp: three different sites are visible. Which site is dark? Which white ?





Workfunction shift:

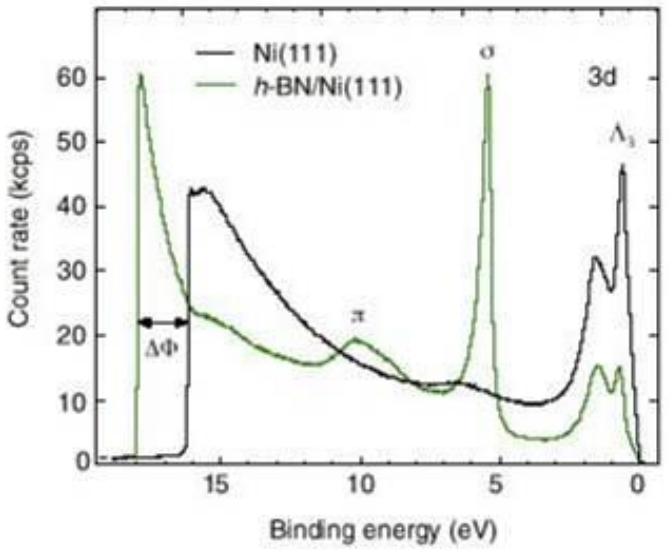


workfunction:

Ni	h-BN/Ni	
5.3	3.5 eV	exp.
5.6	3.9 eV	theory

charge transfer
(Bader's AIM method):

	N	B	Ni
free h-BN-l:	-0.56	+0.56	e⁻
h-BN/Ni:	-0.59	+0.65	-0.06



Intensity drop!

FIG. 2. He I normal emission UP-spectra for Ni(111) and *h*-BN/Ni(111). The work function decrease and the shift of the Λ_3 Ni *d* band feature upon formation of the the *h*-BN layer indicate a decrease of the Ni magnetic moment (for details see text).

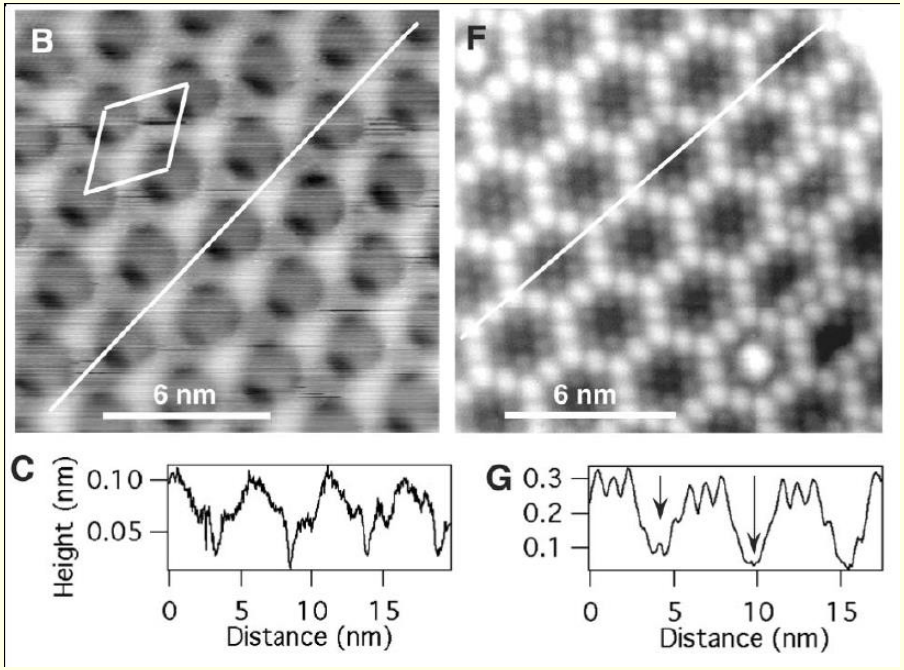
electrostatic picture with 1A charge separation➔ 2eV shift

additional 0.06e should fill Ni-dn states: ➔ smaller moment

h-BN/Rh(111) superstructure

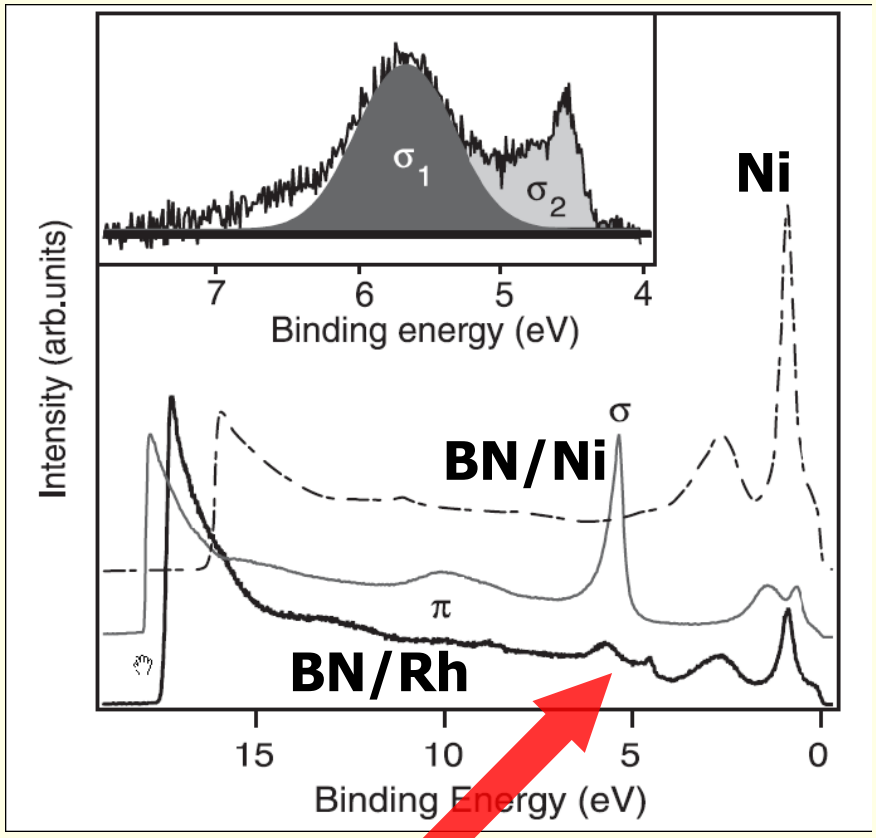
STM, h-BN/Rh(111)

h-BN/Rh(111) C_{60} decorated



M.Corso et. al, Science, 303, 217 (2004)

Normal emission UPS (21.2 eV)

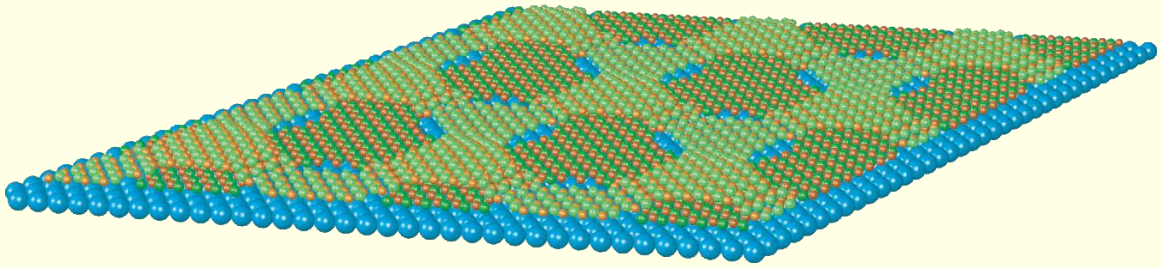


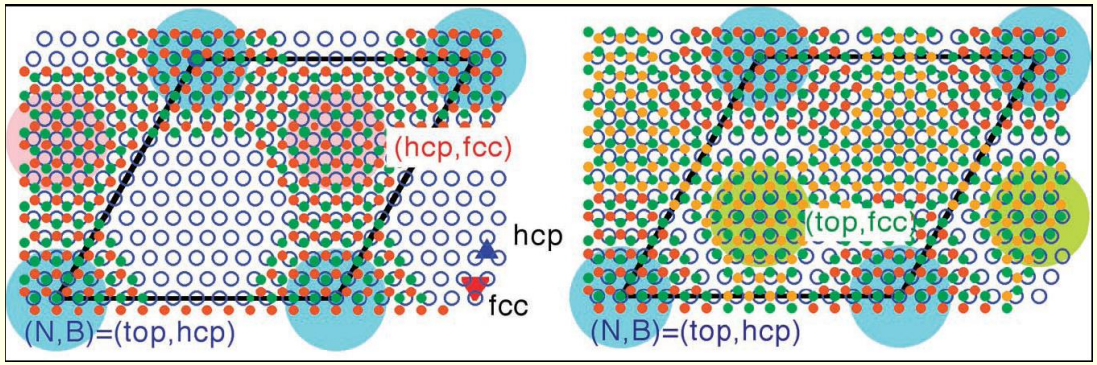
- periodicity 3.2 nm, 3 different regions
- corrugation ~0.5 -1 Å

- σ band splitting (1 eV)
- indicates two species of BN

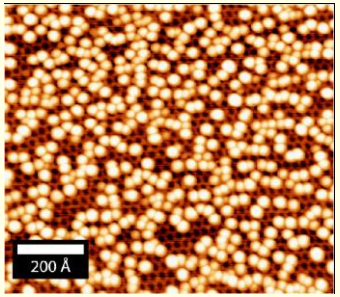
Nanomesh- double layer model

M.Corso et. al, Science, 303, 217 (2004)



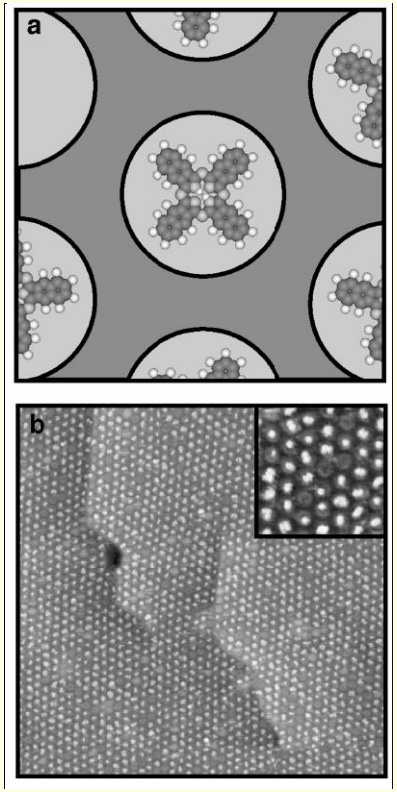


Co clusters



T.Brugger

naphthalocyanine on h-BN/Rh(111) (annealed at 550K)



S.Berner etal., Angew.Chemie

- formation driven by Rh-BN lattice mismatch (7%)
  → 12x12 Rh / 13x13 BN superlattice
- two incomplete layers of h-BN
- holes in h-BN can dock molecules or clusters

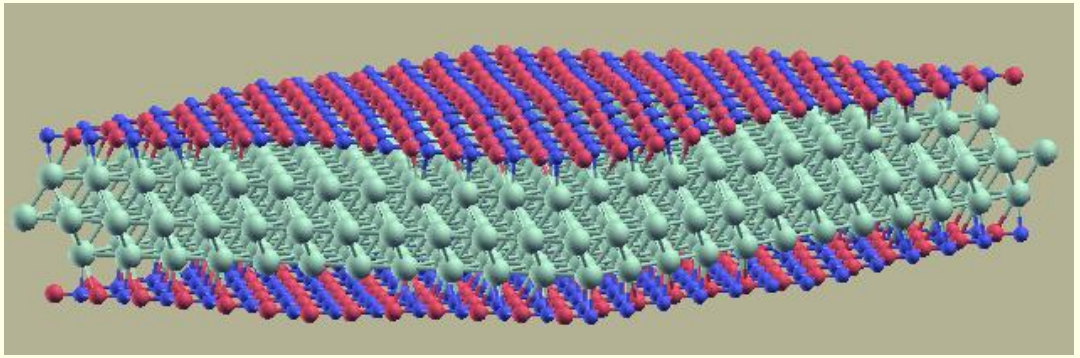
double layer model – weak points?

- high energy costs due to broken BN bounds **!**
- no reason for second layer to be incomplete **!**
- STM measured corrugation is small compared to distance between layers in h-BN **!**

- interaction of h-BN with Rh(111) **?**
- why is h-BN/Rh(111) so different from h-BN/Ni(111) and does not form a flat overlayer **?**
- propose an alternative model, that **explains** observed **STM** images and **UPS σ band splitting ?**

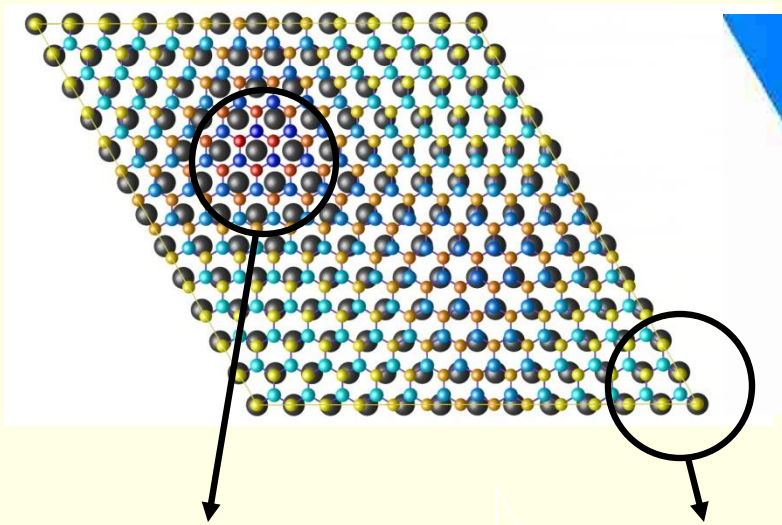
single layer model of the h-BN/Rh(111) nanomesh

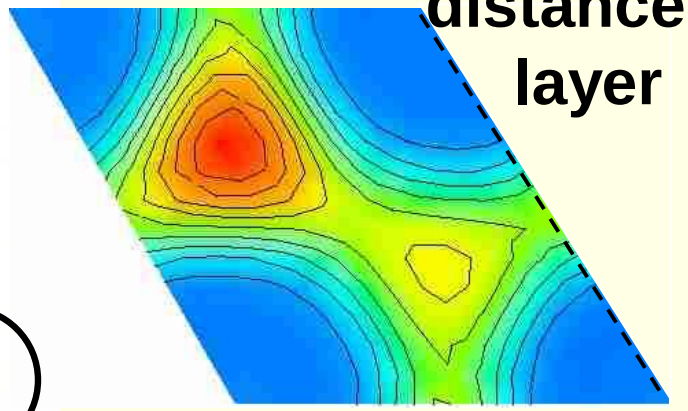
- single continuous BN layer: 13x13 BN on top of 12x12 Rh(111)



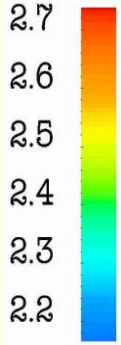
- DFT simulation:
  - quite heavy: 3 layers TM + BN: **1108 atoms/cell (metal!)**
  - **WIEN2k** (all electron APW+lo full-potential calculations)
    - **Hamiltonian size ~50000-70000 (50-100GB memory)**
    - **64-512 cores (Xeons), 120-20min per SCF iteration, 30 iterations/scf**
    - **full structural optimization**

corrugated h-BN layer on Rh(111)

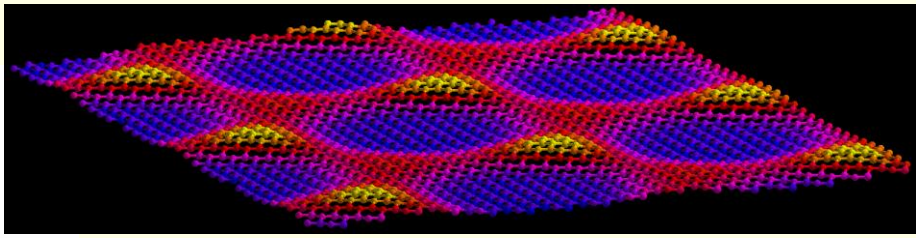


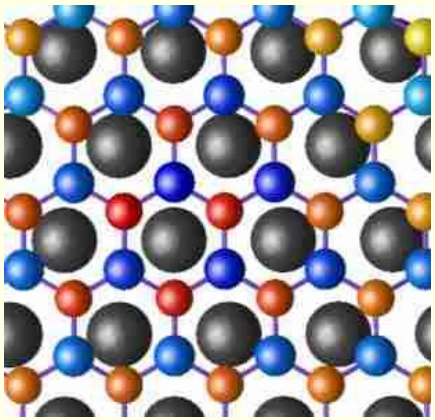


distance of N from metal layer

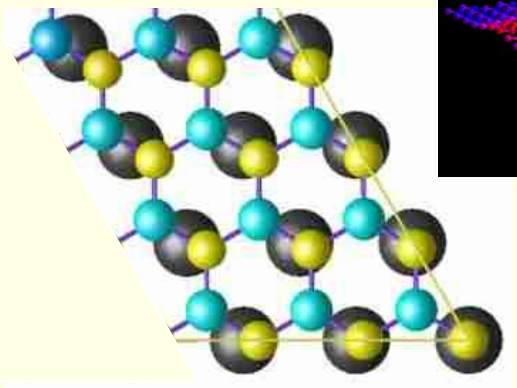


3 nm





"high": "top" empty



"low": N on "top"

N-high B-high

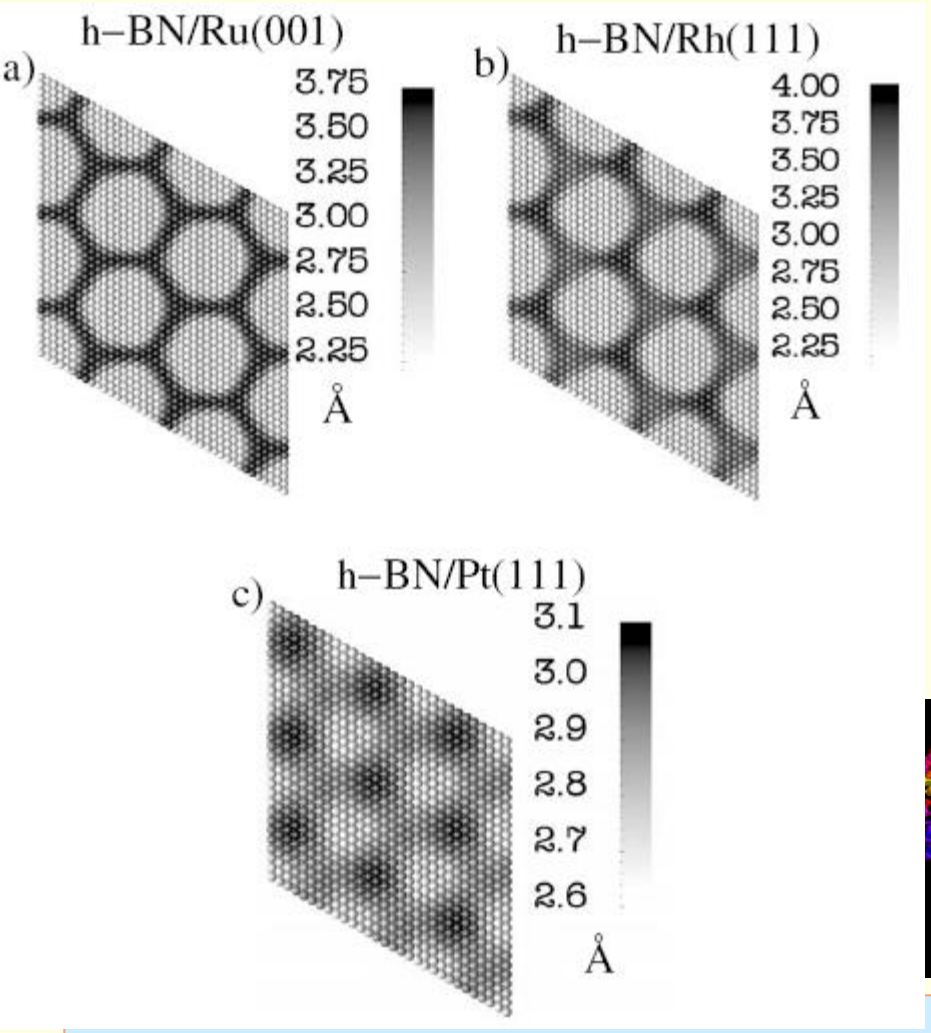
N-low B-low

Rh

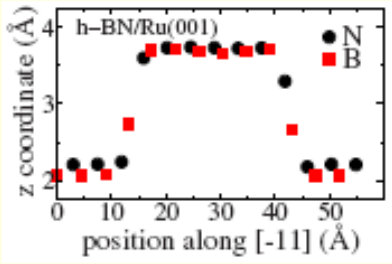
R.Laskowski, P.Blaha, Th.Gallauner, K.Schwarz,
Single layer model of the h-BN nanomesh on the Rh(111) surface
Phys.Rev.Lett. 98, 106802 (2007)

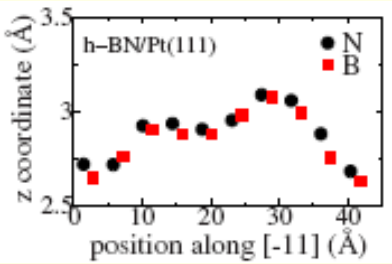
Single h-BN layer on TM(111)

distance of N from metal layer (shown in 3x3 supercell)

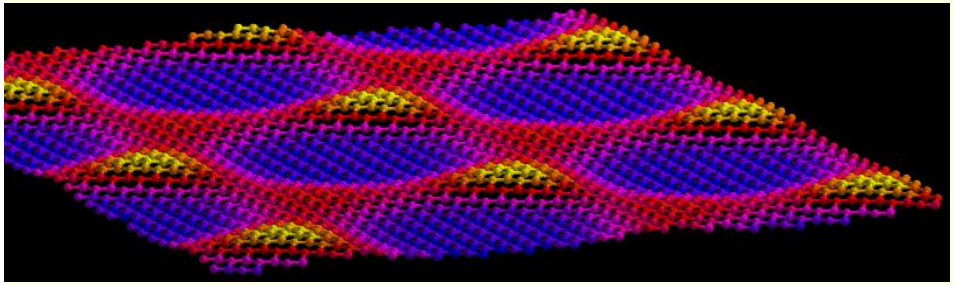


- h-BN layer is corrugated, amplitude ~ 0.5 (Pt) -1.6 (Ru,Rh) Å
- flat region of BN close to metal
- surrounding rims are made of two maxima with slightly different height





enhanced side view

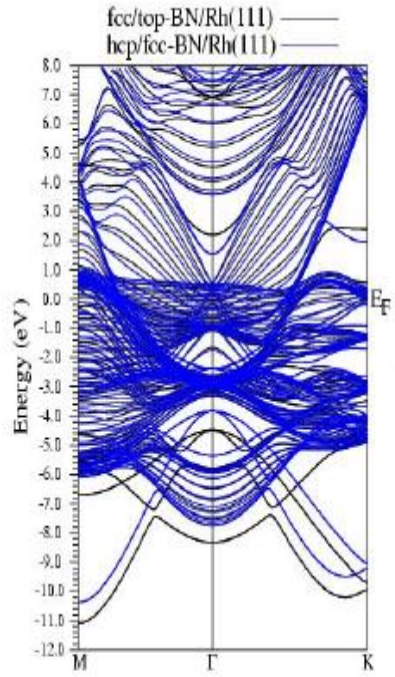


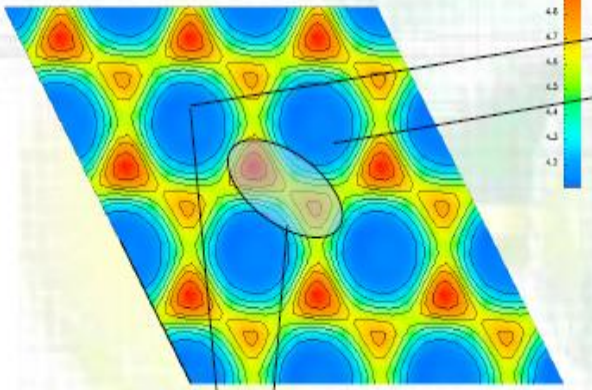
Ab initio study of h-BN nanomeshes on Ru(001), Rh(111), and Pt(111)
R.Laskowski, P.Blaha, PRB 81, 075418 (2010)

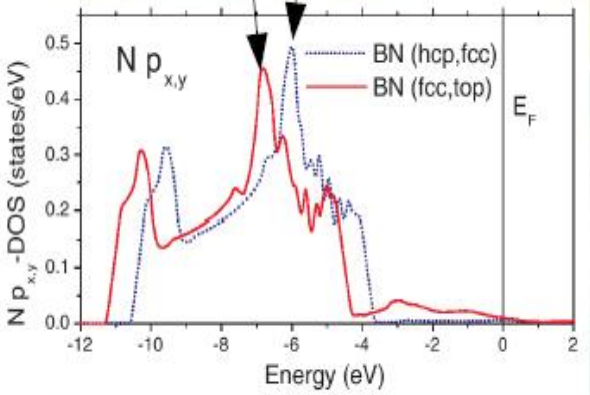
Can the new model explain experiment ?

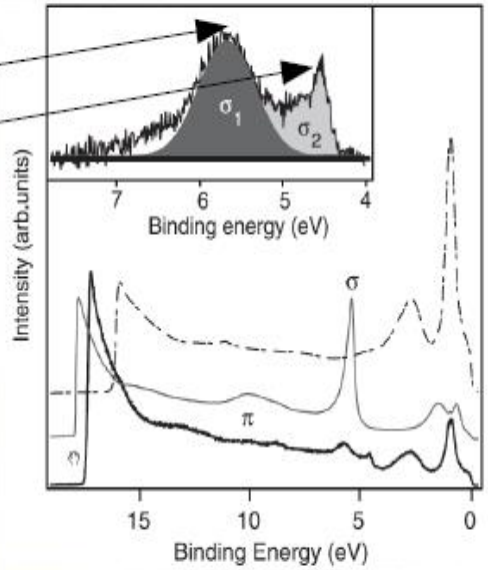
σ (N-$p_{x,y}$) band splitting

experimental UPS









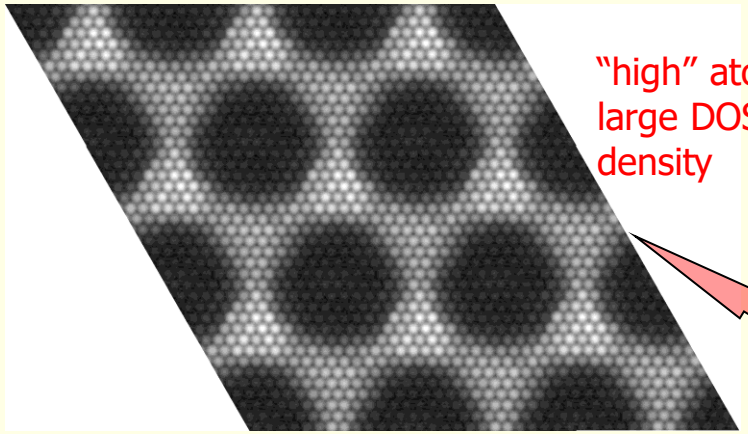
force field (low/high positions 1x1 h-BN/Rh(111)

- band splitting – signal from different regions
- area of the peaks σ_1 σ_2 corresponds to surface areas of the low/hight regions

Comparing STM images (Tersoff-Hamann)

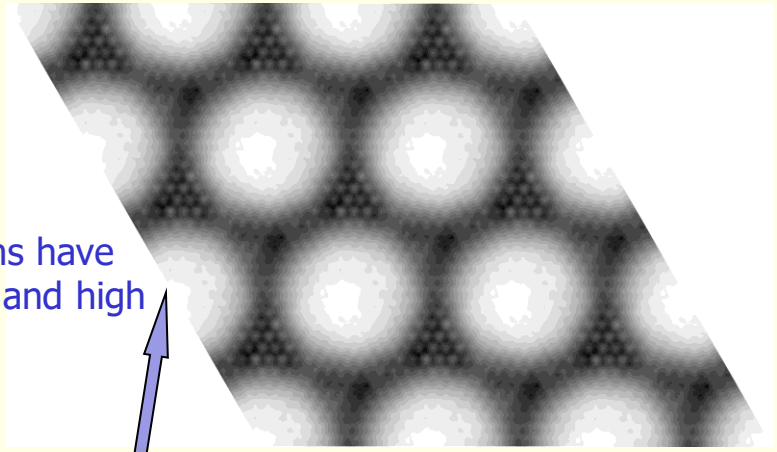
WIEN2k: -2 eV, 2A above surface

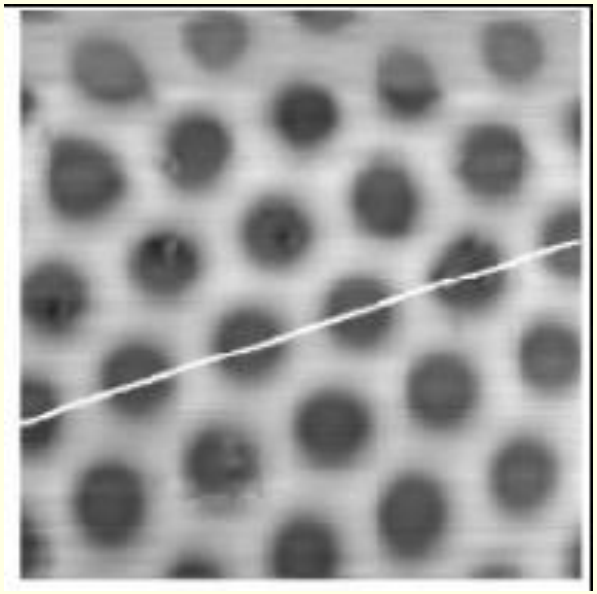
WIEN2k: + 2eV, 3A above surface

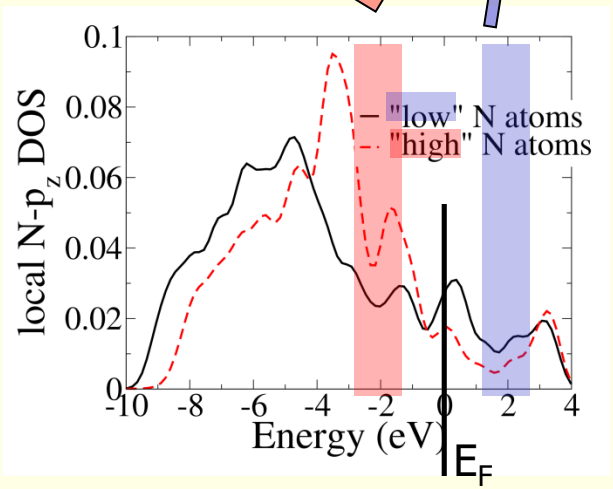


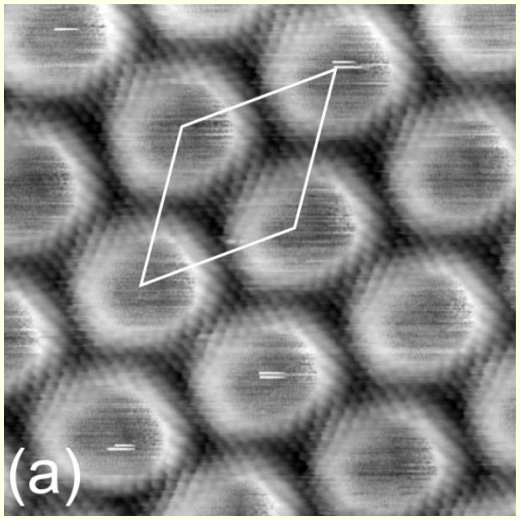
"high" atoms have large DOS and high density

"low" atoms have large DOS and high density







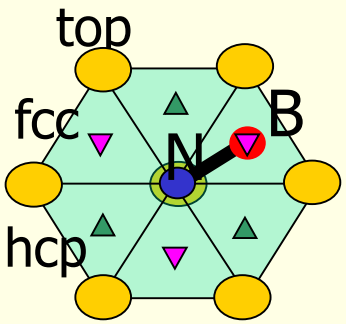


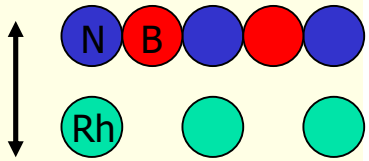
-2V: Goriachko et al., Langmuir **2007,** *23,* 2928

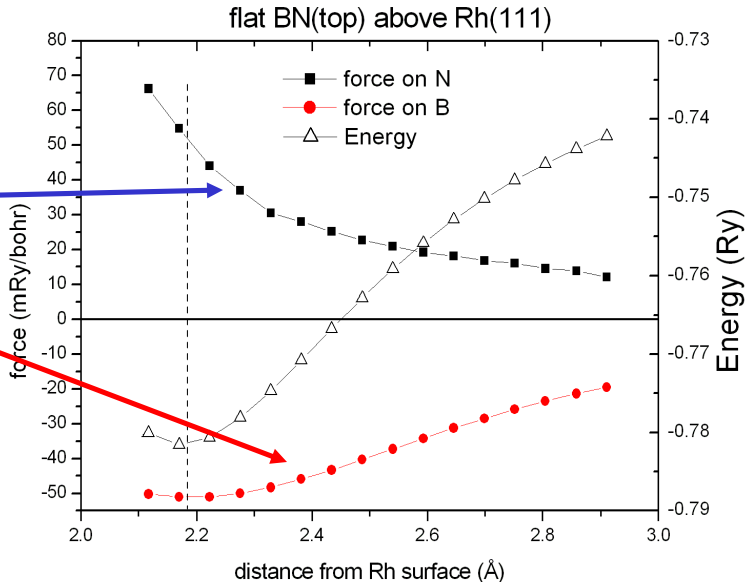
+0.07V: Preobrajenski *et al.* PRB **75**, 245412

What binds BN to Rh ?

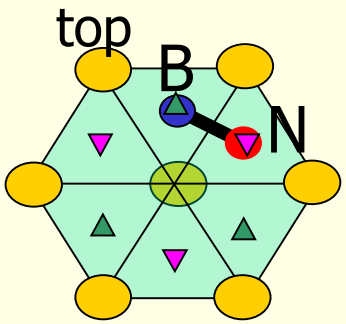
- BN at (fcc,top) position:
  - *attractive B forces dominate repulsive N-forces*

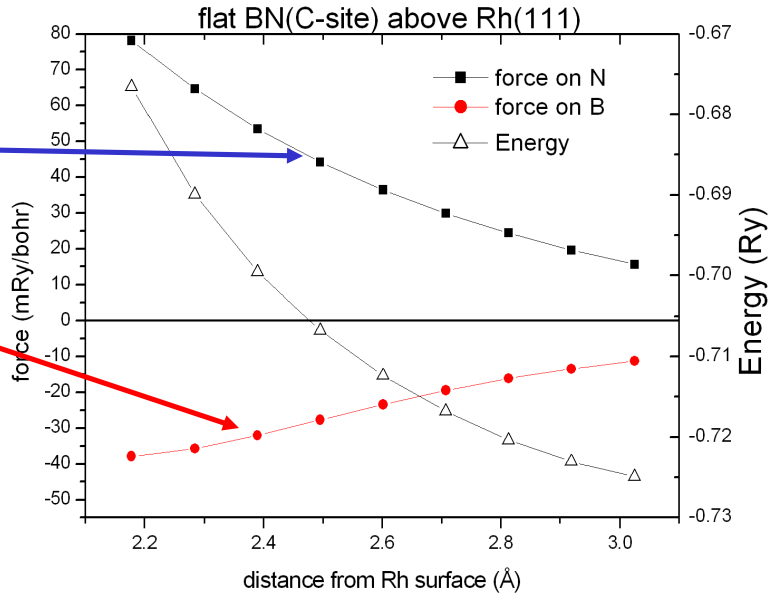




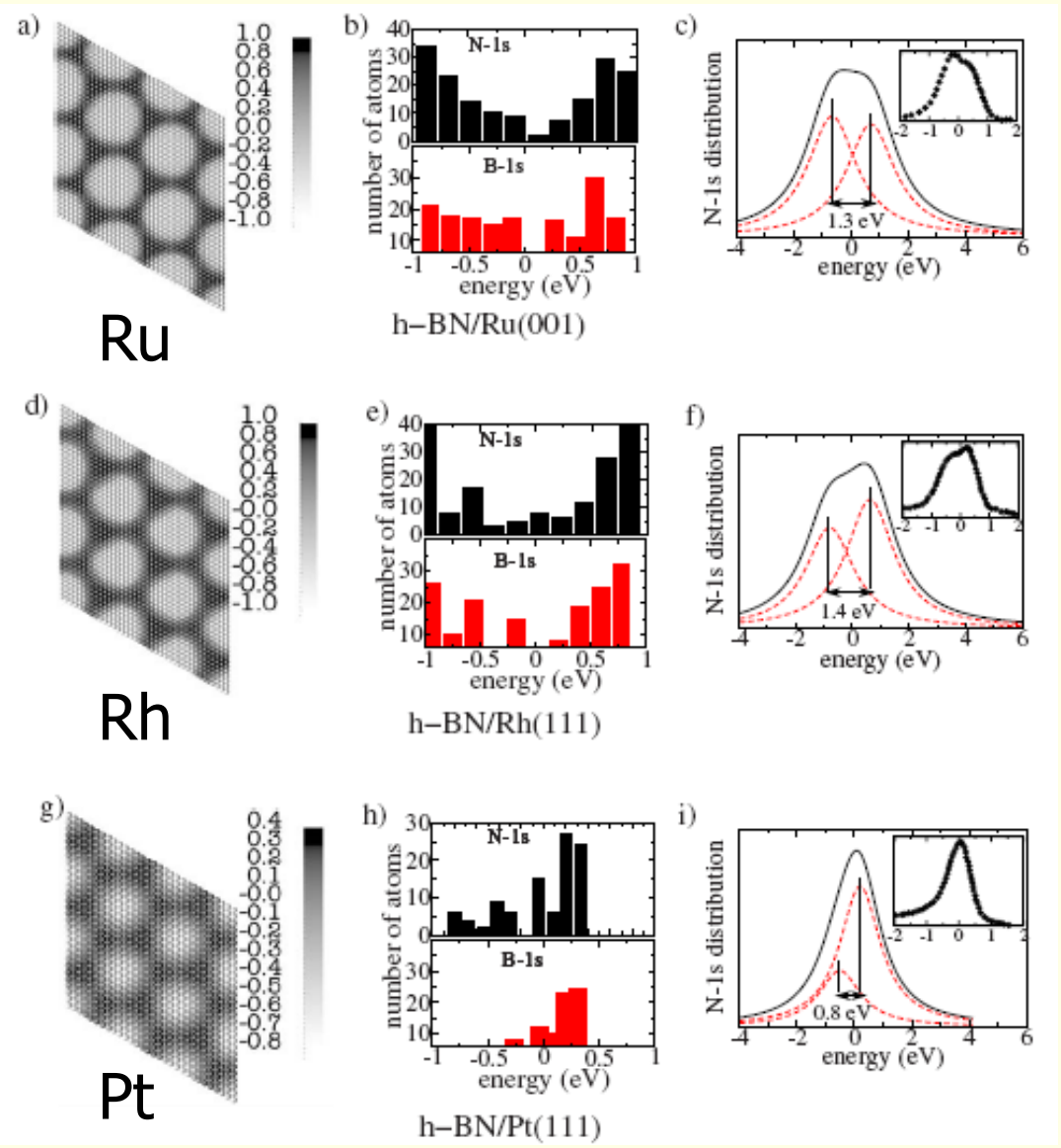


- BN at (hcp, fcc) position:
  - *repulsive N-forces dominate attractive B-forces*

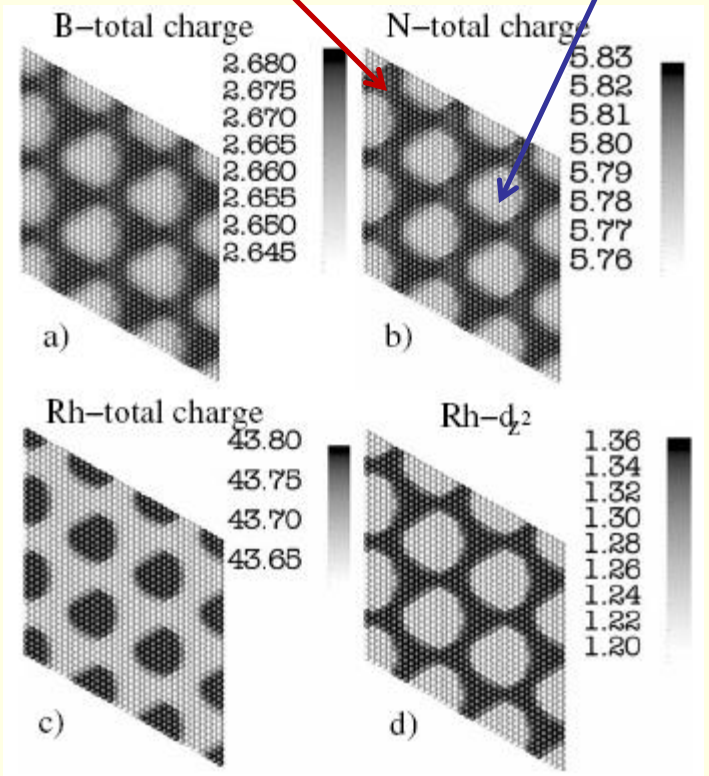




N 1s -XPS core level shifts



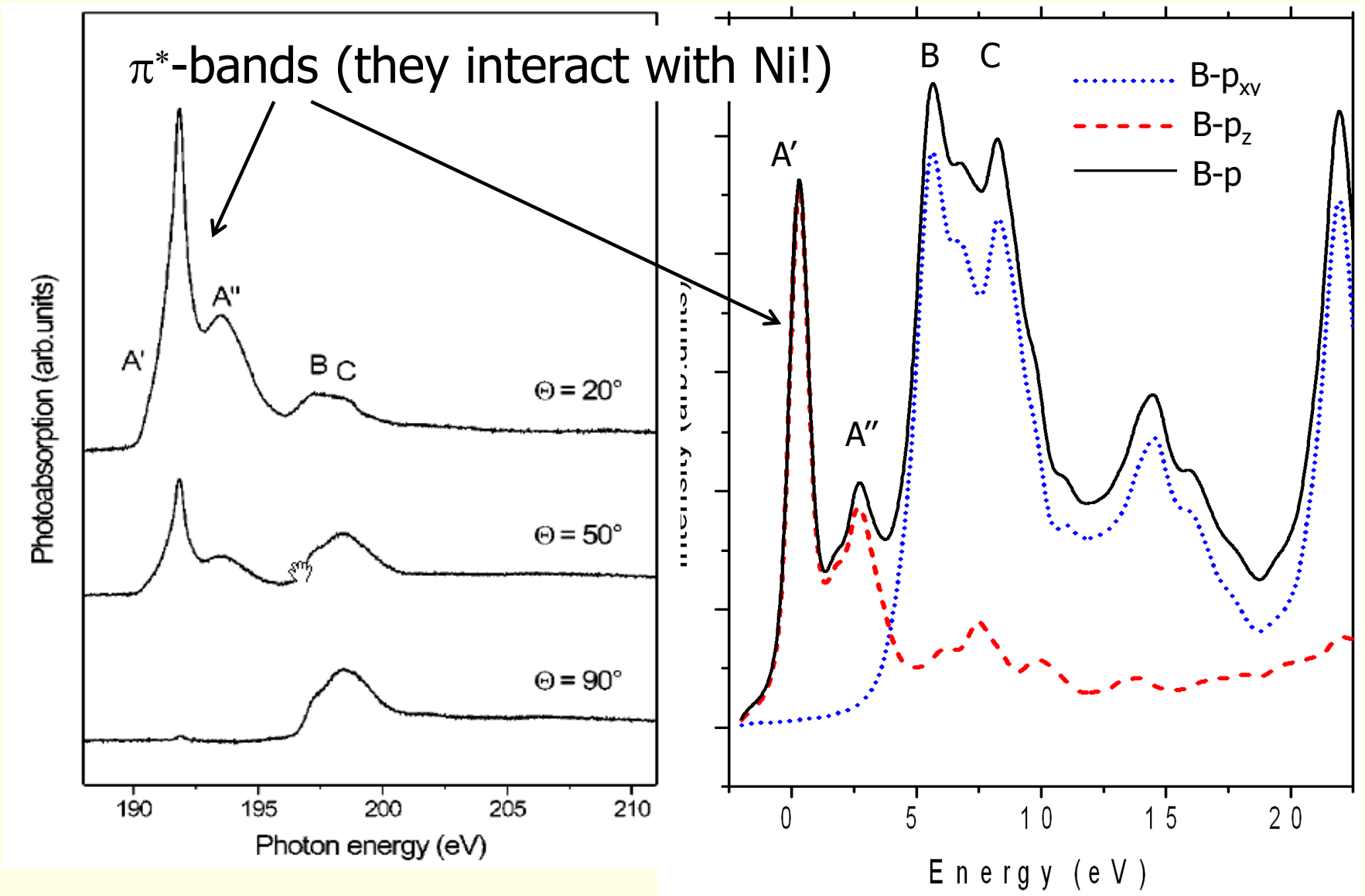
Core level shifts can be explained by different charge transfer at "low" and "high" positions

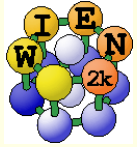


B-K XANES in h-BN/Ni(111)

- B-K edge in BN and BN/Ni(111)
- Preobrajenski etal, PRB70, 165404 (2004): "The experiments contradict recent DFT calculations by Grad etal."

Angle dependency of B-K edge in h-BN/Ni(111)




T
E
W
N
2k


TU
WIEN

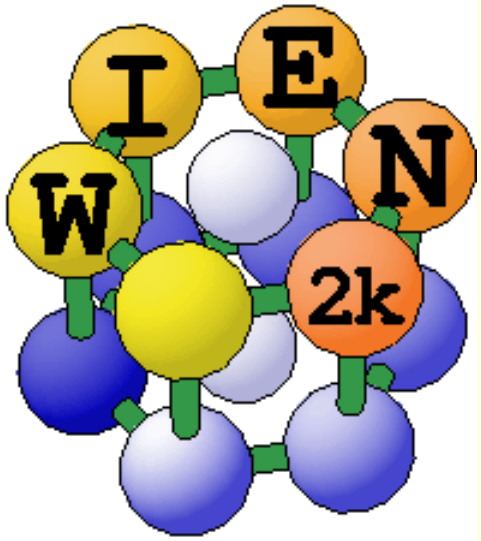
TECHNISCHE UNIVERSITÄT WIEN

Subsurface Cation Vacancy Stabilization of the Magnetite (001) Surface

Peter Blaha

Institute of Materials Chemistry

TU Wien



R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M.A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, G. S. Parkinson, **Science** 346, 1215 (2014)

R.Bliem et.al., **PRB** 92, 075440 (2015)

Magnetite Fe_3O_4

- Magnetite is a natural mineral (lodestone)

- it is a permanent magnet (T_C=858 K) and was used as first compass in ancient time
- technological important material
  - *magnetic recording*
  - *biomagnetism (magnetoreception)*
  - *catalyst for ammonia synthesis*
  - *half-metallic ferromagnet (spintronics)*
  - *corrosion*
- Cubic spinel structure at room temperature
- "Verwey" transition at ~120 K

Magnetite Fe_3O_4

Fe_3O_4, magnetite

phase transition between a mixed-valence and a charge-ordered configuration

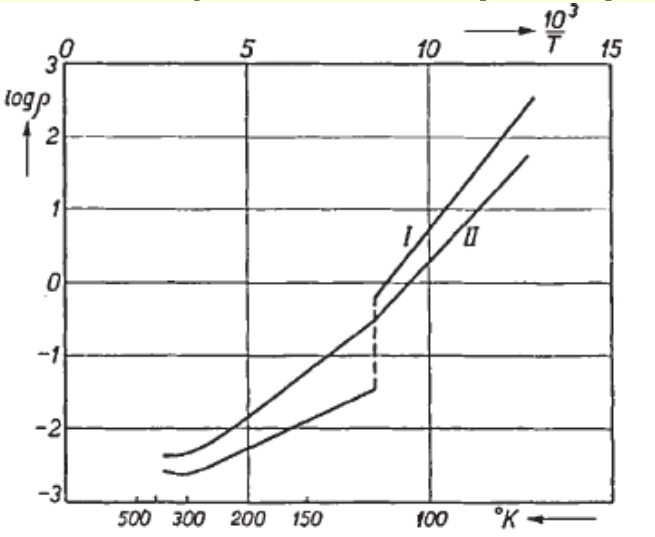
$$2\ Fe^{2.5+} \rightarrow Fe^{2+} + Fe^{3+}$$

cubic inverse spinel structure AB_2O_4

~~$Fe^{2+}_A (Fe^{3+},Fe^{3+})_B O_4$~~

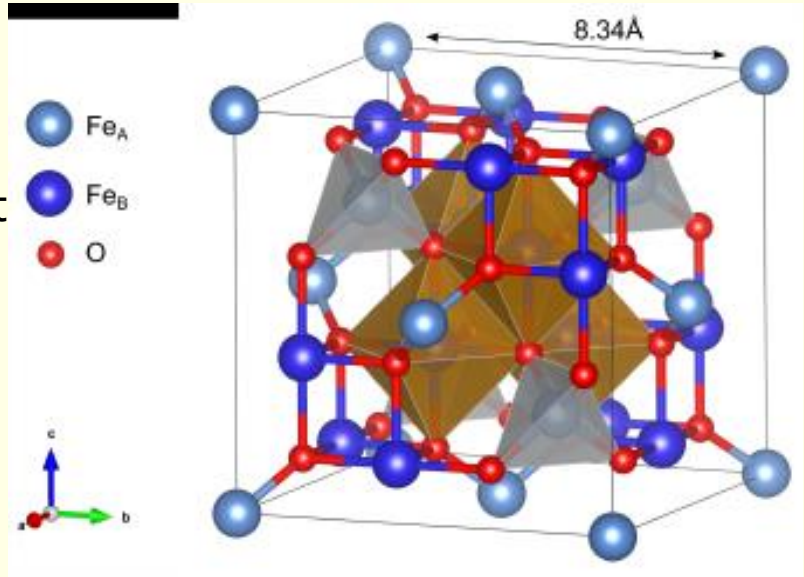
$Fe^{3+}_A (Fe^{2+},Fe^{3+})_B O_4$

Verwey transition (1939)



The accompanying graph shows log ρ against $1/T$ for two bars: I with $FeO : Fe_2O_3 = 1 : 1{\cdot}025$, and II with $FeO : Fe_2O_3 = 1 : 1{\cdot}08$. All details of the curves are in full accordance with the picture proposed above for the nature of the transition and our concept of the cation arrangement in the Fe_3O_4 (and the γ-Fe_2O_3) lattice. In further support of our views, we found that sample I shows a distinct drop in the susceptibility for weak magnetic fields at about 117° K., whereas with sample II the corresponding effect is much weaker.

Fe_{tet}
Fe_{oct}



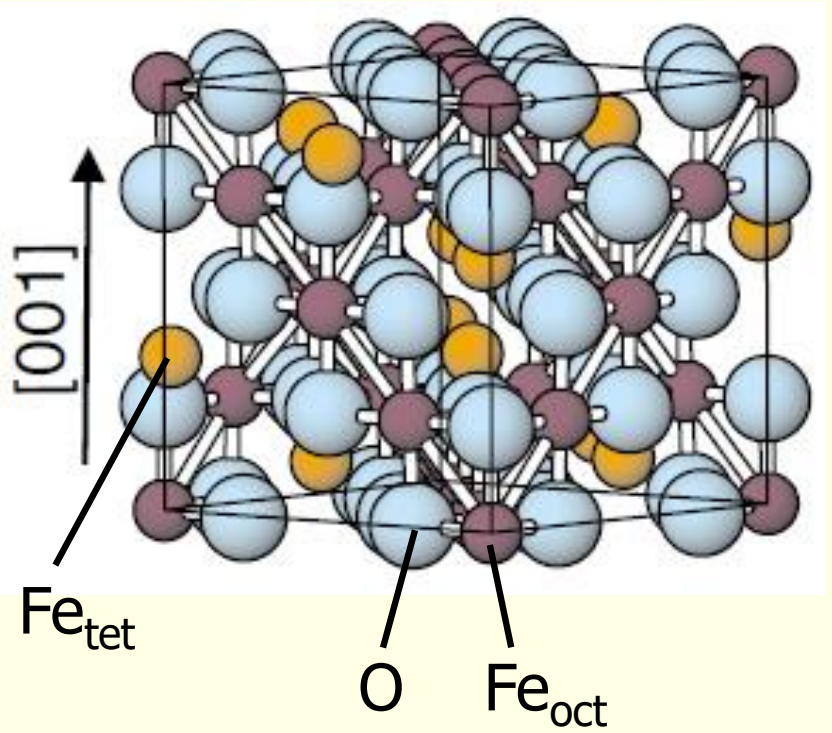
→ small, but complicated coupling between lattice and charge order

Fe_{oct}-terminated Fe_3O_4 (001) surfaces

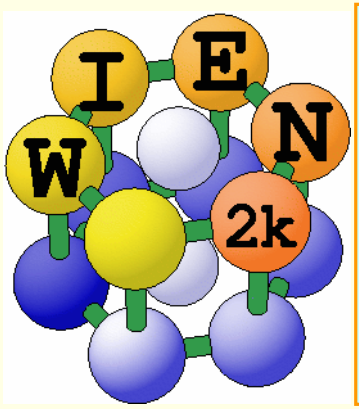
- stimulated by U. Diebold (Z.Novotny et al., PRL 108, 216103 (2012))

  - *$Fe_{oct}^{2.5+}O_2$ - planes, forming „rows" along [110]*
  - *Fe_{tet}^{3+} - planes*
  - *$Fe_{oct}^{2.5+}O_2$ - planes, forming „rows" along [1-10]*
  - *.....*

  - *surface Fe_{oct} atoms are all Fe^{3+} to compensate (partly) the charged surface layer*

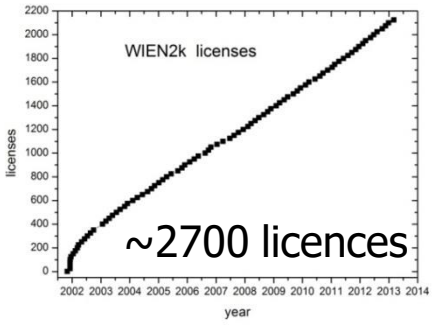


DFT calculations using WIEN2k



An Augmented Plane Wave Plus Local Orbital Program for Calculating Crystal Properties

Peter Blaha et al. (Vienna University of Technology)
http://www.wien2k.at

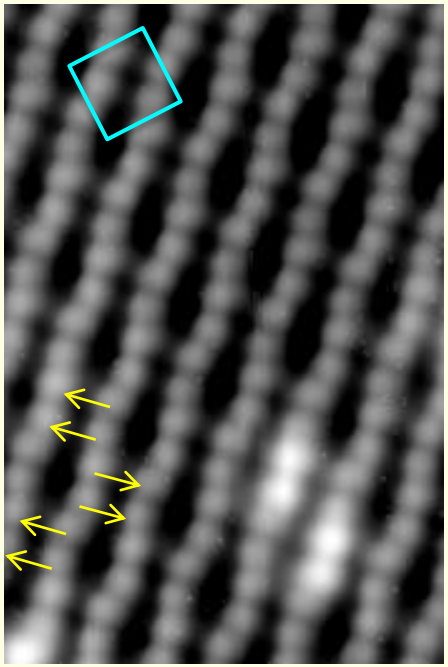


- surface slab calculations using (√2×√2)-17 and (2×2)-17 layer models (up to 248 atoms/cell)
- GGA+U (Fe-3d: U=3.8 eV)
- Rkmax=7, 3x3x1 k-points

The $Fe_3O_4(001)$ Surface

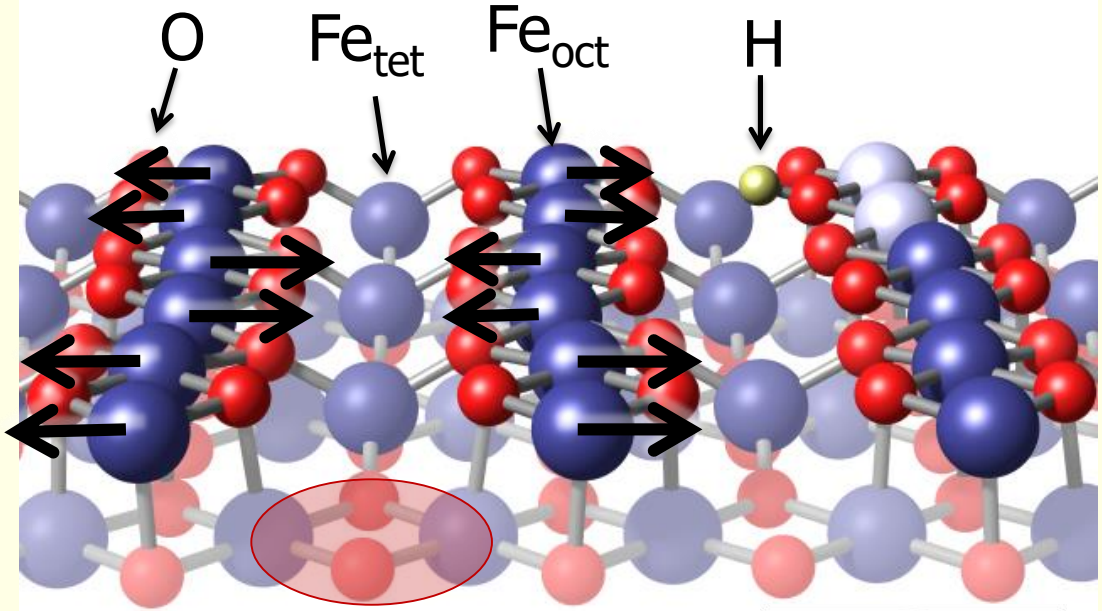
$Fe_3O_4(001)$ exhibits $(\sqrt{2}x\sqrt{2})R45°$ superstructure due to small lateral relaxations of surface atoms ($\approx$ 0.1 Å)

In STM, we see the Fe_{oct} atoms



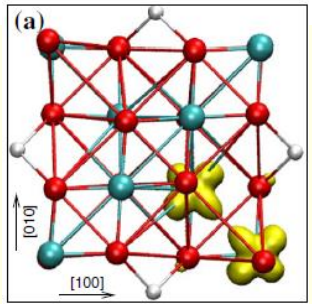
(4.38 x 6.43) nm^2
1 V, 0.1 nA

Structure determined by DFT and LEED-IV:



found by R. Pentcheva *et al.*, PRL **94**, 126101 (2005)

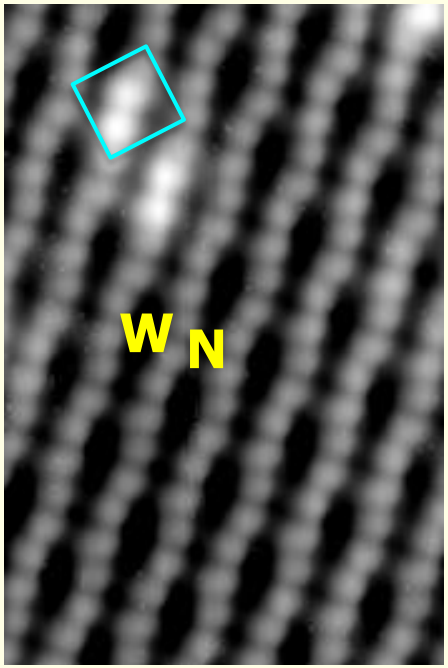
explained by DFT+U calc.: Lodziana, PRL 99, 206402 (2007):
charge and orbital order in **sub-surface** $Fe_{oct}O_2$-rows



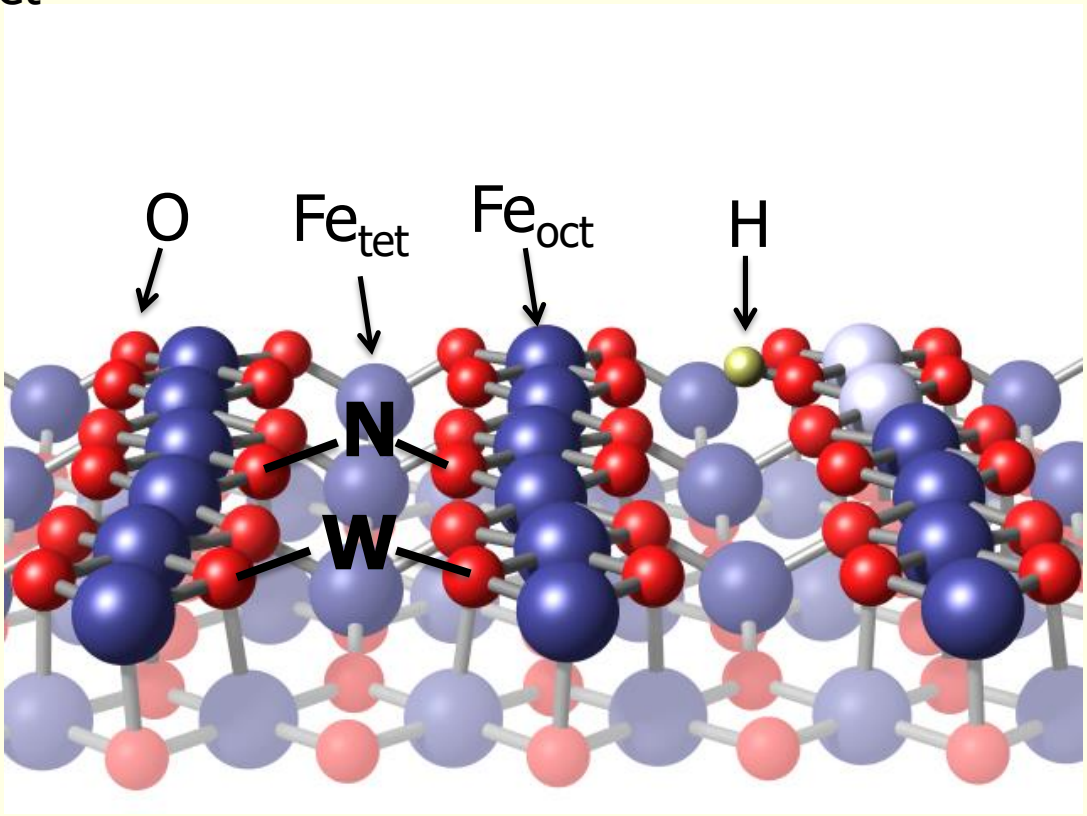
The $Fe_3O_4(001)$ Surface

Two obvious sites for **ad-atom adsorption**:
Bulk continuation Fe_{tet} sites **"W"** and **"N"**

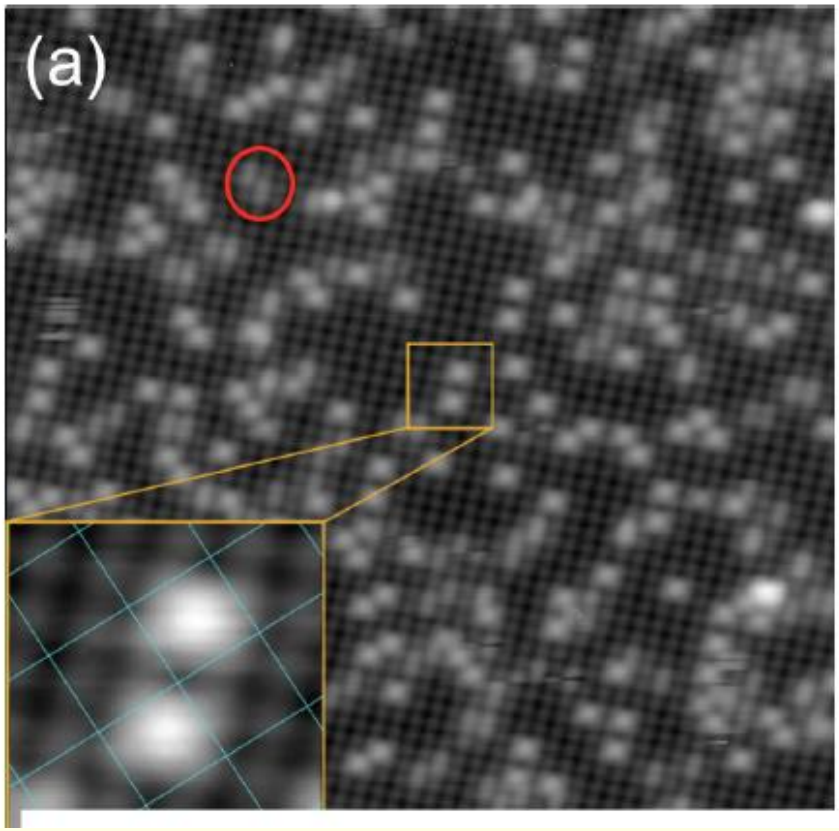
In STM, we see the Fe_{oct} atoms



(4.38 x 6.43) nm^2
1 V, 0.1 nA



Au atoms on Fe_{oct} terminated Fe_3O_4:



experiments in U.Diebolds group:

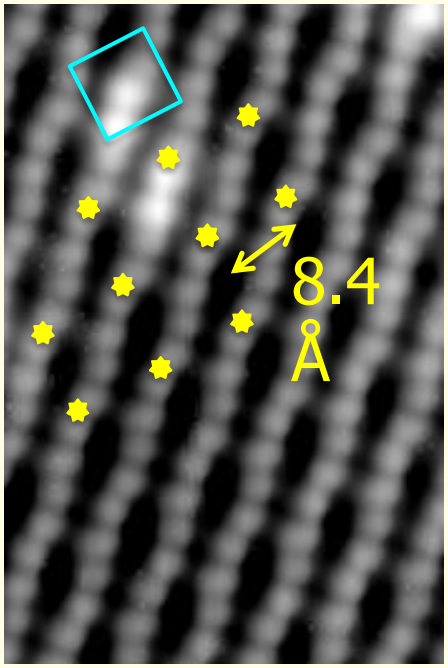
Z.Novotny et al., PRL 108, 216103 (2012)

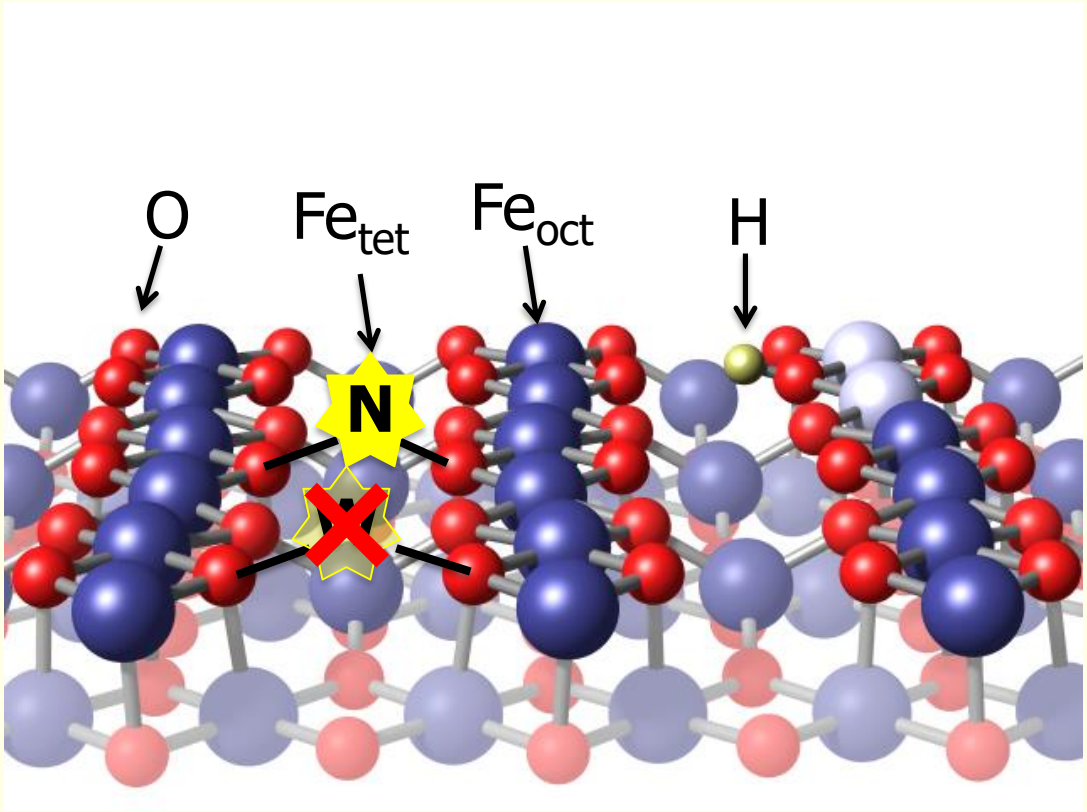
single Au atoms stable up to 400 C

Au adsorbs exclusively on narrow site

The Fe_3O_4(001) Surface

In STM, Au, Ag, Pt, Pd adsorb **only** at the **N** site.





DFT does not find any difference between Me-adsorption on the W or N site

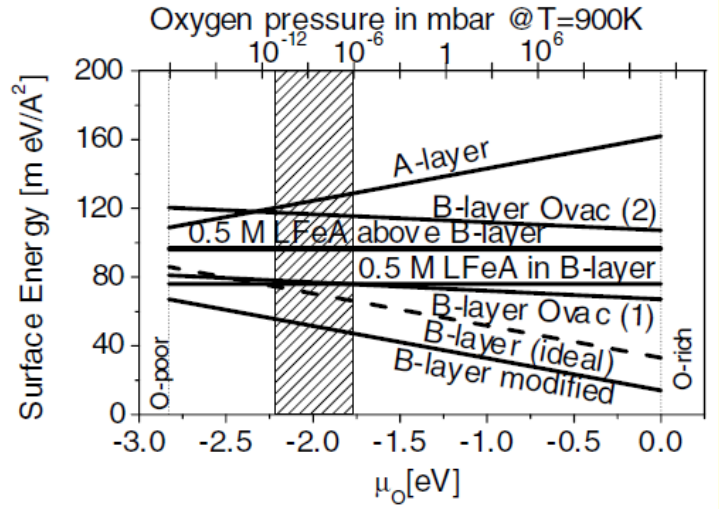
G.Parkinson et al., Nature Mat. 12, 724 (2013)

something must block this site !!!

A new structural model for $Fe_3O_4(001)$

- Surface reconstruction including non-stoichiometry ?

- Pentcheva (and we also) have tried several different O-vacancy structures - non of them are stable.



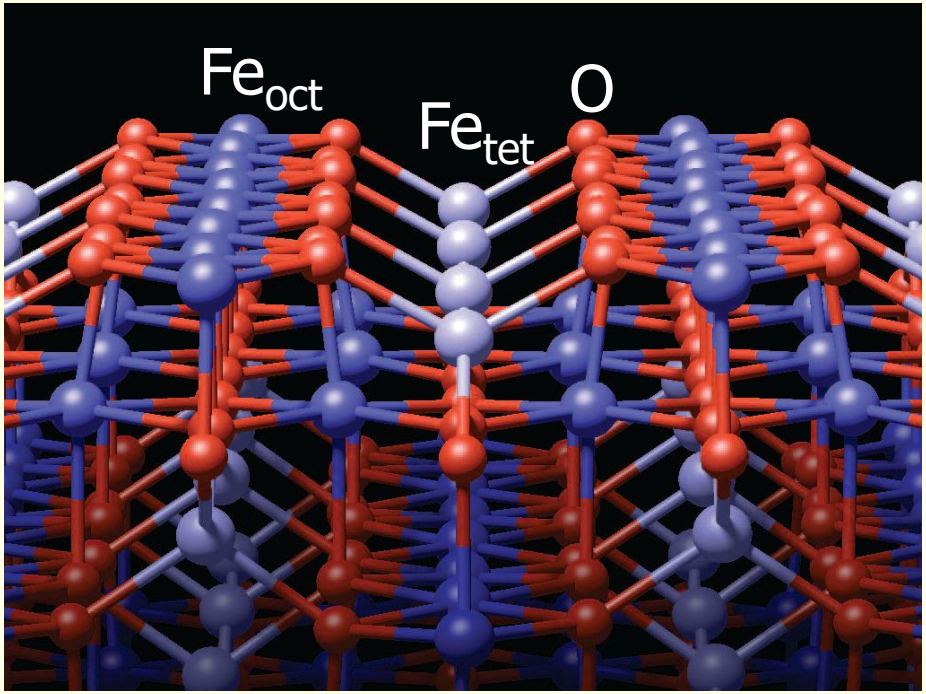
- Fe-oxides contain mostly Fe-vacancies, not O-vacancies
- γ-Fe_2O_3: Maghemite is a "Magnetite" with 1/6 Fe_{oct} vacancies

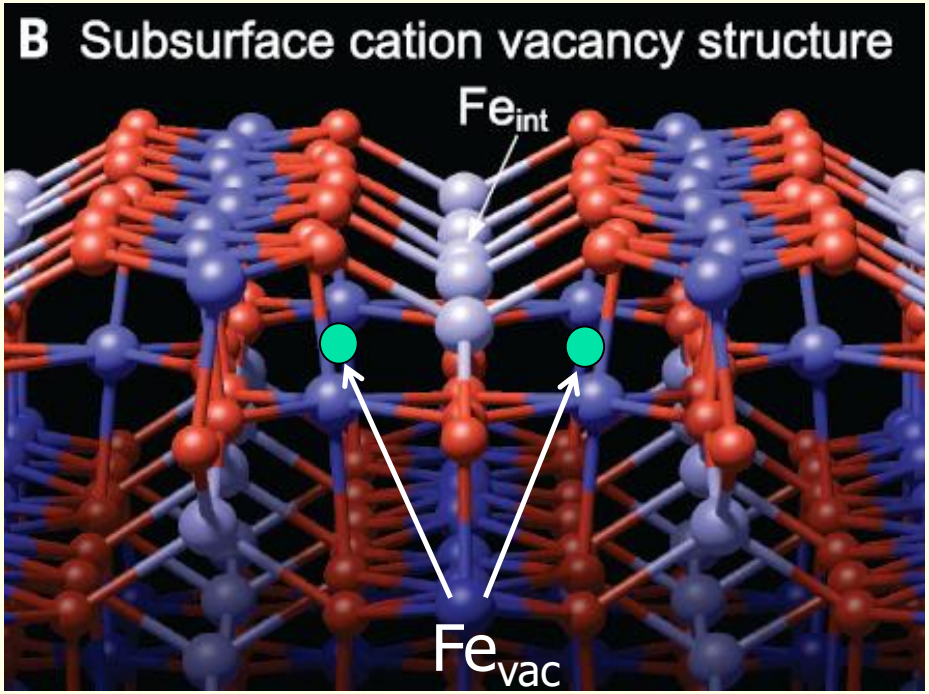
→ **Subsurface cation vacancy structure**

$Fe_3O_4(001)$ surface reconstruction

Distorted bulk truncation

Fe_{tet}-interstitial +
sub-subsurface Fe_{oct}

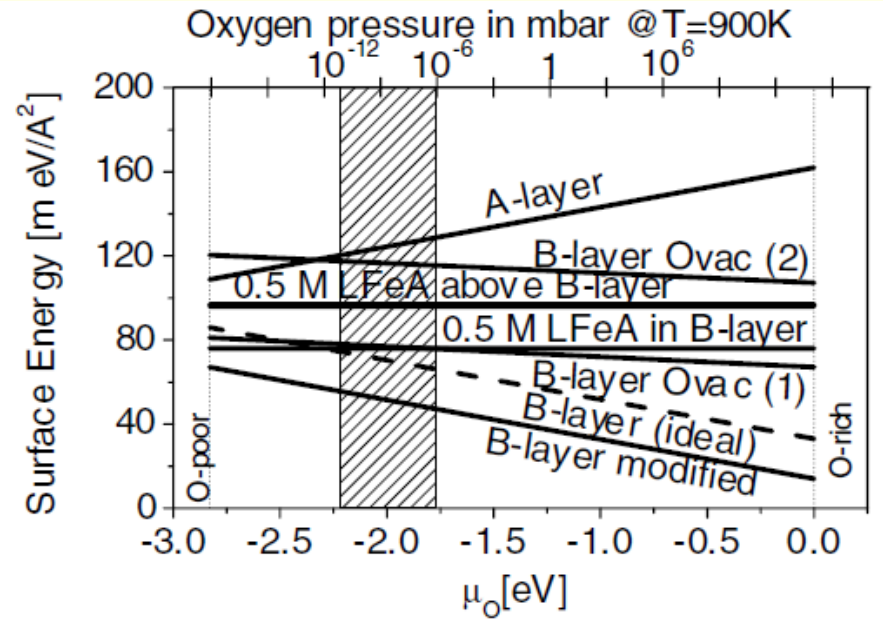




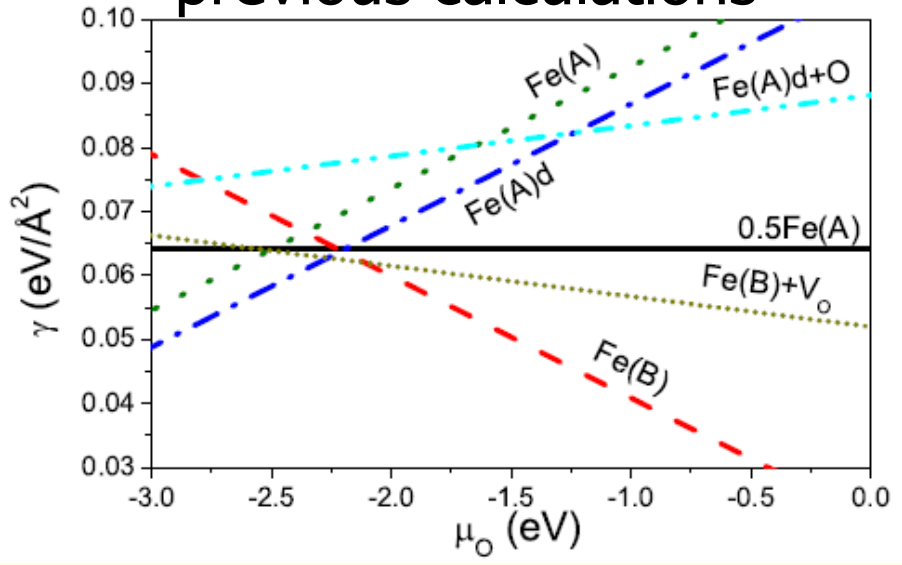
new model:

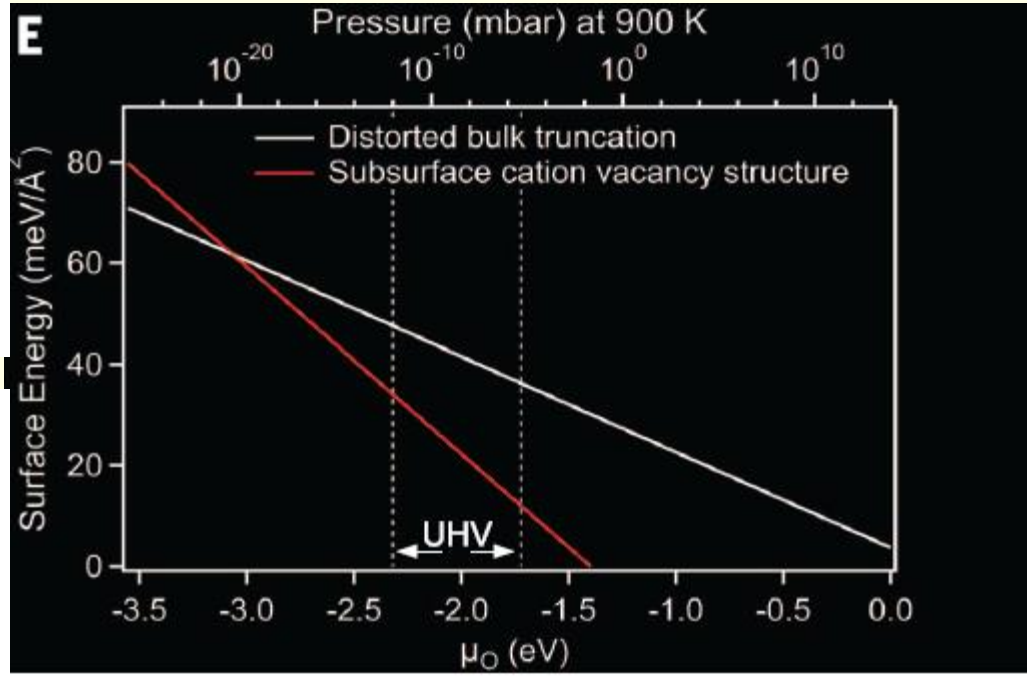
much stronger Fe_{oct} corrugation

Thermodynamic stability



previous calculations

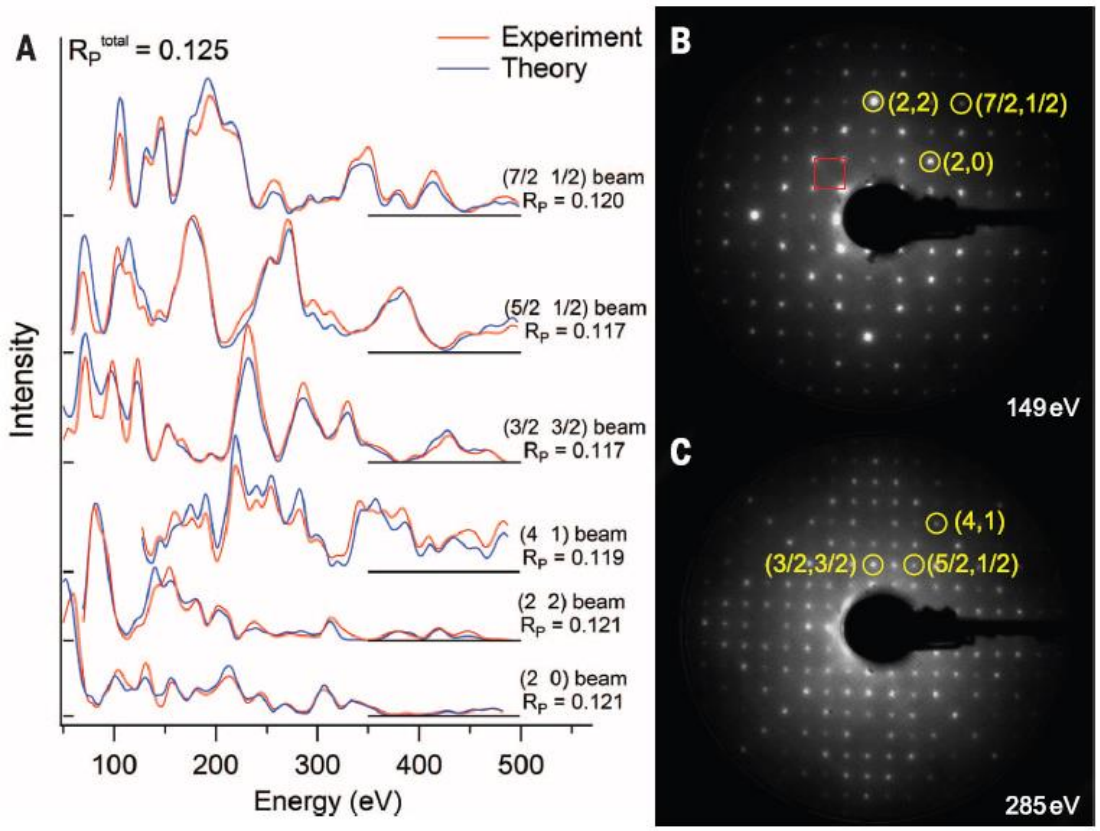




The subsurface vacancy model is more stable than bulk-termination

Quantitative LEED IV-measurements

- Pentcheva et al. 2008: Refinement of the distorted bulk-terminated structure with **R=0.34**
- new exp. by L.Hammer: new model refines to **R=0.12**
- **old exp**. can be refined with new model to the same R=0.12

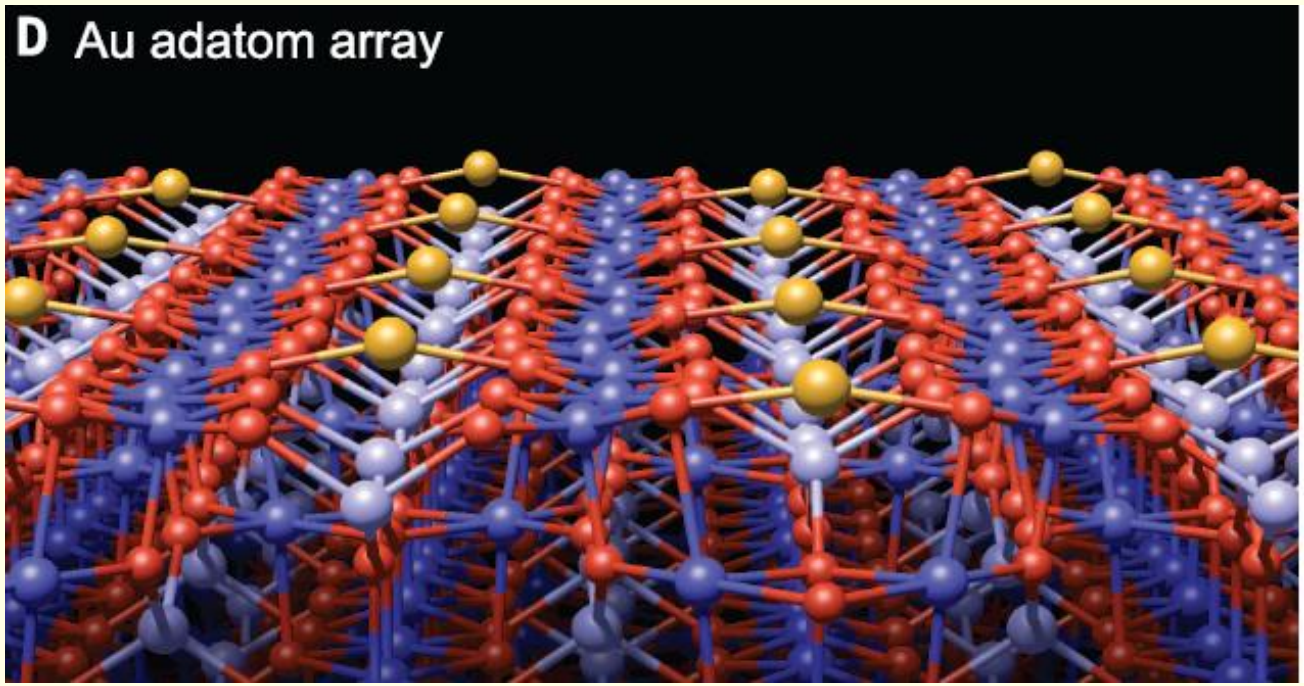


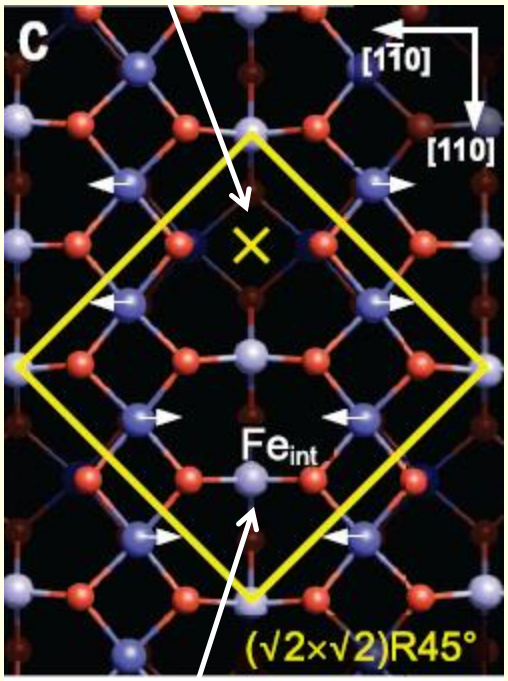
refined exp. positions and theor. positions agree within 0.05 Å

(all within the exp. error)

Au adatom adsorption blocked by Fe_{int}

Fe_{int} blocks selectively adatom adsorption on this site





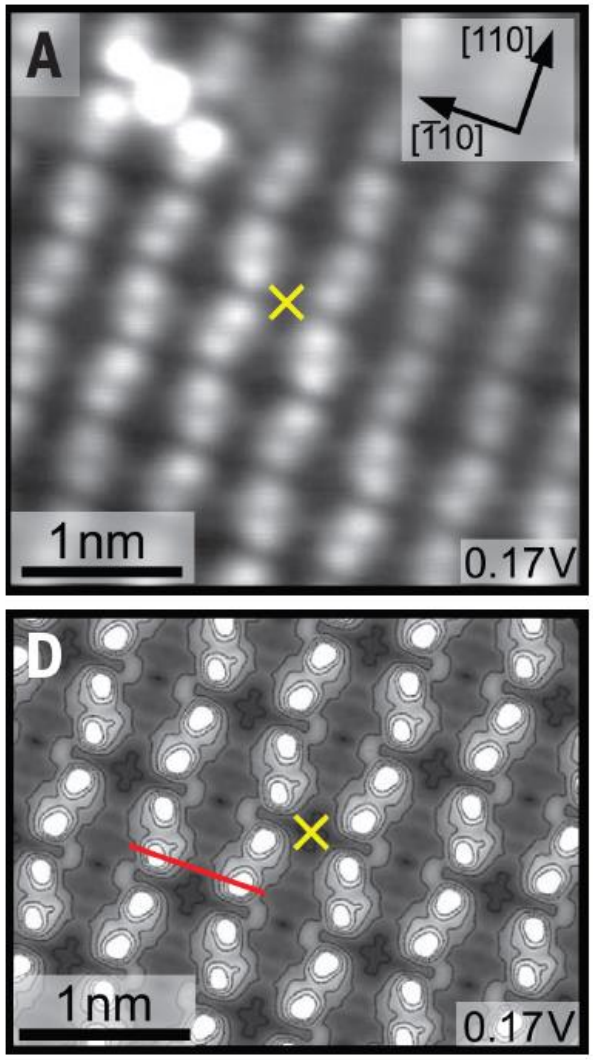
adsorbtion site

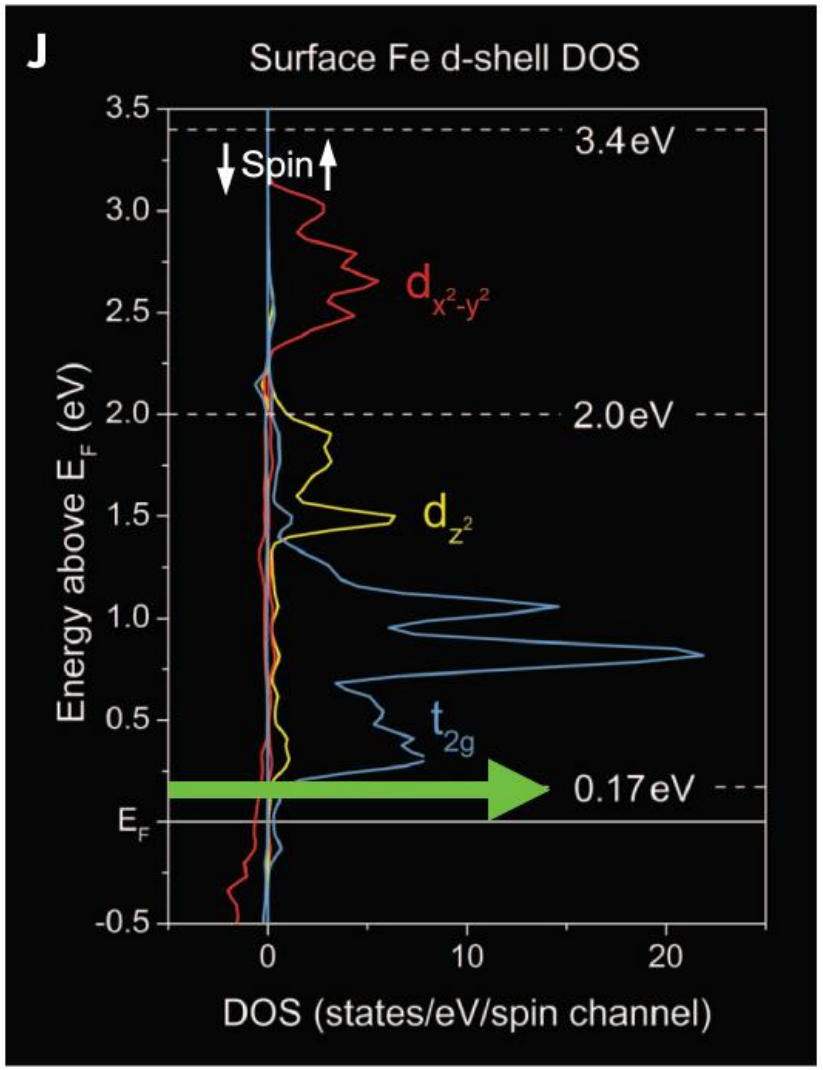
blocked site

But: the **blocked** site is the **N** site (in contrast to exp.) !!??

STM measurements and simulations

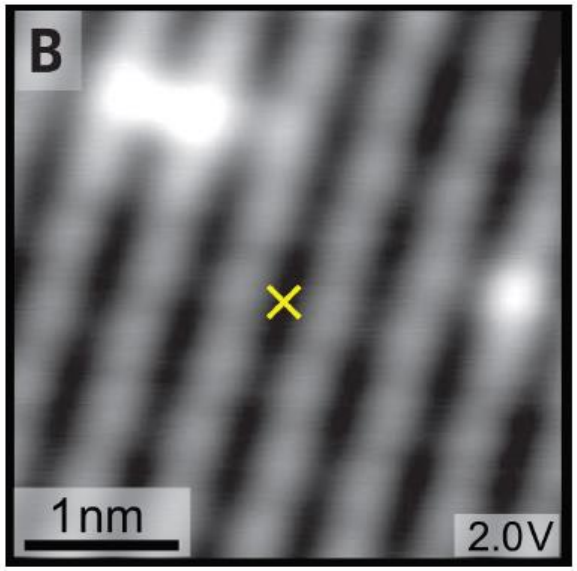
- large corrugation at low bias voltage (narrow site at **x**)

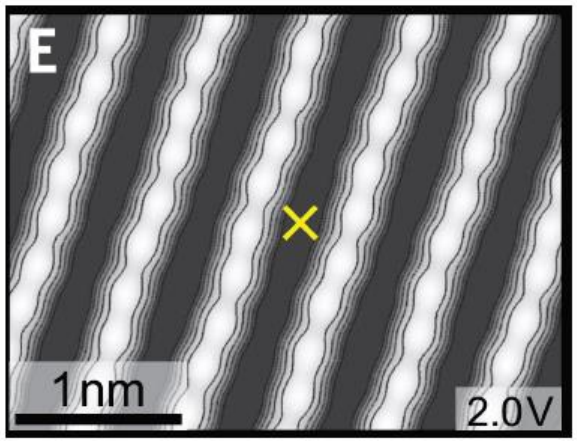


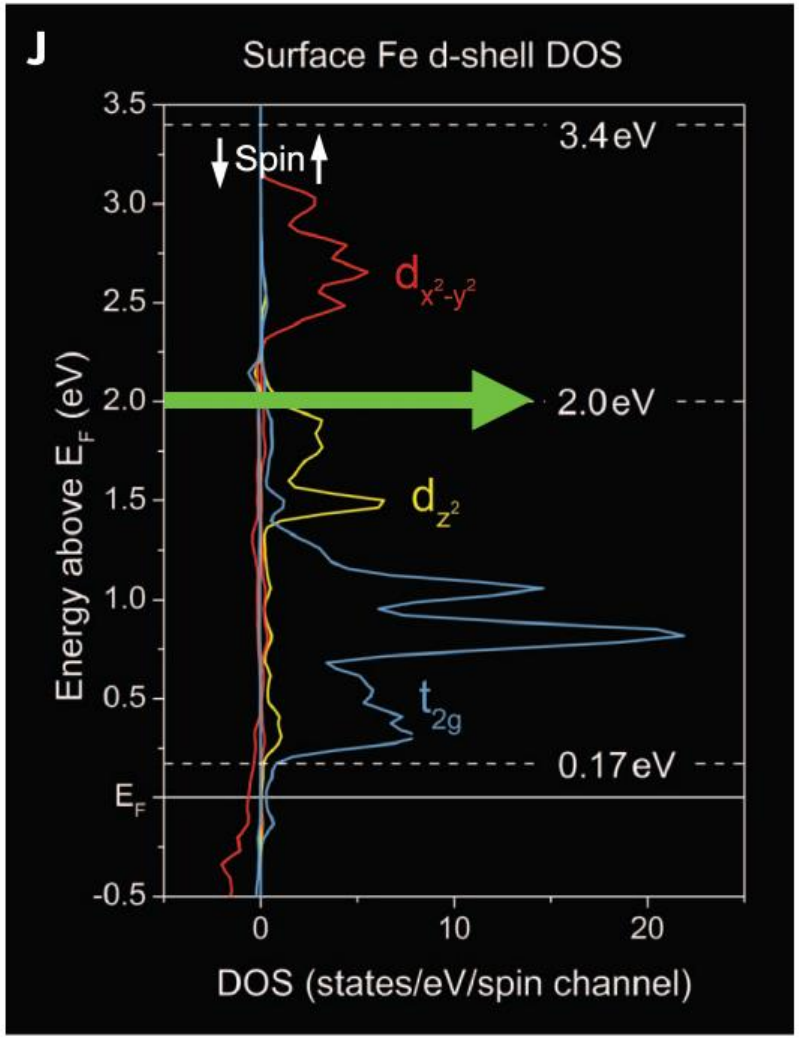


STM measurements and simulations

- at intermediate bias the rows „straighten“

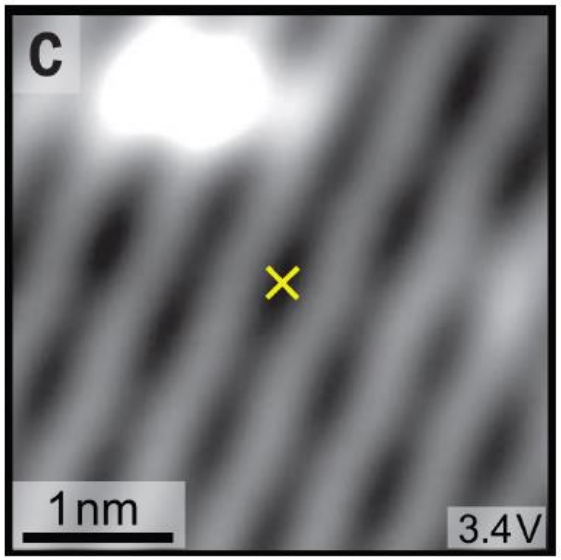


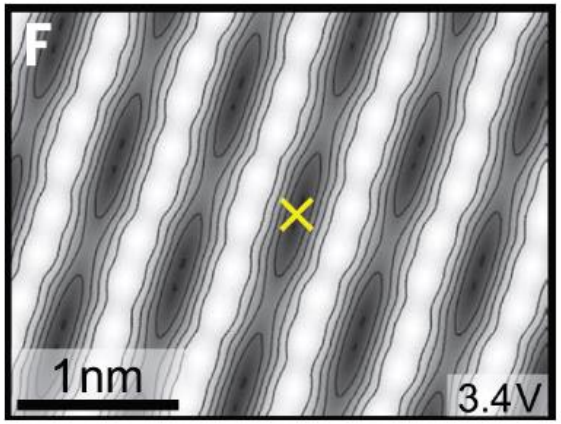


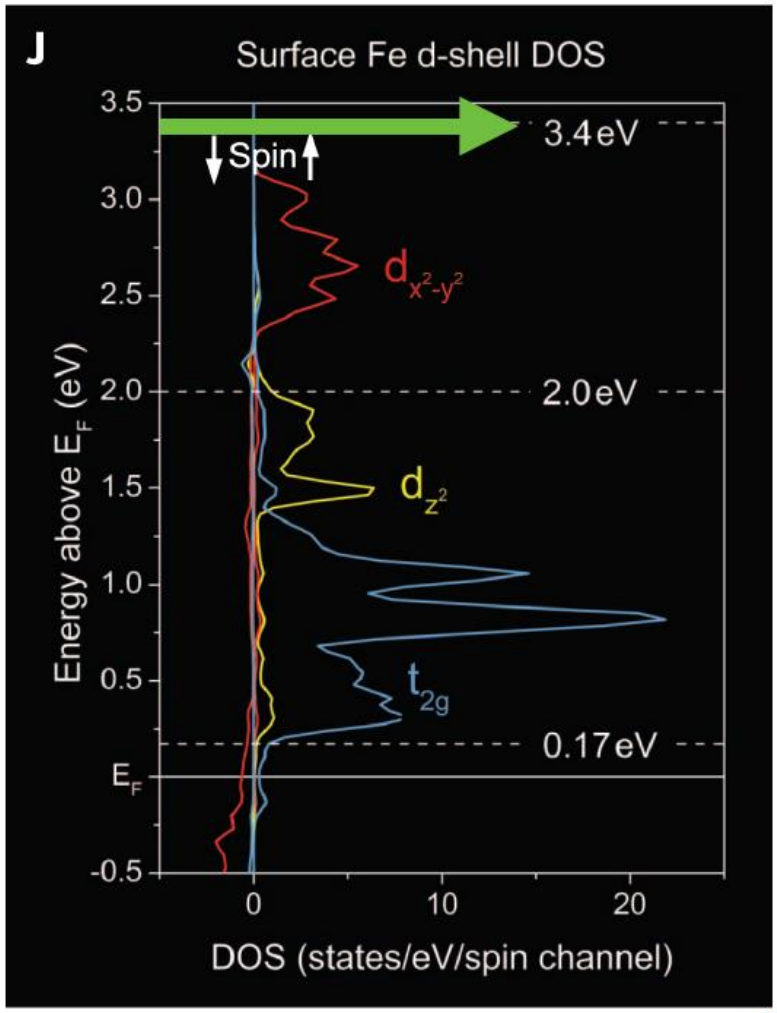


STM measurements and simulations

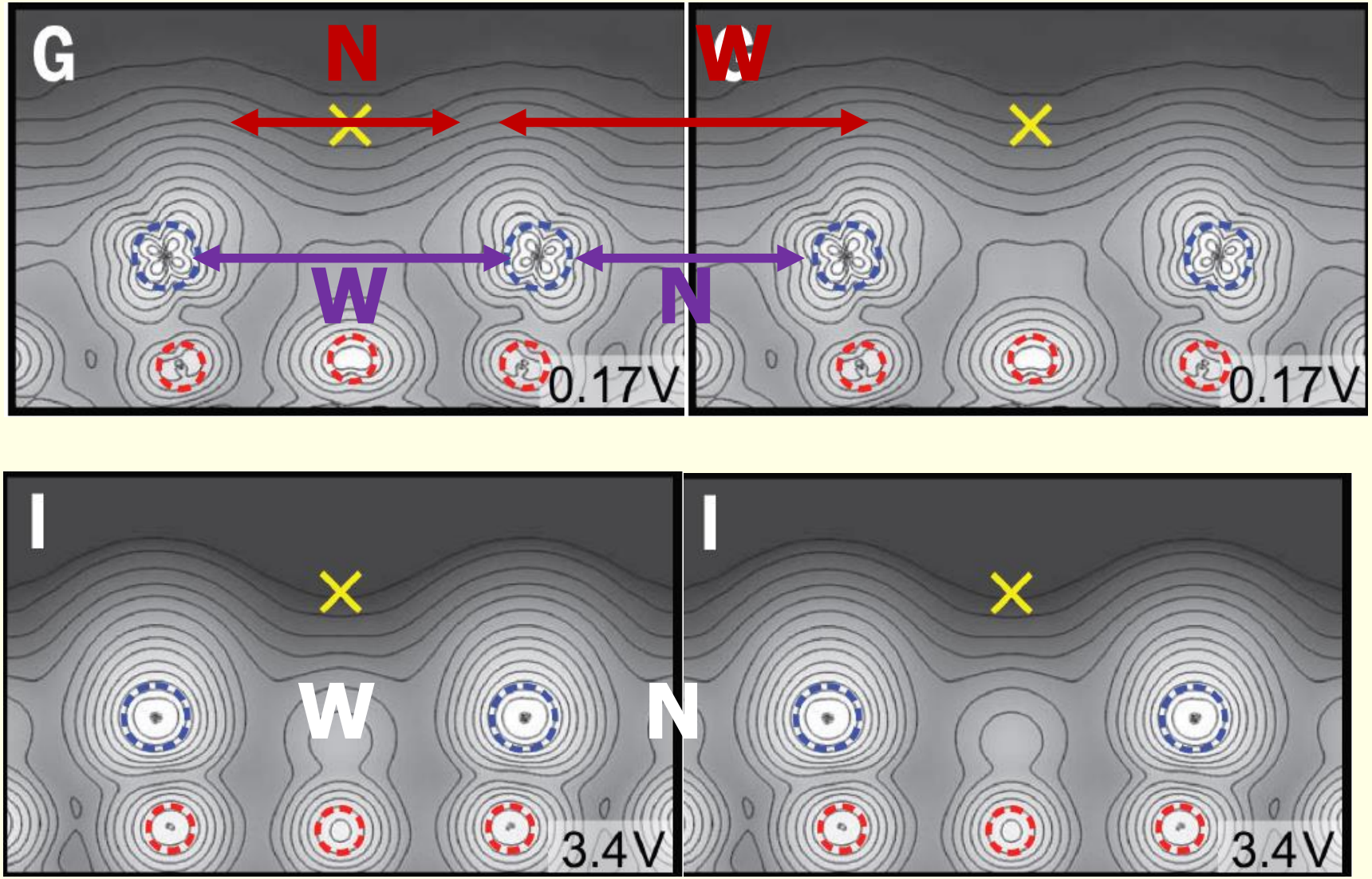
- at large bias the previous „narrow" site looks „wide"



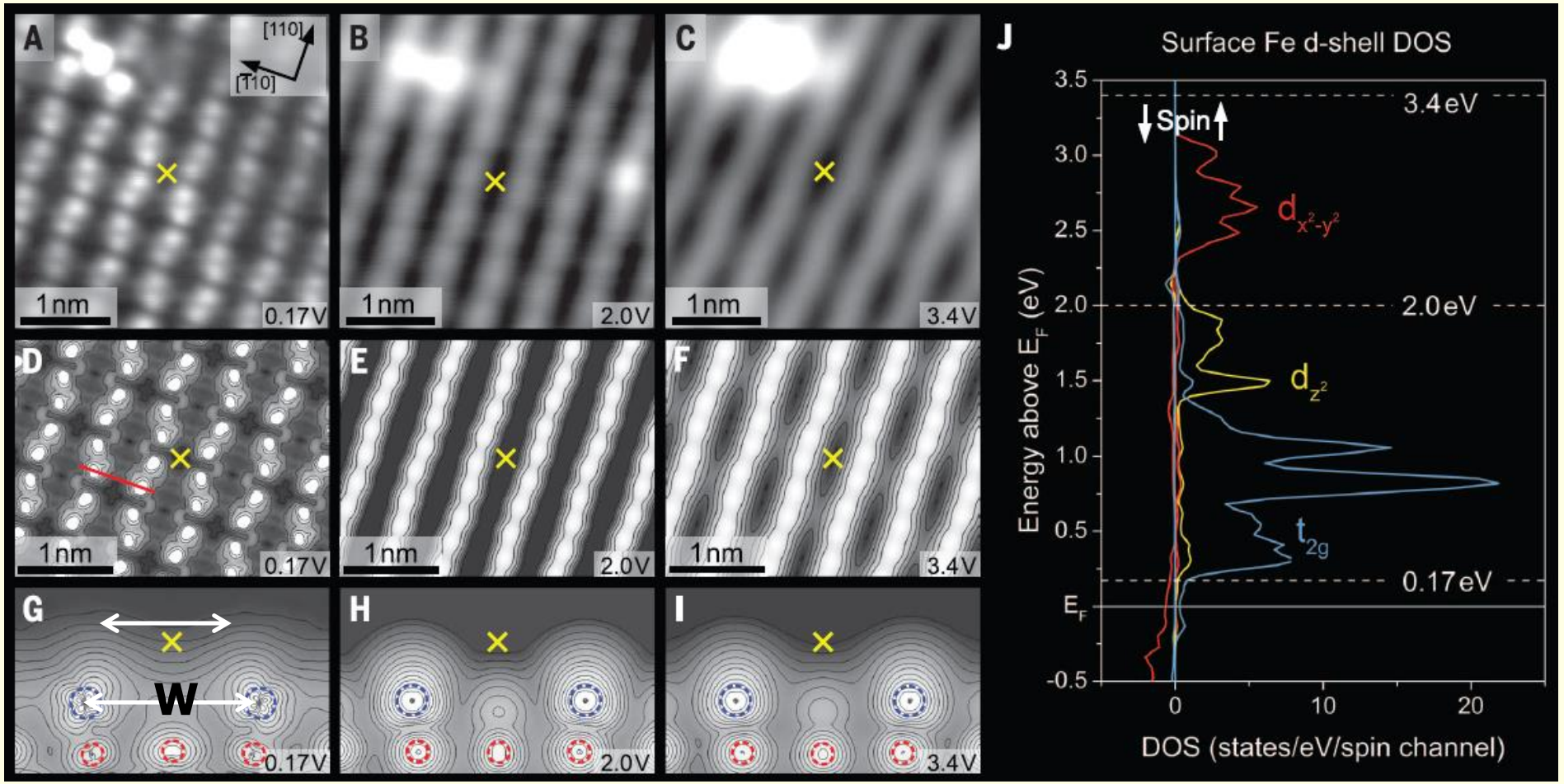




STM probes charge densities, not atomic positions



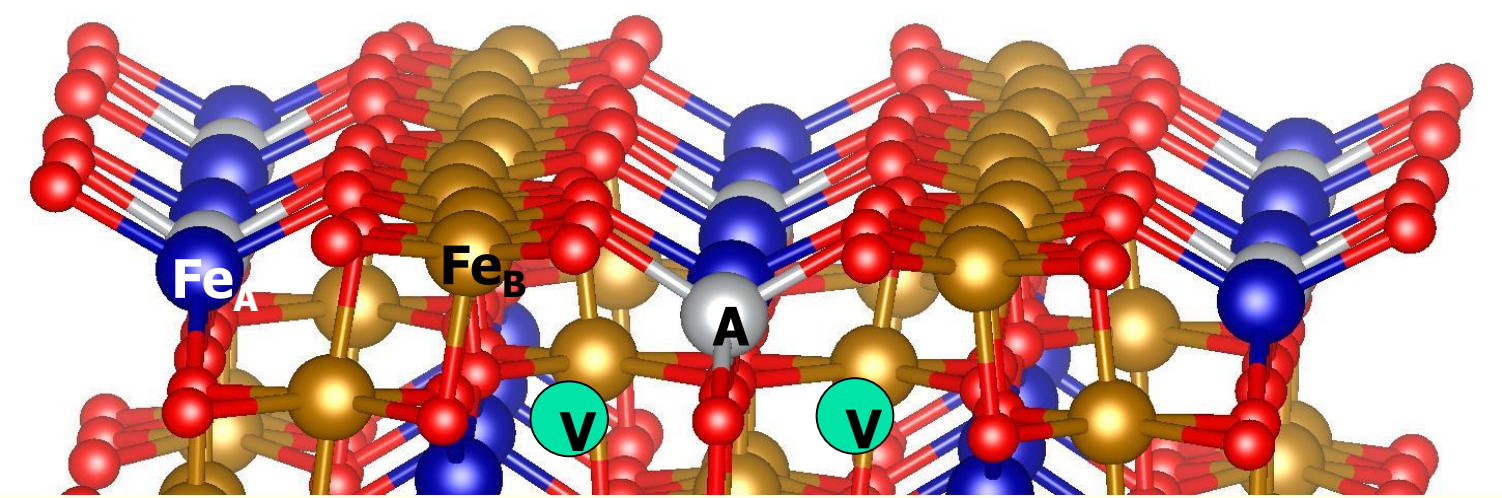
STM with different bias voltage



- "**N**" site is actually the "**wide**" site for low bias
- "N" and "W" change in STM with the bias voltage
- STM probes **electron densities**, not "**atomic positions**"

Summary

- The new SCV-model of the Fe_3O_4 (001) surface explains
  - *LEED-IV measurements*
  - *fixes polar catastrophe*
  - *explains STM images (bias dependency)*
  - *explains site-selective TM-atom adsorption*
  - *spintronics problems*



- *allows investigations of „single-atom" catalysis (CO oxidation with Pt)*

Acknowledgment

U. Diebold + G. Parkinson + group at IAP (TU Vienna)

L. Hammer (Univ. Erlangen)

E. McDermott + R. Bliem (calculations)

R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M.A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, G. S. Parkinson, Science 346, 1215 (2014)

Vienna Computational Materials Laboratory

ViCoM

Thank you for your attention !