DFT simulations of surfaces, interfaces and multilayers

Peter Blaha

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Concepts when solving Schrödingers-equation

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

Form of potential

"Muffin-tin" MT
atomic sphere approximation (ASA)
pseudopotential (PP)
Full potential : FP

Relativistic treatment of the electrons

non relativistic
semi-relativistic
fully-relativistic

electron-electron interactions

Hartree-Fock (+correlations)
Density functional theory (DFT)
  Local density approximation (**LDA**)
  Generalized gradient approximation (**GGA**)
  Beyond LDA: e.g. **LDA+U**

$$\left[-\frac{1}{2}\nabla^2 + V\right]\Psi = \varepsilon\,\Psi$$

Schrödinger - equation

Representation of the solid

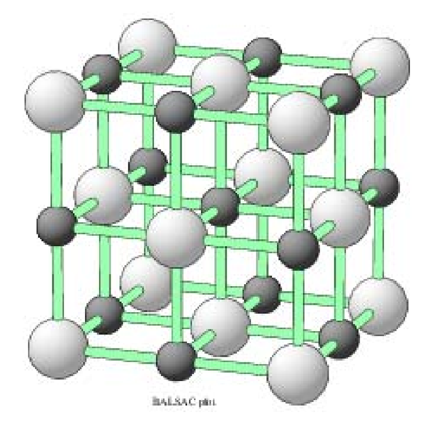
non periodic cluster model
periodic (infinite solid) bandstructure model

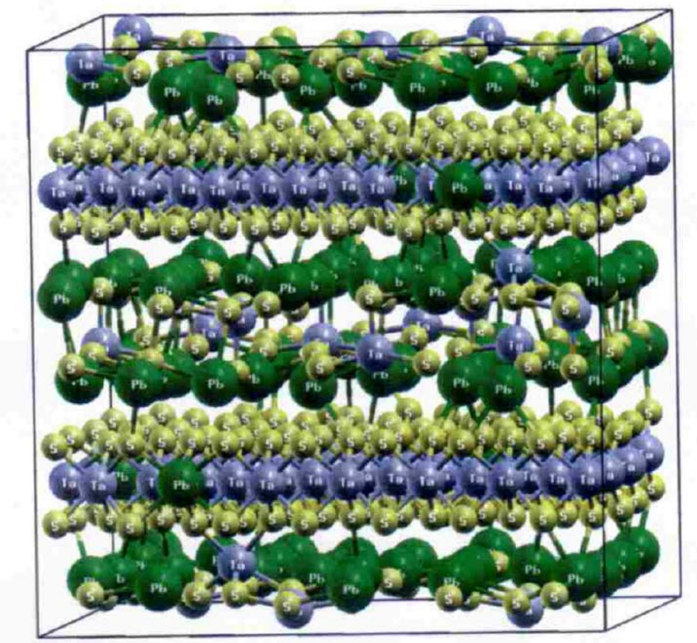
Basis functions

plane waves : PW
augmented plane waves : APW
atomic oribtals. e.g. Slater (STO), Gaussians (GTO),
  LMTO, numerical basis

Representation of the solid

- **infinite "ideal" crystal** (with "small" unit cell) ➔ band structure methods
  - *"supercells" for "realistic materials"*
    (surfaces, multilayers, impurities, disorder, …)
  - *structure optimization possible*
  - *allows to model an "unknown" system*





disorder in the "missfit"-layer compound
$\mathbf{(PbS)_{1.14}TaS_2}$

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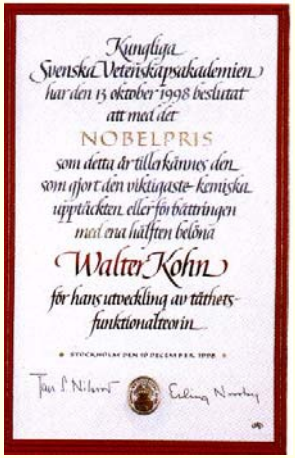
DFT Density Functional Theory

Walter Kohn

Hohenberg-Kohn theorem: (exact)

$$E = \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho]$$

Kohn-Sham: (in principle still exact!)



Kungliga
Svenska Vetenskapsakademien
har den 13 oktober 1998 beslutat
att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste kemiska
upptäckten eller förbättringen
med ena hälften belöna
Walter Kohn
för hans utveckling av täthets-
funktionalteorin

STOCKHOLM DEN 10 DECEMBER 1998

The many body problem of interacting electrons is mapped to **one-electron reference system** that leads to the same density as the real system.

$$\{-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_C(\rho(\vec{r})) + \underset{\Uparrow}{V_{xc}}(\rho(\vec{r}))\}\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r})$$

$$\frac{\partial E_{xc}(\rho)}{\partial \rho}$$

E_{XC}: exchange-correlation E in

various approximations (LDA, GGA)

ε_i **are "illegitimate children of DFT"**

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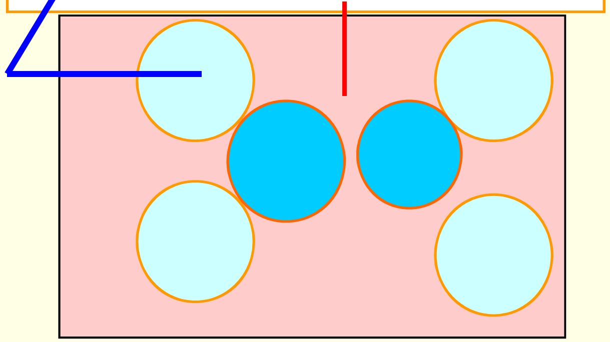
WIEN2k software package

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

Peter Blaha et al. (2001)

http://www.wien2k.at

The unit cell is partitioned into:
atomic spheres
Interstitial region

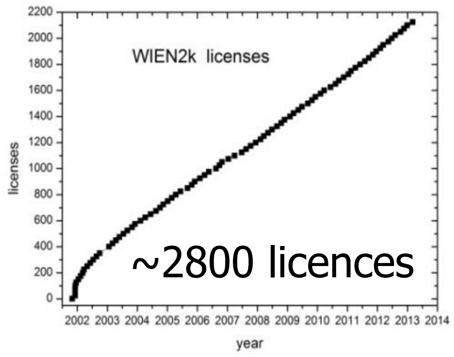


Basisset:

PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$

Atomic partial waves
$$\sum_{\ell m} A_{\ell m}^{K} u_\ell(r',\varepsilon) Y_{\ell m}(\hat{r}')$$

join

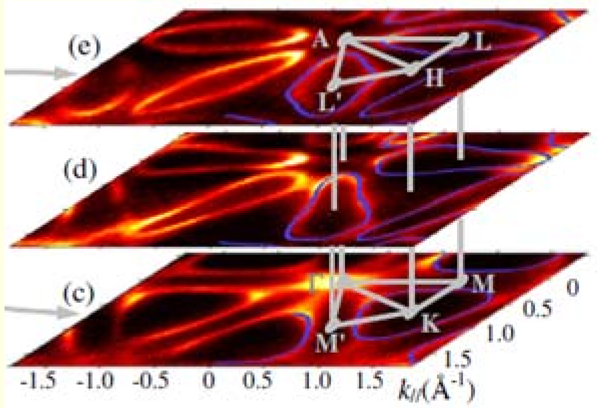


~2800 licences

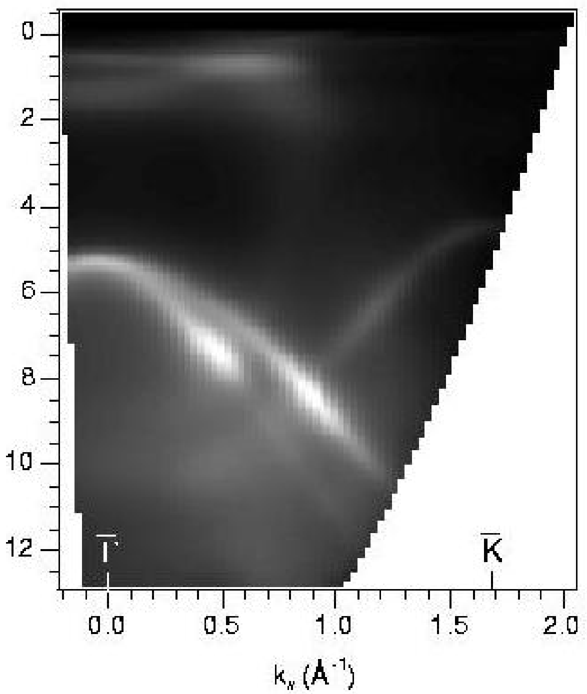
properties with WIEN2k

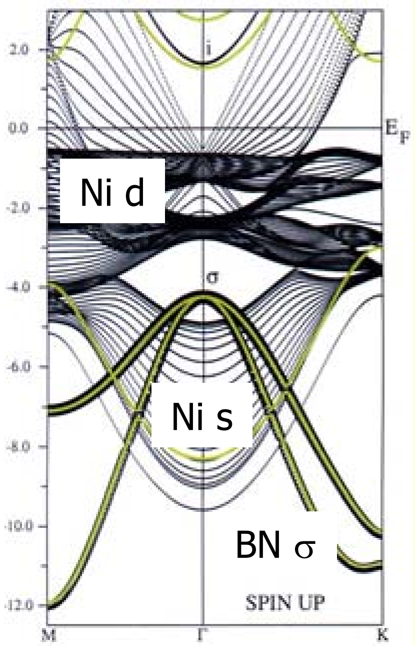
Properties with WIEN2k - I

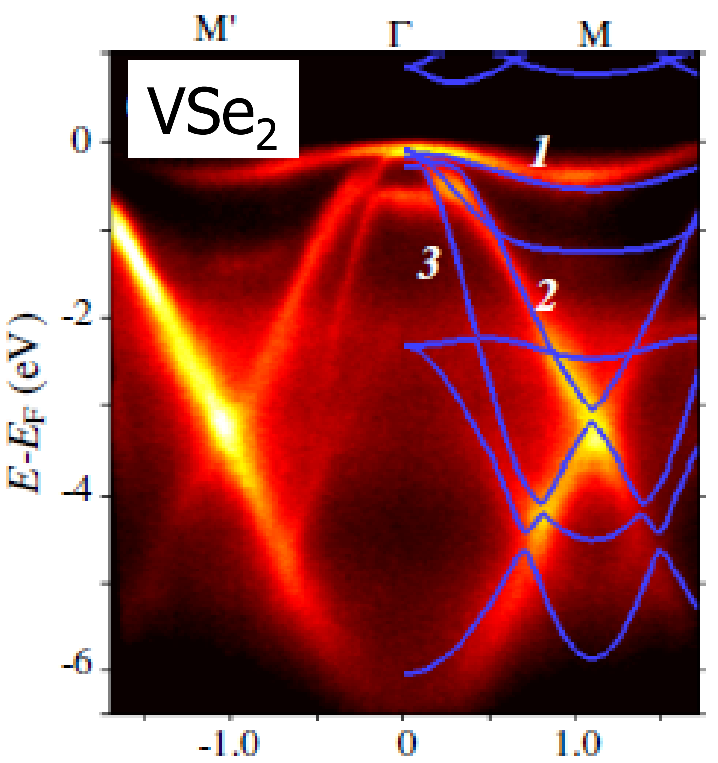
- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize certain band-character)*
- Density of states
  - *including partial DOS with l and m- character*
- Fermi surfaces



h-BN/Ni(111): σ and π bands





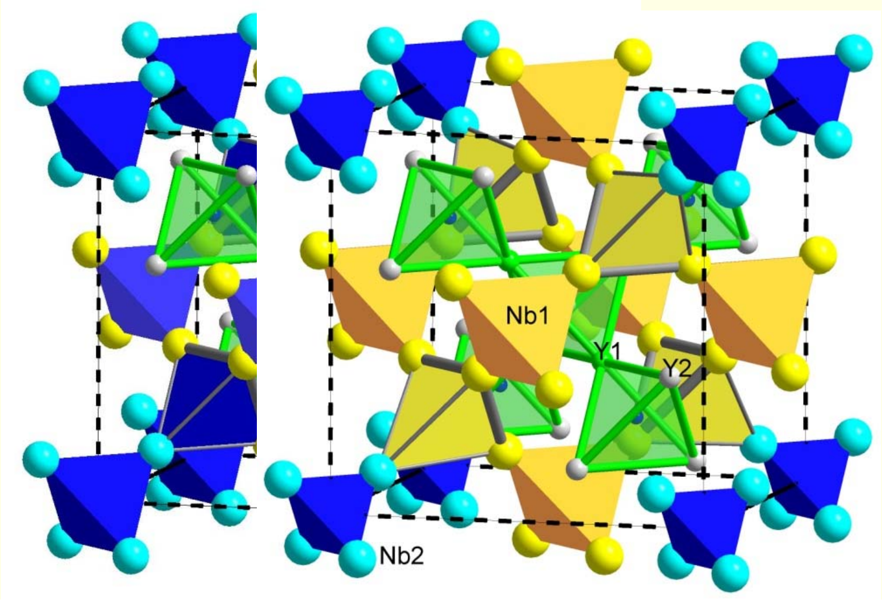


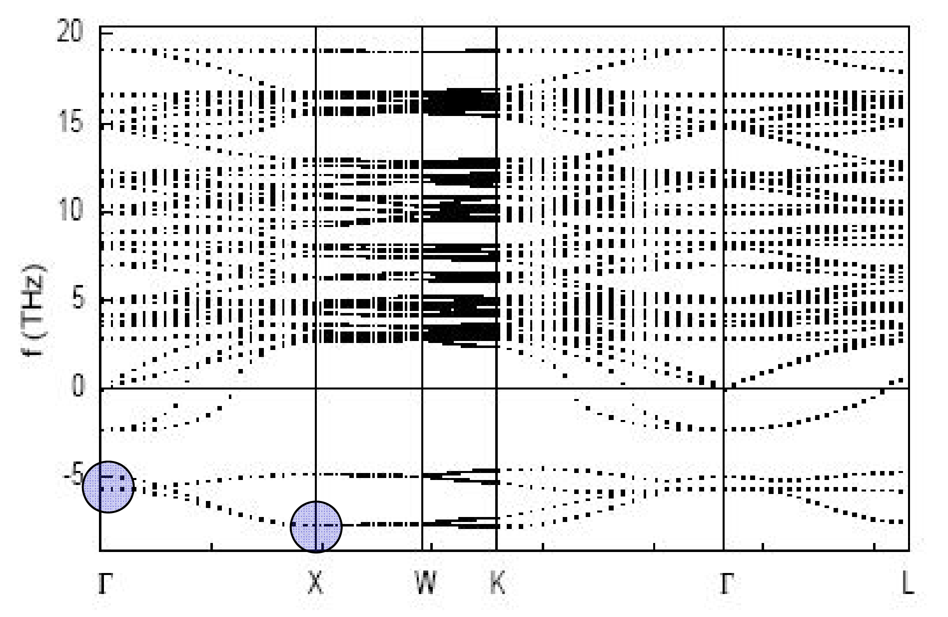
V.Strocov et al., PRL **109** (2012), 086401

Properties with WIEN2k - II

- **Total energy** and **forces: structural optimization**
  - *optimization of internal coordinates, (damped MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *Phonons via a direct method (based on forces from supercells)*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

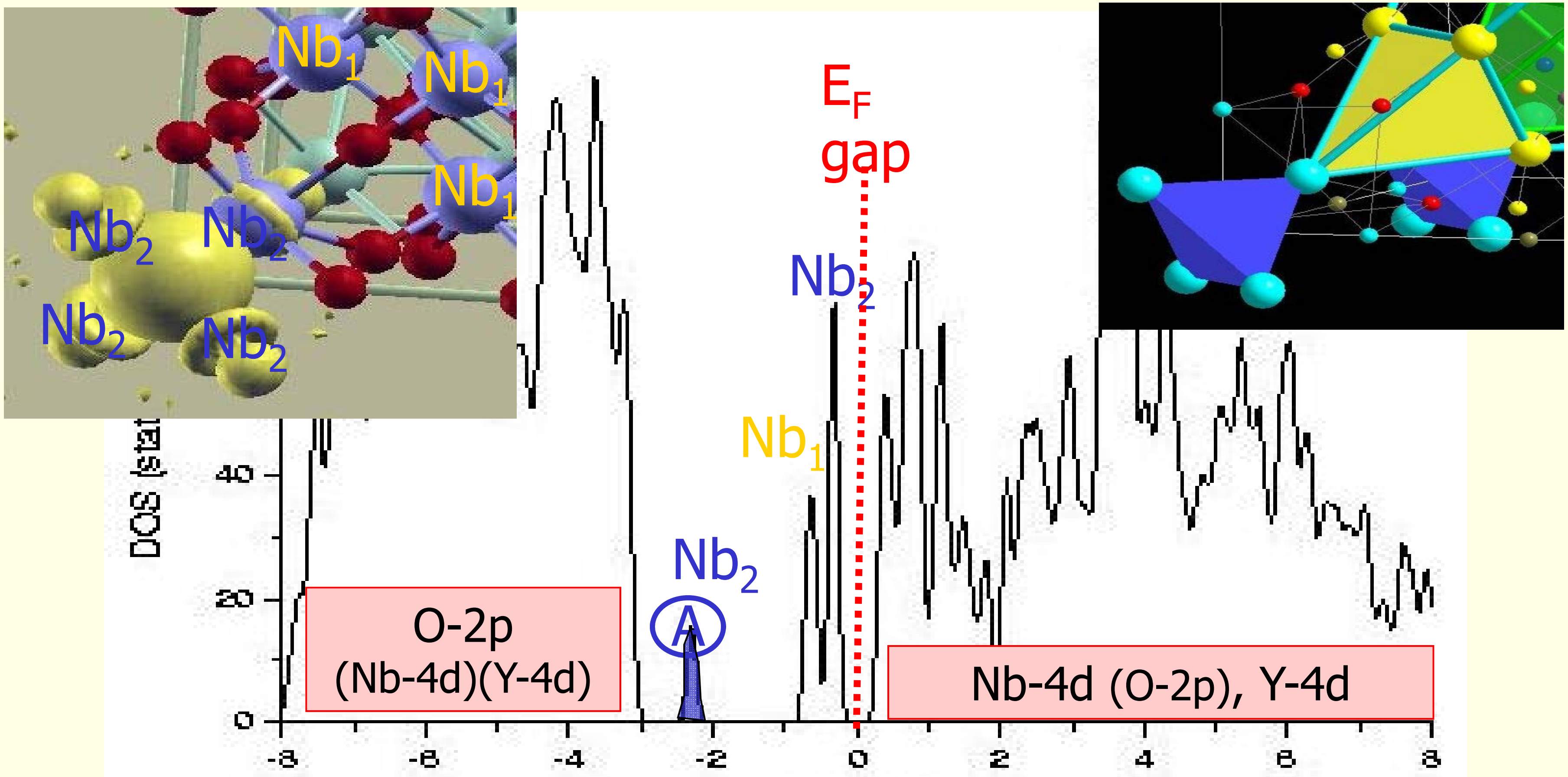
Pyrochlore structure of $Y_2Nb_2O_7$: **metallic** instead of an **insulator**
strong **phonon instabilities**→ phase transition → **insulator**





Properties with WIEN2k - III

- Electron density, potential, X-ray structure factors, spin + orbital moments
  - *total-, valence-, difference-, spin-densities, ρ of selected states*
  - *Bader´s atom-in-molecule analysis, BCP, atomic basins and charges* ($\nabla\rho.\vec{n}=0$)



$Y_2Nb_2O_7$: Peak A 4-center bond (d-z^2)

Properties with WIEN2k - IV

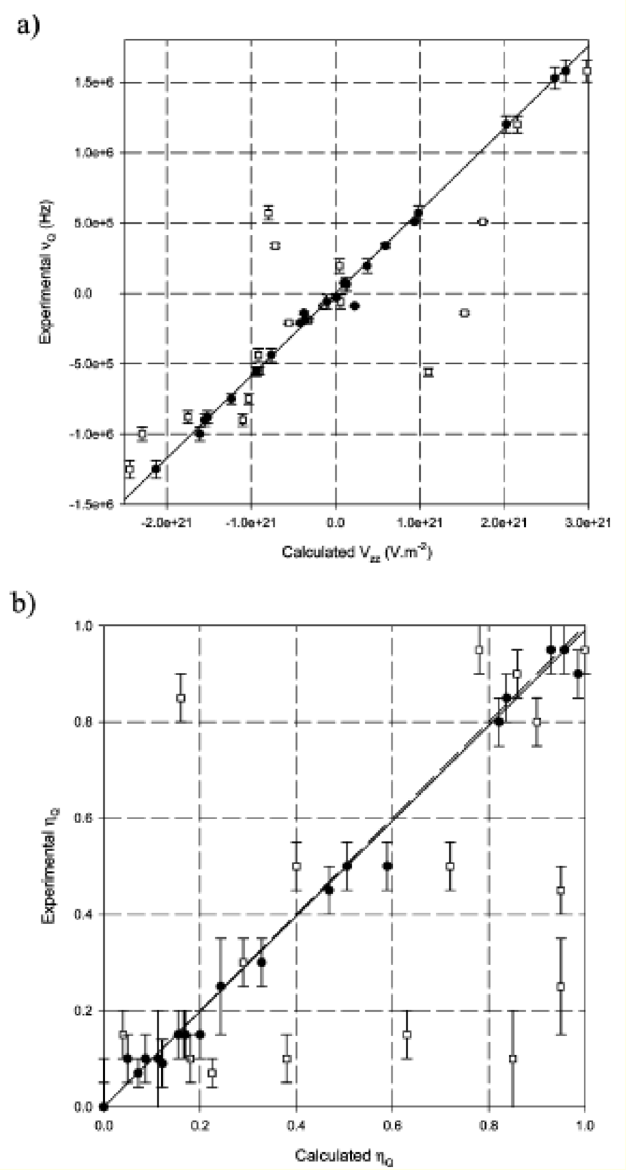
- **Hyperfine parameters** (NMR, Mössbauer, PAC)
  -
  - **hyperfine fields** (contact + dipolar + orbital contribution)
  - **Mössbauer Isomer shifts**
  - **NMR chemical shifts + knight shifts**
  - **Electric field gradients**

$$V_{zz} = \int \frac{\rho(r) Y_{20}}{r^3} dr$$

$$\nu_Q = \frac{3eQV_{zz}}{2I(2I-1)h} \qquad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

- Al-EFG of 16 different Al-fluorides
- before (open symbols)
- after (filled symbols) structural optimization

M.Body et al., *J.Phys.Chem. A 2007, 111, 11873*

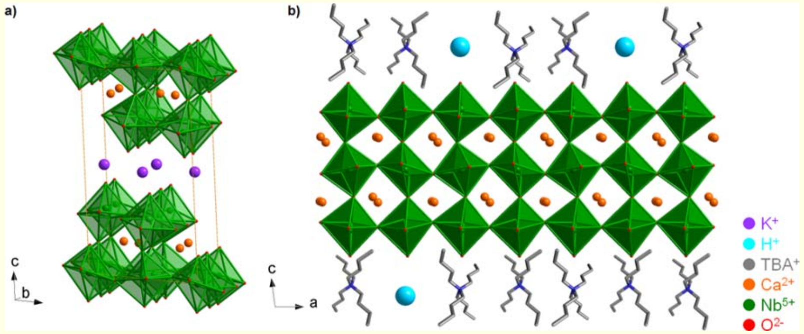


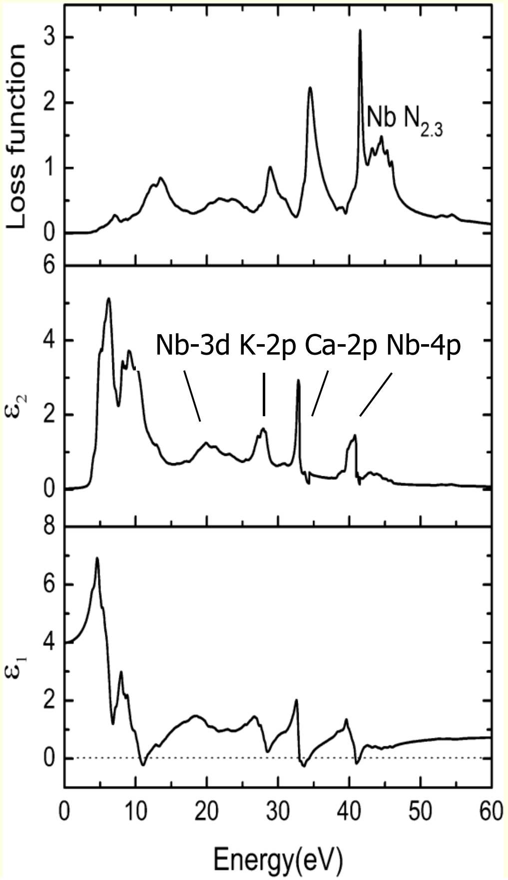
Properties with WIEN2k: Spectroscopy

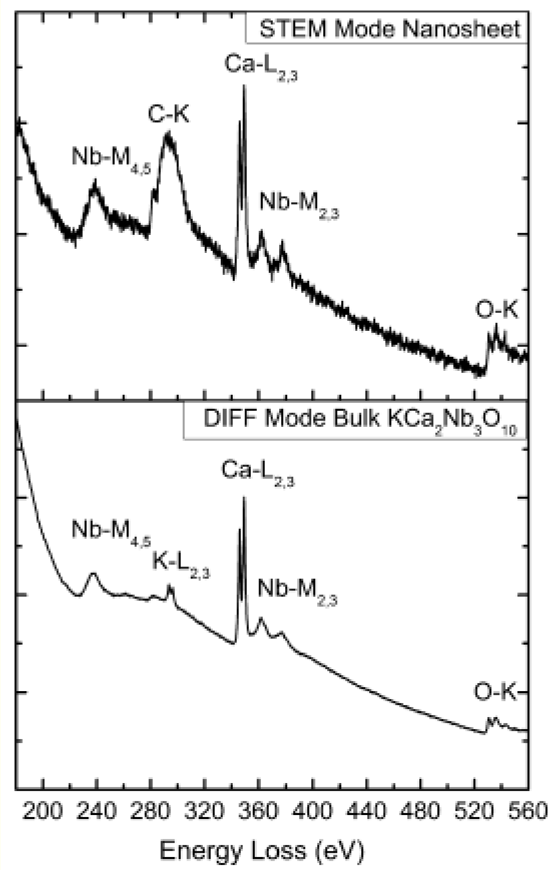
- ***XPS core levelshifts*** *(with half-core holes, Slater's transition state)*
- ***X-ray emission, absorption, electron-energy-loss***
  - (core - valence/conduction-band transitions with matrix elements and angular dep.)
  - EELS including possible non-dipol transititons (momentum transfer)
- ***optical properties*** *(UV-VIS): dielectric function in IPA, JDOS including momentum matrix elements and Kramers-Kronig*

$KCa_2Nb_3O_{10}$: layered material

tripple NbO layers can be exfoliated







Using
Oxide Hetero-structures
for Solar Cells

Oxide Hetero-structures for Solar Cells

Proposal:

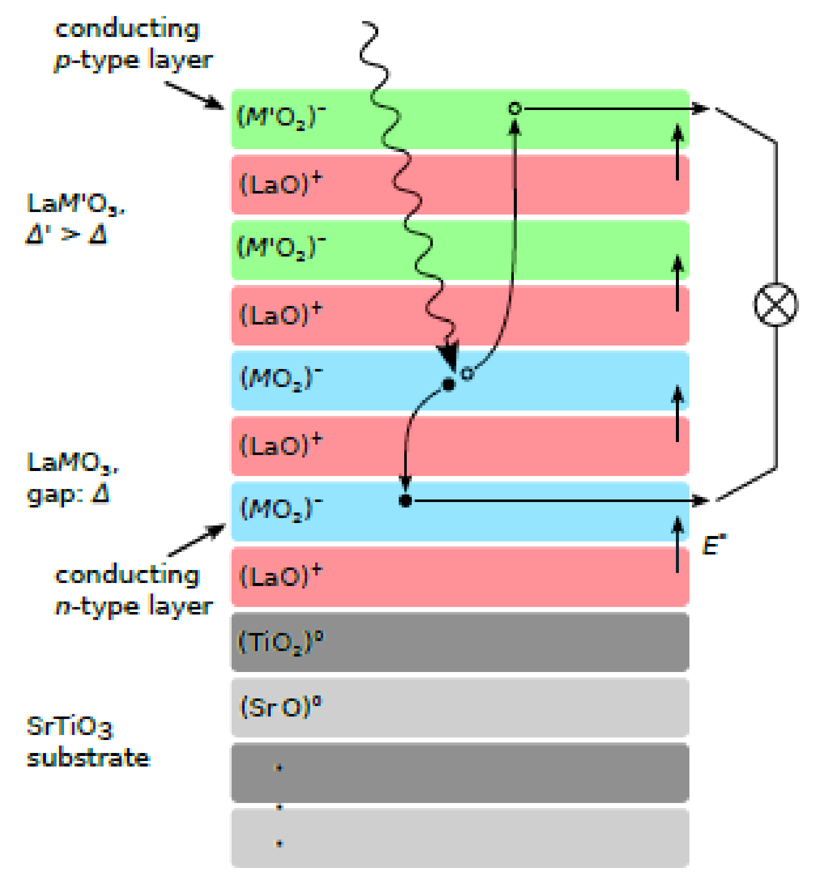
$LaVO_3/SrTiO_3$ heterostructure as **photovoltaic** absorber

- direct gap of 1.1 eV
  - Shockley-Queisser limit (1.0-1.5 eV)
- large intrinsic electric field

➡ separation of holes/electrons

- conducting n- and p-type interface(s)

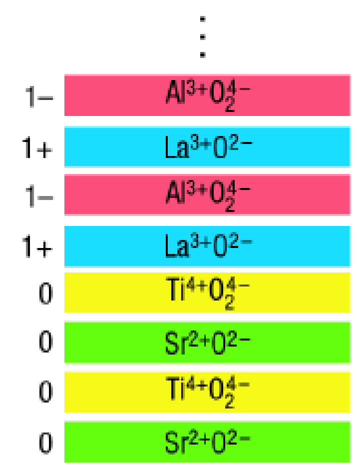
- flexible multi-junction design:
  - different metals M and M‵
  - band gap Δ‵>Δ
  - higher energy photons absorb at M‵
  - lower energy photons at M



E.Assmann et al., Phys. Rev. Lett. 110, 078701 (2013))

prototype $SrTiO_3$ | $LaAlO_3$ multilayer system

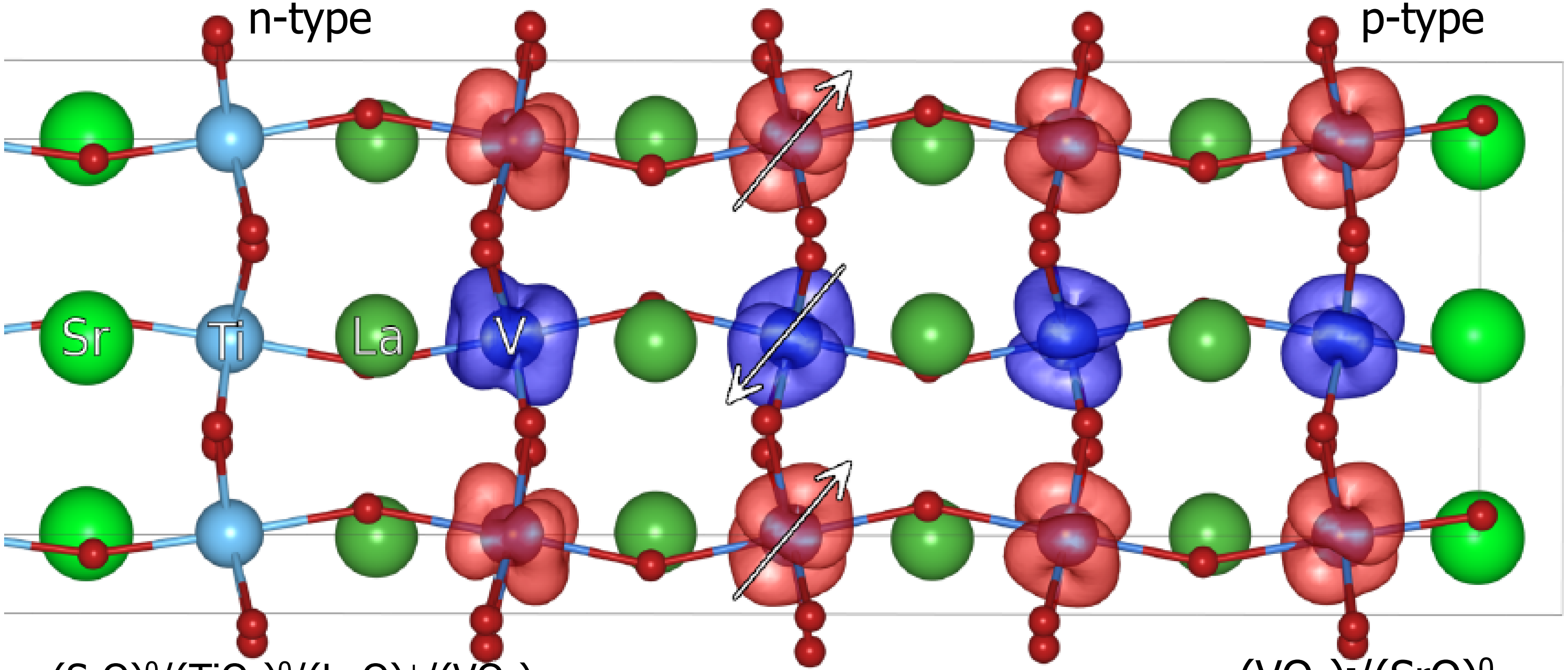
- according to formal valences Sr^{2+}, Ti^{4+}, O^{2-} we have:
  - ***neutral TiO_2|SrO layers***



adapted from N. Nakagawa et al., Nature Mat. 5, **204** (2006)

SrTiO$_3$ / LaVO$_3$ interface

Computational method: GGA + $U_V = 3\,\mathrm{eV}$, $U_{Ti} = 9.8\,\mathrm{eV}$

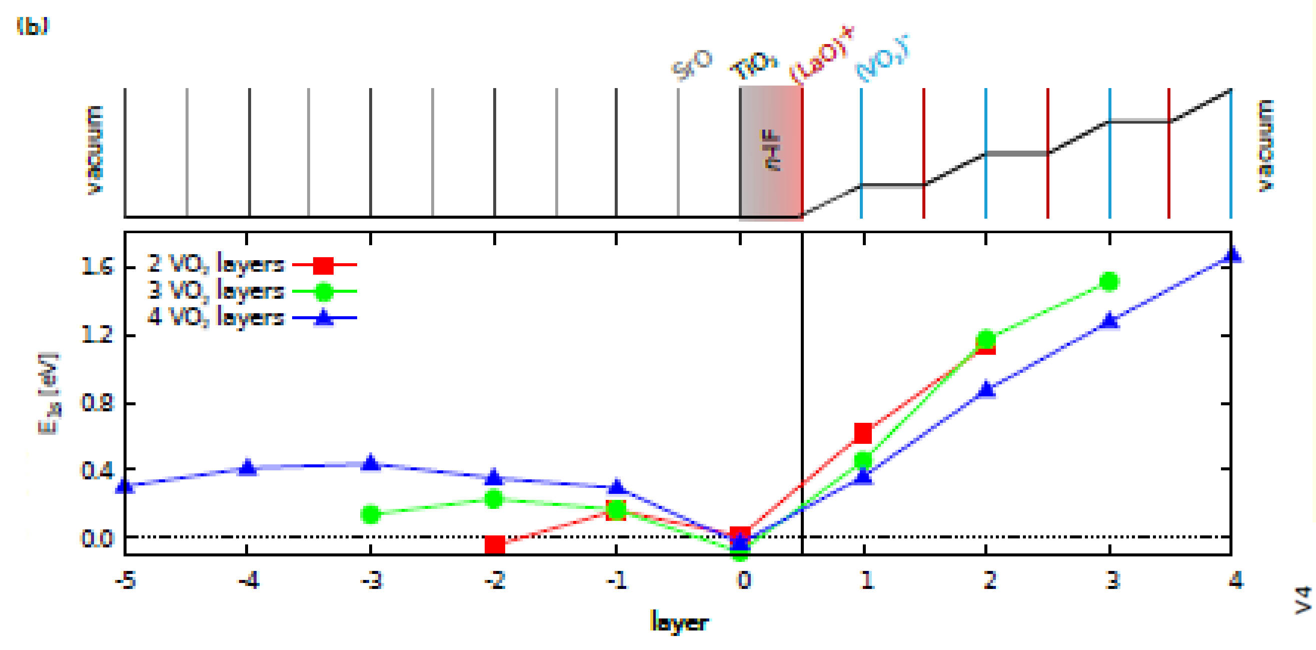


$(SrO)^0/(TiO_2)^0/(LaO)^+/(VO_2)^-$

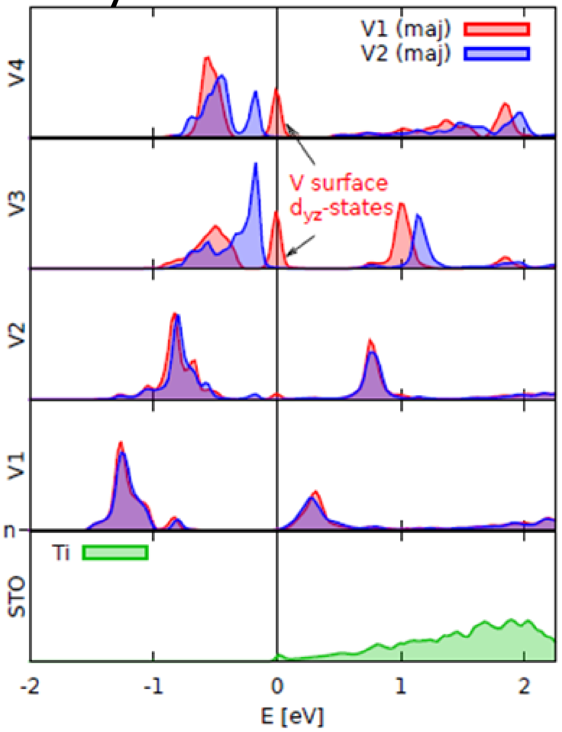
$(VO_2)^-/(SrO)^0$

- spin order: AF-C
- orbital order: AF-G (d_{xz} | d_{yz}) + d_{xy}
- *multi-layer* vs. *thin-film*

electric field due to polar interface



layer-resolved DOS



- thin film geometry (with vacuum)
  - *potential flat in STO (except band bending)*
  - *potential gradient in LVO : 0.4 eV/u.c.=0.1 eV/Å*
    (obtained from O-1s XPS core level shifts)
  - *metallic V states at the surface*
    (beyond critical thickness)

strong optical absorption of $LaVO_3$

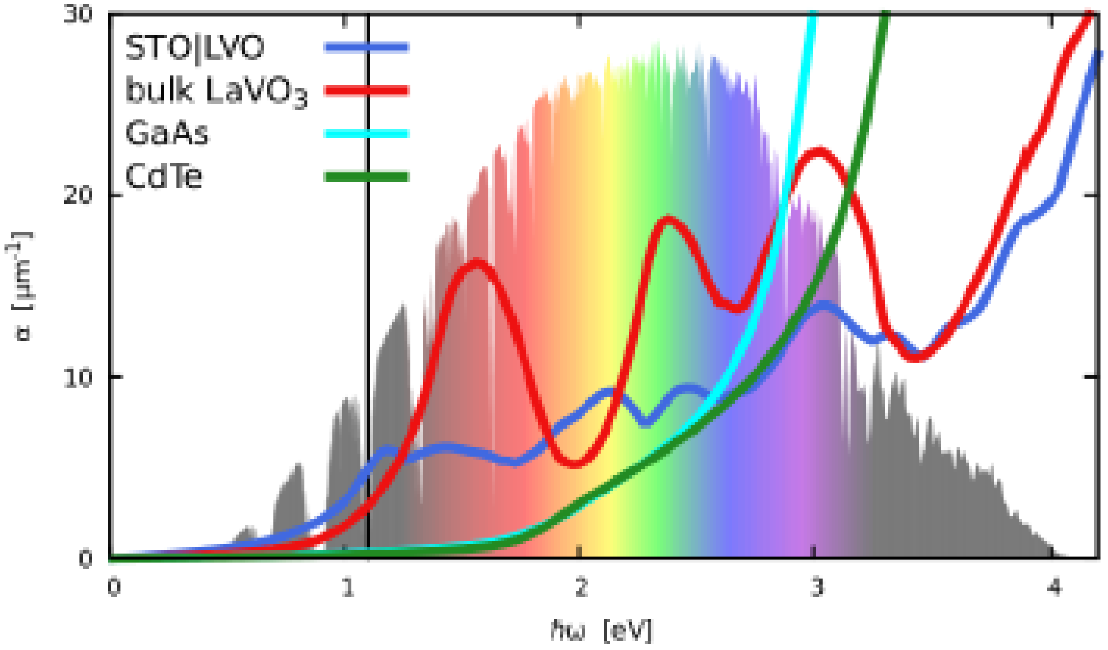
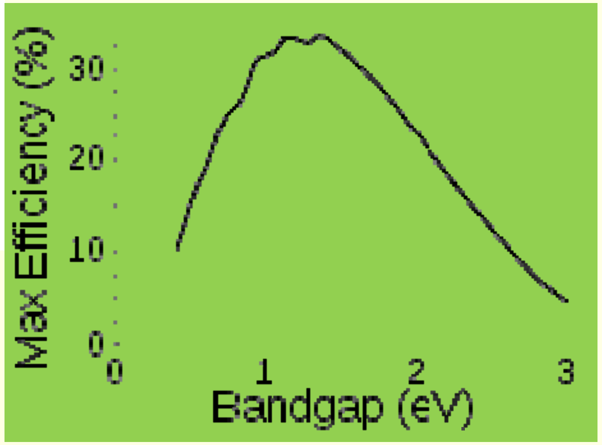


Figure 5: Optical absorption and solar spectrum. The solid lines show the absorption coefficients of $LaVO_3$ and, for comparison, CdTe and GaAs, which are widely used in current high-efficiency solar cells. In the background, the solar spectrum as measured on the Earth's surface is shown (standard global air mass 1.5, in arbitrary units).

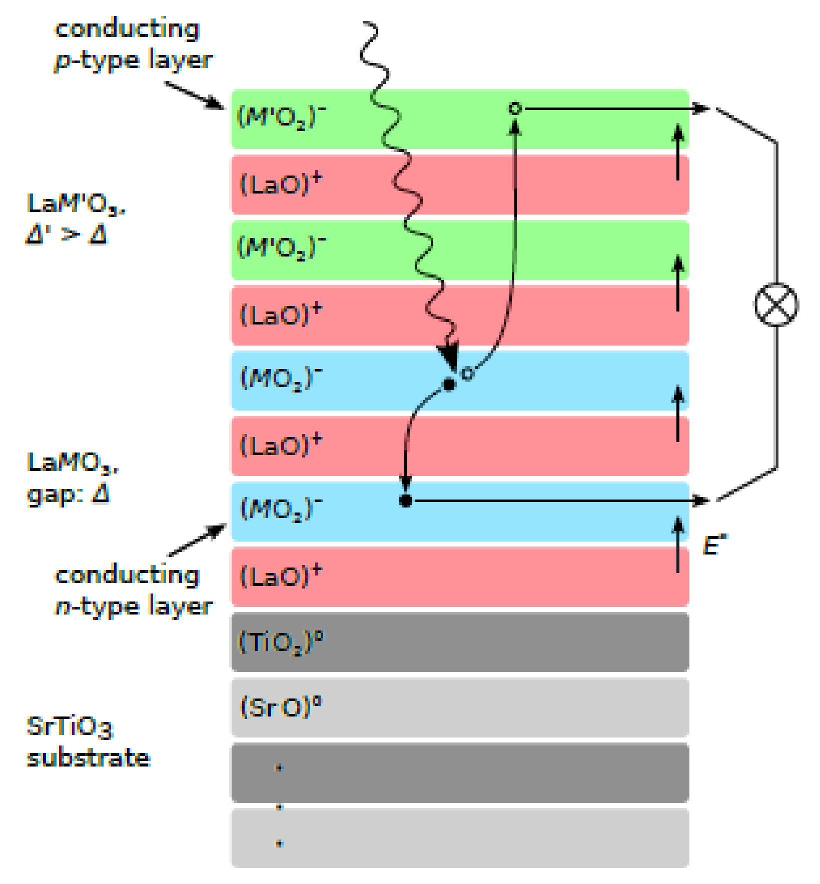
- band gap of 1.1 eV in optimal range

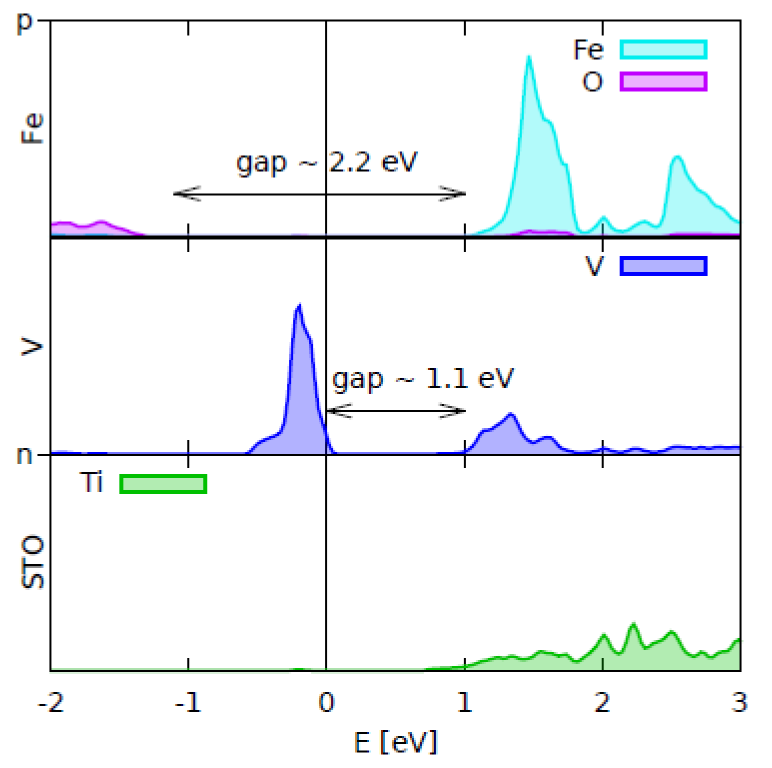
Shockley-Queisser limit:



multi-gap solar cells

- combine 2 TMO with different gaps:





Supplementary Figure S1: The relevant contributions to the density of states around the Fermi level for the "gap-graded" $LaFeO_3|LaVO_3|SrTiO_3$ structure. In this case, the two V/Fe sites give almost identical contributions (in opposite spin channels). A p- and an n-type interface appear, as marked, due to periodic boundary conditions.

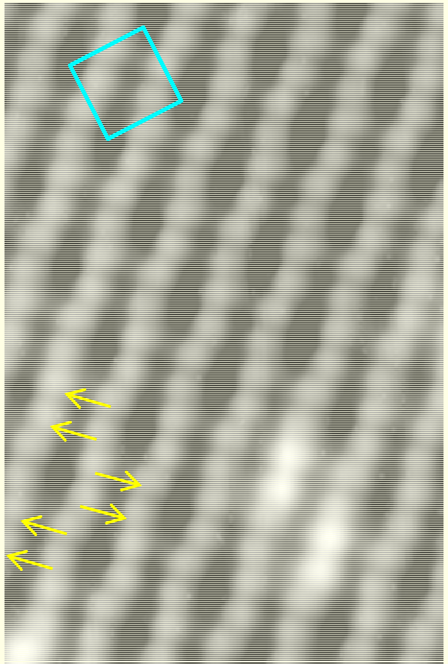
- „tandem solar cell" La**Fe**O_3/La**V**O_3/$SrTiO_3$ for higher efficiency (34 % for single p-n junction)

Surface reconstruction of Fe_3O_4 (001)

The Fe_3O_4(001) Surface

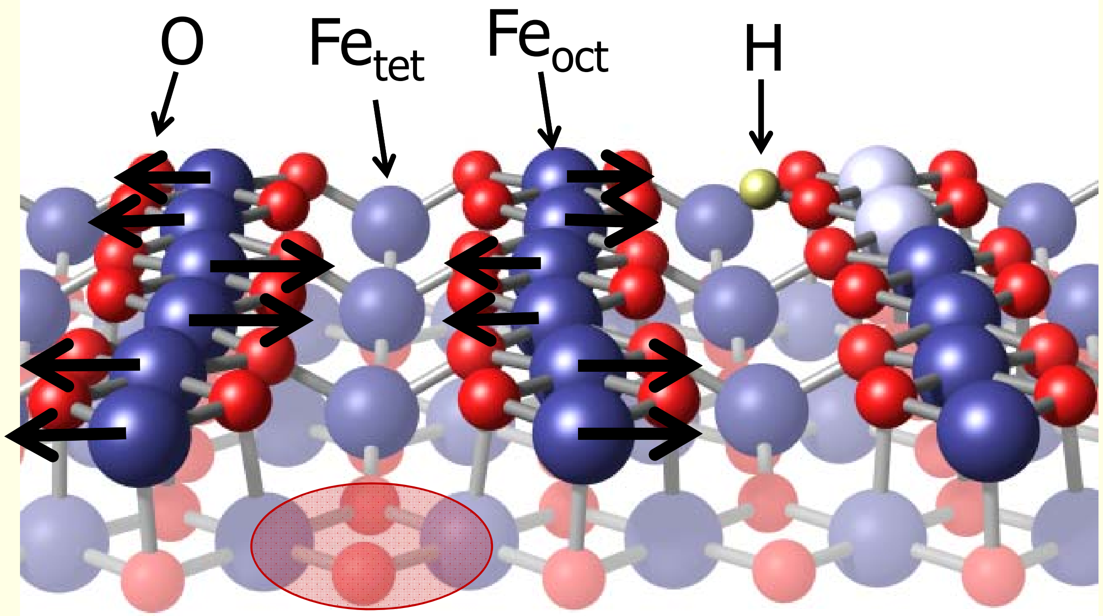
Fe_3O_4(001) exhibits (√2x√2)R45° superstructure due to small lateral relaxations of surface atoms (≈ 0.1 Å)

In STM, we see the Fe_{oct} atoms



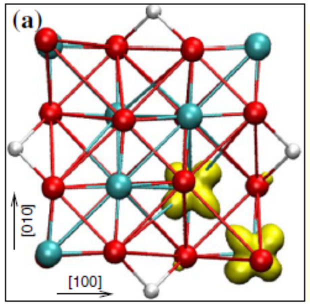
(4.38 x 6.43) nm^2
1 V, 0.1 nA

Structure determined by DFT, SXRD 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

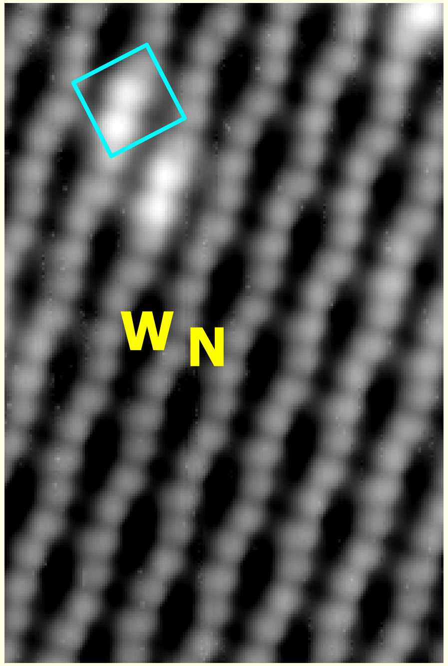


The Fe_3O_4(001) Surface

Two obvious sites for **ad-atom adsorption**:

Bulk continuation Fe_{tet} sites **"W"** and **"N"**

In STM, we see the Fe_{oct} atoms



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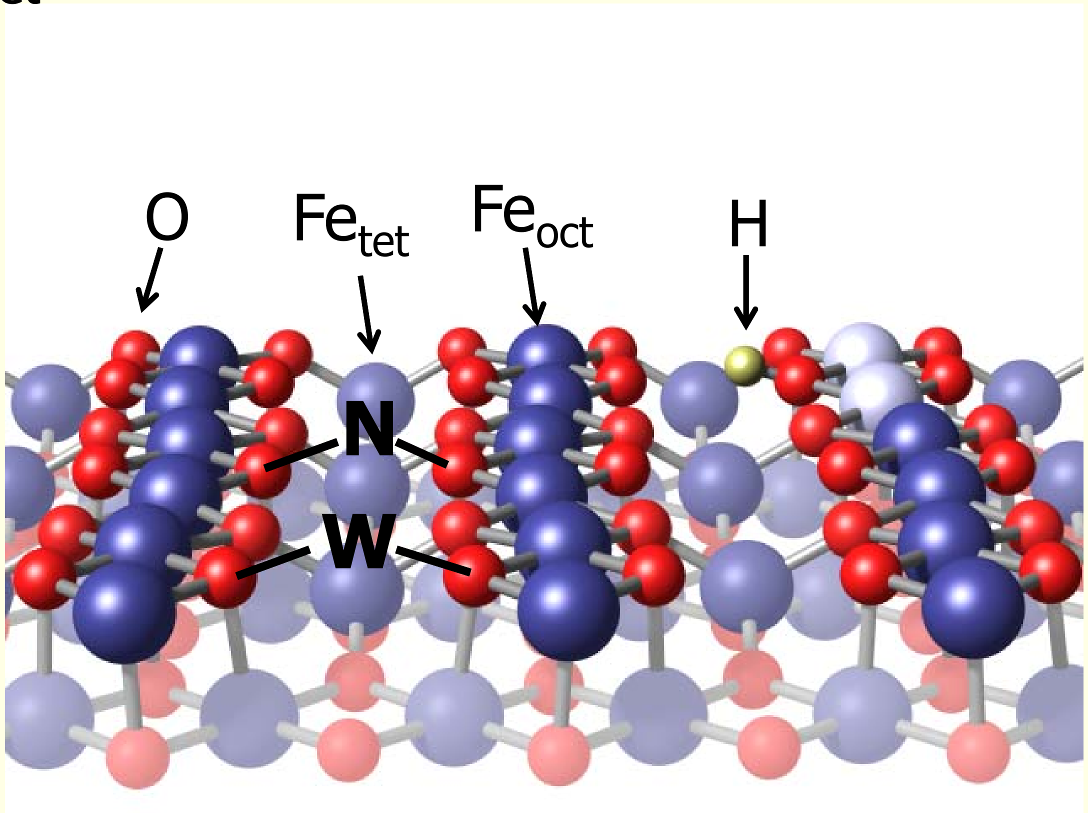
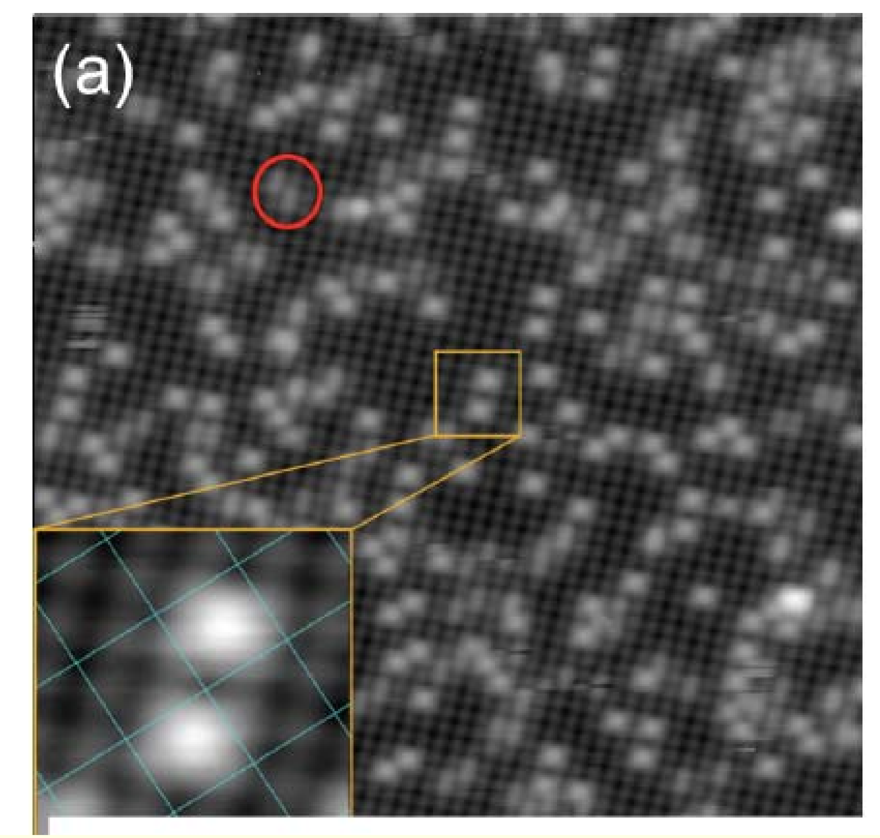


Au atoms on Fe_{oct} terminated Fe_3O_4:



experiments in U.Diebolds group:

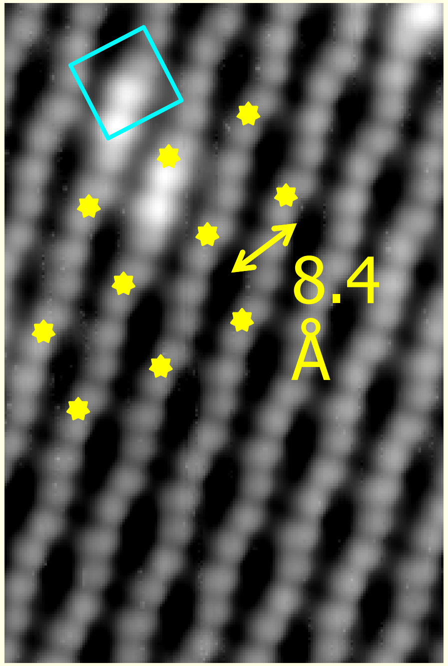
Z.Novotny et al., PRL 108, 216103 (2012)

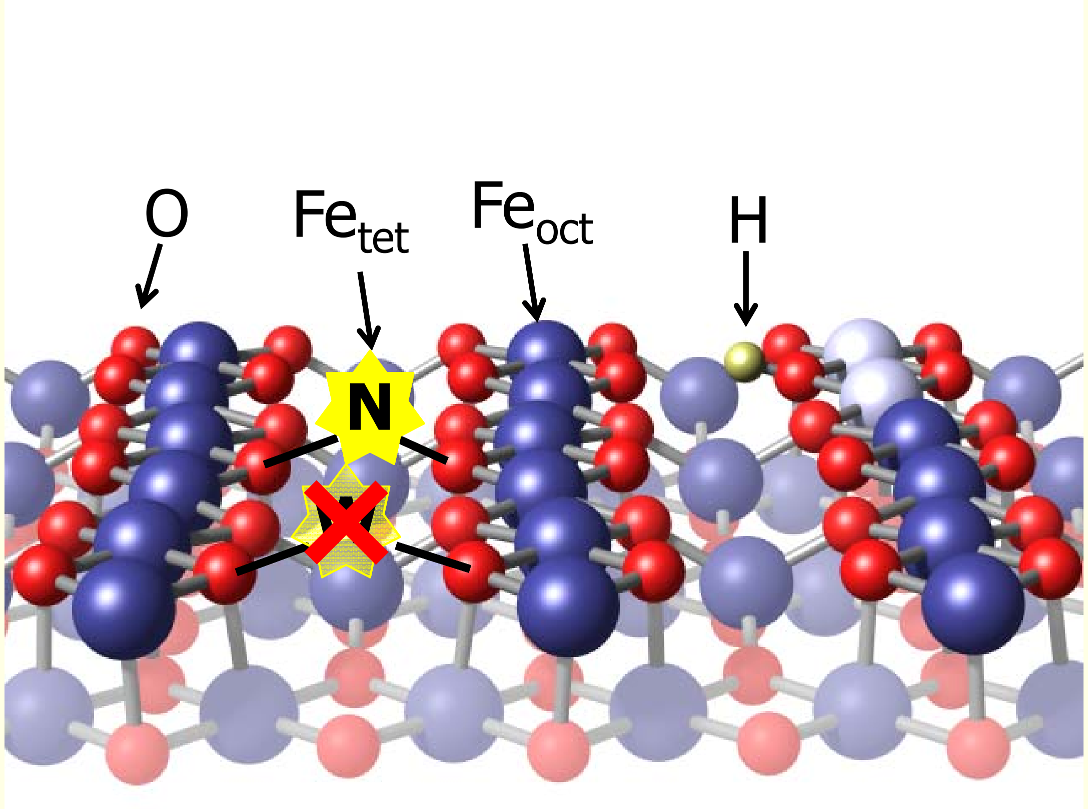
single Au atoms stable up to 400 C

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)

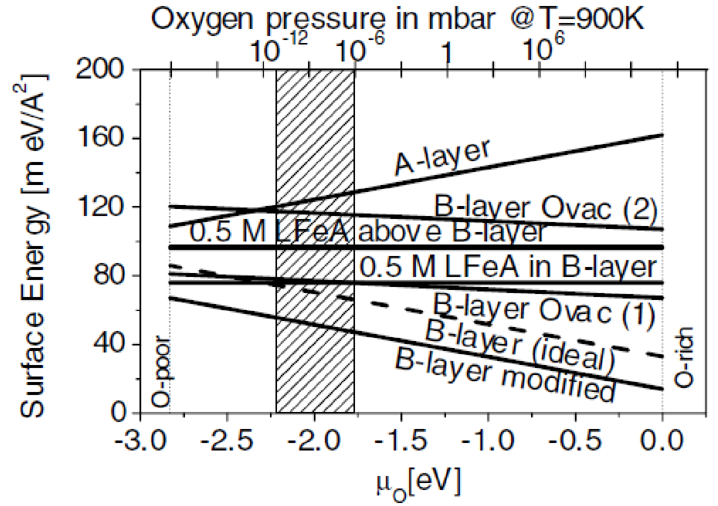
something must block this site !!!

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

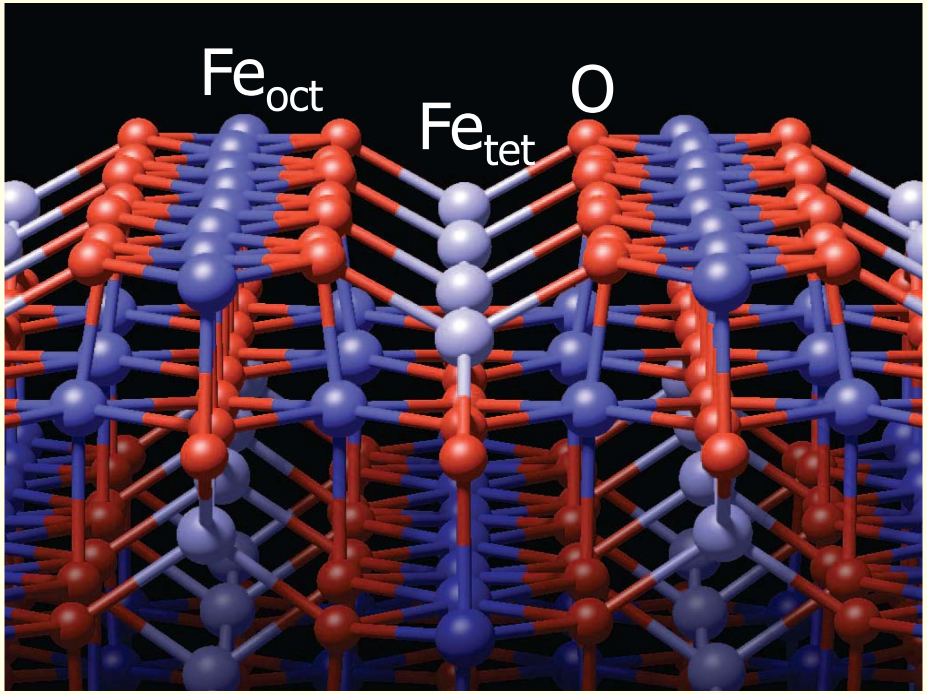
- γ-Fe_2O_3: Maghemite is a “Magnetite” with 1/6 Fe_{oct} vacancies

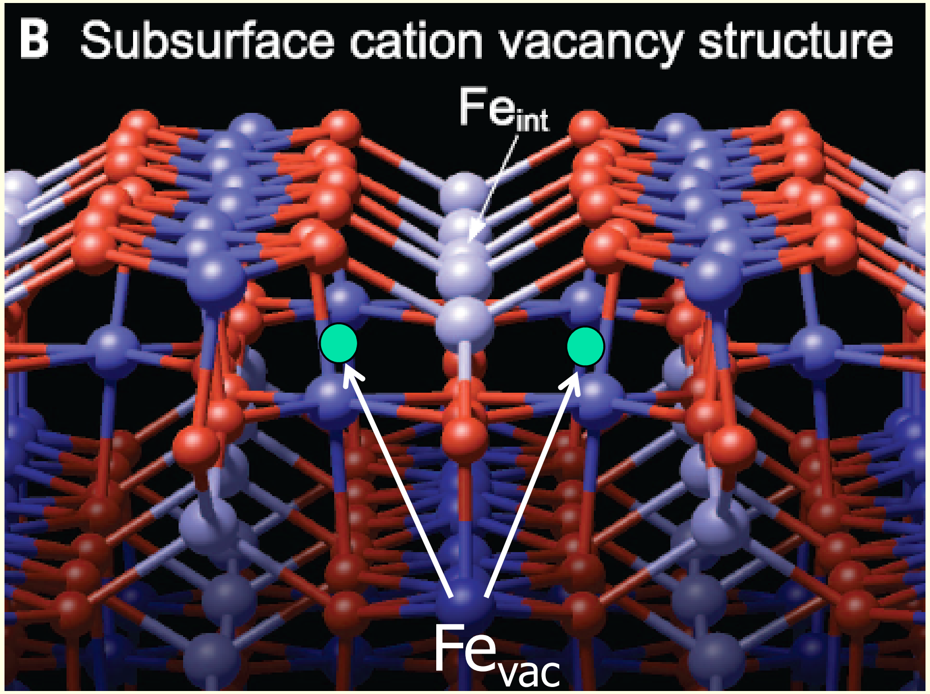
➡ **Subsurface cation vacancy structure**

$Fe_3O_4(001)$ surface reconstruction

Distorted bulk truncation

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

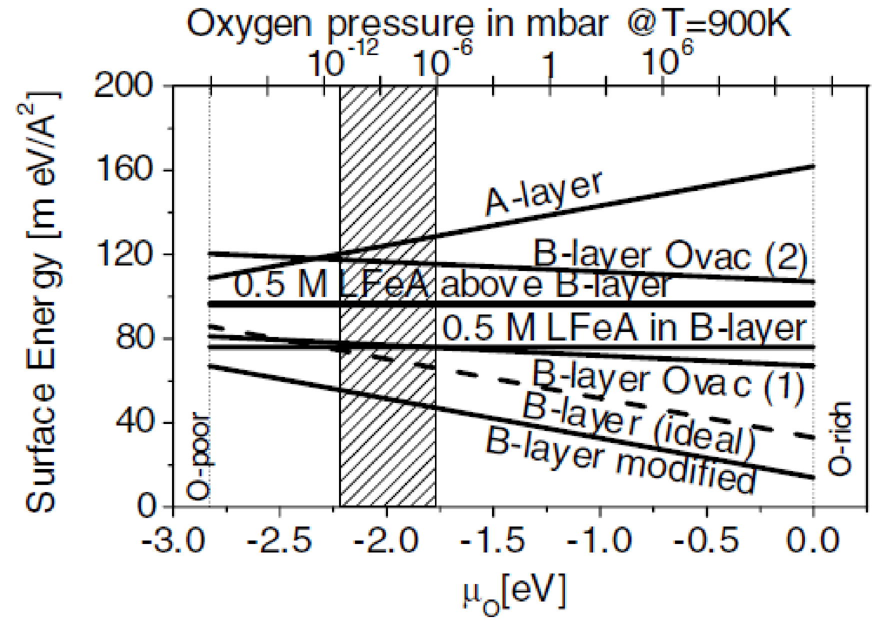




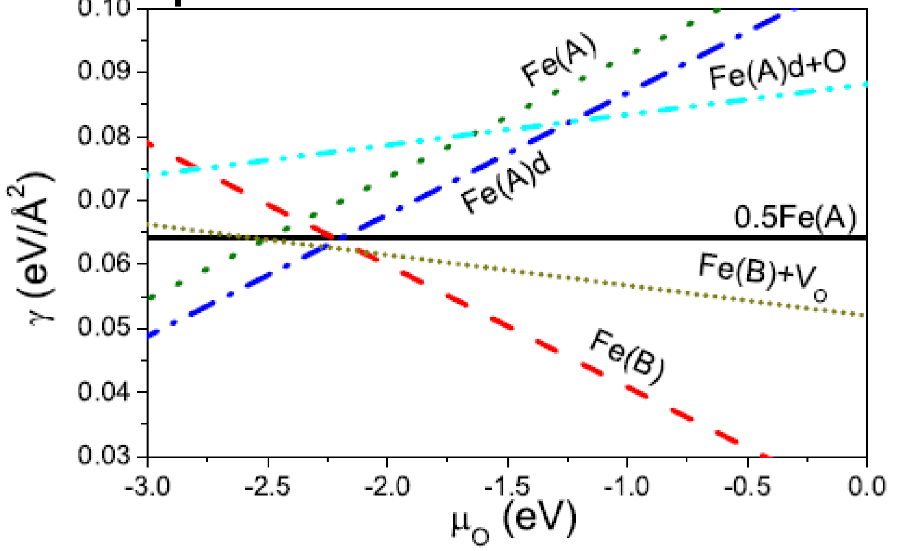
new model:

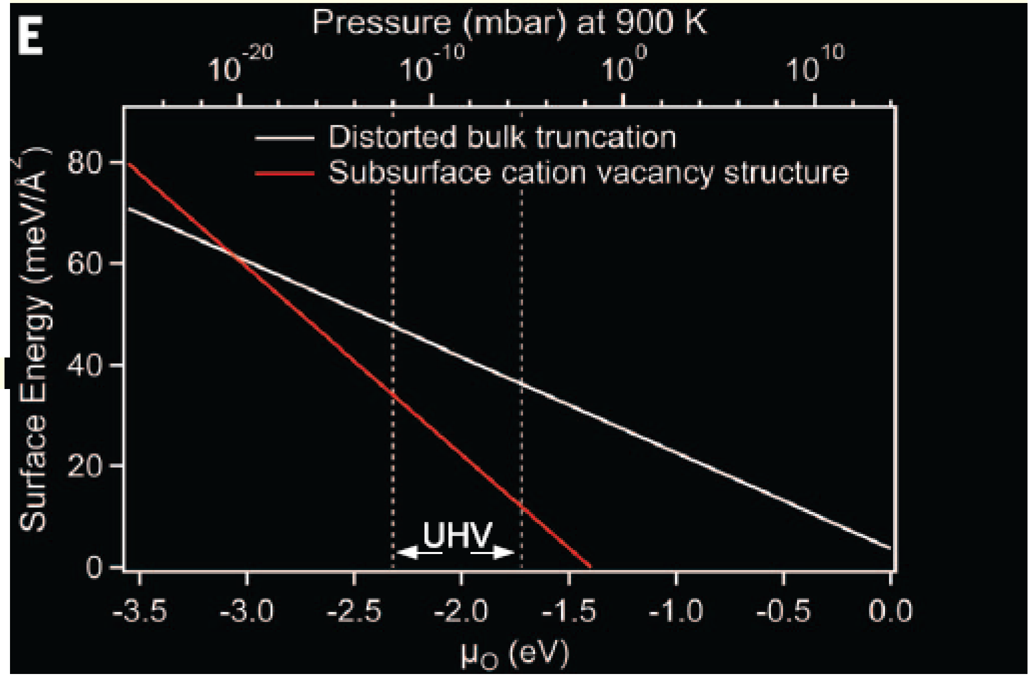
much stronger Fe_{oct} corrugation

Thermodynamic stability



previous calculations

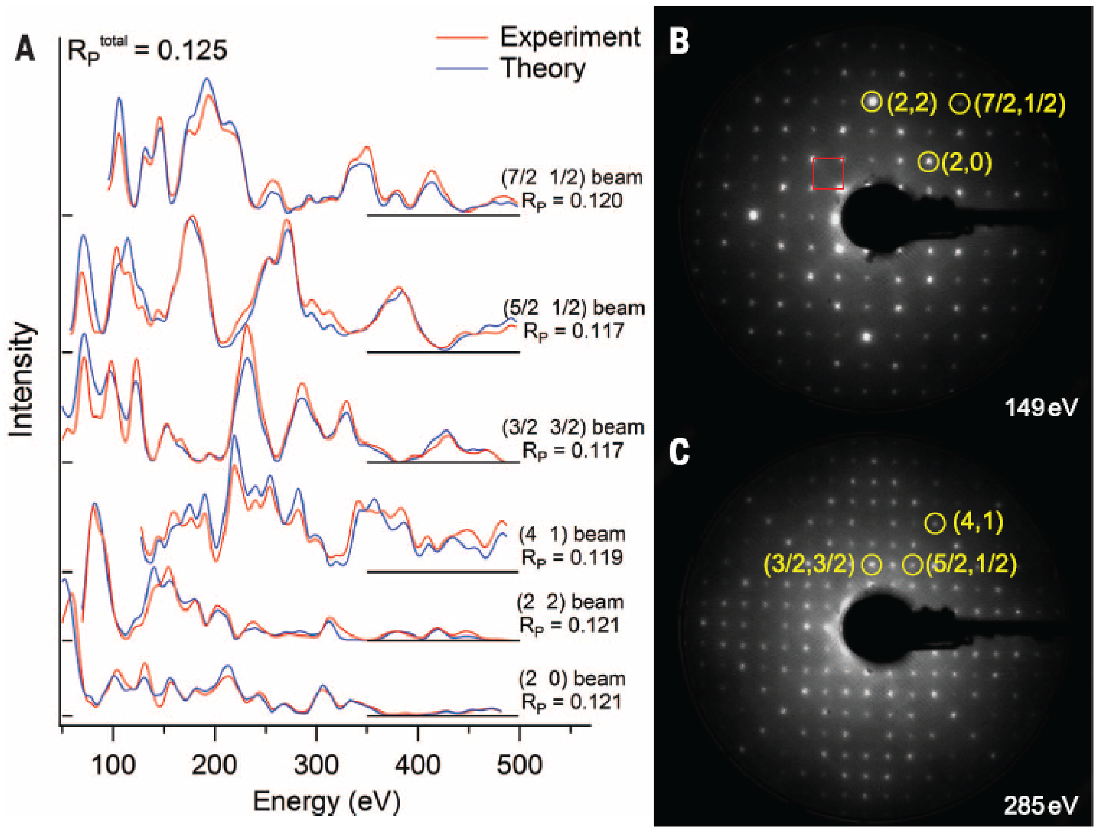




The subsurface vacancy model is more stable than bulk-termination

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



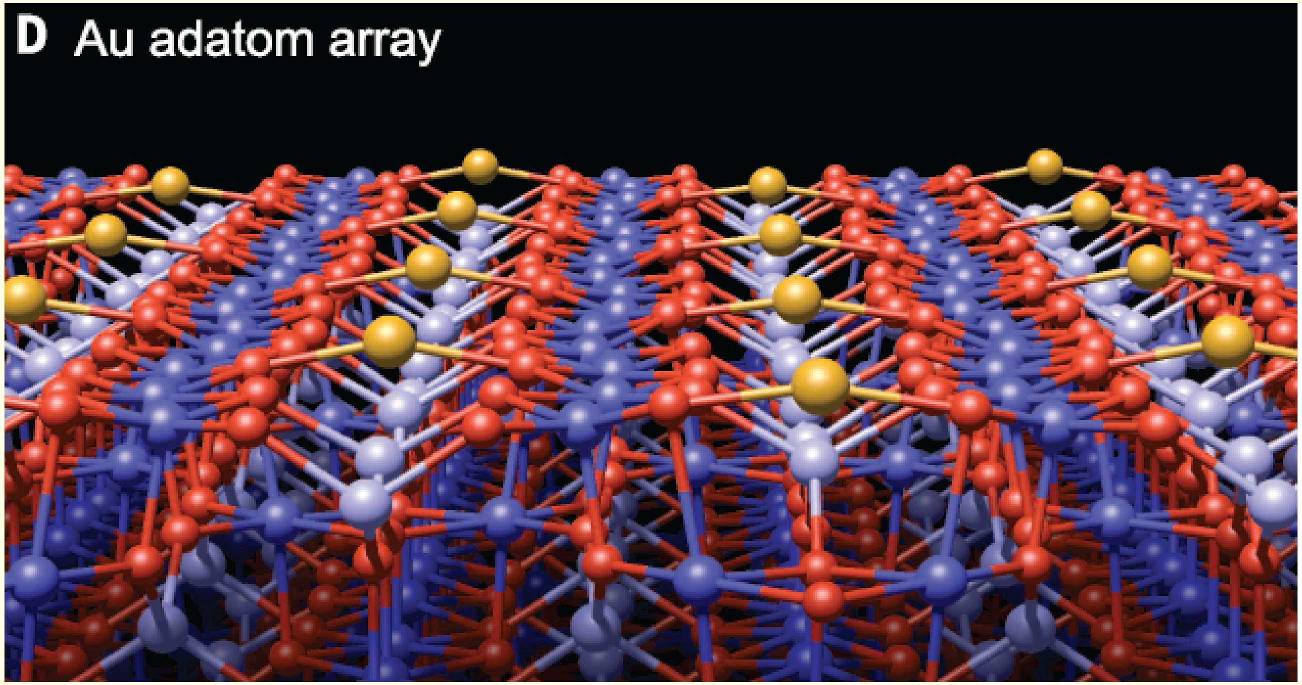
refined exp. positions and theor. positions agree within 0.05 Å

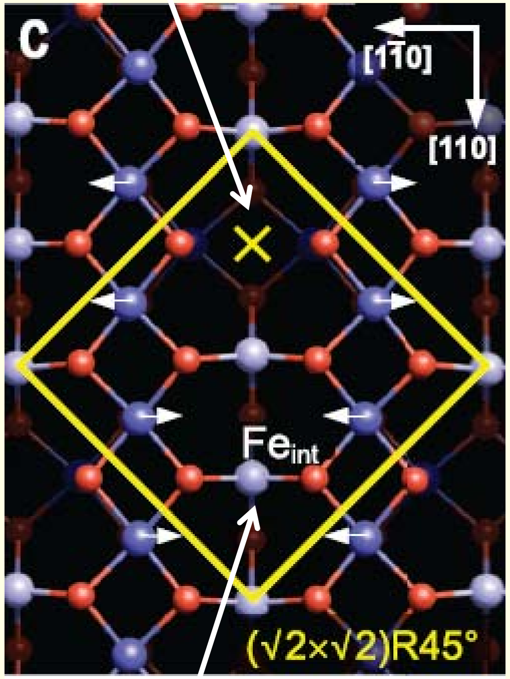
(all within the exp. error)

Au adatom adsorption blocked by Fe_{int}

Fe_{int} blocks selectively adatom adsorption on this site

adsorbtion site

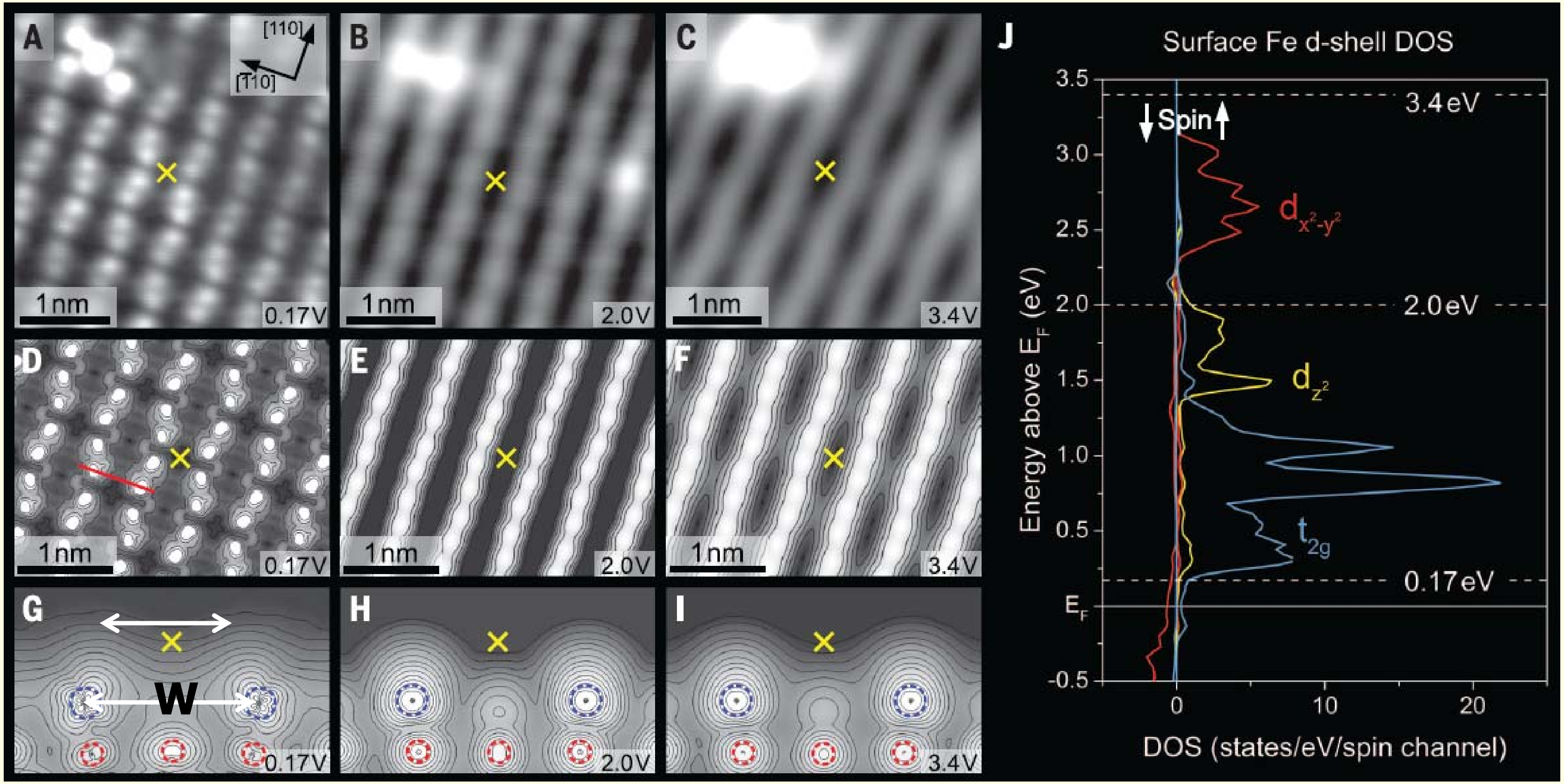




blocked site

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

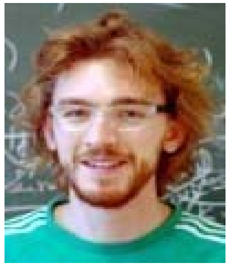
STM with different bias voltage



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

Acknowledgment

STO/LVO:



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Thank you for your attention !