PAUL SCHERRER INSTITUT

PSI

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Extended defects modelling of functional oxides

the intriguing case of UO_2

Empa Postdocs-II & PSI-FELLOW II-3i RETREAT 2018

Functional Oxides in Emerging Technologies

Li-ion Battery Cathodes

All-Oxide Photovoltaics Light absorbers Charge conductors

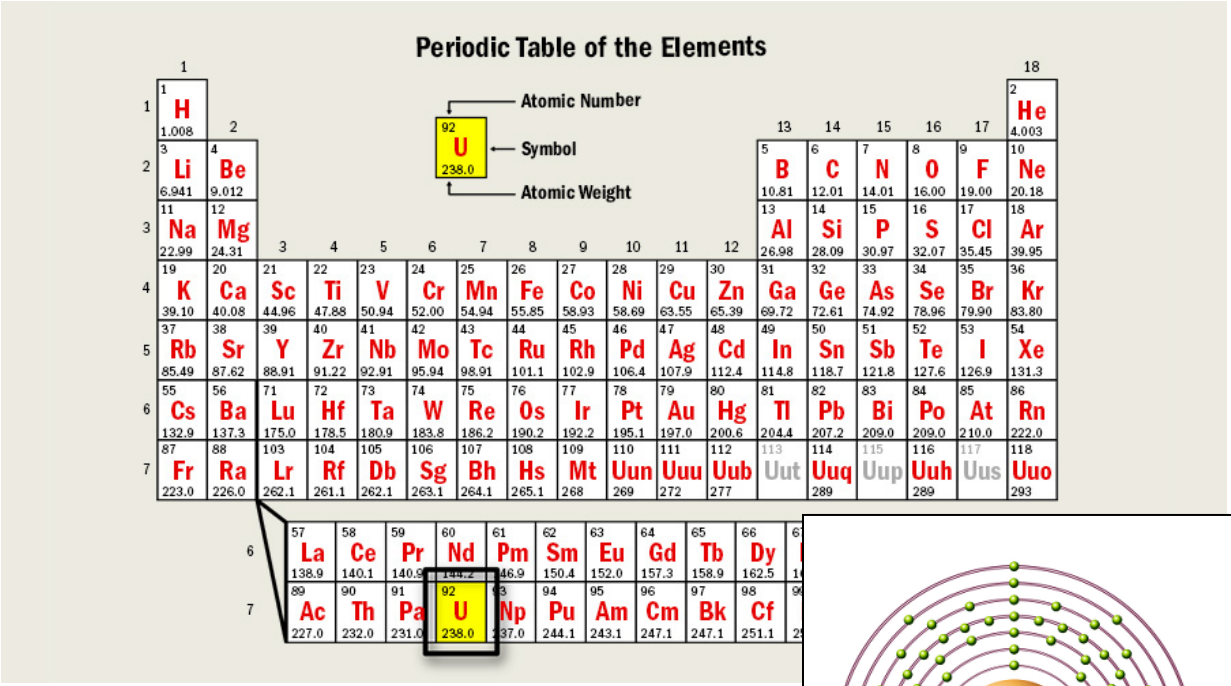
Fuel Cells Non precious metal electro catalysts

Nuclear Fuels safety, UO_2

Unifying Motif: complex electronic structure enables functionality

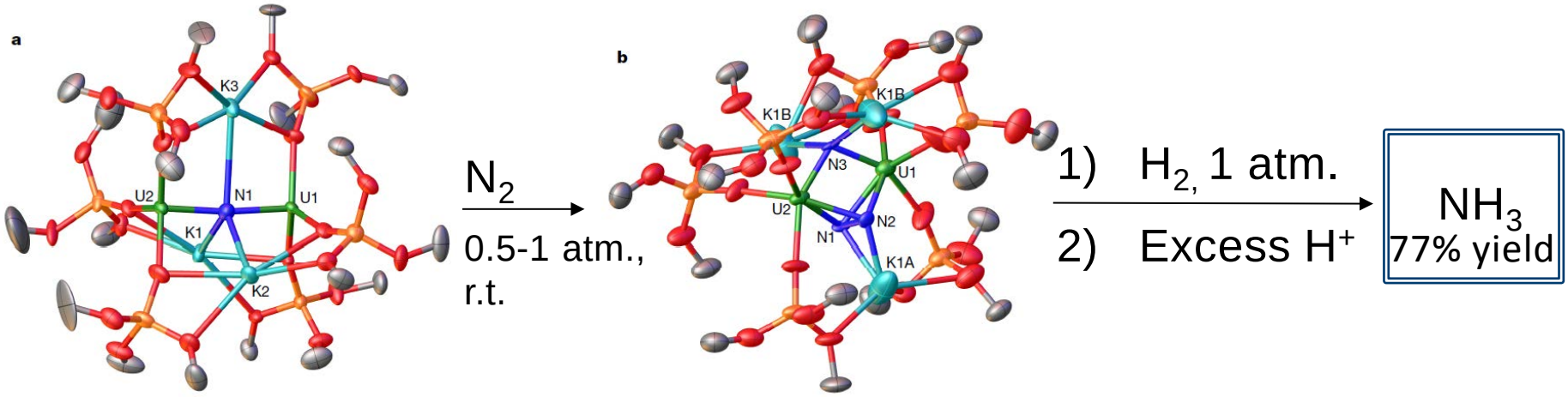
Practical Utilization: how MATERIALS respond to stress?

Functional Oxides – Complex Electronic Structure, UO_2 nuclear fuel



Versatility of Uranium based materials
a catalyst for N_2 Functionalization

- Industrial Haber–Bosch process: $N_2 + 3H_2 \rightarrow 2NH_3$ 450°C, 300 bar.
- Biological N_2 fixation, $N_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ NH_3 + H_2$



X-ray structure

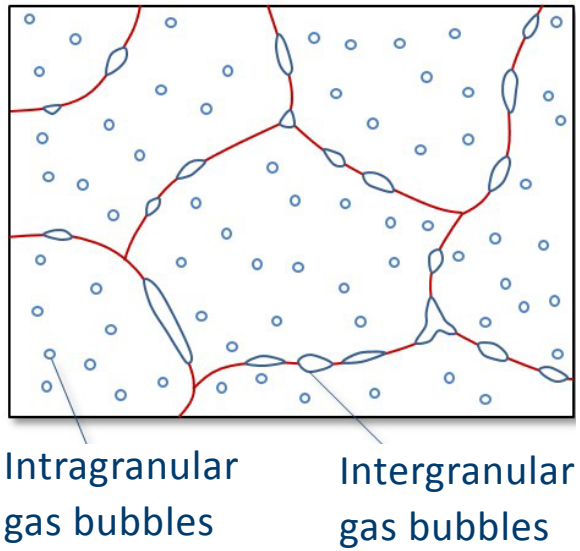
M. Falcone, L. Chatelain, R. Scopelliti, I. Živković, M. Mazzanti *Nature*, 2017, *547*, pp. 332–335

Nuclear Fuel UO_2
Mechanical Properties in the Plastic Regime

- Irradiation:
  compositional changes
  temperature jumps

- U fission process:
  noble gases, Xe, Kr, release
  insoluble in the fuel matrix
  precipitate within the fuel body.

- Extended defects:
  dislocations/grain boundaries can pin
  and immobilize gas bubbles < 1 micron.



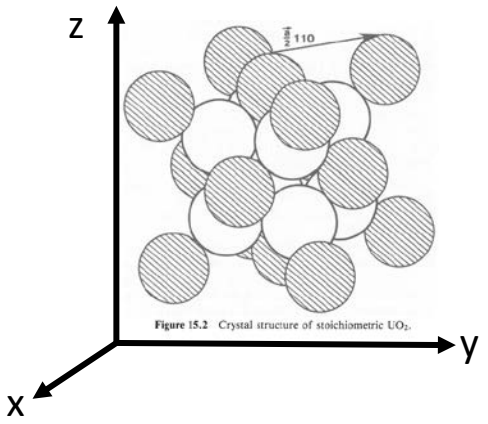
Structure - Property relationship of Dislocations in UO_2

G. W. Greenwood, A. J. E. Foreman, D. E. Rimmer, *J. Nuc. Mater.,* **1959**, 305-324.
D. R. Olander, *in Fundamental Aspects of Nuclear Reactor Fuel Elements,* **1976**.

Image source: http://www.hhallberg.com/?tag=grain-boundary

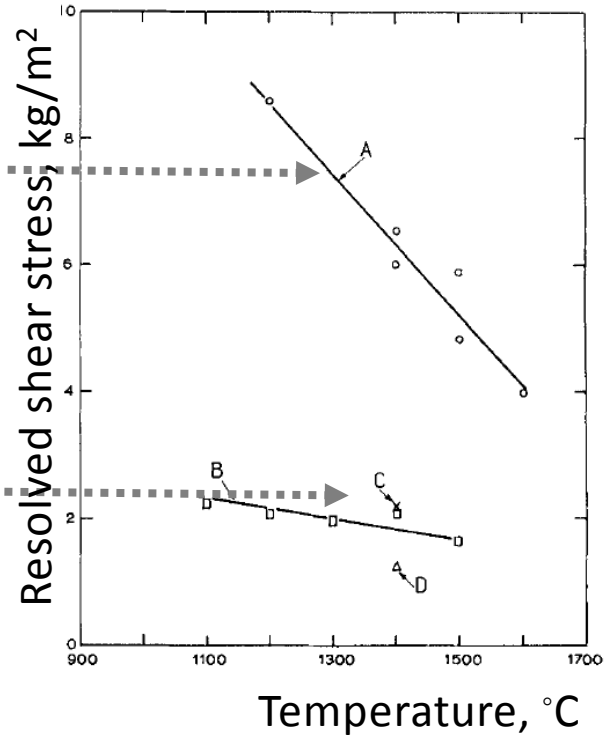
I. Experimental characterization of slip systems in UO_2 *compression tests*

Stoichiometric UO_2 slip systems



A difficult slip system:
{110}<110> (A)

An easy slip system:
{001}<110> (C)



Exp. characterization of slip systems: J. S. Nadeau, *J. A. Ceram. Soc.*, **1969**, *52*, 1.

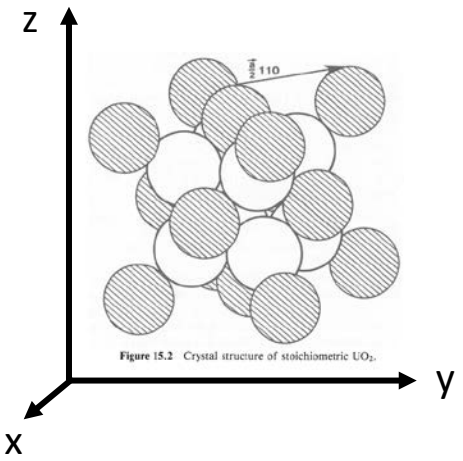
A. H. Heuer, R. J. Keller, T. E. Mitchell in *Deformation Processes in Minerals, Ceramic and Rocks*, **1990**, Ch. 15, pp. 377-390.

II. Experimental characterization of slip systems in UO_2 *compression tests*

Stoichiometric UO_2(U/O=2.0001) at 873K and 523K:

A primary slip system: {111}<1-10>*

with presence of {001}<1-10>



The reason for the dominance of {111} slip for $T < 873$ K is not well understood. It was demon-

Why this behavior should be observed in UO_2, but not in CaF_2, is not clear; we speculate that differences in details of the bonding between anions and cations (the amount of ionic vs covalent character) may be responsible.

*50% difference in yield stresses w.r.t previous experimental studies.

Exp. characterization of {111} slip systems using slip traces and TEM analysis: R. J. Keller, T. E. Mitchell, A. H. Heuer, *Acta Metall.*, **1988**, *36*, 1061-1071.

A. H. Heuer, R. J. Keller, T. E. Mitchell in *Deformation Processes in Minerals, Ceramic and Rocks*, **1990**, Ch. 15, pp. 377-390.

The Goal and the Tasks

Understand how fission product gases interact with dislocations

Understand structure property relationship of dislocation

Develop computational tools for modelling dislocations of materials with complex electronic structure

Modelling Extended Defects

Empirical Potentials - Force fields

$$U(\vec{R}) = \underbrace{\sum_{bonds} k_i^{bond}(r_i - r_0)^2}_{U_{bond}} + \underbrace{\sum_{angles} k_i^{angle}(\theta_i - \theta_0)^2}_{U_{angle}} + \ldots$$

Cheap computationally: Systems of 10,000-100,000 atoms.

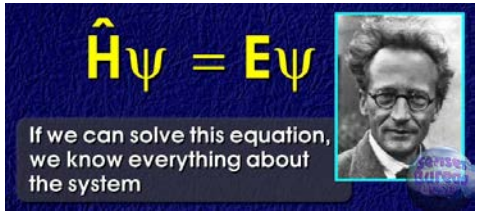
Neglect electronic structure: Covalence in the U-O bond and change in the oxidation state.

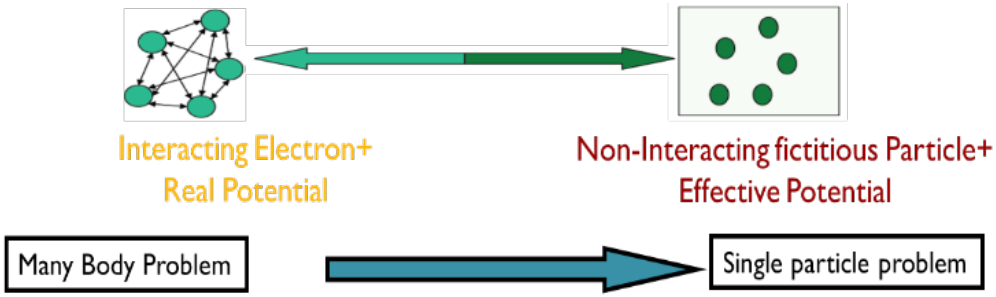
Modelling Extended Defects

First principles methods: DFT+U

CPU intensive: 600-3000 atoms

Detailed electronic structure: bond formation, possible change in the oxidation state during dislocations.





M. Krack, *Phys. Scr*. **2015**, *90*, 094014.
Quickstep: Make the atoms dance, M. Krack and M. Parrinello, Forschungszentrum Jülich, *NIC Series*, Vol. 25, 29 (2004).

Density Functional Theory modelling of UO_2

_f_-electrons in a standard DFT:

➢ **dispersed among all f orbitals**

f-electrons via

***f orbital Occupation Pattern, FOP*:**

- ➢ restoring the band gap of UO_2
- ➢ magnetic structure

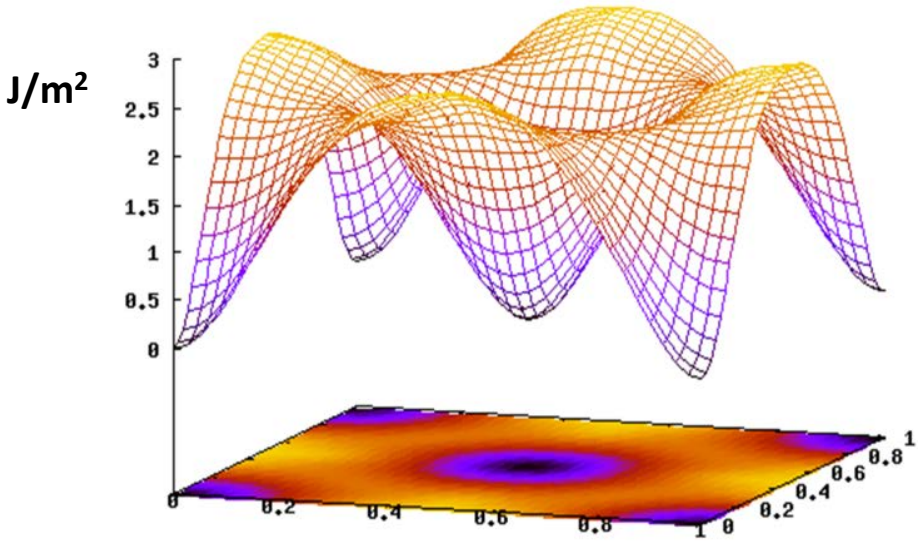
➢ **f orbitals' localized electrons**

M. Krack, *Phys. Scr.* **2015**, *90*, 094014.

Computational studies of dislocations in UO_2

general computational scheme

Plotting energy of crystal as function of displacement



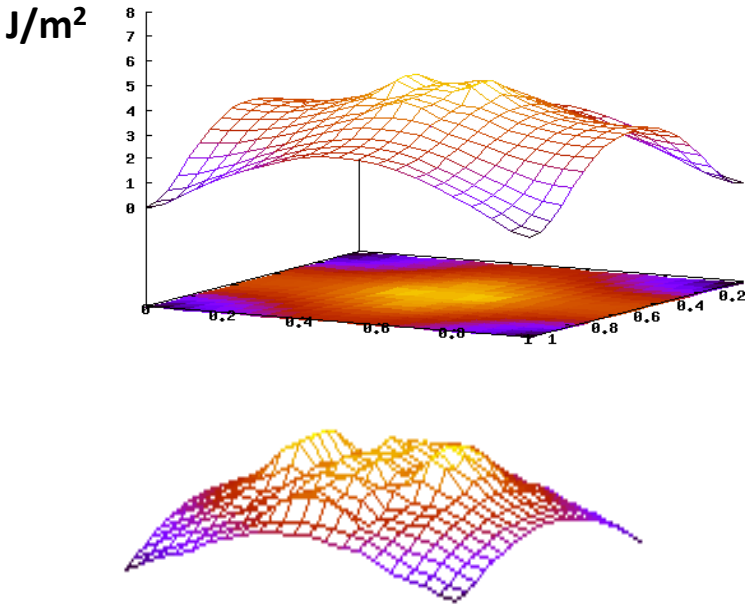
γ-surface, Generalised Stacking Fault Energies

V. Vitek, Philos. Mag., **1968**, *40*, 903.
V. Vitek, *Progress in Materials Science*, **1992**, *36*, 1-27.

Validating Empirical Potentials with DFT+U

{110}

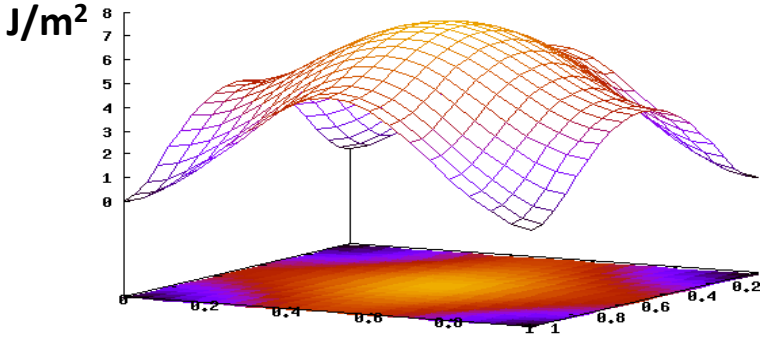
PBE+U



Fine grid of the 0.25-0.75 region

convergence w.r.t z axis

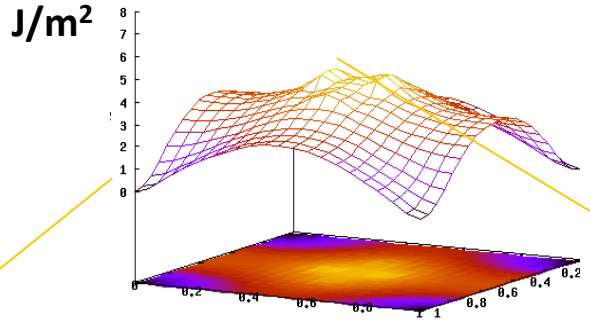
Force Field, Yakub

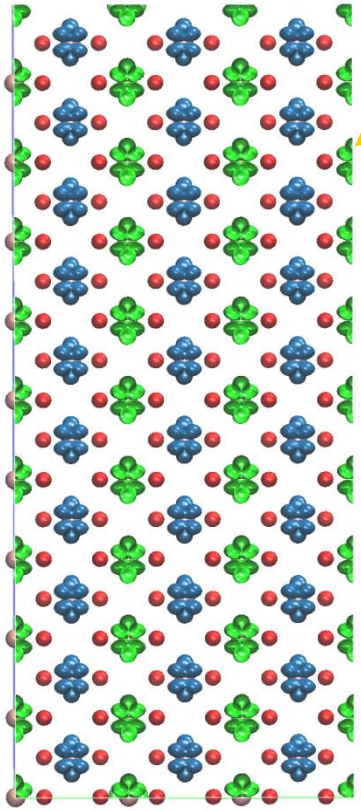


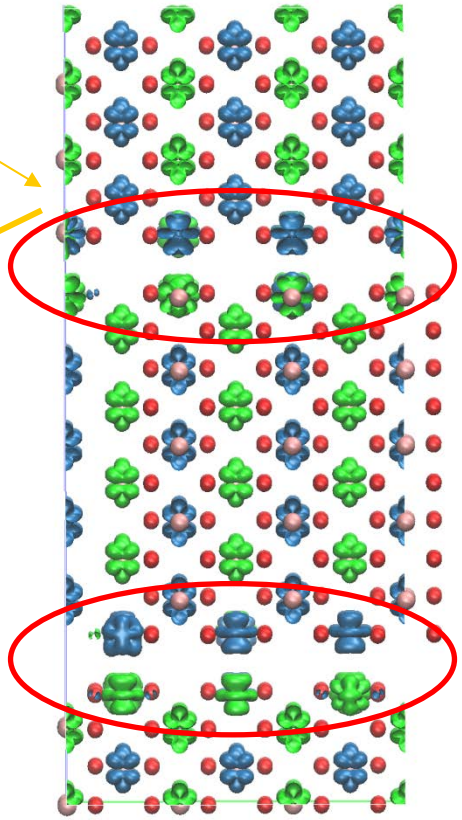
Why the DFT+U γ-surface is corrugated?

M. Kosa, M. Krack, preliminary results, DFT+U, Energies in J/m^2, {110}, FOP: -2 0 -2 0

Electronic structure evolution during the {110} sampling







Repulsion between U ions:

the interfacial U ions redistribute the charge to reduce the repulsion between populated f-orbitals.

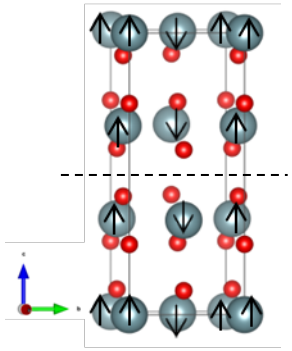
M. Kosa, M. Krack, preliminary results, DFT+U, Energies in J/m², {110}, starting FOP configuration: -2 0 -2 0

Validating Empirical Potentials with DFT+U

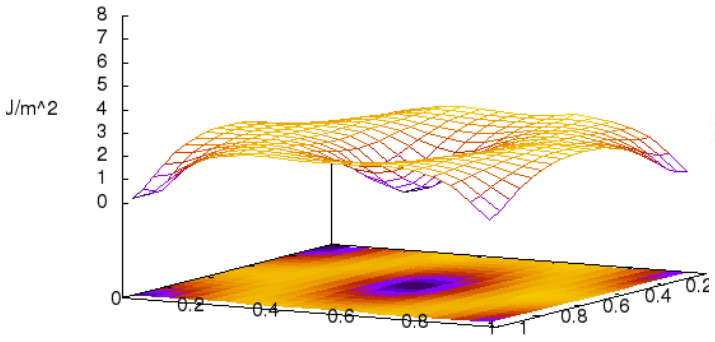
{111}

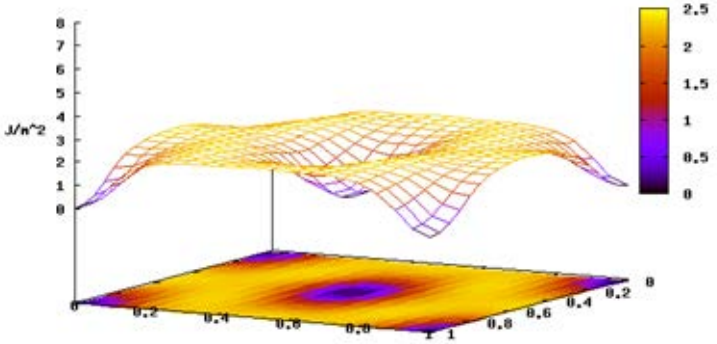
PBE+U

Force Field (Yakub)



4x3x12 cell
2592 atoms (!)



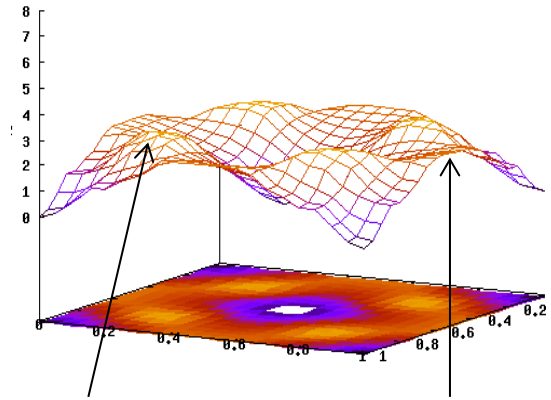


- Qualitative and quantitative agreement between DFT+U and Empirical Potentials.
- The glide is governed by distortion of weak O-O interactions.

M. Kosa, M. Krack, preliminary results, DFT+U, Energies in J/m^2, {110}, FOP: -3 1 -3 1

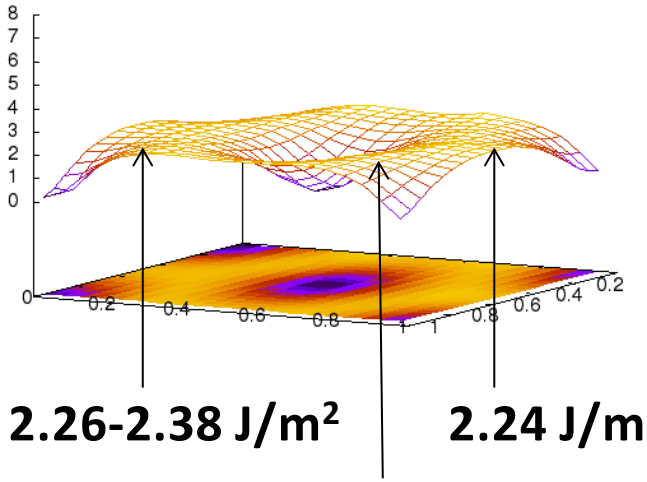
{001} and {111} lowest energy glides

{001}



2.75-3.09 J/m² **2.27-2.65 J/m²**

{111}



2.26-2.38 J/m² **2.24 J/m²**

2.23-2.24 J/m²

- **{111} and {001} planes have comparable GSF energies, with {111} being slightly lower.**
- **The spread of DFT computed GSF energies: ~0.3 J/m², *f-orbital population scheme.***
- **The spread of EP computed GSF energies: ~3 J/m².**

Summary

- Set of tools for computing and analysing the γ – surfaces was devised.
- Capablity of modelling materials with complex electronic structure.
- DFT data: {001} and {111} γ-surfaces have comparable GSF energies, with {111} having slightly lower values.

My thanks go to

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- Dr. Raoul Ngayam Happy, PSI, CH
- Dr. Sébastien Groh, UniBas, CH

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INSPYRE
CSCS

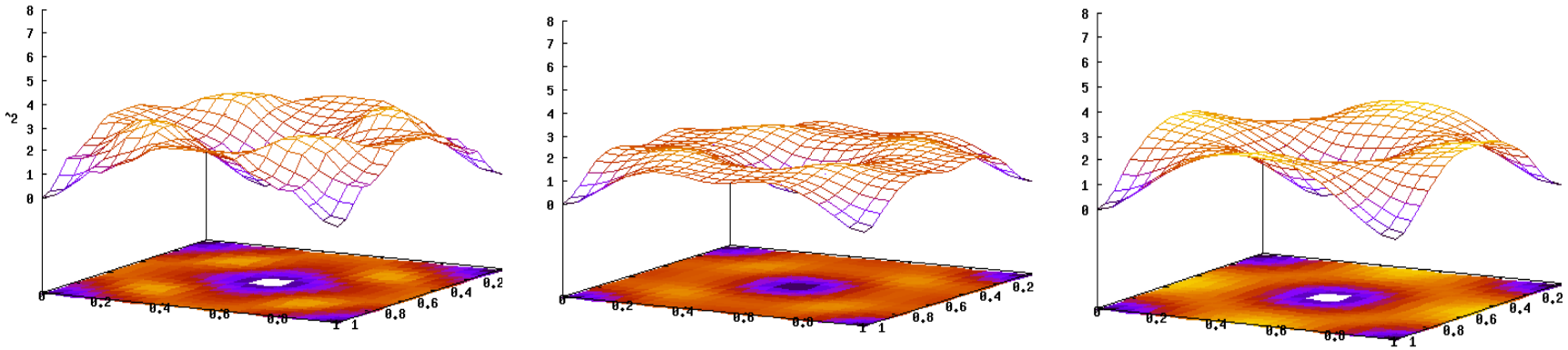
Thank you very much for your kind attention!

Validating Empirical Potentials with DFT+U

{001}

DFT+U | Force Field, Yakub | Force Field, Morelon

J/m^2



DFT+U results in a surface with shape similar to Yakub EP

Electronic degrees of freedom, *i.e.* the f-orbital populations, allow accommodation of lower energy geometric configurations.
Will be demonstrated for the {110} surface

M. Kosa, M. Krack, preliminary results, PBE+U(=2 eV), Energies in J/m^2, {001}, FOP: -3-1+1+3