

# Simulation of pure and Cr-doped $\text{UO}_2$ using molecular dynamics and density functional theory

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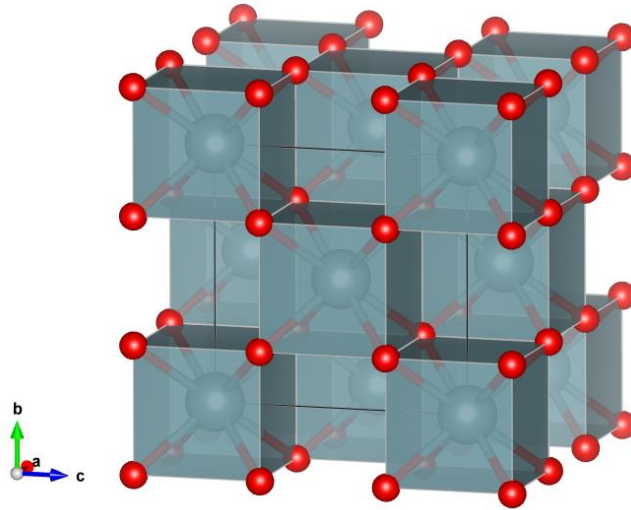
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# UO<sub>2</sub> structure and motivation

Fluorite structure,  
Space Group *Fm3m*  
(No. 225)

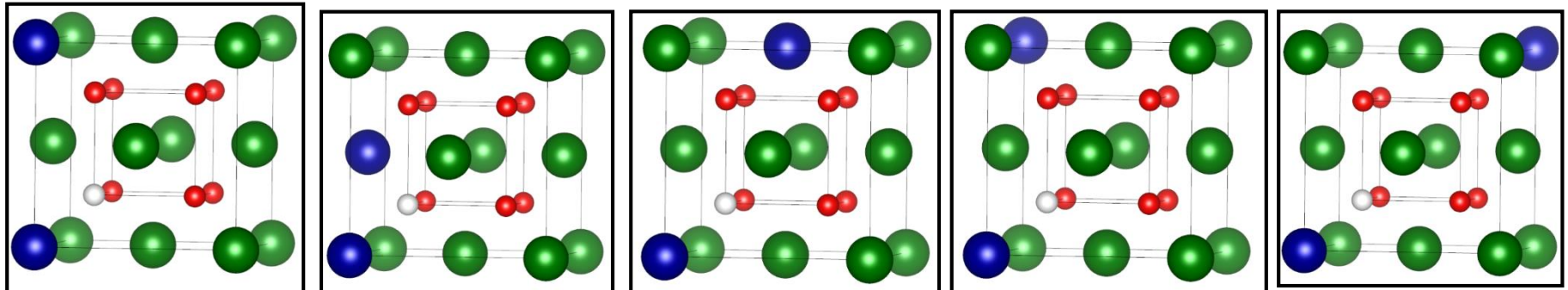
Primitive cell  
contains 12  
atoms



- Doping of urania (UO<sub>2</sub>) with small amounts of chromium is technically applied to obtain a larger average grain size
- Detailed structure of the chromium-bearing precipitates and their interface with the UO<sub>2</sub> host lattice is not yet completely explained.

(«Alchemically» found observation)

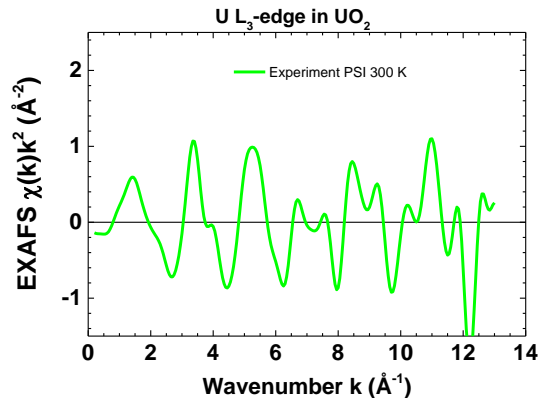
## Where is Cr?



... et.al. configurations

(at this moment ~25 configurations were observed in this study)

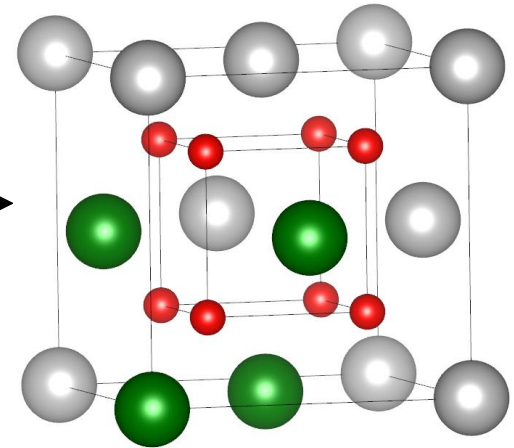
# Comparison with XAS experiment



Experimental XANES/EXAFS spectrum



How to compare?



We are using four theory levels in our study:

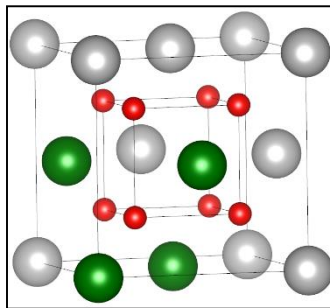
- 1) *ab initio* EXAFS theory (multiple scattering, FEFF)
- 2) Force-field approach (empirical potentials)
- 3) Density functional approach (DFT)
- 4) Molecular dynamics (based on FF or DFT)

4 experiments for UO<sub>2</sub> L<sub>3</sub>-edge are available:

- Cr-doped pristine irradiated UO<sub>2</sub> measured by G. Kuri et.al. in PSI [C. Mieszczyński J. Phys.: Condens. Matter 26 (2014) 355009], 300 K
- Pristine non-irradiated UO<sub>2</sub> measured by M. Chollet et.al. in December, 2014 in PSI, 300 K
- Pristine non-irradiated UO<sub>2</sub> measured by Latvian co-author J. Purans at ESRF synchrotron radiation facility (reference measurement for [G. Heisbourg, S. Hubert, N. Dacheux, and J. Purans, J. Nucl. Mater. 335, 5 (2004)] )
- Data received from S.D. Conradson (Authors thankful to him), USA [Phys. Rev. B 88, 115135 (2013)], 200 K

## A. "Static" calculations:

- Geometry from crystallographic data base ("ideal" structure)
- **FF**, **DFT** (optimized geometry)

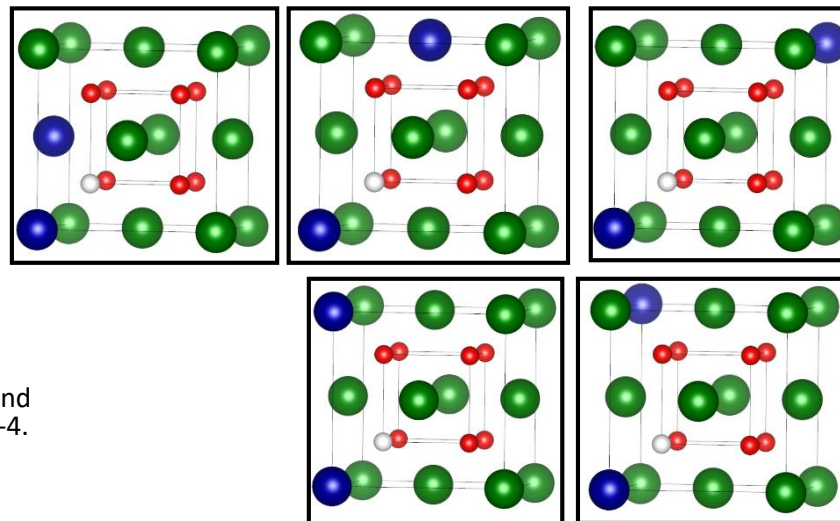


spectrum produced in FEFF

Only one configuration is used to produce spectra in **FEFF**

(N.B. No thermal disorder !)

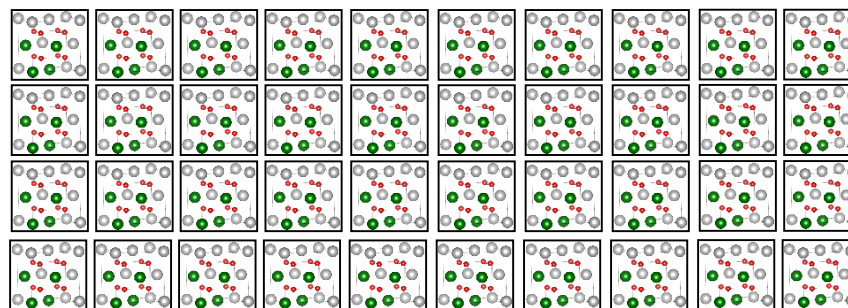
[1] E. Blokhin, E. Kotomin, A. Kuzmin, J. Purans, R. Evarestov, J. Maier, Theoretical modeling of the complexes of iron impurities and oxygen vacancies in SrTiO<sub>3</sub>, Appl. Phys. Lett. 102 (2013) 112913:1-4.



## B. MD calculations:

- the ensemble of atomic configurations ('snap-shots') is calculated for the temperature of the EXAFS experiment

[2] A. Kuzmin and R.A. Evarestov, Quantum mechanics-molecular dynamics approach to the interpretation of X-ray absorption spectra, J. Phys.: Condens. Matter 21 (2009) 055401



MD snapshots → averaging of spectra produced in FEFF

# Force-field MD: we tested potentials published in literature using FT obtained from EXAFS

- **Best force-field** is Meis.

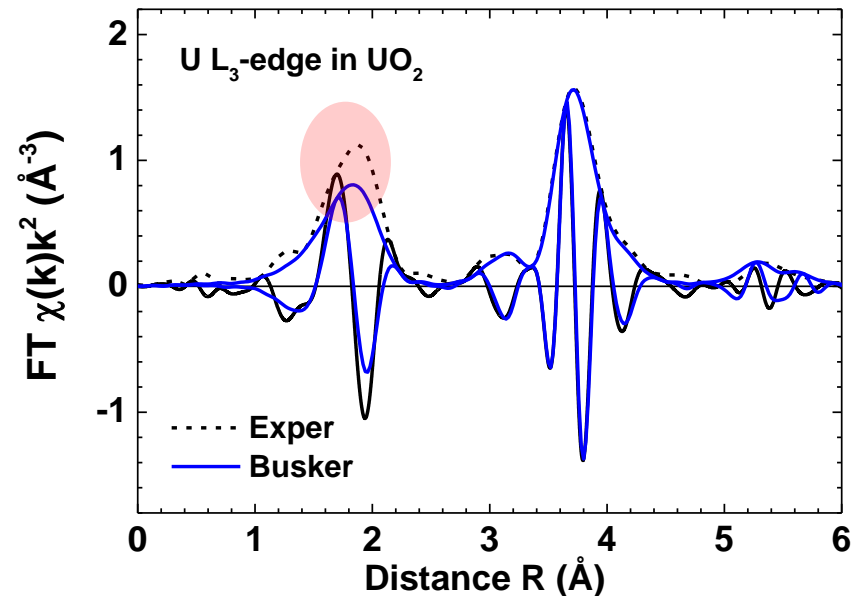
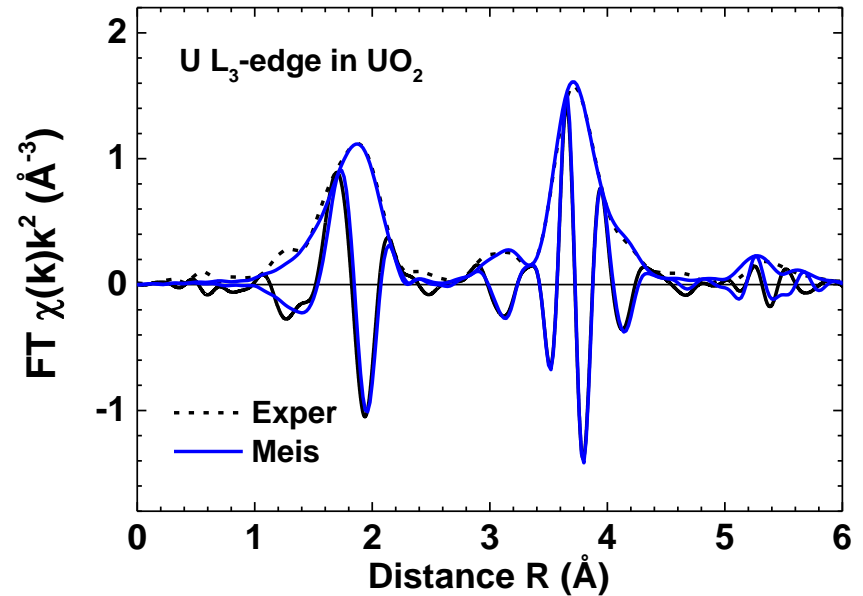
- **Good force-fields** are:

- Read (slightly overestimates disorder in the 1<sup>st</sup> and 2<sup>nd</sup>/3<sup>rd</sup> shells)
- Yakub (slightly overestimates disorder in the 1<sup>st</sup> shell)
- Yamada (slightly overestimates disorder in the 1<sup>st</sup> shell)

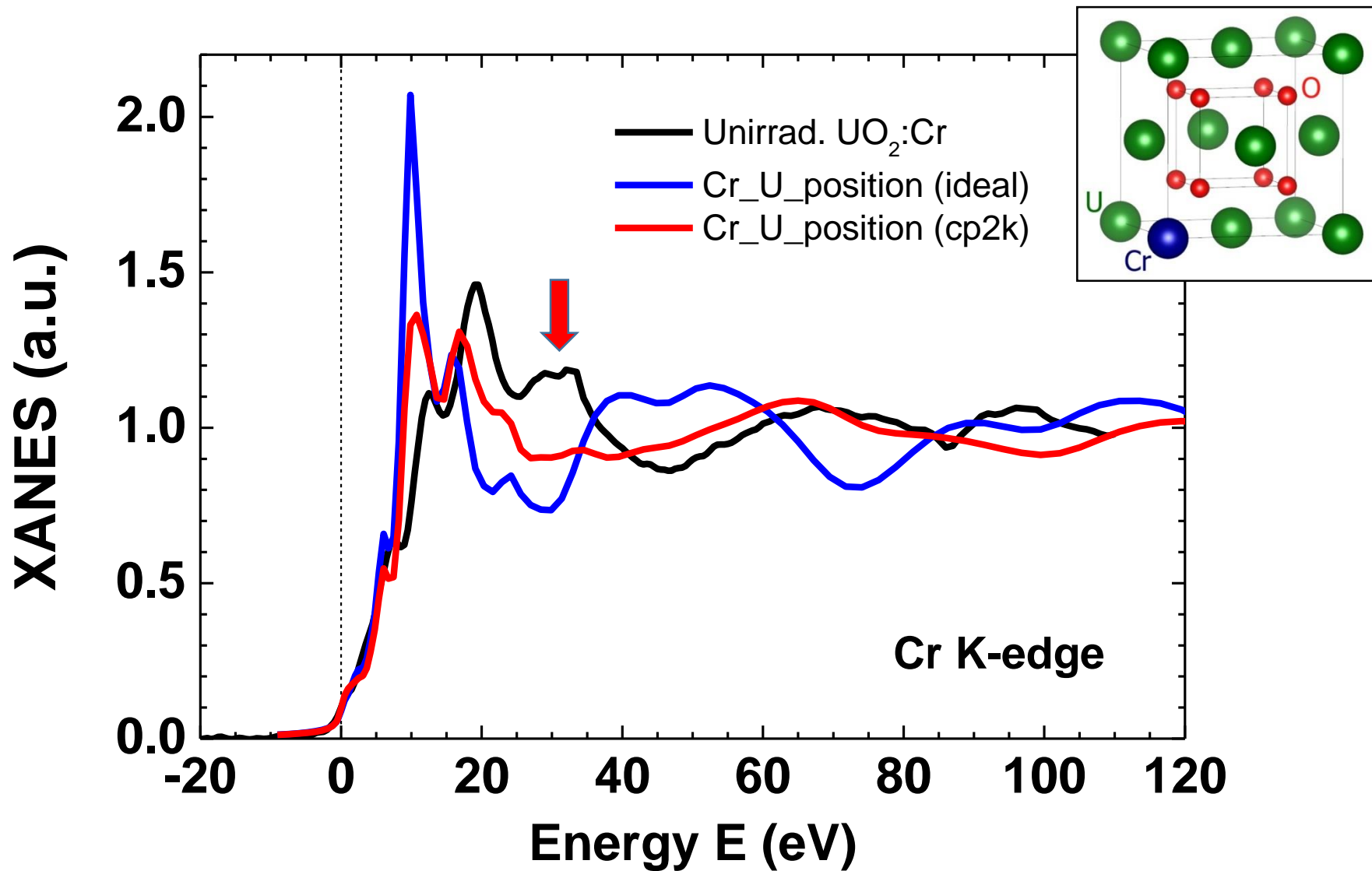
- **Bad force-fields** are:

- Busker, Imperial, Karakasidis, Morelon – fail in the first shell (all overestimate disorder)
- Arima – fails in the second shell (underestimates U-U<sub>2</sub> & U-O<sub>3</sub> disorder)
- Basak – fails in the second shell (overestimates U-U<sub>2</sub> & underestimates U-O<sub>3</sub> disorder)

- **Main conclusion:** MD-EXAFS method is sensitive to details of force-field models and allows one to select the best one.



# Comparison between DFT simulations and XANES experiment based on FEFF



Model can't reproduce a peak at 30 eV !