Actinide Science: A focus on the properties of Uranium Dioxide

Nuclear waste actinide immobilisation 2018

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School of Physics, University of Bristol, Bristol, BS2 8BS, UK.

1999-2003 MSci Physics, UCL

2003-2006 PhD, UCL U-multilayers

2006-2009 post-doc, ESRF

Actinide physics

2009-2012 post-doc, UCL

spin ladders, iridates ($Sr_3Ir_2O_7$)

2012 - present 1851 Research Fellow

Condensed matter → nuclear materials

2015 - lecturer at University of Bristol

teach on nuclear MSc, have research group in the IAC.

Dr. Sophie Rennie, J. Sutcliffe, E. L Bright, D. Chaney, E. Gilroy, J. Wasik, Y. Sasikumar, L. Harding, G. Griffiths

Overarching theme – using cutting edge techniques in condensed matter research and applying them to materials science problems in the nuclear industry.

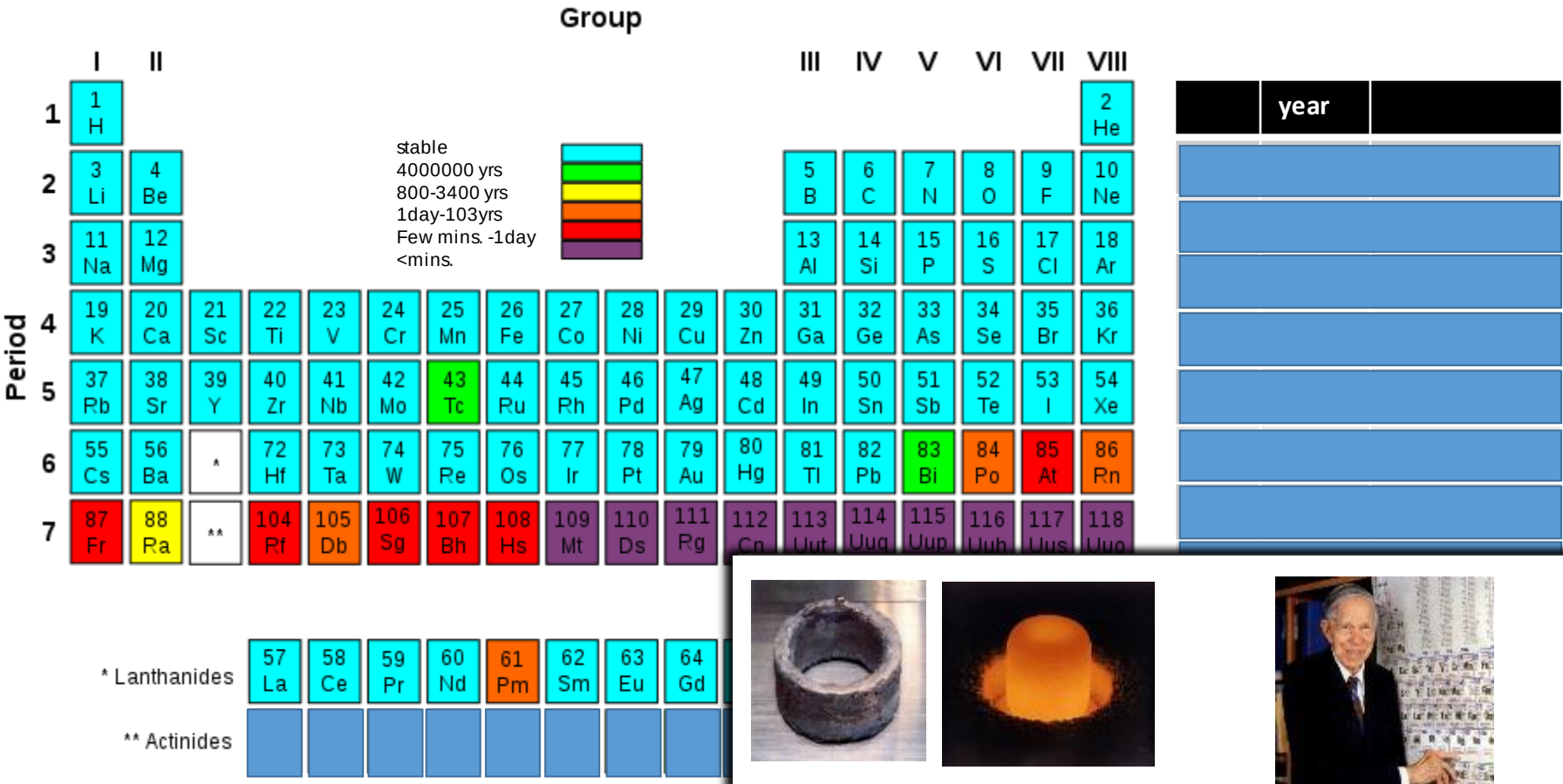
Learning outcomes:

Explain the relationship between the nature of electronic states and the complexity of structures and physical behaviour of actinide elements and compounds. To use this relationship to predict the likely properties in actinide compounds, specifically the ceramic, uranium dioxide.

Explain the mechanism of thermal conductivity in UO_2. To use this mechanism to predict the likely affects of temperature or irradiation damage.

Explain the mechanism of uranium dioxide oxidation and the possible oxidation states and compounds that it can adopt.

Explain the mechanism of uranium dioxide oxidative dissolution. To place this mechanism in the context of stored waste in order to appreciate its relevance in predictive tools for spent fuel storage.



^{239}Pu and ^{238}Pu (1940)

Glenn T. Seaborg *et al.*

$$^{238}_{92}\mathrm{U} + {}^{2}_{1}\mathrm{D} \longrightarrow {}^{238}_{93}\mathrm{Np} + 2\,{}^{1}_{0}\mathrm{n} \quad ; \quad {}^{238}_{93}\mathrm{Np} \xrightarrow[2{,}117\ \mathrm{d}]{\beta^-} {}^{238}_{94}\mathrm{Pu}$$

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow[23{,}5\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow[2{,}3565\ \mathrm{d}]{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Ac and Pa are found in nature as decay
others An are synthetic elements, alth
been found in U ores. Small amount of Np, Pu 1972 at Oklo, Gabon - Francis Perrin

Why is Solid State Physics of *5f* Important?

Pushing boundaries of experiment and theory.

Exotic magnetic and superconducting ground states.

Unusual crystal structures – instabilities

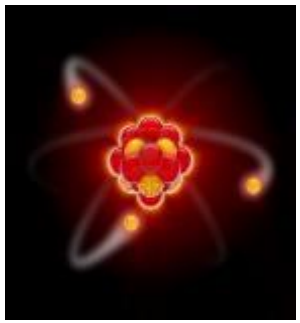
Localised/itinerant – relativistic effects - large SOC

Understanding of fundamental behaviour is a pre-requisite for a deeper knowledge of nuclear materials – especially electronic and phononic properties.

Theoretical Tools

Materials are conceptually very simple structures:

- Just nuclei and electrons
- Only one fundamental force (EM)
- QED theoretical framework
- Solve Dirac equation – calculate all macroscopic properties



Unfortunately, we are able to solve the Dirac equation only in the case of two interacting particles. For a three-body system we need approximations or numerical solutions - just powerful enough computers!

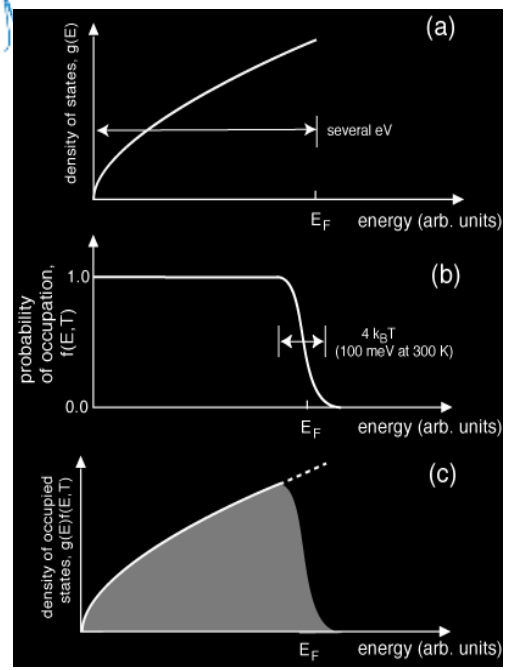
For N particles, the Schrödinger equation is a partial differential equation in 3N dimensions. For 1 uranium atom, N = 92+1 Let us calculate the wavefunction on a 10×10×10 space grid, considering 2 spin states per electron. To represent ψ we need 5×10^{306} complex numbers!

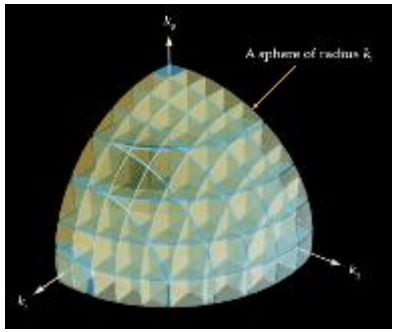
Hard disk with diameter ~ 10^{145} light-years!

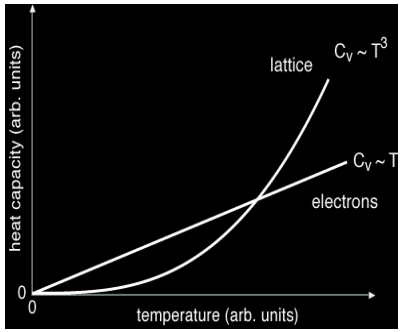
Approximations – Free electron gas (FEG)

Most drastic approximation - electrons as non-interacting particles

N Ψ in 3-D instead of one in 3N-D → from 10^{306} to 10^{5} complex numbers







Thanks to the Pauli exclusion principle, the FEG model is reasonably successful despite the high electron density in a solid and the long-range Coulomb interaction.

Can improve with tight binding or nearly free.

Cannot ignore Coulomb interaction between electrons or relativistic effects in actinides.

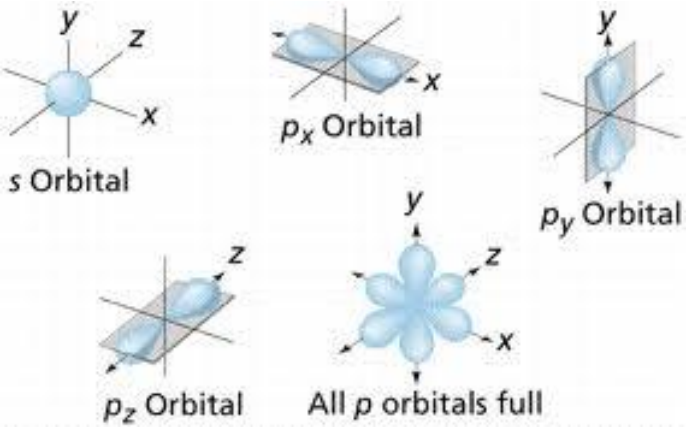
Many actinide materials lie at the brink of magnetic instability, in a regime where quantum fluctuations of the magnetic and electronic degrees of freedom are strongly coupled.

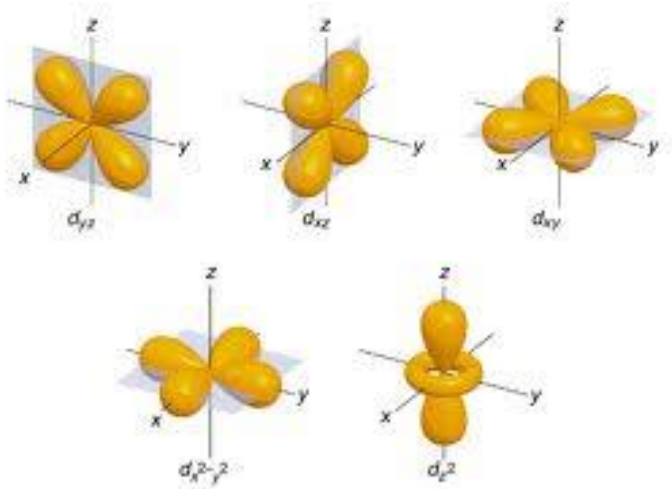
The properties of *5f* electrons determine the behavior of fuel cycle materials: understanding these properties is of considerable importance for the development of simulation codes and safety assessments.

So how do we describe the *5f* electronic states?

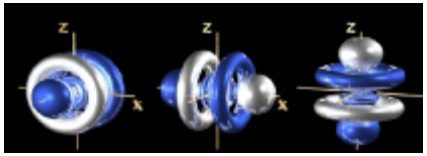
Electronic Configuration

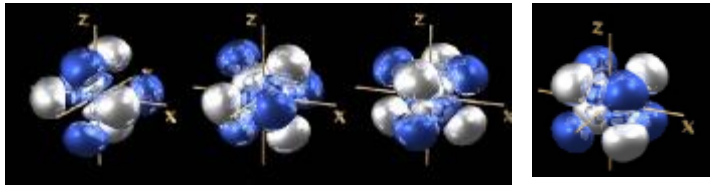
Actinide elements → new transition metal-like series (6d)
However, as the atomic number increases, electrons enter the *5f* electron orbital.





Example config. [Rn]5f?6d7s^2


5*fy*^{3} 5*fx*^{3} 5*fz*^{3}


5*fx*(z^2-y^2) 5*fy*(z^2-x^2) 5*fz*(x^2-y^2) 5*fxyz*

Compare the radial extent of the wave functions. What do you notice?

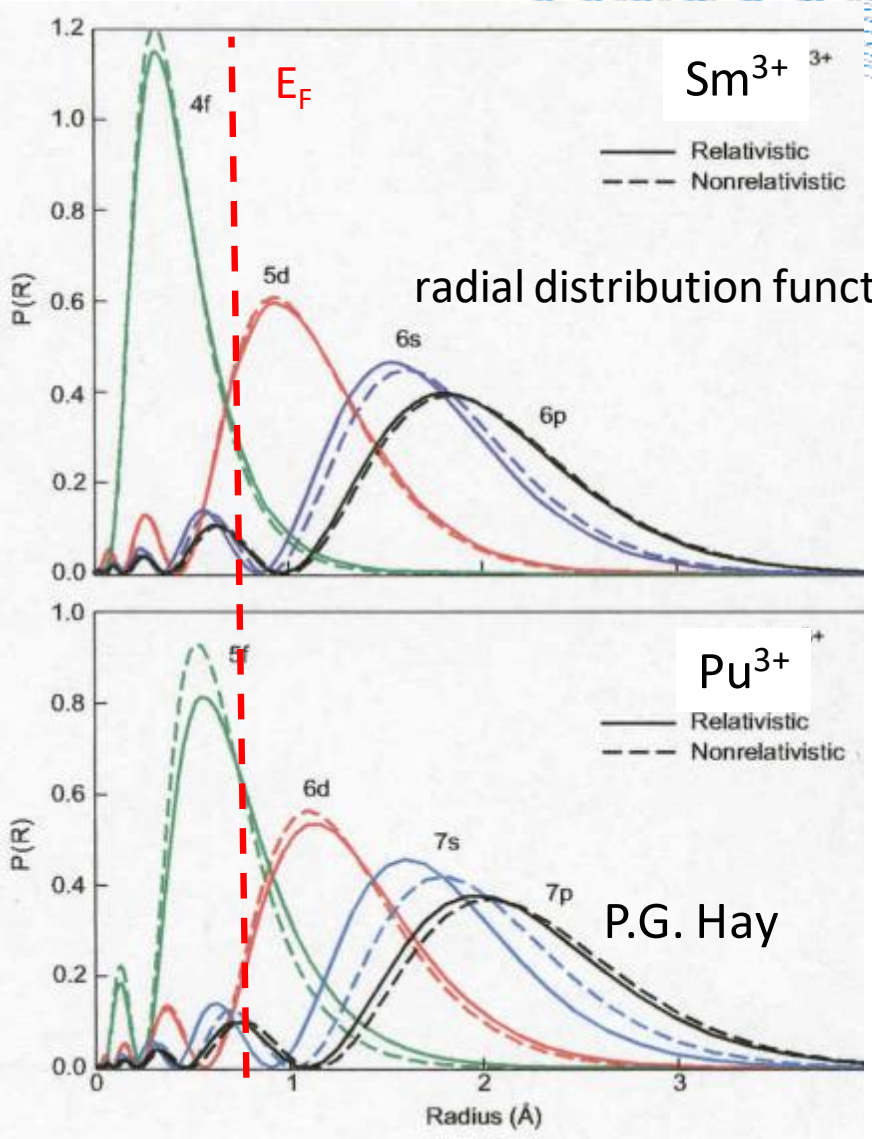
4f electrons are localized and do not participate to bonding.

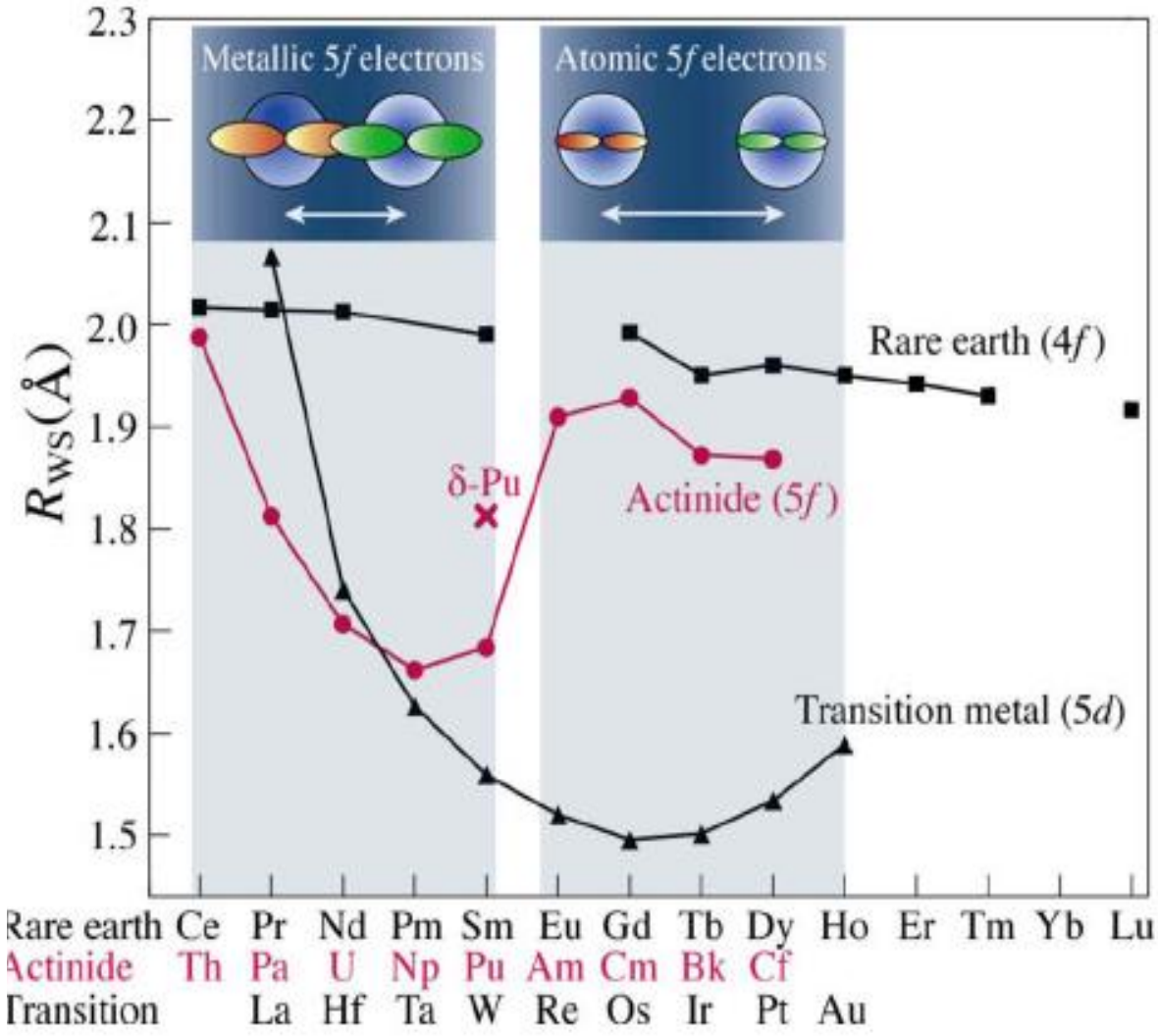
6d, 7s, 7p electrons are delocalized and bonding.

5f electrons are in an intermediate situation (confused about who they are!)

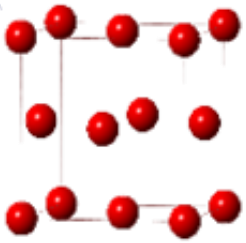
Hybridisation?

Overlapping bands in a solid?

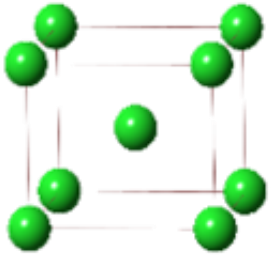



Metallic 5f electrons
Atomic 5f electrons
R_{WS}(Å)
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
Rare earth (4f)
δ-Pu
Actinide (5f)
Transition metal (5d)
Rare earth Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinide Th Pa U Np Pu Am Cm Bk Cf
Transition La Hf Ta W Re Os Ir Pt Au

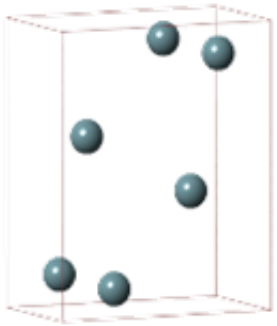
Light actinide structures



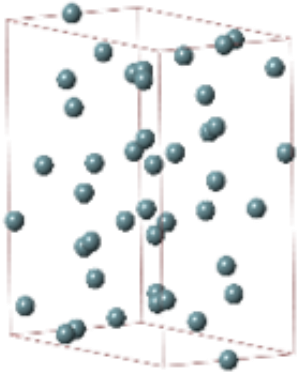
Th, Fm3m



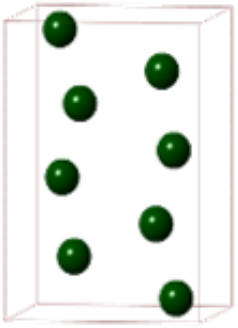
Pa, I4/mmm



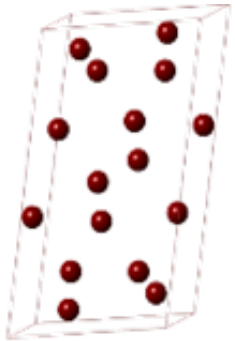
α-U, Cmcm



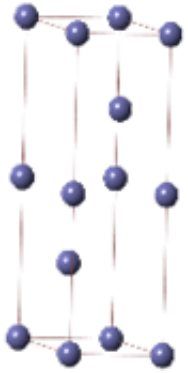
β-U, P42/mnm



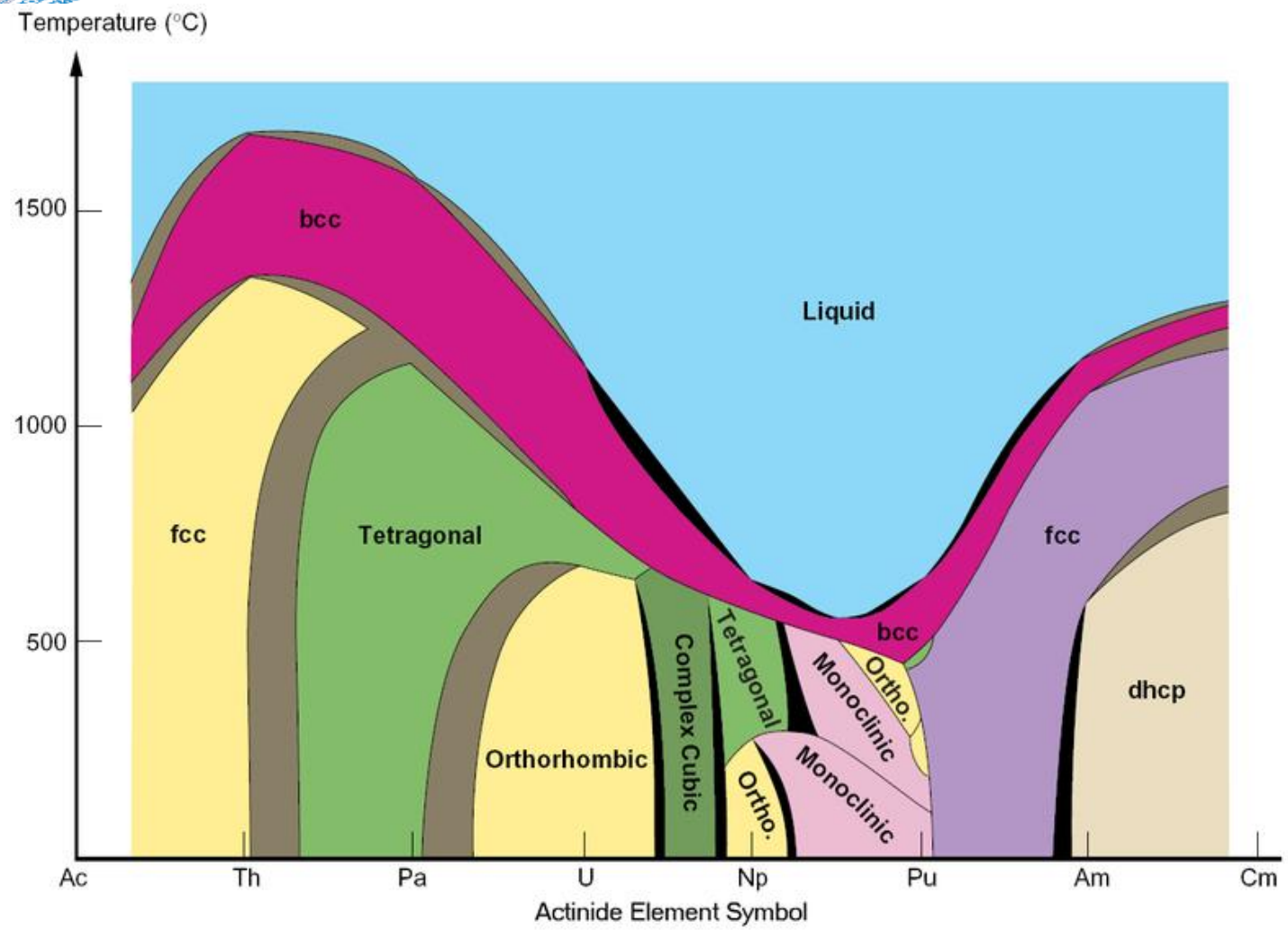
Np, Pnma



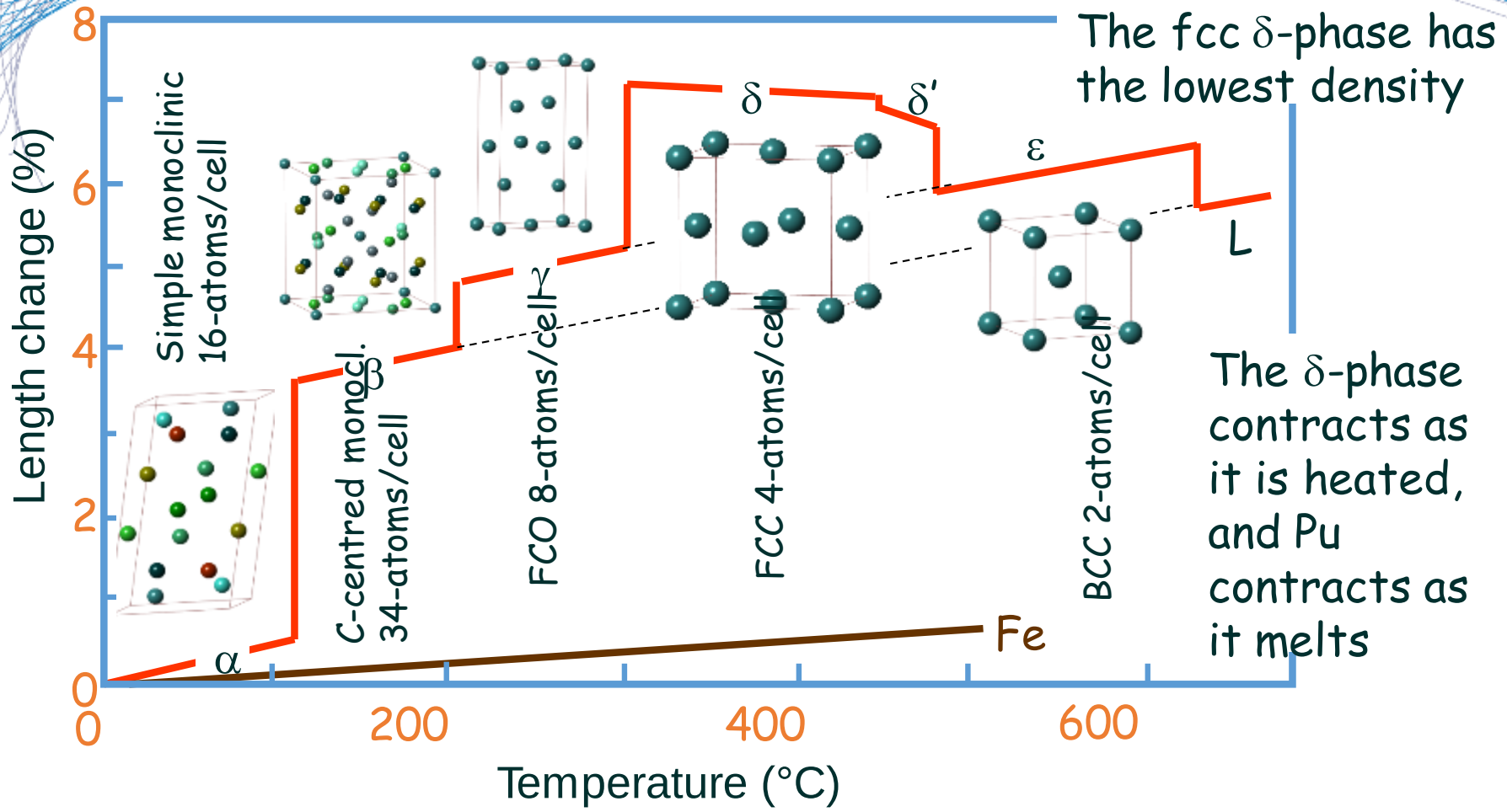
α-Pu, P121/m1



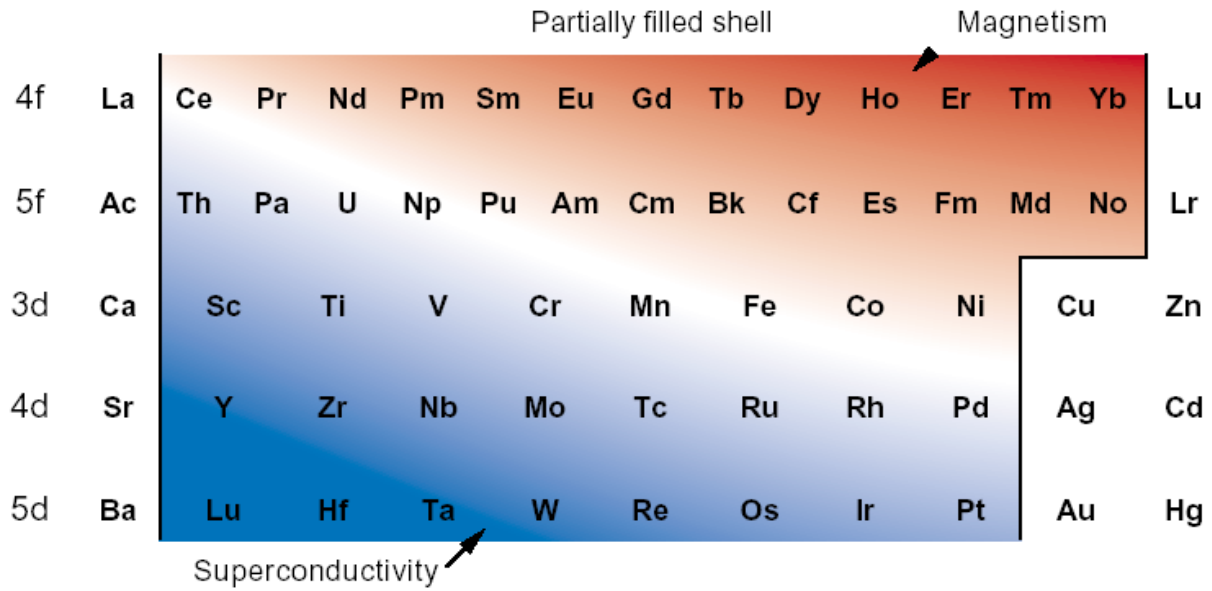
Cm, P63/mmc

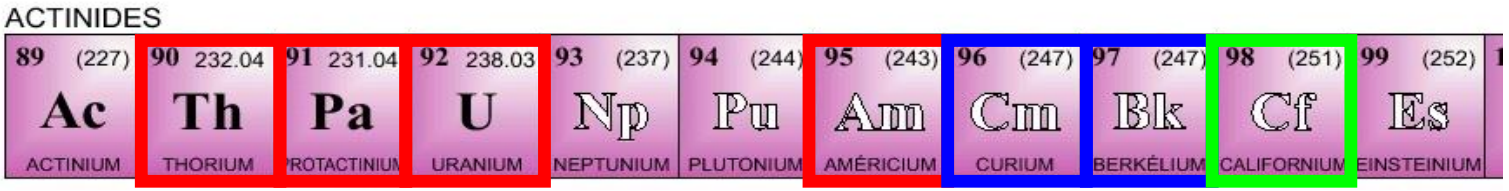

Temperature (°C)
1500
1000
500
bcc
Liquid
fcc
Tetragonal
Orthorhombic
Complex Cubic
Tetragonal
Ortho.
Monoclinic
Monoclinic
bcc
fcc
dhcp
Ac
Th
Pa
U
Np
Pu
Am
Cm
Actinide Element Symbol

Allotropic phases of Pu and anomalous thermal expansion



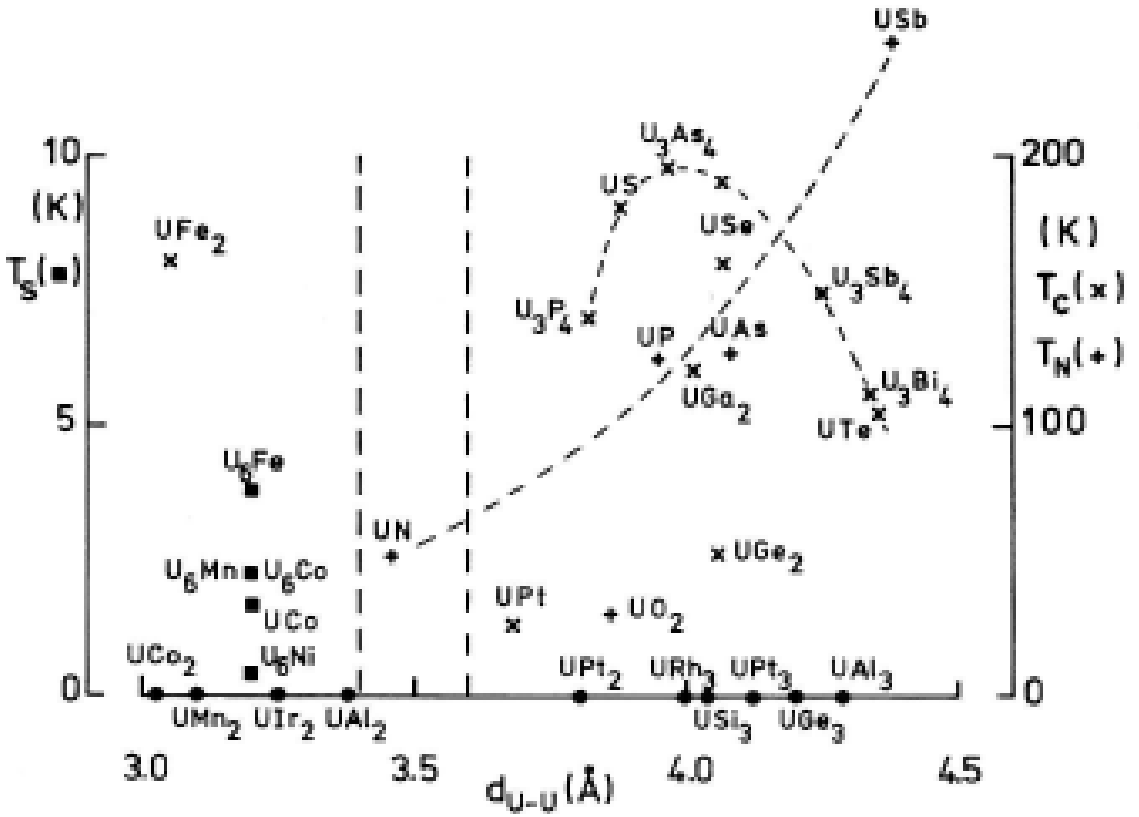
A Revised Periodic Table of the *f* and *d* series





1.4K 0.4K 0.9K 0.8K 52K 25K 52K

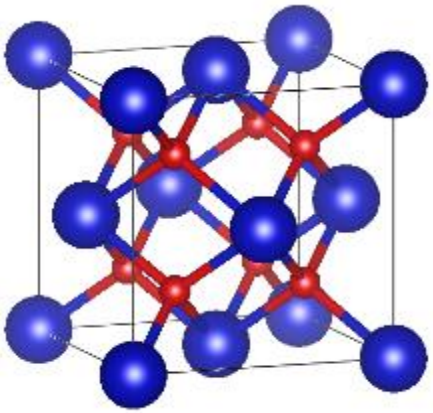
s/c AF FM

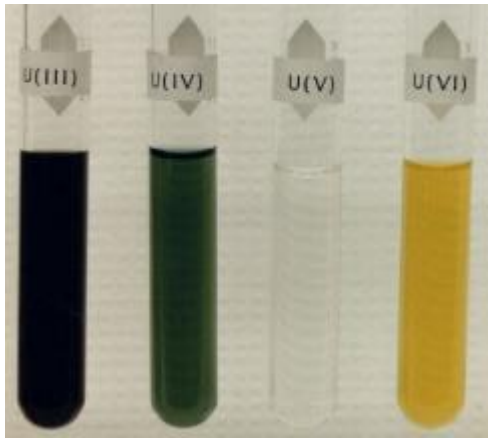


The Hill criterion for uranium (3.4 to 3.6 Å). Superconducting to the left and magnetic to the right

Let’s consider UO_2?

Properties of UO_2





Fcc, CaF_2 crystal structure (a=5.469Å)

Mott-Hubbard *f-f* Insulator, band gap of about 2eV

Range of valence states

Unusual oxidation behaviour

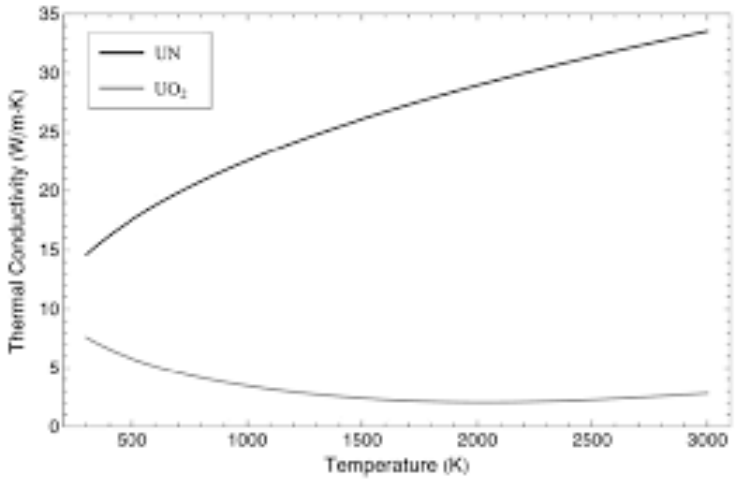
U-U distance is about 3.8 Å

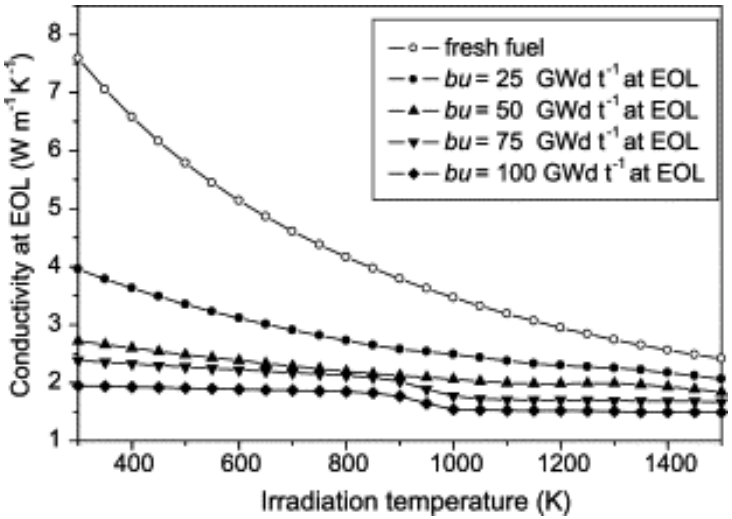
Antiferromagnet at T_N = 30.2 K

Quadrupolar order at T_N

Jahn-Teller distortion at T_N

Why is UO_2 so bad at conducting heat?

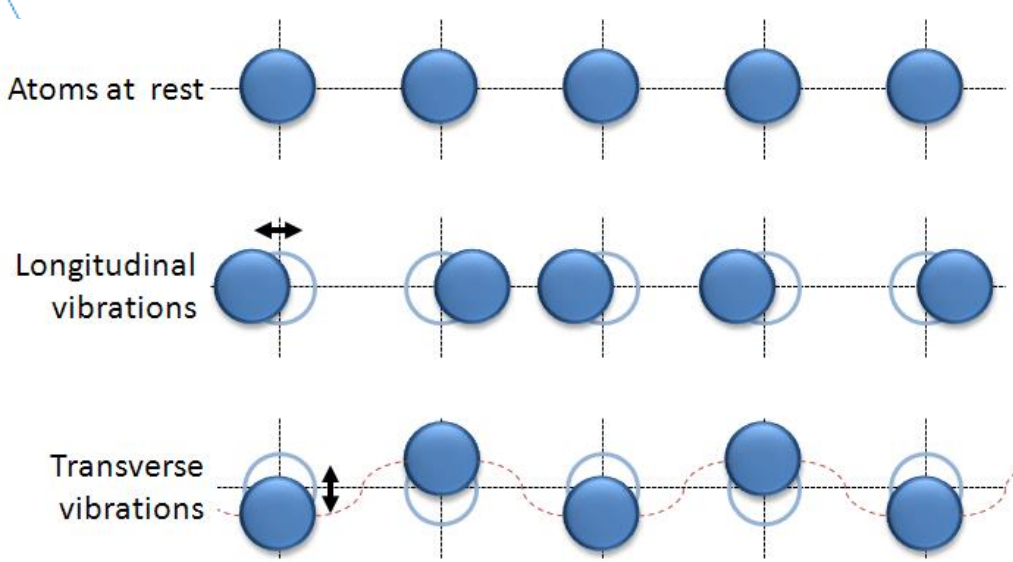


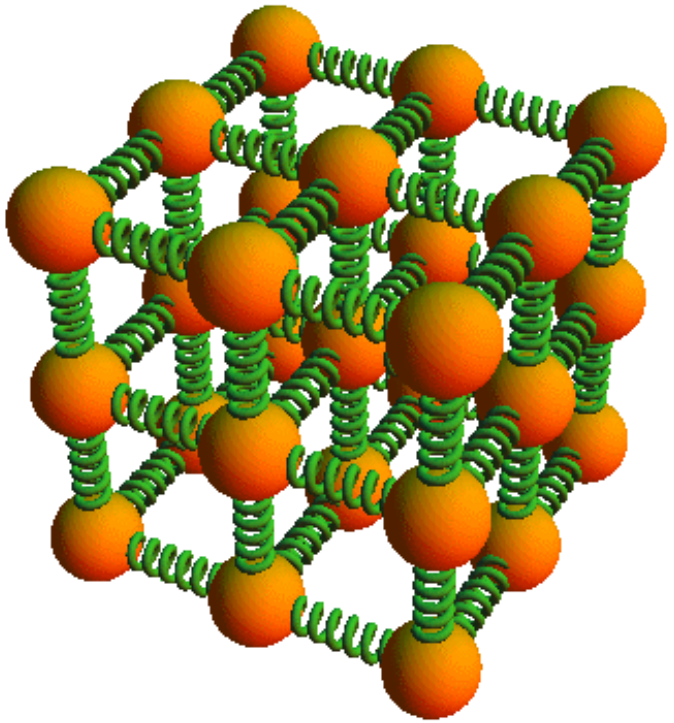


A recap of phonons…

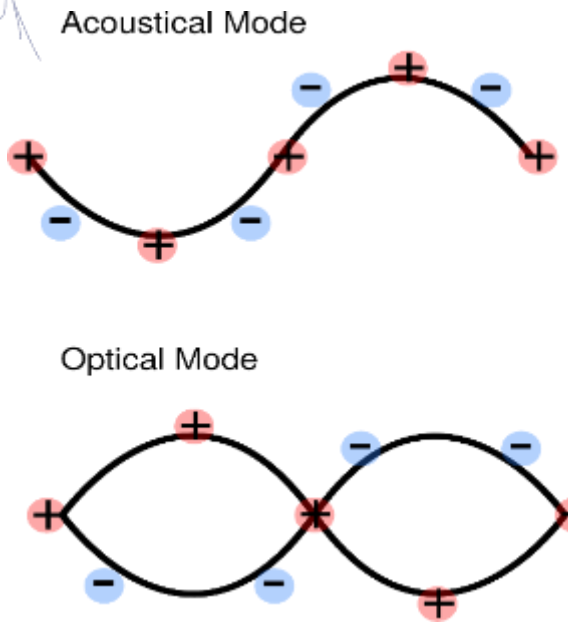
A ***phonon*** is a discrete unit of vibrational energy that arises from oscillating atoms within a crystal.

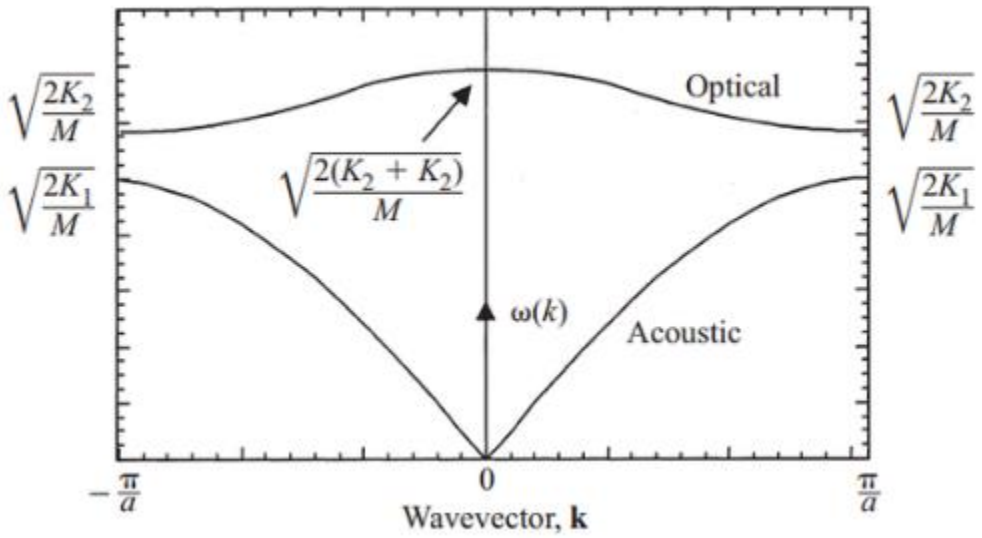
Just as a photon is a quantum of electromagnetic or light energy, a phonon can be considered as the equivalent for vibrational energy.





Phonons again…

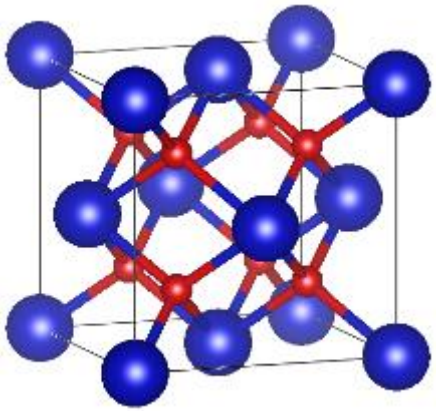


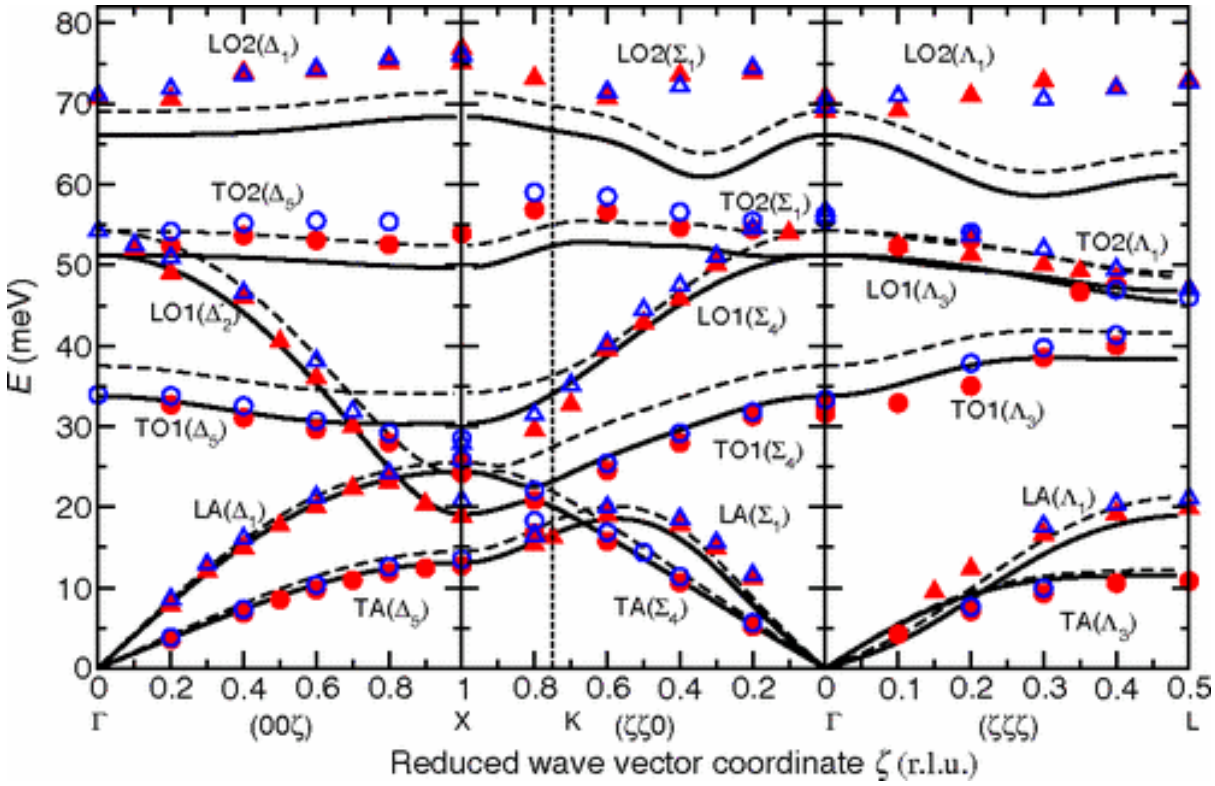


Acoustic – ions move in unison, Optical – ions move opposite to one another

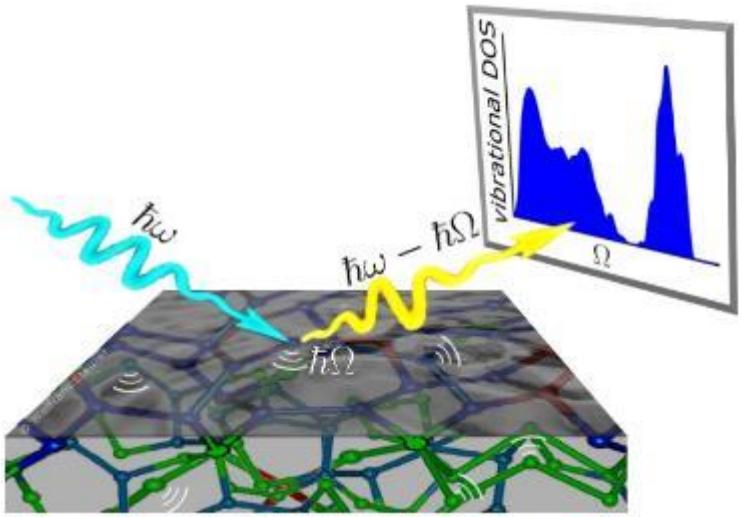
The slope gives the group velocity, speed of sound for acoustic phonons

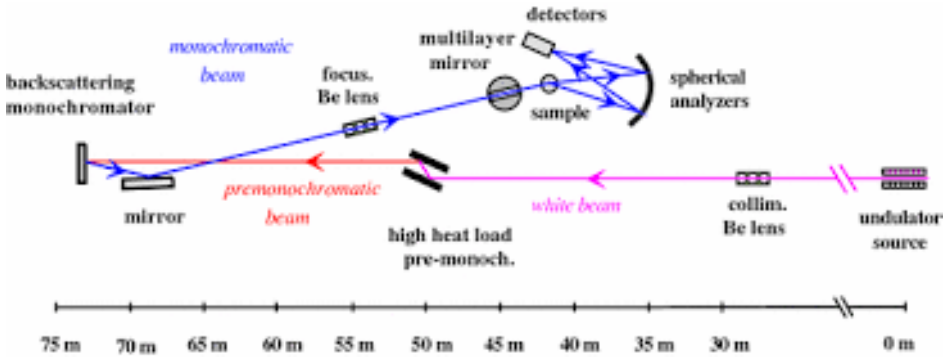
UO_2 Phonon dispersion



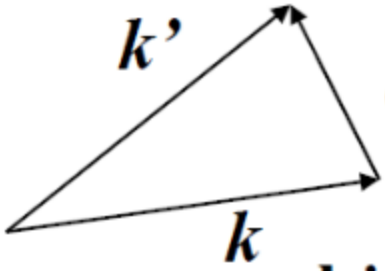


Measuring Phonons – inelastic scattering





Elastic Scattering:



$$\mathbf{k'} = \mathbf{k} + \mathbf{G}$$

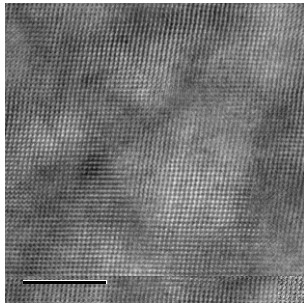
In-elastic Scattering:

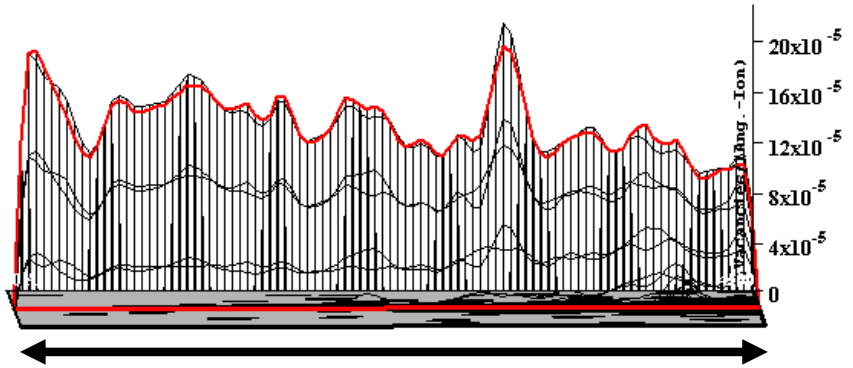
$$\mathbf{k'} = \mathbf{k} + \mathbf{G} - \mathbf{K}$$

$$\mathbf{k'} = \mathbf{k} + \mathbf{G} + \mathbf{K}$$

What’s new?

Radiation damage

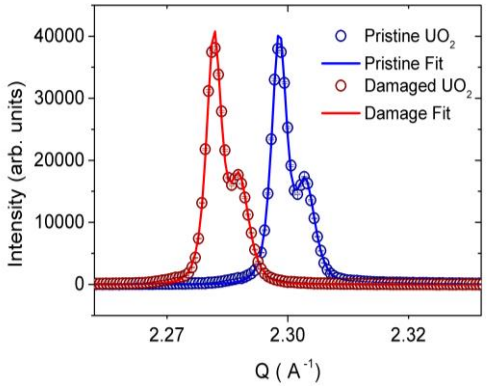




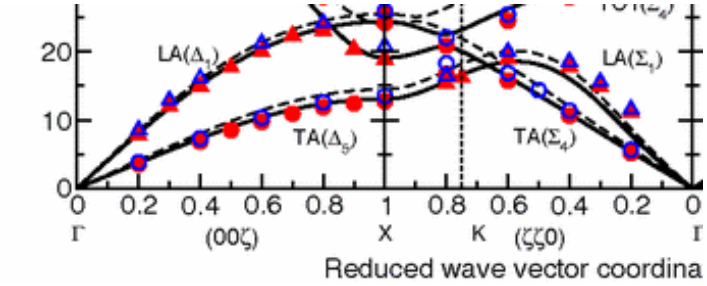
Sputter deposited UO_2, TEM image

450 nm

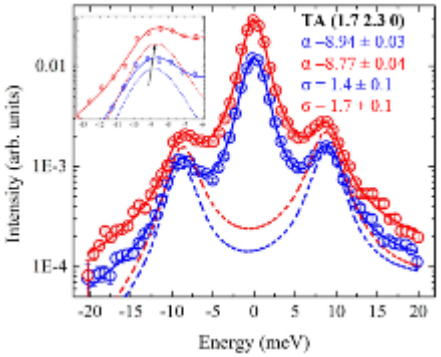
Damage profile, 2MeV He ions



XRD, lattice parameter



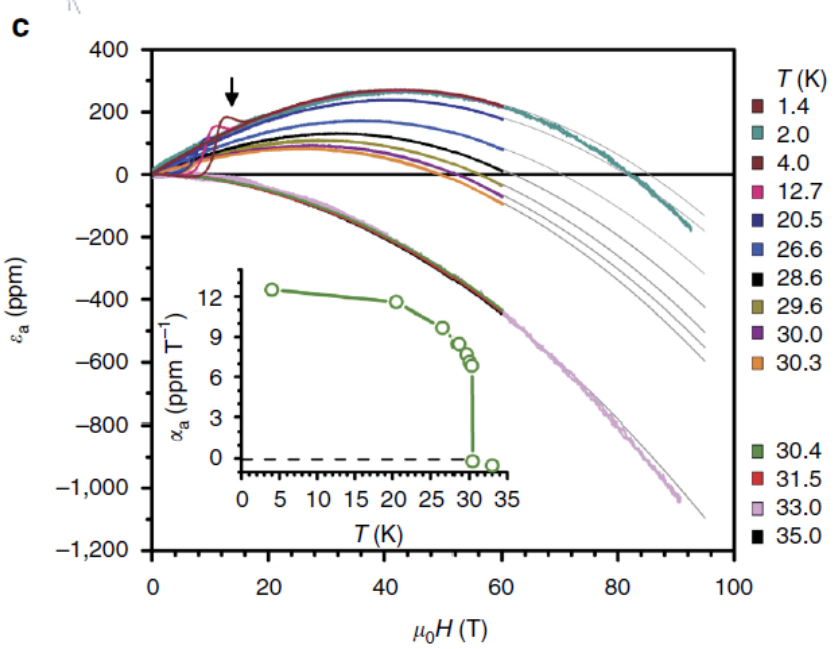
IXS over limited Brillouin zone range



Phonon width change

Rennie *et al.* Phys. Rev. B **97**, 224303 (2018)

Why is UO_2 so bad at conducting heat?

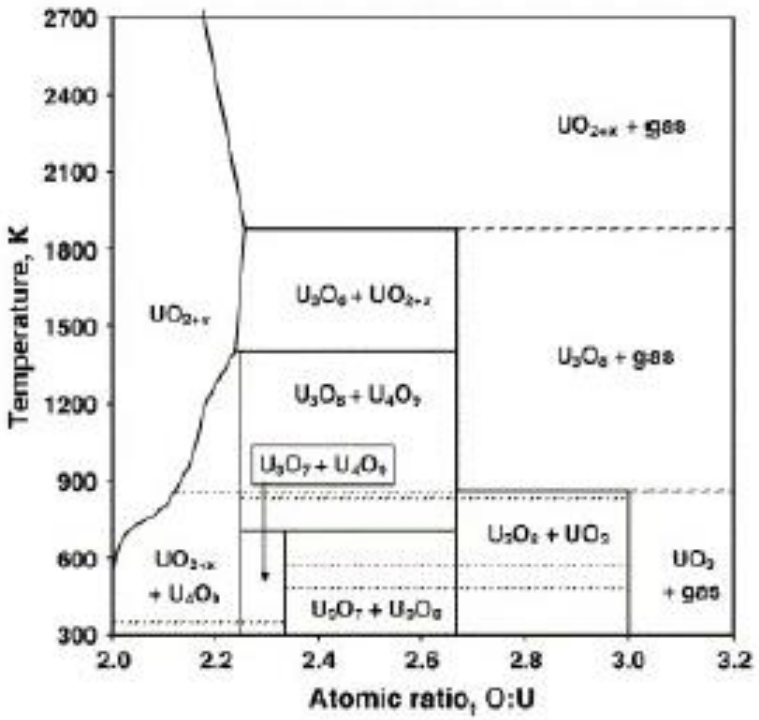


Jaime, Gofryk *et al.* Nat. Comms. (2017)

The unusually low thermal conductivity of UO_2 cripples its performance as a fuel in nuclear reactors. Here we uncover first-order coupling between the magnetism in U-atoms and lattice degrees of freedom that could be the origin of scattering of phonons against spin fluctuations dressed with dynamic Jahn-Teller oxygen modes well above T_N. These effects should be explored further.

UO_2 is insoluble in water right?

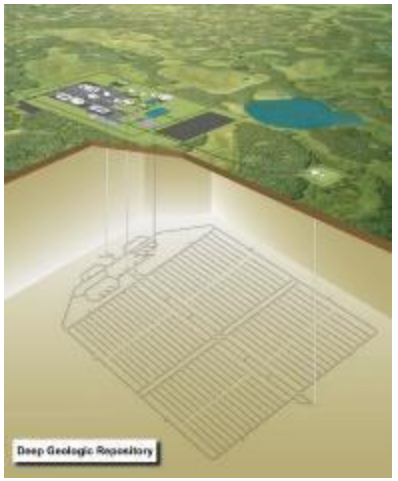
UO_2 oxidation



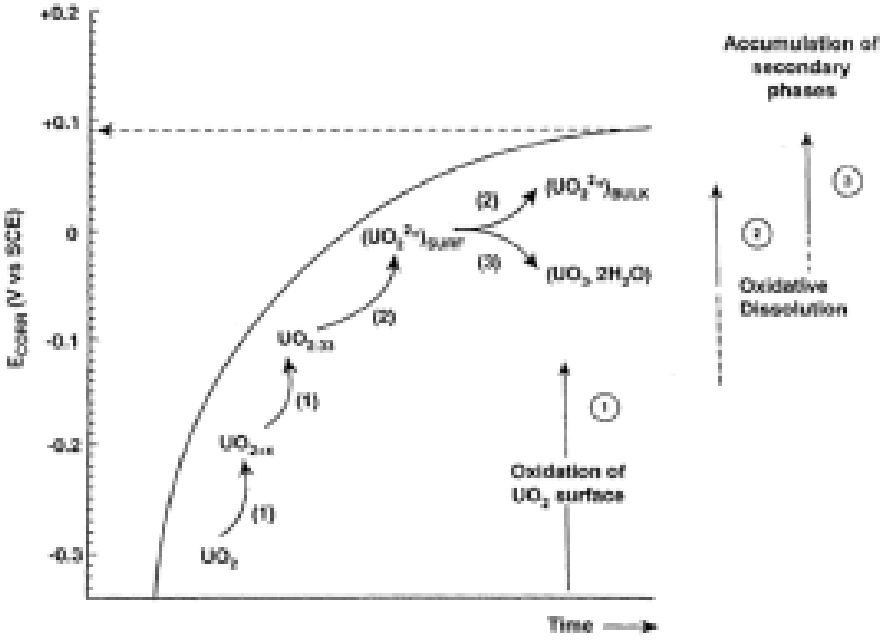
U-O phase diagram – a number of stable oxide states towards the highest oxide UO_3

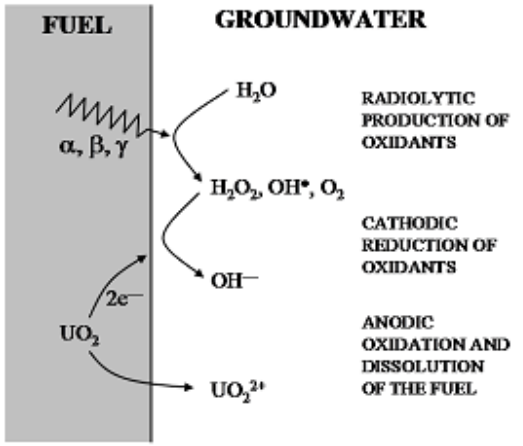
U^{6+} is soluble!

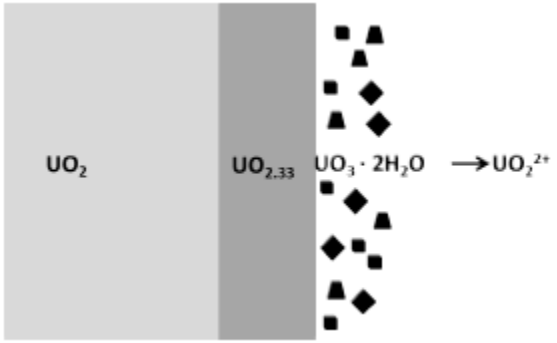
Do we need to worry?



UO_2 oxidative dissolution

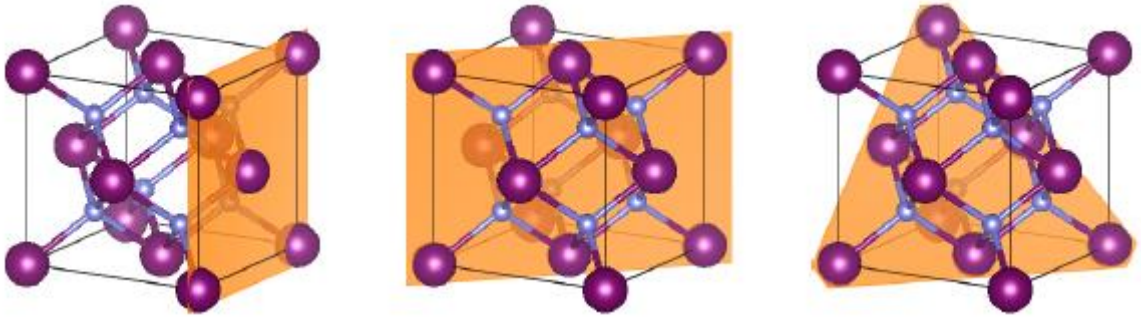




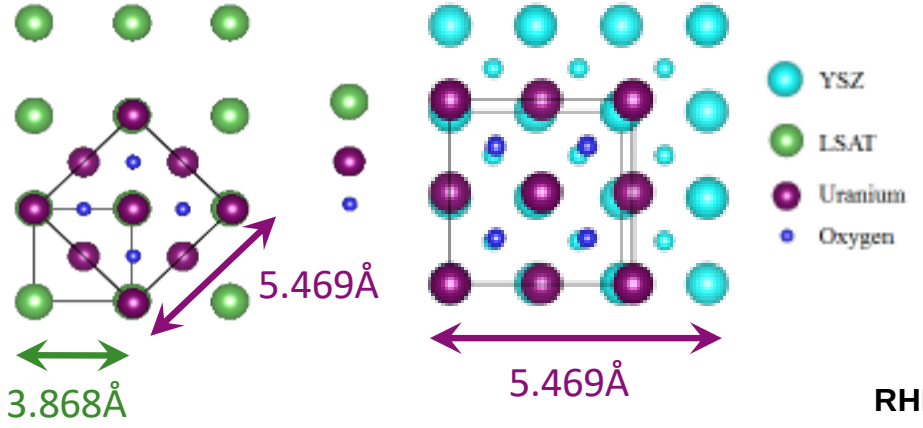


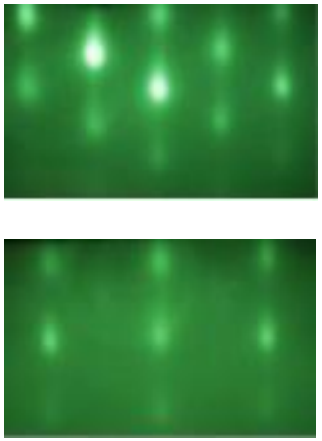
What’s new?

Epitaxial Film Growth



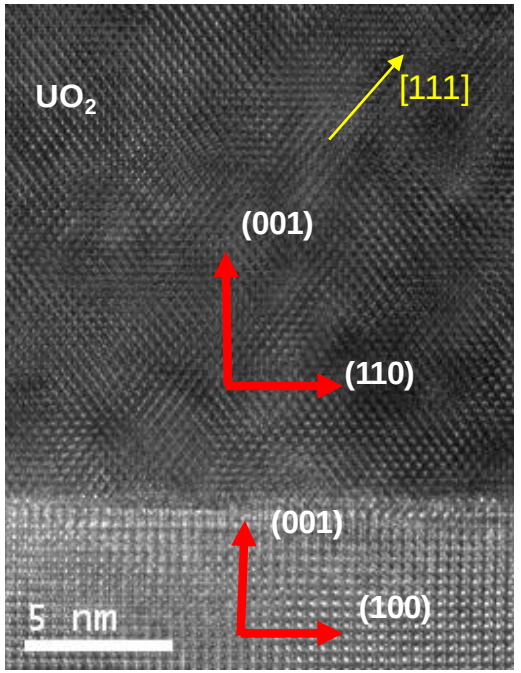
Uranium dioxide has the cubic fluorite crystal structure, space group Fm3m, (a = 5.469Å)





RHEED of [001]-oriented UO_2

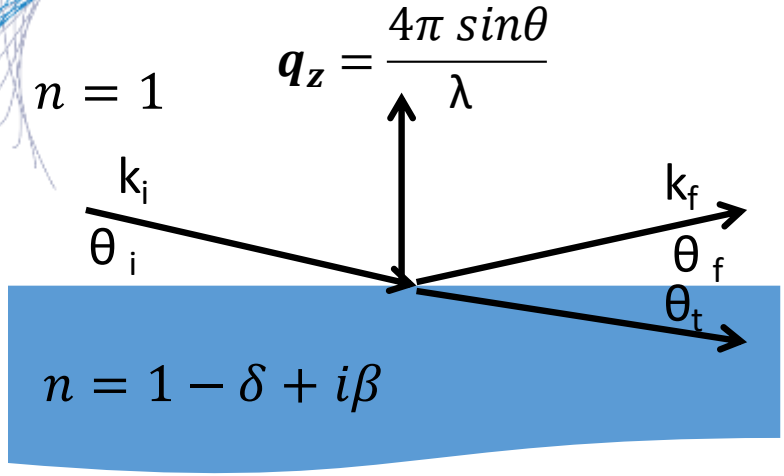
TEM of UO_2 on LSAT



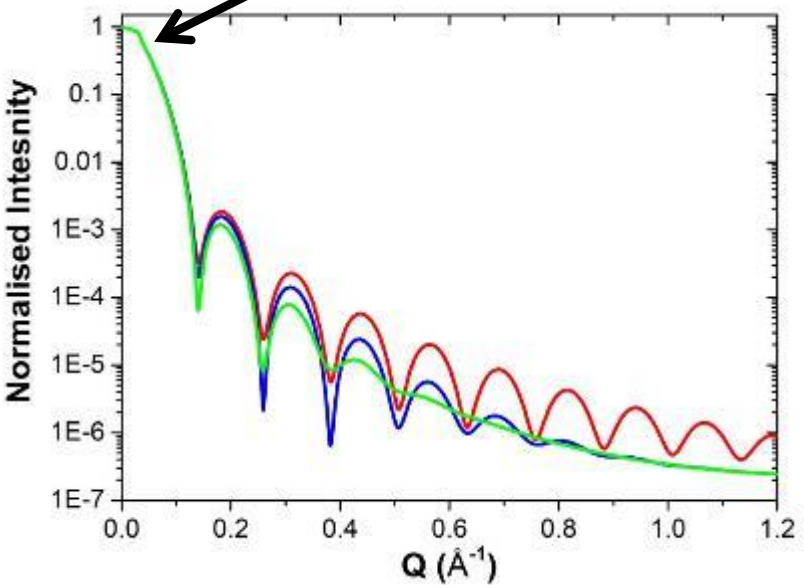
X-ray Reflectivity

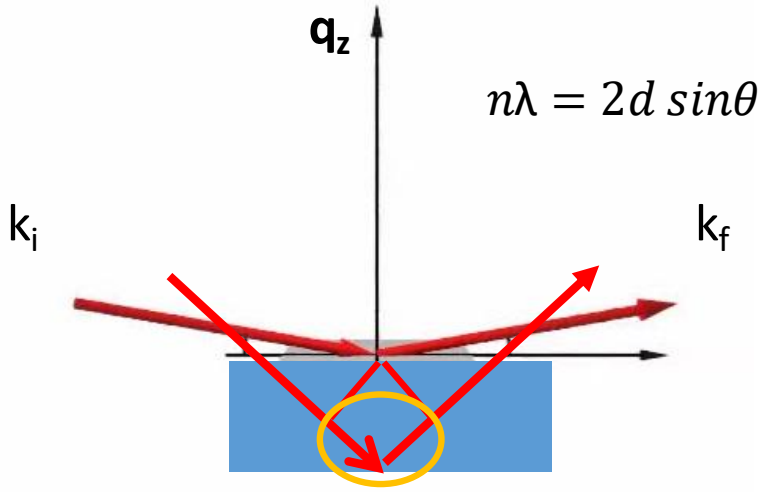
$$q_z = \frac{4\pi \sin\theta}{\lambda}$$

$n = 1$

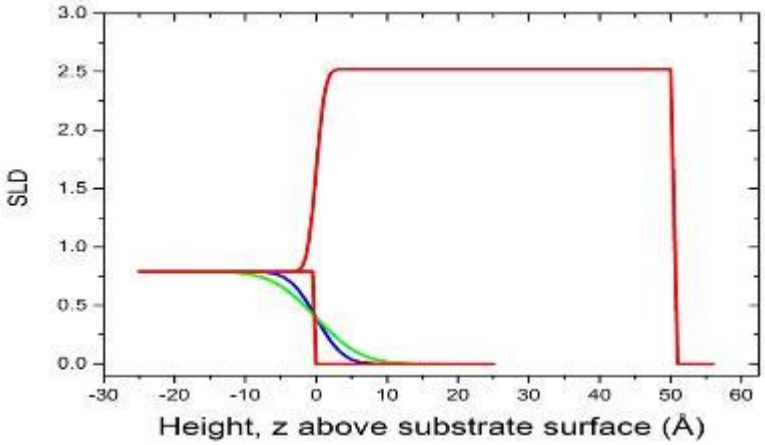


$$\theta_c = \sqrt{2\delta}$$

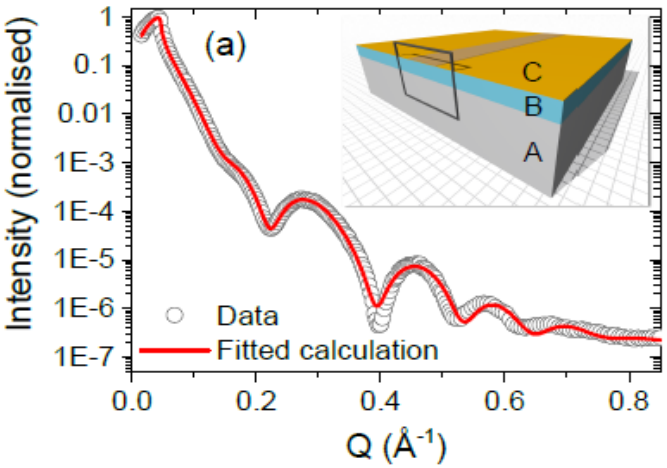


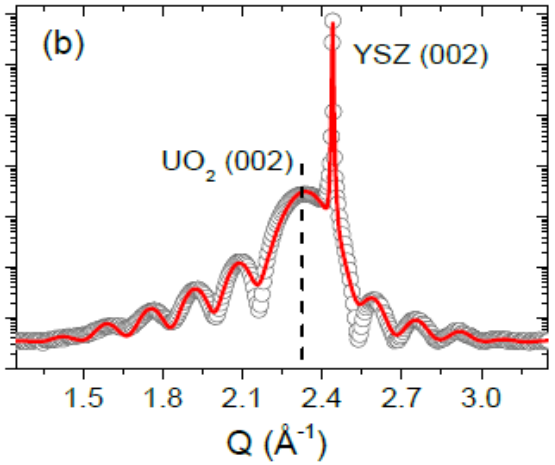


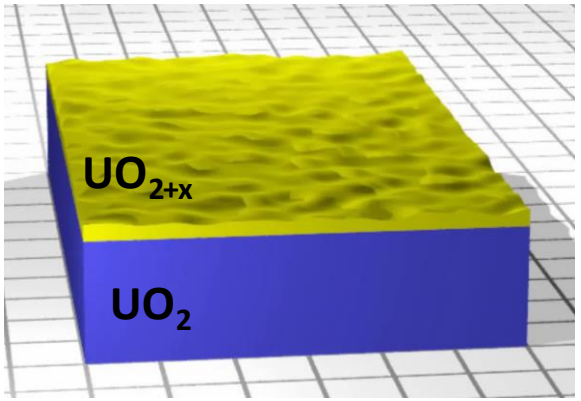
$$n\lambda = 2d\sin\theta$$

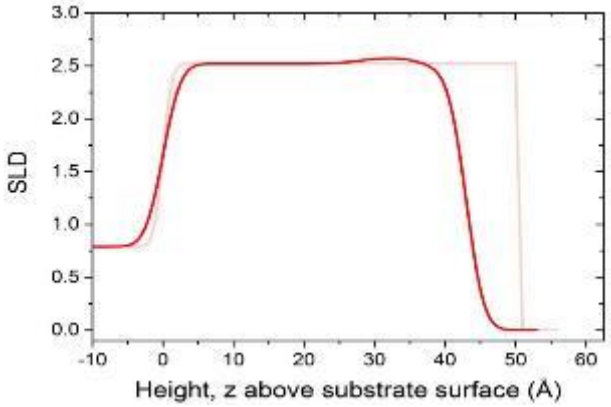


I07and XMaS Expt. – Results









1×10^{12} photons/s, at 17.116 keV

Reflectivity 1) electron density as a function of depth.
2) total thickness
3) interfacial roughnesses

High angle 1) number of lattice planes contributing (i.e. thickness of crystalline material)
2) total thickness
3) surface roughness

Rennie *et al.* Corrosion Science (2018)

Summary:

Hopefully, you now have a good overall view of the cause behind such a variety of rich physics in the actinide elements and compounds. You might even be able predict the likely observable properties depending on the crystal structure and Ac-Ac separation that you observe.

The focus on the predominant fission fuel, UO2, was centred around two of the most important properties: thermal conductivity and interaction with water.

You should now be able to explain the mechanism of heat transfer and how it might be affected by radiation damage. You also have appreciation for the most cutting edge propositions for the origin of the poor conduction in UO_2.

You should be able to explain how UO_2 might dissolve in contact with water, with a particular appreciation for why this may be an issue today.

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