Actinide Science: A focus on the properties of Uranium Dioxide
Nuclear waste actinide immobilisation 2018

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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$_3$Ir$_2$O$_7$)
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.

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

Dr. Sophie Rennie, J. Sutcliffe, E. L Bright, D. Chaney, E. Gilroy, J. Wasik, Y. Sasikumar, L. Harding, G. Griffiths
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.
Ac and Pa are found in nature as decay products of some Th and U isotopes. All the others An are synthetic elements, although small amounts of Np and Pu have 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 $10 \times 10 \times 10$ space grid, considering 2 spin states per electron. To represent $\psi$ we need $5 \times 10^{306}$ complex numbers!

Hard disk with diameter $\sim 10^{145}$ light-years!
Approximations – Free electron gas (FEG)

Most drastic approximation - electrons as non-interacting particles

\[ N \Psi \text{ in 3-D instead of one in 3N-D} \rightarrow \text{from } 10^{306} \text{ to } 10^5 \text{ complex numbers} \]

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 $\rightarrow$ new transition metal-like series (6d)
However, as the atomic number increases, electrons enter the 5f electron orbital.

Example config. [Rn]5f$^2$6d$^7$s$^2$

- 5f$^3$
- 5f$^3$
- 5f$^3$
- 5f($z^2$-$y^2$)
- 5f($z^2$-$x^2$)
- 5f($x^2$-$y^2$)
- 5f$xyz$
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?

P.G. Hay
Light actinide structures

Th, Fm3m
Pa, I4/mmm
α-U, Cmcm
β-U, P42/mnm
Np, Pnma
α-Pu, P121/m1
Cm, P63/mmc
Allotropic phases of Pu and anomalous thermal expansion

The fcc δ-phase has the lowest density.

The δ-phase contracts as it is heated, and Pu contracts as it melts.
A Revised Periodic Table of the $f$ and $d$ series

<table>
<thead>
<tr>
<th>$4f$</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5f$</td>
<td>Ac</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td>Lr</td>
</tr>
<tr>
<td>$3d$</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5d$</td>
<td>Ba</td>
<td>Lu</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Superconductivity**

**ACTINIDES**

<table>
<thead>
<tr>
<th>Ac</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
<th>Cm</th>
<th>Bk</th>
<th>Cf</th>
<th>Es</th>
</tr>
</thead>
<tbody>
<tr>
<td>89 (227)</td>
<td>90 (232.04)</td>
<td>91 (231.04)</td>
<td>92 (238.03)</td>
<td>93 (237)</td>
<td>94 (244)</td>
<td>95 (243)</td>
<td>96 (247)</td>
<td>97 (247)</td>
<td>98 (251)</td>
<td>99 (252)</td>
</tr>
</tbody>
</table>

- **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 $\text{UO}_2$ 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
$\text{UO}_2$ Phonon dispersion
Measuring Phonons – inelastic scattering

Elastic Scattering:

\[ k' = k + G \]

In-elastic Scattering:

\[ k' = k + G - K \]

\[ k' = k + G + K \]
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

Why is UO$_2$ so bad at conducting heat?

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.

$\text{UO}_2$ is insoluble in water right?
UO₂ oxidation

U-O phase diagram – a number of stable oxide states towards the highest oxide UO₃

U⁶⁺ is soluble!

Do we need to worry?
$\text{UO}_2$ oxidative dissolution
What’s new?
Epitaxial Film Growth

Uranium dioxide has the cubic fluorite crystal structure, space group Fm\(\overline{3}m\), \((a = 5.469\,\text{Å})\)

TEM of \(\text{UO}_2\) on LSAT

RHEED of [001]-oriented \(\text{UO}_2\)
**X-ray Reflectivity**

\[ n = 1 \]

\[ q_z = \frac{4\pi \sin \theta}{\lambda} \]

\[ n = 1 - \delta + i\beta \]

\[ n\lambda = 2d \sin \theta \]

\[ \theta_c = \sqrt{2\delta} \]
I07 and XMaS Expt. – Results

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

1 × 10^{12} photons/s, at 17.116 keV

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 UO2.

You should be able to explain how UO2 might dissolve in contact with water, with a particular appreciation for why this may be an issue today.
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Lander et al. Rev. Mod. Phys. 81, 807 (1994) (uranium)