Development of actinide studies using MeV ultrafast electron diffraction

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Status: Funding pending.
Funding source: Applied for funding from New Mexico Consortium and Los Alamos National Laboratory.
Special Equipment Requirements and Hazards

Special equipment:

• *Liquid He* will be required for cooling.
• *Femtosecond pulse acquisition spectrometer* (if available).
• *Elements for convergent beam configuration*.

Hazards:

• *Depleted uranium* is very mildly radioactive and chemically toxic as a heavy meta. However, the thin film samples of UO₂ to be used contain at most a few hundred micrograms (relative to an average body burden of 20 micrograms from natural sources) and their activity is below background.

• Other potential hazards include the *laser* of the MUED instrument and the *cryogenic system* necessary to cool the samples to the desired temperatures. We will work with the BNL collaborators to exercise the necessary precautions.
## CY2022 Time Request

<table>
<thead>
<tr>
<th>Capability</th>
<th>Setup Hours</th>
<th>Running Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>UED Facility</td>
<td>24</td>
<td>56</td>
</tr>
</tbody>
</table>

## Time Estimate for Remaining Years of Experiment (including CY2022)

<table>
<thead>
<tr>
<th>Capability</th>
<th>Setup Hours</th>
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<td>UED Facility</td>
<td>24</td>
<td>56</td>
</tr>
</tbody>
</table>
Overview of the proposal

We propose two activities, including a feasibility study, to be conducted on UO$_2$ thin films employing MeV ultrafast electron diffraction to advance the research on actinide materials.

We focused this proposal on UO$_2$ given the interesting properties of this material, ranging from magnetic phase transitions to the possible presence of polarons and a likely insulator-metal phase transition. In addition, recently high crystalline quality epitaxial UO$_2$ films were produced by collaborators at LANL enabling now the use of samples suitable for this technique.

We present a proposal comprising of a research activity to explore lattice dynamics in a range of temperatures to access both magnetic phases of the material and a feasibility study for transmission Kikuchi diffraction.

We expect the proposed experiments will establish the suitability and importance of the MUED instrument in the area of actinide research.
Specifics objectives of the proposal

**Lattice dynamics**

1. **RT** – Signatures of polarons in this phase

2. **RT** – Presence of photoinduced metal-insulator transition

3. **Low temperature** – Characterize phase transition using pump laser to drive it.

**Transmission Kikuchi diffraction**

4. **Feasibility study** – Requires use of a convergent beam geometry and tilt sample.
Introduction

- UO$_2$ is a line compound with near neighbor compositional line compounds of other phases.
- UO$_2$ is not reactive with O$_2$ or H$_2$O (compared to other actinides Pu or Pu-Ga alloys).
- No concerns of radioactivity as UO$_2$ thin films are formed from depleted U.
- It is a Mott insulator with a magnetic phase transition at 30 K.


Introduction

At RT: paramagnetic Mott Hubbard-type insulator.
- Studies on this phase suggest presence of polarons.
- Conflicting reports of a photoinduced metal-insulator transition.

Below 30 K: transition to antiferromagnetic phase.
- Structurally, this induces the collapse of the unit cell volume.
- This phase displays piezomagnetism after it undergoes a trigonal distortion under magnetic field.

UO₂ thin films by pulsed laser deposition

Epitaxial samples of good crystalline quality were obtained for UO₂

Substrates employed: SrTiO₃, (LaAlO₃)₀.₃(SrAlTaO₆)₀.₆ and LaAlO₃

Table 1. Structural Properties of UO₂, U₁₋ₓO₃ₓ and UO₁₋ₓ

<table>
<thead>
<tr>
<th>phase</th>
<th>c/aoe</th>
<th>space group</th>
<th>symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td></td>
<td>cccP</td>
<td></td>
<td>5.471</td>
<td>5.471</td>
<td>5.471</td>
<td></td>
</tr>
<tr>
<td>U₁₋ₓO₃ₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₁₋ₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 2. Summary of the Optical Band Gaps of Epitaxial UO₂, α-U₁₋ₓO₃ₓ, and α-UO₁₋ₓ Thin Films Grown by PLD, Compared with Literature Data

<table>
<thead>
<tr>
<th>growth</th>
<th>methods</th>
<th>UO₂</th>
<th>α-U₁₋ₓO₃ₓ</th>
<th>α-UO₁₋ₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>films by PLD</td>
<td>2.61</td>
<td>2.92</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>Tauc (direct)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tauc (indirect)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>2.72</td>
<td>2.15</td>
<td>2.54</td>
</tr>
</tbody>
</table>

| literature data      | Tauc (direct)   | 2.47  | 1.89       | 2.26    |
|                      | Tauc (indirect)|       |            |         |
|                      | 2.1             |       |            |         |
|                      | 2.3             |       |            |         |
|                      | 2.39            |       |            |         |
|                      | 2.68            |       |            |         |
|                      | 2.60–2.65       |       |            |         |
We will collaborate with the group led by Aiping Chen at LANL to obtain samples.

As epitaxy requires a certain substrate, we will explore methods to thin the substrate such as ion milling or etching.

Deposition on supported TEM grids will also be employed but likely polycrystalline samples will be obtained.
Characterization of paramagnetic phase

Can we discern signatures of polarons in this material?

- Inspired in the manganite work done in this system, we want to perform pump-probe experiments.

- For this experiment, we will operate at room temperature.

- Also the temperature dependence of the Debye-Waller factor can be compared with theoretical models (which in turn explain melting behavior).
Specifics objectives of the proposal

Lattice dynamics

1. **RT** – Signatures of polarons in this phase

2. **RT** – Presence of photoinduced metal-insulator transition
Is there a photoinduced metal-insulator transition? Can we observe this metastable phase?

- To the best of our knowledge, the only ultrafast technique applied to study this was spectroscopy which indicated no MIT but a robust Mott gap due to strong Coulomb interaction.

- Inspired by UED experiments on VO$_2$, we will use the pump laser to induce this transition by varying the fluence.
Characterization of paramagnetic phase

Is there a photoinduced metal-insulator transition? Can we observe this metastable phase?

- Additionally, we would like to employ the OPA system to perform ultrafast IR transmittance measurements.

- This will be possible if a femtosecond pulse acquisition spectrometer is available.

- If available, enabling IR ultrafast spectroscopy capabilities in the MUED instrument will be of benefit to several users.
Lattice dynamics

3. **Low temperature** – Characterize phase transition using pump laser to drive it.
Characterization of antiferromagnetic phase

Can we induce and characterize the phase transition?

- These experiments will be performed at low temperatures using liquid He cooling.
- Pump laser will be employed to induce the transition.
- Unit cell collapse can be characterized.
- Performing pump-probe measurements, we could study lattice dynamics of this phase compared to the paramagnetic one.

Figure 3. Temperature dependence of the integrated intensity of the (1 1 2) reflection from a UO$_2$ single crystal in both the $\sigma \to \pi$ (black squares) and $\sigma \to \sigma$ (red circles) polarization channels at the $M_4$ resonant energy of 3.74 keV, and the (0 1 4) Bragg reflection measured (green diamonds) at 10 keV. These represent the magnetic dipole (found in 1965 [7, 8]), electric quadrupole order, and the Jahn–Teller internal distortion of the oxygen atoms (found in 1976 [19, 20]). Adapted from Wilkins et al [40]. Reprinted figure with permission from [40], © 2006 American Physical Society.

Some desired capabilities to discuss in the future

Study of magnetic materials

- UO$_2$ has a large of variety of interesting magnetic behavior in both phases, if we could apply magnetic fields to the sample (up to 25 T), we will be able to characterize it further.

- Other materials have been presented previously that would also benefit from this capability.

Study of strain induced effects

- UO$_2$ presents several polymorphs under high compressive and tensile stress.

- Other materials, such as SrTiO$_3$, have strain-dependent behavior as well.

- In the last case, membranes are available so new sample holder design is needed to apply stress to these types of samples.
Specifics objectives of the proposal

Transmission Kikuchi diffraction

4. **Feasibility study** – Requires use of a convergent beam geometry and tilt sample.
Transmission Kikuchi diffraction

Can we perform transmission Kikuchi diffraction (TKD) measurements?

- In UO$_2$ and other actinides (Pu and Pu-Ga alloys most prominently), the presence of defects has large effect on the crystal structure. This is an active field of research for actinides!

- Stress/strain studies on UO$_2$ can open the door to ultrafast studies of defect mediated phase transformation and even directionally preferred corrosion dynamics.

- Also, could be an option in the case of presence of dynamical scattering effects in MUED when dealing with high Z materials.

- The ideal technique for this is EBSD, but no ultrafast capabilities and low energy.

- TKD has been implemented already in a UED/UEM system to study of the dynamics of elastic waves propagation in a material.
Can we perform transmission Kikuchi diffraction (TKD) measurements?

- **TKD has been implemented already in a UED/UEM system** to study the dynamics of elastic waves propagation in a material.
Transmission Kikuchi diffraction

Can we perform transmission Kikuchi diffraction (TKD) measurements?

- We would need to set up a convergent beam geometry (so extensive interaction with ATF staff will be needed)

- Kikuchi diffraction can be interpreted as originating from a virtual source located inside the sample and forms bands as opposed to spots in Bragg diffraction.

- For positive time delays, the intensity of the Kikuchi lines increases due to diffuse thermal scattering as the sample is heated (so better signal-to-noise ratio than MUED).

- Measuring the Kikuchi lines as a function of time delay, we can characterize the stress and strain in the sample.

- Exploration of electron energy and sample tilt will be necessary to obtain high quality Kikuchi patterns.
Actinide research with MUED

- Our proposal includes ‘traditional’ MUED experiments to characterize specifics of RT and low temperature phases.
- Lattice dynamics, including the presence of MIT, will be evaluated for this system.
- High quality epitaxial UO$_2$ films are now possible and within our reach.
- Our proposal also includes a feasibility study for transmission Kikuchi diffraction that has not been implemented at MeV energies and would allow stress/strain studies (major interest from actinides research community).

Ultimate goal: establish and enable study of actinides with MUED
Thank you for your attention

We appreciate all the support from our team members on the development of this proposal.