SCHOOL OF ENGINEERING

Development of actinide studies using MeV ultrafast electron diffraction

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Collaborators: Salvador Sosa (UNM); Anna Llobet Megias, Franz Freibert (LANL); Alan Hurd (UNM / LANL).

BROOKHAVEN NATIONAL LABORATORY

Status: Funding pending.

Funding source: Applied for funding from New Mexico Consortium and Los Alamos National Laboratory.

Los Alamos NATIONAL LABORATORY

Special Equipment Requirements and Hazards

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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 UO_2 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.

Experimental time request

CY2022 Time Request

Capability	Setup Hours	Running Hours
UED Facility	24	56

Time Estimate for Remaining Years of Experiment (including CY2022)

Capability	Setup Hours	Running Hours
UED Facility	24	56

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

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Lattice dynamics

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

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

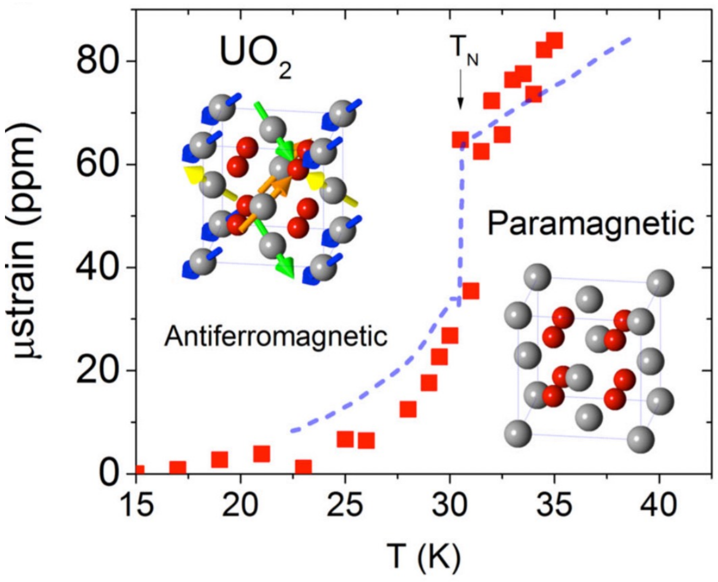
3. **Low temperature** – Characterize phase transition using pump laser to drive it.

Transmission Kikuchi diffraction

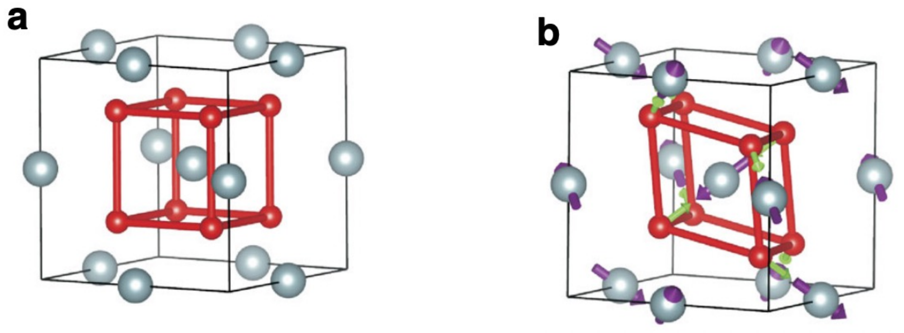
4. **Feasibility study** – Requires use of a convergent beam geometry and tilt sample.

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_2O (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.



Antonio, Daniel J., et al. "Piezomagnetic switching and complex phase equilibria in uranium dioxide." *Communications Materials* 2.1 (2021): 1-6.



Jaime, M., et al. "Piezomagnetism and magnetoelastic memory in uranium dioxide." Nature communications 8.1 (2017): 1-7.

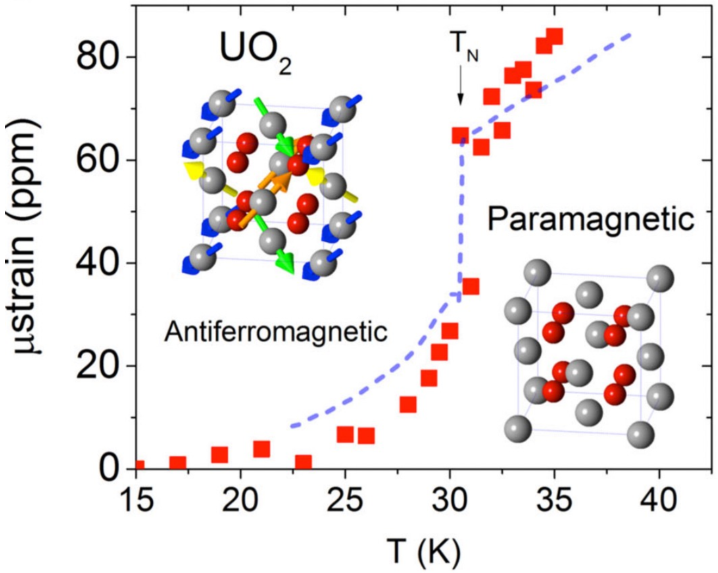
Introduction

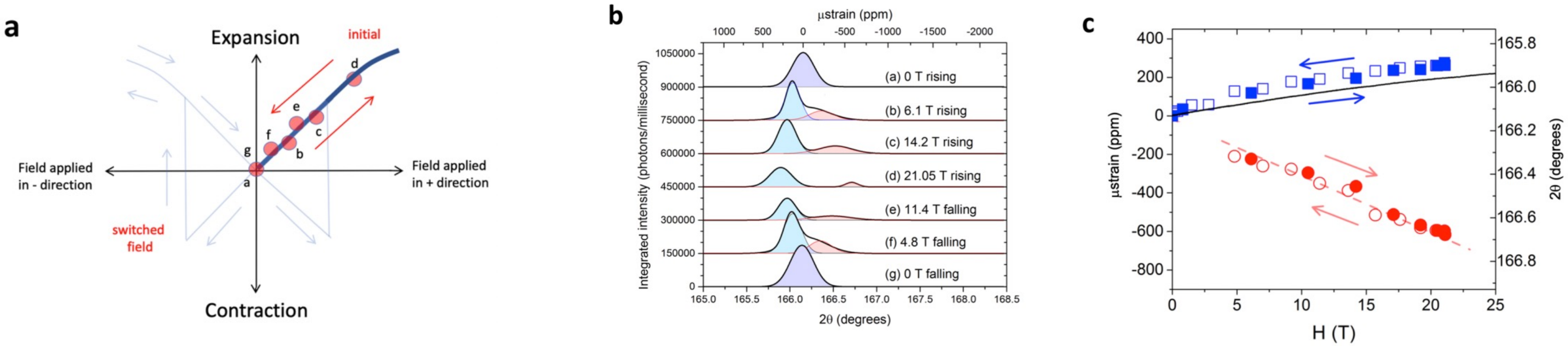
At RT: paramagnetic Mott Hubbard-type insulator.

- 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.





Antonio, Daniel J., et al. "Piezomagnetic switching and complex phase equilibria in uranium dioxide." *Communications Materials* 2.1 (2021): 1-6.

UO_2 thin films by pulsed laser deposition

Structural and Optical Properties of Phase-Pure UO_2, α-U_3O_8, and α-UO_3 Epitaxial Thin Films Grown by Pulsed Laser Deposition

Erik Enriquez,△ Gaoxue Wang,△ Yogesh Sharma, Ibrahim Sarpkaya, Qiang Wang, Di Chen, Nicholas Winner, Xiaofeng Guo, John Dunwoody, Joshua White, Andrew Nelson, Hongwu Xu, Paul Dowden, Enrique Batista, Han Htoon, Ping Yang, Quanxi Jia, and Aiping Chen*

- Epitaxial samples of good crystalline quality were obtained for UO_2
- Substrates employed: $SrTiO_3$, $\mathbf{(LaAlO_3)_{0.3}(SrAlTaO_6)_{0.6}}$ and $LaAlO_3$

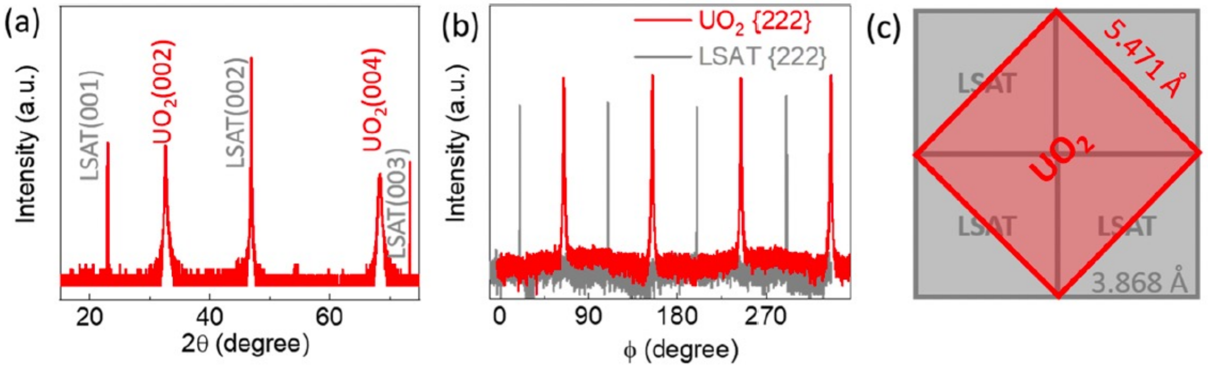


Table 1. Structural Properties of UO_2, U_3O_8, and UO_3

					lattice parameters			
phase	T (K)	color	space group	symmetry	a (Å)	b (Å)	c (Å)	β
UO_2			$Fm\bar{3}m$	cubic[32]	5.471	5.471	5.471	

Table 2. Summary of the Optical Band Gaps of Epitaxial UO_2, α-U_3O_8, and α-UO_3 Thin Films Grown by PLD, Compared with Literature Data

	growth	methods	UO_2	α-U_3O_8	α-UO_3
this work	films by PLD	Tauc (direct)	2.61	2.92	2.87
		Tauc (indirect)	2.47	1.89	2.26
		K	2.72	2.15	2.54
literature data	single-crystal[60]		2.1		
	film (sol−gel)[61]	Tauc (indirect)	2.0−2.5		
	GGA + U method[64]	Tauc (indirect)	2.3		
	HSE03 method[65]	Tauc (direct)	2.39		
	HSE06 method[62]	Tauc (direct)	2.68		
	film (sputtering)[16]	Tauc (indirect)		1.67−1.81	2.60−2.65
	diluted powder[63]	Tauc (indirect)		1.72−1.86	

UO_2 thin films by pulsed laser deposition

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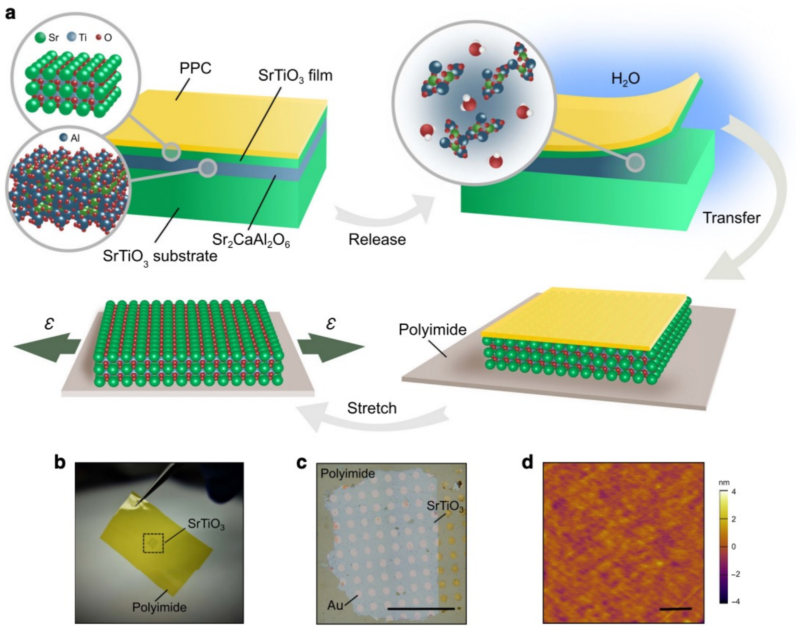
- We will collaborate with the group led by Aiping Chen at LANL to obtain samples.

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

https://doi.org/10.1038/s41467-020-16912-3 OPEN

Strain-induced room-temperature ferroelectricity in $SrTiO_3$ membranes

Ruijuan Xu[1,2✉], Jiawei Huang[3], Edward S. Barnard[4], Seung Sae Hong[1,2], Prastuti Singh[1,2], Ed K. Wong[4], Thies Jansen[1], Varun Harbola[2,5], Jun Xiao[2,6], Bai Yang Wang[2,5], Sam Crossley[1,2], Di Lu[5], Shi Liu[3] & Harold Y. Hwang[1,2✉]



- Deposition on supported TEM grids will also be employed but likely polycrystalline samples will be obtained.

Characterization of paramagnetic phase

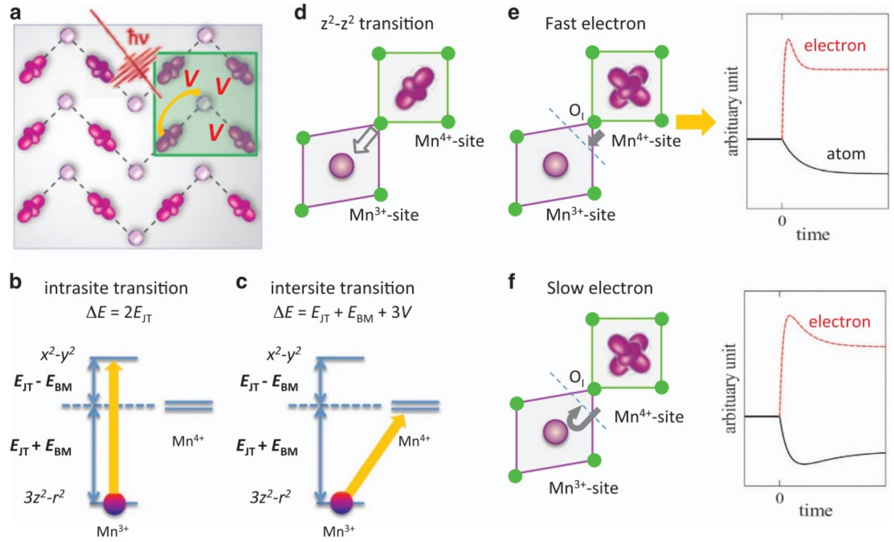
Can we discern signatures of polarons in this material?

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

ARTICLE OPEN

Dichotomy in ultrafast atomic dynamics as direct evidence of polaron formation in manganites

Junjie Li[1], Wei-Guo Yin[1], Lijun Wu[1], Pengfei Zhu[1,2], Tatianna Konstantinova[1,3], Jing Tao[1], Junjie Yang[4], Sang-Wook Cheong[4,5], Fabrizio Carbone[6], James A Misewich[1,3], John P Hill[1], Xijie Wang[1,7], Robert J Cava[8] and Yimei Zhu[1,3]



- 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)

Phonon Spectrum and UO_2 Debye–Waller Factors in a Sublattice Model

A. S. Poplavnoi[a] and T. P. Fedorova[b]
Faculty of Physics, Kemerovo State University, Kemerovo, 650043 Russia
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Specifics objectives of the proposal

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Lattice dynamics

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

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

Characterization of paramagnetic phase

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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.

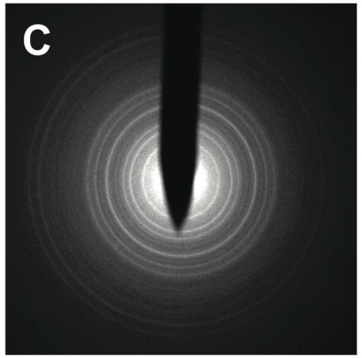
- Inspired by UED experiments on VO_2, we will use the pump laser to induce this transition by varying the fluence.

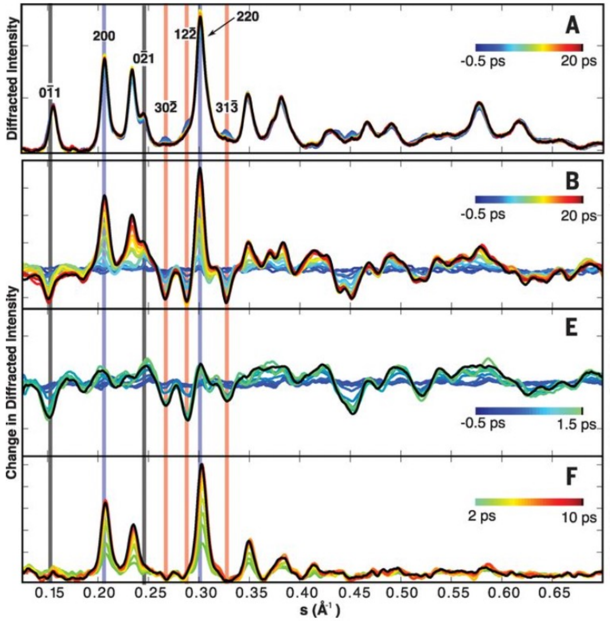
REPORT

A photoinduced metal-like phase of monoclinic VO_2 revealed by ultrafast electron diffraction

VANCE R. MORRISON, ROBERT. P. CHATELAIN, KUNAL L. TIWARI, ALI HENDAOUI, ANDREW BRUHÁCS, MOHAMED CHAKER, AND BRADLEY J. SIWICK Authors Info & Affiliations

SCIENCE • 24 Oct 2014 • Vol 346, Issue 6208 • pp. 445-448 • DOI: 10.1126/science.1253779

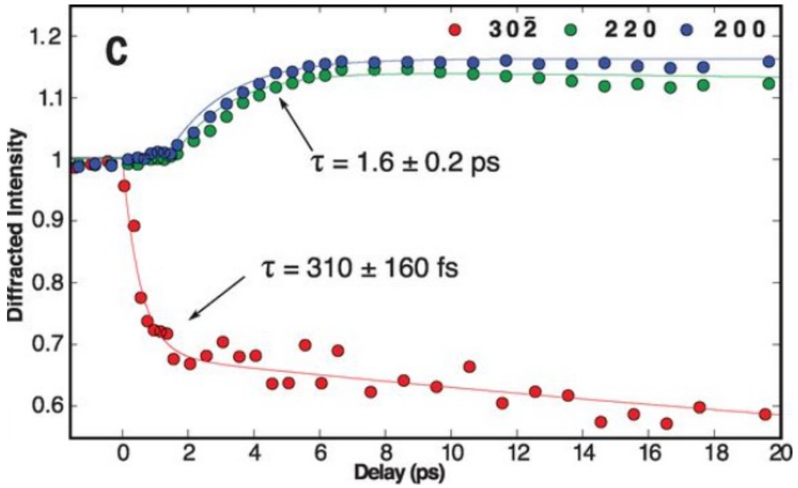


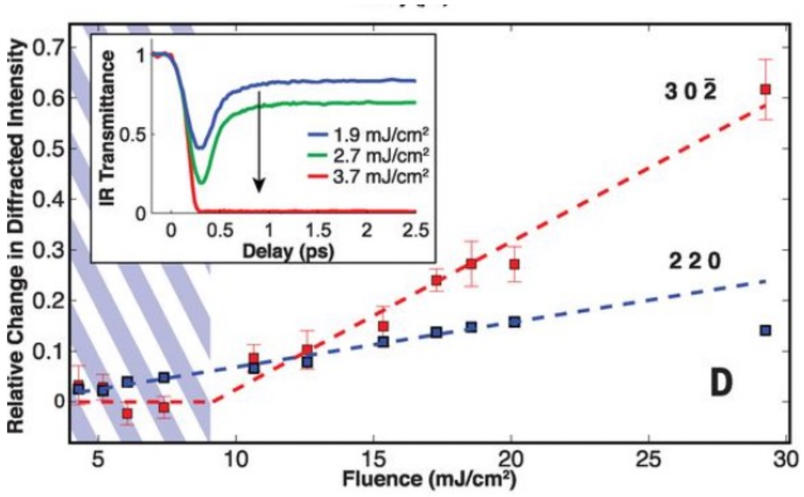


Characterization of paramagnetic phase

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.

Specifics objectives of the proposal

Lattice dynamics

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

Characterization of antiferromagnetic phase

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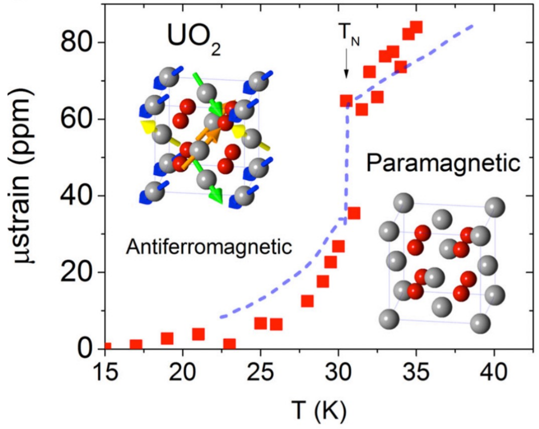
Can we induce and characterize the phase transition?

- 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.



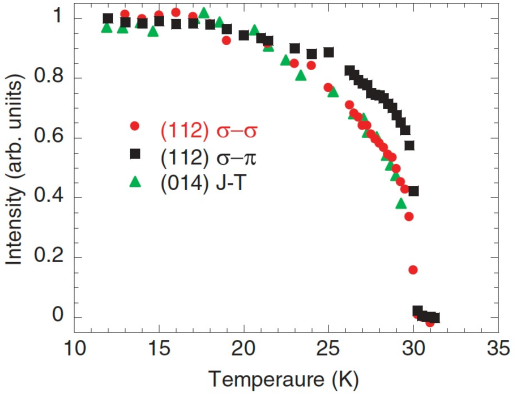


Figure 3. Temperature dependence of the integrated intensity of the (1 1 2) reflection from a UO_2 single crystal in both the $\sigma \rightarrow \pi$ (black squares) and $\sigma \rightarrow \sigma$ (red circles) polarization channels at the M_4 resonant energy of 3.74 keV, and the (0 1 4) Bragg reflection 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.

Lander, G. H., and R. Caciuffo. "The fifty years it has taken to understand the dynamics of UO2 in its ordered state." Journal of Physics: Condensed Matter 32.37 (2020): 374001.

Some desired capabilities to discuss in the future

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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

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Transmission Kikuchi diffraction

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

Transmission Kikuchi diffraction

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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.

Transmission Kikuchi diffraction

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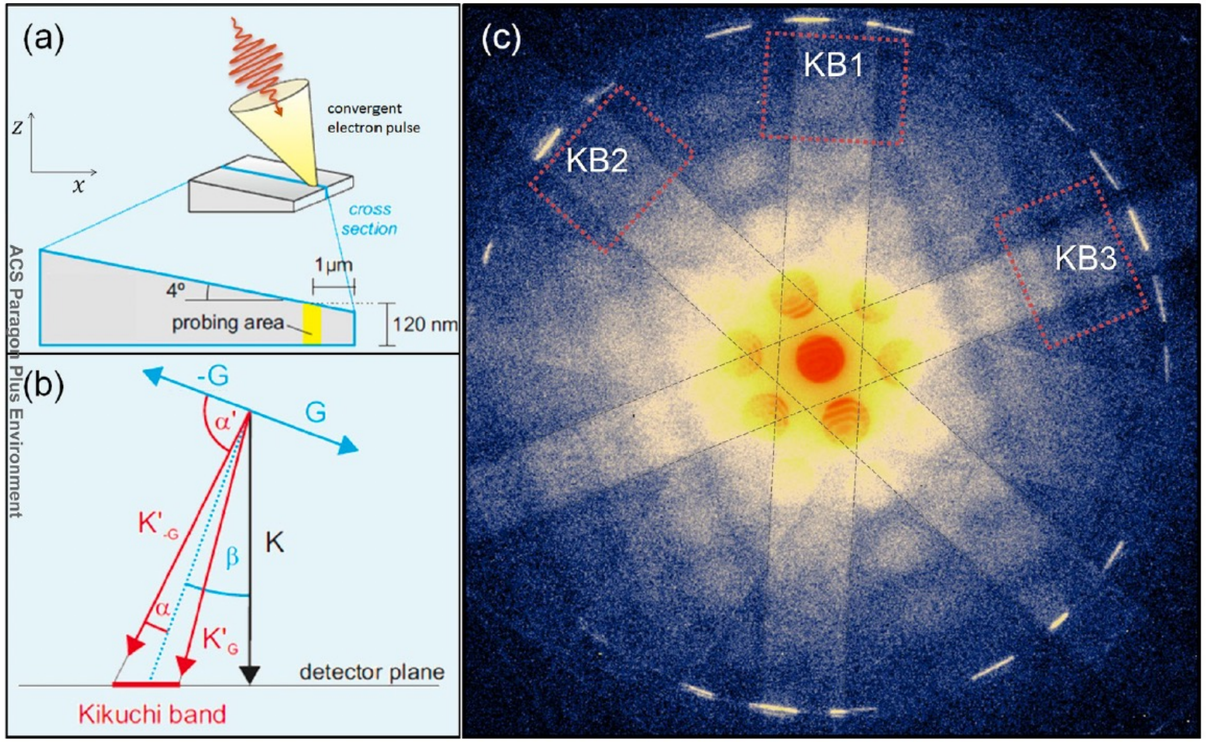
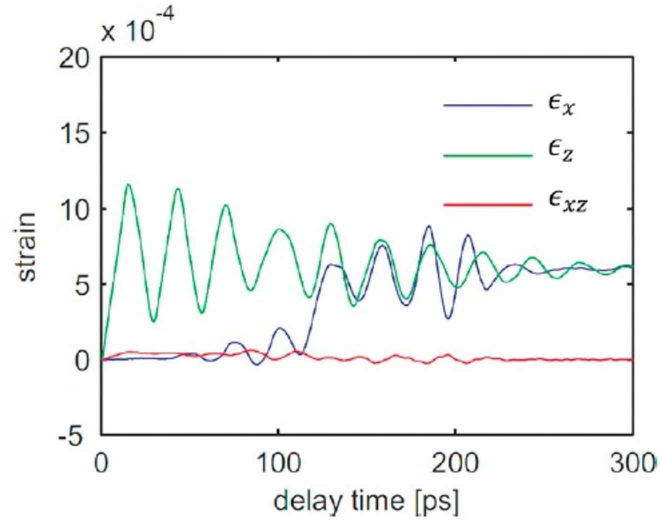
Can we perform transmission Kikuchi diffraction (TKD) measurements?

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




NANO LETTERS
Letter
pubs.acs.org/NanoLett

Ultrafast Kikuchi Diffraction: Nanoscale Stress−Strain Dynamics of Wave-Guiding Structures

Aycan Yurtsever, Sascha Schaefer, and Ahmed H. Zewail*

Transmission Kikuchi diffraction

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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.
- Forpositive 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

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Ultimate goal: stablish and enable study of actinides 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).

Thank you for your attention

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