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Energy Frontier Research Center

Center for Materials Science of Nuclear Fuels

Todd R. Allen

April 2014

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EXECUTIVE SUMMARY

The mission of the Center for Material Science of Nuclear Fuels (CMSNF) is to develop a first-principles-based understanding of thermal transport in UO_2, the most widely used nuclear fuel. The goal is to build an experimentally validated, multiscale modeling capability that provides a predictive understanding of the impact of lattice anharmonicity and radiation induced defects on thermal transport in nuclear fuel. This mission is implemented by integrating the physics of thermal transport in crystalline solids with microstructure science under irradiation. The center brings together a multi-institutional experimental team (from Idaho National Laboratory, Oak Ridge National Laboratory, University of Florida, and the University of Wisconsin) and a multi-institutional computational materials theory team (from Idaho National Laboratory, University of Florida, and Purdue University). The EFRC is led by Director Todd Allen and is organized around the closely related research thrust areas of thermal transport and microstructure science under irradiation. Key scientific and personnel successes since the April 2013 report are highlighted below.

Scientific Successes

- The first phonon density of states (PDOS) measurements for UO_2 to include anharmonicity were obtained using time-of-flight inelastic neutron scattering at the Spallation Neutron Source (SNS), and an innovative, experimental-based anharmonic smoothing technique has enabled quantitative benchmarking of *ab initio* PDOS simulations.
- Direct comparison between anharmonic-smoothed *ab initio* PDOS simulations for UO_2 and experimental measurements has demonstrated the need for improved understanding of UO_2 at the level of phonon dispersion, and, further, that advanced lattice dynamics simulations including finite temperatures approaches will be required for handling this strongly correlated nuclear fuel.
- PDOS measurements performed on polycrystalline samples have identified the phonon branches and energy ranges most highly impacted by fission-product and hyper-stoichiometry lattice defects in UO_2. These measurements have revealed a broad-spectrum impact of oxygen hyper-stoichiometry leading to a reduction in thermal conductivity by hyper-stoichiometry many times stronger than that by substitutional fission-product impurities.
- Laser-based thermo-reflectance measurements on UO_2 samples irradiated with light (i.e., He^+) ions to introduce point defects have been coupled with MD simulations and lattice parameter measurements to determine the role of uranium and oxygen point defects in reducing thermal conductivity.
- A rigorous perturbation theory treatment of phonon lifetimes in UO_2 based on a 3D discretization of the Brillouin zone coupled with experimentally measured phonon dispersion has been implemented that produces improved predictions of the temperature dependent thermal conductivity.
- Atom probe investigations of the influence of grain boundary structure on the segregation behavior of Kr in UO_2 have shown that smaller amounts of Kr are present at low angle grain boundaries than at large angle grain boundaries due to the more dense dislocation arrays associated with large angle boundaries; this observation has potentially important ramifications for thermal transport in the high burn-up rim region of light water reactor fuel.
- A variable charge interatomic potential has been developed that not only provides an accurate representation of the fluorite UO_2 phase, it is further capable of describing continuous stoichiometry changes from UO_2 to hyper-stoichiometric UO_{2+x}, to U_4O_9 and U_3O_7, and possibly to orthorhombic U_3O_8. This is the first potential that features many-body effects in all possible interactions (U-U, U-O and O-O) combined with the variable charge.

- A theoretical proof has been formulated showing that it is necessary to use the so-called model C phase field approach, consisting of Cahn-Hilliard and Allen-Cahn equations, to describe void evolution in irradiated materials. This work resolved a longstanding literature controversy regarding how to model voids at the mesoscale.
- A novel cluster dynamics model has been developed for the nucleation of voids and loops in UO_2 under irradiation. This model is important in understanding the defect state of UO_2 after irradiation and, more importantly, reveals off-stoichiometric states of irradiated UO_2 that are critical for understanding the impact of irradiation on thermal transport.

Personnel Successes

A number of postdoctoral fellows and staff members of CMSNF have taken new positions. Of these, the most recent ones include:

- Dr. Srujan Rokkam, an EFRC Alumni who obtained his Ph.D. at Florida State University and now working with Advanced Cooling Technology, Inc., Lancaster, PA, has been promoted to Research and Development Engineer II. In March 2014.
- Clarissa Yablinsky, from the University of Wisconsin, obtained a postdoctal position at Los Alamos National Laboratory.
- Sarah Khalil successfully defended her doctoral dissertation in February 2014 at the University of Wisconsin and is now an Assistant Professor at Alexandria University in Egypt.
- Dr. Jianliang Lin from Colorado School of Mines obtained a staff position at the Southwest Research Institute.
- Hunter Henderson successfully defended his Ph.D at the University of Florida and will be working as a post-doc with Dr. Michele Manuel during the summer of 2014.
- Dr. Michele Manuel was chosen for the following awards:
  - TMS Early Career Faculty Award
  - Japanese Institute of Materials (JIM)/TMS Young Leader International Scholar
  - American Vacuum Society (AVS) Recognition for Excellence in Leadership
  - ASM Bradley Stoughton Award for Young Teachers.

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ACRONYMS

APT	atom probe tomography
BSU	Boise State University
BTE	Boltzmann Transport Equation
CD	cluster dynamics
CMSNF	Center For Materials Science of Nuclear Fuels
CSM	Colorado School of Mines
DPA	displacements per atom
EBSD	Electron Backscatter Diffraction
EFRCs	Energy Frontier Research Centers
FY	fiscal year
HAGBs	high angle grain boundaries
HRTEM	high resolution transmission electron microscopy
INL	Idaho National Laboratory
INS	inelastic neutron scattering
ISU	Idaho State University
ITU	Institute for Transuranium Elements
IVEM	Intermediate Voltage Electron Microscope
LAGBs	low angle grain boundaries
LANL	Los Alamos National Laboratory
MC	Monte Carlo
MD	Molecular Dynamics
NRC	National Research Council Canada
ORNL	Oak Ridge National Laboratory
PDOS	phonon density of states
PhonTS	Phon Transport Simulator
PI	principal investigator
PKA	primary-knockon-atom
PNNL	Pacific Northwest National Laboratory
RISE	Research and Innovation in Science and Engineering
SNS	Spallation Neutron Source
SRIM	Stopping and range of ions in materials
STEM	Scanning transmission electron microscopy
TEM	Transmission Electron Microscopy
UIUC	University of Illinois at Urbana-Champaign
XRD	X-Ray diffraction

Energy Frontier Research Center

Center for Materials Science of Nuclear Fuels

1. ACCOMPLISHMENTS AGAINST GOALS AND OBJECTIVES

1.1 Thermal Transport

This thrust area includes inelastic neutron scattering measurements and first principles modeling of phonon lifetimes, density of states, and dispersion; it also includes experimental thermal conductivity measurements, phonon transport simulations, and atomistic modeling in support of these efforts.

1.1.1 Neutron Measurements and Phonon Modeling in UO_2

As planned, incoherent inelastic neutron scattering measurements at Oak Ridge National Laboratory (ORNL) have been made of the phonon density of states (PDOS) of stoichiometric UO_2 and of hyper-stoichiometric $UO_{2.08}$ as a function of temperature using the Wide Angular-Range Chopper Spectrometer at the Spallation Neutron Source (SNS). In addition, first-principles lattice dynamics simulations have been performed on the temperature dependence of the PDOS of UO_2 at UF, and 3D Brillouin zone discretization calculations of phonon lifetimes in UO_2 have been performed at Purdue for use in a Monte Carlo solver for the Boltzmann transport equation (BTE). Comparisons of the PDOS measurements as a function of temperature with the first principles simulations have been used to test fundamental understanding of phonon physics in strongly correlated UO_2.

Planned investigations to probe the impact of fission-product lattice defects and hyper-stoichiometry defects on phonons in UO_2 have been performed using PDOS measurements on polycrystalline 5% ceria-doped UO_2 and polycrystalline $UO_{2.08}$. Single crystals of Ce-doped and oxygen hyper-stoichiometric UO_2 single crystals are not yet available. However, the PDOS measurements performed on polycrystalline samples have provided detailed quantitative information on the overall impact of fission-product and hyper-stoichiometry lattice defects on the vibrational spectra of UO_2. Moreover, these time-of-flight neutron scattering measurements at the SNS provide direct information on the most highly impacted phonon branches to be studied individually using time-intensive single crystal phonon lifetime measurements with reactor neutrons at the High Flux Isotope Reactor.

1.1.2 Thermal Transport Measurements and Simulation

As planned, unit mechanism studies in samples irradiated with light ions have been performed at Idaho National Laboratory (INL). The evolution of irradiation damage and its effect on thermal conductivity were examined in He^{2+} irradiated UO_2 (irradiation performed at University of Wisconsin). Laser-based thermo-reflectance measurements coupled with detailed analysis indicated that the thermal conductivity reduction was mainly caused by irradiation induced point defects. Additional work aimed at understanding the role of dislocation loops in limiting phonon mediated thermal transport was performed. Dislocation loops were introduced by irradiation of polycrystalline sintered cerium dioxide sample using 1.6 MeV protons at 700°C. Analysis of the experimental data using a classical conductivity model reveals that the conductivity reduction at larger damage levels is primarily due to dislocation loops, while point defects play only a minor role. More detailed work on proton irradiated UO_2 has been limited by experimental issues related to low frequency laser noise. This issue is being addressed by leveraging a Fuel Cycle Research and Development project to develop a continuous wave laser-based thermal wave system.

To bring closure to a previous measurement and help set the stage for future studies, a phonon wave packet method has been applied to elucidate the details of the interfacial resistance in $Si/SiO_2/Si$ system [1]. Application of this method to grain boundaries in UO_2 is currently in progress. This simulation effort

will dovetail with ongoing experimental work to measure thermal transport across well-characterized, individual grain boundaries in UO_2.

1.1.3 Phonon Transport Modeling at the Mesoscale

The effort at Purdue on phonon transport simulations has focused on the development of a Monte Carlo solver for the BTE for phonons in UO_2. Earlier solutions were based on the use of an isotropic idealization of the Brillouin zone in calculating phonon lifetimes. While that approximation yielded good results, the plan over the past year has been to carry out a rigorous treatment of phonon lifetime calculations based on a 3D discretization of the Brillouin zone of UO_2. This task has been completed as planned. This new discretization scheme enabled the use of anisotropic dispersion relations in the Brillouin zone, which will provide more accurate predictions of the phonon lifetime following the perturbation theory framework. The predicted lifetime will be compared with INS measurements and used in Monte Carlo transport simulations.

1.2 Microstructure Science Under Irradiation

The microstructure science thrust encompasses computational modeling of defect and microstructure evolution, UO_2 sample irradiation and microstructure characterization, and investigation of the stoichiometry of UO_2. As summarized below, the team has made progress on all fronts over the past year.

1.2.1 Irradiation Experiments

As planned, the team has conducted a large number of irradiation tests, post-irradiation annealing and characterization experiments targeting various aspects of the irradiation response of UO_2. Irradiation and post-irradiation annealing experiments were conducted to provide samples for thermal transport measurements and to understand the irradiation-induced defect clustering and microstructure evolution of UO_2. A list of the important investigations that were performed is given below:

- H^+ and He^{2+} ion irradiations of UO_2 were performed to produce samples with point defect or dislocation loop dominated microstructures for thermal transport measurements.
- Grain growth annealing of polycrystalline UO_2 was performed at Boise State University (BSU) to validate the phase field models developed at Purdue and to enable thermal transport measurements on individual grain boundaries. The effect of irradiation on grain growth of UO_2 was evaluated using Electron Backscatter Diffraction (EBSD).
- *In situ* Kr and Xe irradiations of UO_2 were carried out at the Intermediate Voltage Electron Microscopy (IVEM) facility at Argonne National Laboratory to study the effect of grain boundary character on defect evolution in UO_2 during irradiation.
- *Ex situ* 1.8 MeV Kr irradiation of UO_2 at the University of Illinois at Urbana-Champaign (UIUC) and post-irradiation annealing at Boise State University were performed to provide either dislocation loop or bubble dominated microstructures for thermal transport measurement.
- Irradiation damage formation and evolution at the atomic scale was characterized by X-ray diffraction (XRD), analytical transmission electron microscopy (TEM) and atom probe tomography (APT). This information will be used to analyze thermal transport measurements of unit phonon scattering mechanisms.

1.2.2 Atomic-Scale Simulation of Defects in UO_2

A variable charge interatomic potential was developed which improves the description of the U-UO_2 system. Traditional, fixed-point charge potentials typically have extremely large cohesive energies and do not satisfy Cauchy's relation. Furthermore, the non-equilibrium oxygen interstitial and oxygen vacancy point defect energies cannot be described by the previous UO_2 potentials due to the lack of an appropriately defined reference state. Our improved potential not only produces a very good

representation of the fluorite phase of UO_2, but also is capable of describing a continuous stoichiometry from UO_2 to UO_{2+x}, U_4O_9 and U_3O_7, and possibly extension to orthorhombic U_3O_8 [2].

In order to interpret thermal transport measurements of He ion irradiated UO_2 we have investigated a method for accurately estimating the density of Frenkel pairs. This indirect approach calculates the lattice expansion in defect-laden crystals using atomistic models and subsequently compares the MD results with the measured lattice parameter as a function of irradiation dose. In particular, a relation between defect concentration and lattice expansion has been obtained using molecular dynamics (MD) modeling; this, in turn enabled the rationalization of measured conductivity values as a function of dose. The simulation also enabled the prediction of the effect of small clusters on thermal conductivity.

1.2.3 Stoichiometry and Microstructure Evolution in UO_2

As planned, the following accomplishments have been made over the past year in the area of stoichiometry and microstructure modeling: (i) A phase field model for grain growth in UO_2 with inter-granular voids was developed and experimentally validated [3] using TEM and APT. The model will be used to understand annealing experiments in UO_2 with voids; (ii) Formulated a theoretical proof that the model C phase field approach, consisting of Cahn-Hilliard and Allen-Cahn equations, must be used to describe void evolution in irradiated materials [4]. This work resolved a controversy in the literature regarding how to model voids at the mesoscale; (iii) Development of a novel cluster dynamics model for the nucleation of voids and loops in UO_2 under irradiation. This model is important in understanding the defect state left in UO_2 after irradiation and, most importantly, reveals off-stoichiometric states of irradiated UO_2, which is critical for understanding irradiation effects on thermal transport.

2. ACCOMPLISHMENTS FOR THE PERIOD

2.1 Thermal Transport

2.1.1 Neutron Measurements and Phonon Modeling in UO_2

We have used time-of-flight neutron scattering measurements of the phonon density of states to investigate the impact of reactor environment defects on phonons in UO_2. Figure 1a shows the PDOS spectrum of UO_2 after doping with 5% Ce as a surrogate fission-product defect and Figure 1b shows the impact of 4% hyper-stoichiometric oxygen, the most pervasive nuclear fuel defect. The effect of 5% substitutional Ce on the PDOS spectrum is small and commensurate with the known ~8% thermal conductivity reduction for 5% Ce doped UO_2. However, the pure uranium LA zone boundary phonon mode in Figure 1a is strongly reduced in height and broadened, suggesting that the mass difference of Ce relative to U impacts predominantly uranium vibrational modes. On the other hand, 4% hyper-stoichiometry (i.e., $UO_{2.08}$) impacts the PDOS spectrum at nearly all energies except that of the pure uranium LA mode. This is in accordance with the rather large ~30% thermal conductivity reduction that is observed for $UO_{2.08}$. These results show that PDOS measurements on polycrystalline UO_2 provide stringent tests for validating simulations of phonon scattering by defects and for testing the underlying theoretical understanding of thermal conductivity of UO_2 in reactor environments.

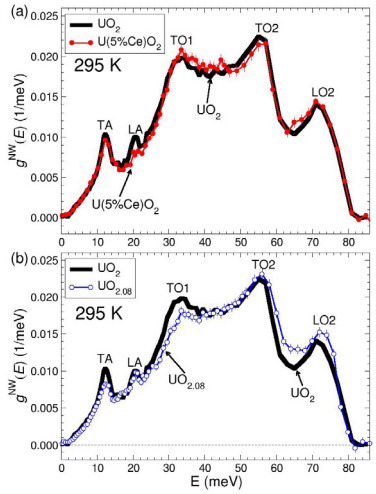

Figure 1. Phonon density-of-states of (a) UO_2 (solid line) and $U(5\%Ce)O_2$ (filled circles); and (b) UO_2 (solid line) and $UO_{2.08}$ (unfilled circles) at 295 K.

We have used the time-of-flight inelastic neutron scattering at the Spallation Neutron Source (SNS) to perform the first temperature dependent PDOS measurements for UO_2 and the first PDOS measurements that include anharmonicity [5]. Detailed comparisons (see Figure 2) of these benchmark PDOS measurements with *ab inito* simulations were made possible by the introduction of anharmonic smoothing of the simulations using our previous linewidth measurements on UO_2 [6]. The results of the comparisons with simulations performed within this EFRC, and with all first principles PDOS simulations reported so far, have shown that first principles simulations overstate the spectral weight of the optical (oxygen) phonon modes significantly and that the quasiharmonic approximation strongly overpredicts temperature induced phonon softening in UO_2. The results show overall that a better understanding of phonon dynamics is needed at a fundamental level for phonon transport simulations in UO_2 and that higher level *ab initio* simulations, including finite temperature approaches, will be required to understand this highly anharmonic, strongly correlated nuclear fuel.

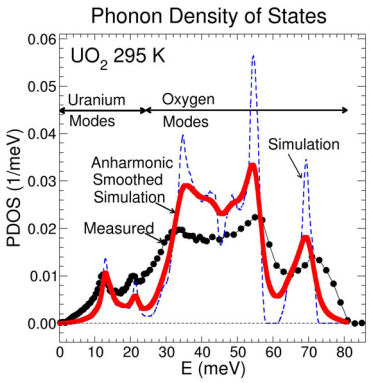

Figure 2. Phonon density of states of UO_2 at 295 K: (symbols) measurements at Spallation Neutron Source (SNS); (dashed) *ab initio* simulation; (solid) simulation convoluted with anharmonic phonon linewidth measurements.

A Monte Carlo (MC) solution of the BTE for phonons in UO_2 showed that the two highest energy phonon branches do not contribute significantly to thermal conductivity due to the low group velocities of these branches. Calculations of the thermal conductivity using the phonon transport properties of the MC solution were found to agree well with the experimental data over the temperature range 300–1000°K. The MC/BTE approach provides critical phonon transport information for confronting the theory of phonon transport and for comparison with INS phonon linewidth data. That is, detailed classical perturbation theory calculations of the branch- and wavevector-specific phonon lifetimes of UO_2 in terms of the Grüneisen parameter and phonon dispersion measurements will provide an alternative approach to *ab initio* simulations for comparison with INS-measurements of phonon lifetimes. Moreover, the ability to simulate phonon transport in UO_2 using the perturbation theory approach will provide a forthcoming framework to study phonon transport in UO_2 crystals containing defect clusters, fission-products, and off-stoichiometry defects associated with reactor environments.

Planned Activities:

- An ORNL-Purdue proposal has been submitted to perform INS measurements on hyper-stoichiometric UO_{2+x} in both the two-phase regime and the disordered high temperature phase. PDOS measurements at the SNS will be used to calibrate and validate a thermodynamic model of the multi-phase material.
- The harmonic and anharmonic contributions to the heat capacity of UO_2 will be determined using PDOS measurements in the temperature range of 77K-1200K.
- A joint ORNL-Purdue-UF investigation of the applicability of the Grüneisen parameter for characterizing anharmonicity in UO_2 will be performed in the context of phonon transport by confronting the perturbation theory predictions with INS measurements of phonon lifetimes.

2.1.2 Thermal Transport Measurements and Simulation

We have continued our work to isolate the role of unit mechanisms on thermal conductivity in UO_2. A portion of this work consists of careful selection of irradiation conditions to introduce either a dislocation loop dominant microstructure or isolated Frenkel pair (i.e., point defect) dominant microstructure. By tuning the thermal diffusion length, the reduction in conductivity in the damage

plateau region caused by light ion irradiation was measured using laser-based thermo-reflectance measurements [7].

For the study of point defects, room temperature irradiations were used. At room temperature, diffusion controlled growth of extended defects is minimized. The reduction in thermal conductivity of polycrystalline UO_2 irradiated with 4 MeV He ions was measured using thermal wave microscopy. The right side of Figure 3 shows a comparison between the measured thermal conductivity and the conductivity obtained from MD simulations. The MD simulations were performed on a series of systems containing residual defects that survive simulations of collision cascades (reported in section 2.1.4). Currently, MD results underestimate the conductivity reduction because the level of defects in the simulated sample is not well defined.

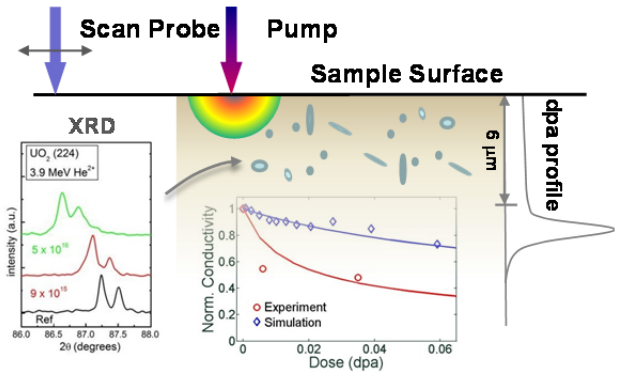

Figure 3. Left: X-ray measurements of lattice expansion in ion-irradiated UO_2. Right: Measurements of the thermal conductivity in the near-surface damage plateau region of 4 MeV He-ion irradiated UO_2.

Completing a study initiated previously [8], we have investigated in detail the influence of irradiation induced dislocation loops on thermal transport in ceria. To retain essentially only dislocation loops, a high temperature irradiation regime was used that promoted loop growth and minimized the concentration of point defects by recombination. Two samples were irradiated at T = 700°C using 1.6 MeV protons. Transmission electron microscopy confirmed that primarily dislocation loops were created using these irradiation conditions. Detailed analysis of the experimental data using the Boltzmann transport framework suggests that dislocation loops are the primary source for the reduction in conductivity at larger damage levels.

For the study of two dimensional defects, the effect of grain boundaries in UO_2 on thermal resistance is being investigated using phonon wave packet dynamics. Results show that at Σ5 twist grain boundaries, acoustic phonons have the dominant role in thermal conductance (~70%). The simulations show further that the energy transmission coefficients of more complex grain boundaries, such as Σ13, show non-monotonic behavior with increasing phonon wave-vector. This behavior is very different from Σ5 boundaries. A simple lattice model has been set up to investigate the source of the difference.

Planned Activities:

- Room temperature thermal transport measurements will be performed on proton irradiated UO_2, Kr irradiated UO_2, and on Kr irradiated and subsequently annealed UO_2 to complete investigations of the impact on thermal transport of individual types of radiation induced defects.
- High temperature (T >600°C) measurement capability will be demonstrated.
- Measurement of the Kapitza resistance across a single grain boundary in UO2 will be performed. This measurement will be coordinated with the UF modeling group to facilitate future modeling efforts.

2.1.3 Phonon Transport Modeling at the Mesoscale

A novel, 3D discretization of the Brillouin zone in UO_2 was carried out as a part of phonon lifetime calculations following the perturbation theory approach. This discretization scheme enabled the use of direction-specific dispersion relations, mode-specific Grüneisen parameters, and an accurate account of the shape of the BZ (truncated octahedron). The total relaxation times for individual phonons were calculated using Matthiessen's rule for the summation of individual contributions from all scattering

processes. Experimental phonon dispersion measurements of UO_2 in high symmetry directions [001], [011] and [111] were employed to model phonon dispersion anisotropy. Phonon lifetimes have been computed for all branches and compared with earlier approximations [9]. These results make thermal conductivity predictions possible using a simple kinetic theory model implemented in terms of the phonon heat capacity, phonon velocities, and phonon lifetimes. The thermal conductivity as a function of phonon branches was found to be consistent with Inelastic Neutron Scattering (INS) determinations.

Planned Activities:

- Implement a new phonon lifetime calculation scheme in the Monte Carlo solution of the BTE to study phonon transport and compare with earlier results.
- Investigate the utility of the Grüneisen parameter appearing in the perturbation theory approximation of phonon lifetime in the context of conductivity calculations by comparing the MC solution with INS results.
- Simulation of phonon transport in UO_2 with point defects and small defect clusters.

2.1.4 Atomic Scale Modeling

To better interpret thermal transport measurements we have investigated new methods to determine the concentration of point defects in ion irradiated UO_2. Two approaches have been used to simulate the lattice expansion of UO_2 as a function of defect concentration using MD. In the first approach, cascade simulations were conducted using primary-knockon-atom (PKA) energies ranging from 2 keV to 100 keV at 300 K. The Basak potential [10] was used for these simulations because we found that it describes defects properties in UO_2 reasonably well [11]. The resulting lattice expansion from cascade damage was found to increase linearly with the total defect concentration. In the second approach, uranium or oxygen Frenkel pairs were created randomly in the system. The U Frenkel pairs generate at least twice the expansion as O Frenkel pairs, indicating that U Frenkel pairs dominate the lattice expansion. As shown in Figure 4, the lattice expansion is almost the same for cascade-induced defects as it is for randomly distributed Frenkel pairs for the same concentration of U Frenkel pairs. This result also predicts that defect clustering in cascades has a negligible effect on lattice expansion as long as they do not form extended defects such as dislocation loops.

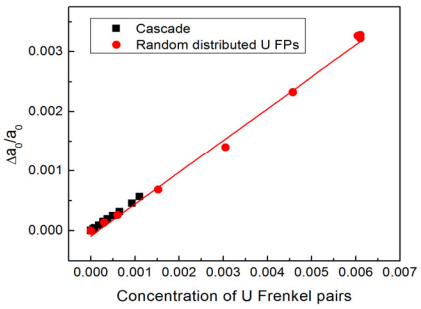

Figure 4. Comparison of lattice expansion simulations for cascade damage and for randomly distributed U Frenkel pairs.

Planned Activities:

- Investigate the degradation of thermal conductivity by isolated uranium and oxygen Frenkel pairs in UO_2 and correlate with cascade simulations, experiments, and kinetic Monte Carlo theory.
- Investigate the structure of oxygen interstitial clusters in hyper-stoichiometric UO_{2+x} by correlating cluster simulations with neutron scattering measurements performed at ORNL.

2.2 Microstructure Science under Irradiation

2.2.1 Irradiation and Characterization Experiments

He^{2+} ion irradiations at low temperature (150–200°C) produced a distinct lattice expansion in XRD and typical low temperature irradiation damage microstructure in TEM. Thermal conductivity of the irradiated layer decreased about 50% as compared to the un-irradiated UO_2 and a Klemens-Callaway model for the thermal conductivity indicated that the reduction was mainly due to point defects. H^+ irradiations at 300°C showed that the blistering limit for UO_2 was much smaller than anticipated (about 1

$\times 10^{18}$ H^+/cm^2). Three damage levels suitable for thermal conductivity measurements were prepared, 0.01, 0.05, and 0.1 DPA. TEM for the damaged regions showed that point defect evolution produced dislocation loops with stacking fault nature (see Figure 5). Further analysis for the thermal conductivity is ongoing.

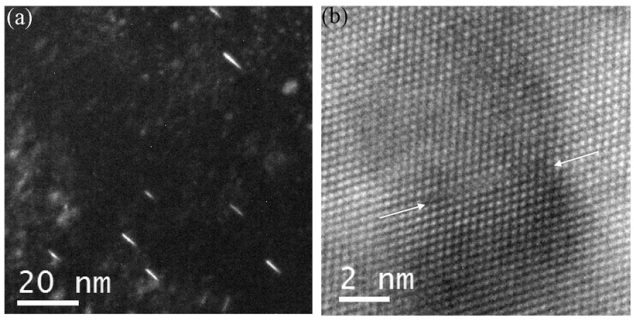

Figure 5. (a) Stacking fault dislocation loops in H^+ irradiated UO_2 imaged using rel-rod contrast in dark field TEM. (b) High-resolution TEM indicating the loops (edge-on at the image) to be of interstitial type.

IVEM *in situ* Kr irradiations for UO_2 showed that defect denuded zones at grain boundaries are not only dependent on the grain boundary character but also dependent on the irradiation temperature. Circular features around 100-200 nm in diameter were found in polycrystalline UO_2 for fluences of 5×10^{16} ions/cm^2 at 600°C. These features may indicate the initial stage of polygonization.

A bubble dominated microstructure for performing thermal transport measurements was developed in 1.8 MeV Kr irradiated UO_2 after high-temperature annealing. Intra-granular bubble sizes increase slightly and bubble densities decrease slightly with increasing annealing temperature. Although bubble spatial distributions follow the Kr depth profile calculated by SRIM, bubbles were found to grow much faster near grain boundaries than in the bulk during annealing as a result of Kr diffusion to the boundaries. Bubble denuded zones appear near grain boundaries after post-irradiation annealing. High-temperature annealing leads to dislocation loop growth and the formation of dislocation segments, which in turn anneal, leading to the formation of dislocation-denuded surface zones. Laser-based thermo-reflectance measurements of the impact of bubbles on thermal transport are in progress.

Planned Activities:

- Grain growth investigations in annealed polycrystalline UO_2 will be completed using EBSD to validate phase field models of grain growth.
- TEM characterization of UO_2 samples irradiated with 1.8 MeV Kr at UIUC will be used to study defect evolution in UO_2 as a function of temperature and dose and to determine the impact on thermal transport.

2.2.2 Atom Probe Tomography Studies

We have performed the first APT analysis of oxide nuclear fuel materials. Due to UO_2's dielectric nature, pulsed ultra-violet laser pulses are required to assist surface evaporation, requiring the optimization of instrument parameters to attain uniform surface evaporation and accurate nanoscale chemical analyses. This study investigated the effect of sample temperature, ion detection rate, and laser energy on the observed stoichiometry, mass resolution, and tip uniformity. Among these parameters, laser energy was found to have the greatest influence on evaporation behavior of UO_2.

We have used APT to study the effect of grain boundary misorientation and post-irradiation annealing on the segregation behavior of Kr ion-irradiated UO_2. Results in Figure 6 indicate that with an increase in temperature, Kr was found to have a propensity to segregate toward grain boundaries and surrounding grain boundary areas. At lower temperatures, Kr was found to segregate only toward grain boundaries and not into the surrounding region, primarily due to the space charge contribution present at lower temperatures in UO_2. APT investigations of the influence of grain boundary structure on the segregation behavior of Kr in UO_2 have shown that only small amounts of Kr are present at low angle grain boundaries (LAGBs) as compared to high angle grain boundaries (HAGBs). This result has been ascribed to the dislocation array structure present at LAGBs because HAGBs contain larger numbers of defects

present the interface and are better able to accommodate Kr. The local chemistry changes near the grain boundaries were too low to infer fuel chemistry changes at grain boundaries reliably in UO_2 by APT.

We have, however, used APT to investigate fuel chemistry changes near voids in UO_2. Due to the detrimental role voids have on thermal conductivity in UO_2, it is important to understand nearby fuel chemistry. In particular, we investigated fuel chemistry changes near voids induced by proton (H^+) irradiation of single crystal UO_2. Evidence so far indicates that the local chemistry does not change greatly near voids, but a slight oxygen deficiency has been observed near voids. These initial results are of interest in connection APT measurements that have been performed near the surface of single crystal UO_2, where we have found the O:U ratio to be slightly greater than 2, i.e., hyper-stoichiometric in nature. These results, for both the planar surface of UO_2 and the near surface of voids are of significance because oxygen stoichiometry is known to decrease thermal conductivity and impact irradiation resistance and reactivity.

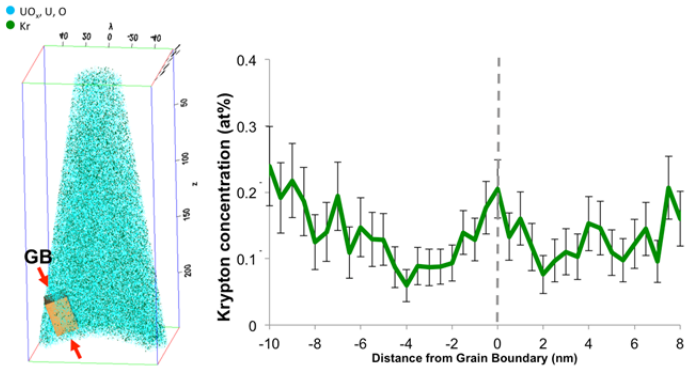

Figure 6. Atom probe reconstruction of Kr irradiated UO_2. The Kr concentration profile on the right indicates both Kr segregation to and depletion near the grain boundary. The depletion zone was further verified with TEM.

Planned Activities:

- Investigations of the effect of intergranular Kr bubbles on grain growth in UO_2 will be completed.
- Studies of diffusion of Kr from matrix defect sites to gas bubbles will be finalized by APT measurements in post-irradiation-annealed samples of proton irradiated UO_2.

2.2.3 Atomic-Scale Simulation of Defects in UO_2

A transferable U-UO_2-O_2 potential has been developed within the COMB3 formalism [2]. This is the first potential that features many-body effects in all possible interactions (U-U, U-O and O-O) combined with the variable charge. The potential was validated by placing an oxygen molecule into bulk uranium metal to observe its expected dissociation and the transition from physisorption to chemisorption. In addition, in a very stringent test of the quality of the potential, oxygen interstitials randomly distributed in uranium metal with U:O ratio of 1:2 were allowed to relax to their energy minima by thermal annealing. After the MD simulation, the system was found to rearrange into the experimentally observed fluorite (see Figure 7) structure. This new potential is now being employed to study defect behavior in U-metal and UO_2.

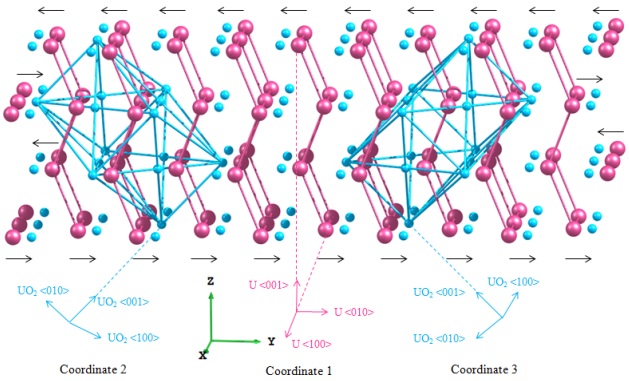

Figure 7. The orientation relation between the orthorhombic α-U and fluorite UO_2. Large purple atoms are U atoms in the original α-U structure under Coordinate 1. As the transformation starts, they move in the <010> direction indicated by a black arrow to become small cyan atoms.

2.2.4 Stoichiometry and Microstructure Evolution in UO_2

We have developed a novel phase-field model for investigating grain growth in porous ceramics. This model has been used to study grain growth in CeO_2, and has now been applied to UO_2. The model showed excellent agreement with experiments in terms of growth exponents (rates), activation energies, and temperature dependence. It also demonstrated that the kinetics of grain growth changes from grain boundary-controlled to pore-controlled with increasing porosity. Although this transition has been used to account for the various growth exponents reported in literature, all of the literature simulations were performed in 2D, which is known to suppress pore breakaway phenomena commonly seen in experiments. We have recently performed 3D simulations showing that our 3D simulations capture the pore breakaway process. In general, basic trends such as the dependence of the growth rates on the pore fraction, and temperature and on the transition from boundary-controlled kinetics to pore-controlled kinetics have been found to be the same in the 3D simulations (see Figure 8); however, growth rates were found to be higher in the 3D simulations. This latter result is consistent with the larger curvature and pore breakaway in the 3D simulations.

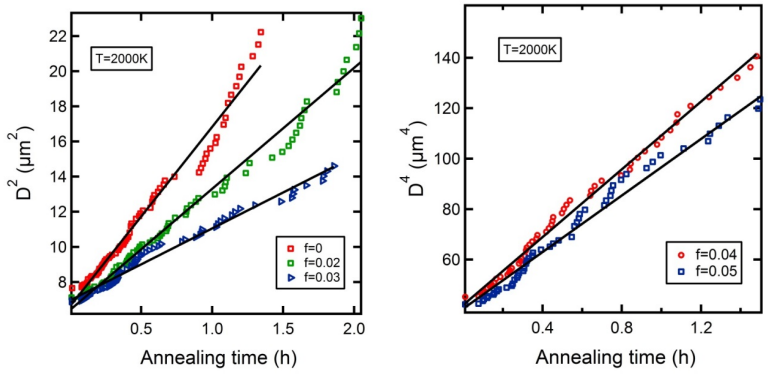

Figure 8. The transition from a boundary-controlled kinetics with exponent of 2 (left) to a pore-controlled kinetics with an exponent of 4 (right) with increasing the amount of porosity during grain growth in UO_2.

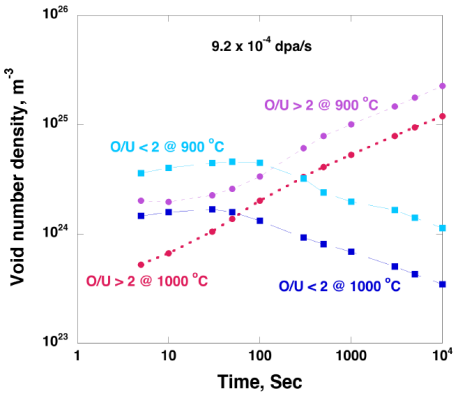

Figure 9. Evolution of hyper- and hypo-stoichiometric vacancy cluster density in UO_2 under irradiation at two different temperatures. Vacancy cluster (void) formation pushes the matric to be hypo-stoichiometric during irradiation.

We have also demonstrated using thermodynamic arguments that phase-field models of type C (i.e., consisting of coupled conserved and non-conserved order parameters) are the most suitable for the problem of void growth in irradiated solids. This is because they are able to take into account the interaction of point defects with the void surface, which influences the kinetics of void growth. Since we developed a sharp-interface model for the void growth in solids under irradiation earlier, the last step in the development of a quantitative phase-field (diffuse-interface) model is to connect the two models using a formal asymptotic analysis based on singular perturbation theory, which is in progress.

We have further developed a novel Cluster Dynamics (CD) model that describes the nucleation and evolution of defect clusters in multi-component systems and we have used this model to predict clustering of vacancies and interstitials into voids and dislocation loops, respectively, in irradiated UO_2. We have found that the model reproduces well a range of experimental measurements on nucleation and growth behavior and their temperature dependences. A very important feature of this model is its ability to predict the off-stoichiometry of defect clusters, allowing, in turn, for the tracking of

off-stoichiometry of the matrix. Preliminary results from this model show that Frenkel defects, as opposed to Schottky defects, dominate the nucleation process in irradiated UO_2. The results in Figure 9 show that under irradiation, vacancy clusters (voids) in stoichiometric UO_2 tend to have both hypo- and hyper-stoichiometric compositions. A hypo- or hyper-stoichiometric cluster composition indicates that the matrix would become off-stoichiometric even if the initial state is perfectly stoichiometric. In order to confirm this finding, we are extending this model to simulate ion irradiation experiments by including the ion species (Xe, Kr, He) as additional defect species that interfere with the dynamics of clustering.

Planned Activities:

- Asymptotic matching of the phase field model of grain growth to its sharp interface counterpart will be used to enable an efficient, quantitative 3D implementation of the approach to void evolution in UO_2 under thermal annealing.
- Asymptotic matching of the phase field model of void growth under irradiation to its sharp interface model will be used to facilitate the simulation of void nucleation under irradiation.
- Extension of the cluster dynamics model to concurrent evolution of loops and voids in irradiated UO_2 will be pursued to couple cluster dynamics with the phase field model above.

2.2.5 Crystal Growth and Sample Preparation

The growth of single-crystal and bi-crystal UO_2 samples for neutron scattering and thermal transport measurements has been pursued through a partnership with the Research and Innovation in Science and Engineering (RISE) Complex at Idaho State University. Figure 10a shows an example of 10-20 gram single crystals extracted from the center of boules as illustrated in Figure 10b, which shows a large central crystal. The crystal growth is by a specially modified float-zone/skull melting method that forms large grain UO_2 cores surrounded by small-grain polycrystalline outer edges. Preliminary results of refinements of the method indicate that single crystal grains up to ~100-200 grams will be possible. Figure 10c is an SEM image of an individual UO_2 grain boundary. The thermal resistance of this boundary will be measured using thermal wave microscopy.

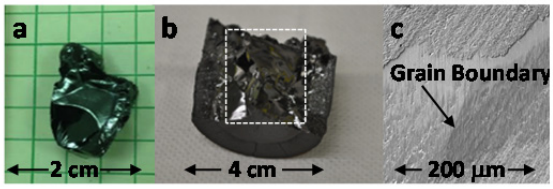

Figure 10. (a) ~15 gram UO_2 single crystal; (b) partially extracted growth boule showing large grain UO_2 central core (dashed outline) prior to removal; (c) Micrograph of an individual grain boundary specially prepared using FIB polishing.

2.3 Education and Outreach

The CMSNF EFRC continues to develop staff through educational efforts. The team routinely co-loans students and team members from different institutions in order to create greater integration and synergy across research tasks. A key outcome is not only to facilitate creative thinking and scientific exchange among team members, but also to provide educational and training opportunities for students and postdocs. To date, students supported under the project are listed in Tables 1 and 3 below.

Table 1. Students and post docs currently involved in the CMSNF.

Name	Location	PI	Status	Project
Yangzhong Li	University of Florida	Phillpot	Ph.D.	Defect evolution using COMB potential for U/UO_2
Bowen Deng	University of Florida	Phillpot	Ph.D.	Thermal transport properties of $Si/SiO_2/Si$ interfaces and grain boundaries in UO_2
Billy Valderrama	University of Florida	Manuel	Ph.D.	Microstructural studies of CeO_2/UO_2 using atom probe
Hunter Henderson	University of Florida	Manuel	Ph.D.	Microstructural studies of CeO_2/UO_2 using atom probe
Philipp Alieninov	University of Florida	Manuel	Ph.D	Microstructural studies of UO_2 using atom probe and EBSD
Mahima Gupta	University of Wisconsin	Allen	Ph.D.	Irradiation and associated microstructural changes
Sarah Khalil	University of Wisconsin	Allen	Ph.D.	Modeling microstructural evolution under irradiation
Lingfeng He	University of Wisconsin	Allen	Post-Doc	Microstructural evolution in irradiated CeO_2 and UO_2
Janne Pakarinen	University of Wisconsin	Allen	Visiting	Microstructural evolution in irradiated CeO_2 and UO_2
Jonathan King	University of Wisconsin	Allen	Undergraduate	Sample preparation at LANL and XPS measurement
Xavier Durawa	University of Wisconsin	Allen	Undergraduate	
Spencer Morris	University of Wisconsin	Allen	Undergraduate	
Karim Ahmed	Purdue	El-Azab	Ph.D.	Phase field modeling of microstructure in UO_2
Abdel-Rahman Hassan	Purdue	El-Azab	Ph.D.	Stoichiometric changes in UO_2 under irradiation
Ahmed Hamed	Purdue	El-Azab	Ph.D.	Monte Carlo simulation of mesoscale phonon transport model
Stephen Taller	INL	Bai	Intern/Graduate	Assessment of structures and stability of defect clusters in UO2 predicted by empirical potentials

3. COST STATUS

The approved budget by period and actual plus trended incurred for the CMSNF is shown in Table 3.

Table 2. Approved budget and actual trended for CMSNF.

CMSNF Project (to Date Funding for FY09 – FY14)	Prior Year Carryover $K (July 31, 2013)	FY-13 Budget $K (through July 31, 2014)	FY-13 Actuals ($K) (based on trend through July 31, 2014)	Expected Carryover into FY-15 (unspent funds)
Allen Oversight/Admin. Package	133.4	772.8	772.8	0.0
Hurley Package	45.1	273.8	273.8	0.0
Gan Package	28.0	65.8	65.8	0.0
University of Wisconsin	31.8	252.8	252.8	0.0
University of Florida	0.0	220.0	220.0	0.0
Florida State University	0.0	0.0	0.0	0.0
Colorado School of Mines	21.9	0.0	0.0	0.0
Purdue University	0.0	220.0	220.0	0.0
INL Planned (through July 31, 2013)	260.2	1,960.2	1,960.2	0.0
Oak Ridge National Lab (allocated directly to ORNL in support of CMSNF)	60.4	360.4	360.4	0.0
Total	320.6	2,320.6	2,320.6	0.0

4. SCHEDULE STATUS

The activities described above are based on the CMSNF roadmap. The CMSNF team developed this roadmap four years ago. It is a living document that is updated at the semiannual project meetings, every 6 months. The roadmap and progress against planned activities is presented to the Advisory Board at its annual meetings. The CMSNF roadmap defines the logical order of implementing the Center's research without specifying fixed dates for the completion of various research tasks.

Our Center has had its most recent meeting with the Advisory Board in August 2013 in Idaho Falls and has had its most recent all-hands meeting in April 2014 at Purdue.

5. CHANGES IN APPROACH

There are no changes in research approach for this reporting period.

6. ACTUAL OR ANTICIPATED PROBLEMS

The Center transitioned from the need for thin film samples to single crystal samples that were not within the expertise of the Colorado School of Mines so it was removed as a member of the Center. A portion of the funding returned has been used to work with Idaho State University to develop the ability to grow large single crystal and bicrystal UO_2 samples. Temperature control issues related to the solidification front that have hindered the growth of large single crystals are currently being addressed.

7. PERSONNEL CHANGES AND/OR LEAVES

Table 3. Individuals that have transitioned from the center, in the last year either graduating and accepting positions with industry or to further pursue educational opportunities within or outside the CMSNF.

Name	Location	PI	Status	Project
Clarrisa Yablinsky	UW	Allen	Post Doc	Research Scientist at Los Alamos National Laboratory
Jianliang Lin	CSM	Lin	PI	Southwest Research Institute
Abdel-Rahman Hassan	Purdue	El-Azab	Ph.D.	Transitioned into the biomedical engineering program at Purdue
Hunter Henderson	UF	Manuel	Ph.D	Post-doctoral research at UF
Sarah Khalil	UW	Allen	Ph.D.	Assistant Professor, Alexandria University

8. PRODUCTS PRODUCED/TECHNOLOGY TRANSFER

8.1 Website

The structure of the current website (http:www.inl.gov/efrc) provides an overview of the Center's five science questions and a detailed explanation of the center's research approach. The website also provides information on team members, a current publication list, collaborations and partnerships, education and outreach information, and upcoming events. The website is continually updated so that new information can be disseminated to the broader research community in a timely manner.

8.2 Networks or Collaborations

1. **ITU:** The Institute for Transuranium Elements (ITU) participates in monthly CMSNF conference calls and is working with CMSNF to identify synergy between the research programs.
2. **Pacific Northwest National Laboratory (PNNL):** Collaborating with Ram Devanathan at PNNL to investigate swift heavy ion damage in CeO_2 and UO_2. Dr. Devanathan has modeled electronic stopping damage under the same conditions that are being performed experimentally by the University of Wisconsin. He is co-authoring a paper with former CMSNF member Dr. Yablinsky.
3. **Los Alamos National Laboratory (LANL):** A collaboration between Dr. Andrew Nelson at LANL and CMSNF has been arranged to provide large-grained, non-stoichiometric UO_2 polycrystals on loan for macroscopic and microscopic thermal transport studies and for neutron PDOS studies.
4. **Idaho State University (ISU):):** A subcontract has been placed with Idaho State University with the goal of providing access to large, single-crystal samples of UO_2.
5. **Boise State University (BSU):** Dr. Janne Pakarinen of the University of Wisconsin and Dr. El-Azab of Purdue have collaborated with Dr. Darryl Butt of Boise State University to conduct grain growth experiments of U_{O2} in controlled oxygen environment and on the modeling of the growth process and effect of oxygen on its kinetics.
6. **National Research Council Canada (NRC):** Retired principal research officer, Dr. William Buyer, has continued collaborations with Dr. Pang and Dr. Larson on the study of phonons in UO_2 using neutron scattering (see section 10) of report for letter of support.

8.3 Technologies/Techniques Developed

8.3.1 Enhanced Capability

Phonon Transport Simulator (PhonTS) code has been developed at the University of Florida and is now available to the wider scientific community. It can be downloaded from http://phonts.mse.ufl.edu and performs lattice thermal conductivity calculations via solution of the BTE by a number of different approaches. It is distributed with an extensive manual, examples of applications and contains a wide selection of classical potentials, as well as interfaces to first principles, third-party codes. It is written in Fortran90, fully parallel, and driven by a single, simple, free-style input file. PhonTS has already being requested by a number of research groups.

As a part of the computational modeling of phonon transport in UO_2 single crystals, a robust MC solution scheme for BTE has been developed that extends beyond previous work of this nature in the literature. A parallel C++ code has been developed at Purdue based on this MC scheme. The code is being enhanced by including 3D representations of the Brillouin zone to provide an accurate representation of phonon-phonon scattering events. When fully tested, the intent is to provide this as a standard code for MC simulation of phonon transport in complex crystals for the scientific community.

A systematic study of APT run parameters was performed and a publication is currently under review. It was determined that the laser pulse evaporation behavior of UO_2 during APT measurements is more sensitive to laser energy than other parameters such as the temperature and the evaporation rate. These results are being disseminated in peer reviewed publications and the mass spectrum is being distributed to other researchers interested in studying nuclear fuels using APT.

8.4 Inventions/Patent

None.

8.5 Other Products

8.5.1 Conference Presentations and Other Non-refereed Publications

- A. Chernatynskiy and S. Phillpot, “Thermal transport in uranium dioxide from first principles,” invited presentation, *International Fuel Performance Working Meeting*, Imperial College London, March 2013.
- M. Khafizov, M. Gupta, J. Pakarinen, C. Yablinsky, L. He, B. Valderamma, M. Manuel, J. Gan, T. Allen, and D. Hurley, “Measurement of Thermal Conductivity in Ion Irradiated Materials,” *2013 MRS Spring Meeting*, San Francisco, CA, April 2013.
- A. Chernatynskiy and S. Phillpot, “Engineering Microstructure for Low Thermal Conductivity,” *2013 MRS Spring Meeting*, San Francisco, CA April 2013.
- A. El-Azab and A.-R. Hassan, “Defect disorder and electrochemical effects of voids in UO2,” *Energy Frontier Research Centers Principal Investigators’ Meeting*, Washington, D.C., July 18-19, 2013.
- L. He, M. Gupta, B. Valderrama, H. Henderson, A.-R. Hassan, J. Pakarinen, J. Gan, M. Kirk, M. Manuel, A. El-Azab, and T. Allen, “Microstructural Investigations of Kr and Xe Irradiated UO_2,” *Energy Frontier Research Centers Principal Investigators’ Meeting*, Washington D.C., July 18-19, 2013.
- B. Valderrama, H. Henderson, L. He, C. Yablinsky, J. Gan, A.-R. Hassan, A. El-Azab, T. Allen, and M. Manuel, “Fission Products in Nuclear Fuel: Comparison of Simulated Distribution with Correlative Characterization Techniques,” *Microscopy and Microanalysis 2013*, Indianapolis, IN, August 4-8, 2013.

- B. Valderrama, H. Henderson, L. He, T. Allen, and M. Manuel, "Comparison of Computationally Simulated Fission Product Distribution with Correlative Characterization Techniques in Surrogate Nuclear Fuel Materials," *2013 SACNAS National Conference*, San Antonio, TX, October 2-6, 2013.
- A. El-Azab and R. Deskins, "Monte Carlo simulation of phonon transport in UO2 crystals with defects," *MMSNF Workshop - Materials Modeling and Simulation for Nuclear Fuels*, October 14-16, 2013, Chicago, Illinois USA
- A. El-Azab, "Continuum theory of defects and materials response to irradiation," *MMSNF Workshop - Materials Modeling and Simulation for Nuclear Fuels*, October 14-16, 2013, Chicago, Illinois USA
- A.-R. Hassan, T. Allen, and A. El-Azab, "Defect disorder and electrochemical effects of voids in UO2," *MMSNF Workshop - Materials Modeling and Simulation for Nuclear Fuels*, October 14-16, 2013, Chicago, Illinois USA
- K. Ahmed, J. Pakarinen, T. Allen, and A. El-Azab, "Phase field modelling of grain growth in porous ceria and uranium dioxide," *MMSNF Workshop - Materials Modeling and Simulation for Nuclear Fuels*, October 14-16, 2013, Chicago, Illinois USAB.
- B.Valderrama, H. Henderson, A.-R. Hassan, J. Gan, A. El-Azab, and M. Manuel, "Characterization of Oxide Fuel Surface Chemistry with Atom Probe Tomography," *2013 ANS Winter Meeting*, Washington, D.C., November 10-14, 2013.
- J. Pang, "Investigations of Phonon Properties and Thermal Transport of UO2 by Inelastic Neutron Scattering and First-Principles Simulations," invited presentation, *2013 Fall MRS Meeting*, Boston, MA, December 1-6, 2013.
- M. Khafizov, J. Pakarinen, L. He, A. Chernatynskiy, J. Gan, S. Phillpot, T. Allen, and D. Hurley, "Influence of Radiation Induced Microstructure on Thermal Transport In Ceramic Materials," *2013 Fall MRS Meeting*, Boston, MA, December 1-6, 2013.
- J. Yu, X-M. Bai, A. El-Azab, and T. Allen, "Influence of Temperature on Oxygen Clustering Dynamics in UO2," *2013 Fall MRS Meeting*, Boston, MA, December 1-6, 2013.
- A. Chernatynskiy, B. Deng, and S. Phillpot, "Role of Microstructure on Thermal Transport in UO_2 from Atomic-level Simulation," invited presentation, *2013 Fall MRS Meeting*, Boston, MA, December 1-6, 2013.
- D. Hurley, M. Khafizov, R. Kennedy, and E. Burgett, "Mechanical Properties of Nuclear Fuel Surrogates using Picosecond Laser Ultrasonics," in *Proceedings of the 2013 International Congress on Ultrasonics*, 686 (2013).
- D. Hurley, E. Piekos, and S. Shinde, "Interaction of Thermal Phonons with Interfaces," book chapter, *Length-Scale Dependent Phonon Interactions* (pp 175-205), Springer, (2013).
- B. Wu and J. Yu, "From Used Oxide Nuclear Fuel to Rechargeable Battery: A First-Principles Study," *Mater. Res. Soc. Symp. Proc.* (DOI: 10.1557/opl.2013).
- B. Valderrama, H. Henderson, L. He, J. Pakarinen, J. Gan, T. Allen, and M. Manuel, "Nano-scale Irradiation Induced Chemistry Variation in Oxide Fuel Materials," *TMS 2014 Annual Meeting & Exhibition*, San Diego, CA, February 16-20, 2014.
- L. He, B. Valderrama, M. Gupta, J. Pakarinen, J. Gan, M. Kirk, A. Nelson, M. Manuel, and T. Allen, "Radiation Effects in UO_2," *TMS 2014 Annual Meeting & Exhibition*, San Diego, CA, February 16-20, 2014.
- L. He, J. Pakarinen, M. Gupta, J. Gan, Y. Wang, M. Kirk, and T. Allen, "Kr and Xe Bubbles in CeO_2," *TMS 2014 Annual Meeting & Exhibition*, San Diego, CA, February 16-20, 2014.

- M. Gupta, J. Pakarinen, S. Conradson, J. Terry, L. He, J. Gan, A. Nelson, and T. Allen, "Damage Structure Evolution in Ion Irradiated UO_2," *TMS 2014 Annual Meeting & Exhibition*, San Diego, CA, February 16-20, 2014.
- J. Pang, A. Chernatynsky, W. Buyers, B. Larson, and S. Phillpot, "Understanding Nuclear Fuel Thermal Conductivity from Phonons in UO2": invited presentation, *TMS 2014 Annual Meeting and Exhibition*. San Diego, CA, February 16-20, 2014.
- X. Bai, J. Yu, A. Chernatynskiy, J. Pakarinen, M. Khafizov, S. Taller, A. El-Azab, T. Allen, "Multiscale Modeling of Defect Production and Clustering in UO2," invited presentation, *2014 MRS Spring Meeting*, San Francisco, CA, April 22-25, 2014.
- J. Yu, X-M. Bai, A. El-Azab, and T. Allen, "Density Functional Theory Calculations of the Structure of Oxygen Interstitials and Electron Localization in UO2+x," *2014 MRS Spring Meeting*, San Francisco, CA, April 22-25, 2014.

8.5.2 Semi-annual Meeting

Purdue University hosted the semi-annual meeting of the EFRC in West La Fayette, Indiana on April 10-11, 2014. The focus of the meeting was to evaluate progress to date and to ensure that team members had a clear understanding of the tasks to be completed by the end of the contract, including planned publications.

8.5.3 Service

Advisory Board and Committees

1. El-Azab: Advisory Board Member, 7th International Conference on Multiscale Modeling of Materials (MMM-14), Berkeley, California, USA, October 6-10, 2014
2. El-Azab: Advisory Board Member, CyberInfrastructure for Atomistic Materials Science (CAMS) Center, University of Florida, Gainesville (cams.mse.ufl.edu).
3. El-Azab: Member, Local Organizing Committee, 51st SES Annual Technical Meeting, Purdue University, October 1-3, 2014
4. Allen: University of Florida Nuclear Engineering Program in the Materials Science and Engineering Department
5. Allen: North Carolina State University Nuclear Engineering Department
6. Allen: University of Michigan Nuclear Engineering Department
7. Phillpot: Materials Science and Technology Division, American Nuclear Society, Executive Committee Member 2012 – present
8. Phillpot: Nuclear Engineering Program, University of Florida, Director, 2011 – present
9. Phillpot: Department of Materials Science and Engineering, University of Florida, Cahir, 2010 – present

Editorial Board

10. El-Azab: Editor-in-Chief, *International Journal of Advance Innovations*, *Thoughts & Ideas,* (2013-present)
11. El-Azab: Editorial Board Member, *Journal of Nuclear Energy Science & Power Generation Technology,* (2012-present)
12. El-Azab: Editorial Board Member, *Journal of Materials Science and Chemical Engineering,* (2013-present)

13. Phillpot: Associate Editor, *Journal of Applied Physics*, 1993-present
14. Phillpot: Editorial Board, *Annual Review of Materials Research*, 2010-present
15. Phillpot: Editorial Board, *Current Opinions in Solid State and Materials Science*, 2012-present
16. Phillpot: Editorial Board, *Journal of Nuclear Materials*, 2012-present
17. Phillpot: Member of Board of Reviewing Editors, *Science*, 2009-2013
18. Allen: *Journal of Nuclear Materials*, 2012-present

Conference Symposium Organization

19. Allen: *TMS 2014 Annual Meeting & Exhibition,* "Accelerated Materials Evaluation for Nuclear Applications Utilizing Test Reactors, Ion Beam Facilities and Modeling Radiation Effects in Oxide Ceramics and Novel LWR Fuels"
20. Bai, Manuel and Allen: *TMS 2014 Annual Meeting & Exhibition*, "Radiation Effects in Oxide Ceramics and Novel LWR Fuels – Experimental Characterization of Radiation Effects in Oxide Ceramics"
21. Yu: *2014 MRS Spring Meeting*, "Materials Behavior under Extreme Irradiation, Stress or Temperature"
22. Hurley: *2013 Fall MRS Meeting,* "Symposium UU: Phonon-Interaction-Based Material Design – Theory, Experiments and Applications," Boston, MA
23. El-Azab: Lead Organizer, Symposium G, *7th International Conference on Multiscale Materials Modeling*, "Microstructure Complexity and Self-Organization in Materials- in Honoring Ladislas Kubin," Berkeley, California, October 6-10, 2014, (Co-organizers, Benoit Devincre, Michael Zaiser, Pascal Bellon, James Belak)
24. El-Azab: Co-organizer, *51st SES Annual Technical Meeting,* "Mesoscale Mechanics of Materials Symposium," Purdue University, October 1-3, 2014 (Co-organizers, Ghadir Haikal and Marisol Koslowski)
25. El-Azab: Co-organizers, *Materials Science and Engineering Congress*, "Atomistic to Mesoscale Modeling and Characterization of Materials for Energy Applications," Darmstadt, Germany, September 23-25, 2014 , (Co-organizer, M.H. Braga)

9. REFERENCES

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[3] Ahmed, Karim, Janne Pakarinen, Todd R. Allen, and Anter El-Azab, "Phase Field Simulation of Grain Growth in Porous Uranium Dioxide," *Journal of Nuclear Materials*, 446, Issues 1-3, 90-99 (2014). [10.1016/j.jnucmat.2013.11.036]

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10. LETTER OF SUPPORT

National Research Council Canada
Conseil national de recherches Canada
Canadian Neutron Beam Centre
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NRC·CNRC

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To: Dr. Todd R. Allen, Director,
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Idaho Nuclear Laboratory
2525 Fremont Avenue
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From: Dr. William J.L. Buyers, O.C., D.Sc. (Hon.), F.R.S.C., F.Inst.P.

Letter of Support for EFRC Research into Thermal Conductivity of UO_2

As a retired Principal Research Officer of the National Research Council of Canada (NRC), I am currently affiliated with the NRC Canadian Neutron Beam Centre, located at Chalk River Laboratories, where I am a Guest Scientist. I contribute my knowledge and know-how to an NRC program of experimental and theoretical research on the basic properties of materials. This research has no intended military or commercial applications.

To support NRC's research program in the basic properties of materials, I regularly travel to perform research in other countries. Such activity is an open collaboration between researchers, addressing the scientific goals of NRC as well as the institutions I visit, with no commercial implications. I am independently and fully funded by a pension from the Government of Canada. I receive no salary from any organization or laboratory in the United States.

The project on thermal conductivity of oxide fuels is of considerable interest to my personal research program. It is also of interest to NRC since the first measurements of phonon energies in uranium dioxide were carried out with neutron inelastic scattering at Chalk River Laboratories as early as 1965. Despite this pioneering start, the transport of heat has never been measured in a microscopic way for each phonon, the quantum of lattice vibration. Development of this new quantum method is what I and my Oak Ridge collaborators have brought to the achievement of the EFRC goal. The EFRC mission requires specific knowledge of the technology of extracting the phonon lifetime from very high resolution neutron scattering measurements. I have

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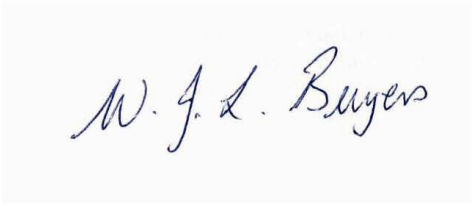
considerable experience dating from the sixties in experimental phonon methods to determine anharmonic phonon collisions.

I have loaned a high-quality, massive single crystal of depleted uranium dioxide to my Oak Ridge collaborators for the work of the EFRC. In this way we were able to make an early start to a key part of the EFRC program focused on how thermal transport is limited by anharmonic phonon collisions. Definitive results, now published in the high impact journal Physical Review Letters, have enabled a direct comparison with ambitious but untested theoretical approaches. Our findings have revealed important weaknesses in current theory, and have pointed the way in which the theory should be improved. Our results provide the first comprehensive benchmark against which future theories maybe tested.

The EFRC program on thermal conductivity was not only needed for a thorough understanding of energy production with its broad benefits, but also presented a challenge requiring development of a new method. The research is of personal interest to me, and I have excellent collaborators to work with at MST, HFIR and SNS at ORNL. I have travelled to Oak Ridge National Laboratory several times since the EFRC began in order to participate in experiments at the HFIR and the SNS. I intend to continue my active participation as required.

I require no salary or fee, but expect to receive appropriate recognition of my scientific contribution in disseminated documents.



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