

Recent Advancements in *In situ* TEM Capabilities Applied to Extreme Environments Including the Synthesis of Surrogate Nuclear Fuel Nanosystems

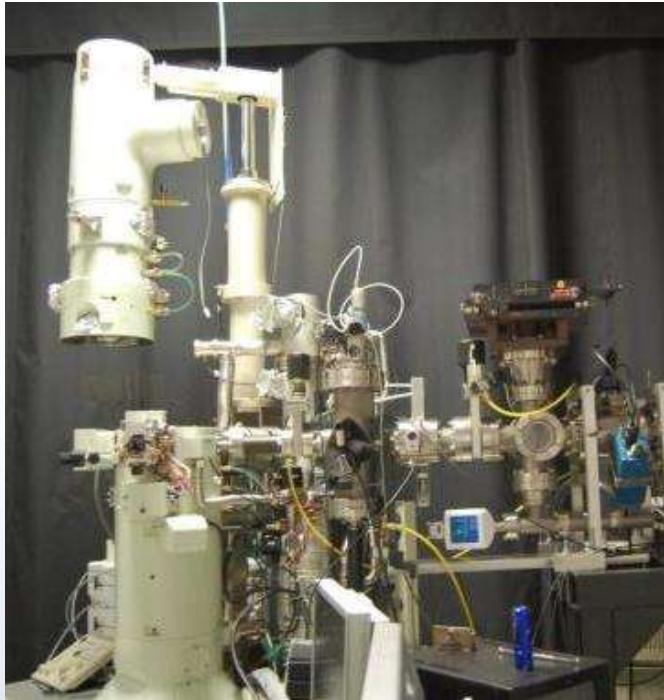
SAND2013-10155C

K. Hattar, S.H. Pratt, and T.M. Nenoff

Ion Beam Lab

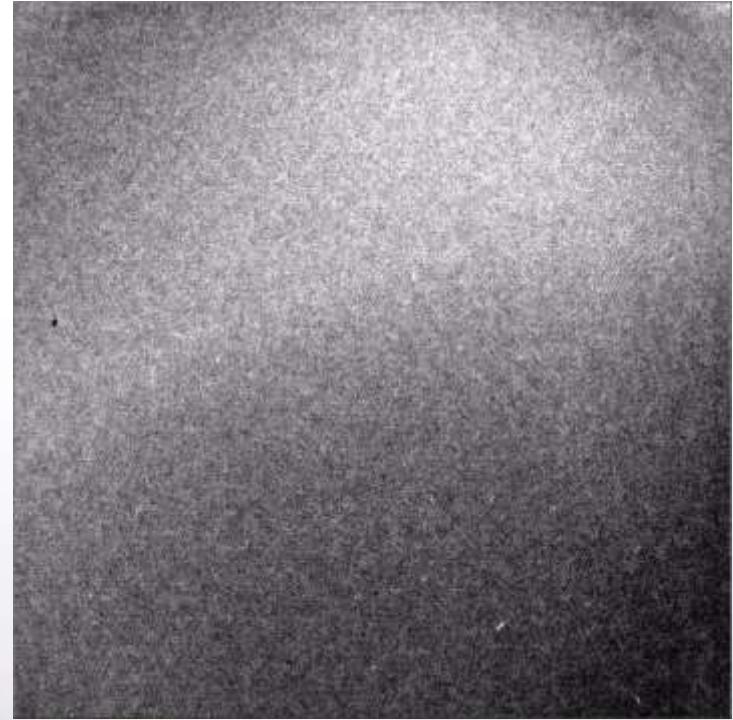
Sandia National Laboratories

December 5, 2013



In situ ion
Irradiation TEM is
operational, while
still in development
it is providing
experimental
insight

Collaborators:



D. Buller, J.A. Scott, D. Masiel, N. Li, A. Misra, B.A. Hernandez-Sanchez, T.J. Boyle, J. Sharon, B. L. Boyce,
C. Chisholm, A.M. Minor, D. Sasaki, B.G. Clark, D. Gross, J. Kacher, P.J. Cappillino, B.W. Jacobs, L.R.
Parent, I. Arslan, M.A. Hekmaty, D.B. Robinson, & I.M. Robertson



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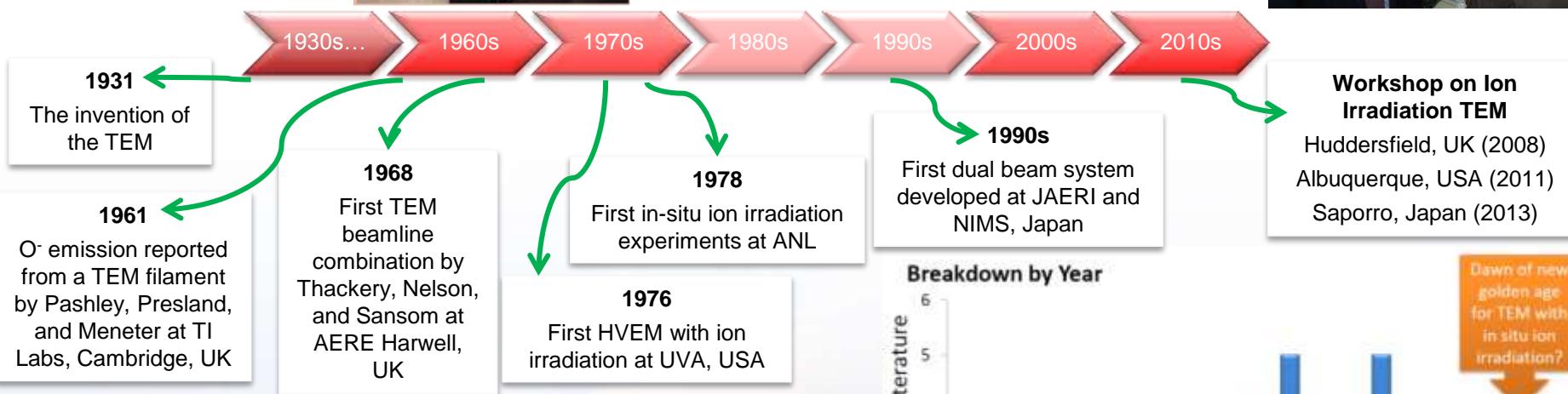


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History of *In situ* Ion Irradiation TEM



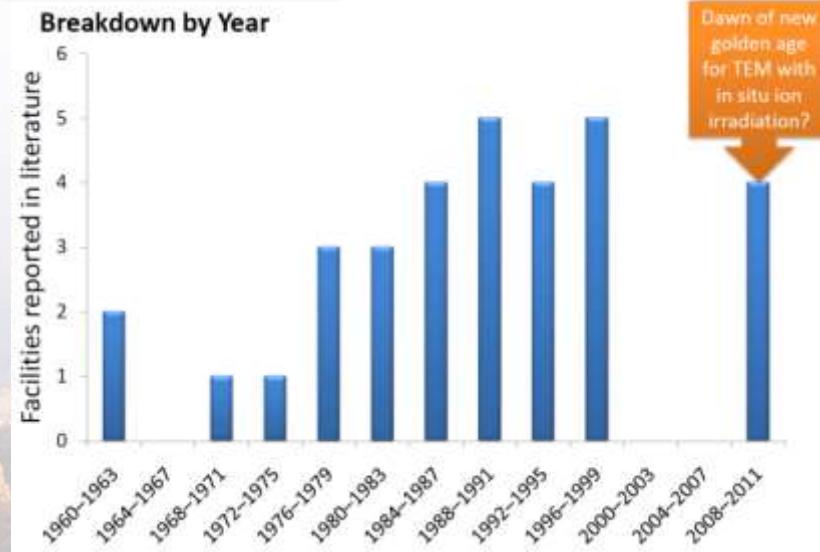
Courtesy of: J. Hinks



“The direct observation of ion damage in the electron microscope thus represents a powerful means of studying radiation damage”



D.W. Pashley and A.E.B. Presland Phil Mag. 6(68) 1961 p. 1003



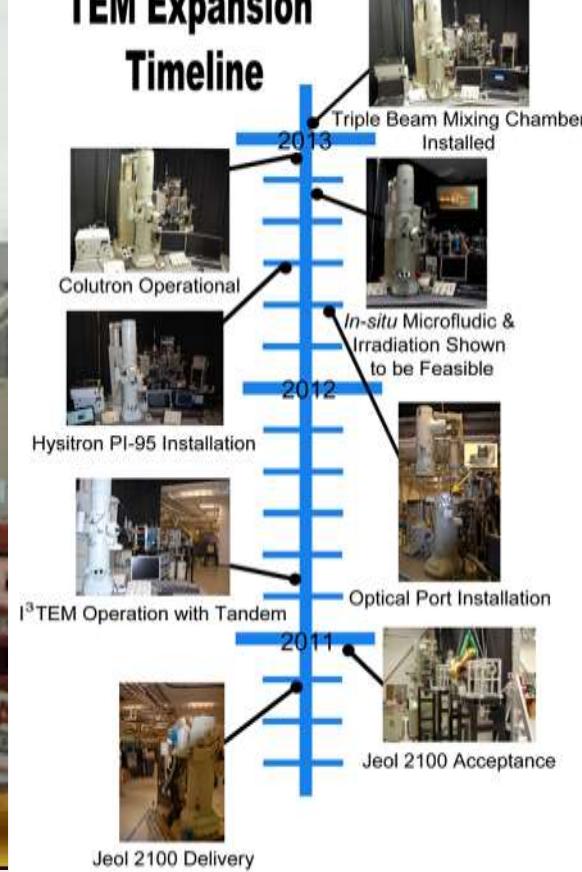
Dawn of new golden age for TEM with in situ ion irradiation?



I^3 TEM History at the Ion Beam Lab



TEM Expansion Timeline



Current Status of the *In situ* TEM Beamlne

Collaborators: D.L. Buller & J.A. Scott



Beam burn from
14 MeV Si

Gas Heating TEM
Stage Controls

Microfluidic TEM
Stage Controls

Double tilt stage
needs to tilt only
12°

10 kV
Colutron

6 MV
Tandem

Pre-TEM Coupon
Irradiation Chamber

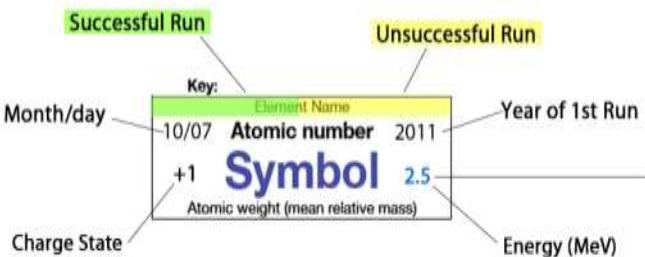
Bending
Magnet to
Mix Beams

Quantitative
Mechanical
Testing
TEM Stage
Controls

I^3 TEM is operational,
but also still in development

Ion Species Attempted as of 7/23/2013

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
Hydrogen 10/7 1 2011 1+ H 2.5 1.008																	Helium 4/18 2 2011 1+ He 2.01 4.0026		
Lithium 3 Li 6.94	Beryllium 4 Be 9.0122																		
Sodium 11 Na 22.990	Magnesium 12 Mg 24.305																		
Potassium 19 K 39.098	Calcium 20 Ca 40.078(4)																		
Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62																		
Caesium 55 Cs 132.91	Barium 56 Ba 137.33	57-70	*	Lutetium 71 Lu 174.97	Hafnium 72 Hf 178.40(2)	Tantalum 73 Ta 180.95	Tungsten 62/74 102 W 183.84	Rhenium 75 Re 186.21	Osmium 76 Os 100.23(2)	Iridium 77 Ir 102.22	Platinum 78 Pt 105.08	Gold 79 Au 106.97 65	Mercury 80 Hg 200.59	Thallium 81 Tl 204.38	Lead 82 Pb 207.2	Bismuth 83 Bi 208.98	Polonium 84 Po [208.08]	Astatine 85 At [200.90]	Radon 86 Rn [222.02]
Francium 87 Fr [223.02]	Radium 88 Ra [226.03]	89-102 **		Lawrencium 103 Lr [262.11]	Rutherfordium 104 Rf [265.12]	Dubnium 105 Db [268.13]	Seaborgium 106 Sg [271.13]	Bohrium 107 Bh [270]	Hassium 108 Hs [277.15]	Meitnerium 109 Mt [276.15]	Darmstadtium 110 Ds [281.16]	Roentgenium 111 Rg [280.16]	Copernicium 112 Cn [285.17]	Ununtrium 113 Uut [284.18]	Flerovium 114 Fl [289.19]	Ununpentium 115 Uup [288.19]	Livermorium 116 Lv [293]	Ununseptium 117 Uus [294]	Ununoctium 118 Uuo [294]



Hydrogen 10/7 1 2011 1+ H 2.5 1.008	Boron 7/30 5 2013 2+ B 2 10.81	Carbon 7/08 6 2013 1+ C 1 12.011	Nitrogen 7/30 8 2013 2+ N 3 14.007	Oxygen 7/30 8 2013 2+ O 3 15.999	Fluorine 18.998 9 Neon 20.180														
Lithium 3 Li 6.94	Magnesium 12 Mg 24.305	Scandium 21 Sc 44.956	Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.038	Iron 26 Fe 55.845(2)	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546(3)	Zinc 30 Zn 65.38(2)	Gallium 31 Ga 69.723	Silicon 32 Si 28.085 5.5	Phosphorus 33 P 30.974	Sulfur 34 S 32.06	Chlorine 35 Cl 35.45	Argon 36 Ar 39.948		
Sodium 11 Na 22.990	Magnesium 12 Mg 24.305	Zirconium 39 Y 88.906	Niobium 40 Zr 91.224(2)	Molybdenum 41 Nb 92.006(2)	Technetium 42 Mo 95.06(2)	Ruthenium 43 Tc [97.01]	Ruthenium 44 Ru 101.07(2)	Rhodium 45 Rh 102.91	Rhodium 46 Pd 106.42	Silver 47 Ag 107.87	Palladium 48 Cd 112.41	Silver 49 In 114.82	Gold 50 Ag 118.71	Indium 51 In 121.76	Antimony 52 Sb 127.60(3)	Tellurium 53 Te 126.00	Iodine 54 I 131.29	Krypton 55 Kr 83.798(2)	
Potassium 19 K 39.098	Calcium 20 Ca 40.078(4)	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224(2)	Niobium 41 Nb 92.006(2)	Molybdenum 42 Mo 95.06(2)	Technetium 43 Tc [97.01]	Ruthenium 44 Ru 101.07(2)	Ruthenium 45 Rh 102.91	Rhodium 46 Pd 106.42	Silver 47 Ag 107.87	Ruthenium 48 Cd 112.41	Silver 49 In 114.82	Gold 50 Ag 118.71	Indium 51 In 121.76	Antimony 52 Sb 127.60(3)	Tellurium 53 Te 126.00	Iodine 54 I 131.29	Krypton 55 Kr 83.798(2)	
Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224(2)	Niobium 41 Nb 92.006(2)	Molybdenum 42 Mo 95.06(2)	Technetium 43 Tc [97.01]	Ruthenium 44 Ru 101.07(2)	Ruthenium 45 Rh 102.91	Rhodium 46 Pd 106.42	Silver 47 Ag 107.87	Ruthenium 48 Cd 112.41	Silver 49 In 114.82	Gold 50 Ag 118.71	Indium 51 In 121.76	Antimony 52 Sb 127.60(3)	Tellurium 53 Te 126.00	Iodine 54 I 131.29	Krypton 55 Kr 83.798(2)	
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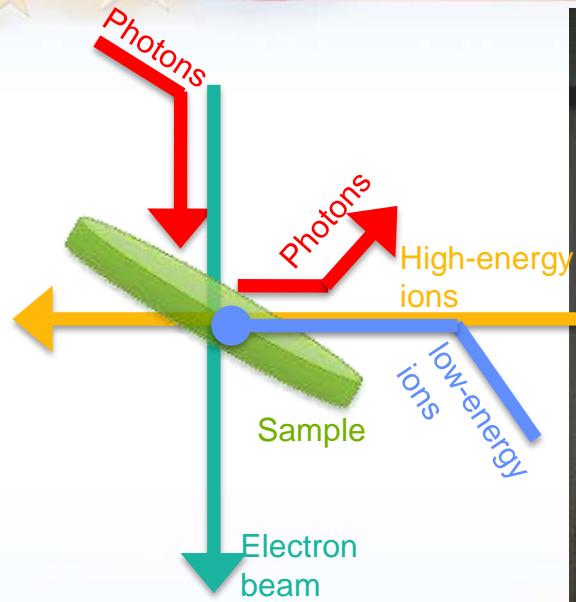
Lanthanum 57 La 138.91	Cerium 58 Ce 140.12	Praseodymium 59 Pr 140.91	Neodymium 60 Nd 144.24	Promethium 61 Pm [144.91]	Samarium 62 Sm 150.36(2)	Europium 63 Eu 151.96	Gadolinium 64 Gd 157.25(3)	Terbium 65 Tb 158.93	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.03	Erbium 68 Er 167.26	Thulium 69 Tm 168.93	Ytterbium 70 Yb 173.05
Actinium 89 Ac [227.03]	Thorium 90 Th 232.04	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Neptunium 93 Np [237.06]	Plutonium 94 Pu [244.06]	Americium 95 Am [243.06]	Curium 96 Cm [247.07]	Berkelium 97 Bk [247.07]	Californium 98 Cf [251.08]	Einsteinium 99 Es [252.08]	Fermium 100 Fm [257.10]	Mendelevium 101 Md [258.10]	Nobelium 102 No [259.10]

*lanthanoids

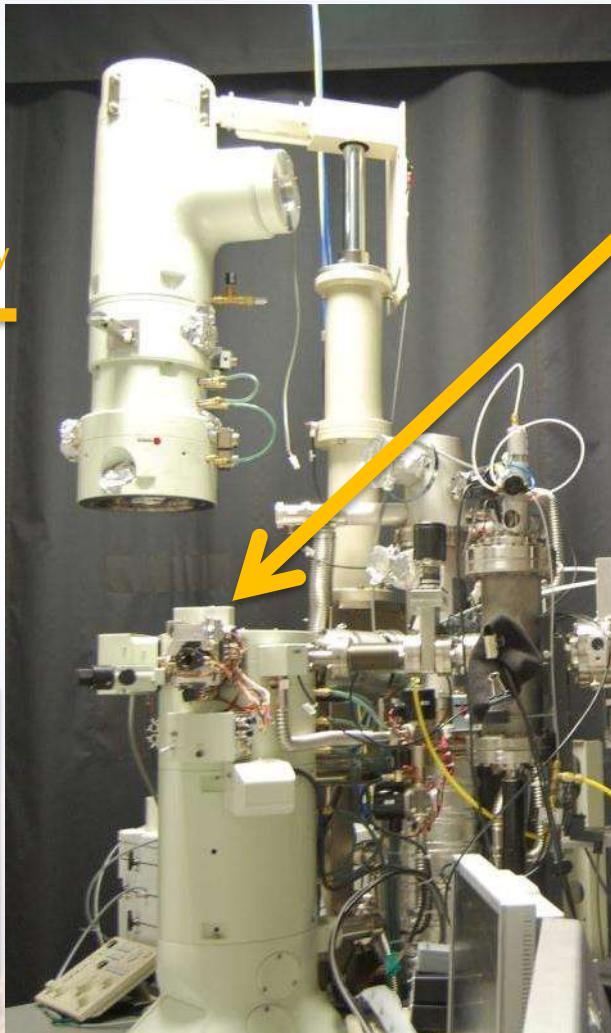
**actinoids

In situ TEM Luminescence

Collaborators: D. Masiel, D. Buller, and C. Chisholm



Two optical port were added to the I³TEM already containing a electron beam and two ion beams, which permits *in situ* TEM luminescence studies



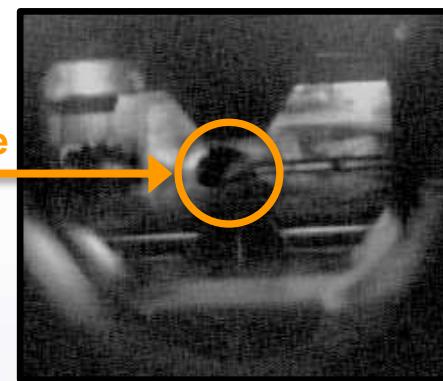
Optical Mirror in TEM



First IBIL in TEM



Sample



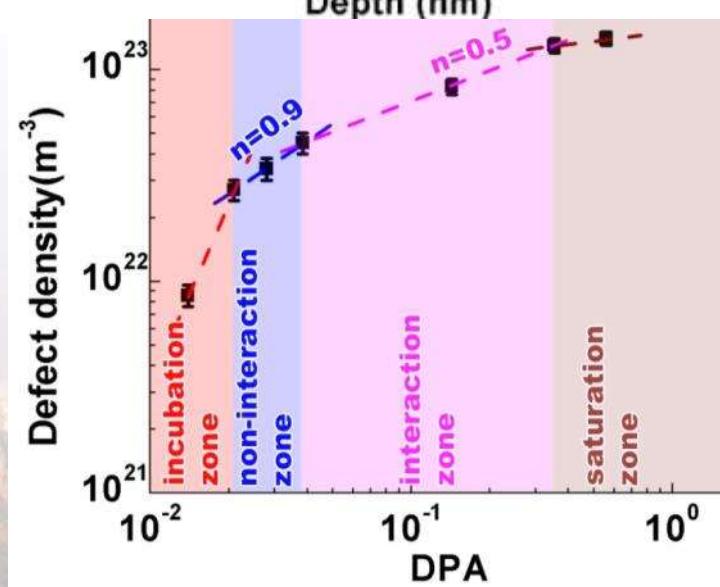
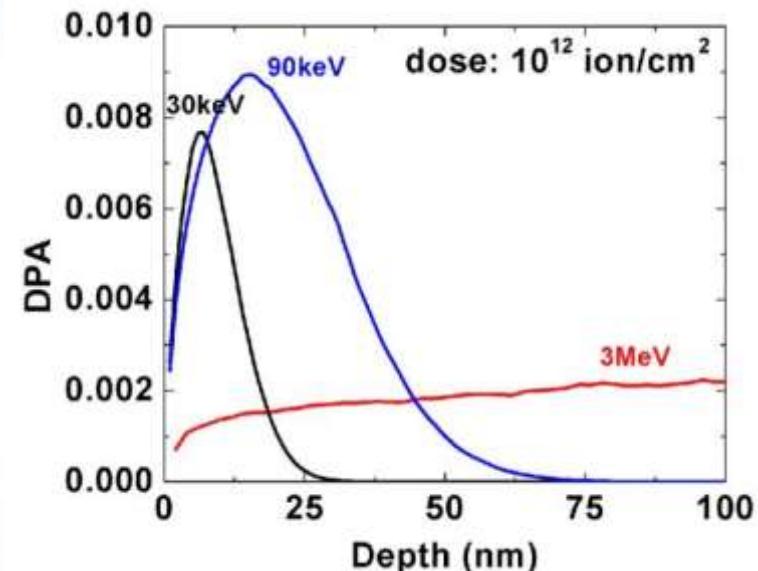
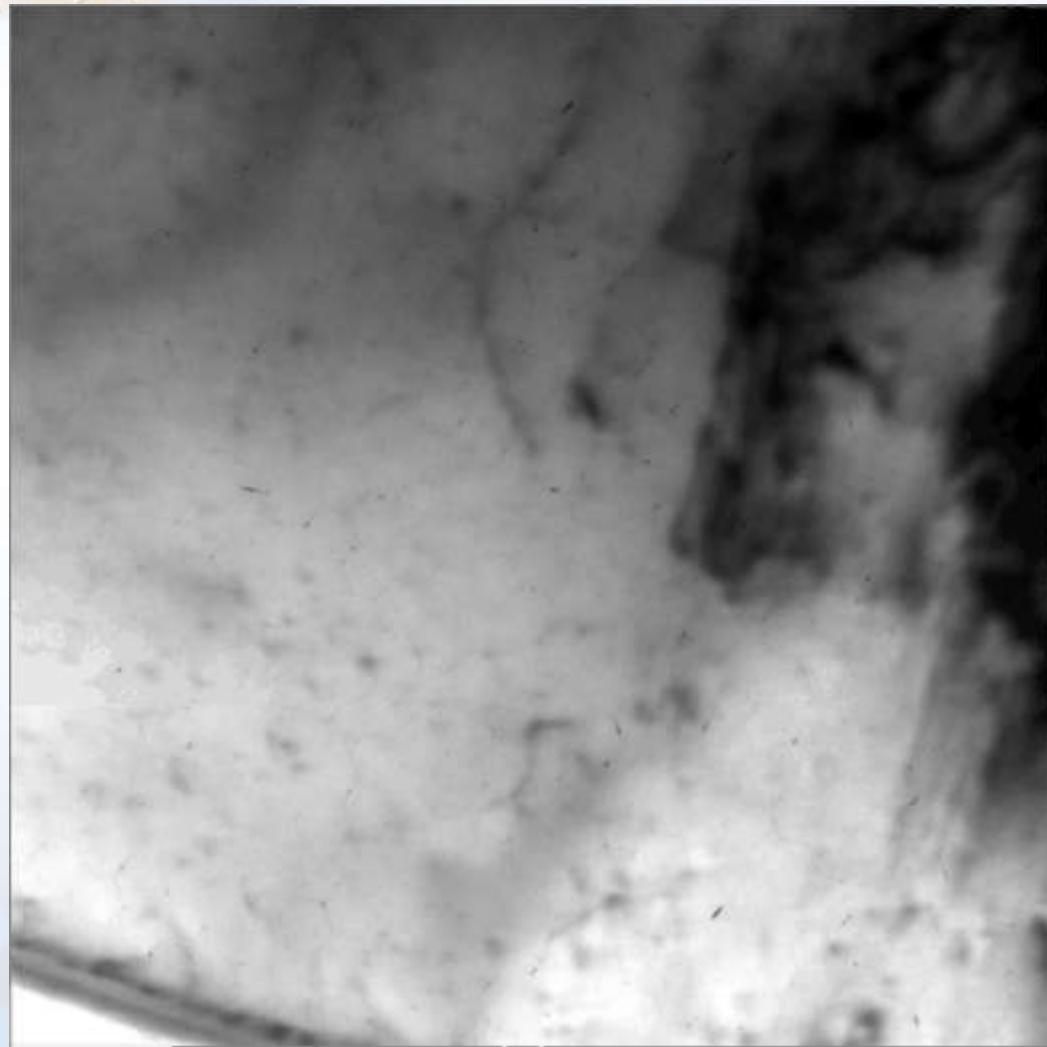
Optical Pathway in an I³TEM

- Angled mirror with bore hole for the electron path was installed above the polepiece
- Another mirror is located just above the ion beams in the beamline
- Two perspective of the sample are possible
- Permits *in situ* IBIL and CL.





Quantifying Defect Evolution

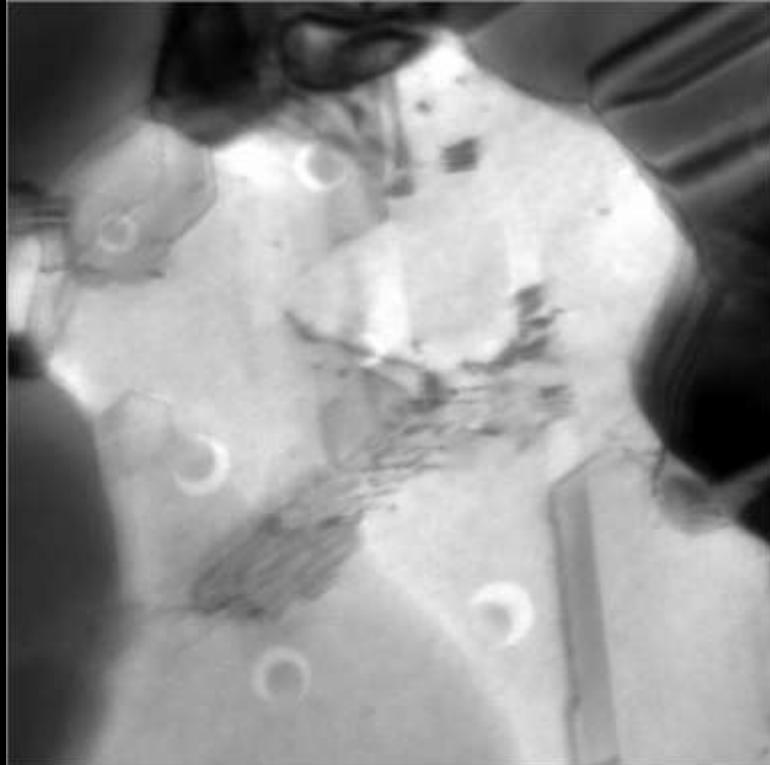




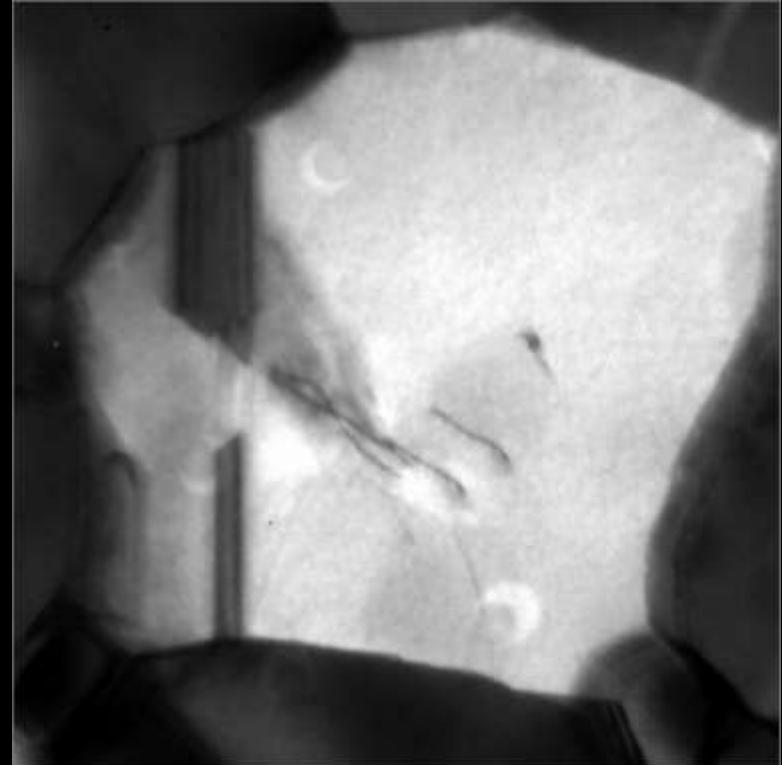
Single Ion Strikes

Collaborators: C. Chisholm & A. Minor

7.9×10^9 ions/cm²/s



6.7×10^7 ions/cm²/s



VS

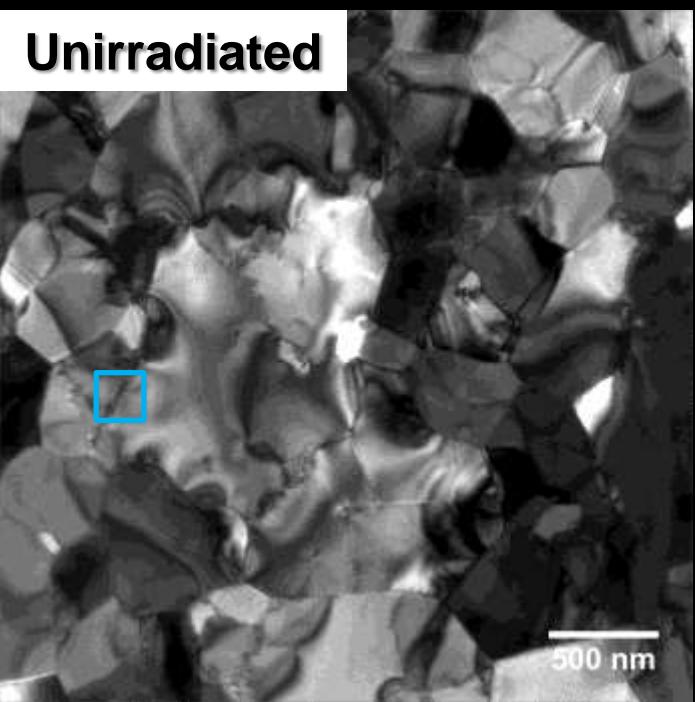
Improved vibrational and ion beam stability permits us to work at 120kx or higher permitting imaging of single cascade events



In situ Implantation

Collaborators: C. Chisholm & A. Minor

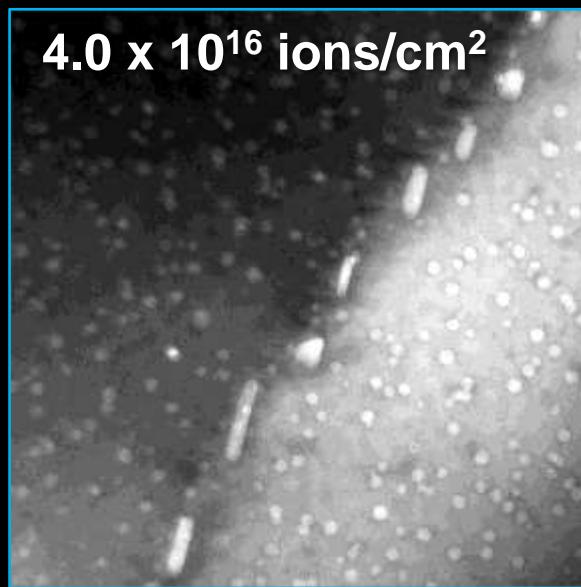
Unirradiated



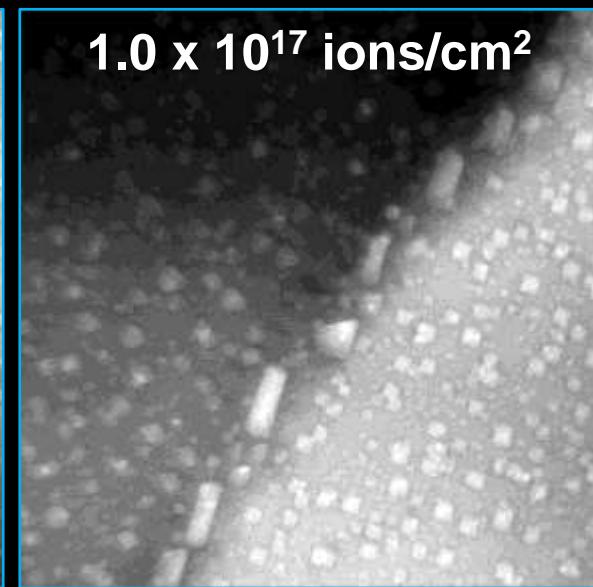
**Gold thin-film implanted
with 10keV He²⁺**

**Result: porous
microstructure**

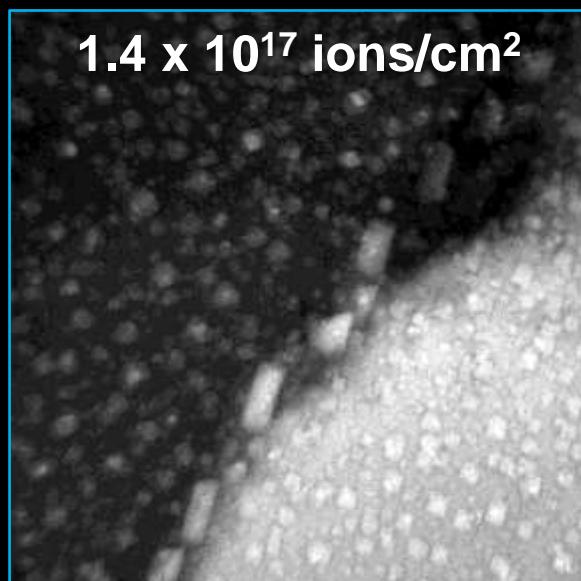
4.0×10^{16} ions/cm²



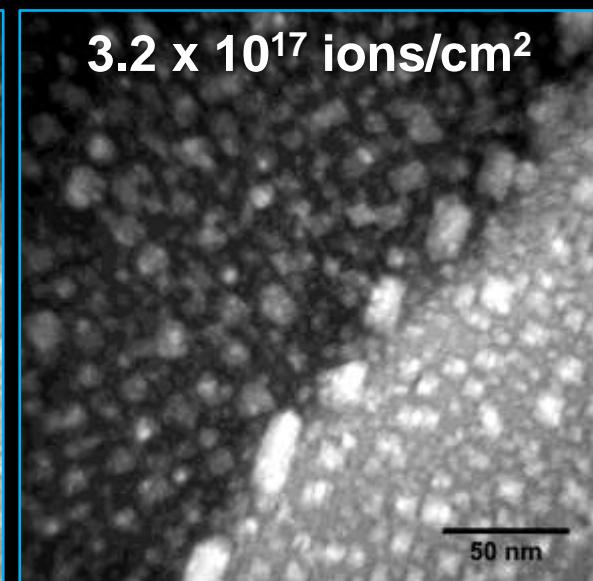
1.0×10^{17} ions/cm²



1.4×10^{17} ions/cm²

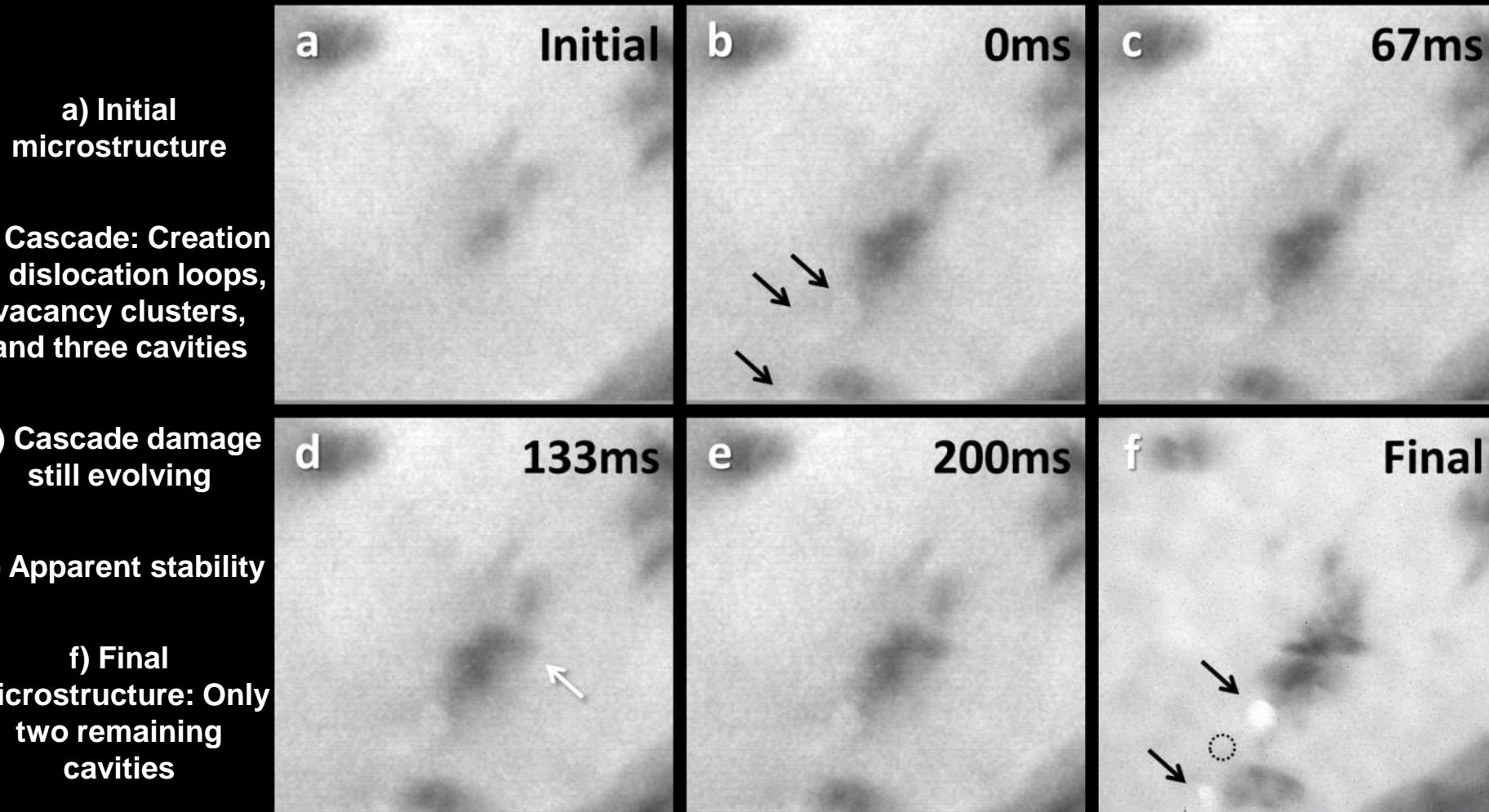


3.2×10^{17} ions/cm²



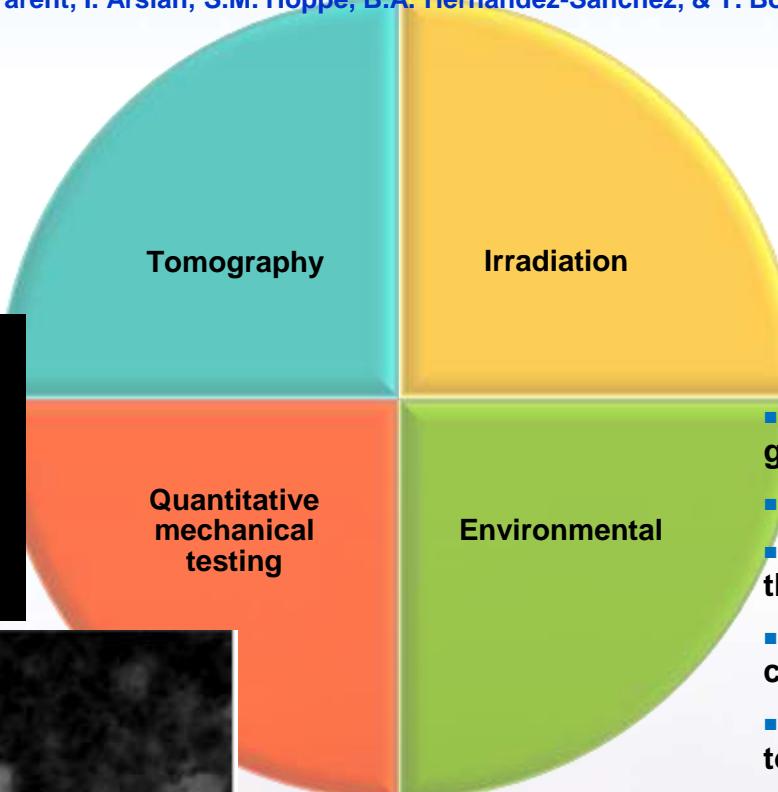
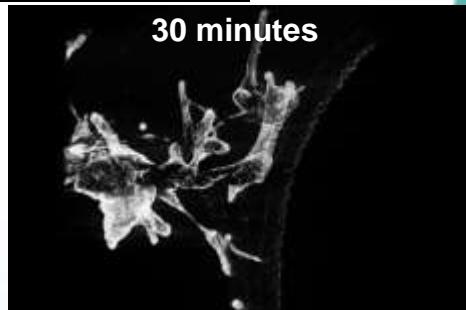
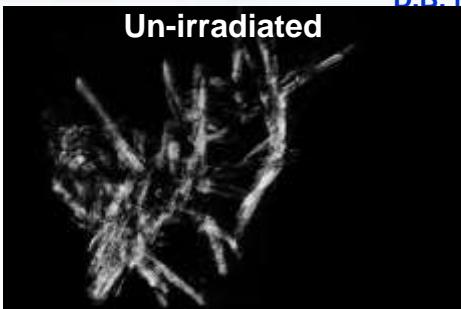
Single Ion Strikes During Concurrent Irradiation: Nucleation of Helium Cavities

Collaborators: C. Chisholm & A. Minor



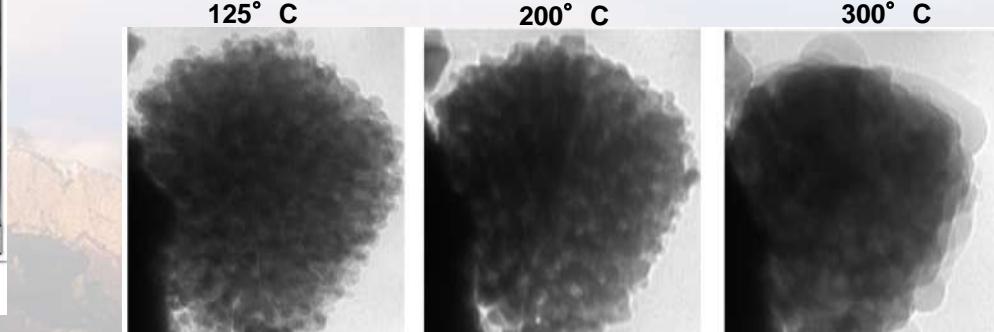
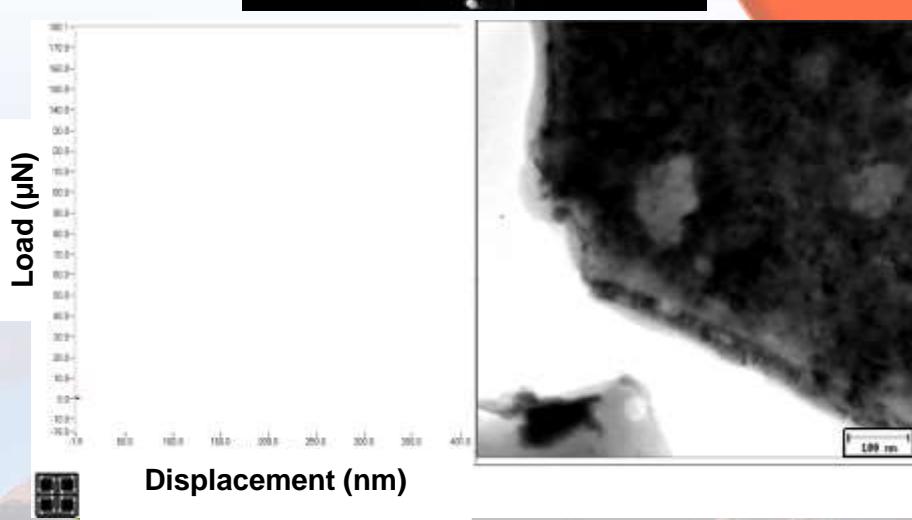
Add in-situ Capabilities from Advancements in TEM Stages

Contributors: J. Sharon, B. L. Boyce, C. Chisholm, A.M. Minor, B.G. Clark, P.J. Cappillino, B.W. Jacobs, M.A. Hekmaty, D.B. Robinson, L.R. Parent, I. Arslan, S.M. Hoppe, B.A. Hernandez-Sanchez, & T. Boyle



Vapor-Phase Heating TEM Stage

- Compatible with a range of gases
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable
- 1 atm H₂ after several pulses to specified temp

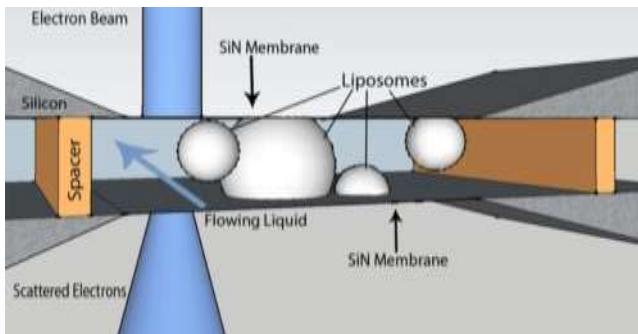


In situ TEM microfluidic Environments

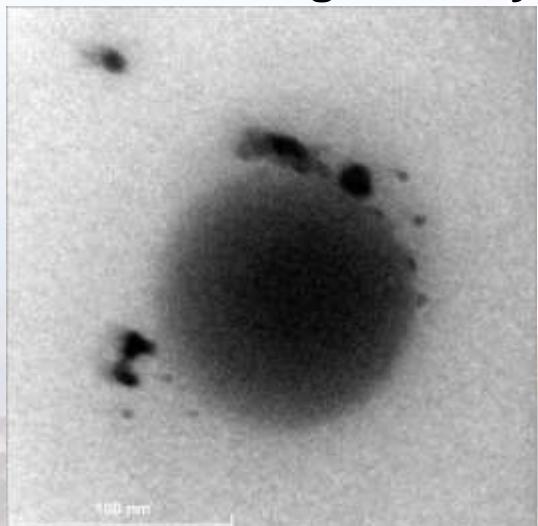
Contributors: S.H. Pratt, E. Carnes, J. Brinker, D. Sasaki, D. Gross, J. Kacher, I.M. Robertson & Protochips Inc.

Microfluidic Stage

- Mixing of two or more channels
- Continuous observation of the reaction channel
- Chamber dimensions are controllable

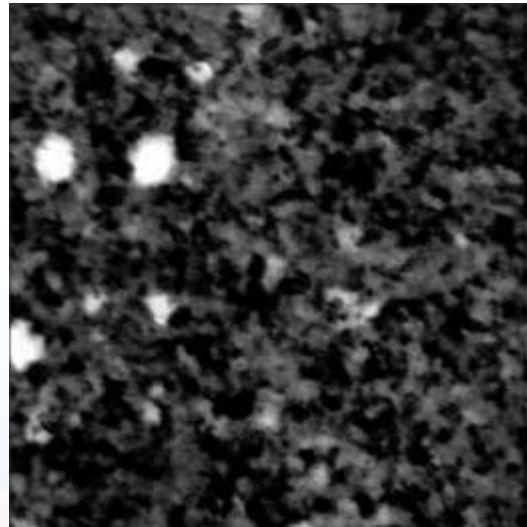


Protocell Drug Delivery

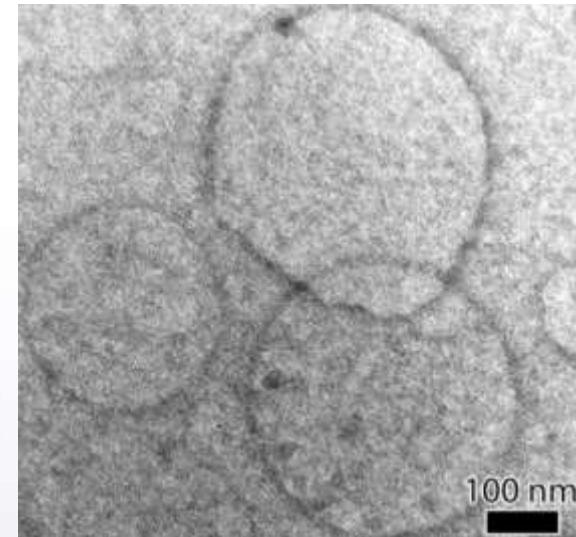


In situ microfluidic TEM can provide insight in events as diverse as corrosion and drug delivery

Fe Corrosion



Liposomes in Water



We hope to go a step further and combine it with ion implantation and irradiation environments

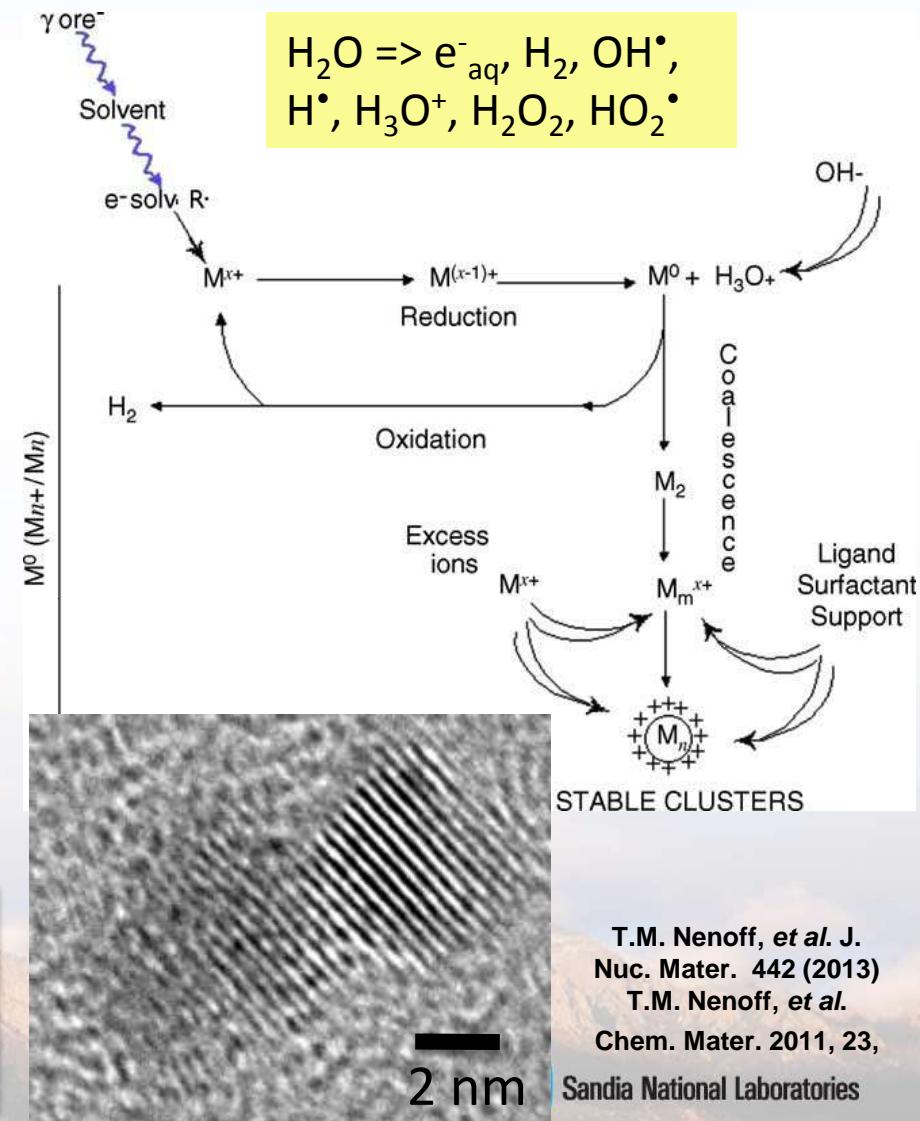


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Low Temperature Synthesis of Lanthanide and Actinide Nanoparticles

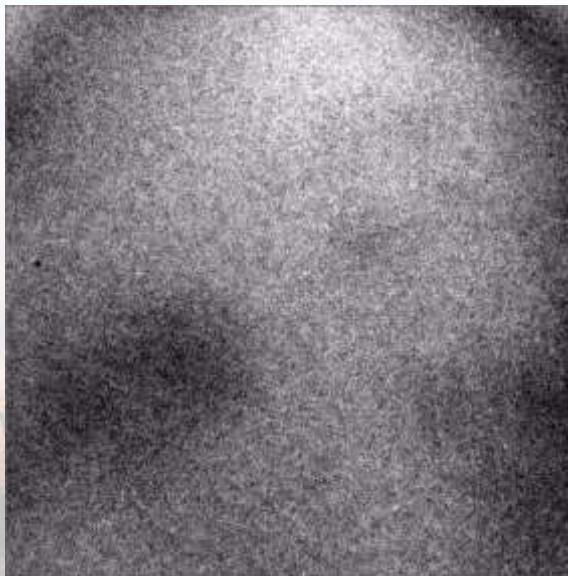
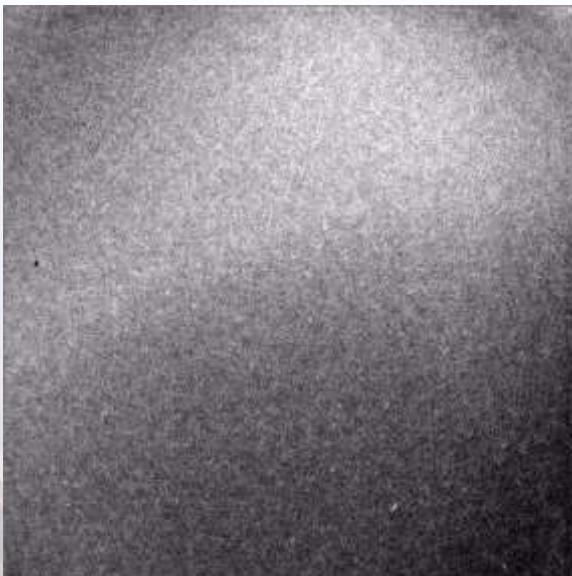
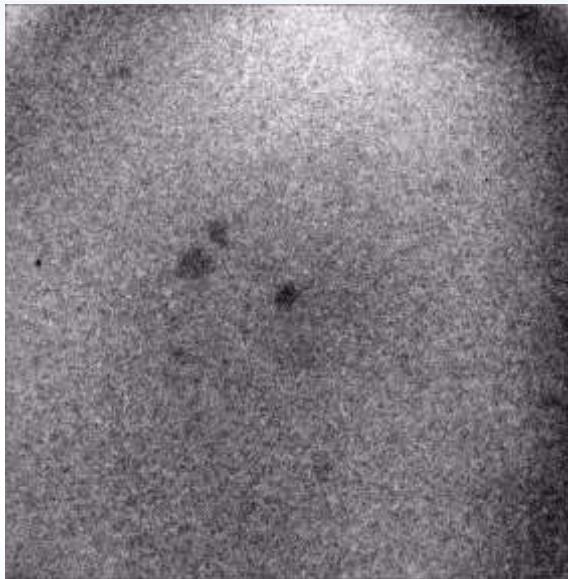
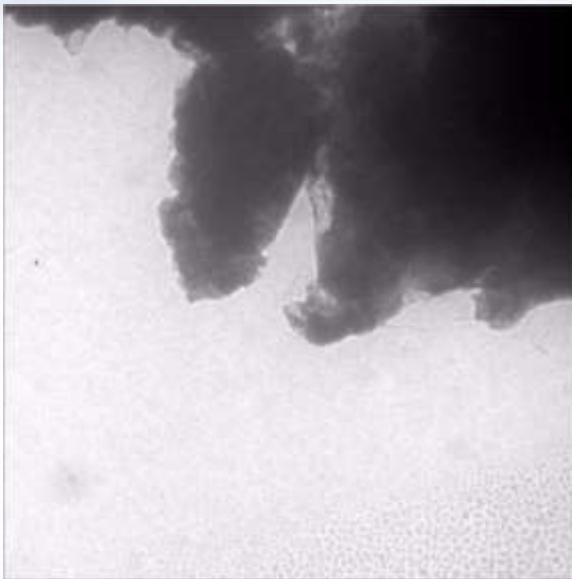
- Fabrication of nuclear fuels at low temperatures allowing for the formation of complex Uranium metal and alloys with minimum volatility of alloy compounds in the process
- Potentially permits the recycling of dissolved uranium and lanthanide ions from acidic solutions (used fuel) into metals and alloys
- Gamma (γ) irradiation is used to reduce uranium and lanthanide ions to metal in solution at room temperature
- result in Limits potential release to the environment and/or other ES&H issues

Radiolytic formation of actinide nanoparticles
RT approach for nuclear fuels synthesis reducing defect formations in bulk metals when compared to normal sintering at 1500-1700°C





In situ Observation of the Various Structural Evolutions

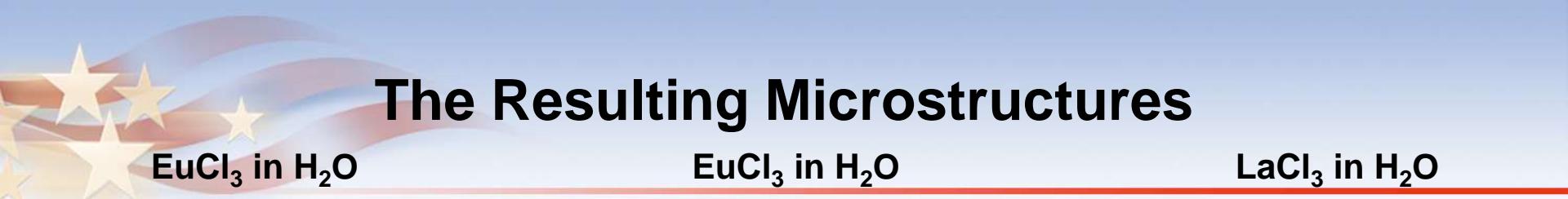


Structural evolution is highly dependent on:

- the lanthanide salt
- local salt conc.
- flow rate
- proximately to other nanostructures
- e^- beam dose
- e^- beam dose rate
- etc.

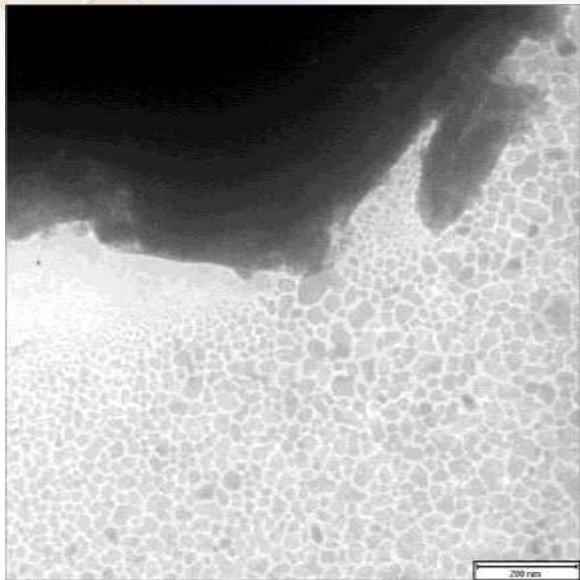


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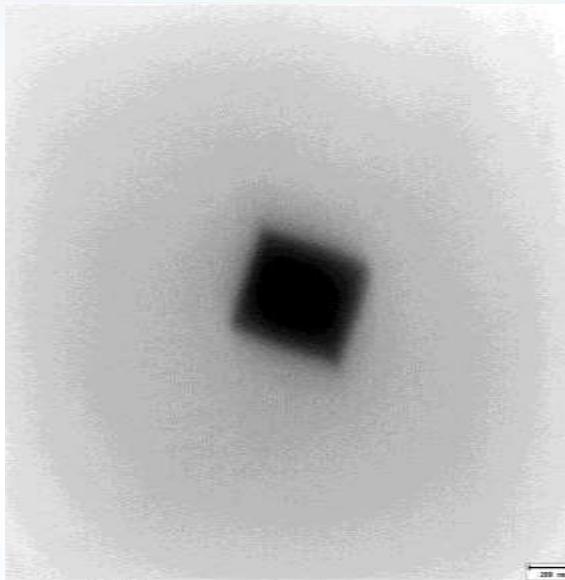


The Resulting Microstructures

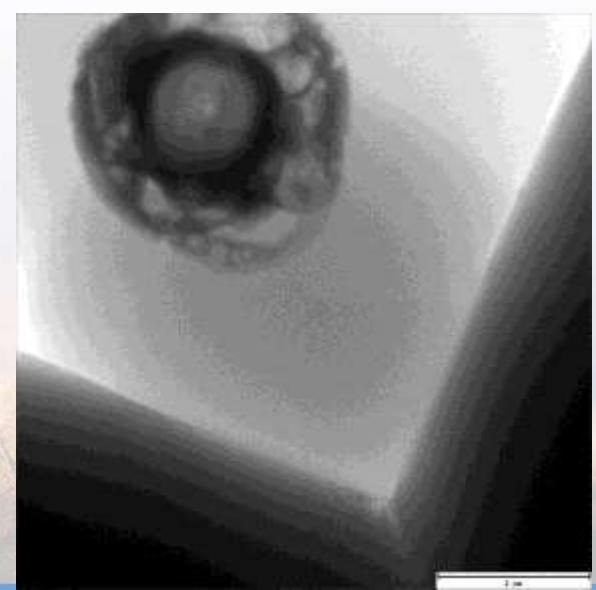
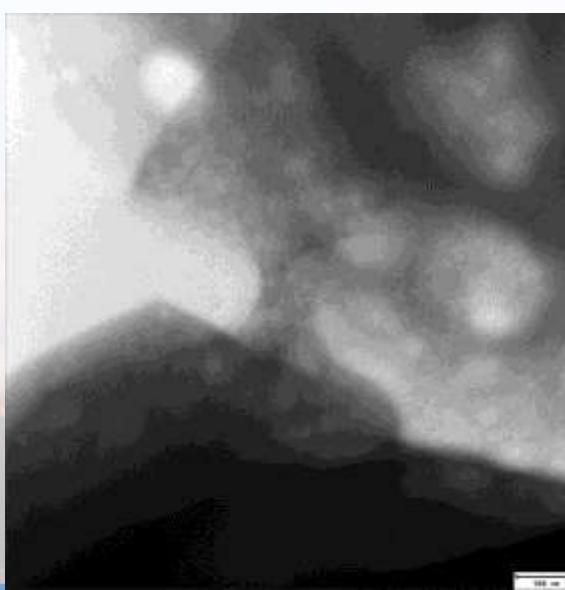
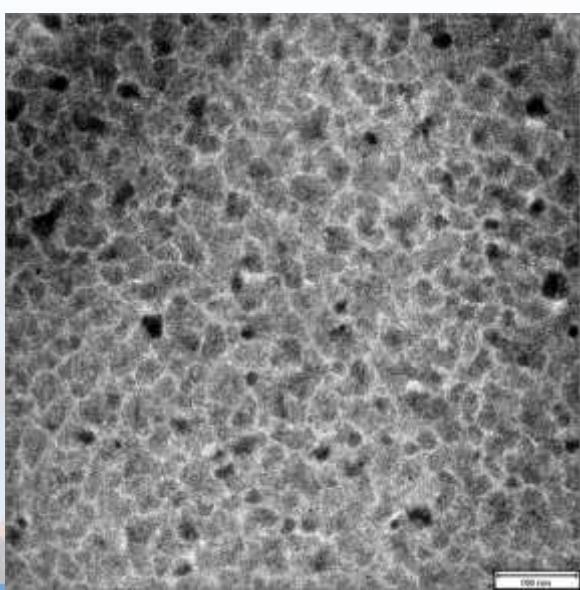
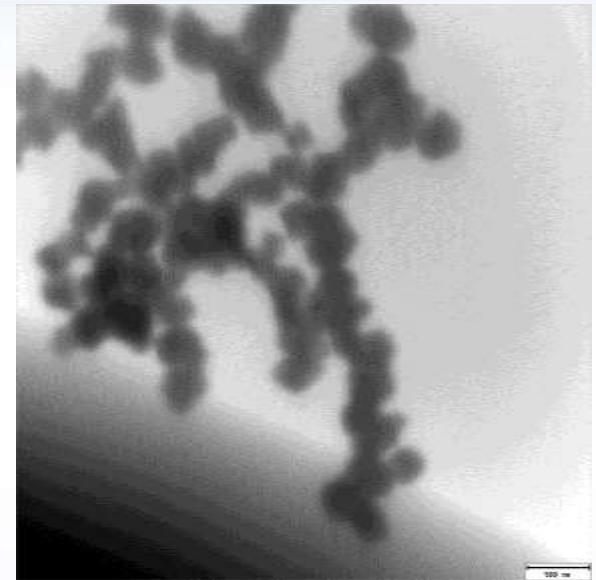
EuCl_3 in H_2O



EuCl_3 in H_2O



LaCl_3 in H_2O



Summary & Future Interests



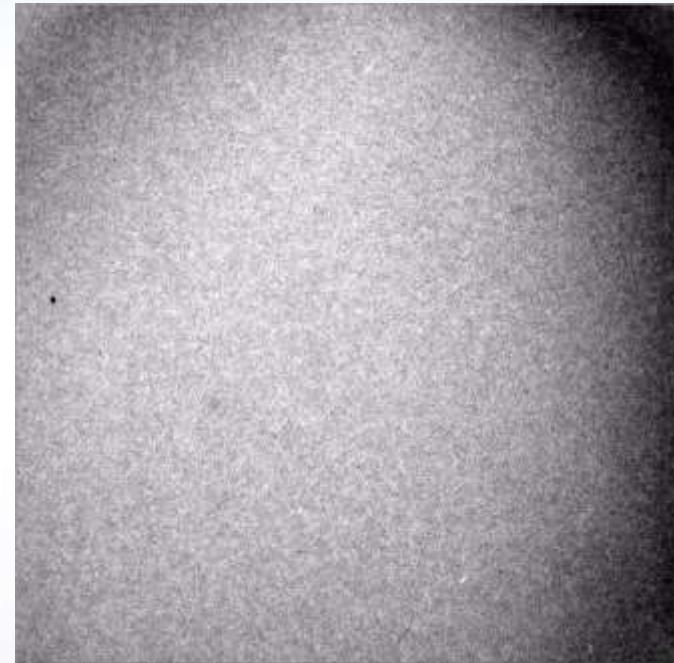
Sandia's I³TEM is one of only two facilities in the US

- *In situ* irradiation from H to Au
- *In situ* gas implantation
- Eight TEM stages with various capabilities (two beta-testing)

I³TEM can provide fundamental understanding to key mechanisms in a variety of extreme conditions

It has provided insight into the formation of lanthanide nanoparticles

The I³TEM capability are still being expanded



Sandia's I³TEM although still under development is providing a wealth of interesting initial observations

Collaborators:

D. Buller, J.A. Scott, D. Masiel, N. Li, A. Misra, B.A. Hernandez-Sanchez, T.J. Boyle, J. Sharon, B. L. Boyce, C. Chisholm, A.M. Minor, D. Sasaki, B.G. Clark, D. Gross, J. Kacher, P.J. Cappillino, B.W. Jacobs, L.R. Parent, I. Arslan, M.A. Hekmaty, D.B. Robinson, & I.M. Robertson



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