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Title:	In Situ Synthesis of Uranium Carbide and its High Temperature Cubic Phase
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In Situ Synthesis of Uranium Carbide and its High Temperature Cubic Phase

Helmut Matthias Reiche, Sven C. Vogel

reiche@lanl.gov, March 16, 2015

Lujan Neutron Scattering Center & Material Science & Technology Division

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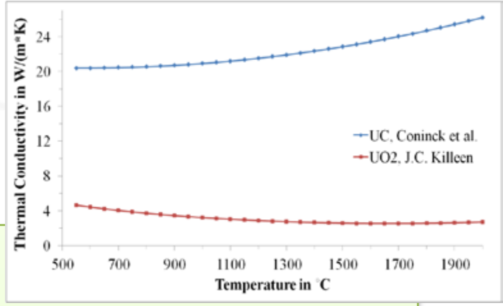
Motivation: New Ceramic Fuels

- Uranium-carbides, -nitrides, -silicides, … are actively researched.
- Phase diagram not fully established

- Safety precautions based on accident scenario models
- Accurate model paramount

Motivation: UO_x & UC_x Nuclear Fuels



UC: higher thermal conductivity and higher fissile density than UO_2

ICSD (*Inorganic Crystal Structure Database*) lists 15 entries for UC_2;

- 12 describe tetragonal phase
- 3 non-quenchable cubic phase, stable 1769 - 2560˚C; conflicting

Uranium powder is pyrophoric

Irradiation of actinides restrictive

Study uranium carbides

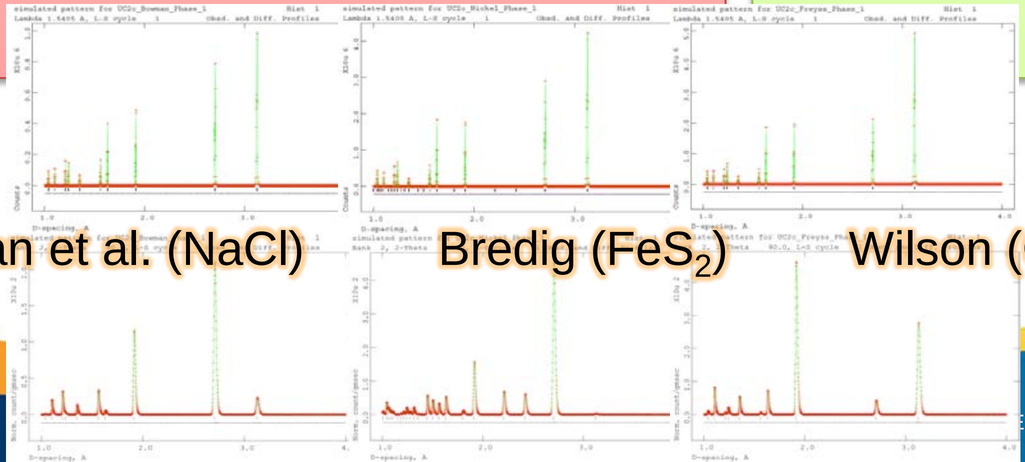
Study UC_2 in situ at T > 1769˚C using neutron diffraction

$UO_2 + 3C \rightarrow UC_2 + CO_2$

LANSCE, LANL

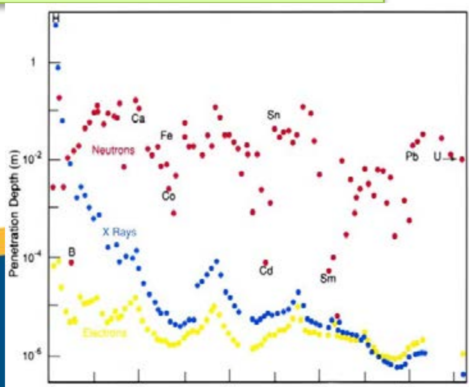
If you can ship it, we can measure it

XRD



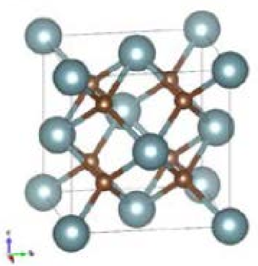
Bowman et al. (NaCl) Bredig (FeS_2) Wilson (CaF_2)

ND

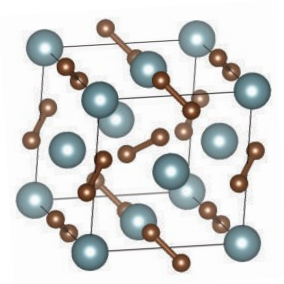


The U-C System

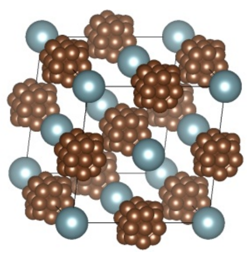
Phase	Structure Form	Space Group	Structure Type	Structure
δ	UC_x	$Fm\bar{3}m$	NaCl	Face centered cubic
ζ	U_2C_3	$I\bar{4}3d$	Pu_2C_3	Cubic
ε	UC_2	$I4/mmm$	CaC_2	Body centered tetragonal



Wilson, W.B.
1960
CaF_2

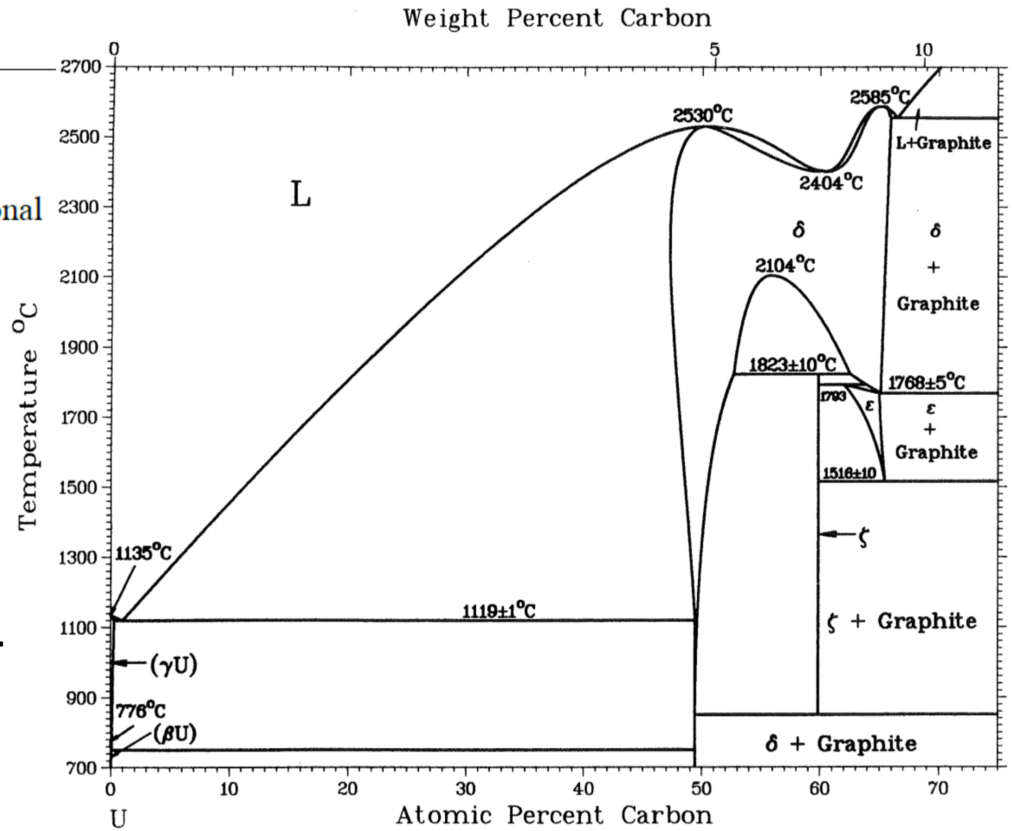


Bredig, M.A.
1960
FeS_2



Bowman et al.
1966
NaCl

In situ investigation required



T.B. Massalski : William W. Scott, Jr. Materials Park, Ohio, 1990.

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Journal of Nuclear Materials 288 (2001) 100–120

journal of nuclear materials

lsevier.nl/locate/jnucmat

Assumes UC_2 structure to be isotypic with CaF_2 according to W.B. Wilson, J. Am. Ceram. Soc. 43 (1960) 77.

Thermodynamic modelling of the C–U and B–U binary systems

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Received 19 June 2000; accepted 7 November 2000

Abstract

The thermodynamic modelling of the carbon–uranium (C–U) and boron–uranium (B–U) binary systems is being performed in the framework of the development of a thermodynamic database for nuclear materials, for increasing the basic knowledge of key phenomena which may occur in the event of a severe accident in a nuclear power plant. Applications are foreseen in the nuclear safety field to the physico-chemical interaction modelling, on the one hand the in-

PHYSICAL REVIEW B **81**, 014101 (2010)

First-principles study of uranium carbide: Accommodation of point defects and of helium, xenon, and oxygen impurities

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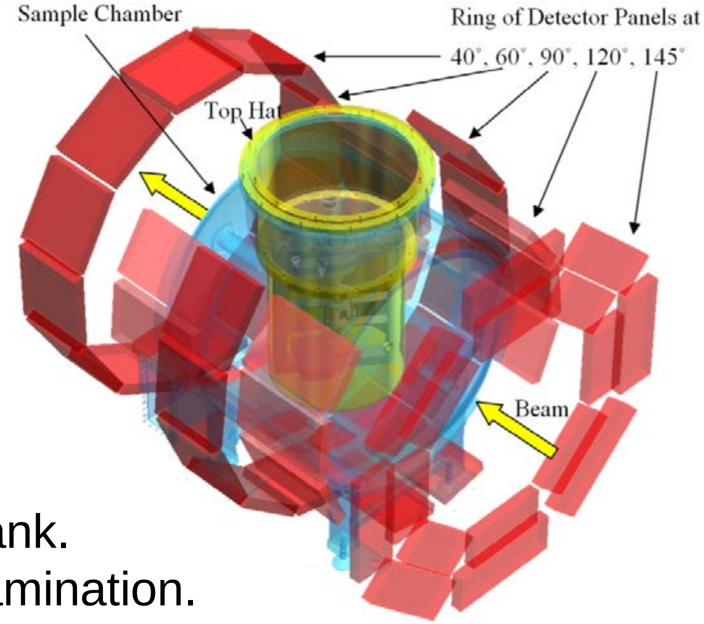
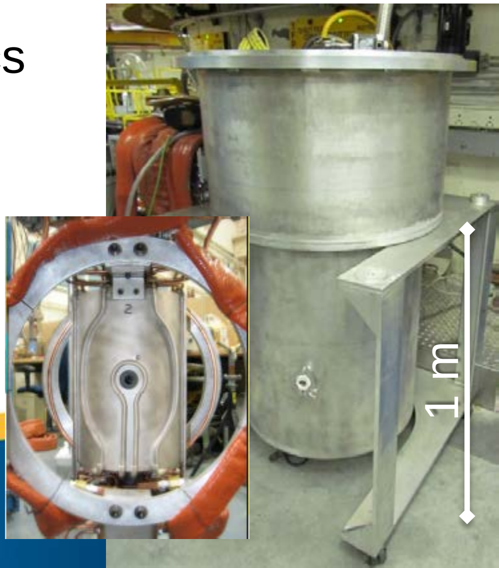
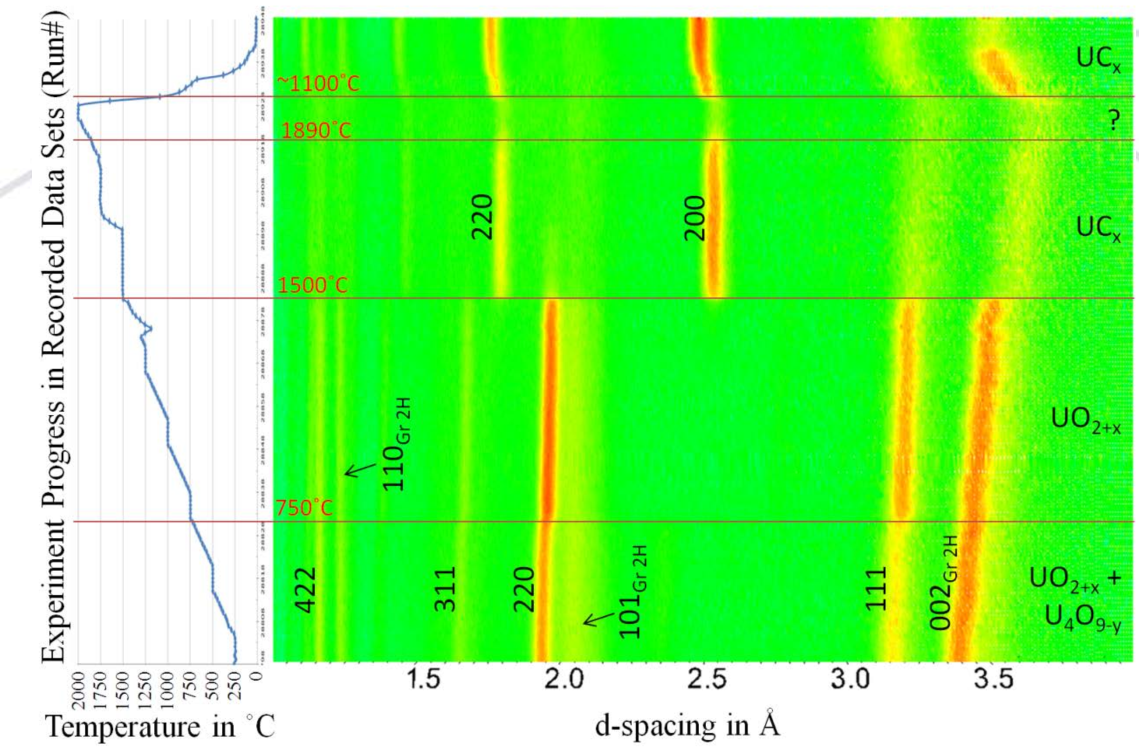
(Received 21 August 2009; revised manuscript received 23 November 2009; published 4 January 2010)

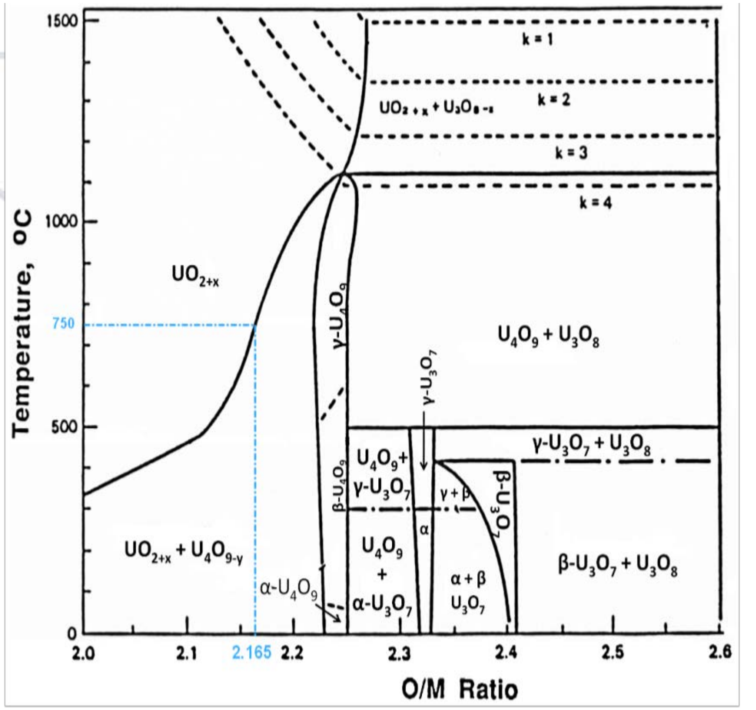
Technique: Neutron Diffraction

- HIPPO: High Pressure – Preferred Orientation
- Thermal flux: $\sim 10^7 \frac{n}{s\ cm^2}$ due to 8.83 m to target
- 51 detector panels with 1200 ^3He tubes, 4.9 m^2
- Custom furnace: T_{Max} ~ 2500 K, ΔT=100 K/min
- Pulsed Neutron Source / TOF
  ➔ Same Bragg peaks occurs in each detector bank.
  Peaks present in only one bank indicate contamination.
- Large detector coverage allows to follow fast reaction kinetics
  ➔ In situ characterization of
  a) reaction kinetics and temperatures
  b) crystal structure

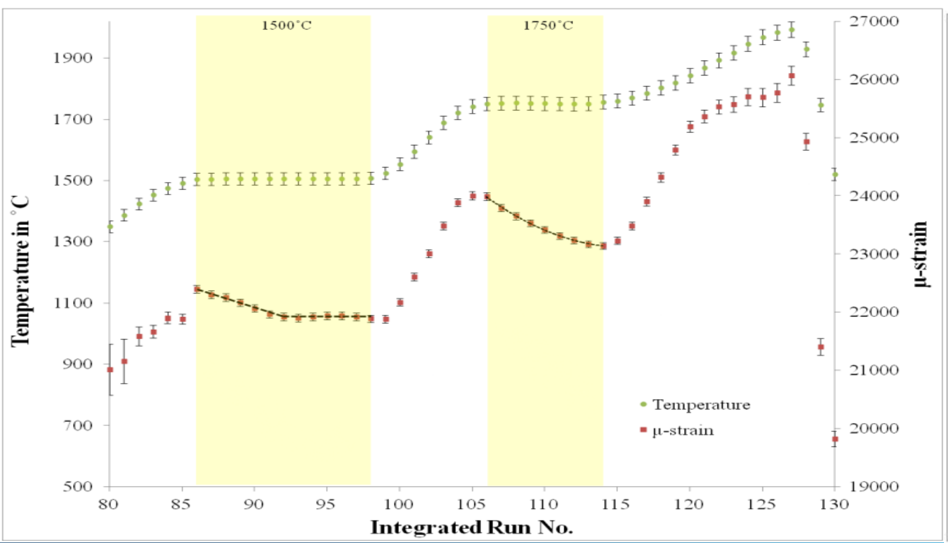


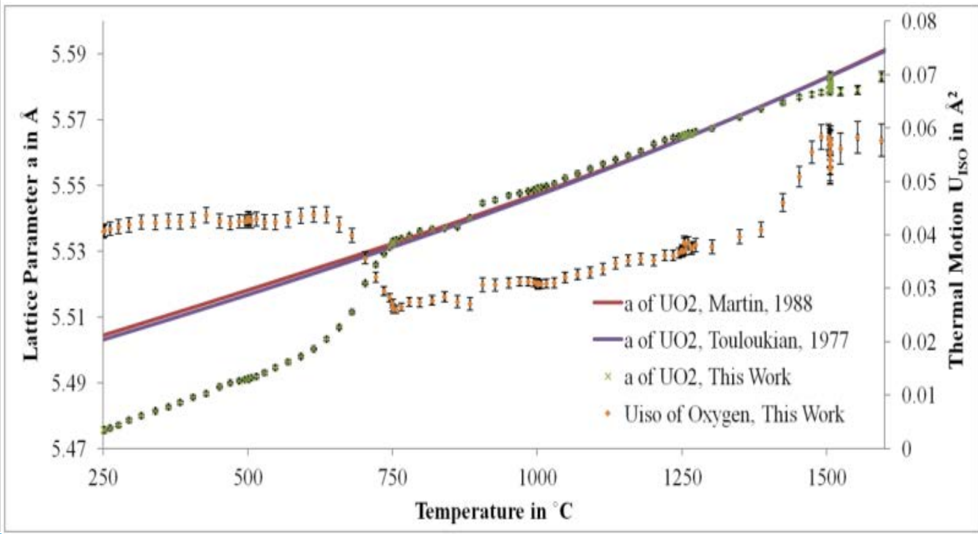


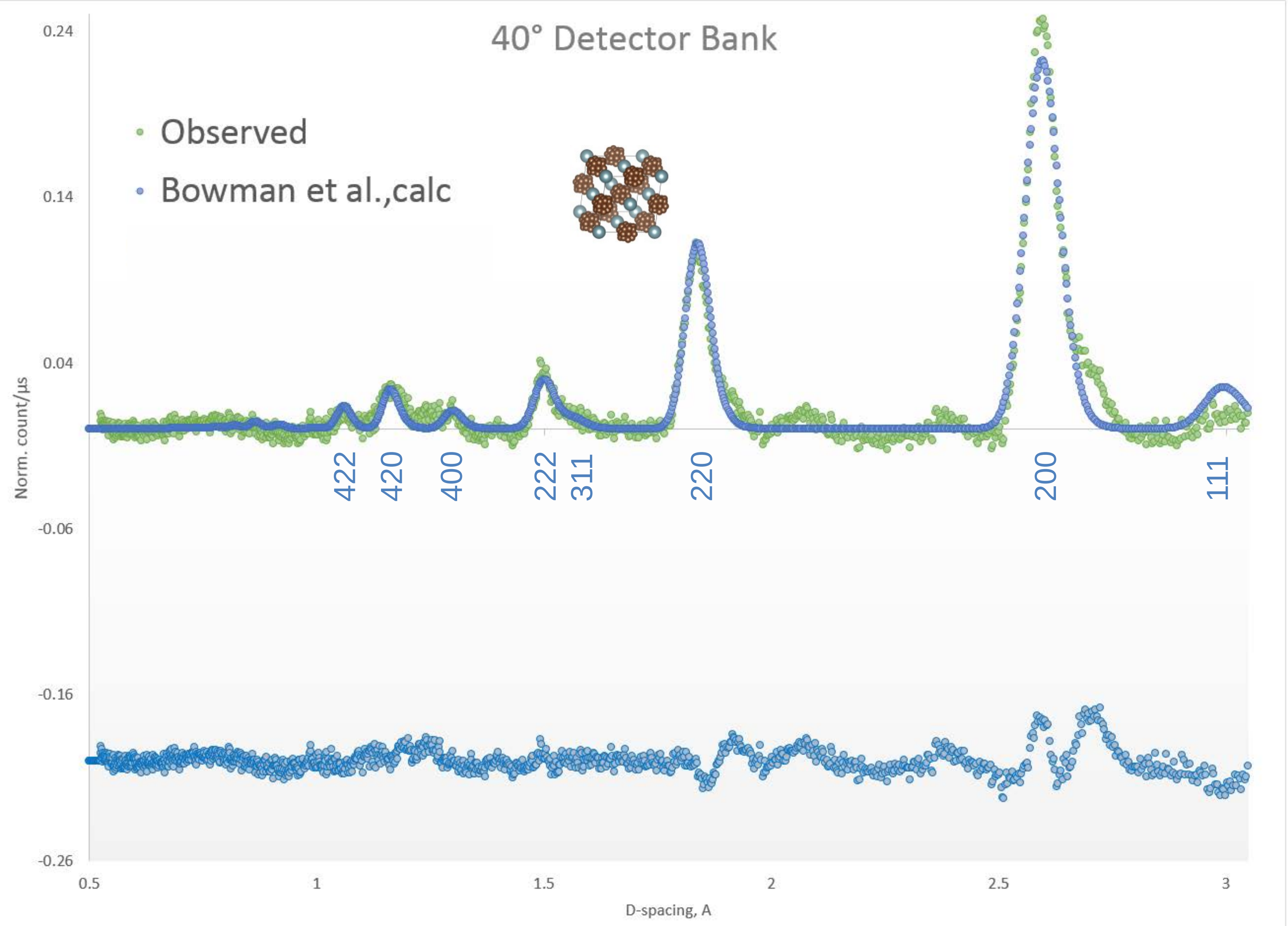




$$UO_2 + 2C \rightarrow UC + CO_2$$







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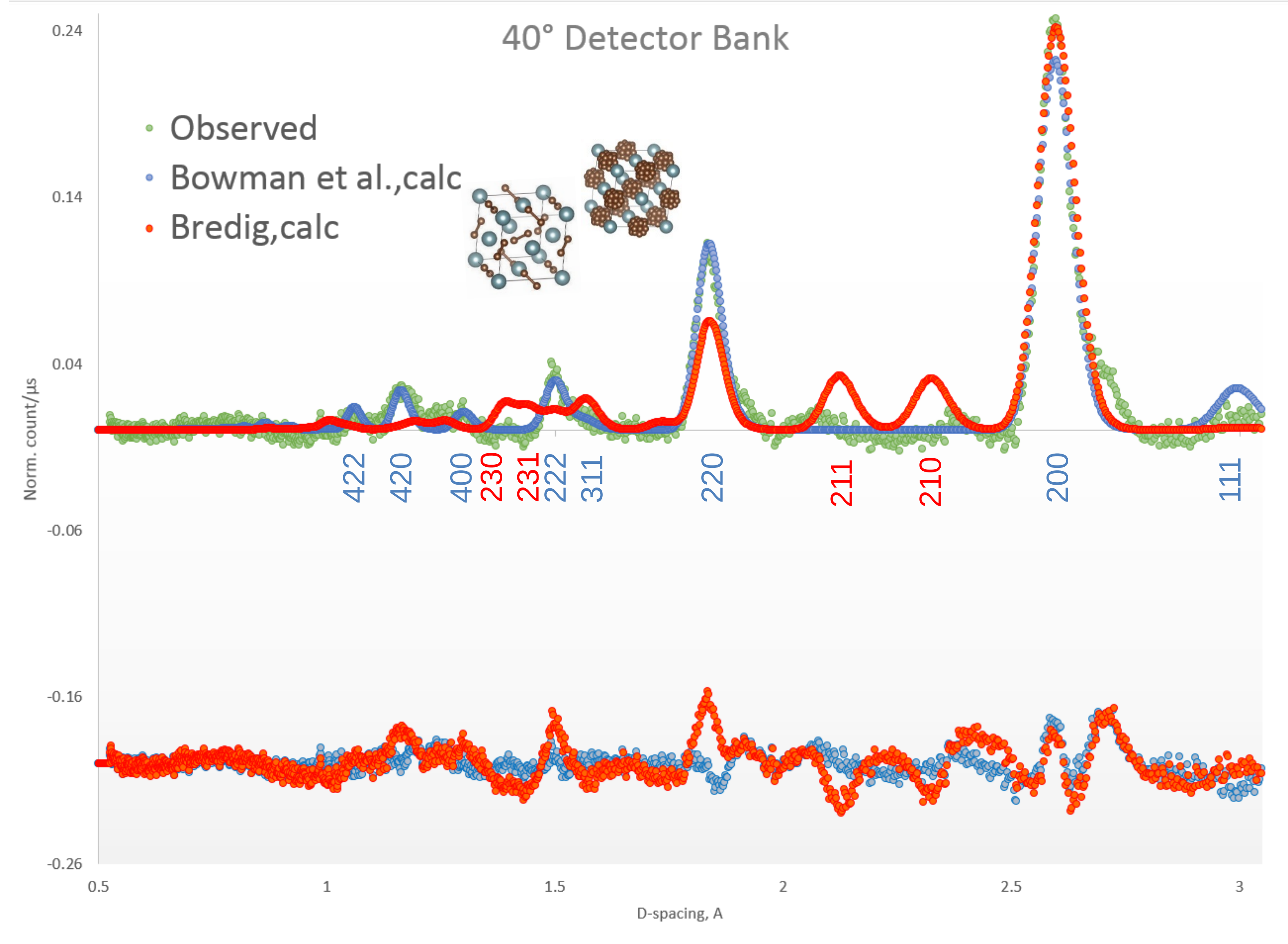

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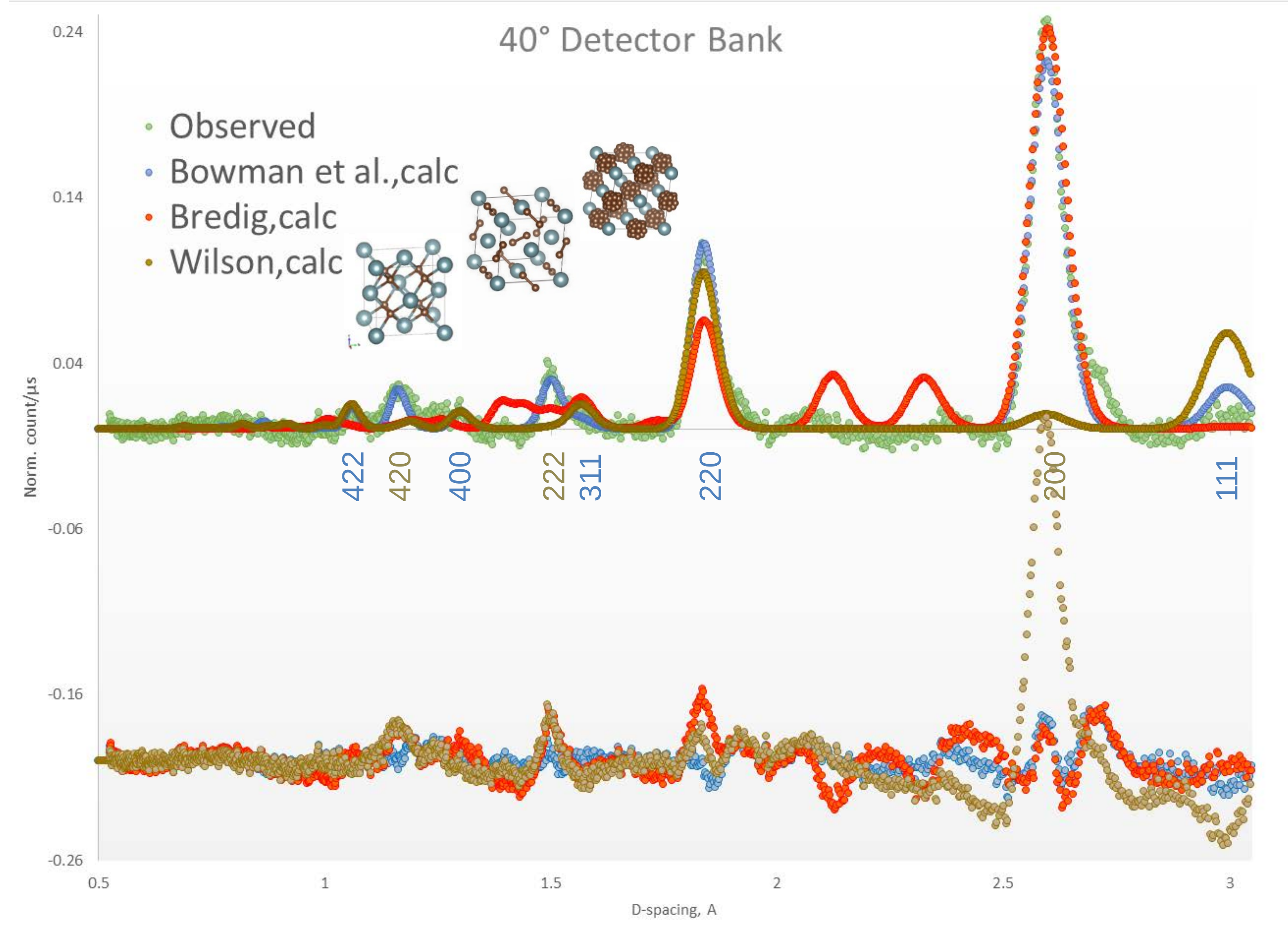

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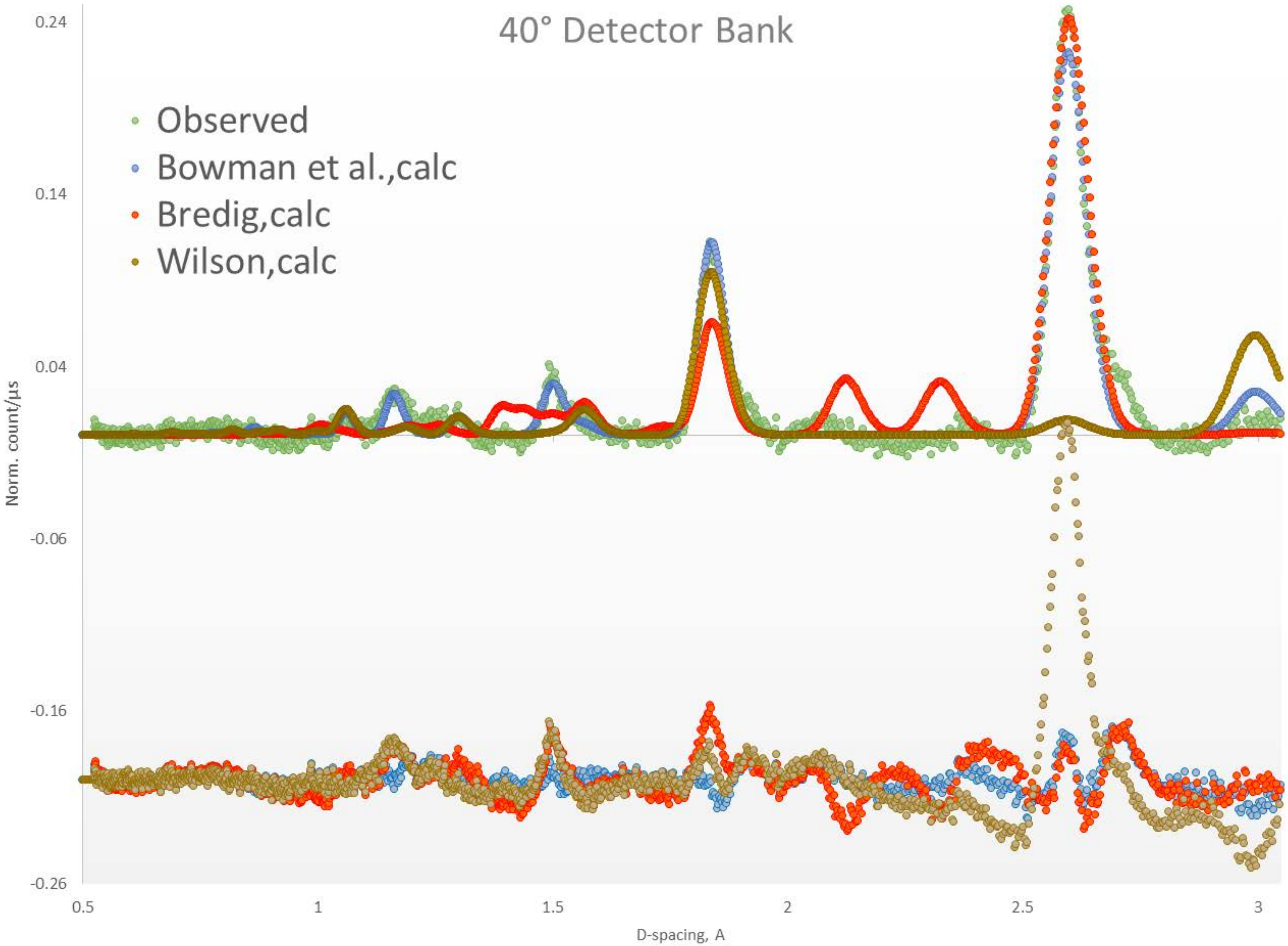

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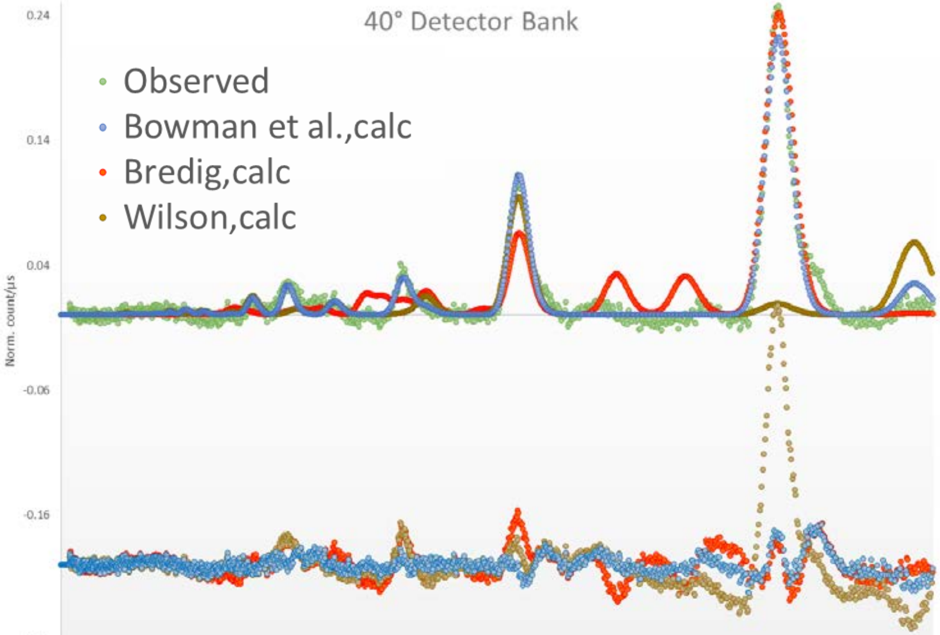
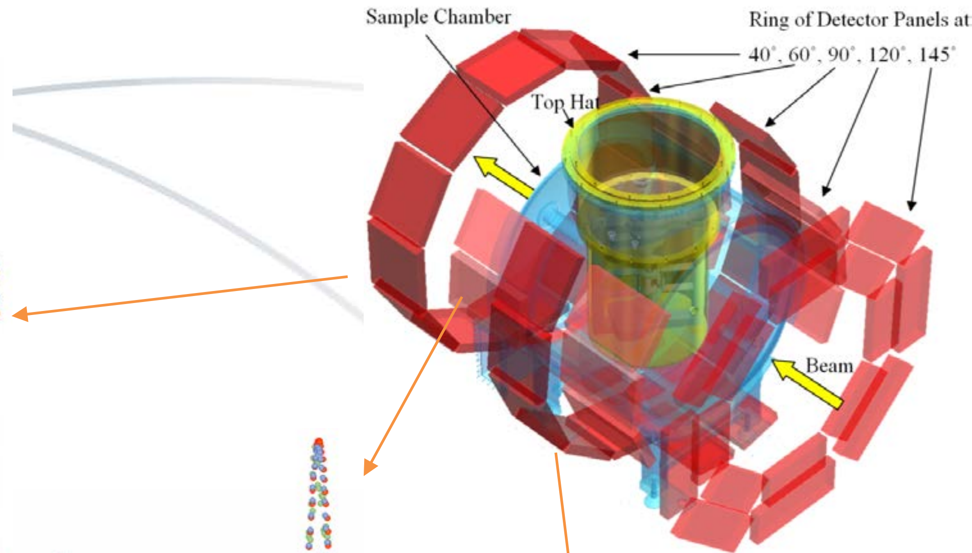
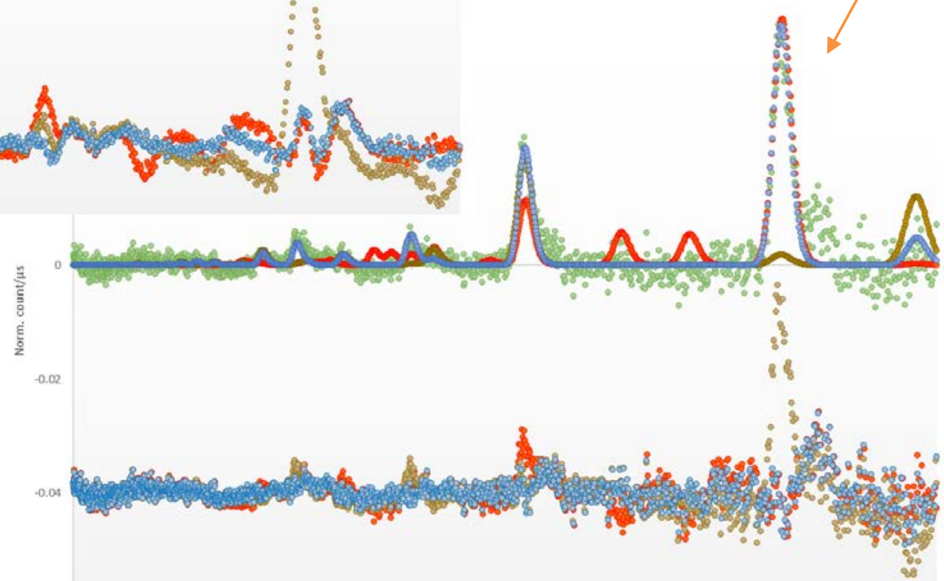
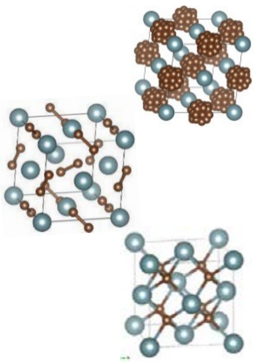




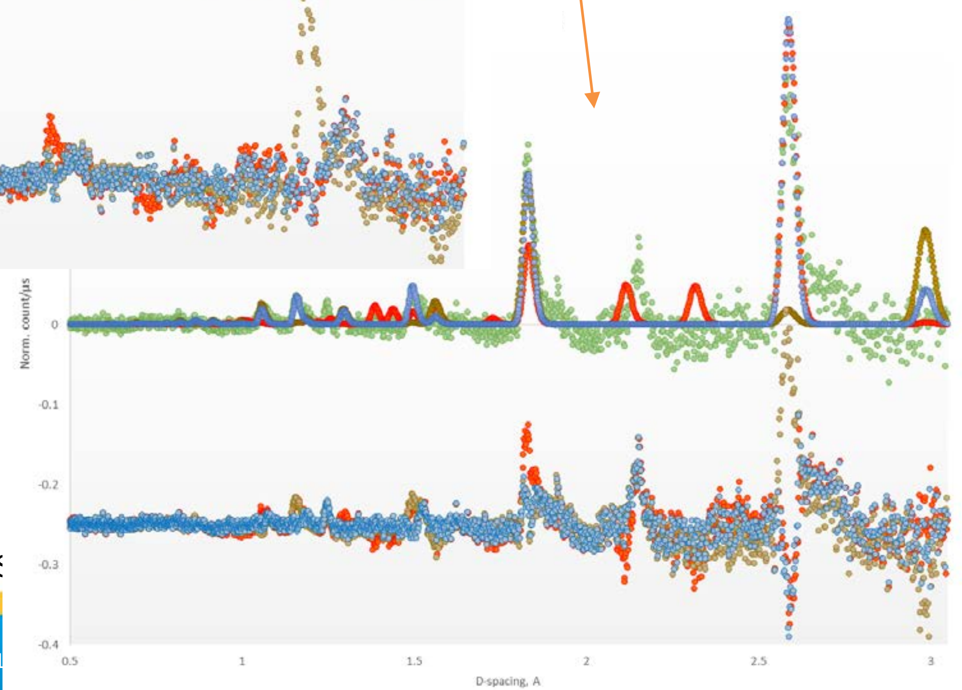




$X^2 = 6.9$

$X^2 = 7.9$

$X^2 = 10.1$



Best fit of in situ data @ 2200°C is structure proposed by Bowman et al.

Summary

- U-C system is actively researched, however, we present first in situ data since 1960. We identified the none quenchable, cubic, δ-phase which in turn is fundamental to computational methods
- Rich datasets of the formation synthesis of uraniumcarbide yield kinetics data which allow to benchmark modeling, thermodynamic parameters etc.
- Order-disorder transition (carbon sublattice melting) observed due equal sensitivity of neutrons to both elements. This dynamic has not been accurately described in some recent simulation-based publications, good agreement with theoretical work by X.D Wen et al.
- LA ... sample env...

Inorganic Chemistry

Article

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Rotational Rehybridization and the High Temperature Phase of UC_2

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Thank you

- My supportive Family (pics)

- Dr. Sven Vogel, Instrument Scientist/Data Analysis
- Dr. Luke Daemon, Sample Synthesis
- Eric Larson, CAD Design

High-Temperature Furnace: Motivation

- Nuclear fuels are generally actinides (Th, U, Pu) with a light element (O,C,…) with T_m > 2500°C → ~~XRD, Synchrotron~~
- Phase transition kinetics require fast acquisition time
- Some models predict a UO_2 fuel centerline of T > 1850°C for SCWR
- Many materials have non-quenchable high temperature phases that are poorly known (e.g. cubic UC_2)

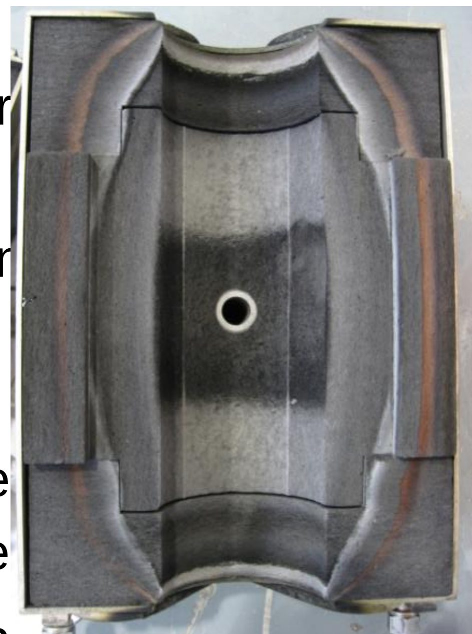
…o source allows for

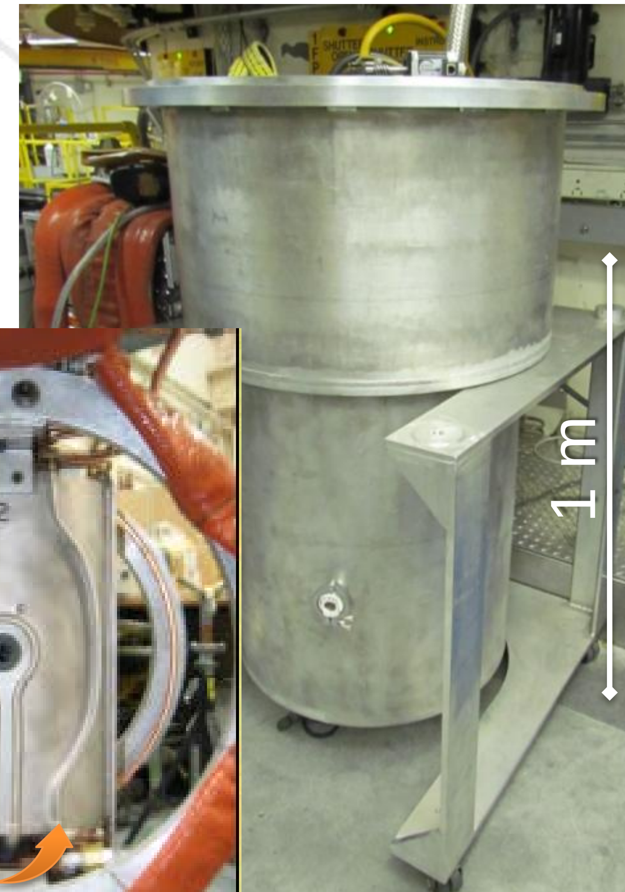
…of T > 1500°C

Facility	Beamline	High Temperature
ILL, France	D20	ILL: 1150°C (1500°C Nb setup)
LANSCE, NM	HIPPO	ILL: 1000°C
HFIR	HB-2A	ILL: 800°C (1340°C Nb setup)
SNS, TN, USA	---	<under development>
ISIS, UK	GEM	1100°C
J-PARC, Japan	iMATERIA	<under development>

High Temperature Furnace: Design

- T_{Max} ~ 2500 K, ΔT=100 K/min
- 360° sample rotation
- 50 mm sample height adjustment
- Heat shield and element made of graphite
- SCR controlled tr
10V@2000A
- Resilient safety ir
  - Water flow
  - Vacuum
  - Temperature s
  - LabVIEW he
- SCADA via Lab
handling and notification





	Space Group	Structure Type	Pearson Symbol	Cell Size	Observation Temperature
Bowman et al.	$Fm\bar{3}m$	Defect NaCl*	cF8	5.488 Å	1900˚C
Wilson, W.B. (Freyss et al.)	$Fm\bar{3}m$	CaF_2	cF12	5.410 Å	1820˚C
Bredig, M.A. (Nickel and Saeger)	$Pa\bar{3}$	FeS_2	cP12	5.472 Å	1820˚C

*Although listed as U0.5C in the ICSD, Bowman actually proposed UC2 with C2 molecules on the C sites of the NaCl structure, following the motion of a free rotator model or a random disorder model (oriented along [111] direction).

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Computational Materials Science 40 (2007) 562–568

COMPUTATIONAL MATERIALS SCIENCE

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Classical molecular dynamics simulation of uranium monocarbide (UC)

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Received 19 January 2007; received in revised form 19 February 2007; accepted 21 February 2007
Available online 16 April 2007

Uranium monocarbide (UC) is an important ingredient in the Indian nuclear fuel program. In Fast Breeder Test Reactor (FBTR), Kalpakkam, India; UC–PuC mixed carbide fuel has been used extensively for the last 15 years. Initially the FBTR was made critical with Mark I fuel (30%UC + 70%PuC) and later on it was continuously fuelled by Mark II (45%UC + 55%PuC) with the expansion of the FBTR core. Clearly, thermophysical and thermomechanical properties of UC are of special interests to us for better understanding and prediction of in-reactor fuel performance. Moreover, fuel behaviour in some sup-

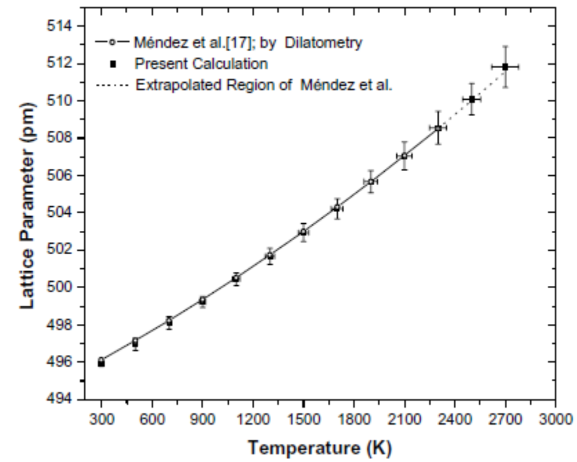

Fig. 2. Variation of lattice parameter of UC with temperature.

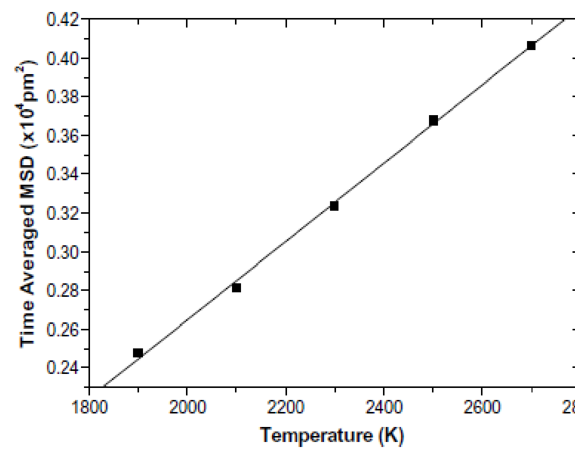

Fig. 6. Variation in time-averaged MSD of carbon ion in UC with temperature.

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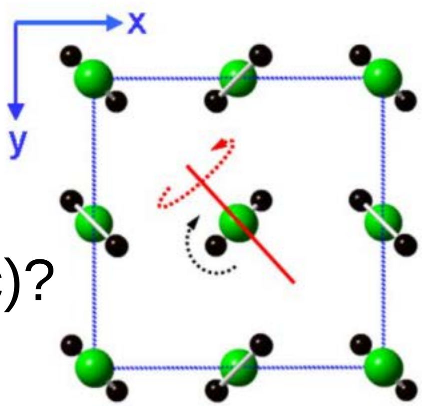
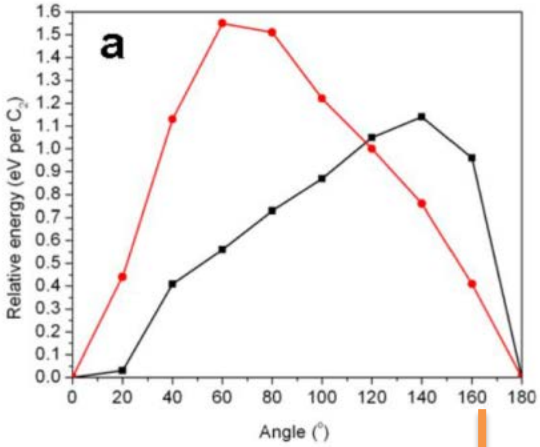
Order-Disorder Transition

Why loss of intensity?

1. Melt?
2. Bredig Transition (Superionic)?
3. Motion of C_2 Molecule
   A. ‘Free Rotation Model’ by Bowman et al., 1966, ND.
   B. ‘Oscillating’ Model by Wen et al., 2012, simulation.





➔ Collaboration with Wen et al. to calibrate their HSE model with our experimental data