2019 NX SCHOOL

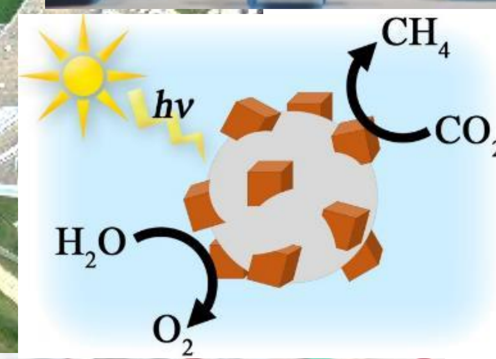
IN SITU AND OPERANDO EXPERIMENTS

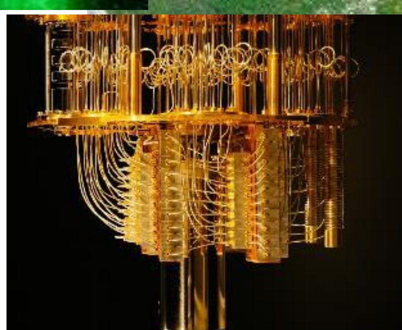
UTA RUETT

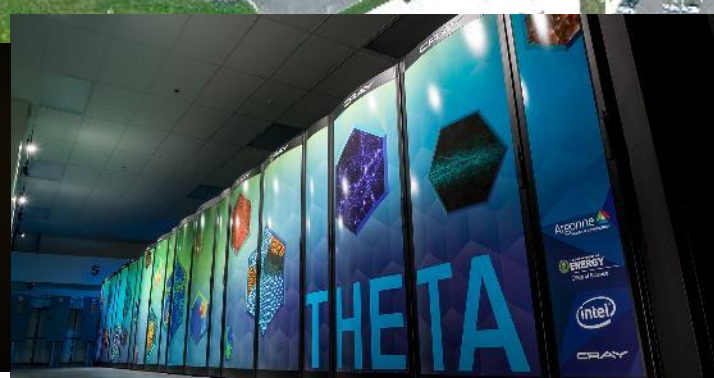
LEADER OF STRUCTURAL SCIENCE GROUP AT APS

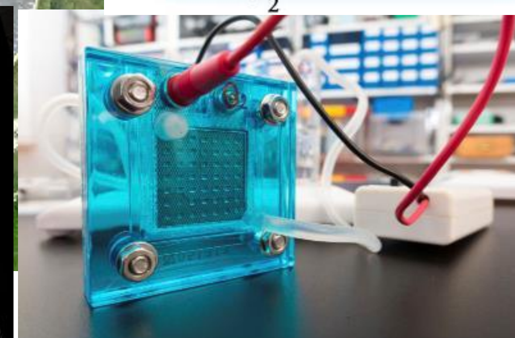
SECTOR 11 & 17-BM

MODERN CHALLENGES









MODERN CHALLENGES

Synthesis of new Materials

- **Understanding intermediates and tuning factors**

→Efficient growth

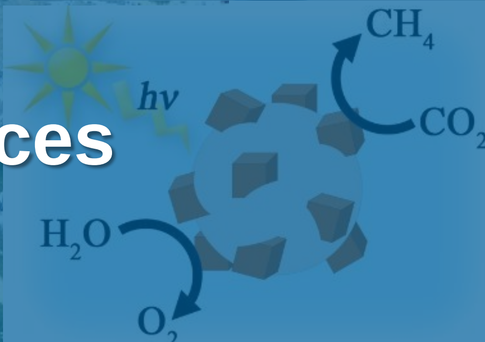
Properties of materials

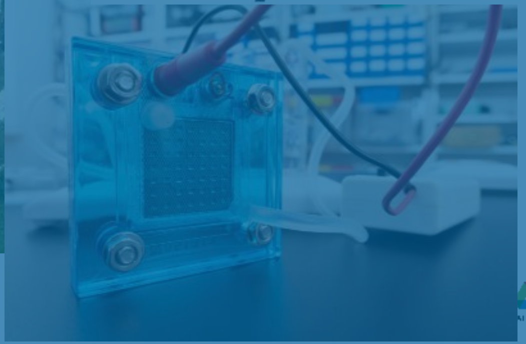
→ Understanding of phenoma

Functionality of materials and devices

- **Observing mechanisms**
- **Understanding limitations**

→ Optimized functionality





MODERN CHALLENGES

Synthesis of new Materials

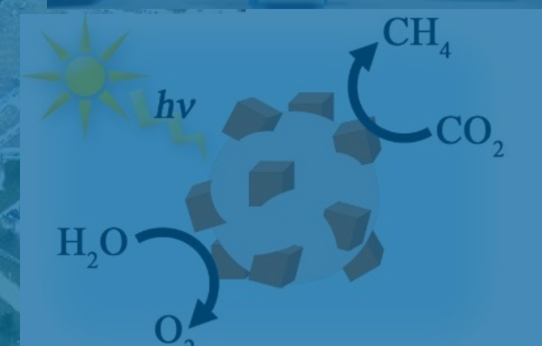
- Reactor
- High pressure cell
- Deposition system
- Furnace for annealing
- Multi-modal

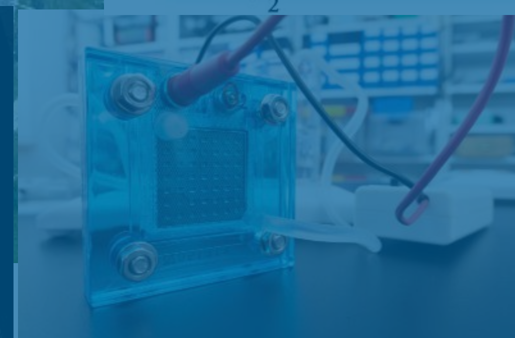
Properties of materials

- Temperature (heating, cooling)
- Magnetic Field
- Electrical field
- Pressure
- Load frame
- Viscosity
- …

Functionality of materials and devices

- Battery cycler
- Gas loading
- Reactor for catalysis
- Load frame
- Rheology



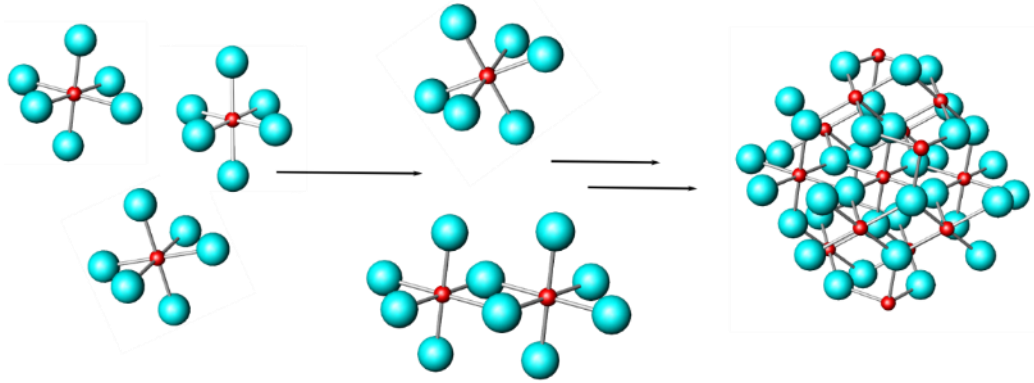


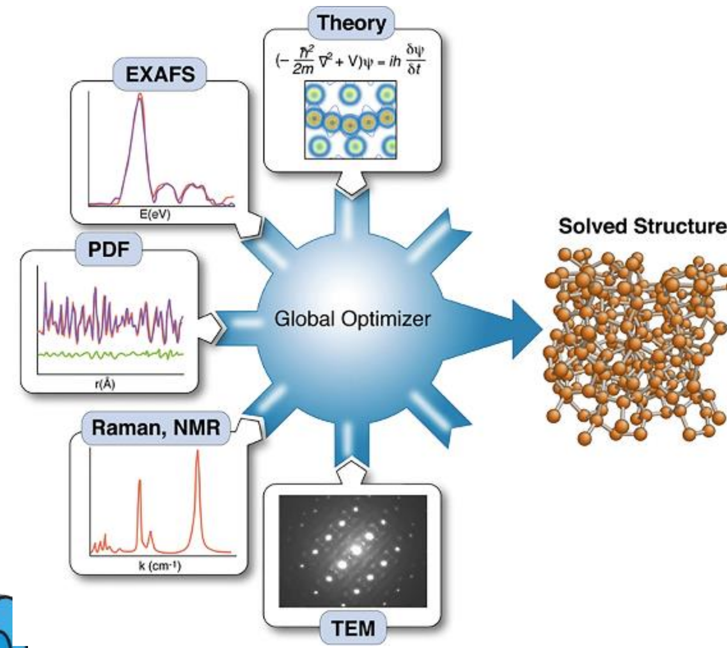
SYNTHESIS

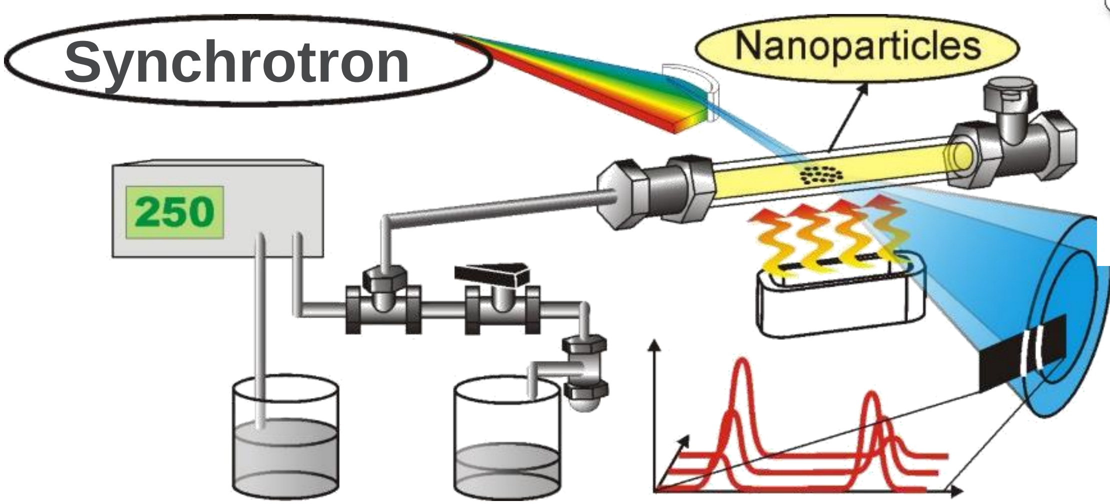
SYNTHESES REACTORS: WATCHING CHEMISTRY IN ACTION

In situ synthesis / annealing / deposition

Courtesy by Kirsten Jensen



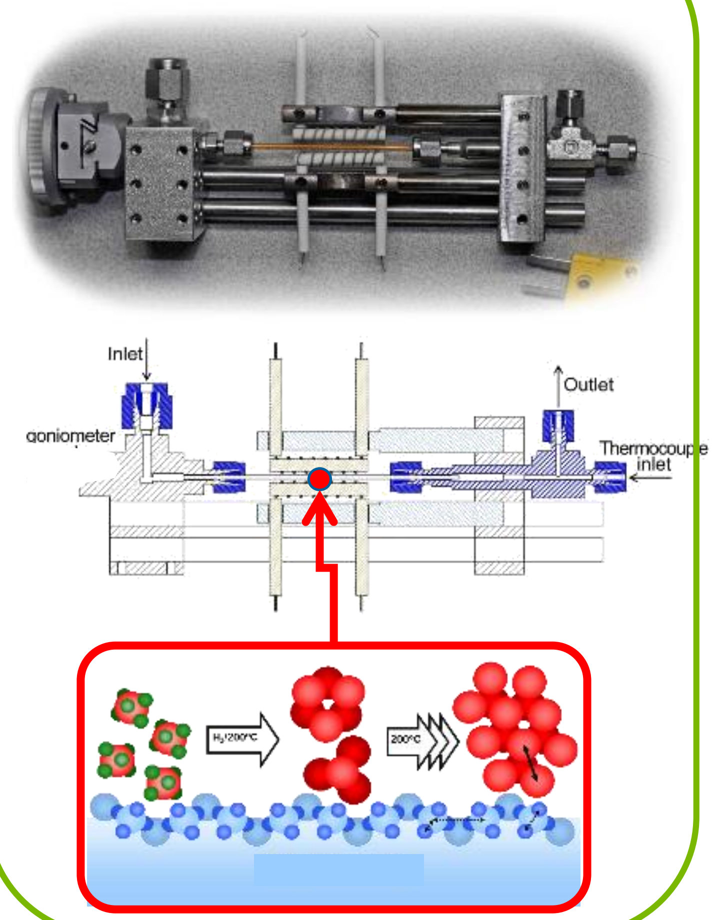




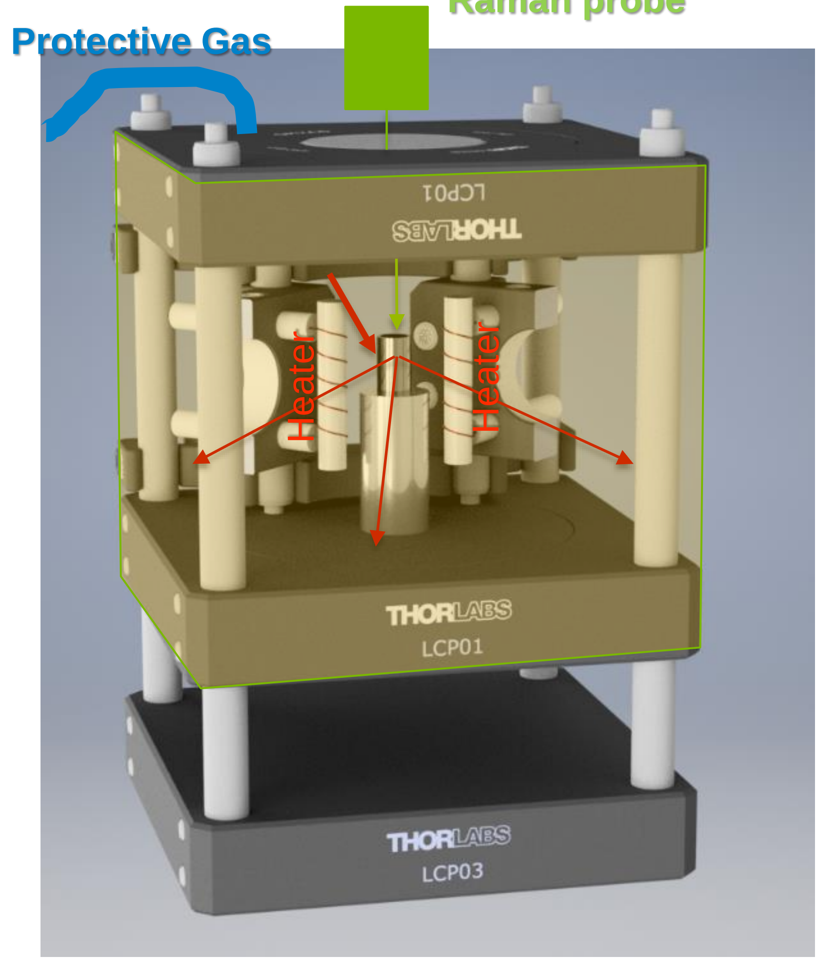
SYNTHESES REACTORS

Diffraction – Total scattering – Small angle scattering – Spectroscopy

Flow cell / Furnace



Synthesis reactor, 600º C

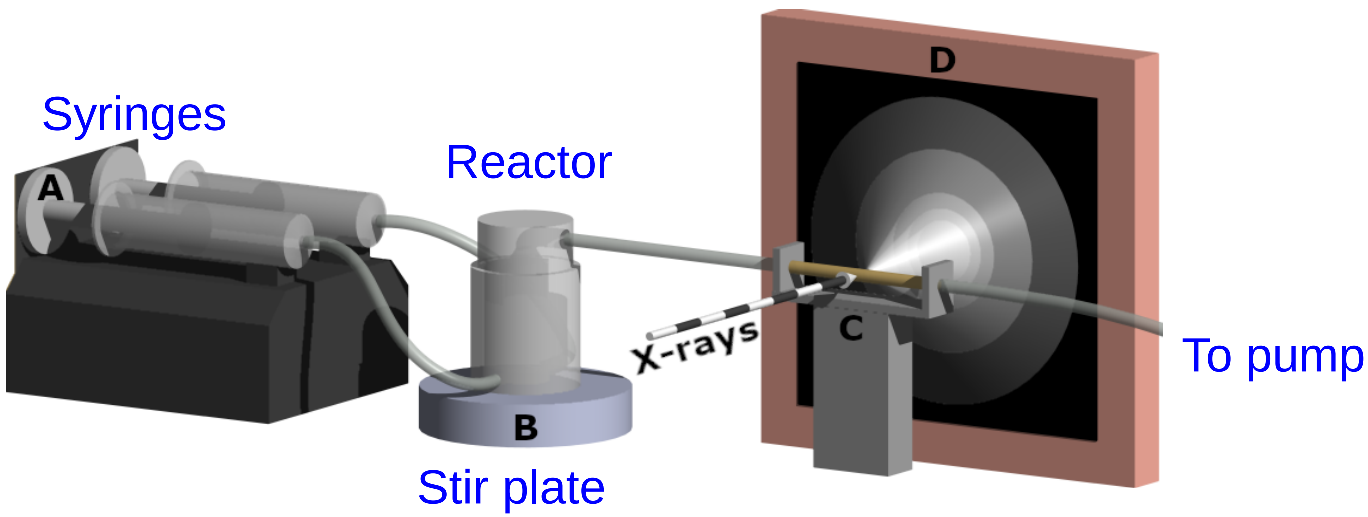


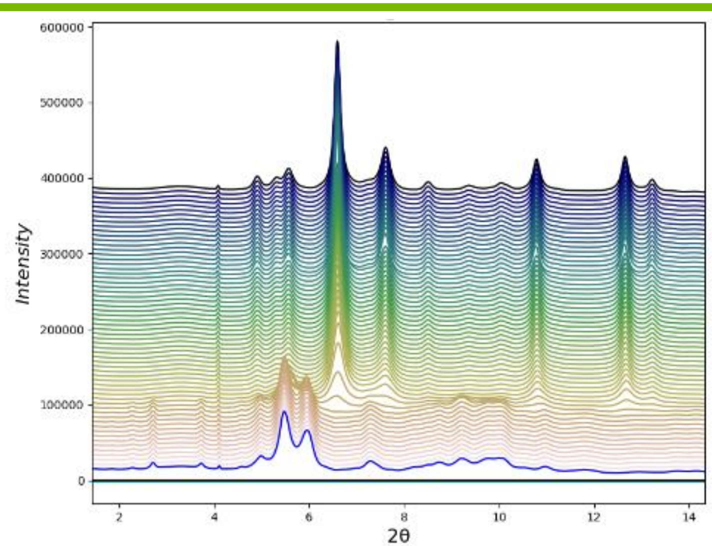
SYNTHESES REACTORS

Diffraction – Total scattering – Small angle scattering – Spectroscopy

Courtesy by Olaf Borkiewicz

Mixed flow reactor





Observation of structural changes

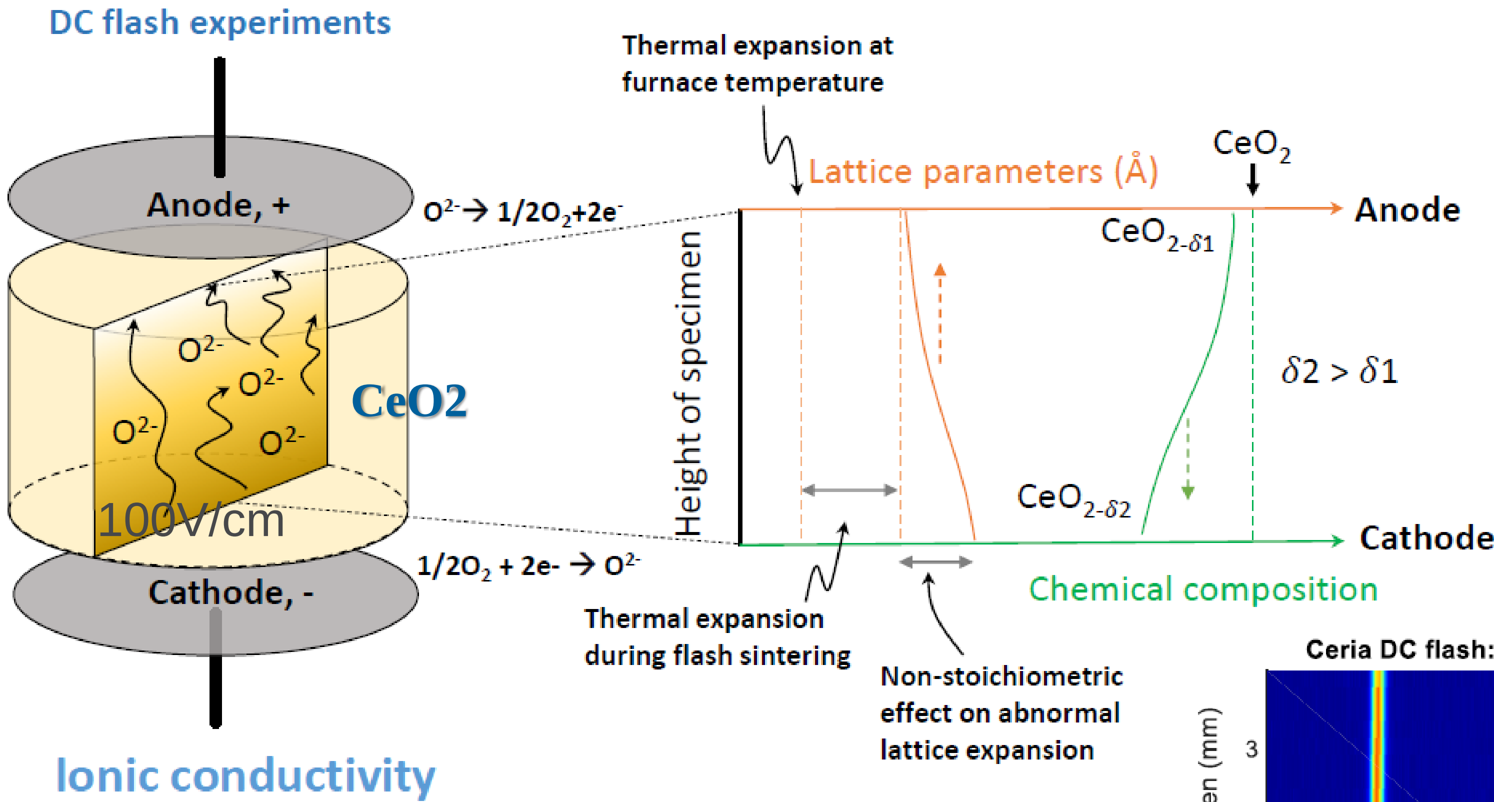
- Morphology
- Intermediates
- Metastable intermediates

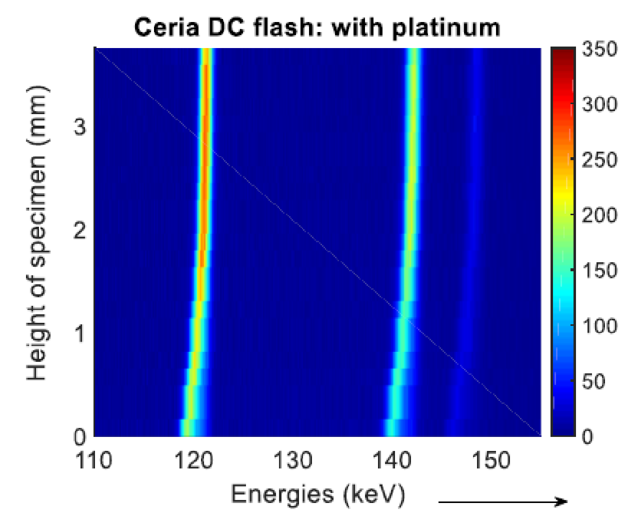
→ Tuning reaction pathway

SYNTHESES REACTORS:

Flash Sintering

Courtesy by Harry Charalambous



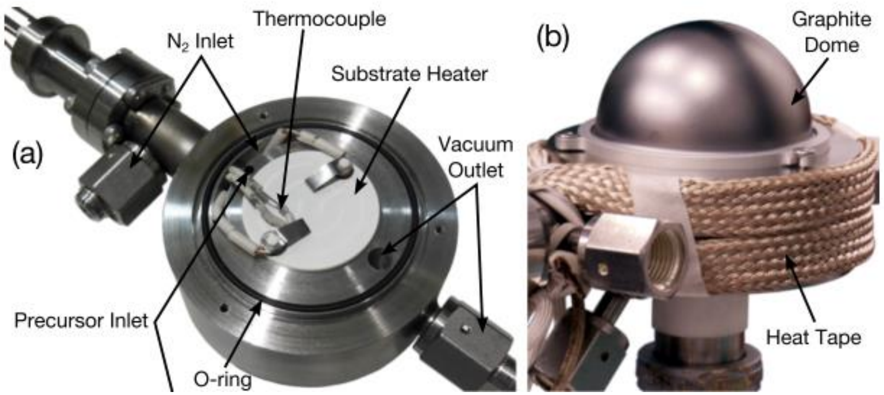


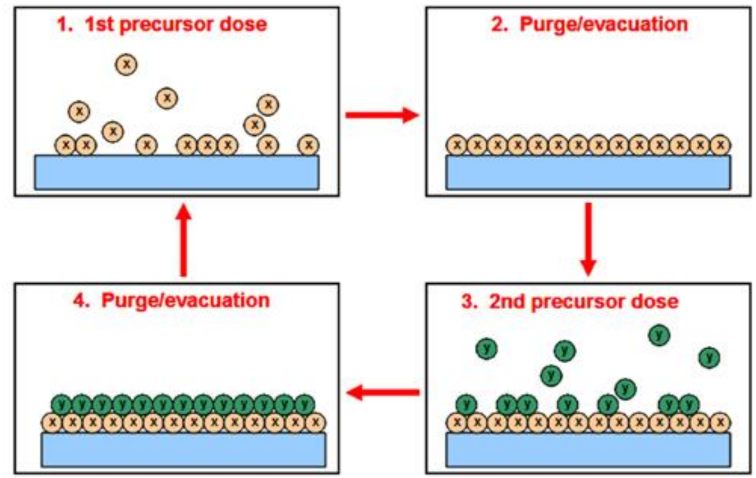
Jha, Charalambous, Wang, Phuah, Mead, Okasinski, Wang, & Tsakalakos, Ceram. Int. 2018

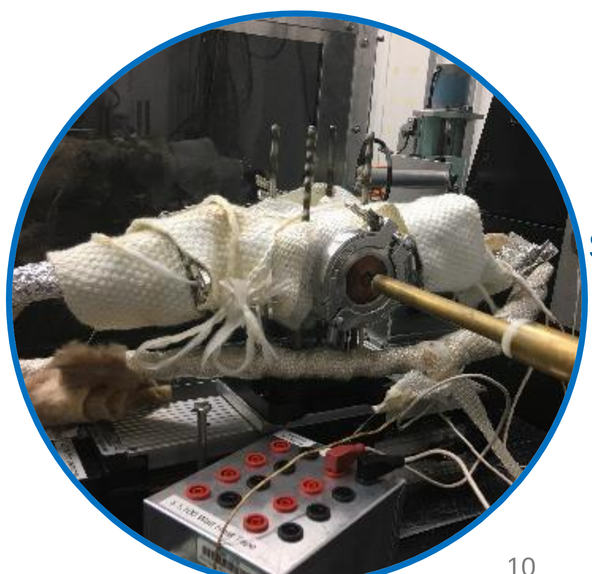
ATOMIC LAYER DEPOSITION

Deposition of precursors on substrates, but also on porous material or nanoparticles through gas flow

commercial

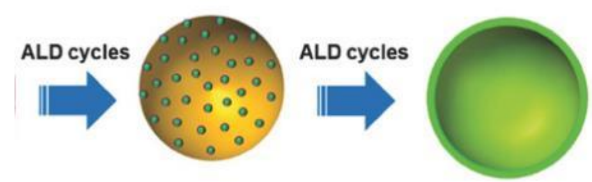






Emergency solution

Coating of nanoparticles



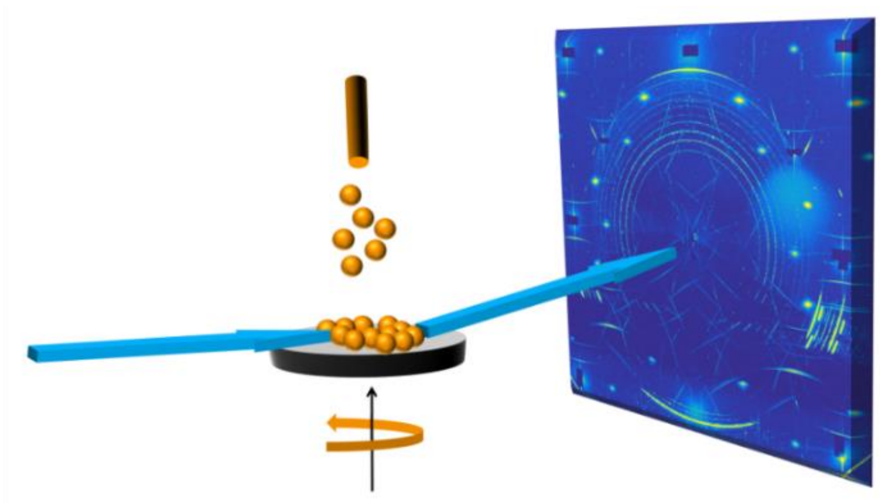
IN SITU FILM GROWTH WITH MULTIMODAL APPROACH

Molecular Beam Epitaxy (MBE) @PETRA III (Germany)

Courtesy by Anita Ehnes and Ann-Christin Dippel

Photonenergy > 60 keV

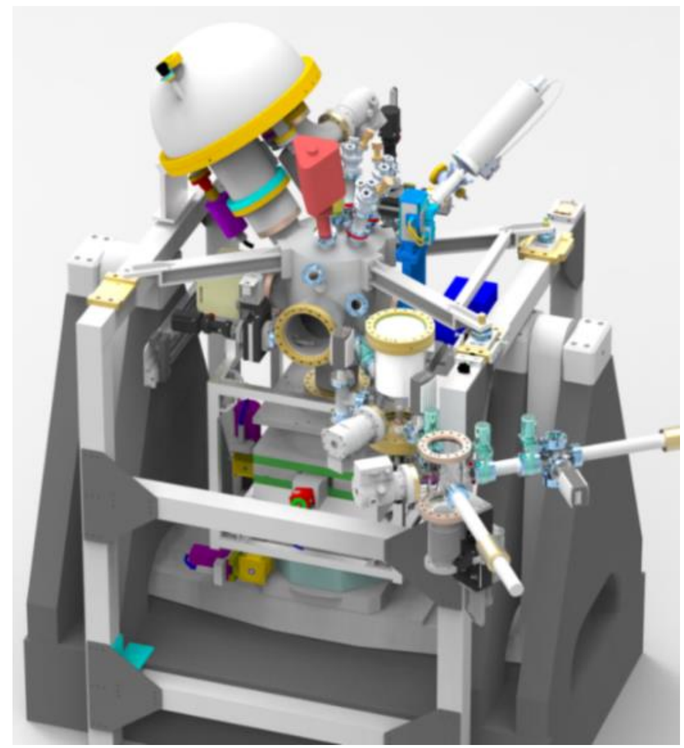
- gazing incident geometry for surface sensitivity
- no detector motion using large 2D detector
- only sample rotation required



→ follow the growth of an epitaxial thin film with time resolution below 5 sec

Collaboration with J. Wollschläger (BMBF project)

- XPS detector & x-ray tube
- RHEED system (offline only)
- LEED system for preparation chamber
- mass spectrometer



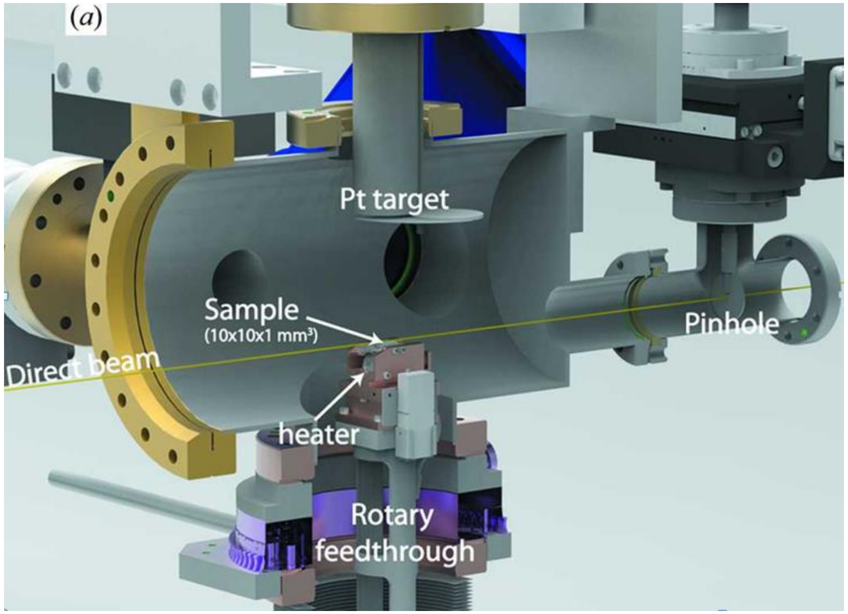
F. Bertram |scientist,DESY
J.T. Röh |engineer,DESY

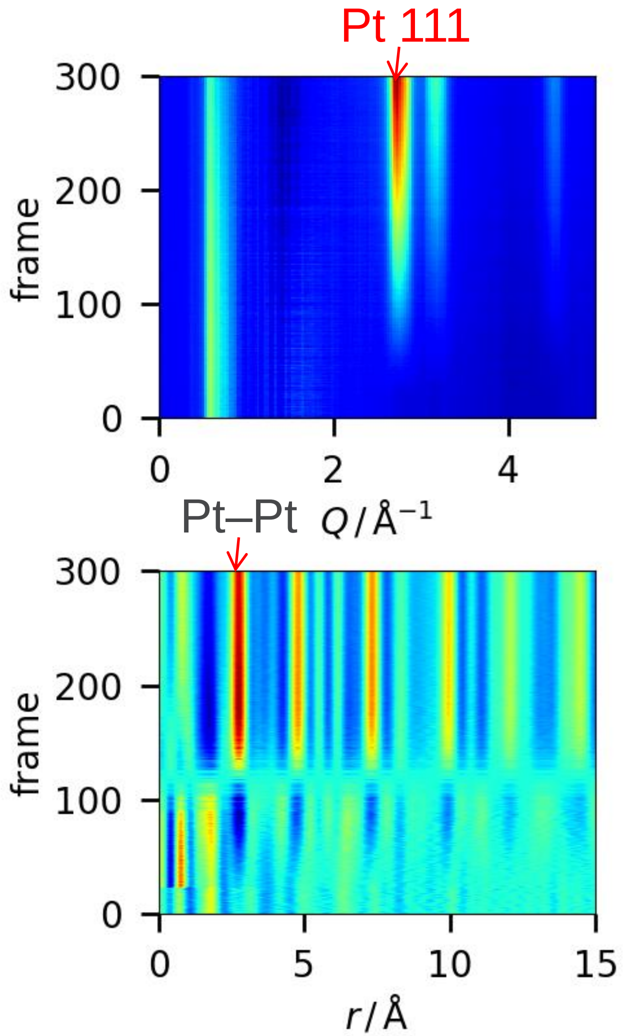
IN-SITU SPUTTER CHAMBER FOR PDF ANALYSIS

Courtesy by Ann-Christin Dippel

Time resolution: 15Hz

Photonenergy > 80 keV





Ann-Christin Dippel et al. IUCrJ (2019). 6

A.C. Dippel |scientist, DESY
M. Roelsgaard | scientist ,Aarhus Uni, Denmark
J.T. Röh |engineer,sample environment,DESY

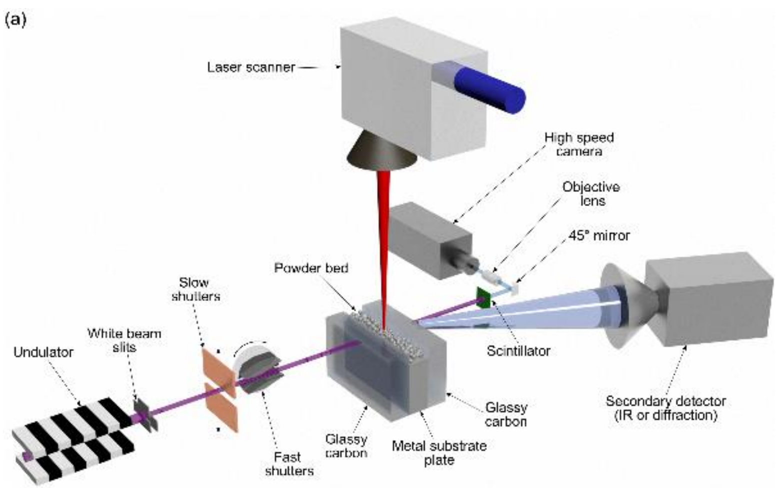
ADDITIVE MANUFACTURING RESEARCH AT APS

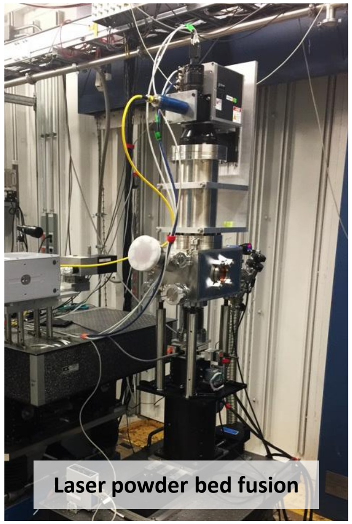
Courtesy by Tao Sun

Address the critical issues in metal additive manufacturing

In situ/operando synchrotron x-ray experiments →

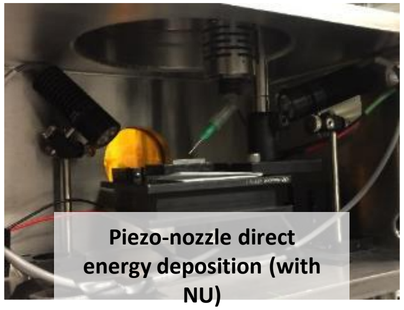
- **Structure defects**
- **Failure mechanisms**
- **High-fidelity models**
- **Reliability and Repeatability**





Laser powder bed fusion

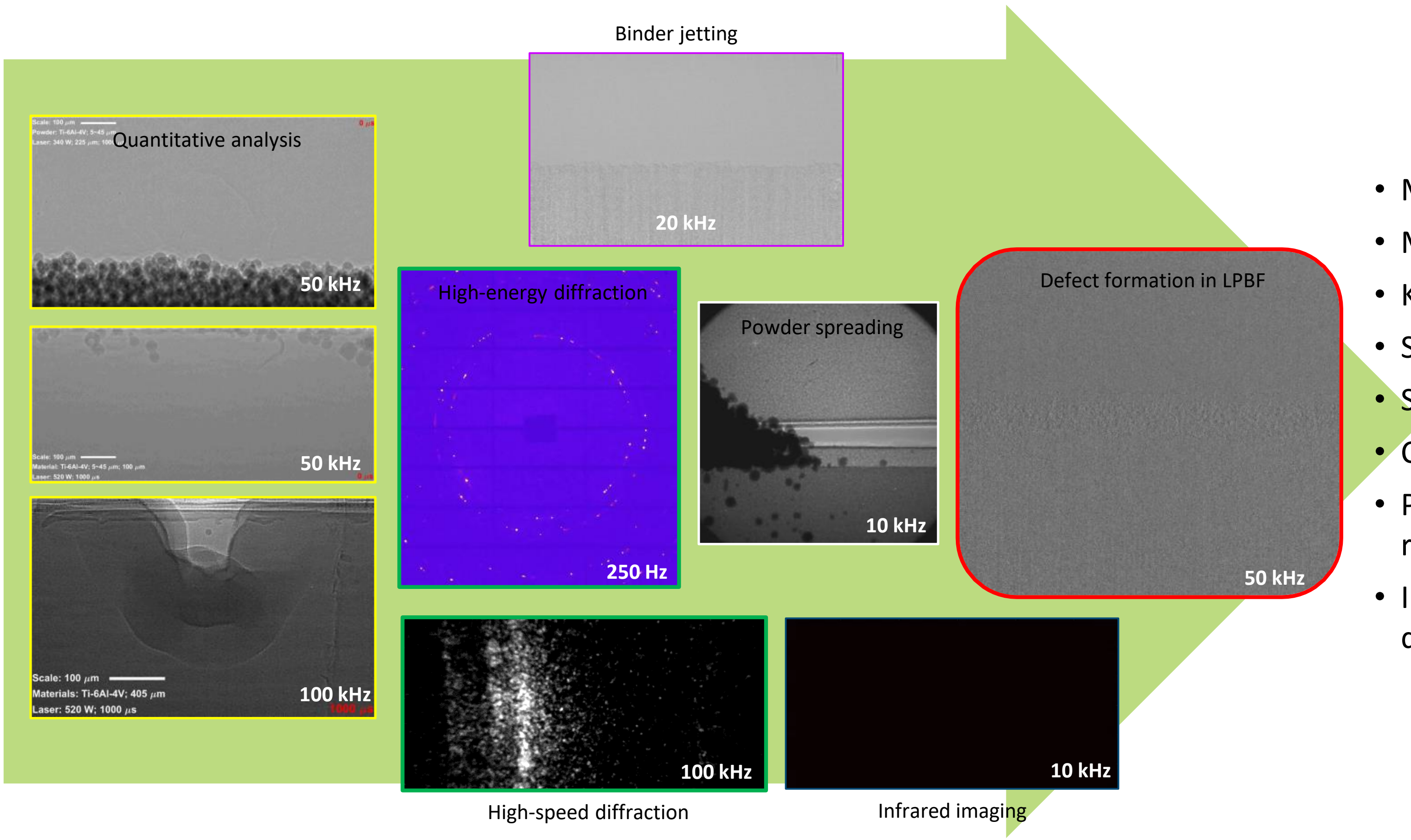
Binder jetting (ExOne machine)



Piezo-nozzle direct energy deposition (with NU)

IN SITU/OPERANDO X-RAY STUDIES ON AM PROCESSES

Courtesy by Tao Sun

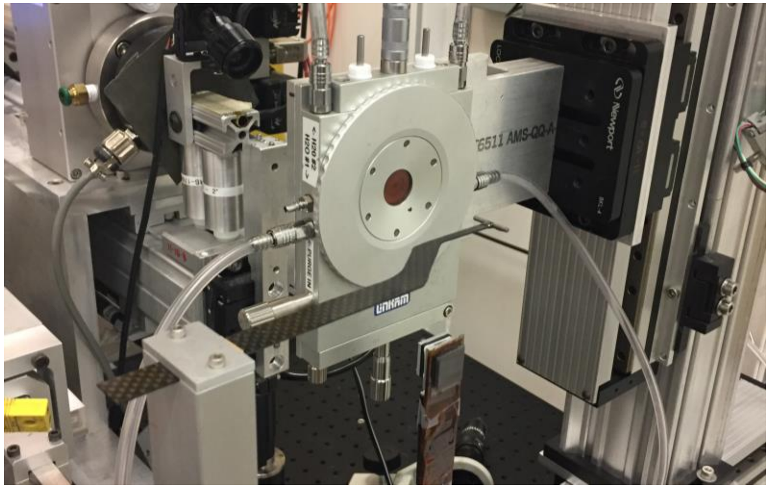


- Melt pool morphology
- Melt flow velocity
- Keyhole dynamics
- Spattering velocity
- Solidification rate
- Cooling rate
- Phase transformation rate
- Internal temperature distribution

PROPERTIES OF MATERIALS

FURNACES

Commercial / modified/ home made



Linkham (~1500º C)

Anton Paar

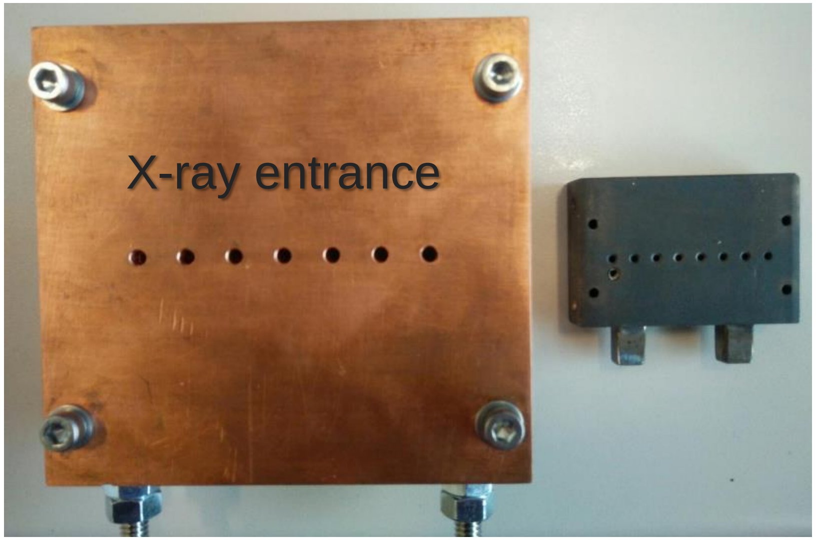
Hot air blower (up to 900º C)

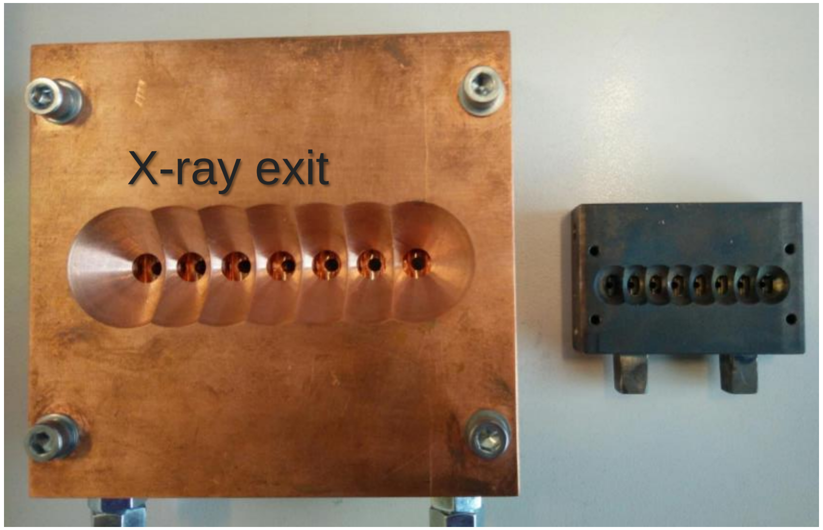
Resistive capillary heater (up to 1000º C)

FURNACES

Home made

Batch reactor for capillaries: simultaneous heating of several samples



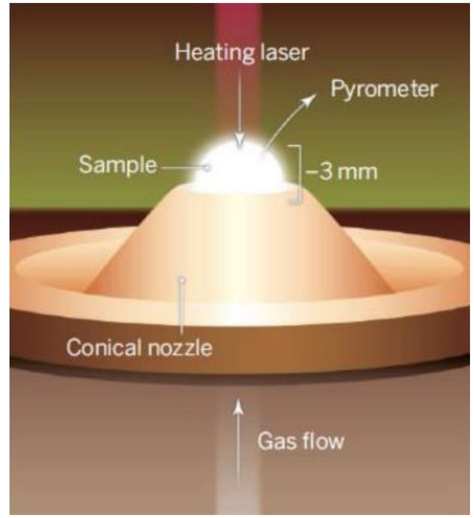


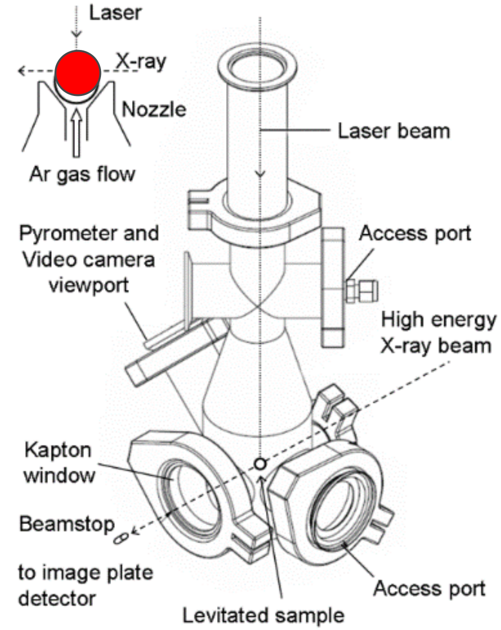
FURNACES

Extreme Conditions: Aerodynamic Levitation

Courtesy by Chris Benmore

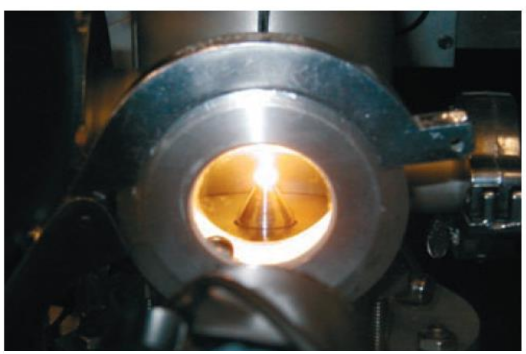
- Laser heating & aerodynamic levitation.
- Access structures at extreme temperatures from 1500 to >3300ºC.
- Oxides processed in Ar, O, N, air, CO/CO_2 atmospheres.
- Containerless: no container contamination, supercool liquids several hundred degrees.
- Observation of meta-stable states.



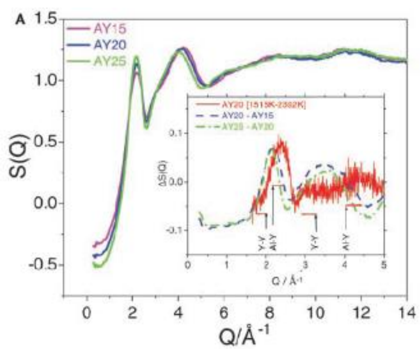


CERAMIC MATERIALS

Levitating liquids



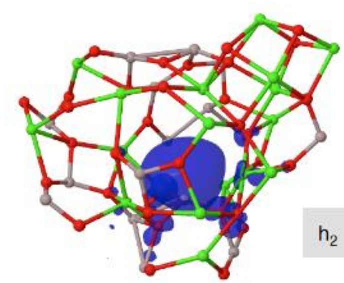
nature materials | VOL 7 | NOVEMBER 2008 |



Detection of First-Order Liquid/Liquid Phase Transitions in Yttrium Oxide–Aluminum Oxide Melts

G. N. Greaves,[1*] M. C. Wilding,[1] S. Fearn,[1] D. Langstaff,[1] F. Kargl,[1] S. Cox,[1] Q. Vu Van,[1] O. Majérus,[2] C. J. Benmore,[3] R. Weber,[4] C. M. Martin,[5] L. Hennet[6]

24 OCTOBER 2008 VOL 322 SCIENCE www.sciencemag.org



Network topology for the formation of solvated electrons in binary CaO–Al_2O_3 composition glasses

Jaakko Akola[a,b,c], Shinji Kohara[d,1], Koji Ohara[d], Akihiko Fujiwara[d], Yasuhiro Watanabe[e], Atsunobu Masuno[e], Takeshi Usuki[f], Takashi Kubo[g], Atsushi Nakahira[g], Kiyofumi Nitta[d], Tomoya Uruga[d], J. K. Richard Weber[h,i], and Chris J. Benmore[i,1]

www.pnas.org/cgi/doi/10.1073/pnas.1300908110

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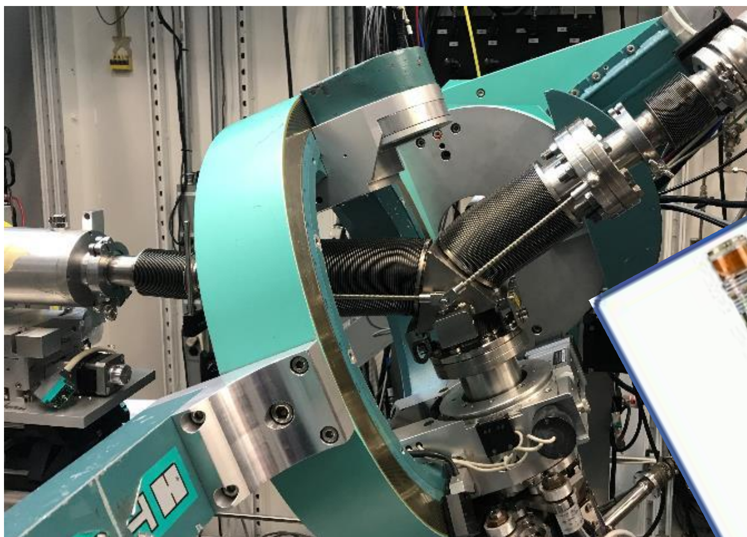
CRYOSTATS – CRYOCOOLER

Displex: sample shielded (<10 K)
Bath cryostat: sample shielded (<10 K)
LN2/He- Cryostream: sample in air (80K/4K)

Courtesy by Joerg Strempfer



Displex cryostat

Cryostream

MAGNETIC FIELDS

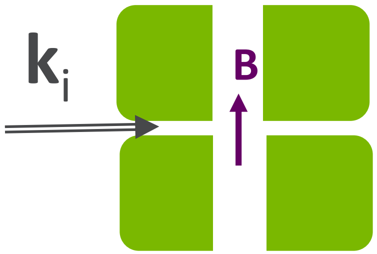
Earth: 0.00004 T
Refigrator magnet: 0.005 T
Permanent magnet neobdynium:1.25 T

Contiunous field Superconductor: <20T
Pulsed field: 100 T

DIFFRACTION STUDIES IN PULSED MAGNETIC FIELD (GEOMETRY)

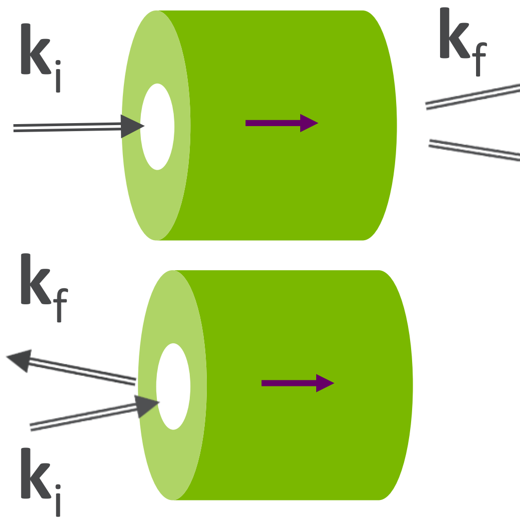
Split-pair magnet:

TRANSVERSE (no optical access limitation)
LONGITUDINAL (out-of-plane; very limited)



Solenoid:

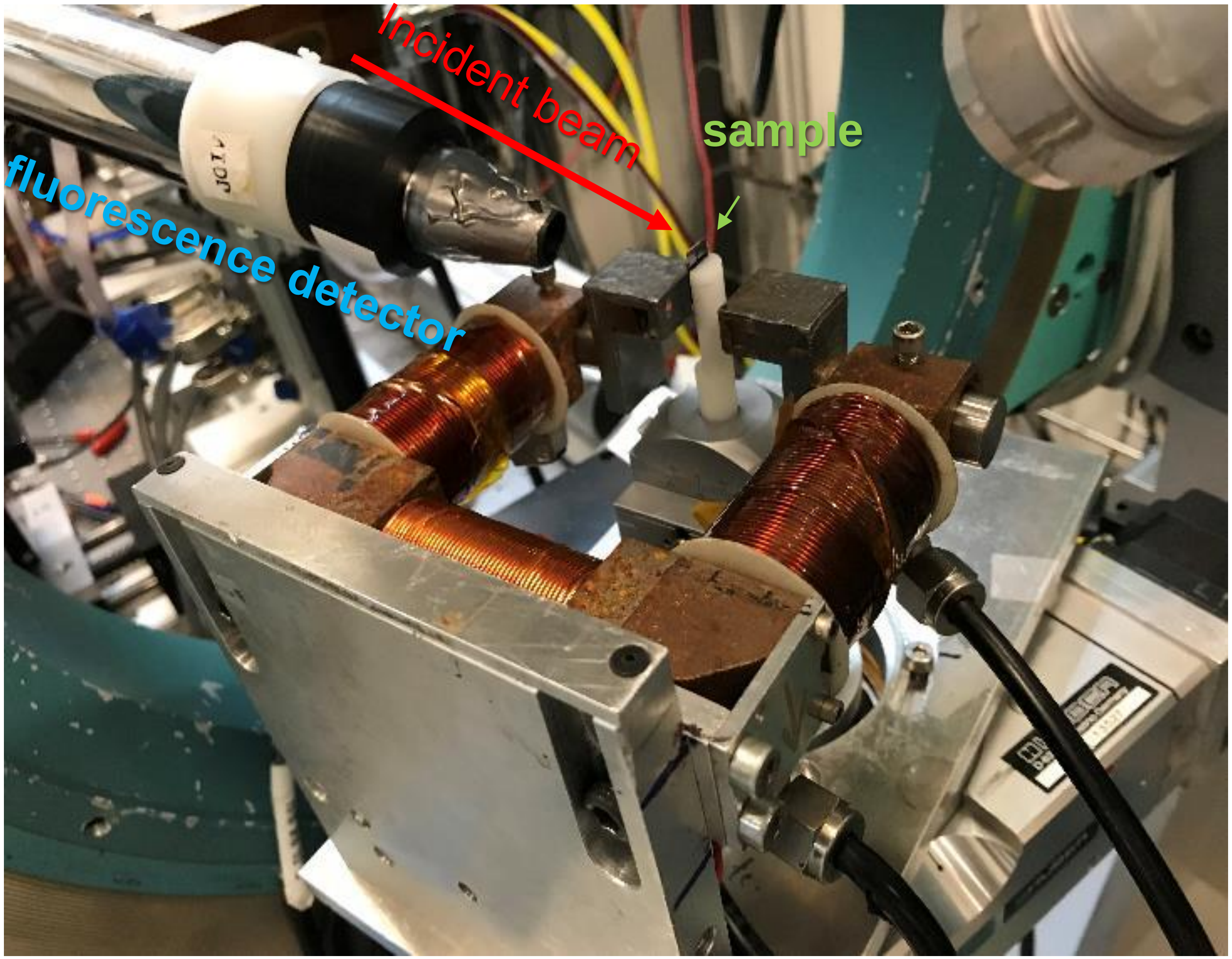
TRANSVERSE (forward scattering; limited)
LONGITUDINAL (back-reflection; sensitive)



MAGNETIC FIELD

Courtesy by Joerg Strempfer

Electromagnet ~ 0.1 T



For XMCD

MAGNETIC FIELD:

Superconducting

6.5 T spectroscopy

APS

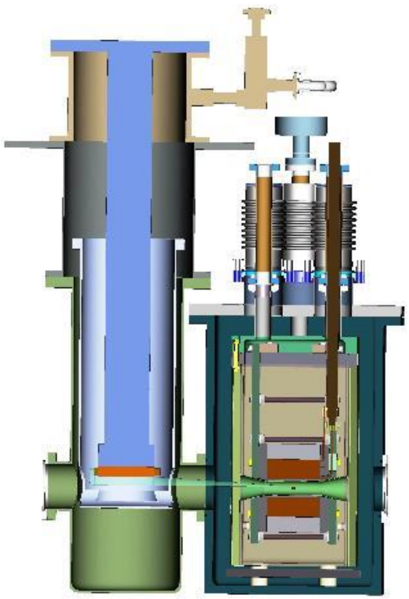
7 T HEX diffraction

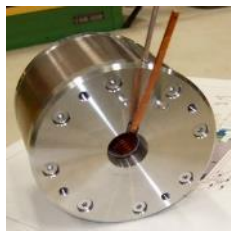
14 T diffraction

PETRA III

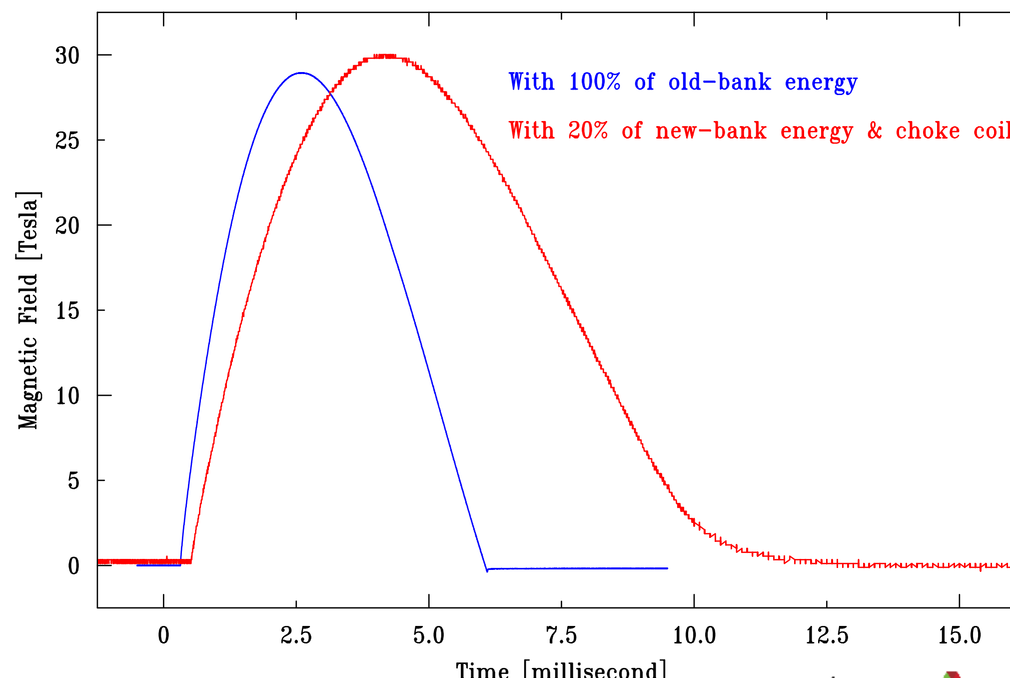
MAGNETIC FIELD: Long-pulse 30 Tesla solenoid

Courtesy by Zahir Islam





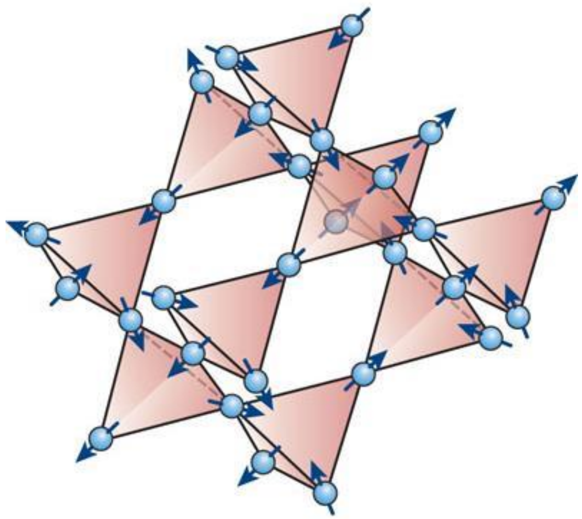
- Large safety margin (use lower voltages than maximum rated voltage of 10 kV reduces chances of capacitor failures
- **30 Tesla, 10 ms pulse every 12 minutes**
- Longer pulse matching fast (~1 kHz) 2D detectors (*e.g.* MMPAD) to improve efficiency



APS: D. Capatina, G. Trento, A. Cours, J. Fuerst; NHMFL: bank; Tohoku: high-field coil & choke coil

FRUSTRATED MAGNETISM: MAGNETO-ELASTICS OF A SPIN LIQUID

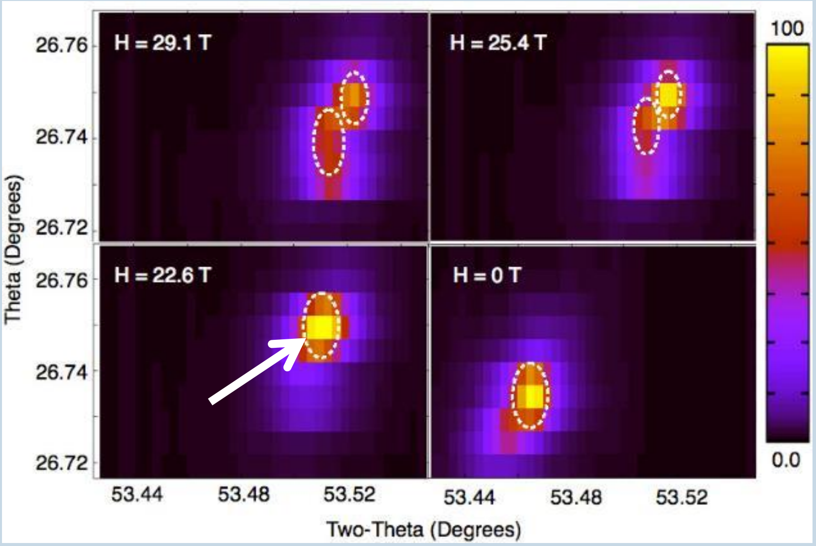
Courtesy by Zahir Islam



Conceptually important model system

- Strong correlations/fluctuations
- Coupled degrees of freedom
- Novel (quantum) phases

$TbTi_2O_7$ spin liquid



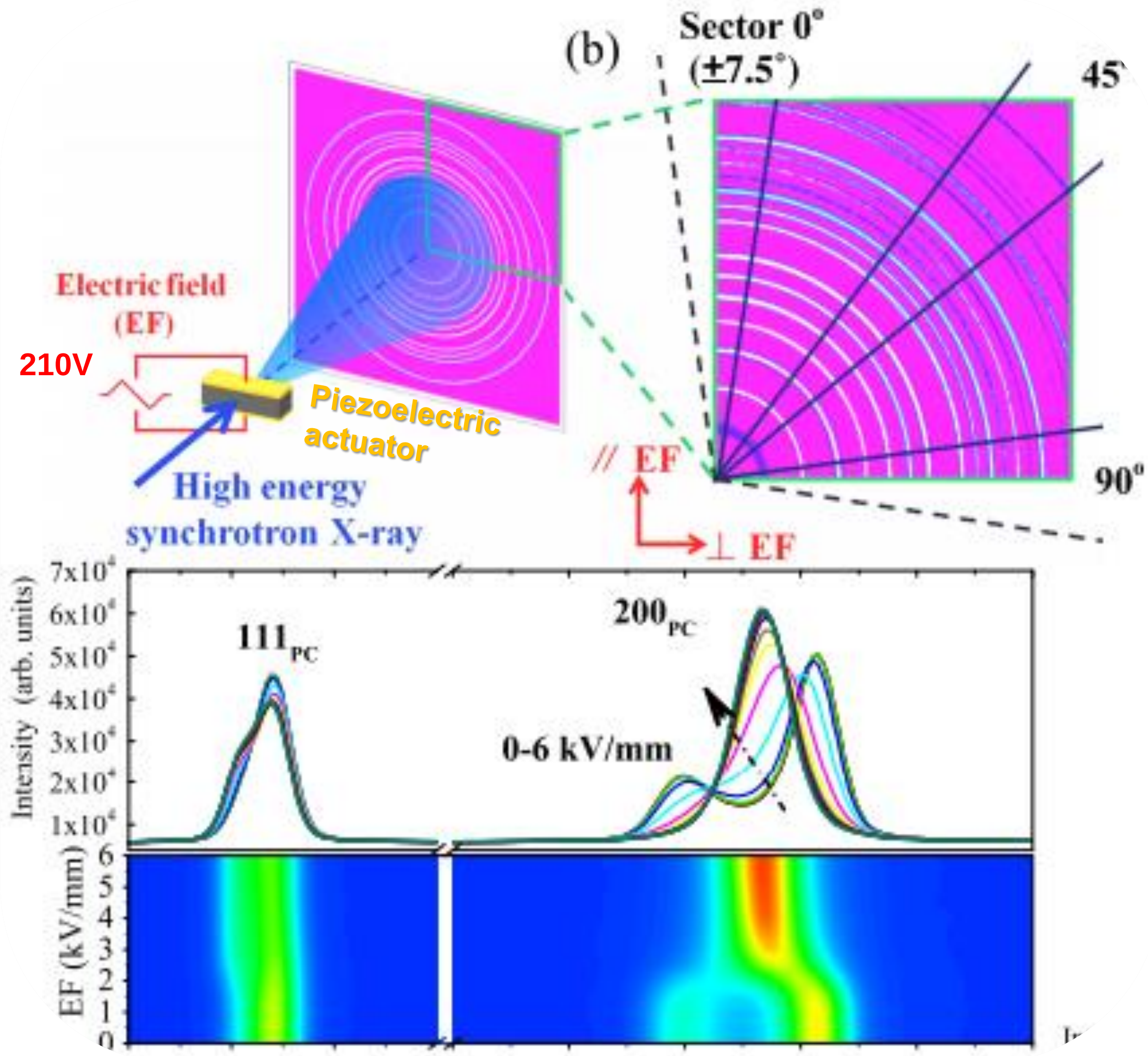
J. Ruff *et al., Phys. Rev. Lett.* **105**, 077203 (2010)

Material has no magnetic order down to ~70mK. Magneto-striction observed below 25T and structural transition above 25T.

1ms pulse every >20 minutes

ELECTRICAL FIELD

Courtesy by Yang Ren



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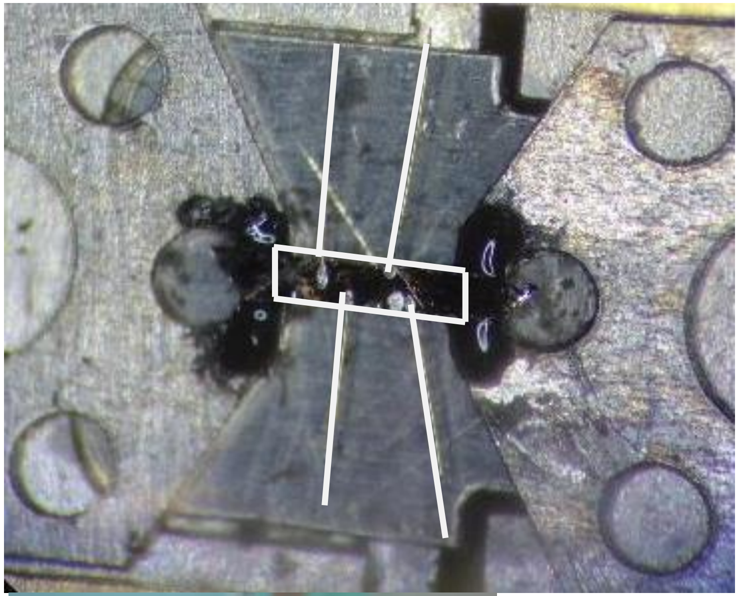
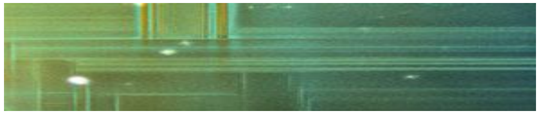
LOAD FRAME

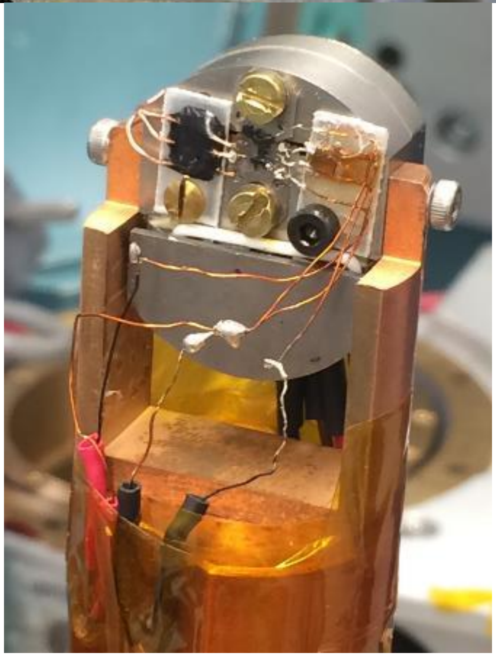
Single Crystal Uniaxial Strain : Razorbill CS100, 5·10^6 N/m, 6 µm displacement



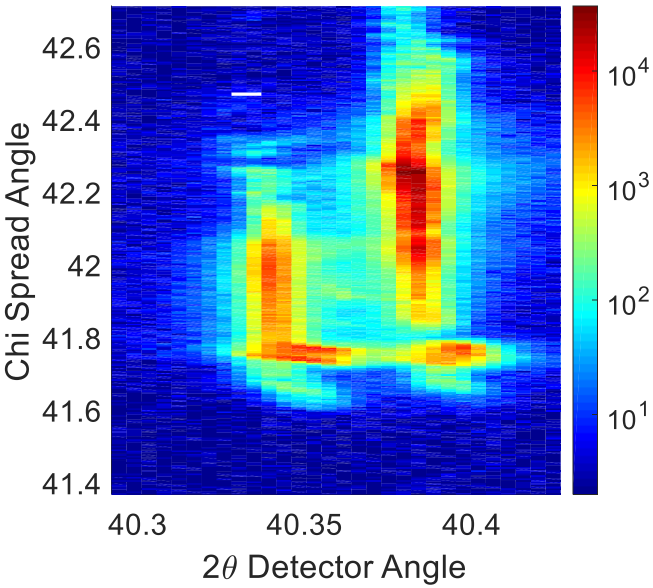
Courtesy by Philip Ryan

1500 x 300 µm^2





Temperature
+
Strain
+
Electrical field



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FUNCTIONALITY

COMPRISES & MODEL SYSTEMS

Actual devices ←→ Reduction to the relevant

Industry standard coin cell

“X-ray enabled coin cell

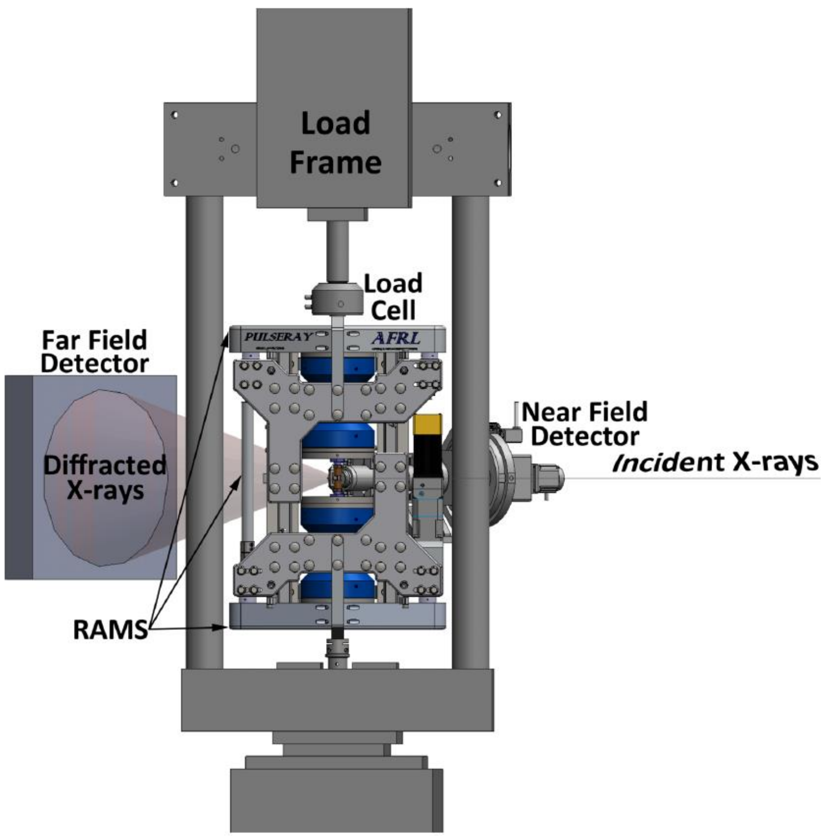
Coin cell substitute

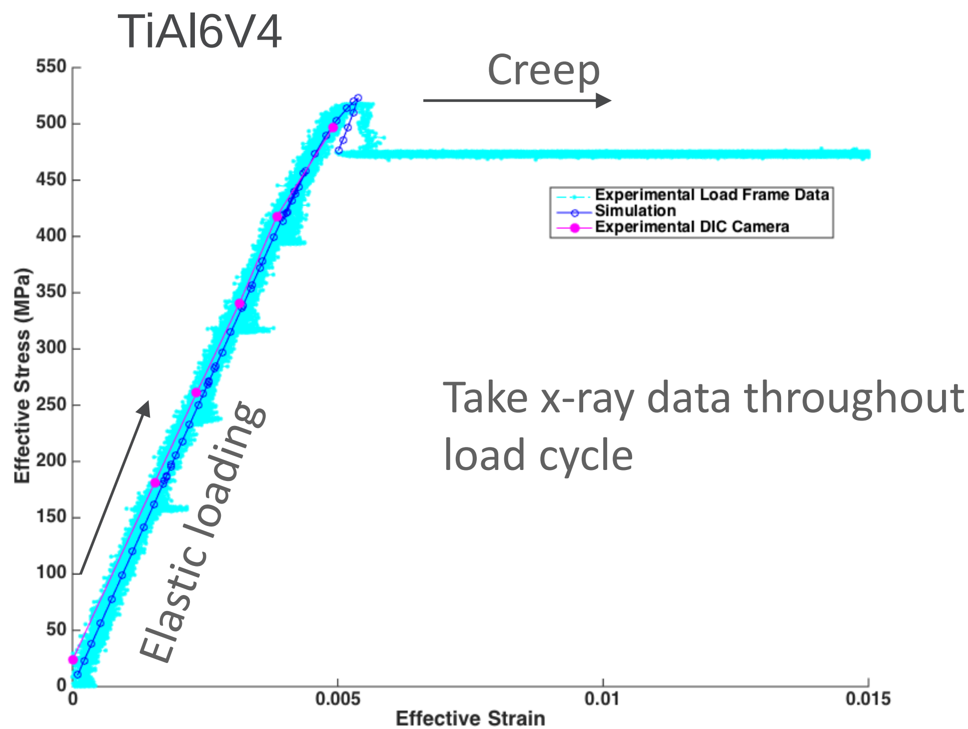
LOAD FRAME

In-grip Rotation During Mechanical Loading

Courtesy by Jon Almer

- Rotation and Axial Motion System (RAMS)
- Enables HEDM and tomographic imaging during mechanical loading





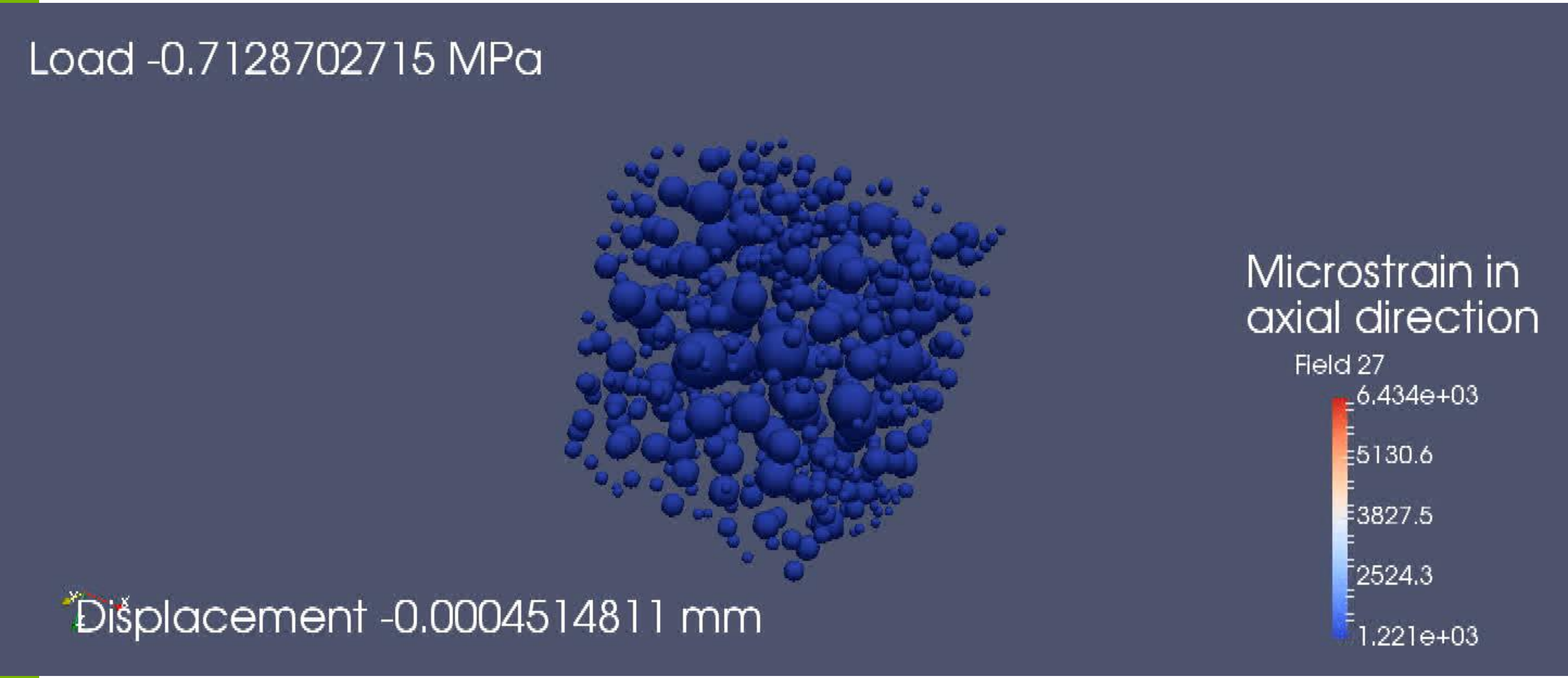
RAMS developed by AFRL/PulseRay and partner users at ANL/CMU/LLNL/Petra-III

P. Shade, B. Blank et al, RSI 86 (2015), 093902

LOAD FRAME

Grain-resolved Strains Along Loading Direction (FF-HEDM)

Courtesy by Jon Almer



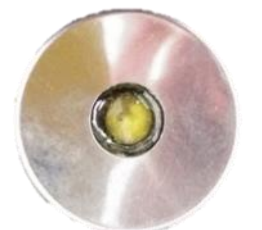
- Full 3D strain/stress tensors of all grains in ~1mm^3 volume
- Axial strains in elastic regime shown – heterogeneous!
- During creep, stress heterogeneity increases (not shown)
- Rich set of data to test material models

J. Schuren, P. Shade et al, COMMS 19 (2015), 235-244

ELECTROCHEMISTRY
Comprises & Model Systems

Actual devices ←→ Reduction to the relevant

Industry standard coin cell



“X-ray enabled coin cell

Coin cell substitute

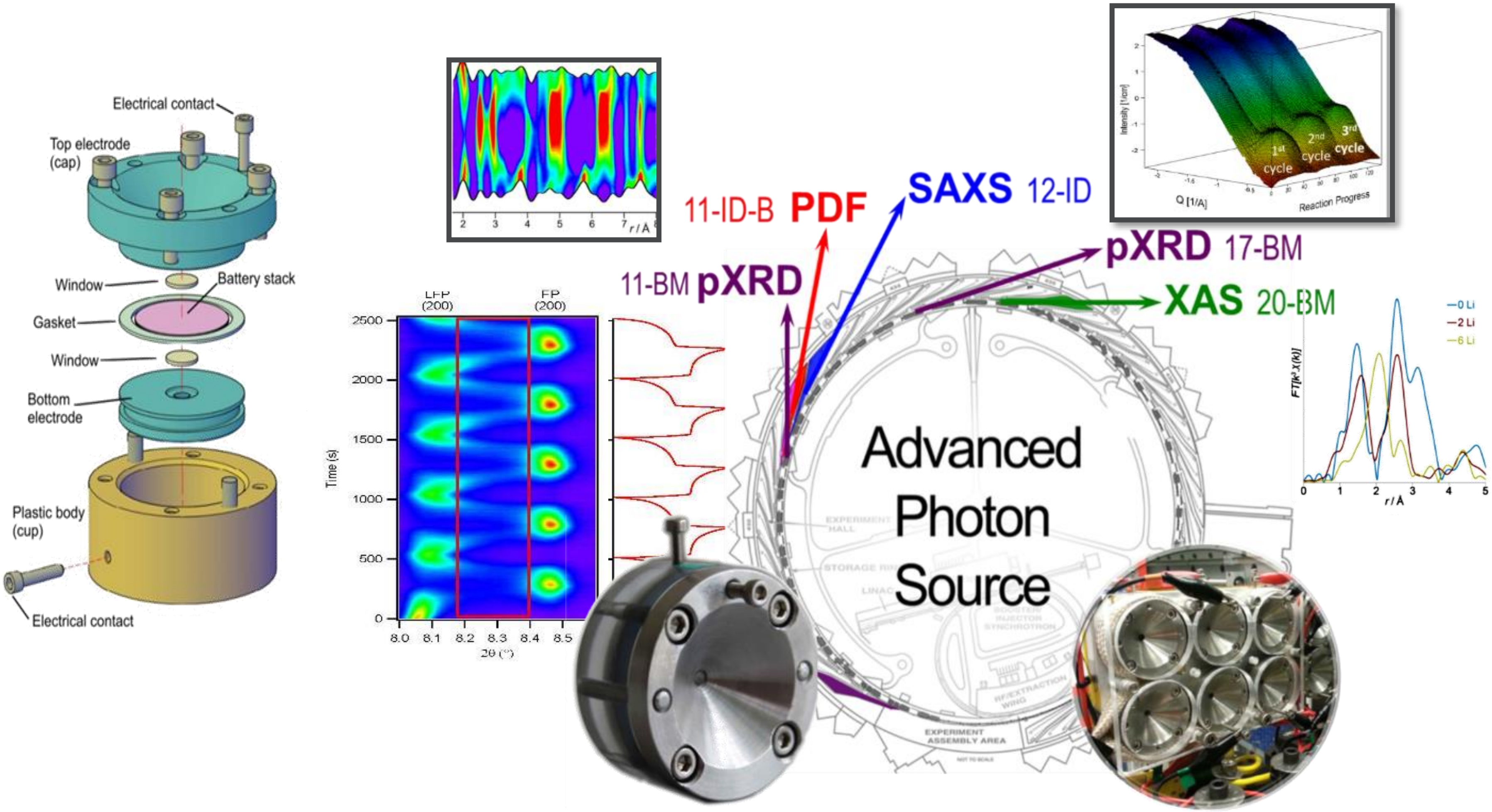
Courtesy by Kamila Wiaderek

ELECTROCHEMISTRY

BRIDGE To The Gap Between Performance And Data Quality; AMPIX cell

Courtesy by Kamila Wiaderek

AMPIX US Patent 9,022,652

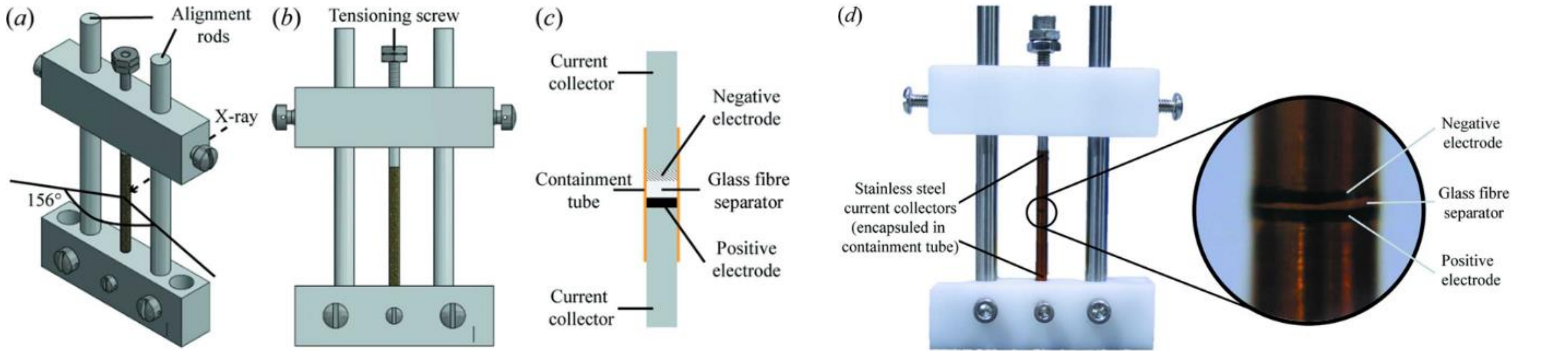


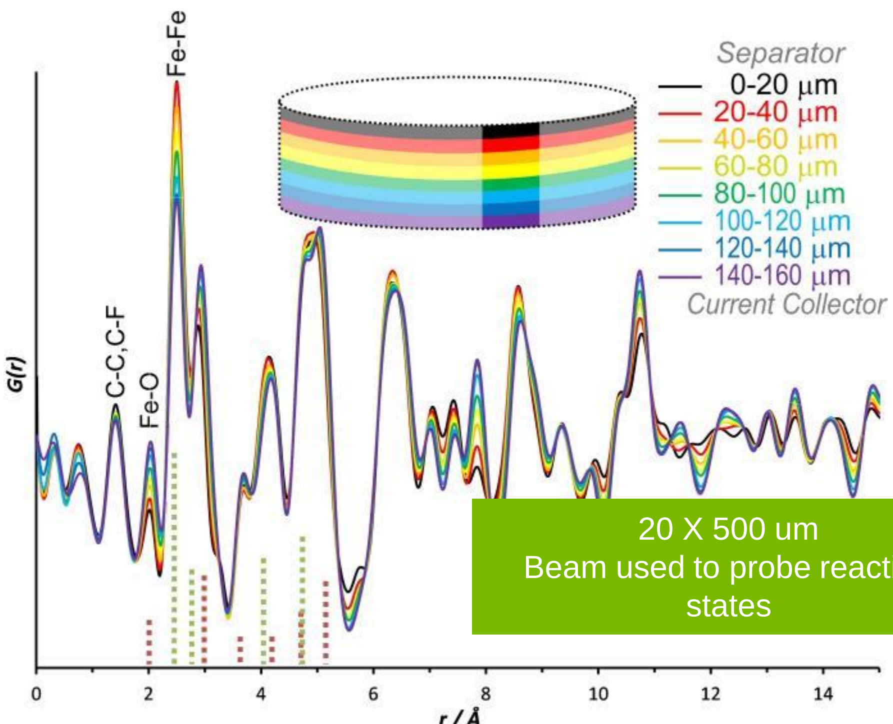
Borkiewicz et. al, J. Appl. Cryst., **2012**, 1261-1269

ELECTROCHEMISTRY

Pellet Horizontal Surface Aligned Parallel To The X-ray Beam

Courtesy by Kamila Wiaderek





20 X 500 um
Beam used to probe reaction states

Electrode homogeneity is true commercial challenge

Sample environments that allow full cell studies and deconvolution of the signal coming from anode and cathode are in demand.

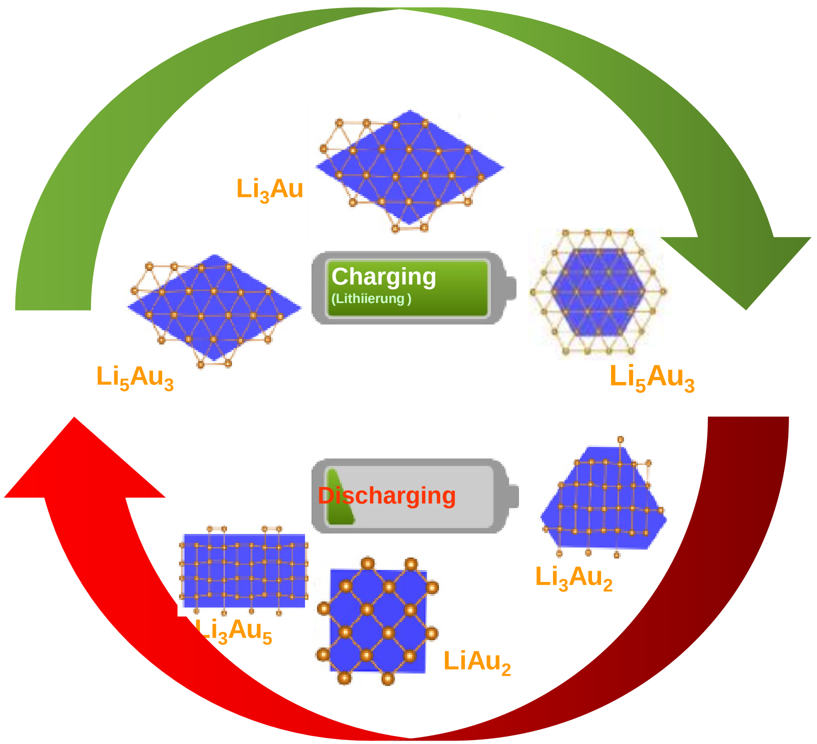
Existing cells are still in the development stages and have poor reliability

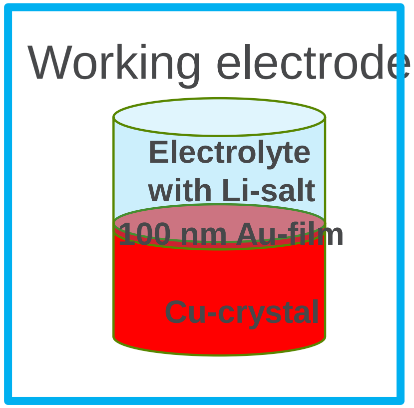
Borkiewicz et. al, Phys. Chem. Chem. Phys., **2013**, 8466-8469

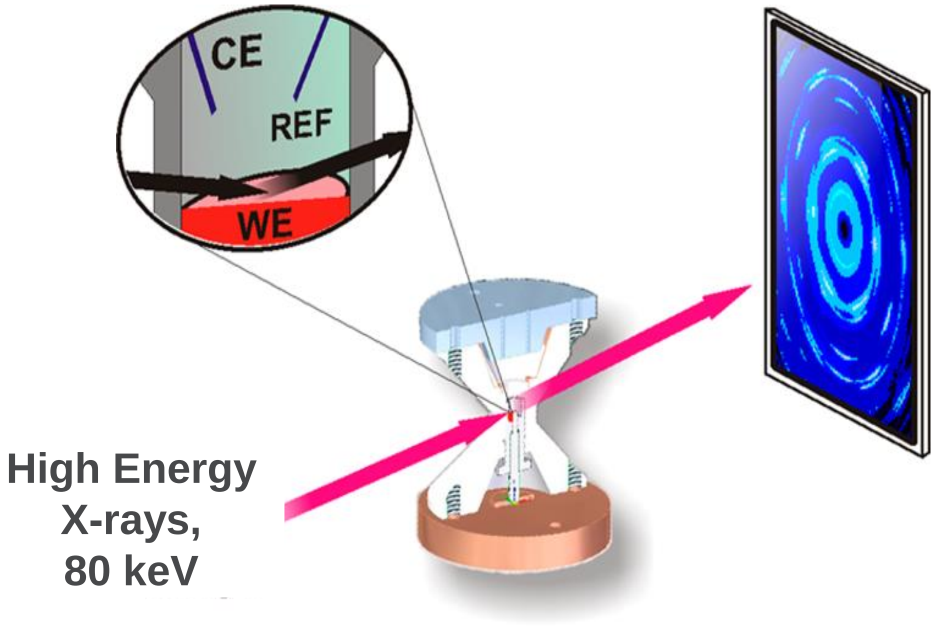
ELECTROCHEMISTRY

Electrochemical Lithiation Cycles Of Gold Anodes In Model System

P. Bach, I. Valencia-Jaime, U. Ruett, O. Gutowski, A.H. Romero, F.U. Renner .Chem. Mater., (2016), **28** (9), 2941

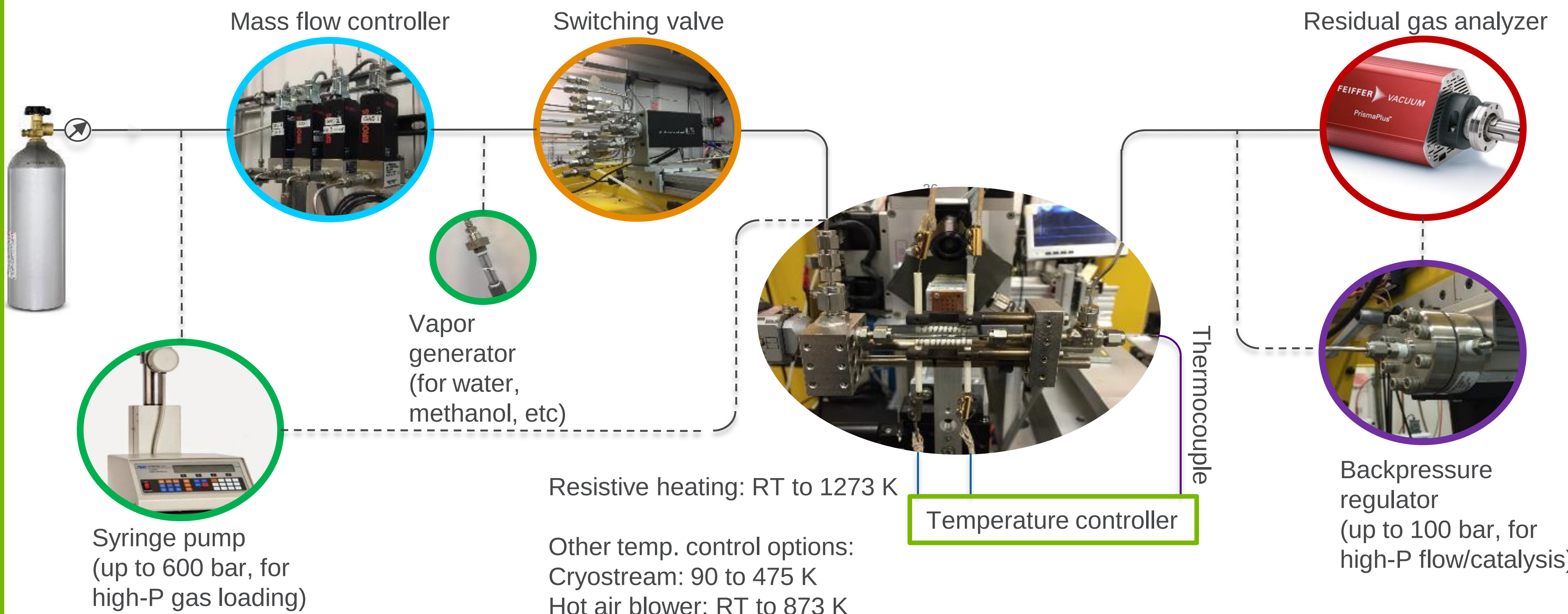


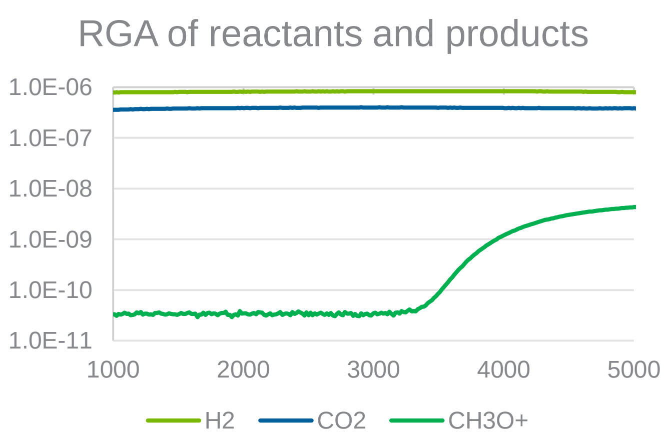


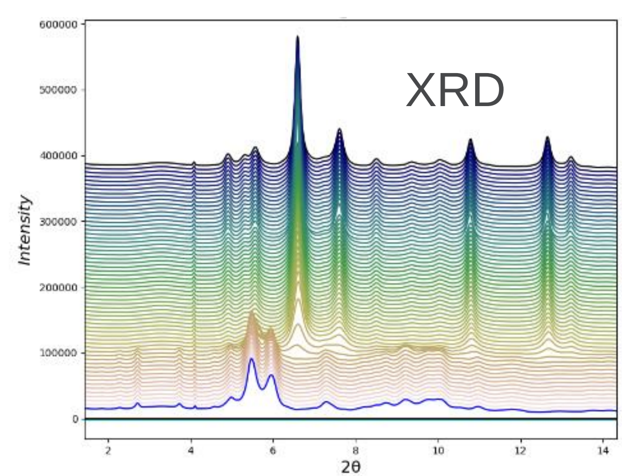


GAS LOADING AND CATALYSIS

Courtesy by Andrey Yakovenko





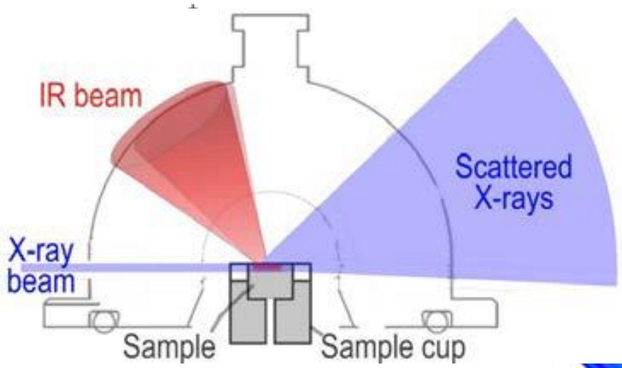


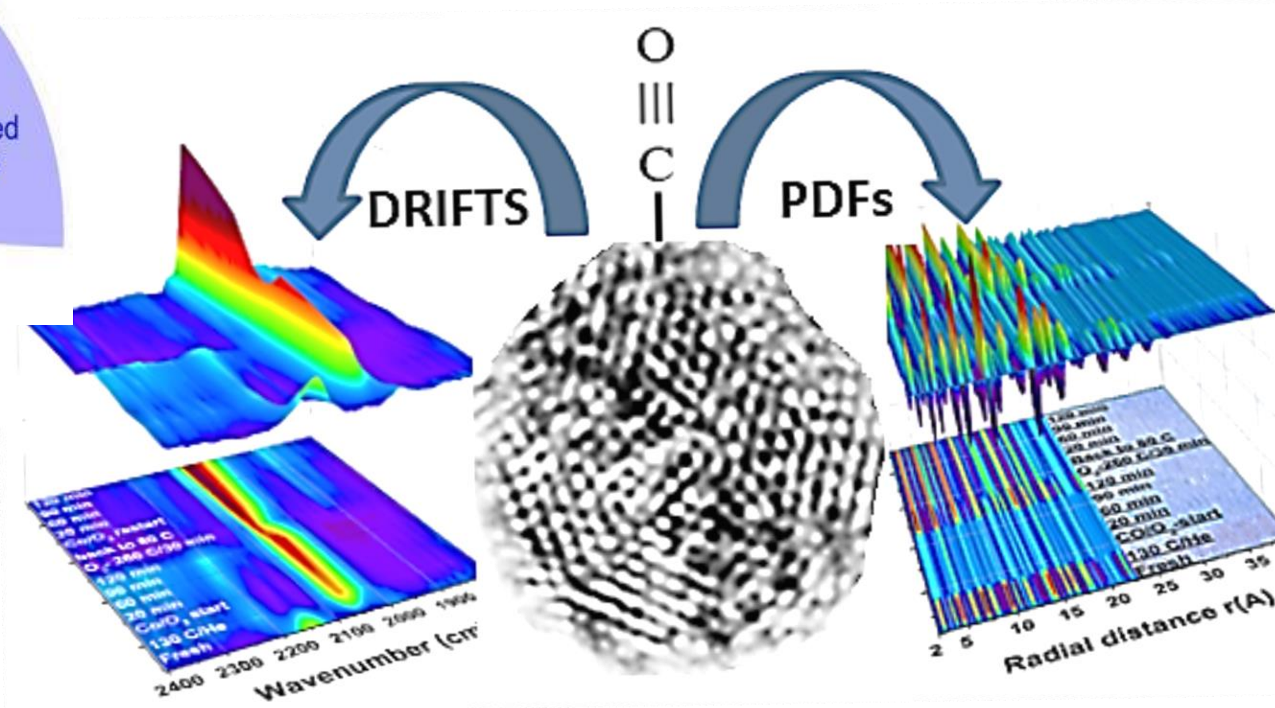
CATALYSIS

ACS APPLIED MATERIALS & INTERFACES
Research Article
Cite This: ACS Appl. Mater. Interfaces 2018, 10, 10870−10881
www.acsami.org

Evolution of Active Sites in Pt-Based Nanoalloy Catalysts for the Oxidation of Carbonaceous Species by Combined in Situ Infrared Spectroscopy and Total X-ray Scattering

Valeri Petkov,*,† Yazan Maswadeh,† Aolin Lu,‡ Shiyao Shan,‡ Haval Kareem,‡ Yinguang Zhao,‡ Jin Luo,‡ Chuan-Jian Zhong,‡ Kevin Beyer,§ and Karena Chapman§

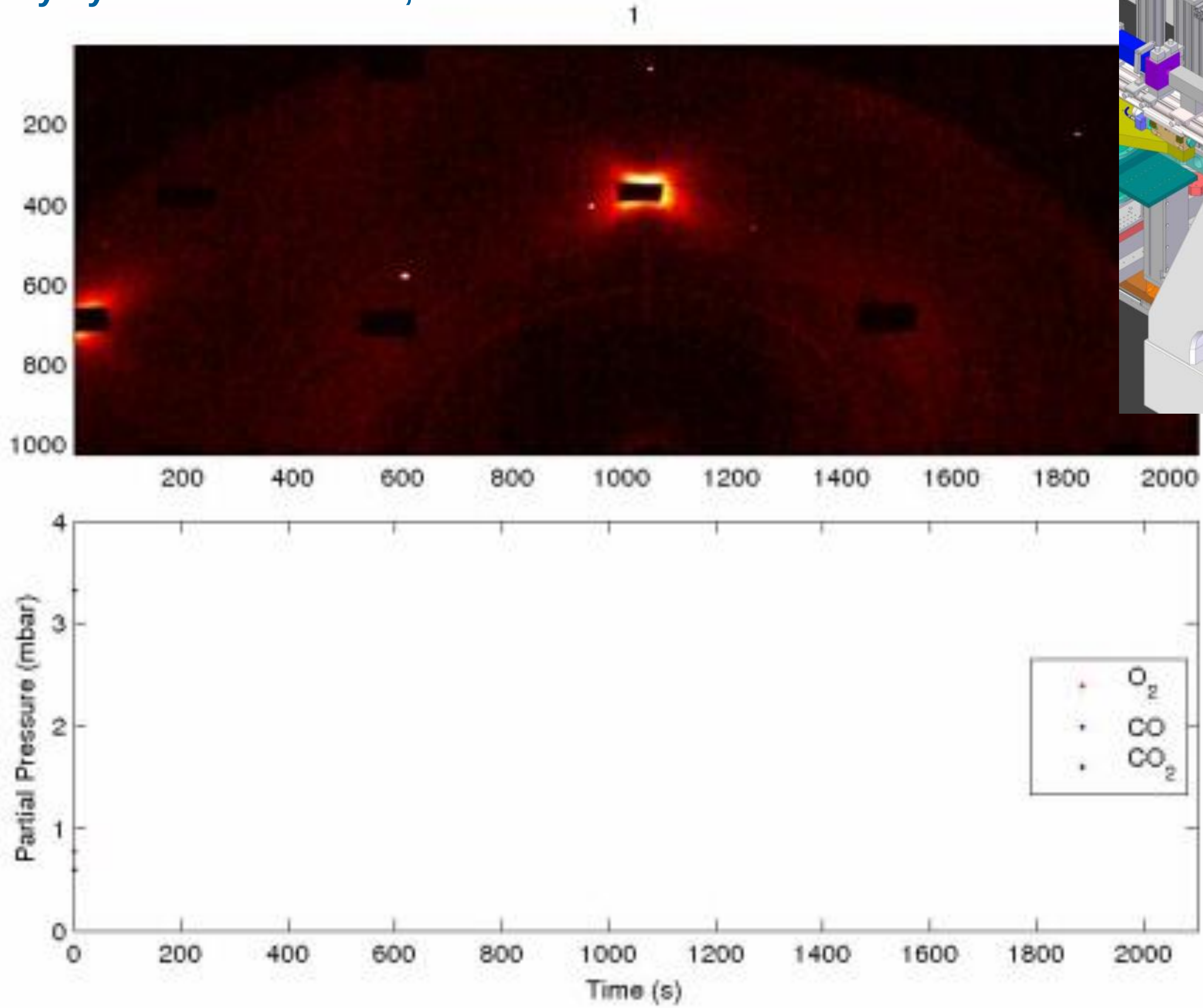


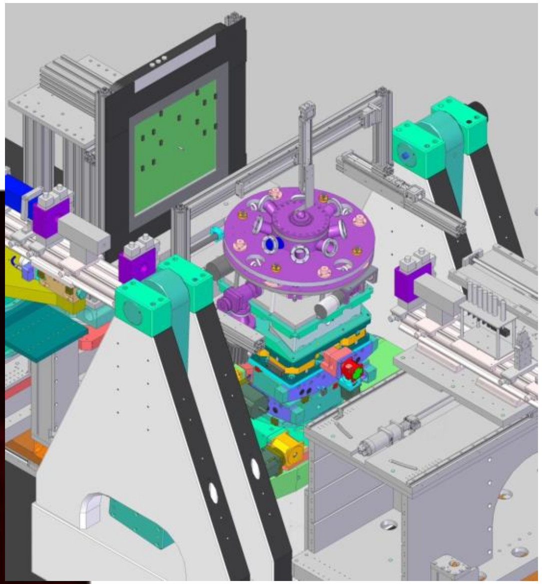


CATALYSIS

Pd surface, CO → CO2

Courtesy by Johan Gustafson, PETRA III





J. Gustafson, M. Shiplin, C. Zhang et al. (2014) **Science** 343, p.758

TAKE HOME MESSAGE:

DON'T LIMIT YOURSELF TO THE EXISTING TOOLS, BUT

GET INSPIRED BY THE VARIETY

THE EXISTING SAMPLE ENVIRONMENTS SHOW WHAT WE CAN DO TODAY, THEY DON'T DETERMINE WHAT YOU WILL DO IN THE FUTURE.

ALBERT EINSTEIN: "YOU HAVE TO LEARN THE RULES OF THE GAME, AND THEN YOU HAVE TO PLAY BETTER THAN ANYONE ELSE."