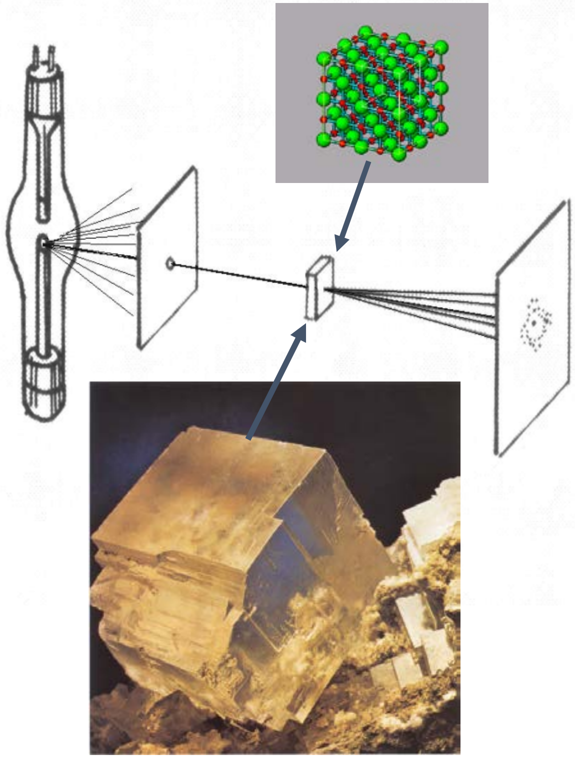
DYNAMIC CRYSTALLOGRAPHY

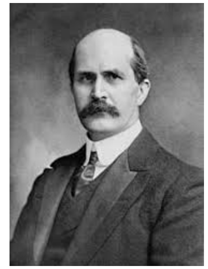
Bo Brummerstedt Iversen
Center for Materials Crystallography
Department of Chemistry
Aarhus University

A talk from a potential future user ?

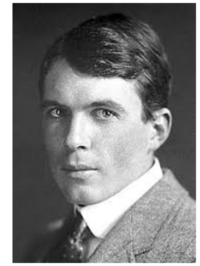
Static Crystallography



Max von Laue

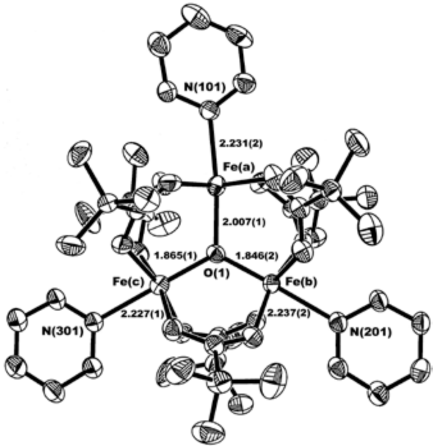


W. H. Bragg

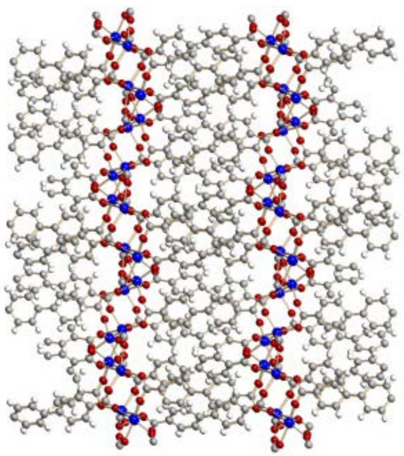


W. L. Bragg

molecular crystals

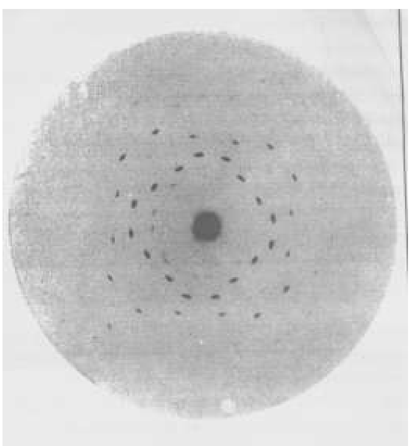


extended structures



Intensity $\propto |F|^2$

$\rho(r) = 1/V\Sigma F(H)\exp(-2piHr)$

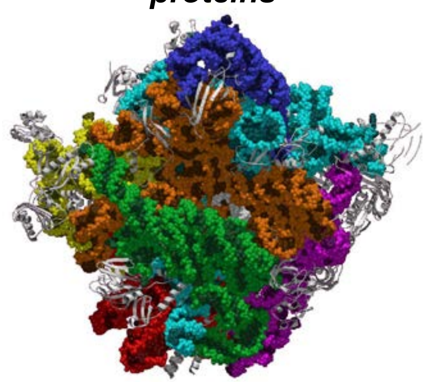


ZnS, von Laue, 1912

Time and spatially averaged electron density in the crystal

Crystal is unperturbed

proteins

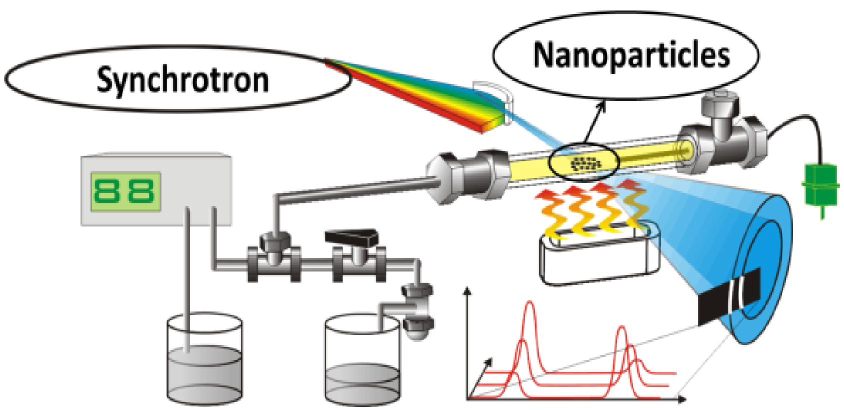


Crystallography is becoming DYNAMIC

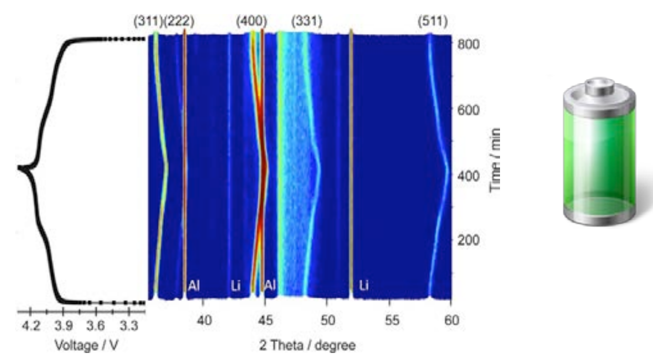
Real Materials, Real Conditions, Real Time

Static experiments Model systems *Ex situ*	Intense radiation → Accurate detectors	Dynamic experiments Real materials *In situ, Operando*

Watching the formation of nanoparticles



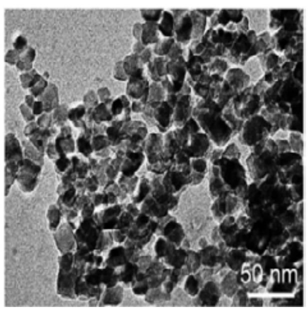
Looking inside operating batteries

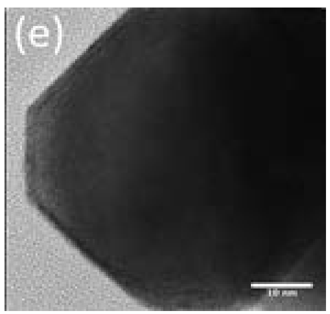


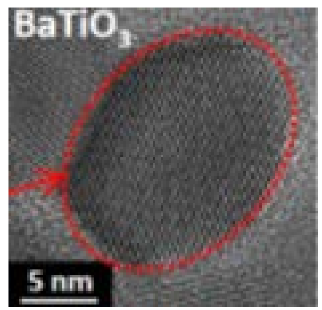
Charge **Discharge** **Structural change**

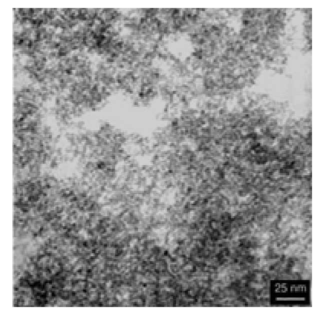
Requires hard X-ray radiation to study inorganic materials and to penetrate sample environments

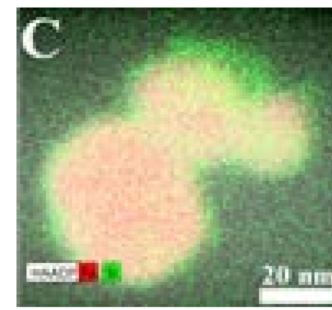
Solvothermal flow reactors – kg scale

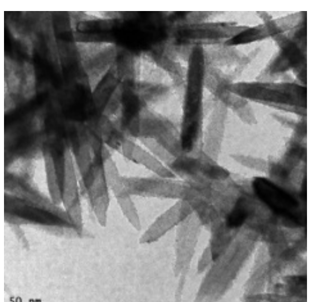


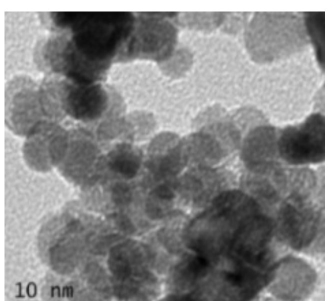


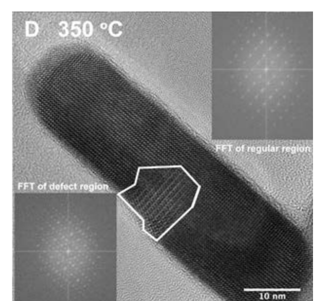


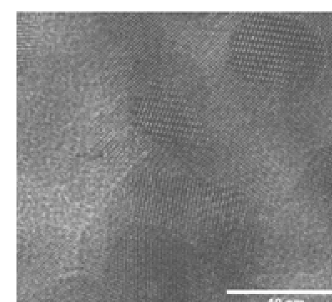




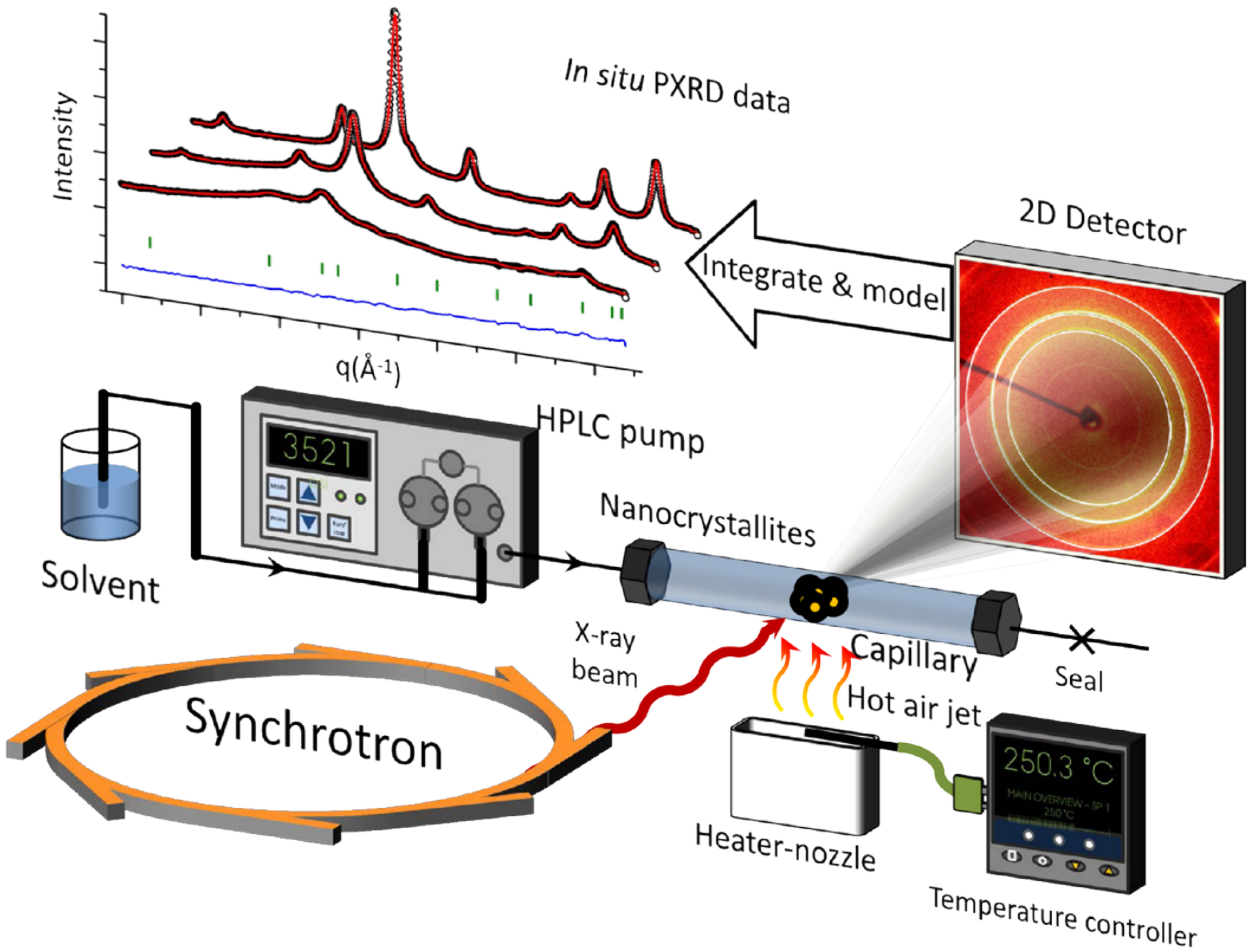








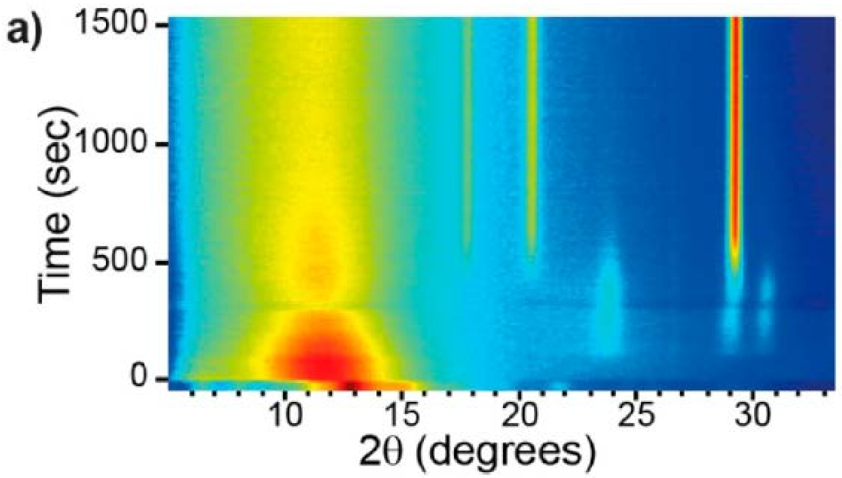
In situ X-ray scattering studies



H. L. Andersen et al., *J. Appl. Crystallogr.* **2018**, 51, 526-540

In situ Powder X-ray Diffraction

$Cu_{2-x}S$



- Phase analysis
- Atomic structure
- Defects
- Crystalite size
- Morphology
- Size distribution

P. Nørby et *al.*, *ACSNANO* **2014**, 8, 4295-4303

In situ PXRD

Nanoscale — RSC Publishing — PAPER

Pulsed supercritical synthesis of anatase TiO_2 nanoparticles in a water–isopropanol mixture studied by *in situ* powder X-ray diffraction†

Jakob Rostgaard Eltzholtz, Christoffer Tyrsted, Kirsten Marie Ørnsbjerg Jensen, Martin Bremholm, Mogens Christensen, Jacob Becker-Christensen and Bo Brummerstedt Iversen*

Communications — Nanoparticles

Time-Resolved In Situ Synchrotron X-ray Study and Large-Scale Production of Magnetite Nanoparticles in Supercritical Water

Martin Bremholm, Marcella Felicissimo, and Bo B. Iversen*

Nanoparticles

Rapid One-Step Low-Temperature Synthesis of Nanocrystalline γ-Al_2O_3

Nina Lock, Mogens Christensen, Kirsten M. Ø. Jensen, and Bo B. Iversen*

Nanoparticles

In Situ High-Energy Synchrotron Radiation Study of Sol–Gel Nanoparticle Formation in Supercritical Fluids

Henrik Jensen, Martin Bremholm, Rudi P. Nielsen, Karsten D. Joensen, Jan S. Pedersen, Henrik Birkedal, Yu-Sheng Chen, Jon Almer, Erik G. Søgaard, Steen B. Iversen, and Bo B. Iversen*

FULL PAPER

In Situ High-Energy Synchrotron Radiation Study of Boehmite Formation, Growth, and Phase Transformation to Alumina in Sub- and Supercritical Water

Nina Lock, Martin Bremholm, Mogens Christensen, Jonathan Almer, Yu-Sheng Chen, and Bo B. Iversen

ADVANCED MATERIALS

High-Pressure, High-Temperature Formation of Phase-Pure Monoclinic Zirconia Nanocrystals Studied by Time-Resolved in situ Synchrotron X-Ray Diffraction

By Martin Bremholm, Jacob Becker-Christensen, and Bo Brummerstedt Iversen*

CRYSTAL GROWTH & DESIGN — Article

Direct Formation of Crystalline Phase Pure Rutile TiO_2 Nanostructures by a Facile Hydrothermal Method

Aref Mamakhel, Christoffer Tyrsted, Espen Drath Bøjesen, Peter Hald, and Bo Brummerstedt Iversen*

CRYSTAL GROWTH & DESIGN — Article

In Situ Powder Diffraction Study of the Hydrothermal Synthesis of ZnO Nanoparticles

Espen D. Bøjesen, Kirsten M. Ø. Jensen, Christoffer Tyrsted, Nina Lock, Mogens Christensen, and Bo B. Iversen*

CHEMISTRY OF MATERIALS — Article

Anisotropic Crystal Growth Kinetics of Anatase TiO_2 Nanoparticles Synthesized in a Nonaqueous Medium

Grethe Vestergaard Jensen, Martin Bremholm, Nina Lock, G. Roshan Deen, Torben R. Jensen, Bo B. Iversen, Markus Niederberger, Jan Skov Pedersen, and Henrik Birkedal*

CRYSTAL GROWTH & DESIGN — Article

Rapid Hydrothermal Preparation of Rutile TiO_2 Nanoparticles by Simultaneous Transformation of Primary Brookite and Anatase: An in Situ Synchrotron PXRD Study

Jian-Li Mi, Casper Clausen, Martin Bremholm, Nina Lock, Kirsten M. Ø. Jensen, Mogens Christensen, and Bo B. Iversen*

CHEMISTRY OF MATERIALS — Article

High-Temperature and High-Pressure Aqueous Solution Formation, Growth, Crystal Structure, and Magnetic Properties of $BiFeO_3$ Nanocrystals

Jian-Li Mi, Thomas N. Jensen, Mogens Christensen, Christoffer Tyrsted, Jens E. Jørgensen, and Bo B. Iversen*

Structure, Size, and Morphology Control of Nanocrystalline Lithium Cobalt Oxide

Kirsten M. Ø. Jensen, Mogens Christensen, Christoffer Tyrsted, Martin Bremholm, and Bo B. Iversen*

CRYSTAL GROWTH & DESIGN — Article — 2011, Vol. 11, 753–758

CRYSTAL GROWTH & DESIGN — Article

Continuous Flow Supercritical Water Synthesis and Temperature-Dependent Defect Structure Analysis of YAG and YbAG Nanoparticles

Peter Nørby, Kirsten M. Ø. Jensen, Nina Lock, Mogens Christensen, and Bo B. Iversen*

CRYSTAL GROWTH & DESIGN — Article

Hydrothermal Synthesis of $CoSb_2O_4$: In Situ Powder X-ray Diffraction, Crystal Structure, and Electrochemical Properties

Peter Nørby, Martin Roelsgaard, Martin Søndergaard, and Bo B. Iversen*

FULL PAPER

In-situ Synchrotron X-ray Diffraction Study of the Formation of Cubic Li_2TiO_3 Under Hydrothermal Conditions

Andreas Laumann, Kirsten Marie Ørnsbjerg Jensen, Christoffer Tyrsted, Martin Bremholm, Karl Thomas Fehr, Michael Holzapfel, and Bo Brummerstedt Iversen

research papers — Applied Crystallography

Real-time synchrotron powder X-ray diffraction study of the antisite defect formation during sub- and supercritical synthesis of $LiFePO_4$ and $LiFe_{1-x}Mn_xPO_4$ nanoparticles

Kirsten Jensen, Mogens Christensen, Christoffer Tyrsted and Bo Brummerstedt Iversen*

The Journal of Supercritical Fluids

Coupling in situ synchrotron radiation with ex situ spectroscopy characterizations to study the formation of $Ba_{1-x}Sr_xTiO_3$ nanoparticles in supercritical fluids

CHEMISTRY OF MATERIALS

Insights into $BaTi_{1-y}Zr_yO_3$ ($0 \leq y \leq 1$) Synthesis under Supercritical Fluid Conditions

Gilles Philippot, Espen D. Bøjesen, Catherine Elissalde, Mario Maglione, Cyril Aymonier, and Bo B. Iversen

RSC Advances — RSC Publishing — PAPER

In situ synchrotron powder X-ray diffraction study of formation and growth of yttrium and ytterbium aluminum garnet nanoparticles in sub- and supercritical water†

Peter Nørby, Kirsten M. Ø. Jensen, Nina Lock, Mogens Christensen and Bo B. Iversen*

CHEMISTRY OF MATERIALS — Article

In-Situ Synchrotron Radiation Study of Formation and Growth of Crystalline $Ce_xZr_{1-x}O_2$ Nanoparticles Synthesized in Supercritical Water

Christoffer Tyrsted, Jacob Becker, Peter Hald, Martin Bremholm, Jan Skov Pedersen, Jacques Chevallier, Yngve Cerenius, Steen B. Iversen, and Bo B. Iversen*

Dalton Transactions — PAPER

In situ powder X-ray diffraction study of the hydro-thermal formation of $LiMn_2O_4$ nanocrystallites†

CRYSTAL GROWTH & DESIGN — Article

Hydrothermal Synthesis and in Situ Powder X-ray Diffraction Study of Bismuth-Substituted Ceria Nanoparticles

Kasper Houlberg, Espen D. Bøjesen, Christoffer Tyrsted, Aref Mamakhel, Xueqin Wang, Ren Su, Flemming Besenbacher, and Bo B. Iversen*

The Journal of Supercritical Fluids

Glucose-assisted continuous flow synthesis of Bi_2Te_3 nanoparticles in supercritical/near-critical water

Nanoscale — COMMUNICATION

The formation mechanism of bimetallic PtRu alloy nanoparticles in solvothermal synthesis†

CHEMISTRY OF MATERIALS

Pulsed-Flow Near-Critical and Supercritical Synthesis of Carbon-Supported Platinum Nanoparticles and In Situ X-ray Diffraction Study of Their Formation and Growth

THE JOURNAL OF PHYSICAL CHEMISTRY C — Article

Controlling Allotropism in Ruthenium Nanoparticles: A Pulsed-Flow Supercritical Synthesis and *in Situ* Synchrotron X-ray Diffraction Study

Jian-Li Mi, Yanbin Shen, Jacob Becker, Martin Bremholm, and Bo B. Iversen*

J. Phys. Chem. C 2010, 114, 12133–12138

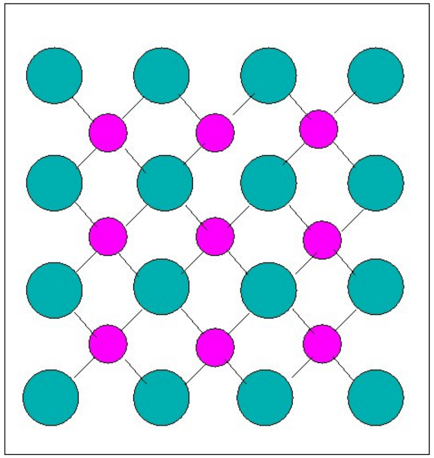
Formation and Growth of Bi_2Te_3 Nanoparticles in Biomolecule-Assisted Near-Critical Water: In Situ Synchrotron Radiation Study

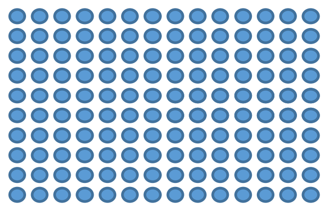
Jian-Li Mi, Mogens Christensen, Christoffer Tyrsted, Kirsten Ø. Jensen, Jacob Becker, Peter Hald, and Bo B. Iversen*

Every system is unique and holds its own story

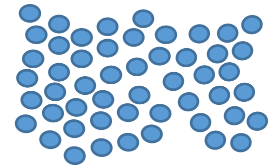
Crystalline and amorphous materials

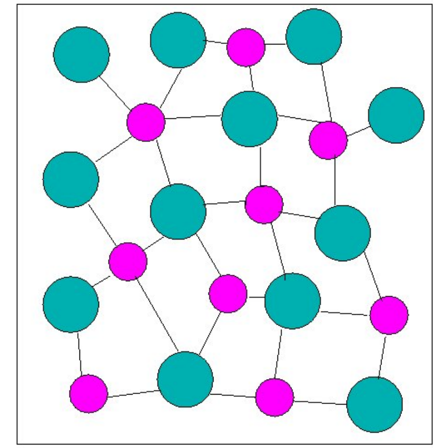
Crystal

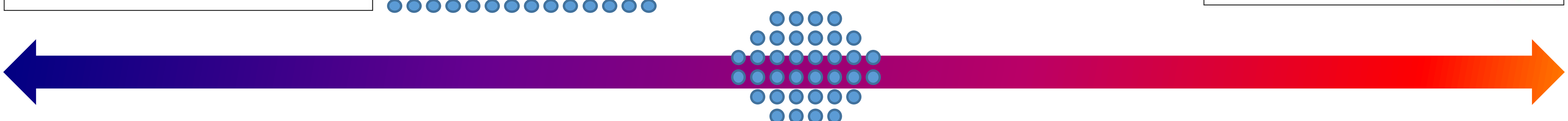




Amorphous



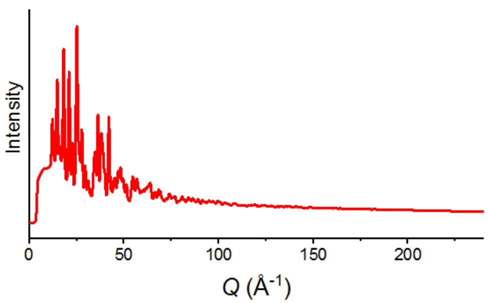


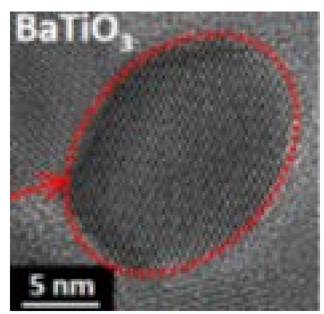


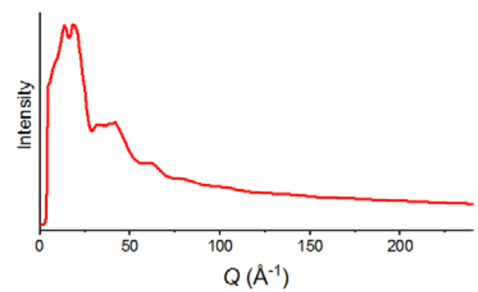
Order

Nanoparticles

Disorder

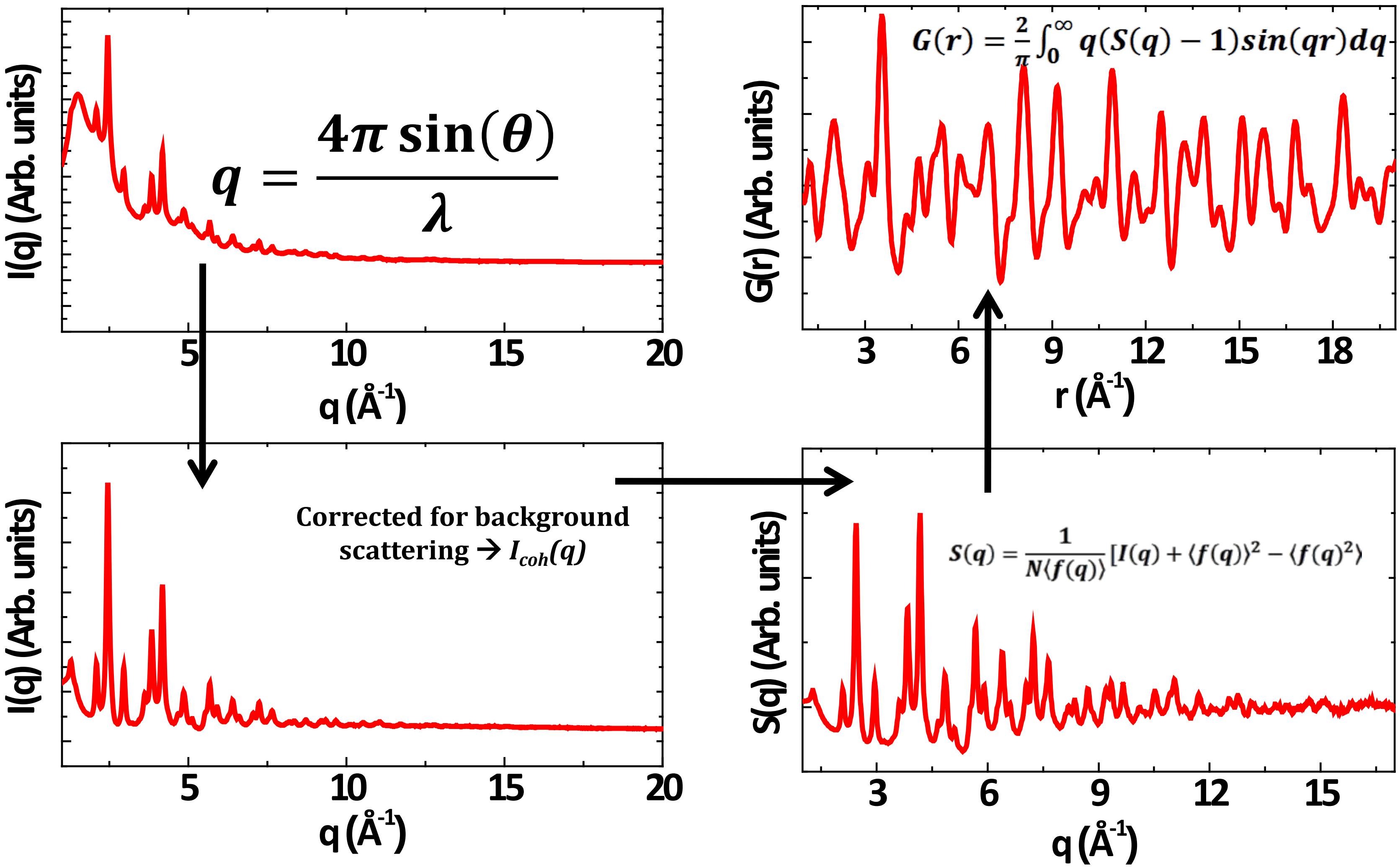




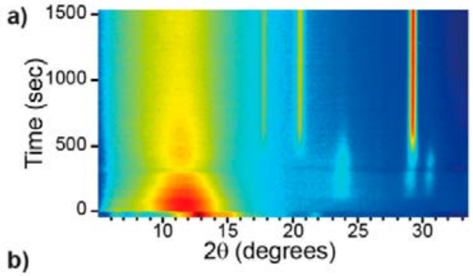


We need structural probes
on the nanoscale

Total Scattering and the Pair Distribution Function



Requires short wavelength X-rays to get resolution in reciprocal space



Pre-Nucleation Cluster structures

Angewandte Communications *Angew. Chem. Int. Ed.* **2012**, 51, 9030–9033
DOI: 10.1002/anie.201204747
Crystal Growth

Understanding the Formation and Evolution of Ceria Nanoparticles Under Hydrothermal Conditions

*Christoffer Tyrsted, Kirsten Marie Ørnsbjerg Jensen, Espen Drath Bøjesen, Nina Lock, Mogens Christensen, Simon J. L. Billinge, and Bo Brummerstedt Iversen**

JACS Journal of the American Chemical Society *J. Am. Chem. Soc.* **2012**, 134, 6785–6792
Article
pubs.acs.org/JACS

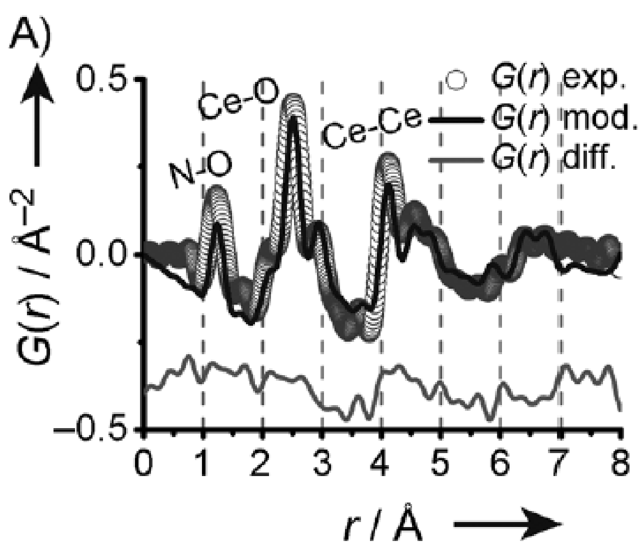
Revealing the Mechanisms behind SnO_2 Nanoparticle Formation and Growth during Hydrothermal Synthesis: An In Situ Total Scattering Study

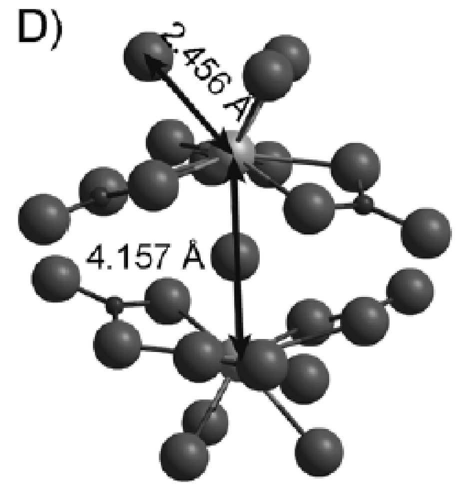
Kirsten M. Ø. Jensen,† Mogens Christensen,† Pavol Juhas,‡ Christoffer Tyrsted,† Espen D. Bøjesen,† Nina Lock,† Simon J. L. Billinge,*‡§ and Bo B. Iversen*†

Chem. Eur. J. **2012**, 18, 5759–5766
FULL PAPER
DOI: 10.1002/chem.201102826

Watching Nanoparticles Form: An In Situ (Small-/Wide-Angle X-ray Scattering/Total Scattering) Study of the Growth of Yttria-Stabilised Zirconia in Supercritical Fluids

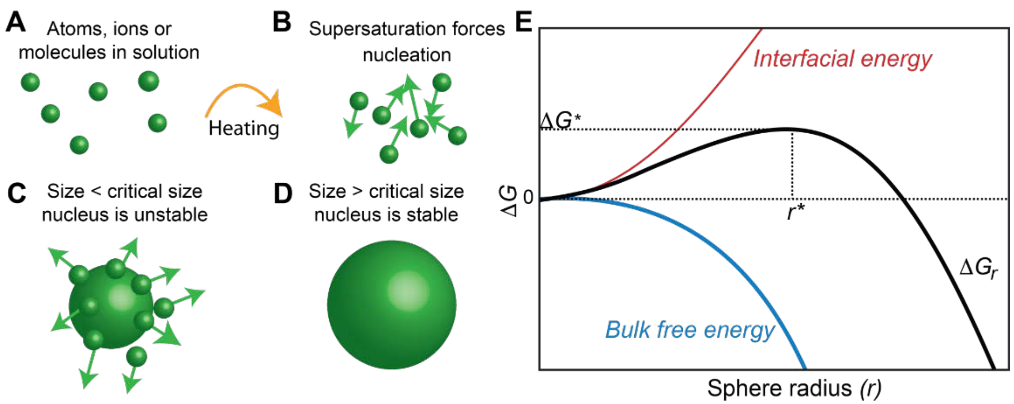
Christoffer Tyrsted,[a] Brian Richard Pauw,[a, b] Kirsten Marie Ørnsbjerg Jensen,[a] Jacob Becker,[a] Mogens Christensen,[a] and Bo Brummerstedt Iversen*[a]



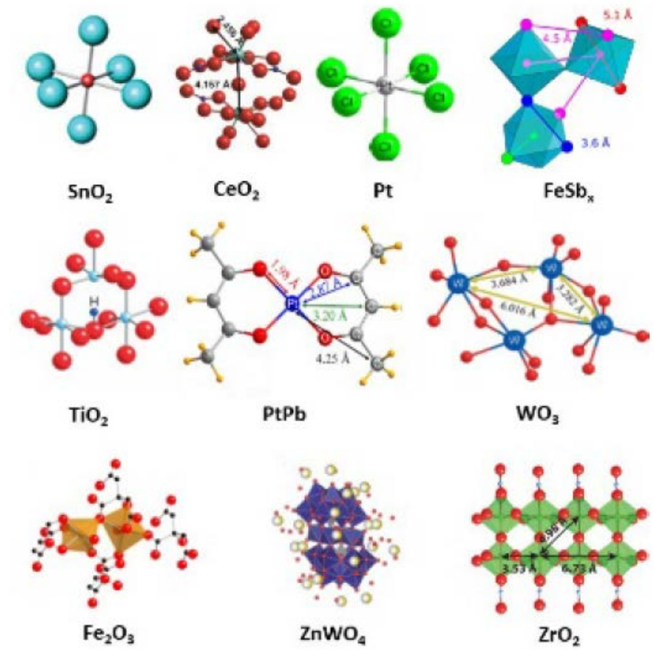


Direct space structural modelling

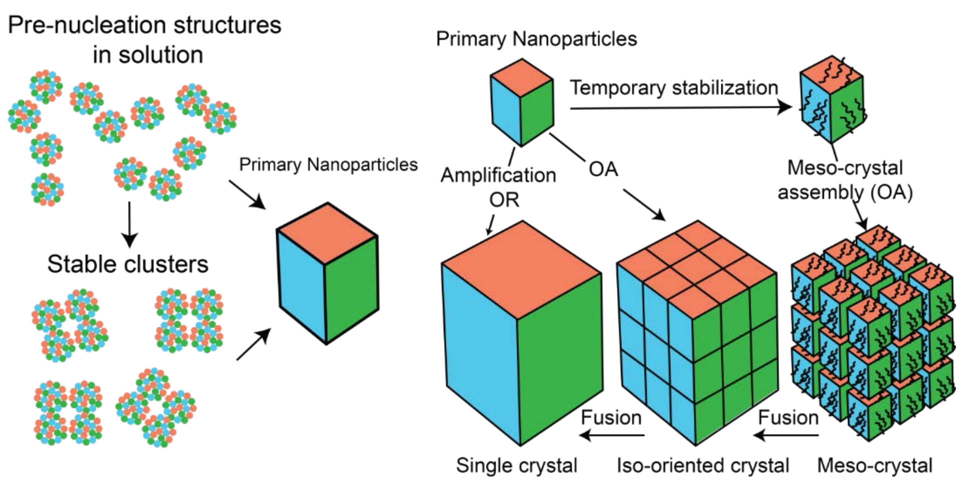
Classic Nucleation



Prenucleation Clusters determined from in situ PDF

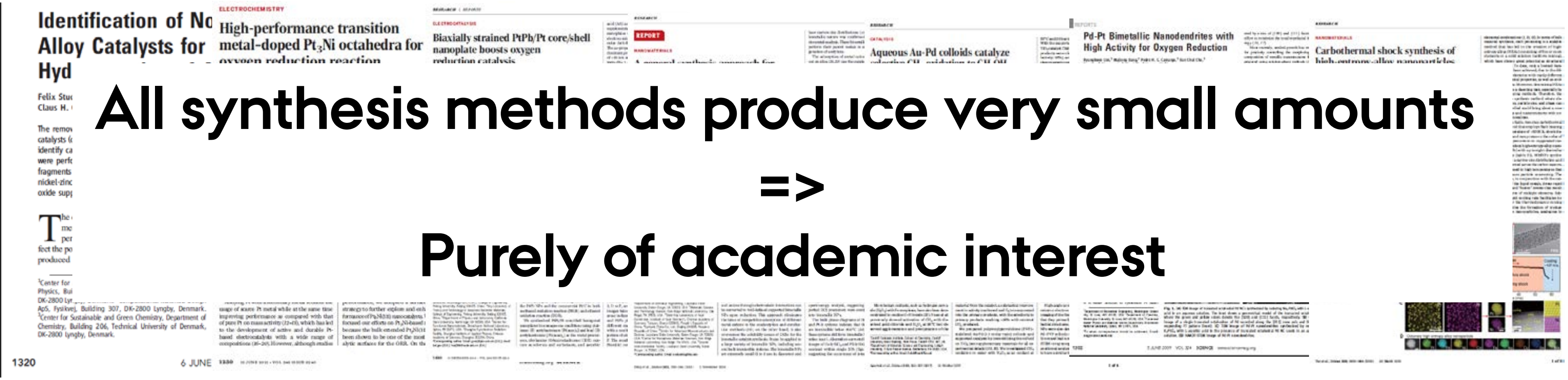


Non-Classical Nucleation



Bøjesen & Iversen, *CrystEngComm* **2016**, 18, 8332 - 8353

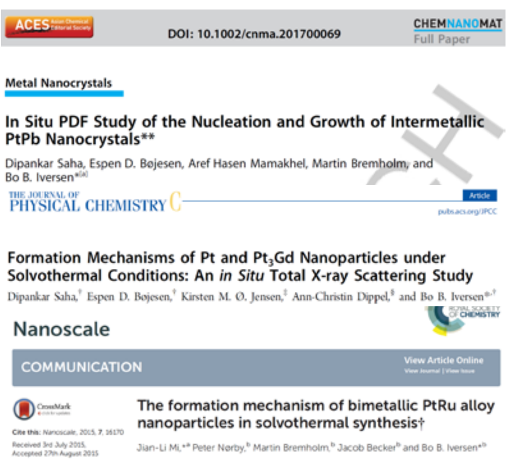
Bimetallic nanoparticles for catalysis



All synthesis methods produce very small amounts

=>

Purely of academic interest


DOI: 10.1002/cnma.201700069 — CHEMNANOMAT Full Paper

Metal Nanocrystals

In Situ PDF Study of the Nucleation and Growth of Intermetallic PtPb Nanocrystals**

Dipankar Saha, Espen D. Bøjesen, Aref Hasen Mamakhel, Martin Bremholm, and Bo B. Iversen[a]

THE JOURNAL OF PHYSICAL CHEMISTRY C — Article

Formation Mechanisms of Pt and Pt_3Gd Nanoparticles under Solvothermal Conditions: An *in Situ* Total X-ray Scattering Study

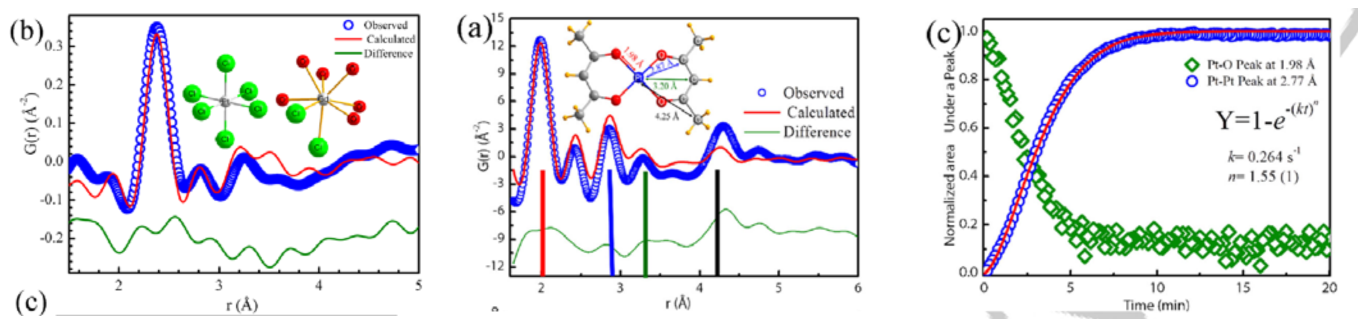
Dipankar Saha, Espen D. Bøjesen, Kirsten M. Ø. Jensen, Ann-Christin Dippel, and Bo B. Iversen

Nanoscale

COMMUNICATION

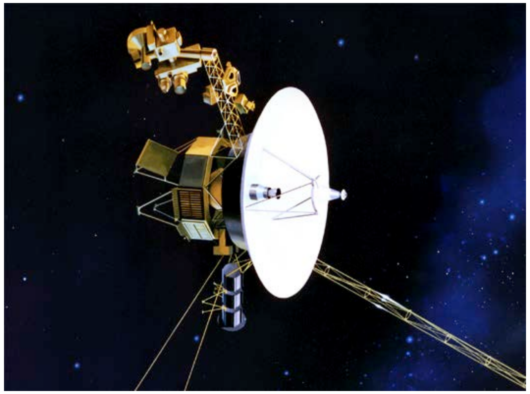
The formation mechanism of bimetallic PtRu alloy nanoparticles in solvothermal synthesis†

Jian-Li Mi, Peter Nørby, Martin Bremholm, Jacob Becker and Bo B. Iversen



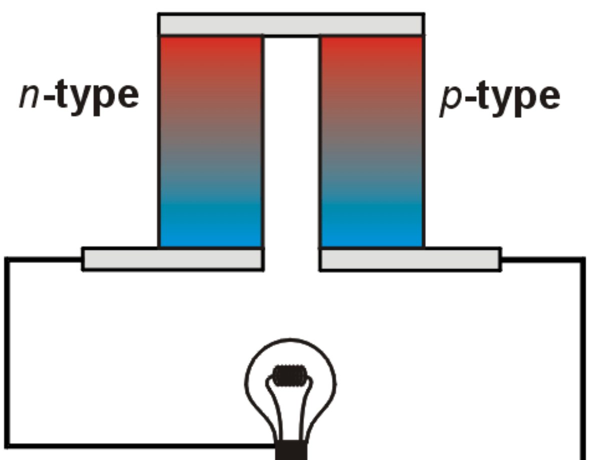
Design solvent and precursor based on in situ data =>
Development of large scale solvothermal synthesis

Thermoelectrics



Power Generation

$$ZT = \frac{S^2\sigma}{\kappa}T$$



LETTERS
PUBLISHED ONLINE: 11 MARCH 2012 | DOI: 10.1038/NMAT3273
nature materials

Copper ion liquid-like thermoelectrics

Huili Liu[1,2], Xun Shi[1,3]★, Fangfang Xu[3], Linlin Zhang[3], Wenqing Zhang[3], Lidong Chen[1]★, Qiang Li[4], Ctirad Uher[5], Tristan Day[6] and G. Jeffrey Snyder[6]

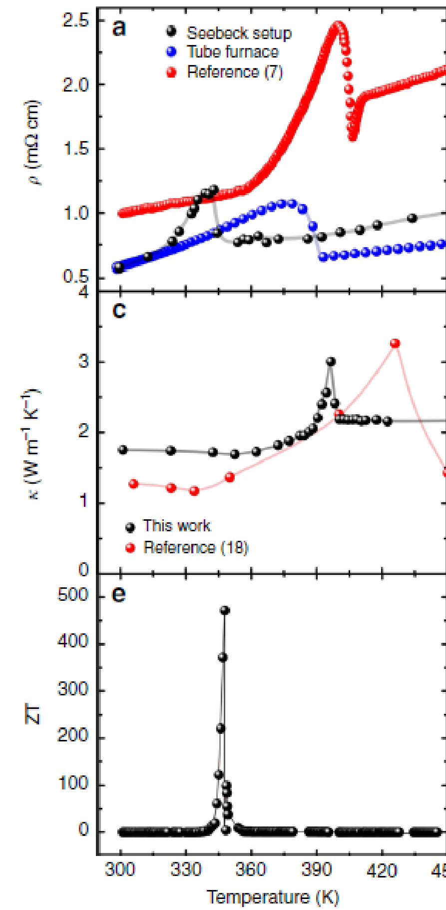
$Cu_{2-\delta}Se$

nature COMMUNICATIONS

ARTICLE
OPEN

Discovery of colossal Seebeck effect in metallic Cu_2Se

Dogyun Byeon[1], Robert Sobota[1], Kévin Delime-Codrin[1], Seongho Choi[1], Keisuke Hirata[1], Masahiro Adachi[2], Makoto Kiyama[2], Takashi Matsuura[2], Yoshiyuki Yamamoto[2], Masaharu Matsunami[1] & Tsunehiro Takeuchi[1]



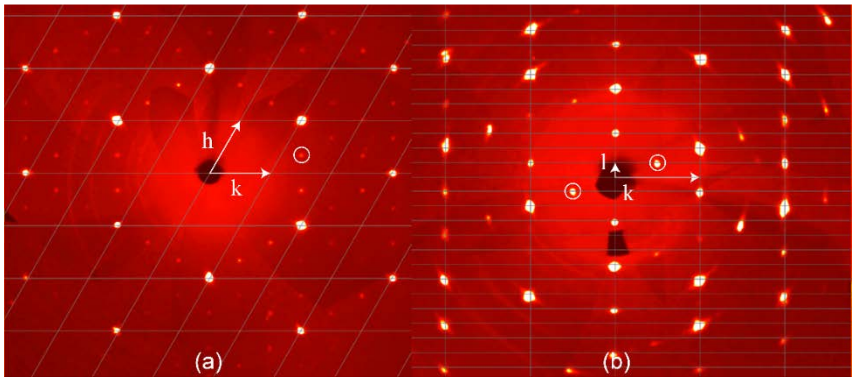
Spatially and time averaged structure of $Cu_{2-\delta}Se$

research papers *IUCrJ (2017). 4, 476-485*

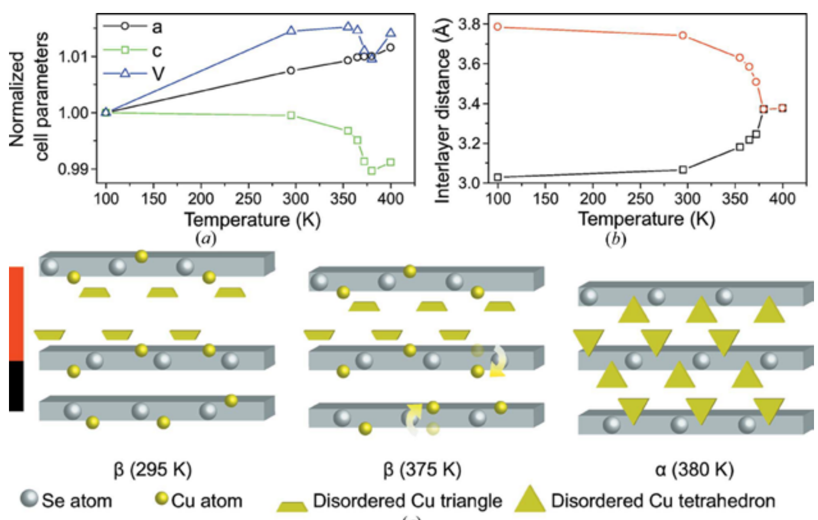
IUCrJ
ISSN 2052-2525
CHEMISTRY | CRYSTENG

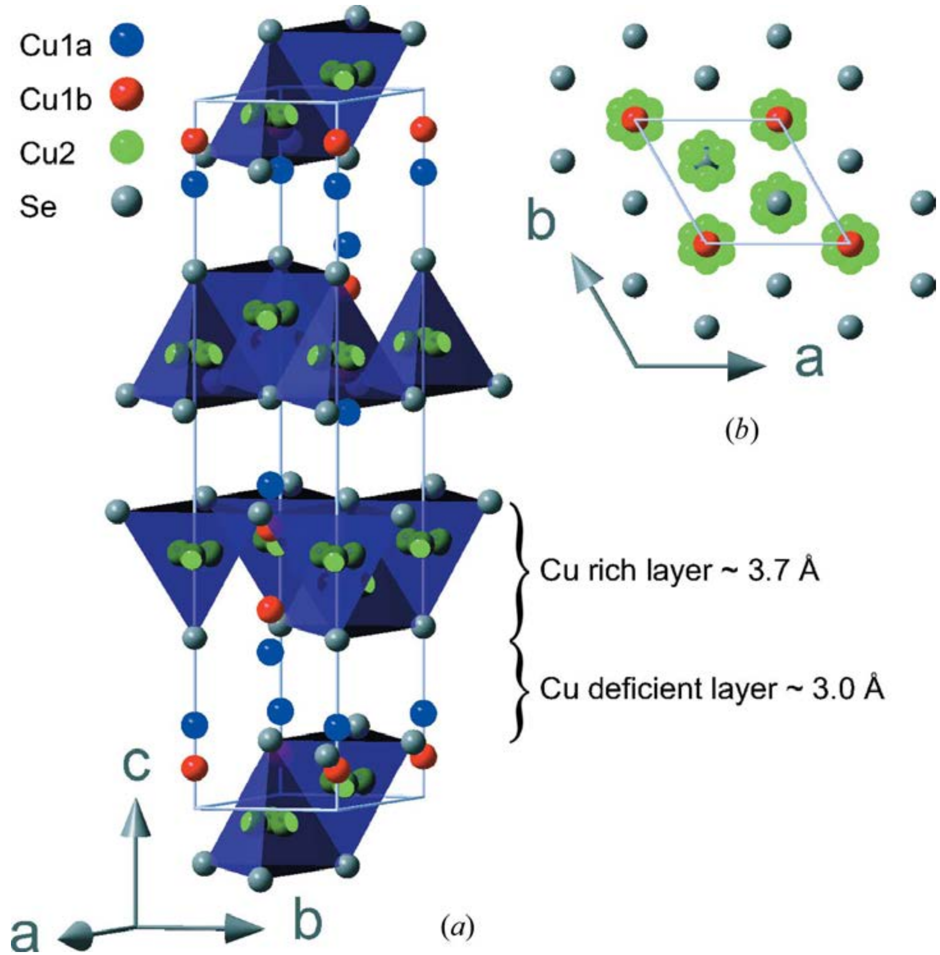
Crystal structure across the β to α phase transition in thermoelectric $Cu_{2-x}Se$

Espen Eikeland,[a] Anders B. Blichfeld,[a] Kasper A. Borup,[a,b] Kunpeng Zhao,[c] Jacob Overgaard,[a] Xun Shi,[c] Lidong Chen[c] and Bo B. Iversen[a]*



Appears to have unresolved superstructure



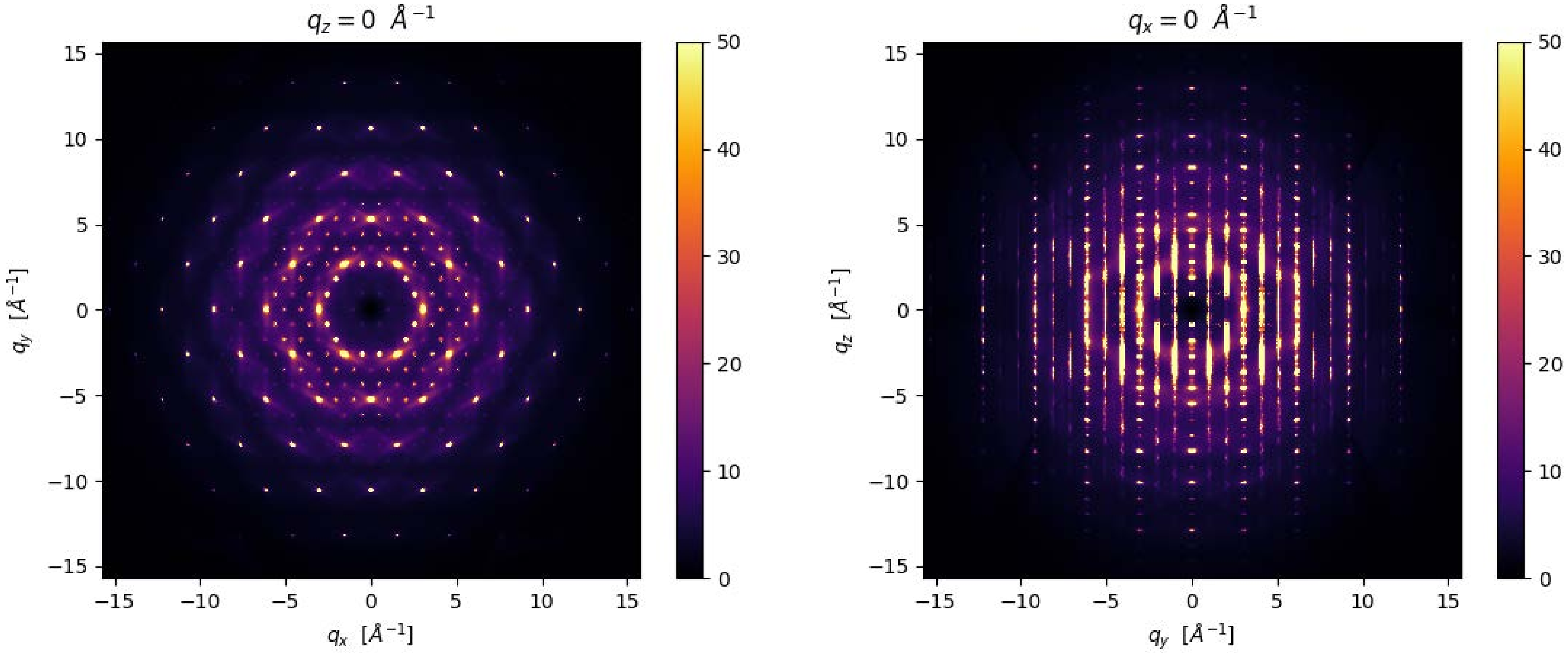


Structure has remained elusive since 1936

Diffuse scattering intensity outside the Bragg peaks

Low noise detectors, intense radiation => Quantitative measurement

Cu_2Se

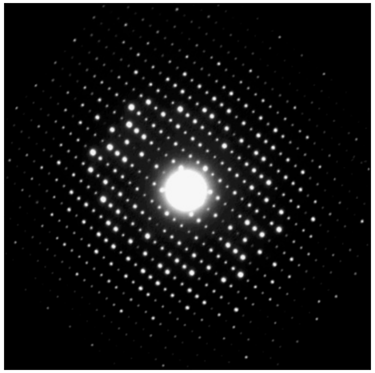


A perfect crystal only has Bragg Peaks
Real crystals are imperfect

Solving Crystal Structures – The Patterson Function

$$P(\mathbf{u}) = \sum |F(\mathbf{H})|^2 \exp(-2\pi i\mathbf{H}\mathbf{u}) = \rho(\mathbf{r}) * \rho(-\mathbf{r})$$

Fourier Transform of the Bragg Intensity

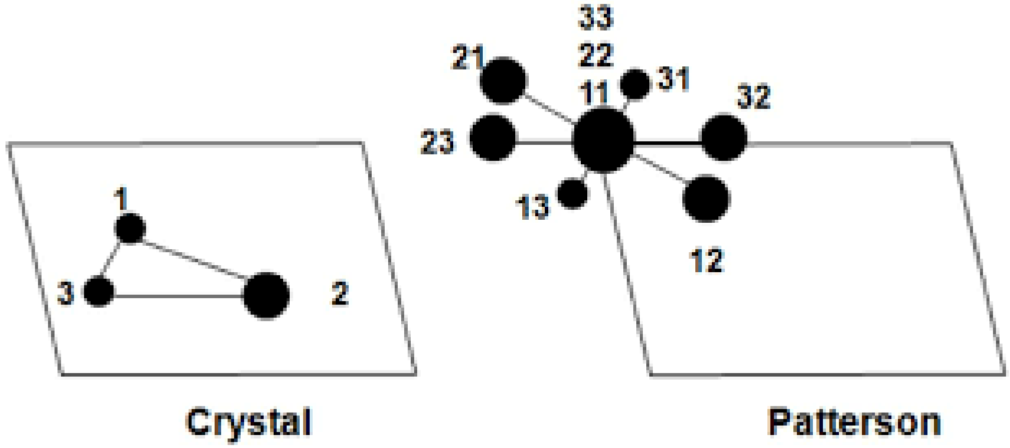


$$\text{Peak Intensity} \propto |F|^2$$

$$\rho(r) = 1/V\sum F(H)\exp(-2\pi iHr)$$

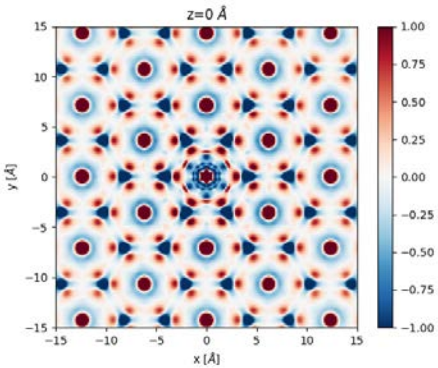
Peaks at interatomic vectors

Locates "heavy" atoms



Generalized Patterson Function

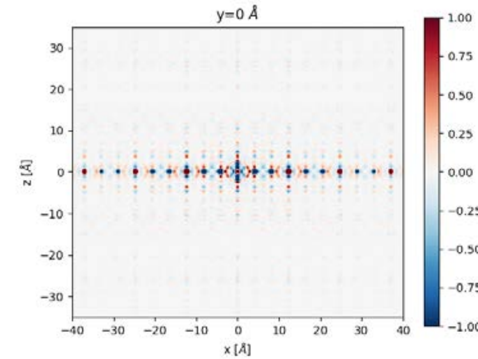
$$3\text{D}-\Delta\text{PDF} = \mathcal{F}^{-1}\left[I_{diffuse}\right] \qquad \rho(\boldsymbol{r}) = \rho_{periodic}(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})$$

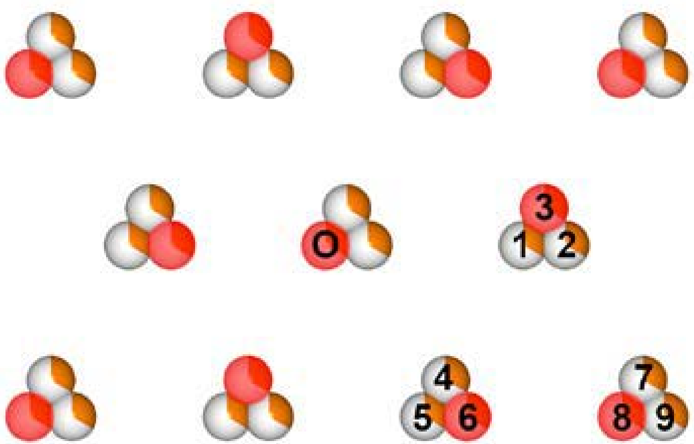


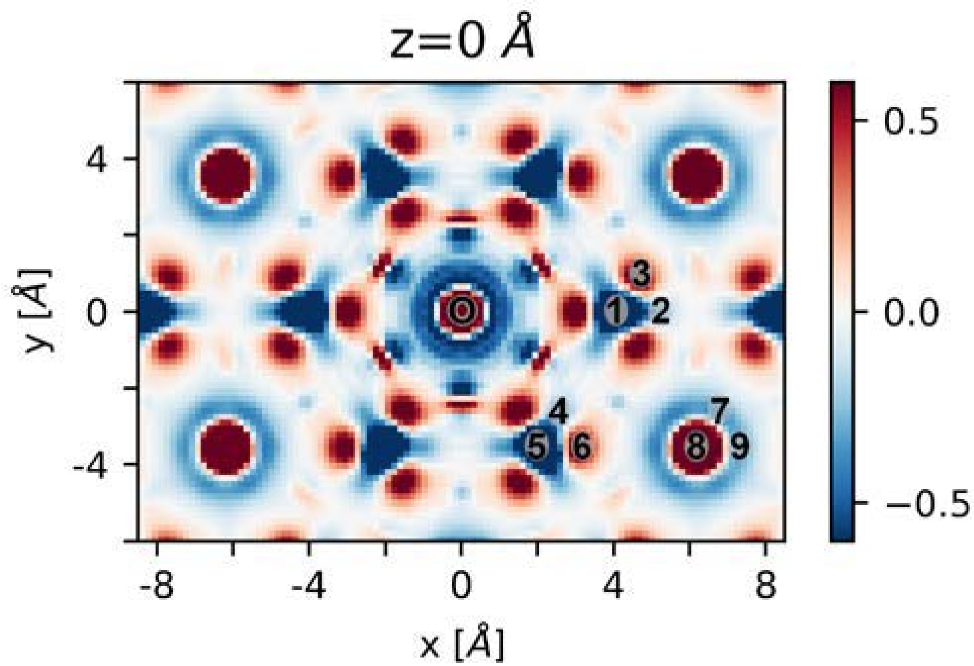
$$\boxed{3\text{D}-\Delta\text{PDF}(\boldsymbol{r}) = \langle \delta\rho \otimes \delta\rho \rangle}$$

Difference from the average density

Cu_2Se





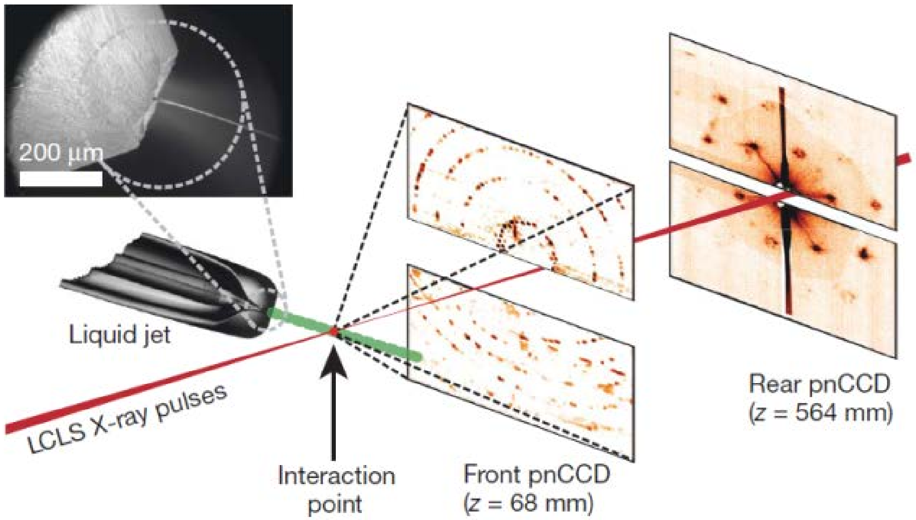


Roth & Iversen, Acta Cryst. A 2019

Determination of true local structure

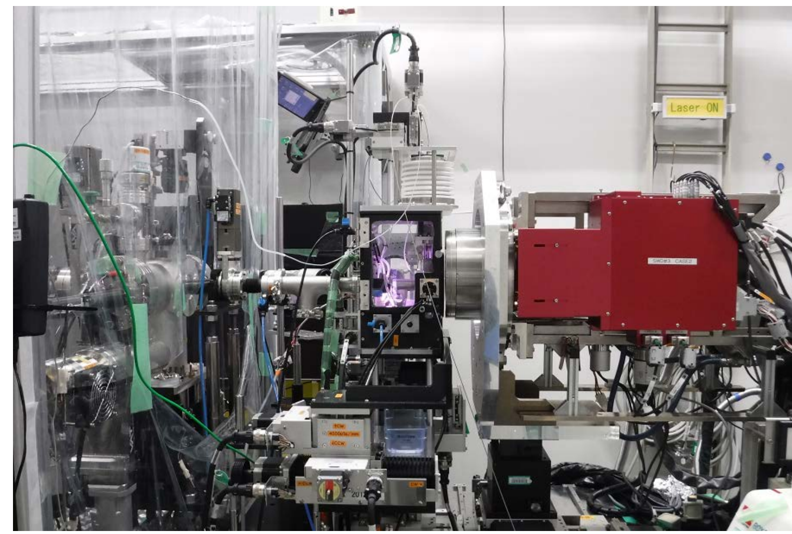
XFEL CRYSTALLOGRAPHY

Serial protein crystallography



Chapman et al., Nature 2011, 470, 73

SACLA

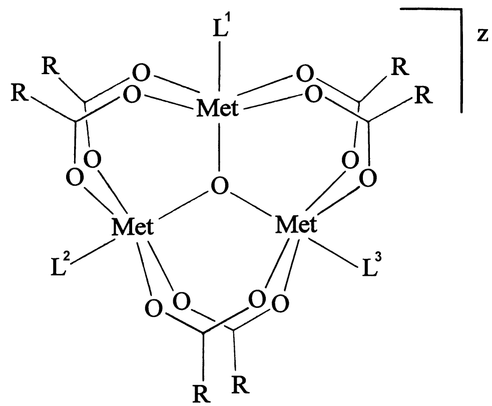


- Indexing of spots is ”easy” for proteins to get orientation matrix
- Small unit cell crystallography lacking
- Need short wavelength to obtain reciprocal space resolution

- **Beam size: 1μm**
- **λ = 22.5 KeV**
- **Delay=0.5 - 330 fs**

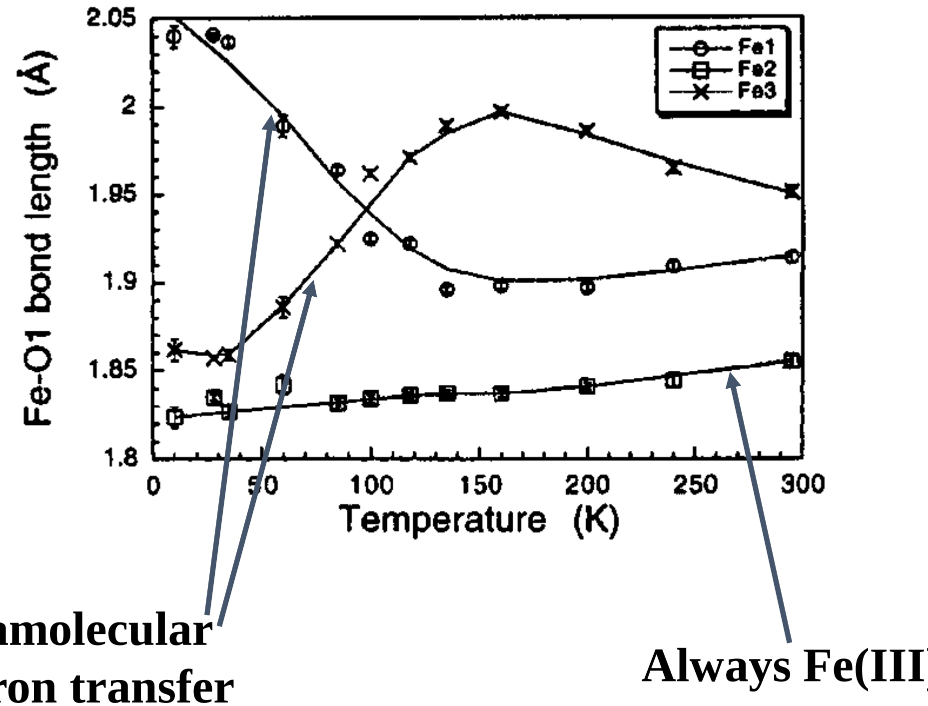
Some typical dynamic phenomena in crystals

Trinuclear carboxylates



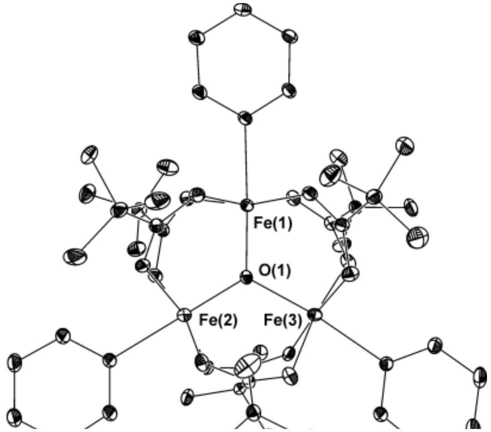
- Model compunds for active sites
- Oxidation catalysts
- Intramolecular electron transfer two M^{3+}, one M^{2+}
- Crystal/solvent effects (supramolecular chemistry)
- Molecular magnetism
- Electronic control through variation of metals, ligands and solvent

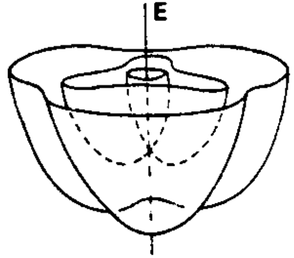
Spatially and time averaged structure



$Fe^{III}\ Fe^{III}\ Fe^{II}$ ⟷ $Fe^{III}\ Fe^{II}\ Fe^{III}$ ⟷ ($Fe^{II}\ Fe^{III}\ Fe^{III}$)

Wilson et al., *J. Am. Chem Soc.* **2000**, 122, 11370-11379

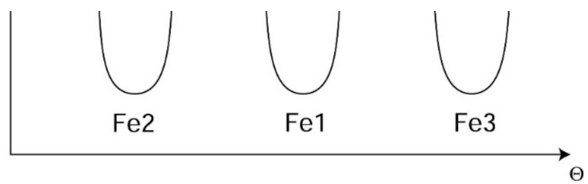




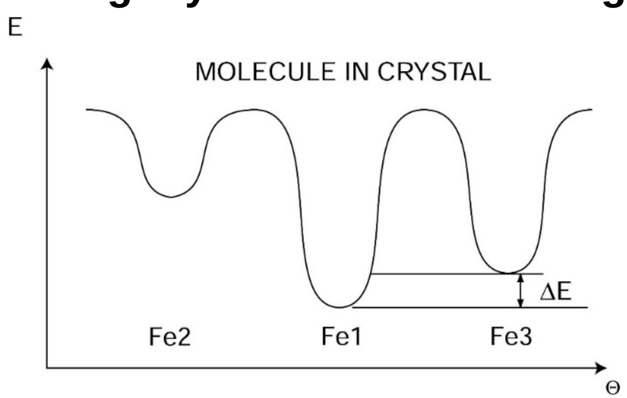
$$P(I)/P(II) = \exp(\Delta E/kT)$$
$$d(obs) = |\,Fe1\text{-}O1\,| - |\,Fe3\text{-}O1\,|$$
$$\Delta E = kT\ln[(d(max)+d(obs)/d(max)-d(obs)]$$

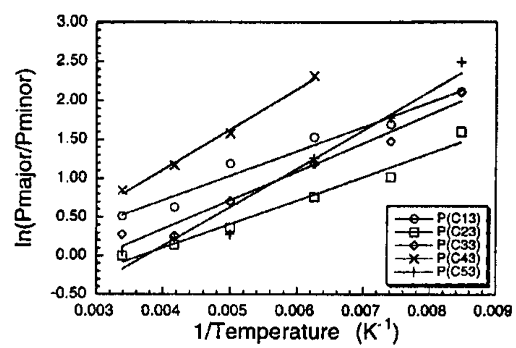
$$\Delta E = 44\ cm^{-1}$$

What would happen if we did XFEL crystallography with fs time resolution (remove time averaging) on nanocrystals (remove spatial averaging)



Strong crystal forces => ΔE big





ΔE = 217, 212, 255, 359, 345 cm^{-1}

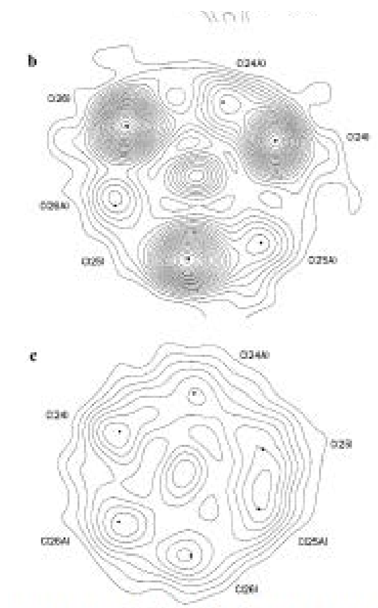
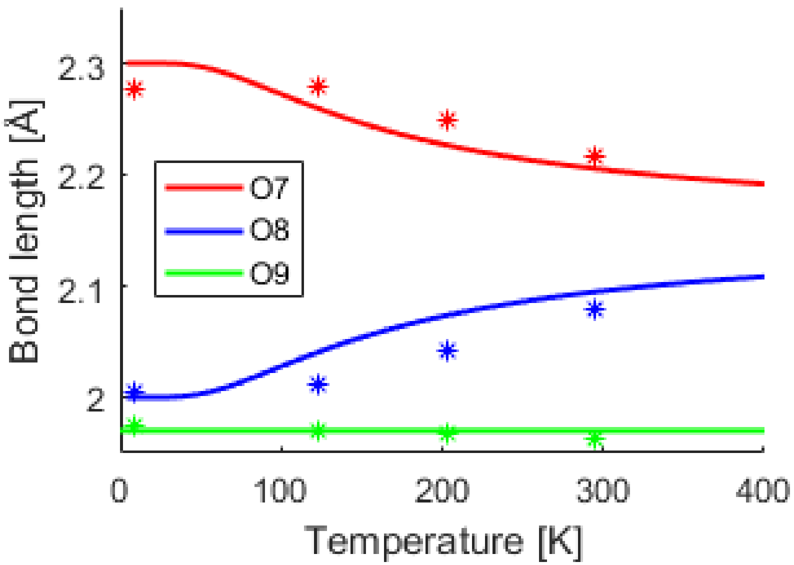
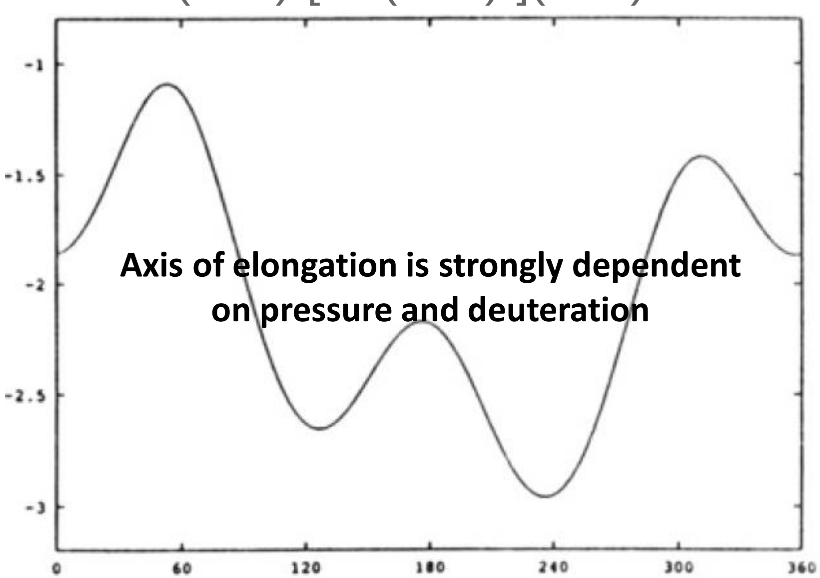


Figure 9. Difference Fourier maps through the plane of the methyl carbons of the tert-butyl group involving C23: (a) 10 K, (b) 135 K,

Dynamical Jahn-Teller systems Tutton Salts

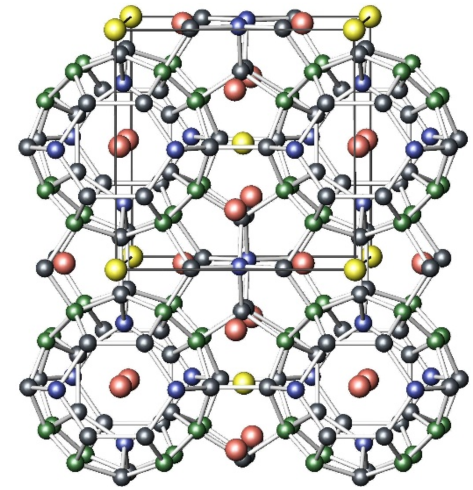


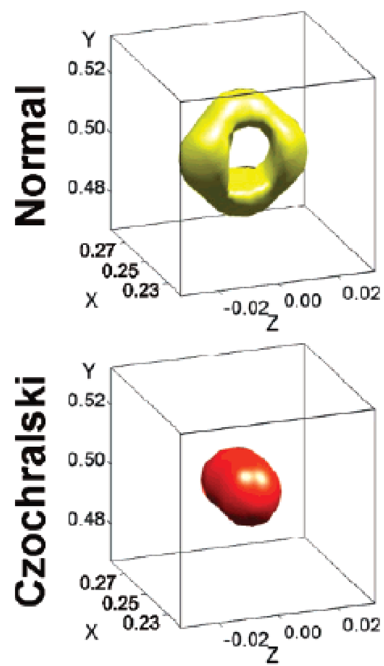
$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$

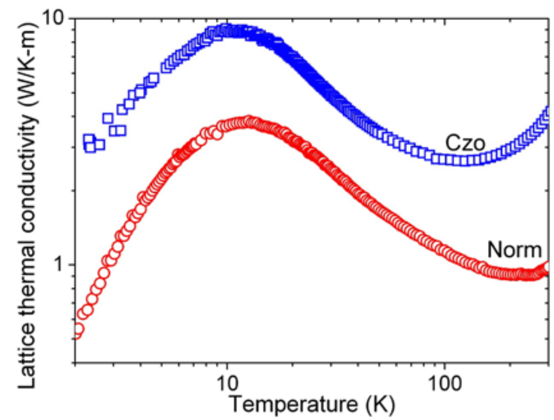


Axis of elongation is strongly dependent on pressure and deuteration

Guest atom disorder in Thermoelectric clathrates







THANKS

Center for Materials Crystallography