Total scattering and atomic pair distribution function analysis: overview and applications

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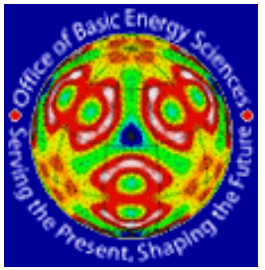

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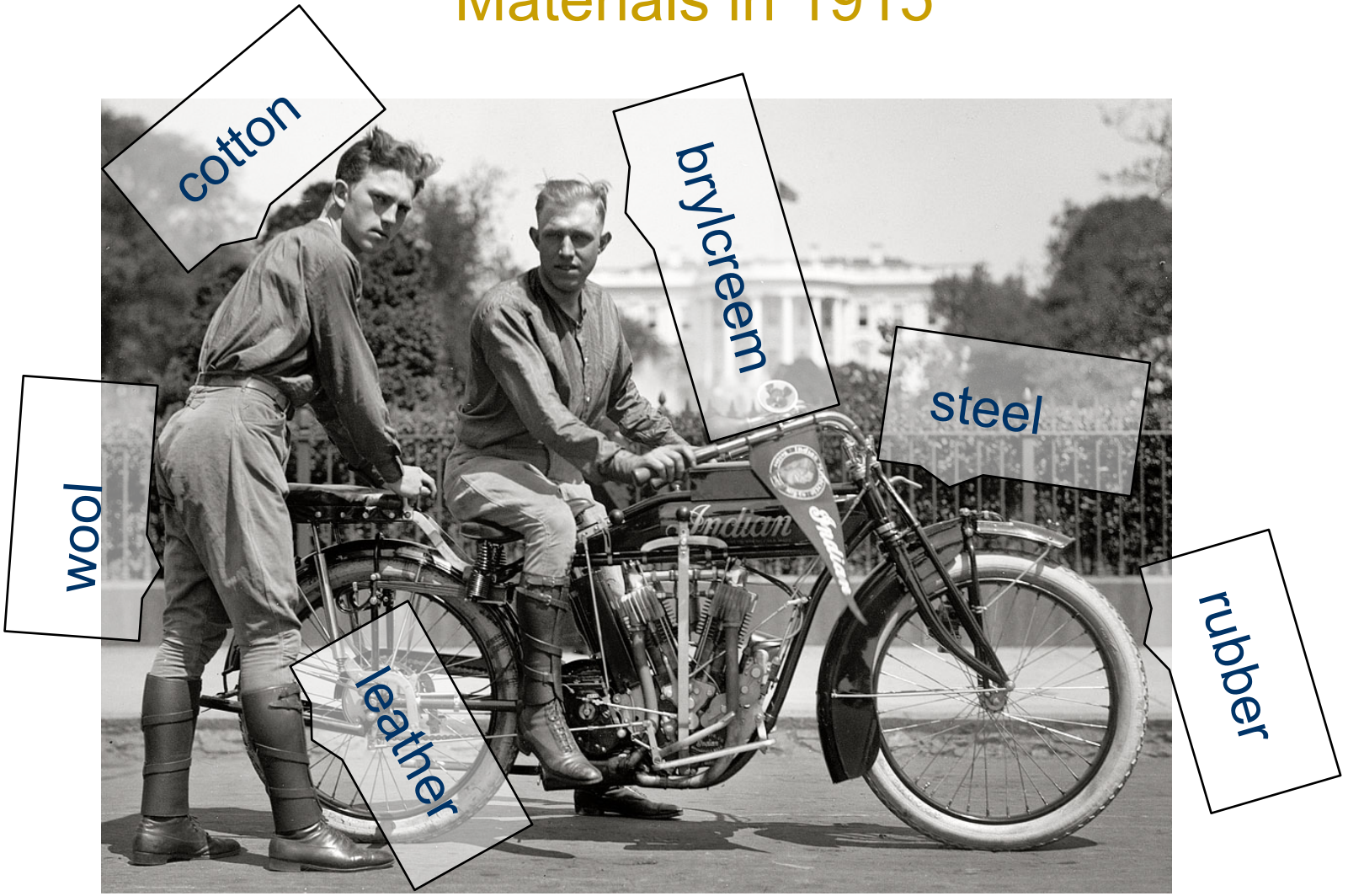
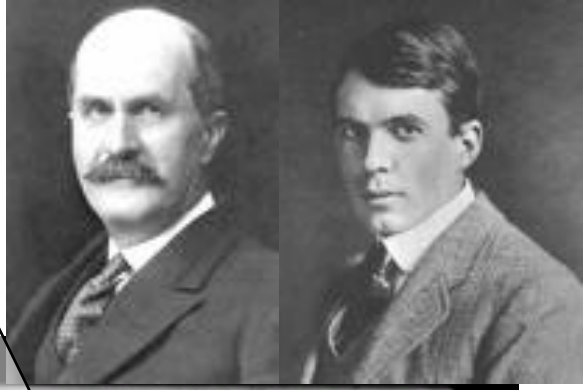
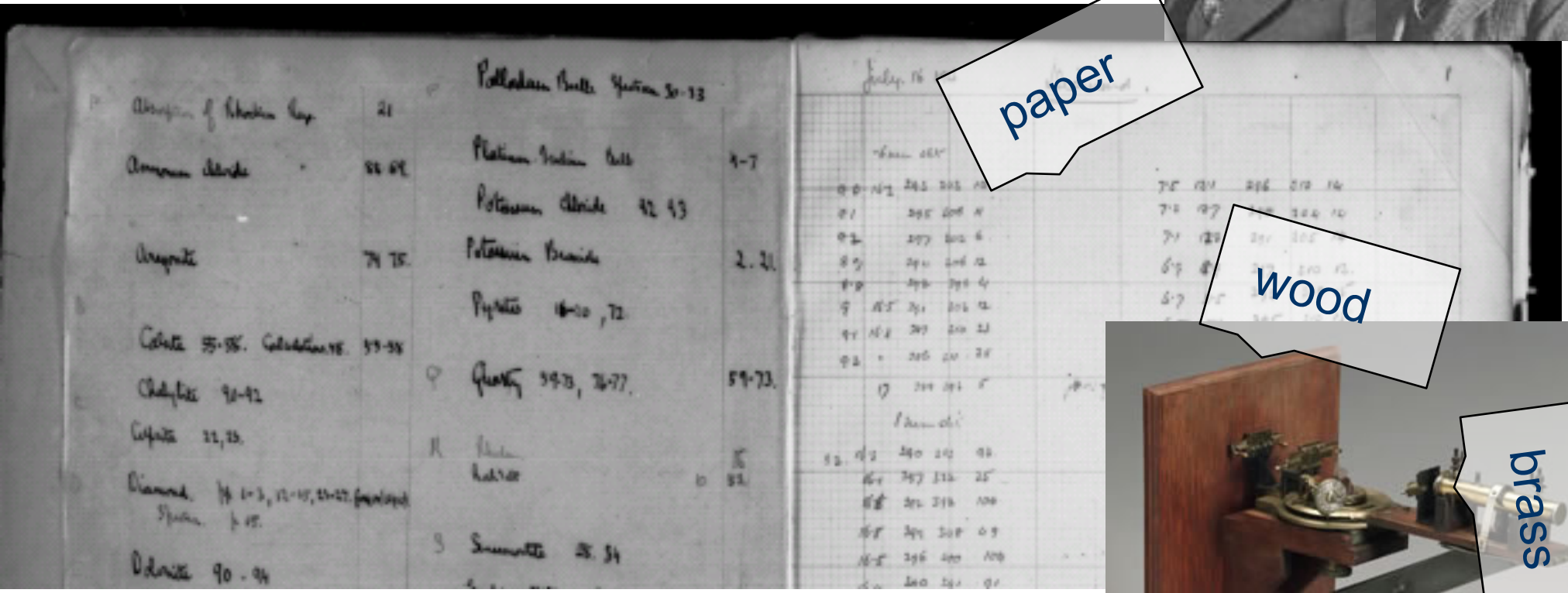
HTTP://thebillingegroup.com

Materials in 1915



W. Henry Bragg's notebook





- Available at U. Leeds website:

http://www.leeds.ac.uk/library/spcoll/bragg-notebook/

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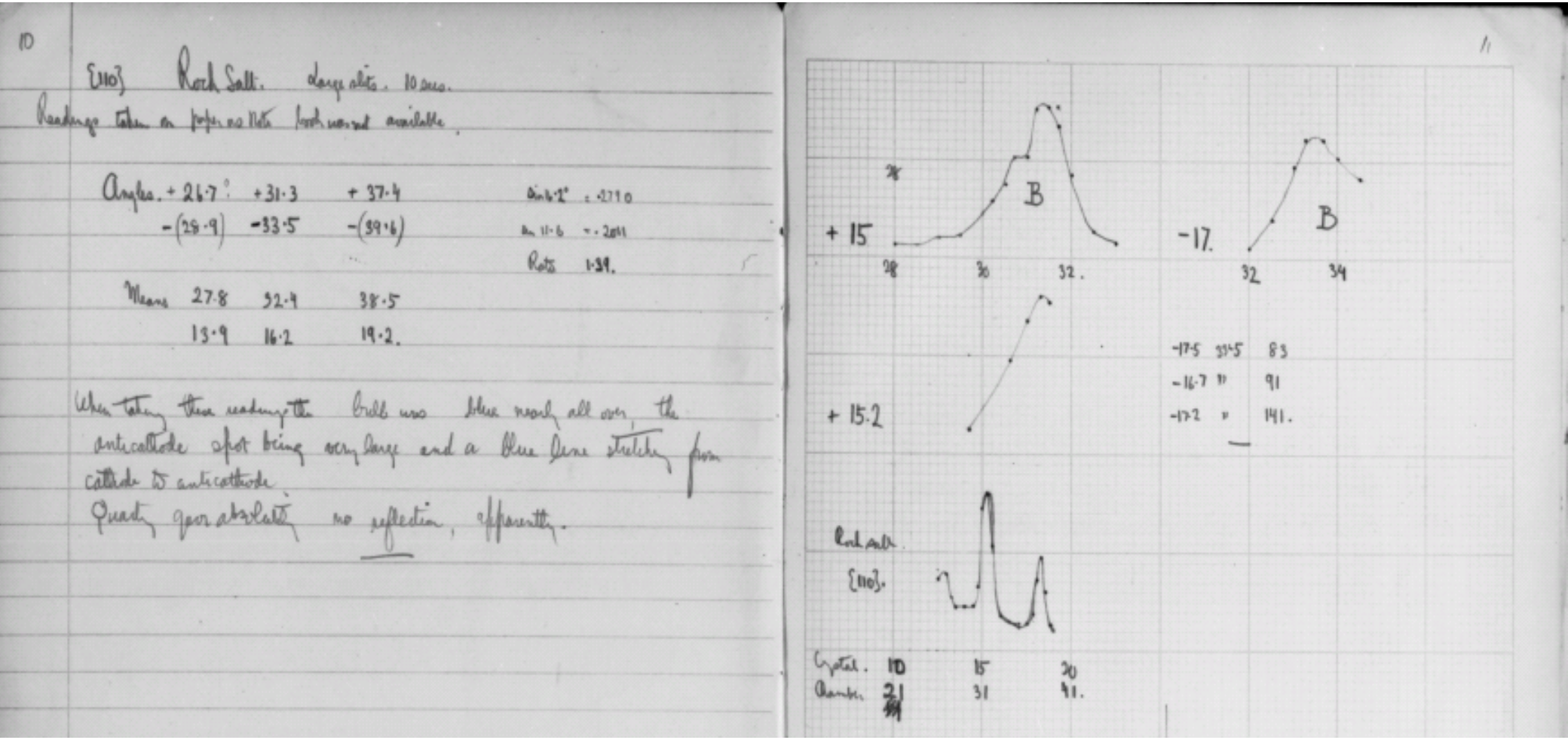
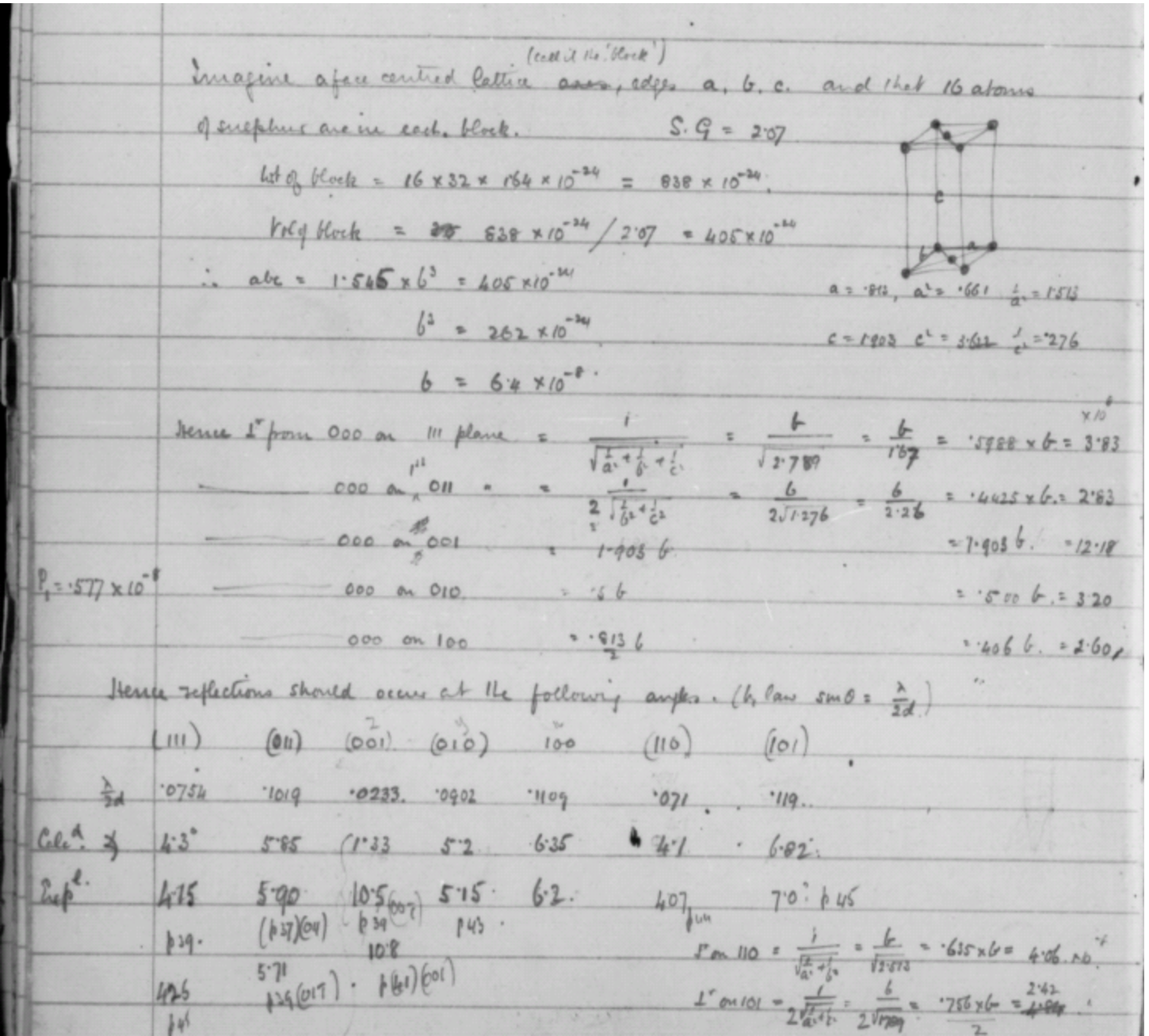
Big data, circa 1915



- Page 11, he has moved from diamond to rock-salt….the first appearance of something looking like a Bragg peak

HPC circa 1915



- Apparently the first structure solution
- Page 43

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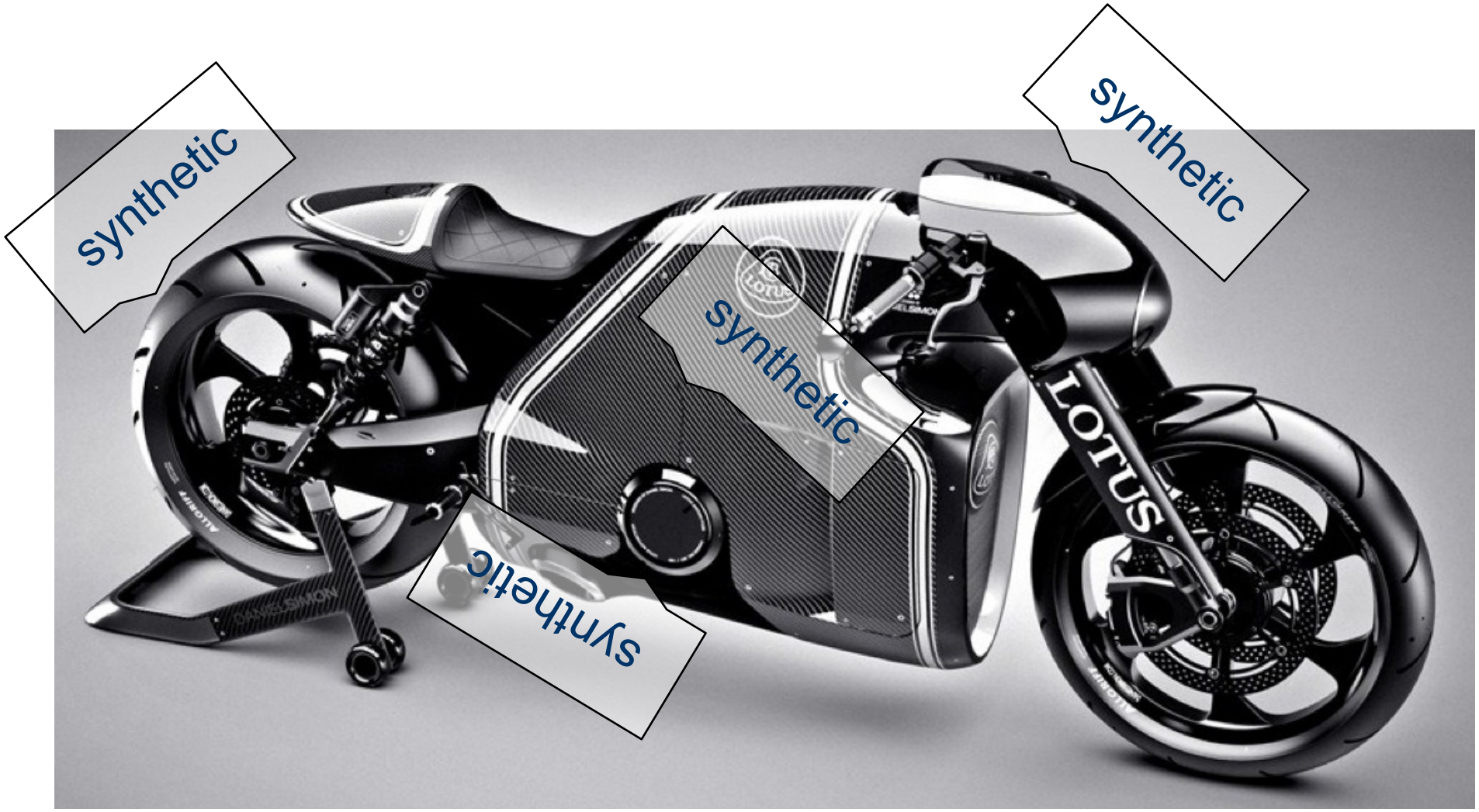
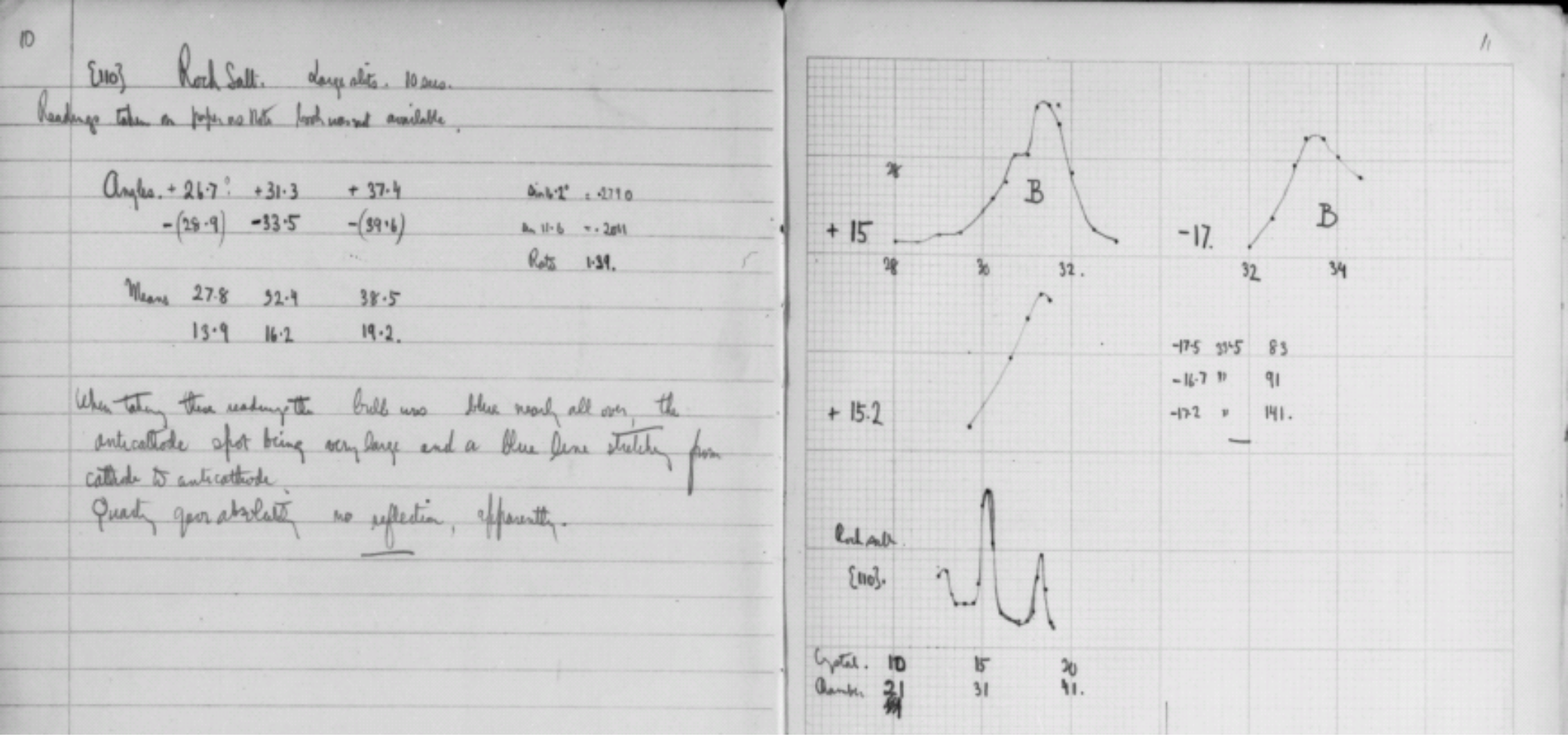
Materials 2015

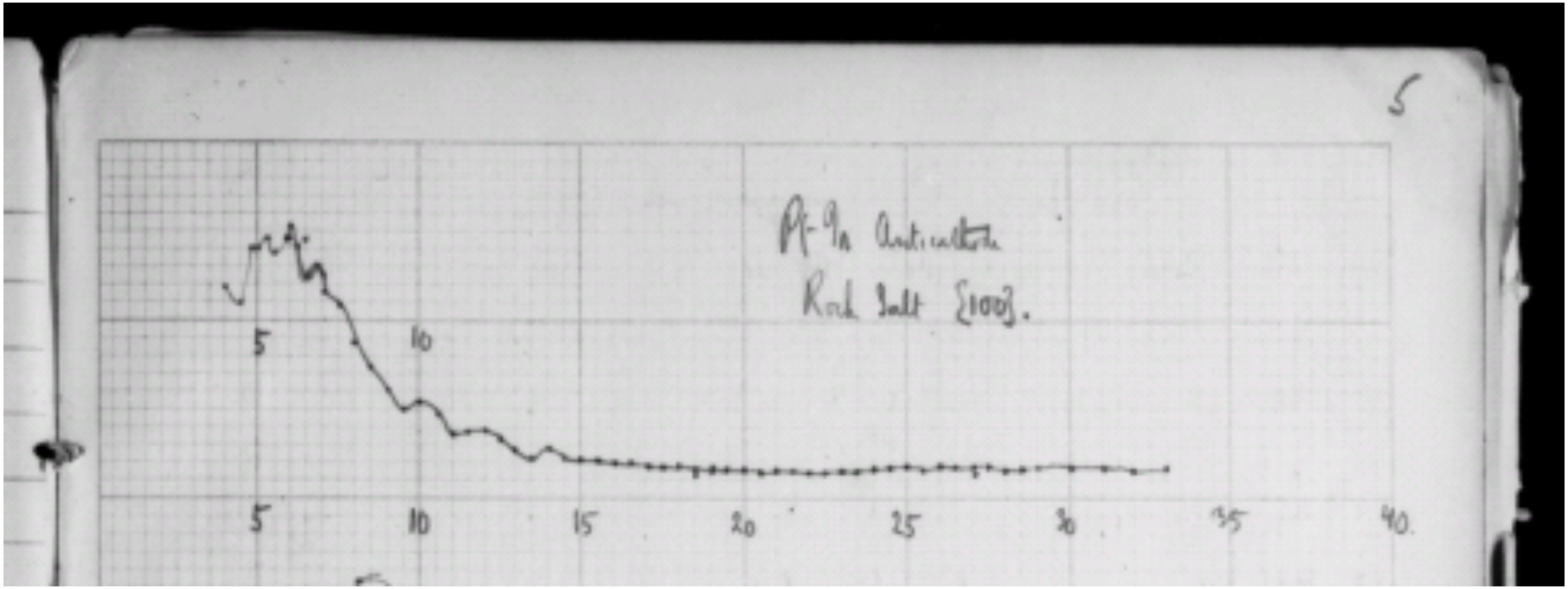




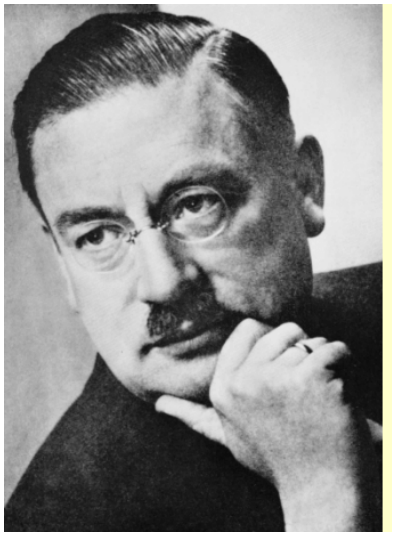
- Page 11, he has moved from diamond to rock-salt….the first appearance of something looking like a Bragg peak

Diffuse Scattering

- The Braggs discovered Bragg scattering on Page 11
- But apparently they discovered diffuse scattering on Page 5!



Computational issues: A Brief History of PDF



- Pieter Debye, 1915:

$$I = \sum_n \sum_m f_m f_n^* \frac{\sin qr_{mn}}{qr_{mn}}$$

- Fritz Zernike and Jon Prins, 1927:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi} \int_0^\infty qi(q) \sin qr dq$$

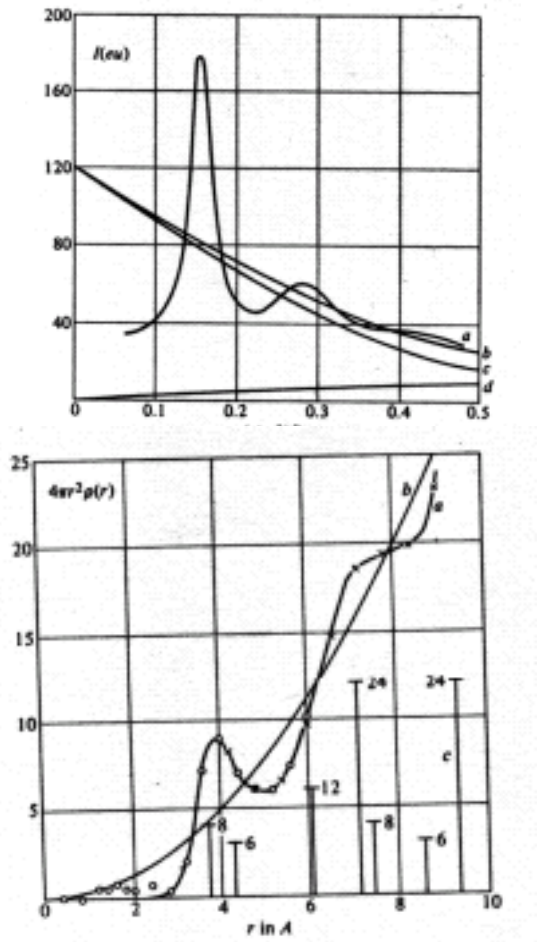
History

Debye and Menke, Z. Phys. (1930)

PDFs of mercury

Tarasov, L. P., and Warren, B. E., (1936) *J. Chem. Phys.*, **4**, 236.

X-ray PDFs of molten sodium



Complex materials

- Photovoltaics with improved efficiency
  - Nanoparticles in the light collecting layer
- High energy density batteries
  - Electrodes
  - Electrolytes
- Fuel cells for transportation applications
  - Electrodes
  - Electrolytes
  - Catalysts
  - Hydrogen storage
- Sequestration
  - Functionalized mesoporous materials

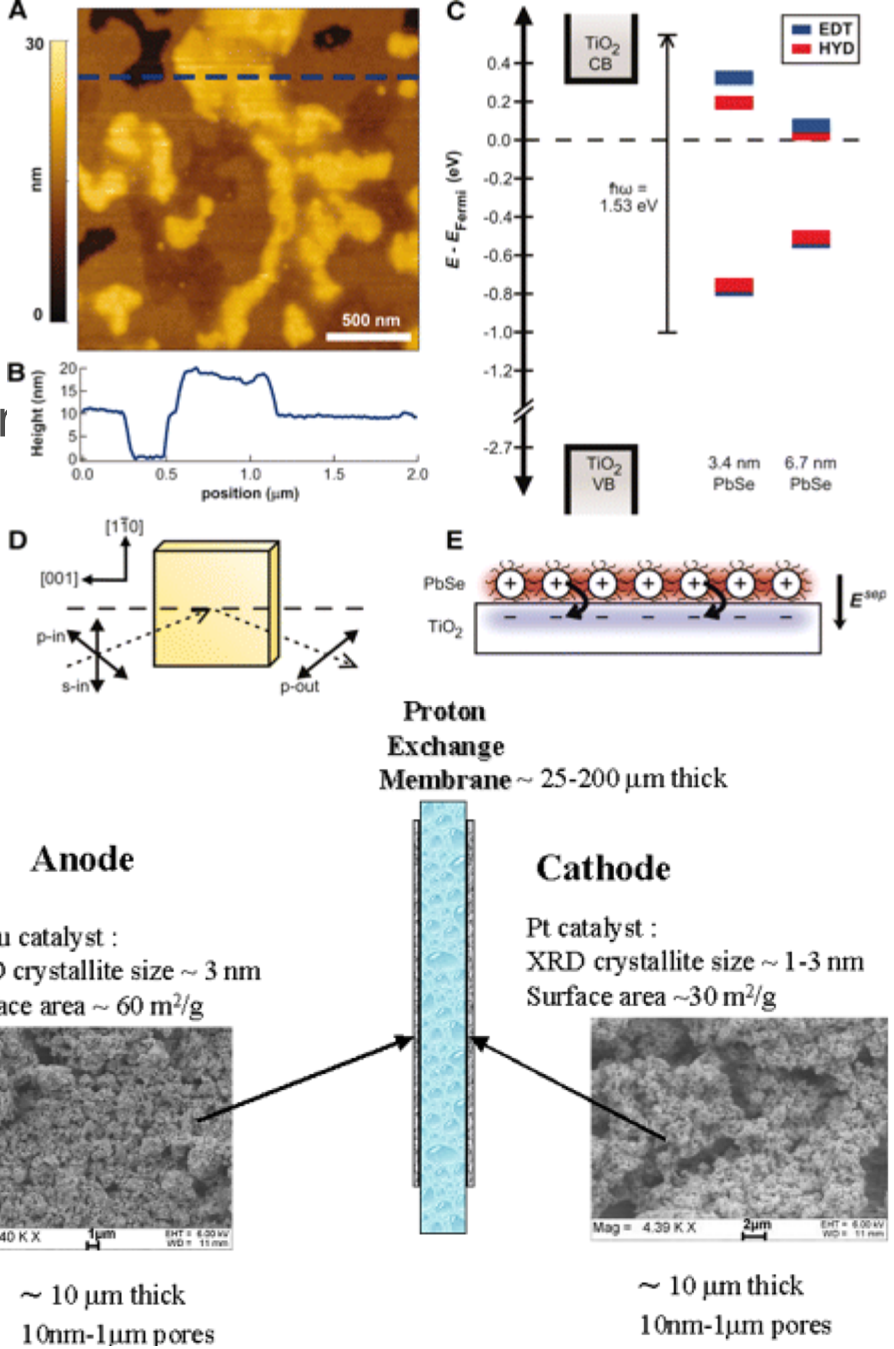


Image credits: 10.1126/science.1185509
U. Uppsala

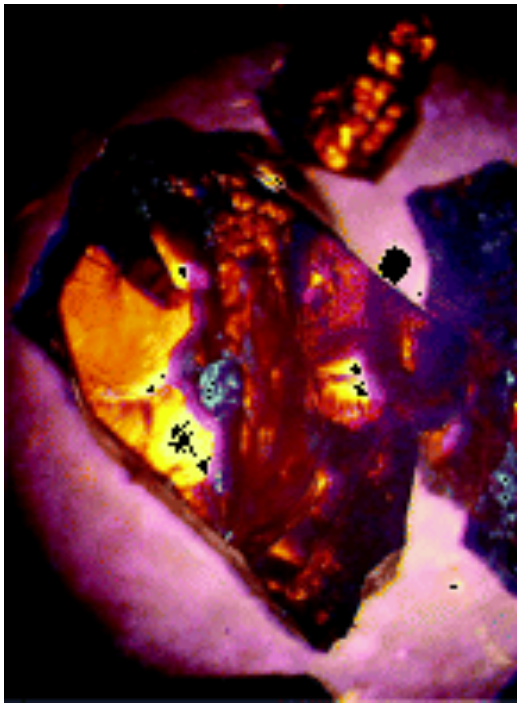
The Nanostructure Problem

- We want to engineer materials at the nanoscale

- But we can't even solve the atomic structure at the nanoscale:

The nanostructure problem

The Crystal Structure Problem

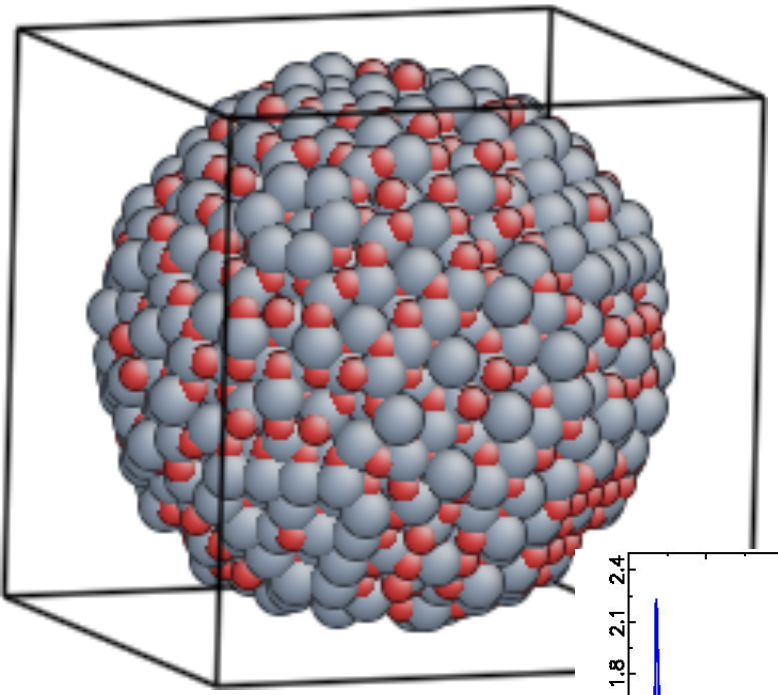


From LiGaTe2: A New Highly Nonlinear Chalcopyrite Optical Crystal for the Mid-IR L. Isaenko, et al., J. Crystal Growth, 5, 1325 – 1329 (2005)

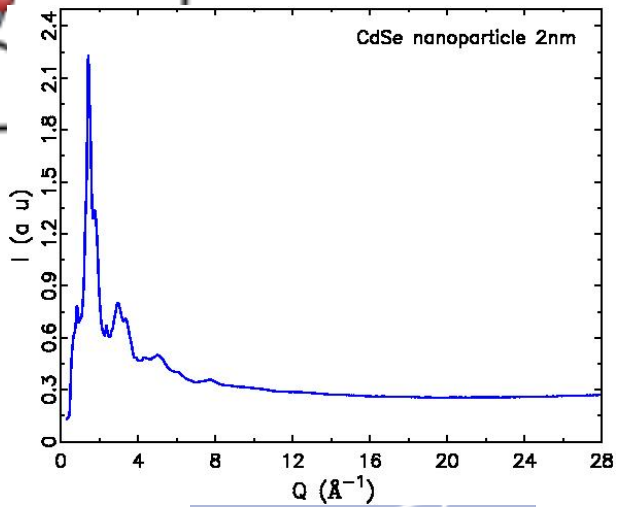
- Problem:
  - Here is a crystal, what is its structure?
- Solution:
  1. Give it to your grad student
  2. She puts it on the x-ray machine
  3. …Pushes the button
     1. Machine tells you the structure
     2. Or Machine gets stuck
        1. Throw away the crystal
        2. Make it the subject of her thesis

Crystallography is largely a solved problem

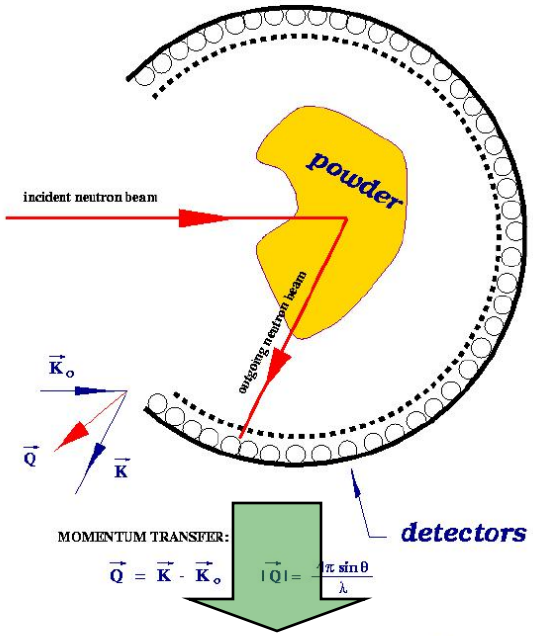
The Nanostructure Problem

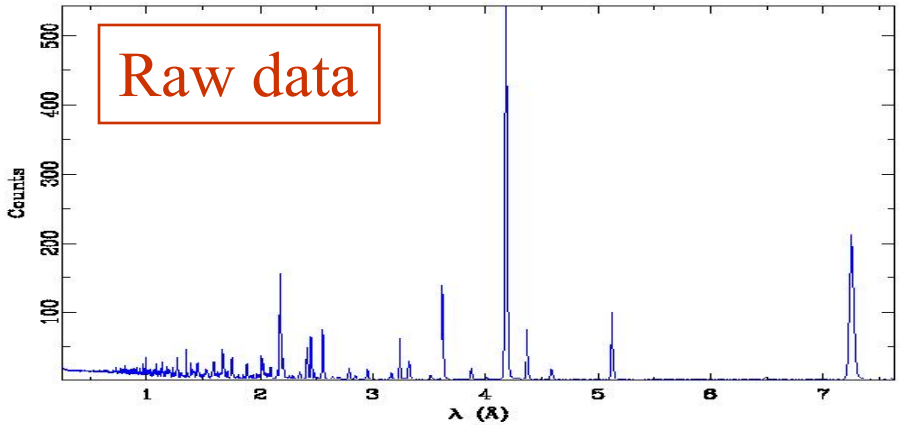


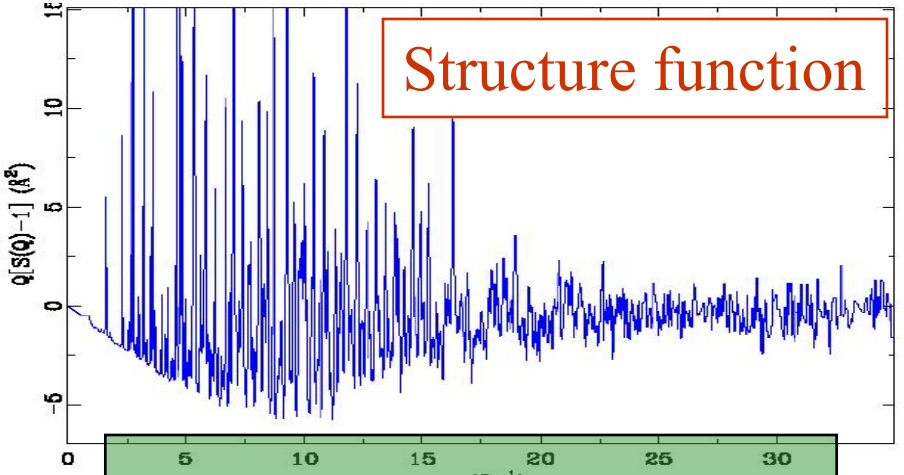
- Problem:
  - Here is a nanoparticle, what is its structure?
- Solution:
  1. Give it to your grad student
  2. She puts it on the x-ray machine
  3. …Pushes the button



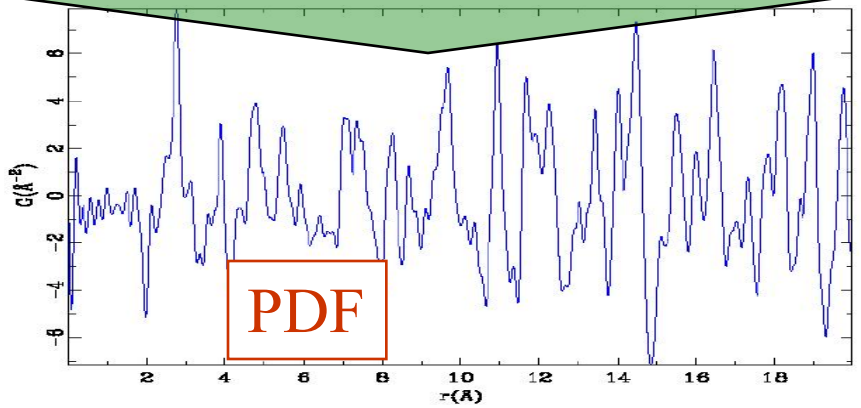
The atomic Pair Distribution Function





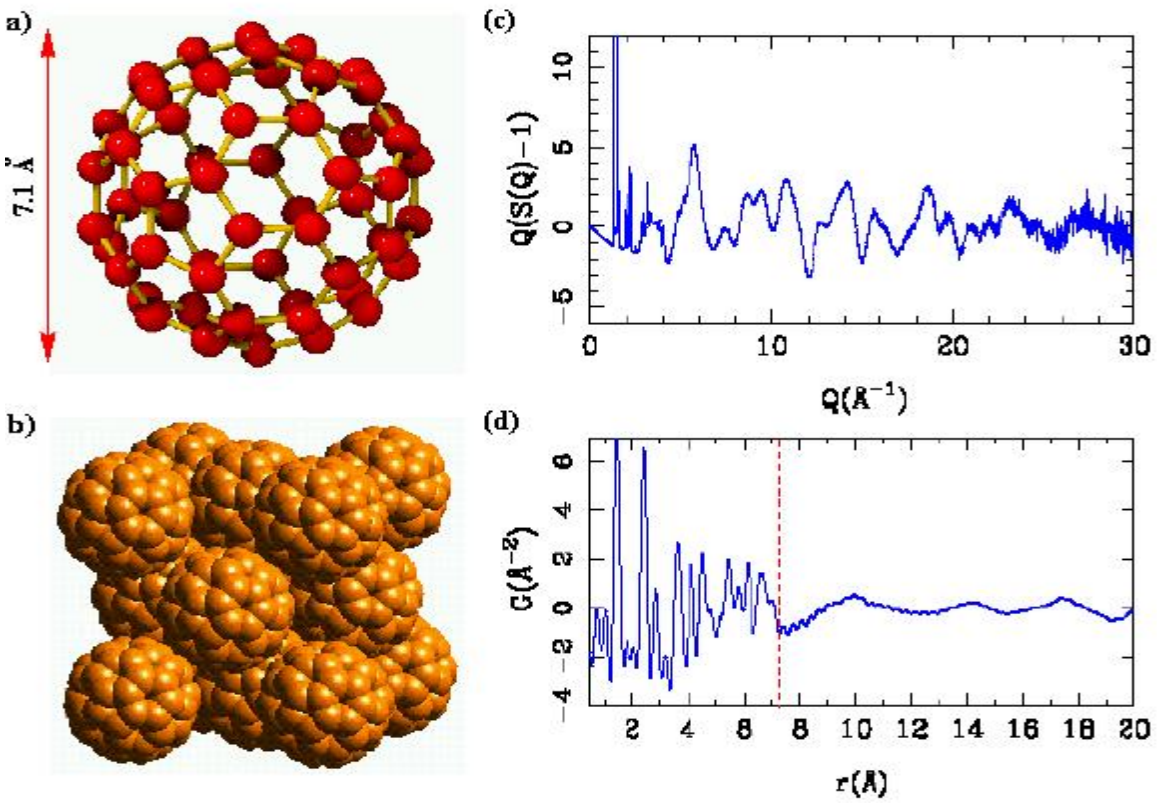


$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr\,dQ$$

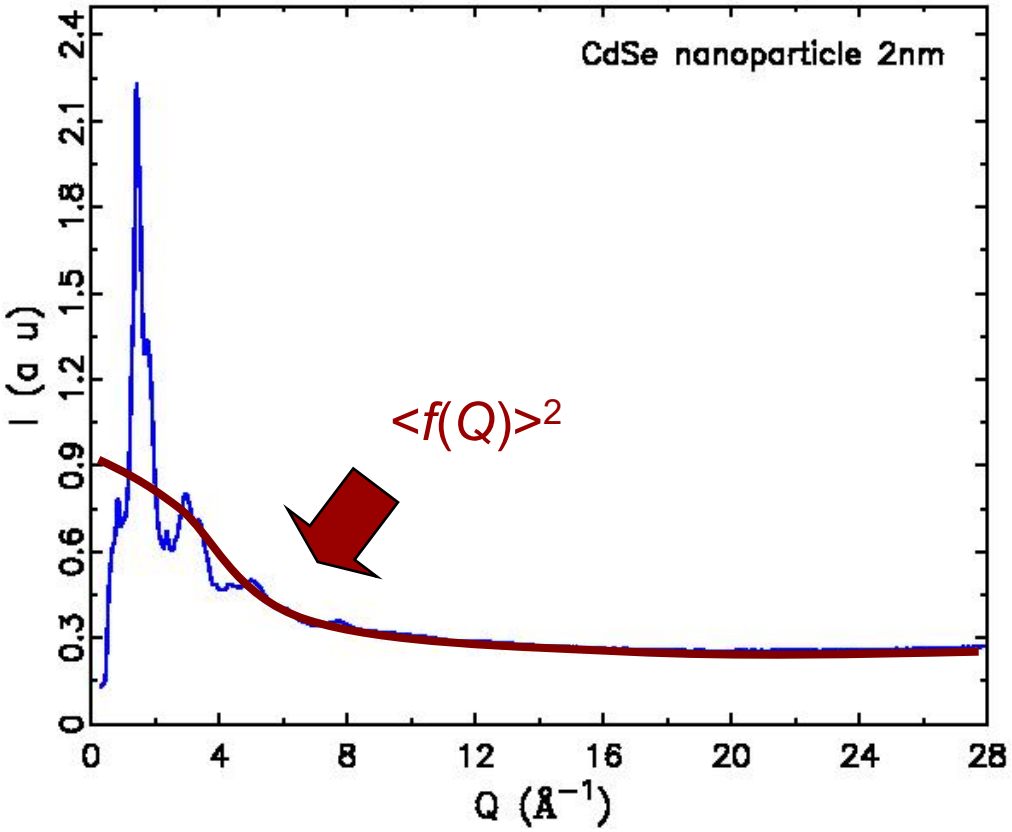


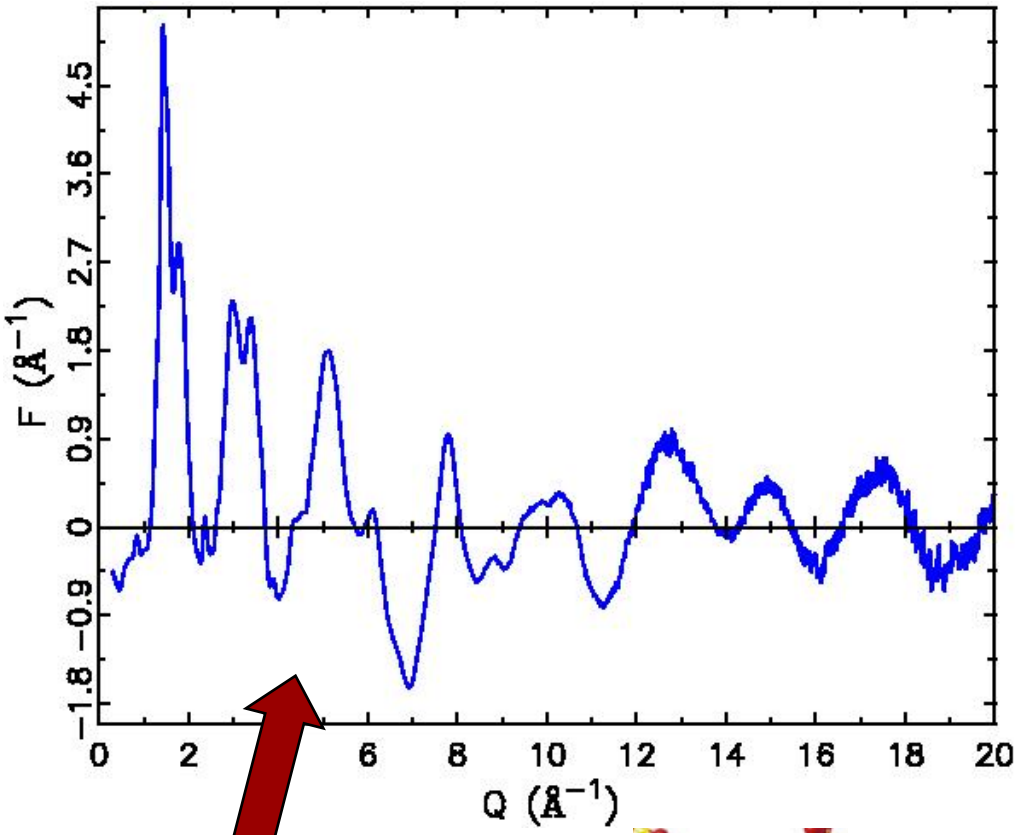
What is the PDF?

- Sit on an atom and look at your neighborhood
- *G(r)* gives the probability of finding a neighbor at a distance *r*
- PDF is experimentally accessible
- PDF gives the local structure



But there is no information at high-Q…?

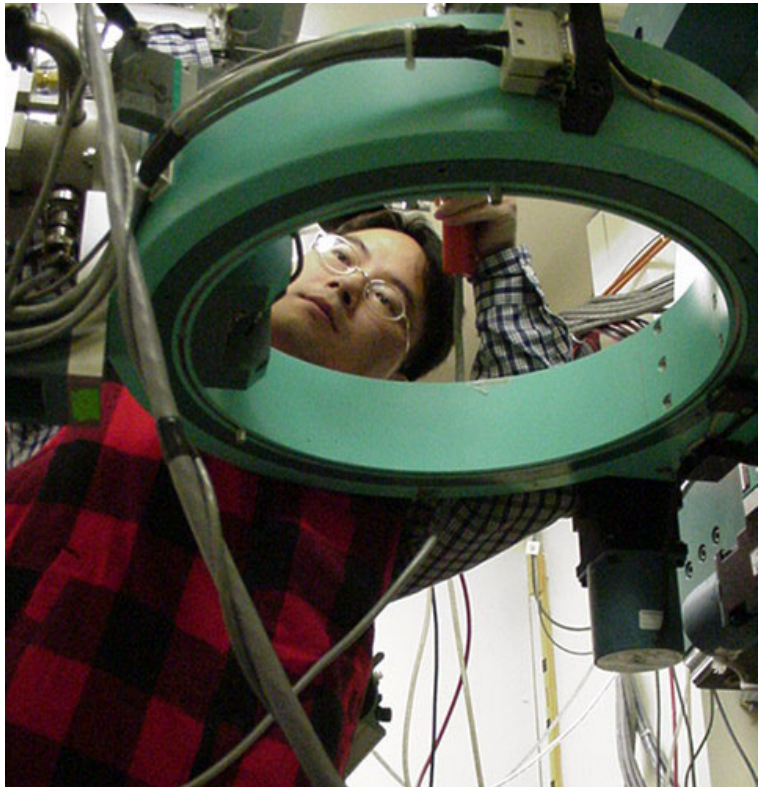


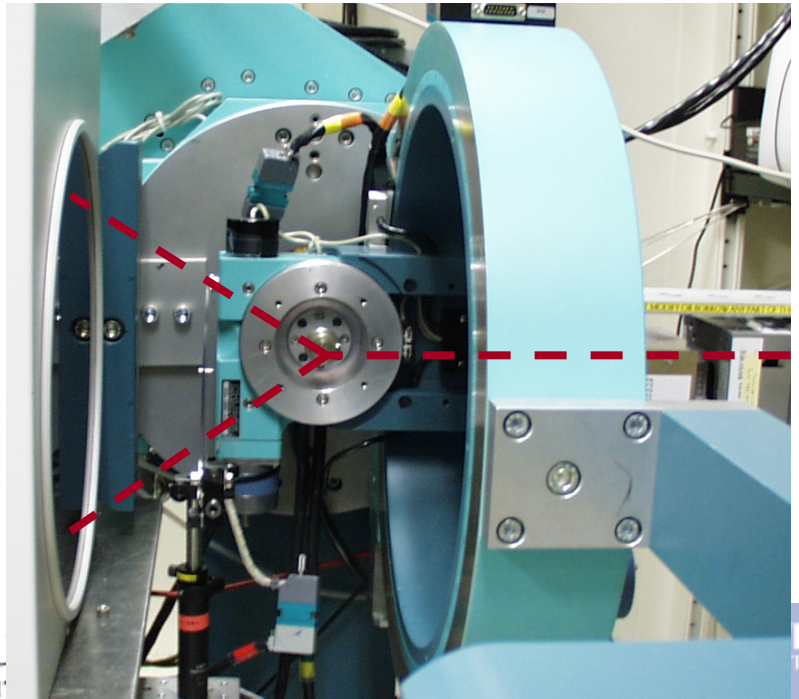


$$G(r) = \frac{2}{\pi}\int_0^\infty \boxed{Q[S(Q)-1]}\sin Qr\,\mathrm{d}Q$$

The Atomic Pair Distribution Function (PDF) Method

- Use modern high intensity x-ray and neutron sources to collect unprecedentedly precise data
- Utilize all the information: Bragg and diffuse scattering
- Use modern computing capabilities to analyze, model and visualize the data



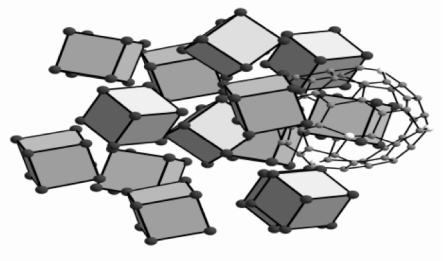


- Chupas et al., J. Appl. Crystallogr. (2003)
- Billinge-group, BNL, SUNY-SB, APS collaboration
- Main developments thanks to Pete Chupas and Xiangyun Qiu

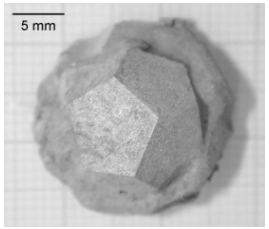
Synchrotron beamlines for PDF work

- NSLS-II @ Brookhaven National Laboratory
  - XPD (28-ID-2)
  - PDF (28-ID-1)
- APS @ Argonne National Laboratory
  - 11IDB, 11IDC
- ESRF
  - ID15, ID11, ID22
- Spring 8
  - various
- DESY
  - P07
- Diamond
  - XPDF

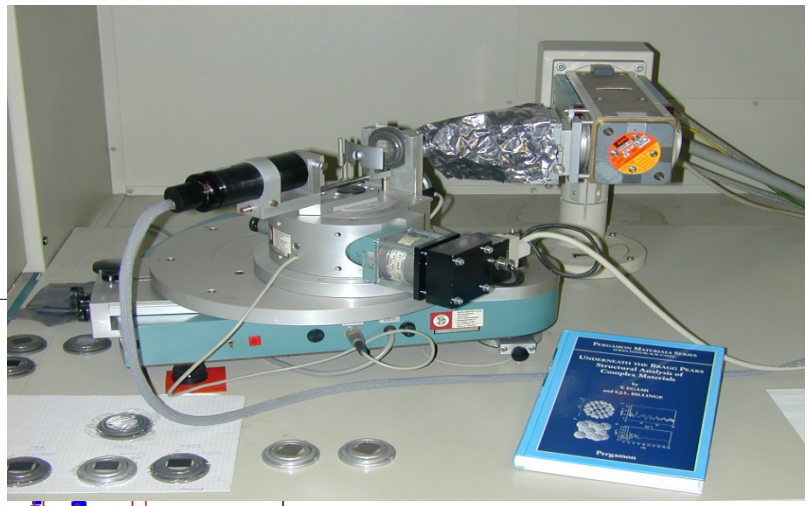
X-ray PDF: In-house measurements

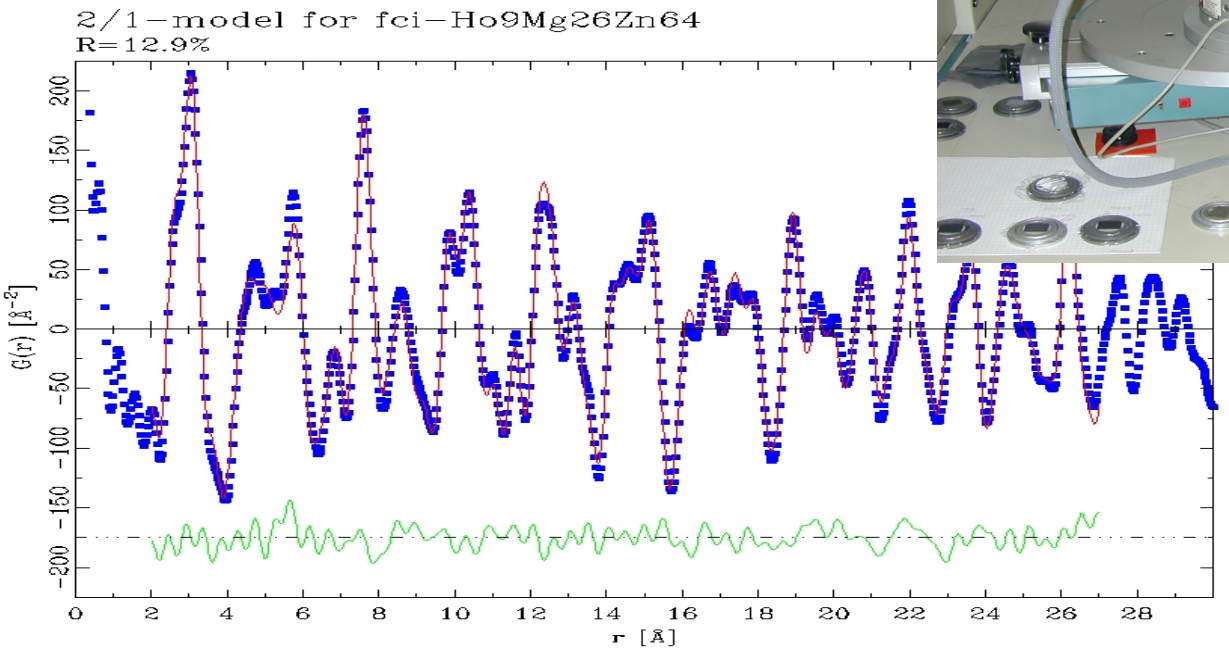


***fci*-Ho-Mg-Zn**



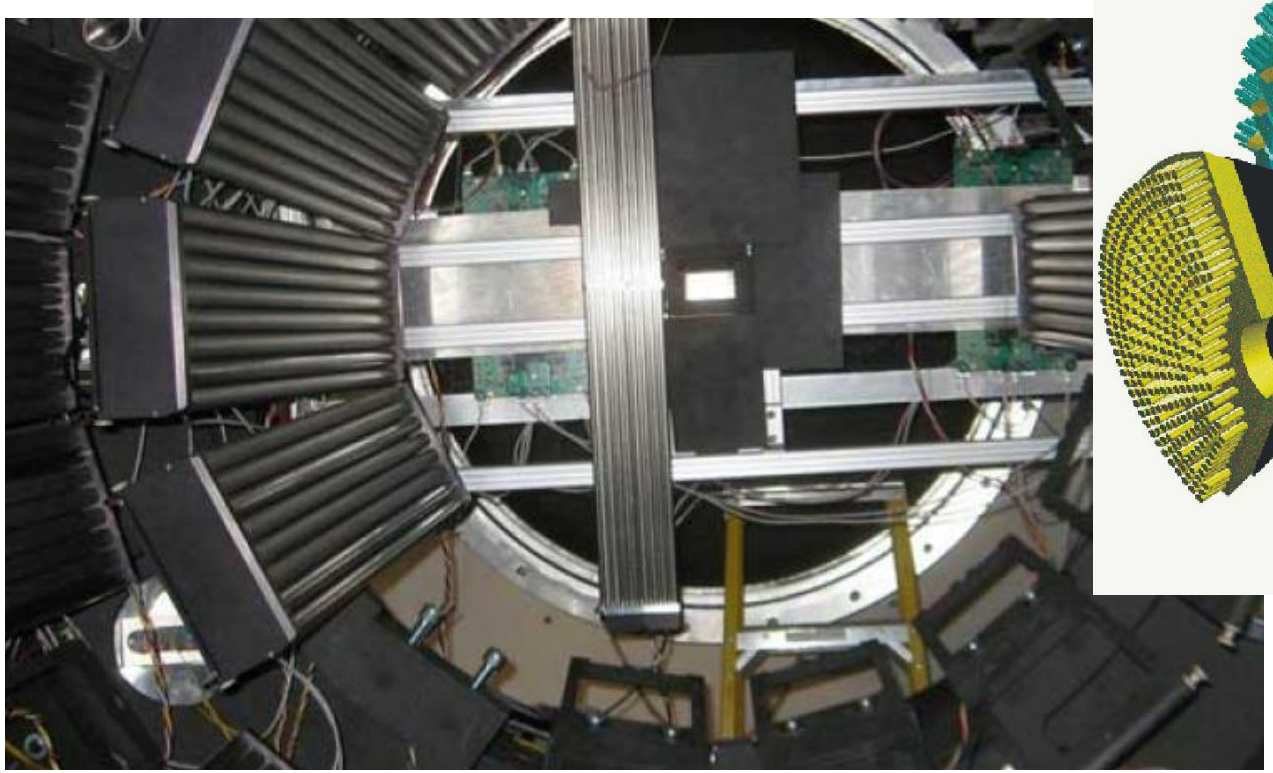
Huber Gunier diffractometer
Q_{max} = 13.5Å^{-1}



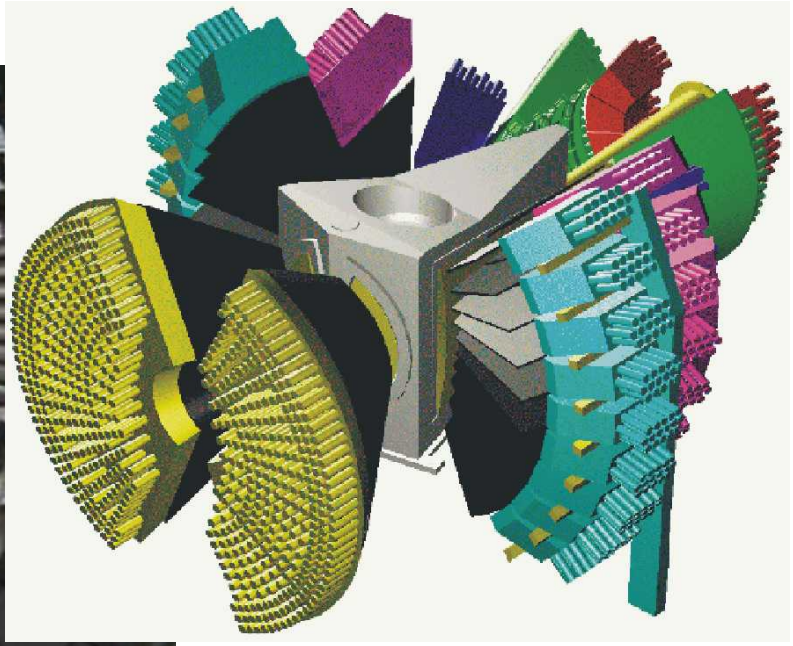


Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

RAPDF with Neutrons



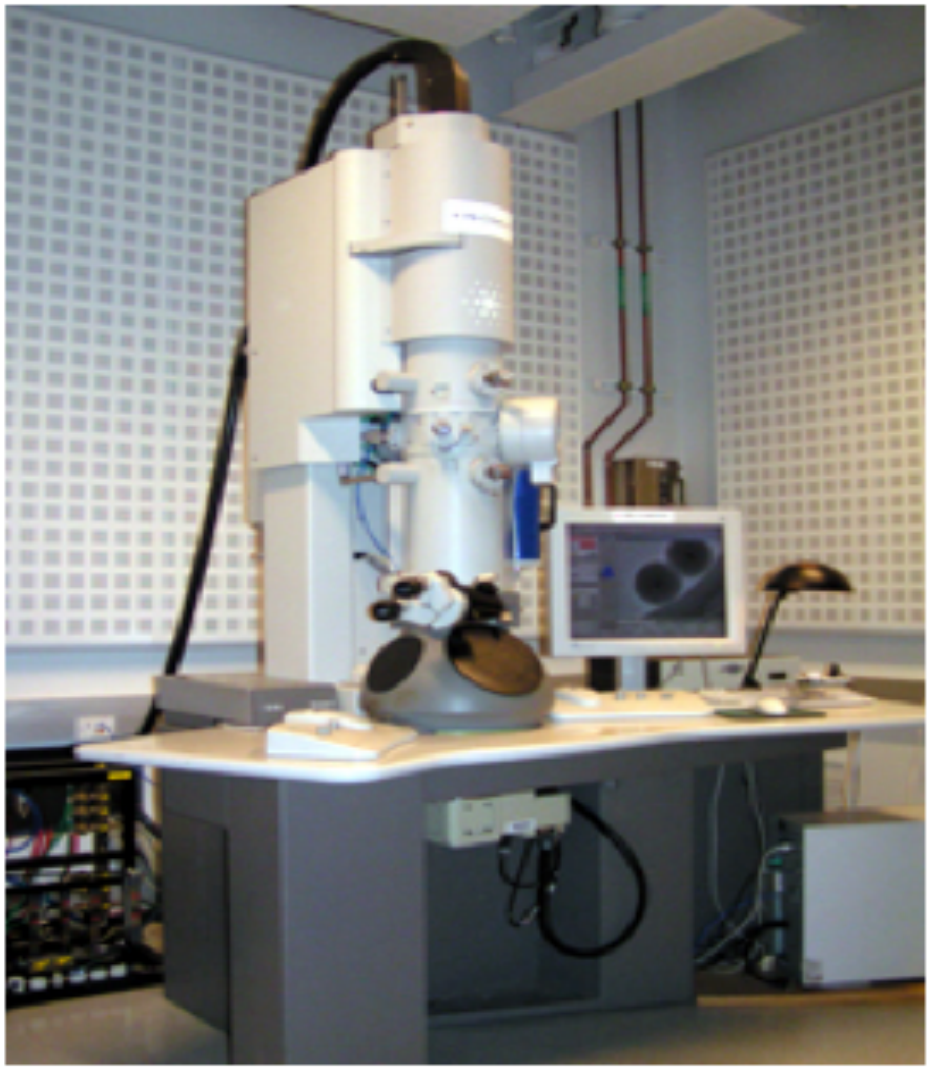
POWGEN & NOMAD @SNS



GEM, POLARIS &
NIMROD @ISIS

D4 @ILL

PDFs from laboratory microscopes



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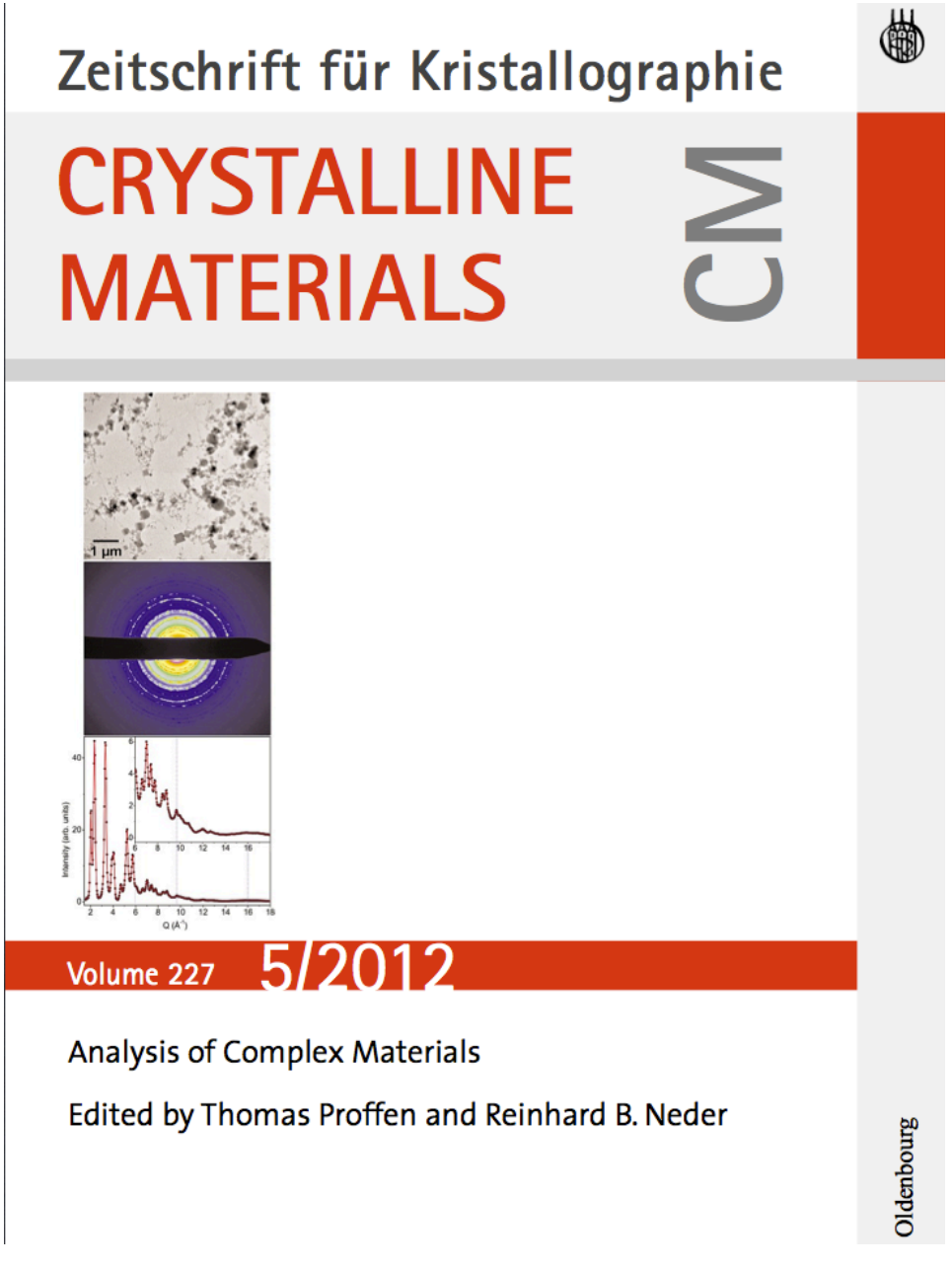
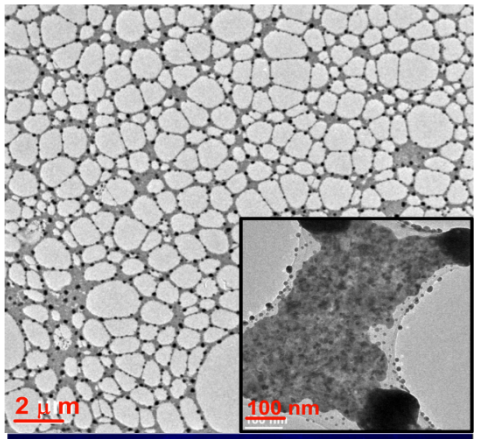


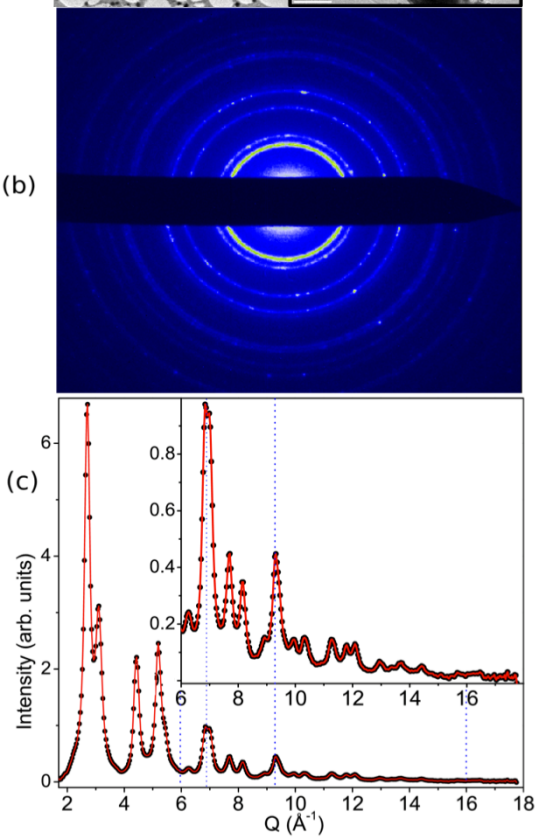
Au (1000) Å particles

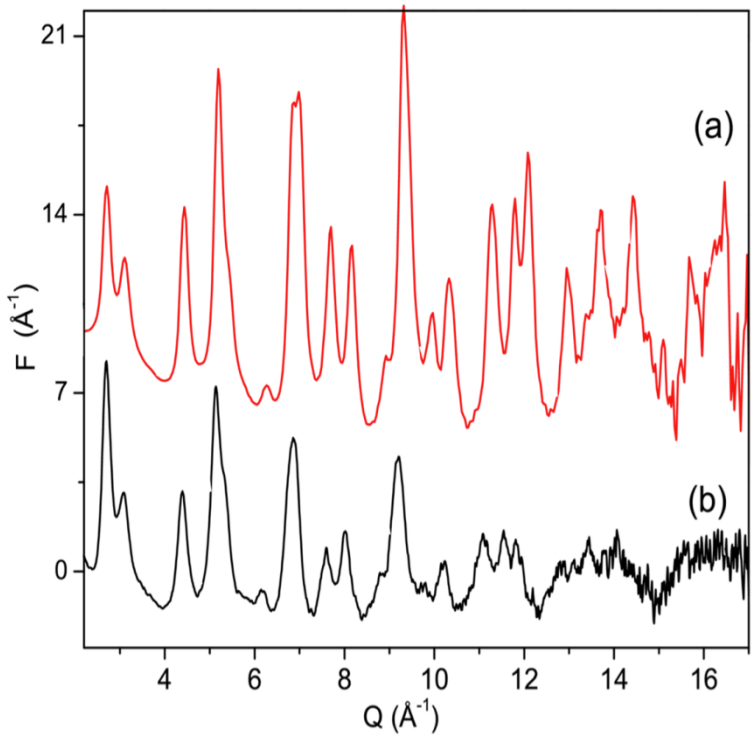
	ePDF (film)	ePDF (NP)	xPDF
Q_{max} (Å^{-1})	15.25	15.25	15.25
Fit range (Å)	1–20	1–20	1–20
Cell parameter (Å)	4.075(3)	4.076(2)	4.058(1)
U_{iso} (Å^2)	0.033(4)	0.006 (3)	0.014(1)
Diameter (Å)	~27[a]	~1000[b]	24.51(9)
Q-damp (Å^{-1})	0.095(5)	0.095(5)	0.047(2)
Rw (%)	17	24	20

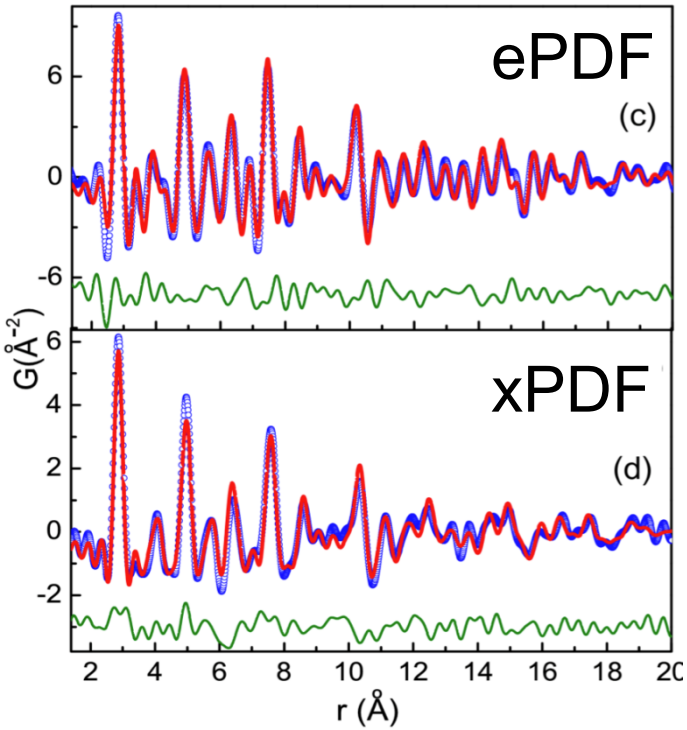
a: film thickness measured during deposition
b: NP diameter estimated directly from the TEM image

ePDFsuite software. Ask for details

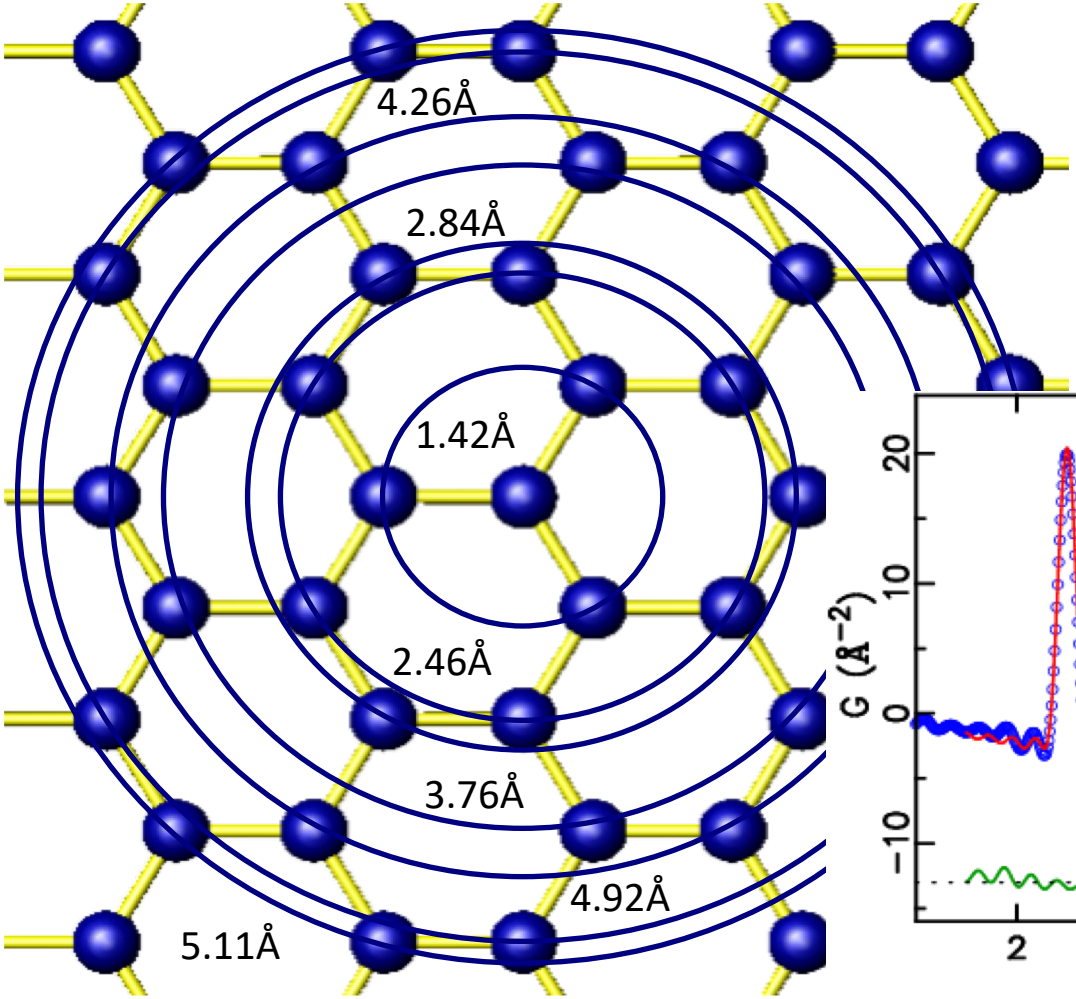




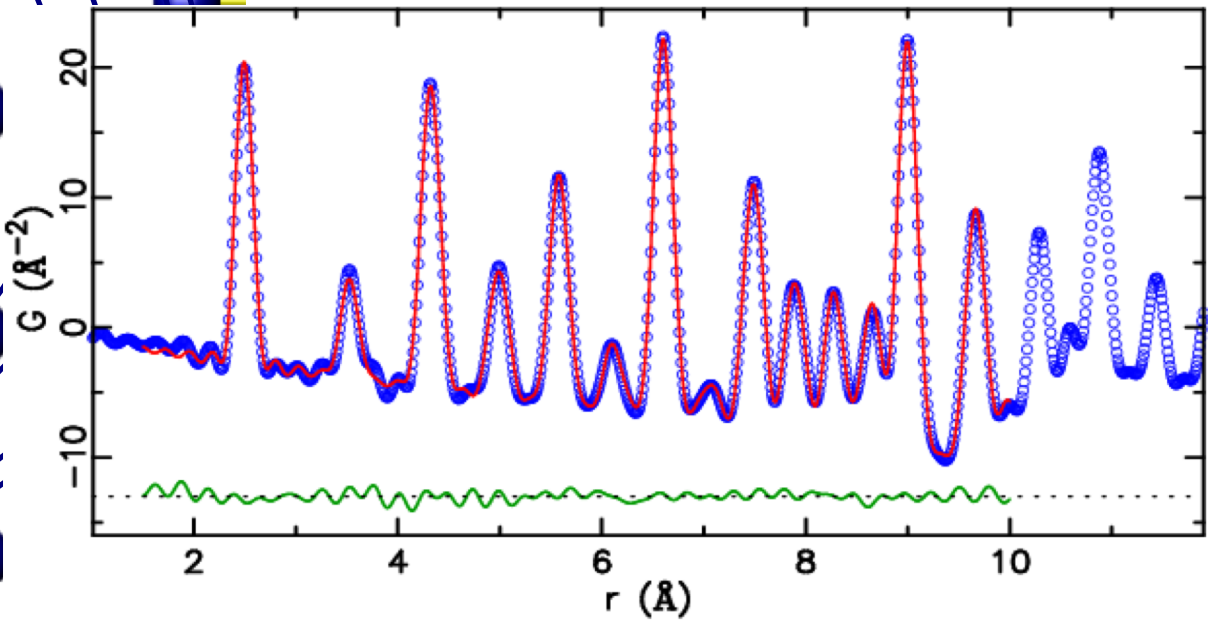




Nanostructure refinement



Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.



Modeling summary

- Small Box modeling
  - Similar in nature to Rietveld refinement of powder diffraction data
  - Small number of parameters, highly constrained fits
  - Danger of model bias, difficult to find distorted solutions.
  - Exemplars: PDFgui
- Large Box modeling
  - Large number of atoms in a box allowed to move aroun
  - Small number of constraints, exploratory unbiased fittin distorted solutions
  - Danger of overfitting and degenerate solutions. Difficult uncertainties
  - Exemplars: RMCprofile, RMC and Diffev in DISCUS, E
- George Box modeling
  - All models are wrong; some models are useful.
    - George E. P. Box, William Hunter and Stuart Hunte *Experimenters*, second edition, 2005, page 440.

PDFgui

- Used to be called “real-space Rietveld”
  - Starting point is a crystallographic description of the model
  - Small Unit cell, periodic boundary conditions
  - Fits to G(r) which is the FT of F(Q)

- PDFgui
  - Available from diffpy.org
  - Development funded by NSF-DANSE program

PbSe-480K.ddp (~\Documents\gl\16papers\16eb_pbse-emphanisis\new\20170412\Structure modeling\Recent data\PbSe-480K.ddp) - PDFgui

File Edit View Fits Phases Data Calculations Help

Fit Tree

- PbSe
  - PbSe.cif
  - PbSe.gr

Plot Control

X

step

Y

lat(1)
lat(2)
lat(3)
pscale
u11(1)
u11(2)

offset -5

Plot Reset

Configure | Constraints | Results

Phase Configuration

a	6.128	b	6.128	c	6.128
alpha	90.0	beta	90.0	gamma	90.0

Scale Factor	1.0				
delta1	0.0	delta2	1.0	spdiameter	0.0
sratio	1.0	rcut	0.0	stepcut	0.0

Included Pairs: all-all

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Pb	0.5	0.5	0.5	0.0186431	0.0186431	0.0186431	0.0	0.0	0.0	1.0
2	Pb	0.5	0.0	0.0	0.0186431	0.0186431	0.0186431	0.0	0.0	0.0	1.0
3	Pb	0.0	0.5	0.0	0.0186431	0.0186431	0.0186431	0.0	0.0	0.0	1.0
4	Pb	0.0	0.0	0.5	0.0186431	0.0186431	0.0186431	0.0	0.0	0.0	1.0
5	Se	0.0	0.0	0.0	0.0143116	0.0143116	0.0143116	0.0	0.0	0.0	1.0
6	Se	0.0	0.5	0.5	0.0143116	0.0143116	0.0143116	0.0	0.0	0.0	1.0
7	Se	0.5	0.0	0.5	0.0143116	0.0143116	0.0143116	0.0	0.0	0.0	1.0
8	Se	0.5	0.5	0.0	0.0143116	0.0143116	0.0143116	0.0	0.0	0.0	1.0

PDFfit2 Output

PbSe-480K.ddp (~\Documents\gl\16papers\16eb_pbse-emphanisis\new\20170412\Structure modeling\Recent data\PbSe-480K.ddp) - PDFgui

File Edit View Fits Phases Data Calculations Help

Fit Tree

- PbSe
  - PbSe.cif
  - PbSe.gr

Plot Control

X

step

Y

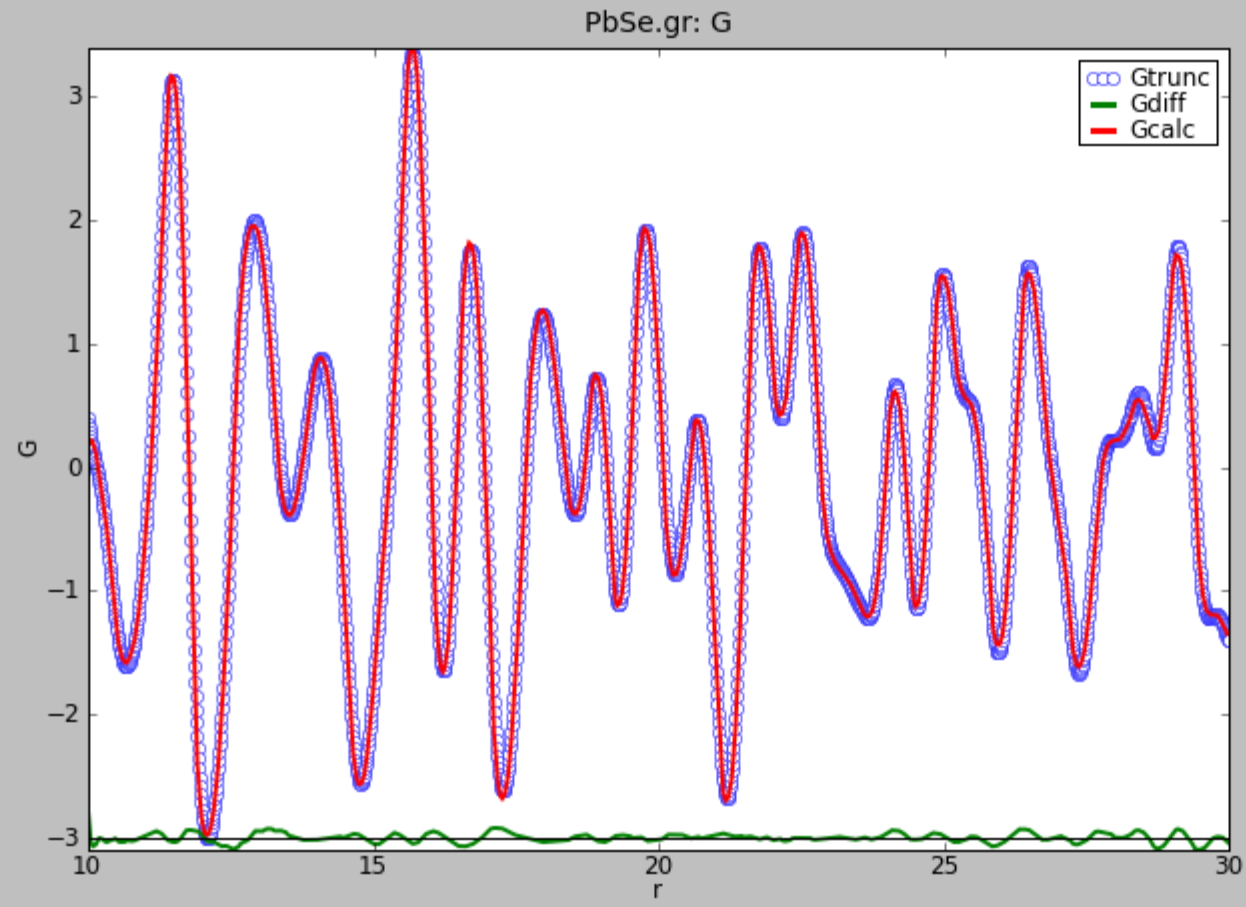
- Gcalc
- Gdiff
- Gobs
- Gtrunc
- crw
- dGcalc

offset -3

Plot Reset

PDFfit2 Output

Plot [2] PbSe.gr: G



x = 22.619, y = 2.69891

Diffpy project (BNL LDRD)
Complex Modeling infrastructure: Diffpy-CMI

Official release of Diffpy-CMI v0.1

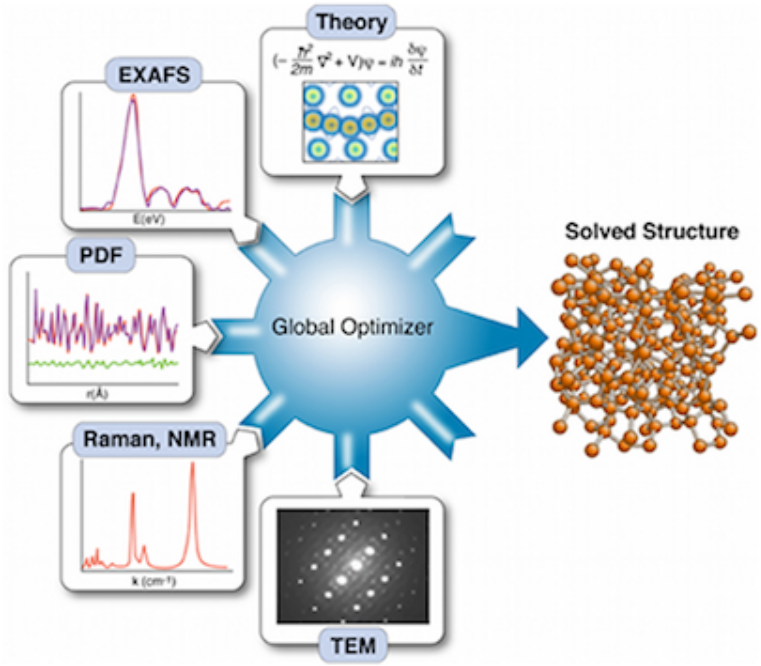
www.diffpy.org

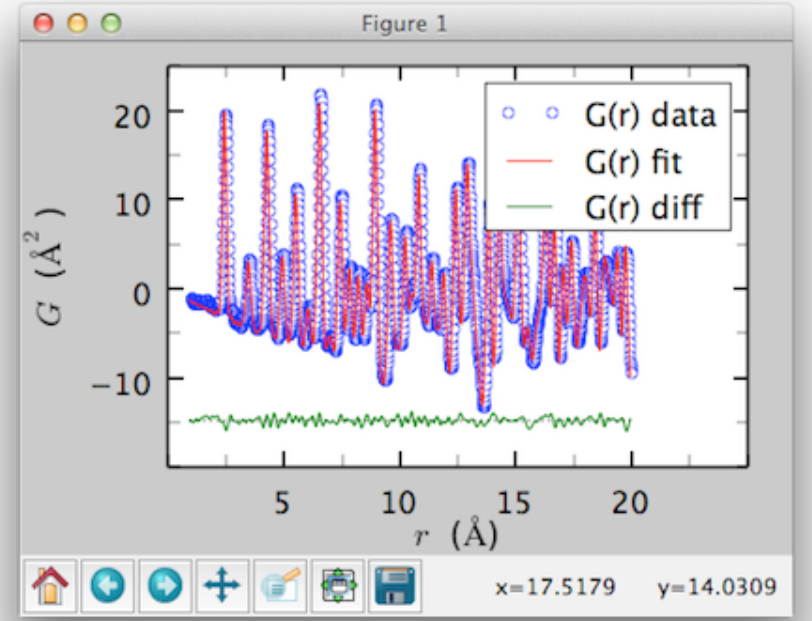
DiffPy Community Publications Products Search

DiffPy-CMI is now available! Get DiffPy-CMI Credits

DiffPy - Atomic Structure Analysis in Python

A free and open source software project to provide python software for diffraction analysis and the study of the atomic structure of materials.





CMI: complex modeling infrastructure

- CMI
  - Very powerful
  - Very difficult to use
  - We are working on a more friendly user interface and better documentation, but for now it is advised to contact us and we can help you get started

Diffpy-Complex Modeling Infrastructure: Diffpy-CMI

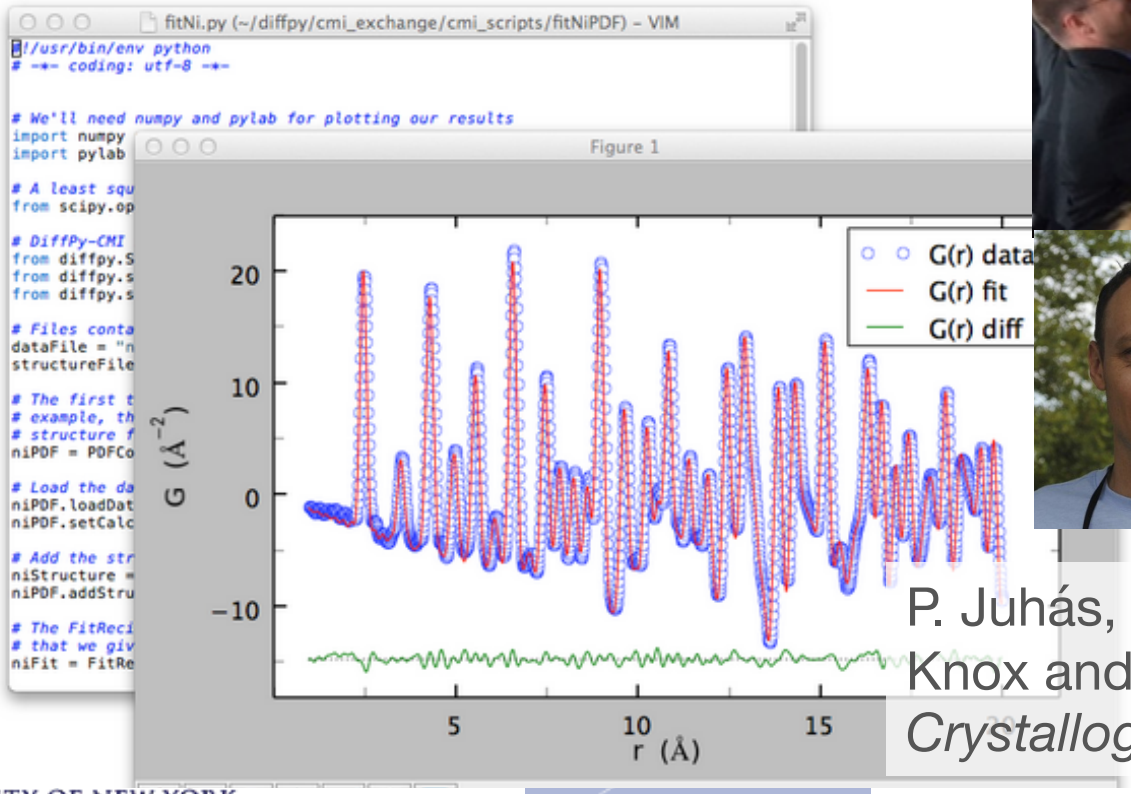
DiffPy Community Publications Products

DiffPy-CMI

DiffPy-CMI is our complex modeling framework. It is a highly flexible library of Python modules for robust modeling of nanostructures in crystals, materials.

The software provides functionality for storage and manipulation of structure data and calculation of structure-based quantities, such as PDF, SA overlaps, bond lengths, and coordinations. Most importantly the DiffPy-CMI package contains a fitting framework for combining multiple experime problem.

This is an early release of code that is under intense development, with support for installation on Unix, Linux, and Macintosh machines. The sco will evolve rapidly, but we want to make the code available at the earliest possible date. Please make use of the software and provide feedback a but please be patient and check back frequently for updates.

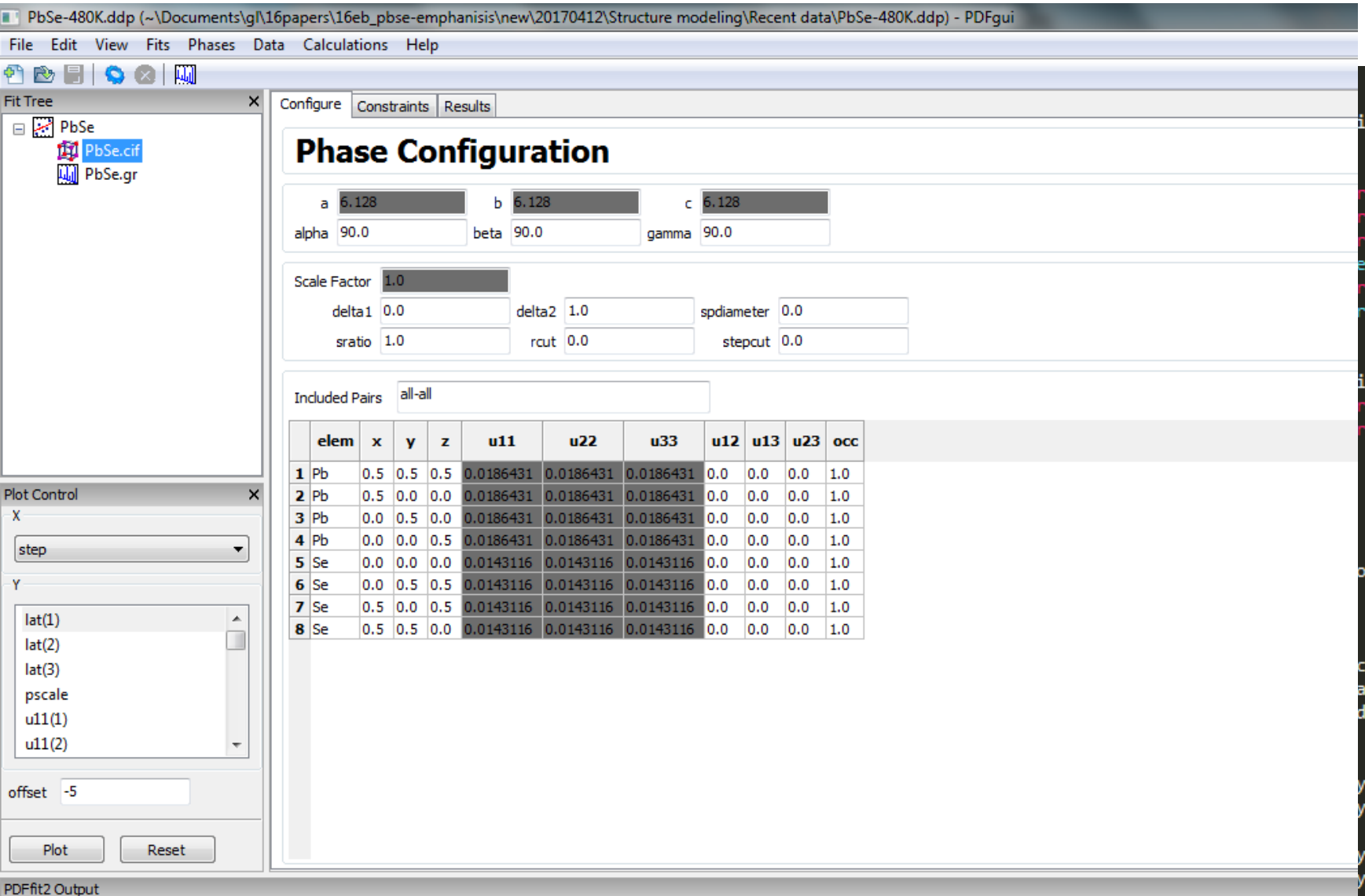


P. Juhás, C. L. Farrow, X. Yang, K. R. Knox and S. J. L. Billinge, *Acta Crystallogr. A*, (2015).

```python
#!/usr/bin/env python
# -*- coding: utf-8 -*-


# We'll need numpy and pylab for plotting our results
import numpy as np
import pylab

# A least squares fitting algorithm from scipy
from scipy.optimize.minpack import leastsq

# DiffPy-CMI modules for building a fitting recipe
from diffpy.Structure import loadStructure
from diffpy.srfit.pdf import PDFContribution
from diffpy.srfit.fitbase import FitRecipe, FitResults

# Files containing our experimental data and structure file
dataFile = "ni-q27r100-neutron.gr"
structureFile = "ni.cif"
spaceGroup = "Fm-3m"

# The first thing to construct is a contribution. Since this is a simple
# example, the contribution will simply contain our PDF data and an associated
# structure file. We'll give it the name "nickel"
niPDF = PDFContribution("nickel")

# Load the data and set the r-range over which we'll fit
niPDF.loadData(dataFile)
niPDF.setCalculationRange(xmin=1, xmax=20, dx=0.01)

# Add the structure from our cif file to the contribution
niStructure = loadStructure(structureFile)
niPDF.addStructure("nickel", niStructure)

# The FitRecipe does the work of calculating the PDF with the fit variable
# that we give it.
niFit = FitRecipe()

# give the PDFContribution to the FitRecipe
niFit.addContribution(niPDF)

# Configure the fit variables and give them to the recipe.  We can use the
```

```
66
67  # Turn off printout of iteration number.
68  niFit.clearFitHooks()
69
70  # We can now execute the fit using scipy's least square optimizer.
71  print "Refine PDF using scipy's least-squares optimizer:"
72  print "  variables:", niFit.names
73  print "  initial values:", niFit.values
74  leastsq(niFit.residual, niFit.values)
75  print "  final values:", niFit.values
76  print
77
78  # Obtain and display the fit results.
79  niResults = FitResults(niFit)
80  print "FIT RESULTS\n"
81  print niResults
82
83  # Plot the observed and refined PDF.
84
85  # Get the experimental data from the recipe
86  r = niFit.nickel.profile.x
87  gobs = niFit.nickel.profile.y
88
89  # Get the calculated PDF and compute the difference between the calculated and
90  # measured PDF
91  gcalc = niFit.nickel.evaluate()
92  baseline = 1.1 * gobs.min()
93  gdiff = gobs - gcalc
94
95  # Plot!
96  pylab.figure()
97  pylab.plot(r, gobs, 'bo', label="G(r) data",
98          markerfacecolor='none', markeredgecolor='b')
99  pylab.plot(r, gcalc, 'r-', label="G(r) fit")
100 pylab.plot(r, gdiff + baseline, 'g-', label="G(r) diff")
101 pylab.plot(r, np.zeros_like(r) + baseline, 'k:')
102 pylab.xlabel(r"r ($\AA$)")
103 pylab.ylabel(r"G ($\AA^{-2}$)")
104 pylab.legend()
105
106 pylab.show()
107
```

In the pipeline: PDFgui2.0

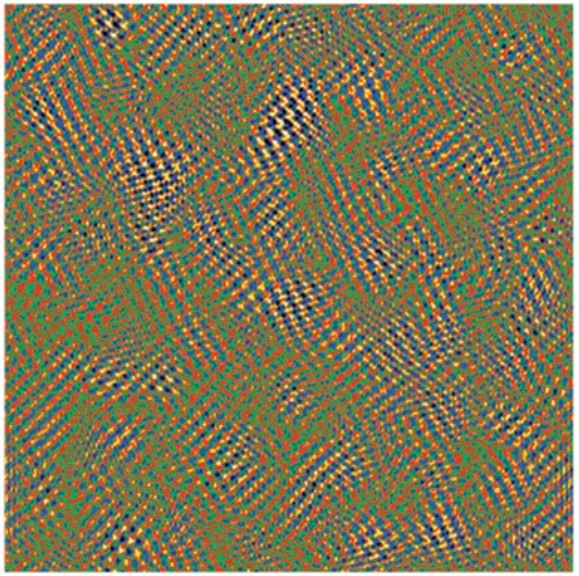


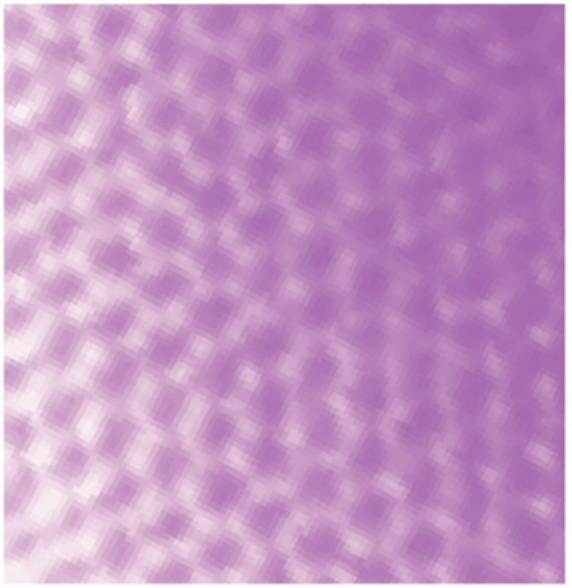

```
Turn off printout of ite
iFit.clearFitHooks()

We can now execute the f
rint "Refine PDF using sc
rint "  variables:", niFi
rint "  initial values:",
eastsq(niFit.residual, ni
rint "  final values:", n
rint

Obtain and display the f
iResults = FitResults(niF
rint "FIT RESULTS\n"
rint niResults

Plot the observed and re

Get the experimental dat
 = niFit.nickel.profile.x
obs = niFit.nickel.profil

Get the calculated PDF a
measured PDF
calc = niFit.nickel.evalu
aseline = 1.1 * gobs.min(
diff = gobs - gcalc

Plot!
ylab.figure()
ylab.plot(r, gobs, 'bo',
        markerfacecolor='n
ylab.plot(r, gcalc, 'r-',
ylab.plot(r, gdiff + base
```

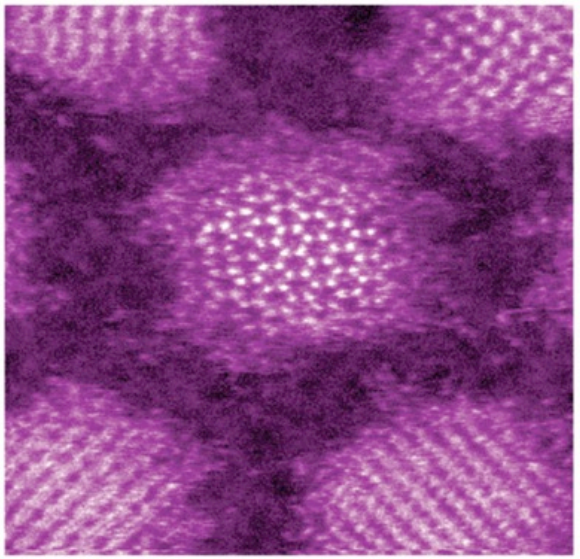
In the Pipeline in the pipeline: PDFgui2.n

- PDFgui2.0 will simply replicate PDFgui functionality but using Diffpy-CMI as the engine
- Later releases (2.1, 2.3, 2.5, etc.) will begin to implement some of the extended capabilities of Diffpy-CMI:
  - Non-spherical particle shape functions
  - Log-normal particle distributions
  - Fitting discrete nanoparticles
  - Magnetic PDF
- Make sure you sign up for the xpd-users Google group to be the first to hear about these developments

Nanomaterials



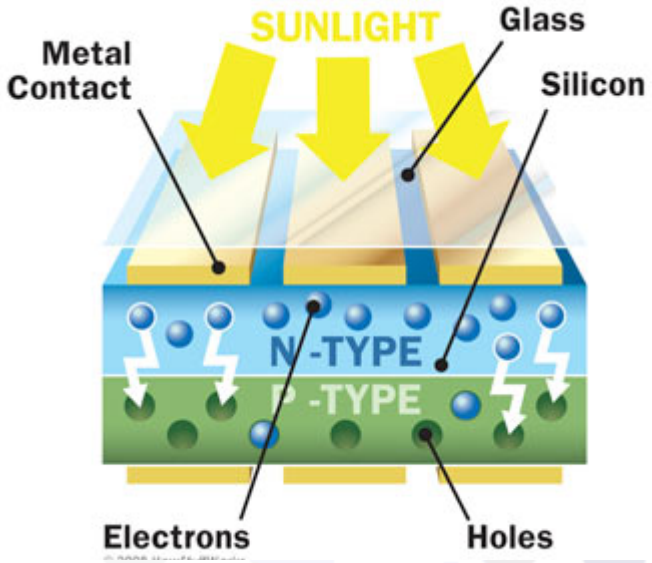


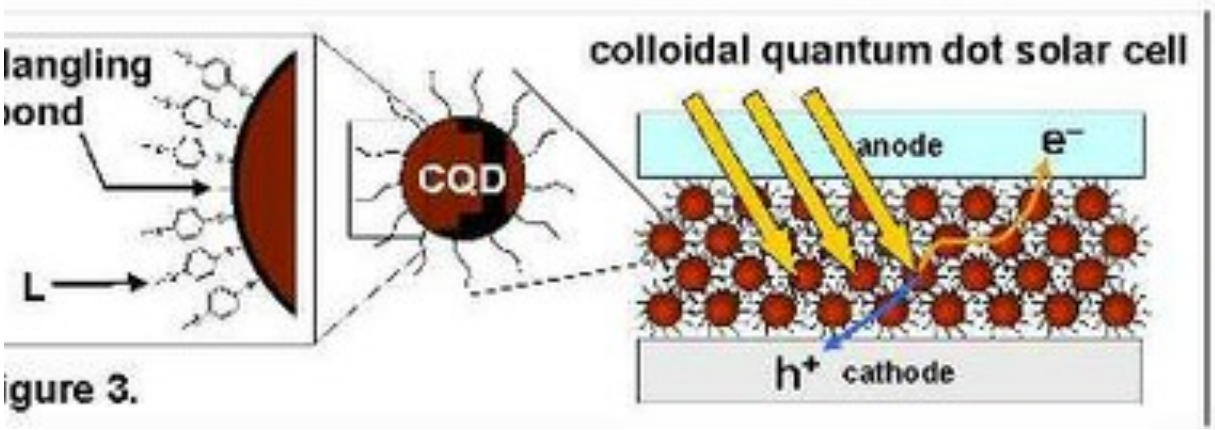


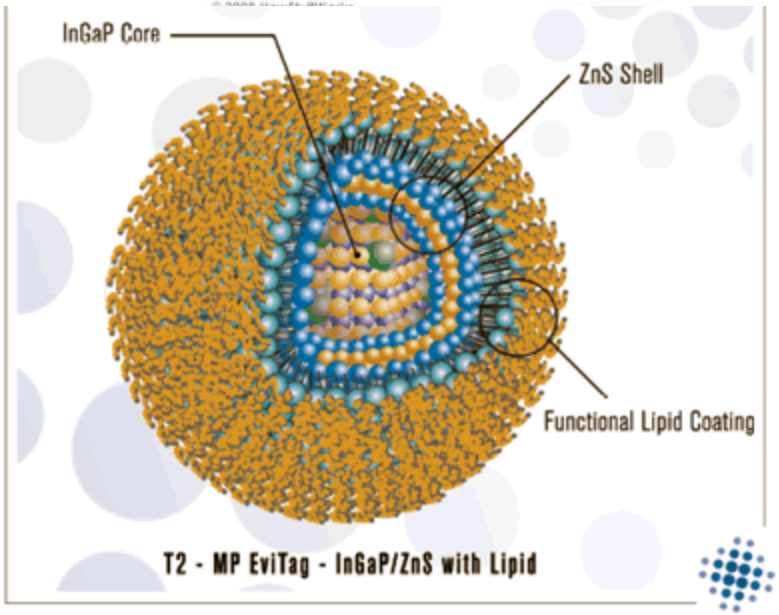
The Nanoparticle structure problem

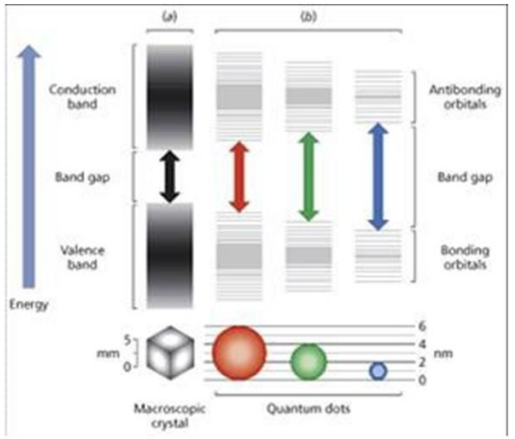
1. Powder of similar but not identical powders
    1. Structure
    2. Defects
    3. TD properties Pt NPs

Quantum Dot solar cells

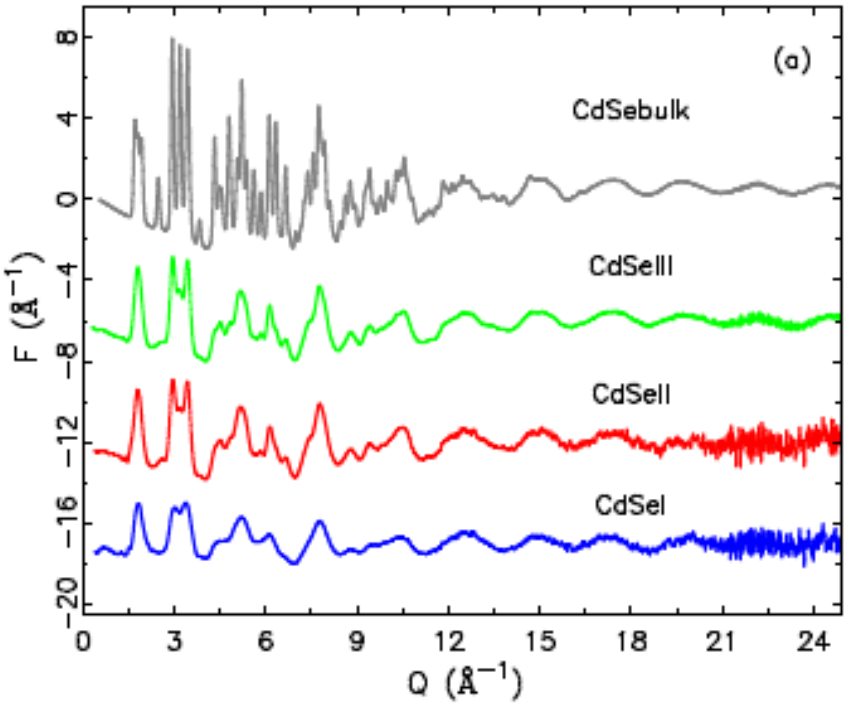


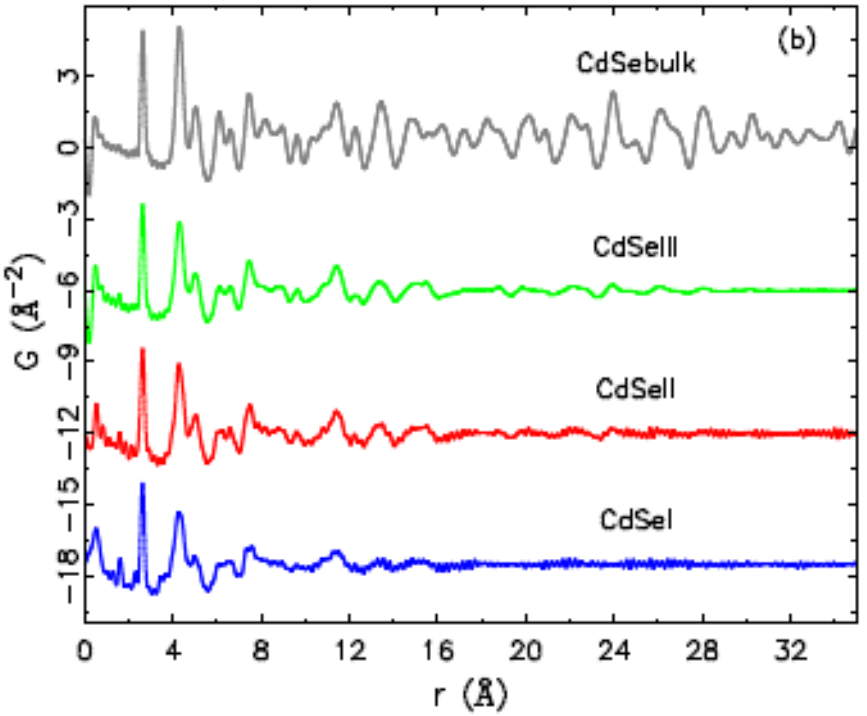




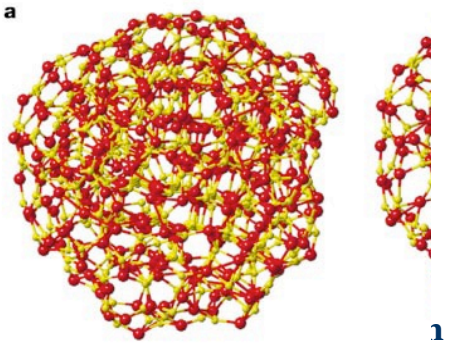


CdSe quantum dots





- RAPDF experiments at APS, Sector 6
- Work of grad student Ahmad Masadeh
- Masadeh, SJB *et al.* PRB **76**, 115413 (2007)



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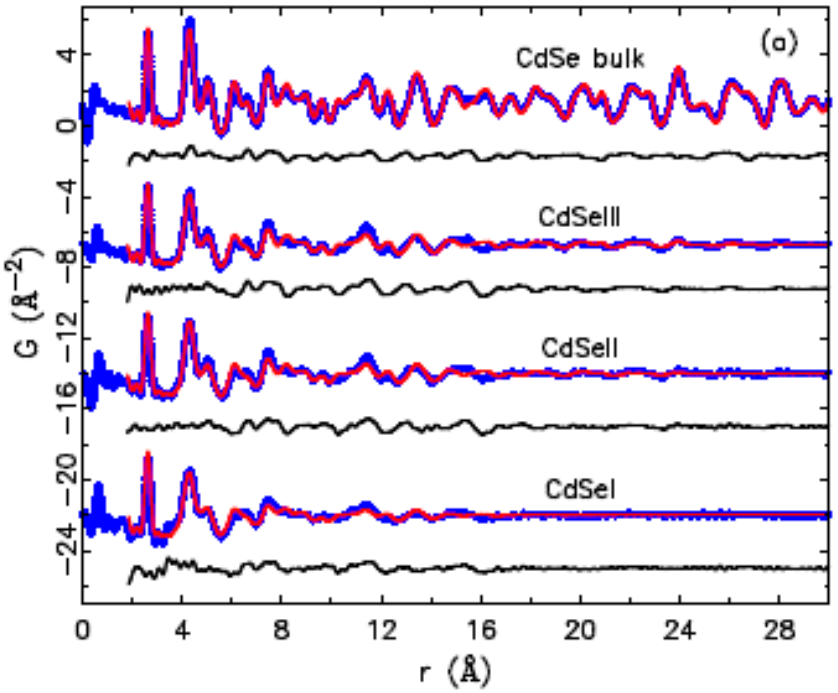
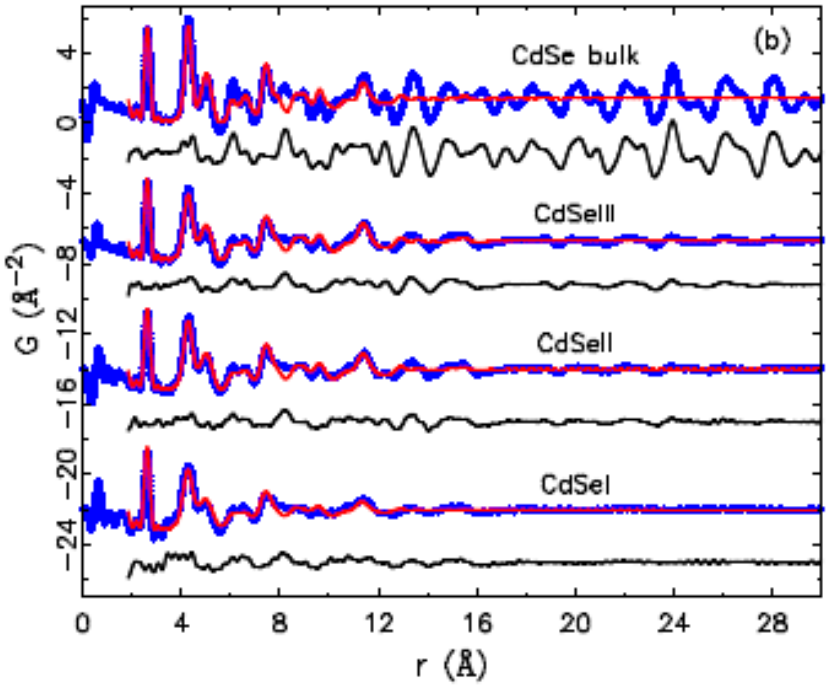
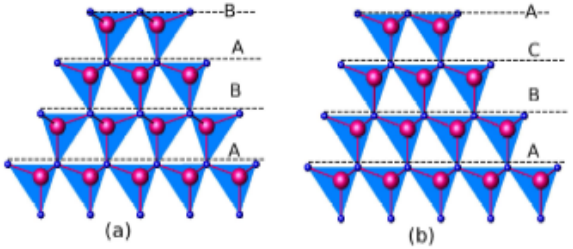
Structure of the CdSe core

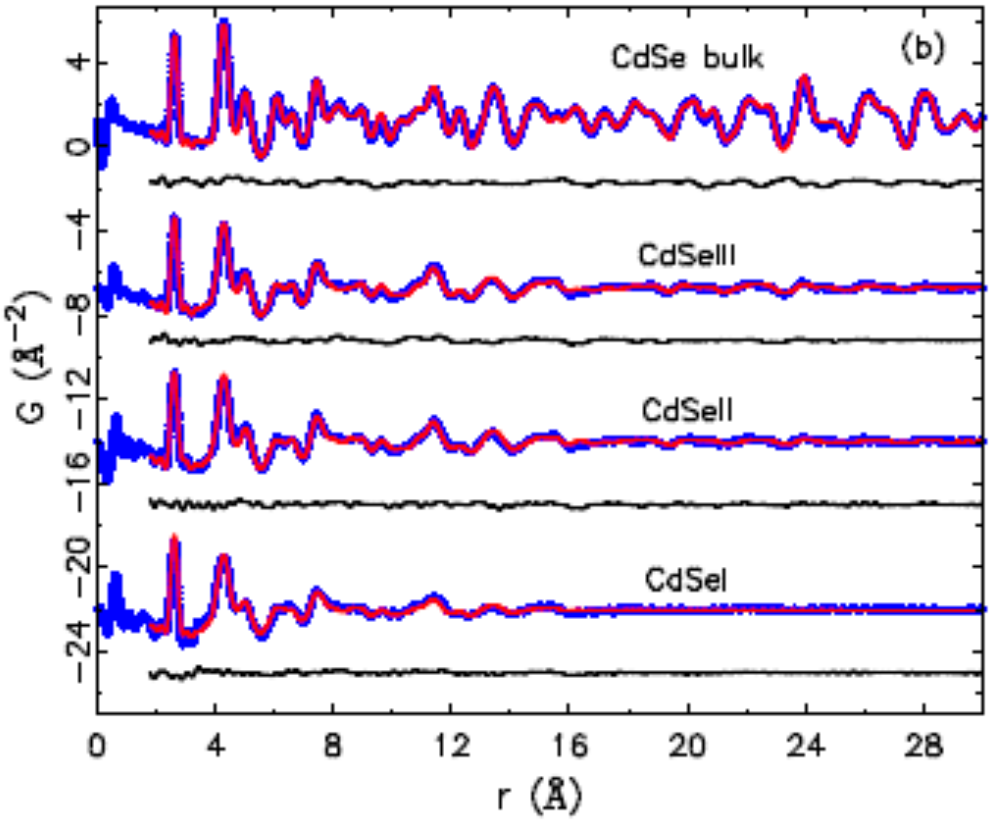




- Wurtzite structure

- Zinc blende structure



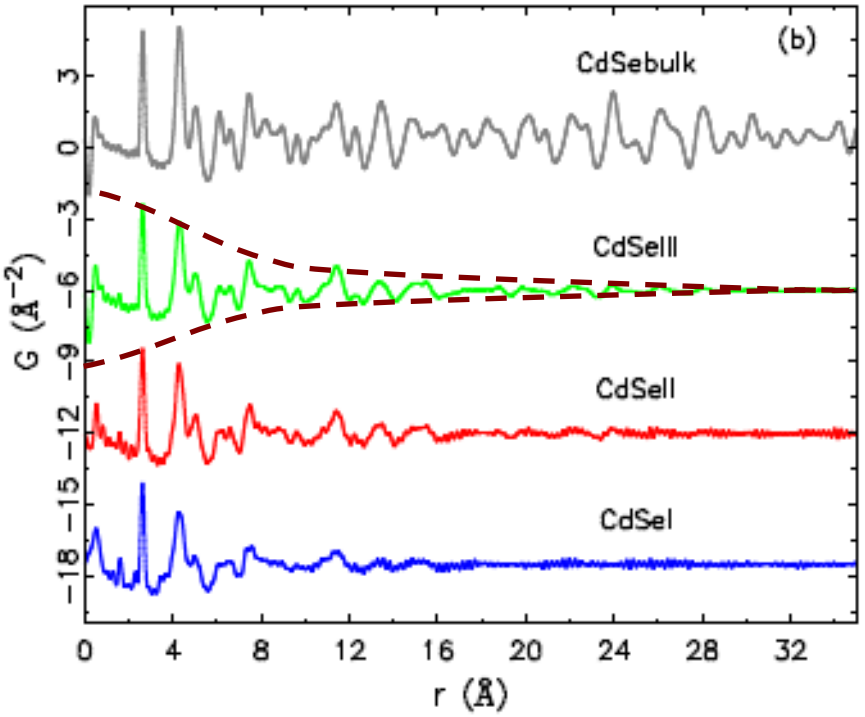


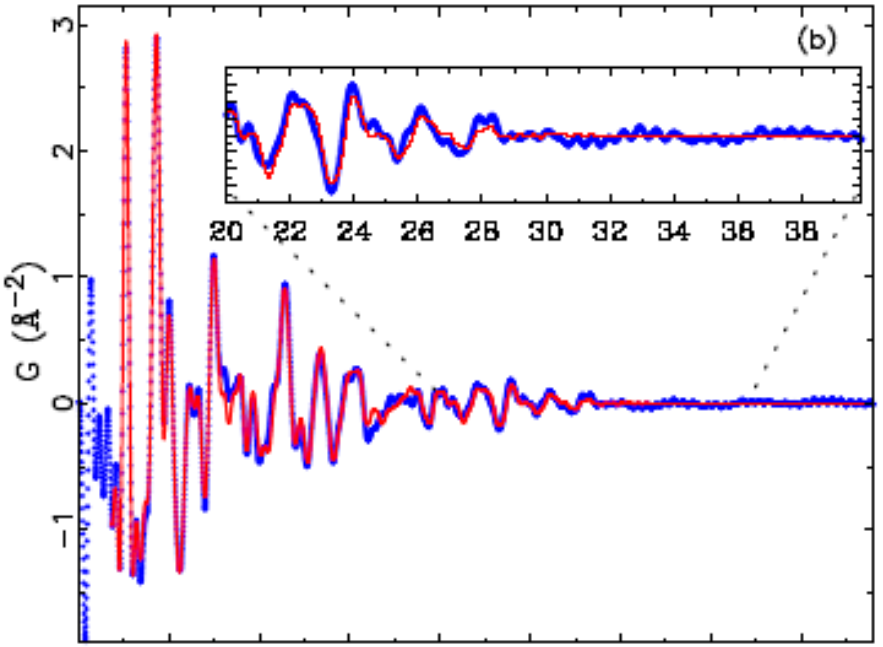
Masadeh, SJB *et al.* PRB **76**, 115413 (2007)

Thanks to Reinhard Neder for help with stacking fault models

	CdSe-bulk		CdSeIII		CdSeII		CdSeI	
Stacking fault density (%)	0.0	33.0	0.0	50.0	0.0	50.0	0.0	50.0
a (Å)	4.3014(4)	4.3012(4)	4.2997(9)	4.2987(9)	4.3028(9)	4.3015(9)	4.2930(9)	4.2930(8)
c (Å)	7.0146(9)	7.0123(9)	7.0145(4)	7.0123(4)	6.9987(9)	6.9975(9)	6.9405(9)	6.9405(7)
Se *Z-frac.*	0.3774(3)	0.3771(3)	0.3761(9)	0.3759(9)	0.3751(6)	0.3747(6)	0.3685(9)	0.3694(9)
Cd $U_{11} = U_{22}$ (Å^2)	0.0108(2)	0.0102(2)	0.0146(7)	0.0149(7)	0.0149(6)	0.0112(5)	0.0237(9)	0.0213(8)
U_{33} (Å^2)	0.0113(3)	0.0112(3)	0.0262(9)	0.0241(9)	0.0274(9)	0.0271(9)	0.0261(9)	0.0281(9)
Se $U_{11} = U_{22}$ (Å^2)	0.0109(9)	0.0102(9)	0.0077(7)	0.0138(7)	0.0083(7)	0.0121(7)	0.0110(9)	0.0191(9)
U_{33} (Å^2)	0.0462(9)	0.0115(9)	0.1501(9)	0.02301(9)	0.1628(9)	0.0265(9)	0.1765(9)	0.0311(9)
NP[a] diameter (nm)	∞	∞	3.7(1)	3.7(1)	3.1(1)	3.1(1)	2.4(2)	2.2(2)
R_w	0.12	0.09	0.20	0.14	0.18	0.15	0.27	0.21

Size of the structural core





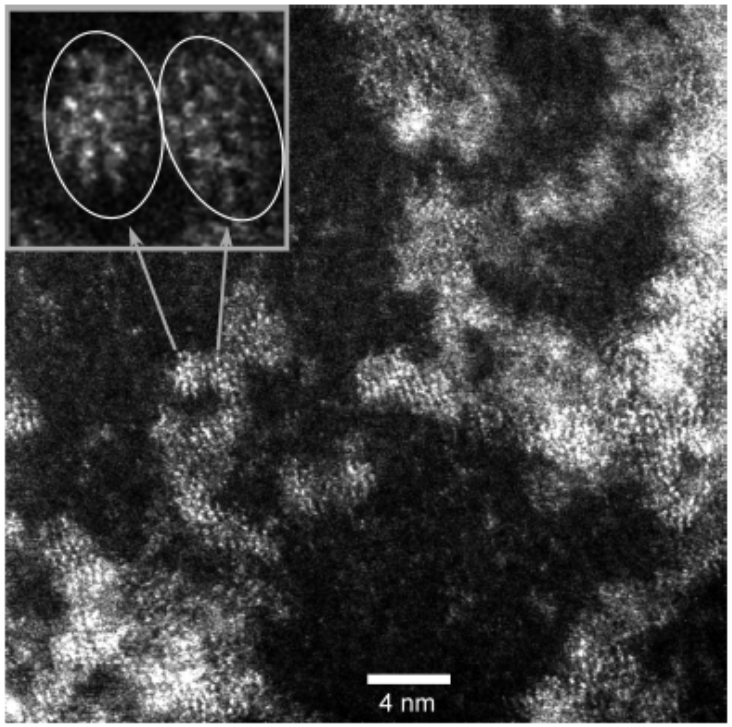
$$f(r,d) = \left[1 - \frac{3r}{2d} + \frac{1}{2}\left(\frac{r}{d}\right)^3\right]\Theta(d-r),$$

- Masadeh, SJB *et al.* PRB **76**, 115413 (2007
- Also see Shamoto paper, JAC 2007

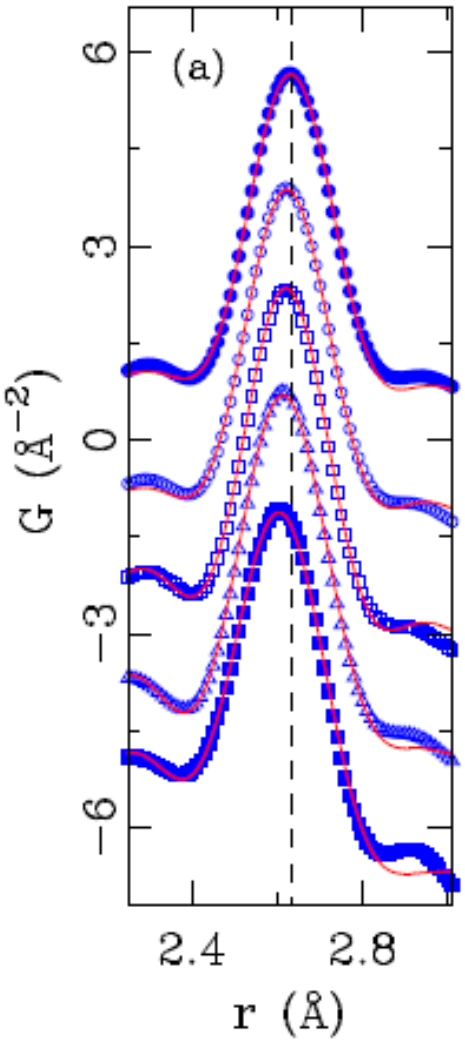
TABLE I: CdSe nanoparticle diameter as determined using various methods.

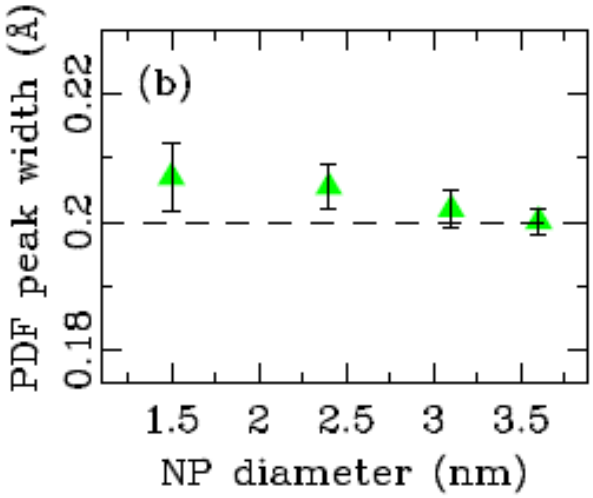
	CdSeIII	CdSeII	CdSeI
Nucleation time (s)	1200	630	15
Diameter (nm)			
TEM	3.5(2)	2.7(2)	2.0(2)
UV-vis	3.5(4)	2.9(3)	$\leq$ 1.90
PL	3.6(4)	2.9(3)	$\leq$ 2.1
PDF	3.7(1)	3.1(1)	2.2(2)

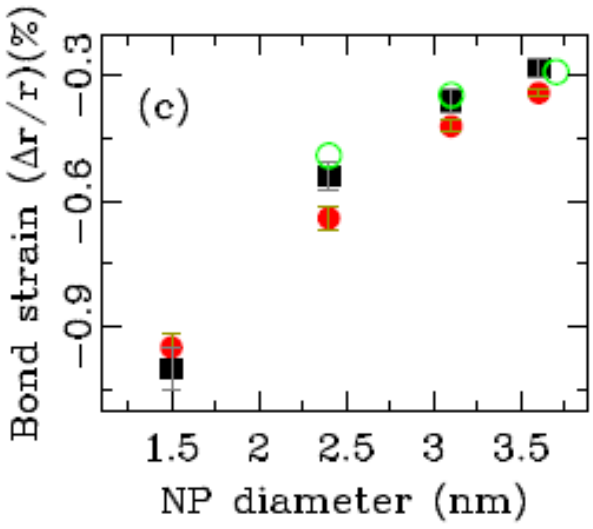
White Light Nanoparticles



- Xiaohao Yang, Masadeh, McBride, Bozin, Rosenthal and SJLB, *Phys. Chem. Chem. Phys.* **15**, 8480-8486 (2013)







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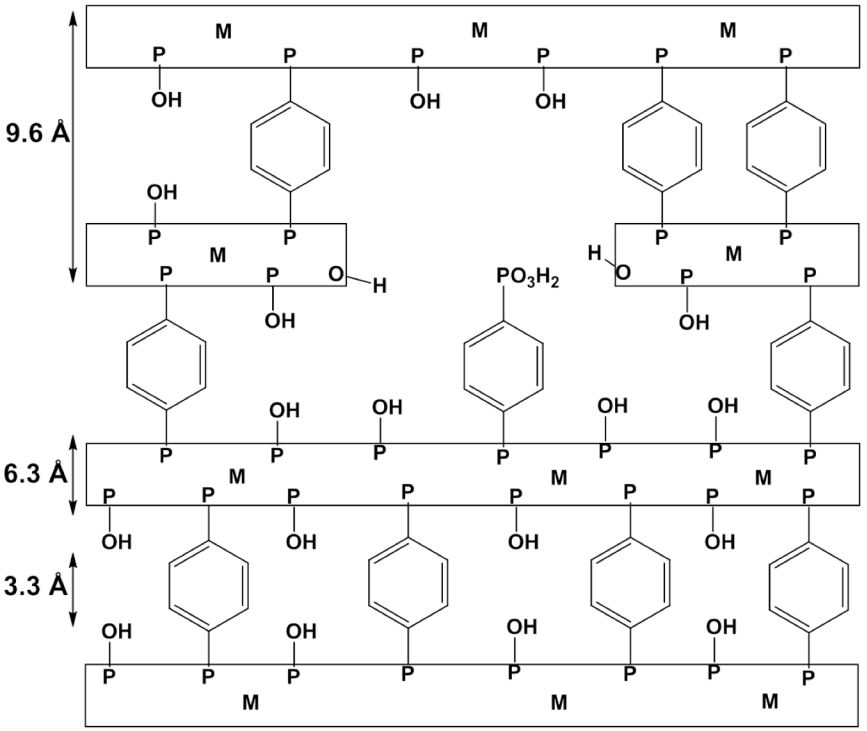
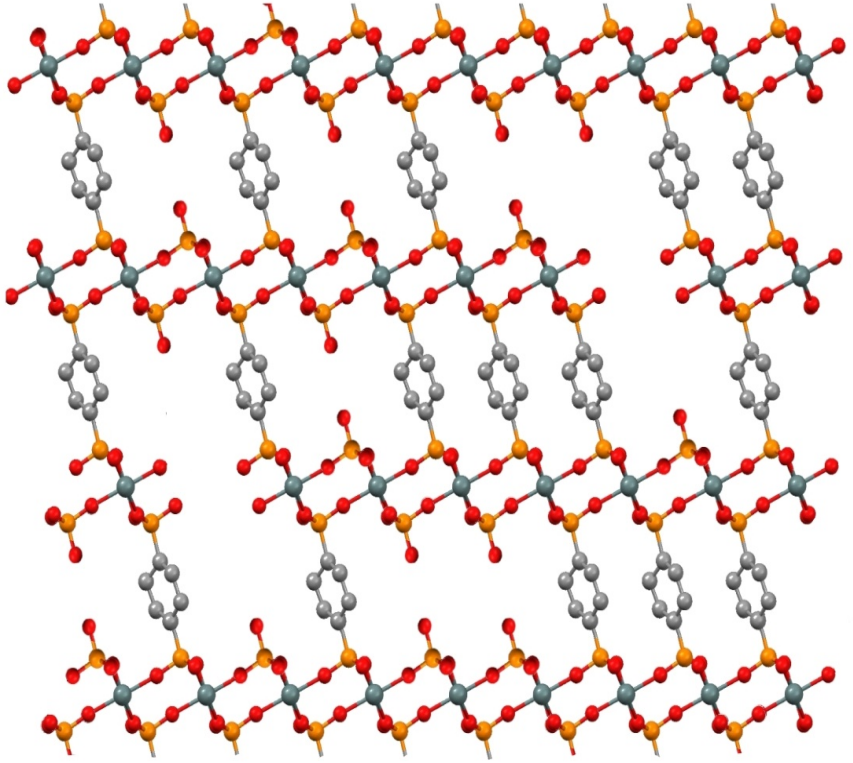
Zr/Sn phenyl phosphate, unconventional MOFs





Clearfield, A. *Dalton Trans*. 2008, **44**, 6089-6102.

- Collaboration with the group of Abe Clearfield, Texas A&
- Work of Chenyang Shi and Rita Silbernagel

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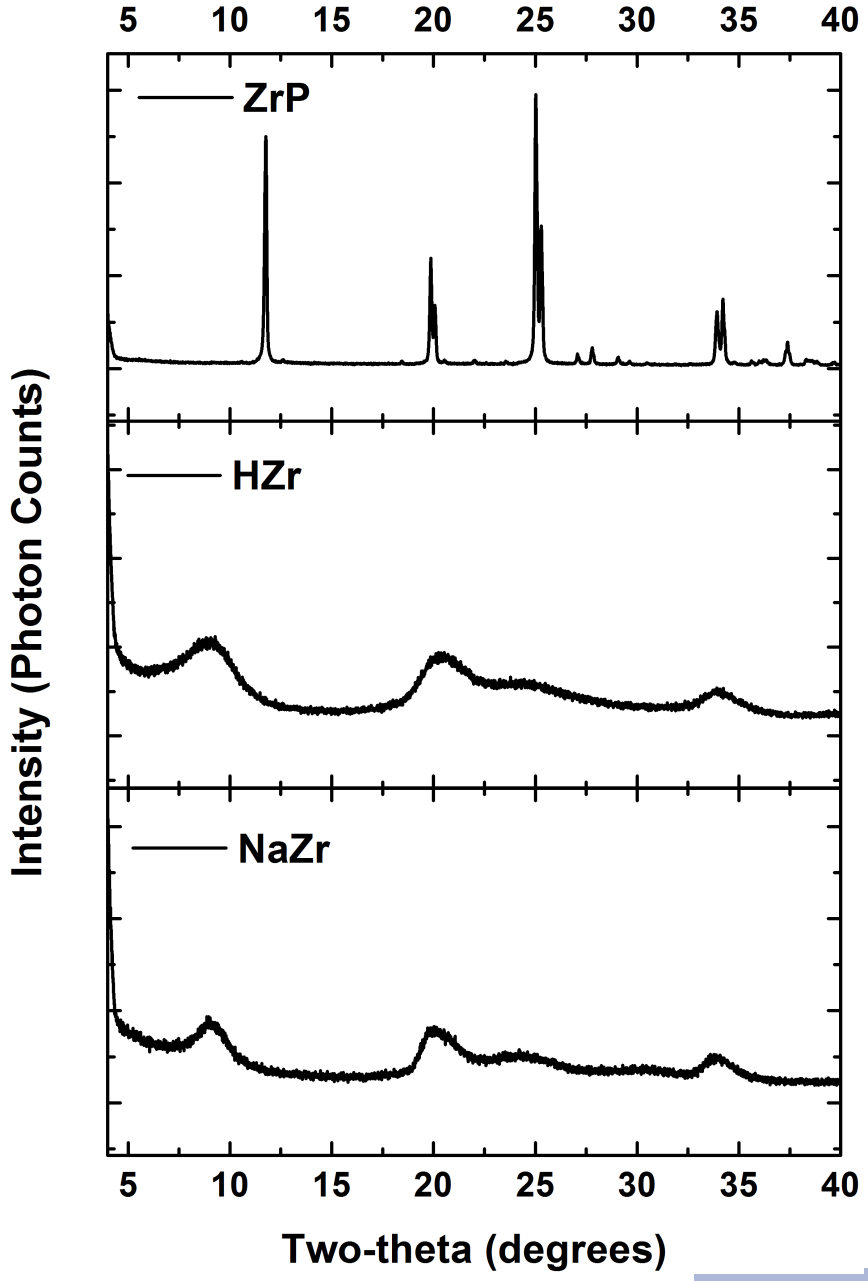
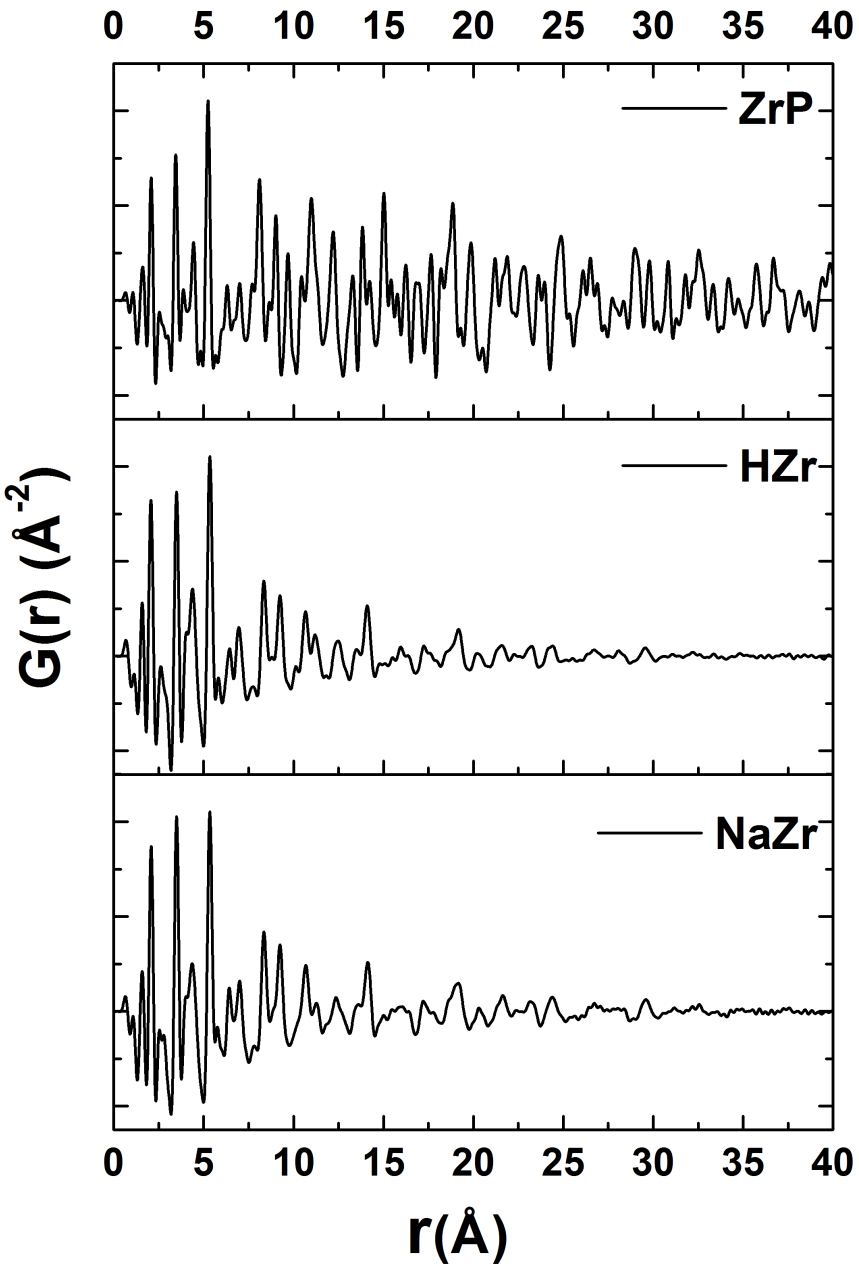
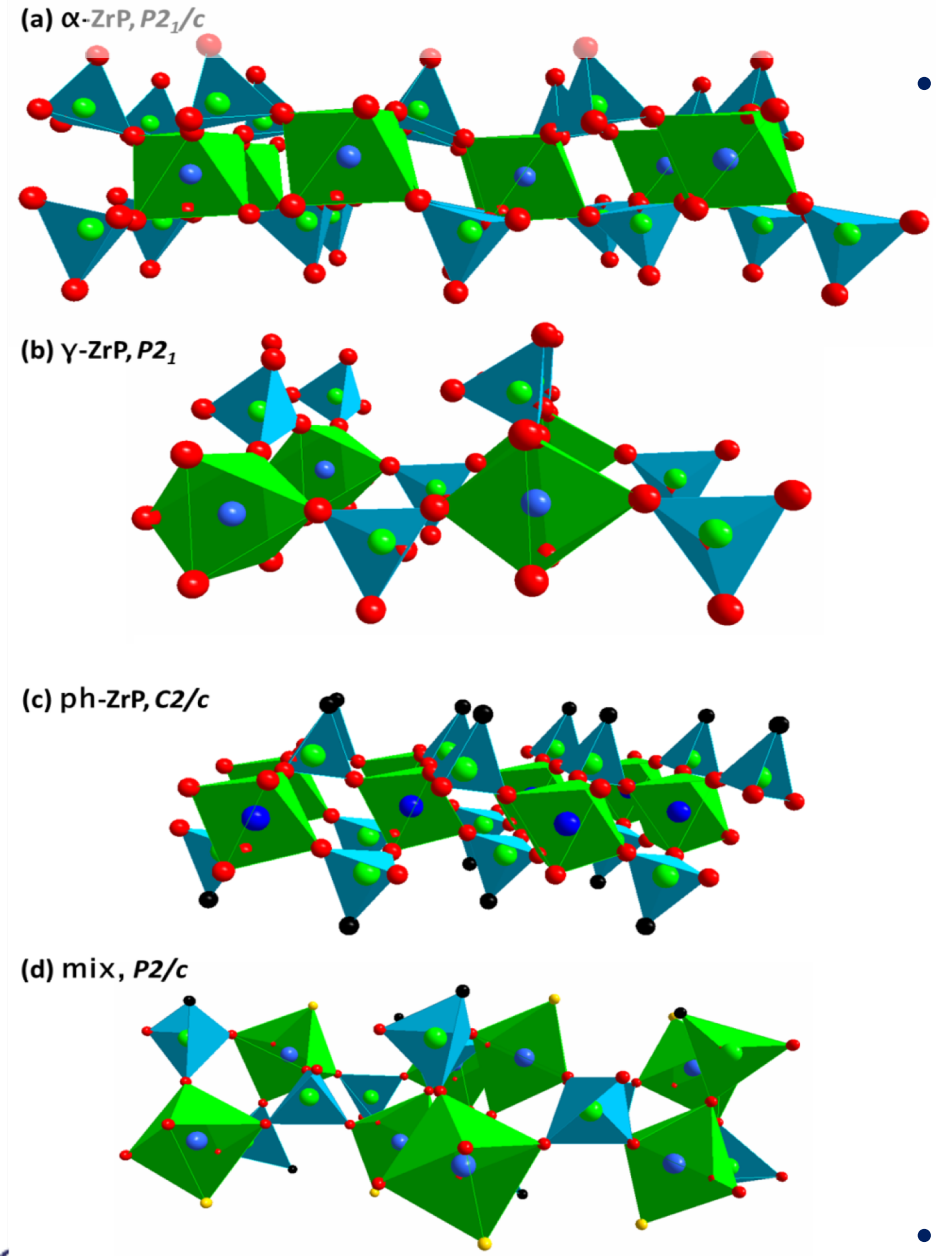

ZrP
HZr
NaZr
Intensity (Photon Counts)
Two-theta (degrees)
5
10
15
20
25
30
35
40


ZrP
HZr
NaZr
G(r) (Å-2)
r(Å)
0
5
10
15
20
25
30
35
40

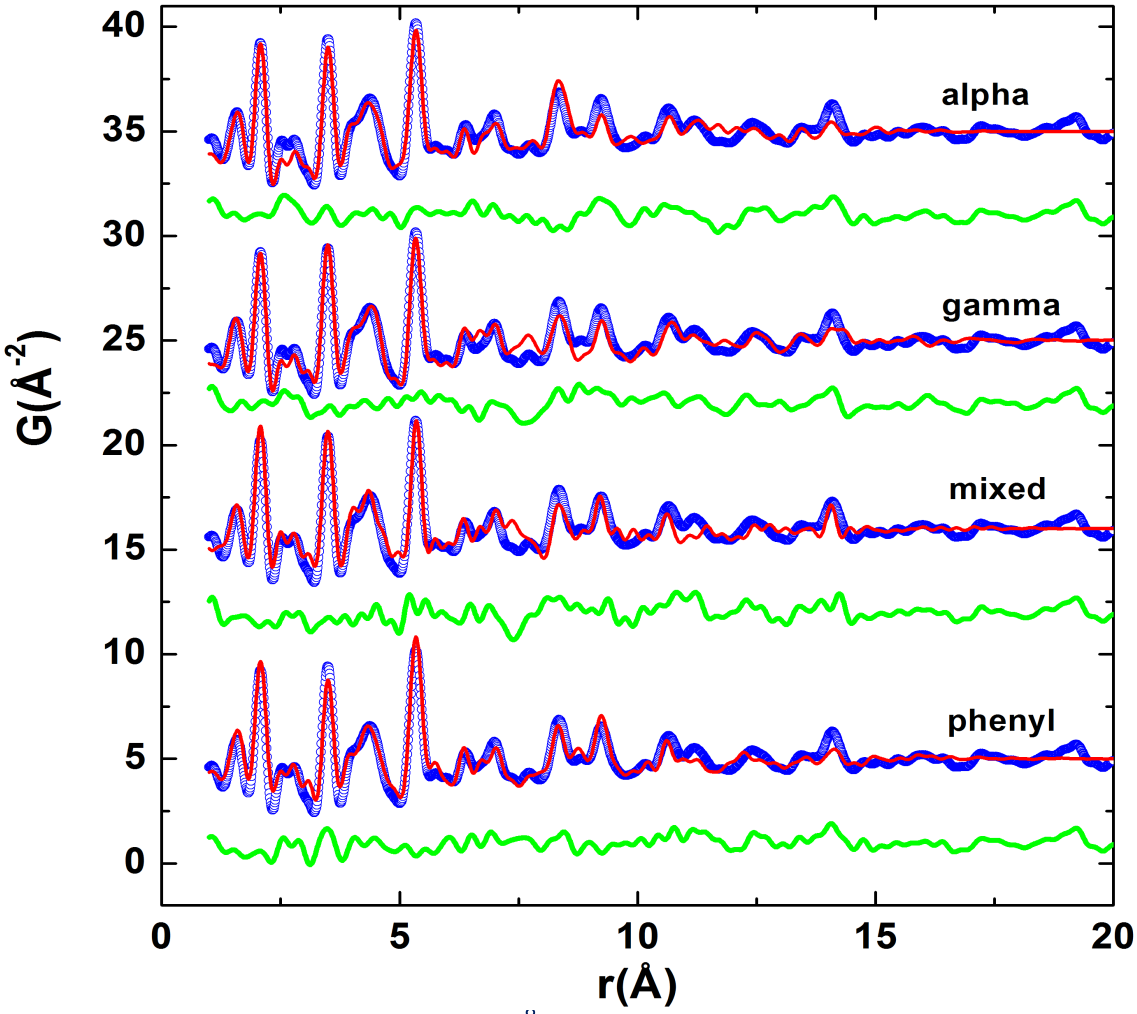
ates

from

Try ZrP structures on H-Zr sample, PDFgui

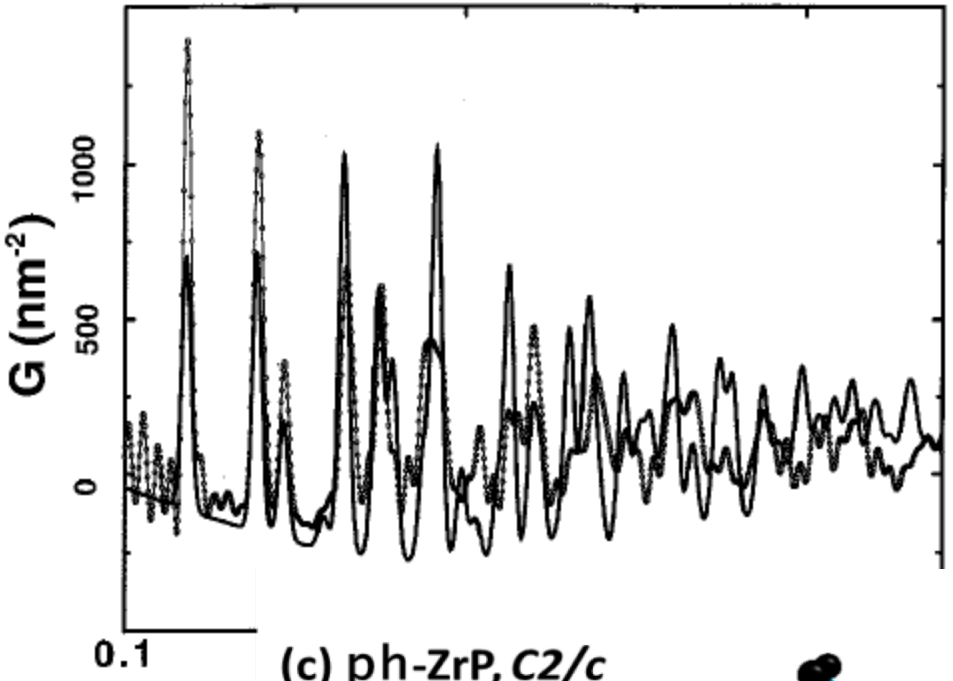


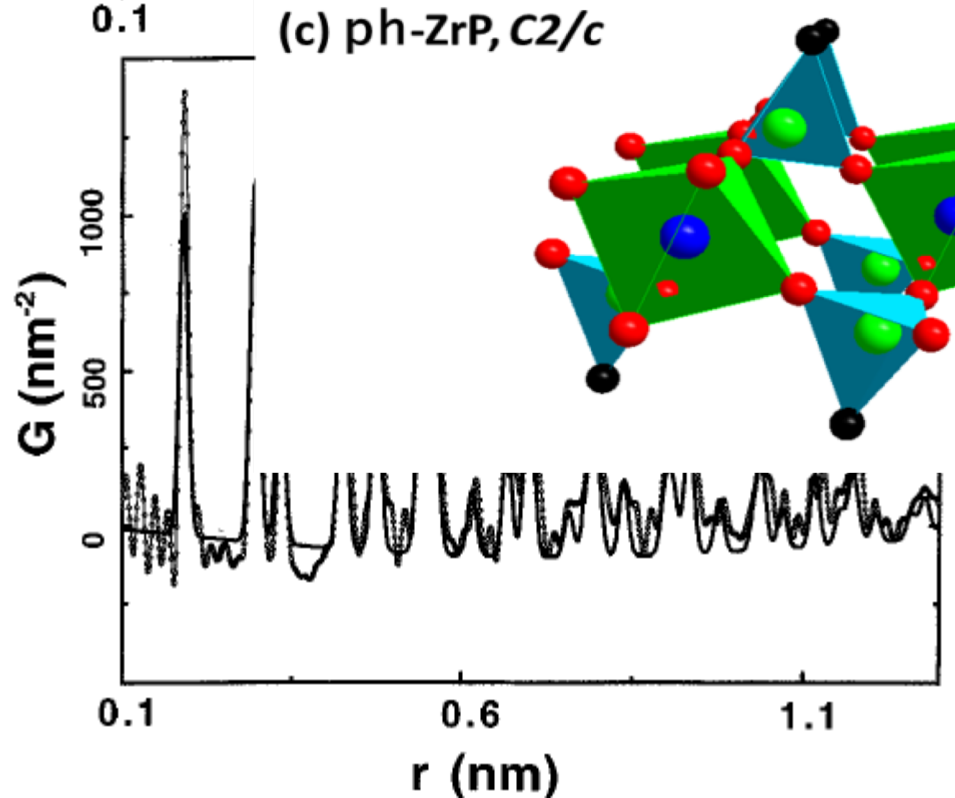
- Use PDFgui to fit 3D crystal structures from the literature (as indicated)

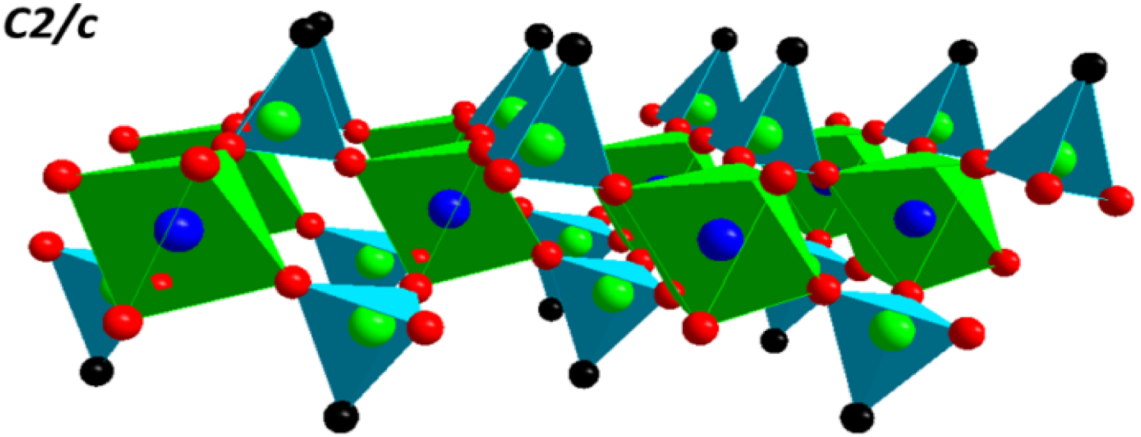


- Fits do well up to ~7Å but less well beyond

Graphene modeling circa 1996







- Poor person's modeling of turbostratic disorder
- Crystal structure of graphite in PDFFIT doesn't fit will (top)

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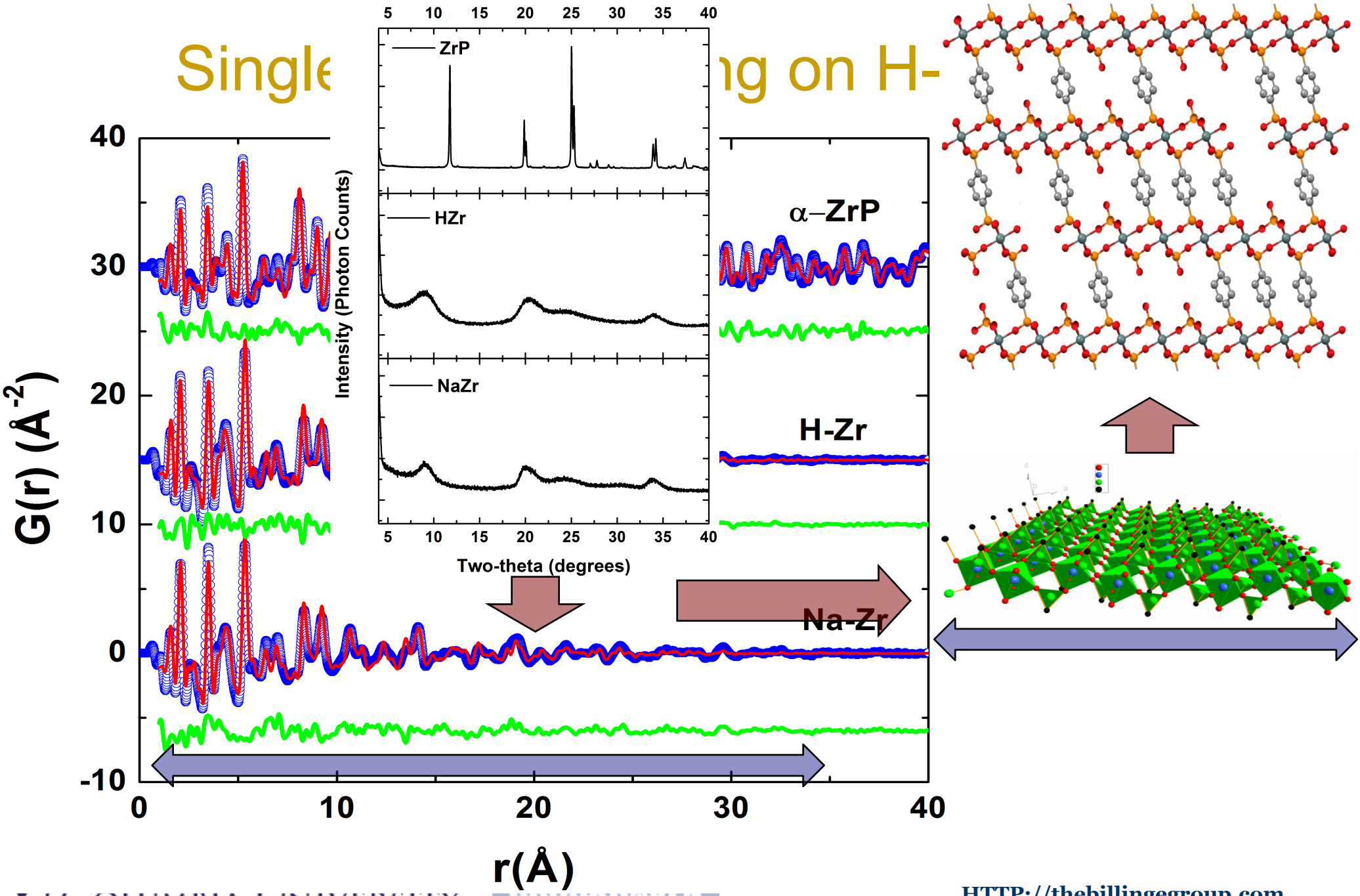
2159 (1996)

- This won't work here:

Single ng on H-



Nanoparticle and cluster solutions

Example: DFT can predict structures

- DFT is one of the most accurate of the theories (but still approximate)
- This is the basis of Materials Prediction, a fundamental of Materials Genomics
- Can DFT predict the stable structure of Au nanoparticles?
  - Yes!

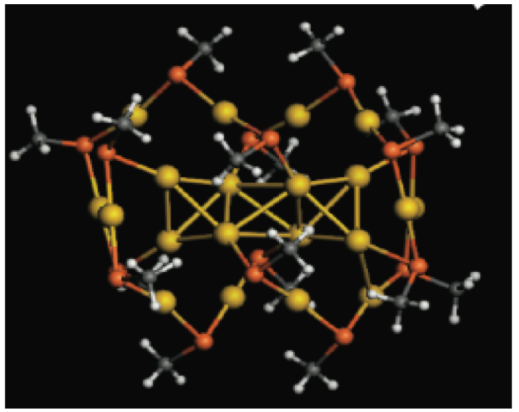
J|A|C|S COMMUNICATIONS

Published on Web 09/02/2009

Thiolate-Protected $Au_{20}(SR)_{16}$ Cluster: Prolate Au_8 Core with New $[Au_3(SR)_4]$ Staple Motif

Yong Pei, Yi Gao, Nan Shao, and Xiao Cheng Zeng*

Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588



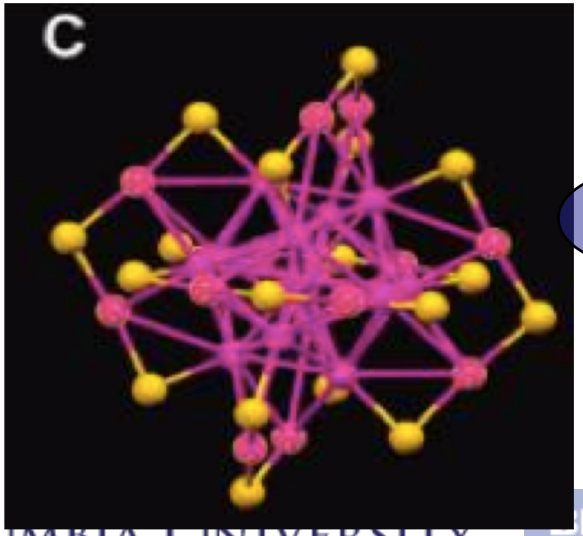
20

J|A|C|S COMMUNICATIONS

Published on Web 04/12/2008

Correlating the Crystal Structure of A Thiol-Protected Au_{25} Cluster and Optical Properties

Manzhou Zhu,† Christine M. Aikens,‡ Frederick J. Hollander,§ George C. Schatz,|| and Rongchao Jin*,†



25

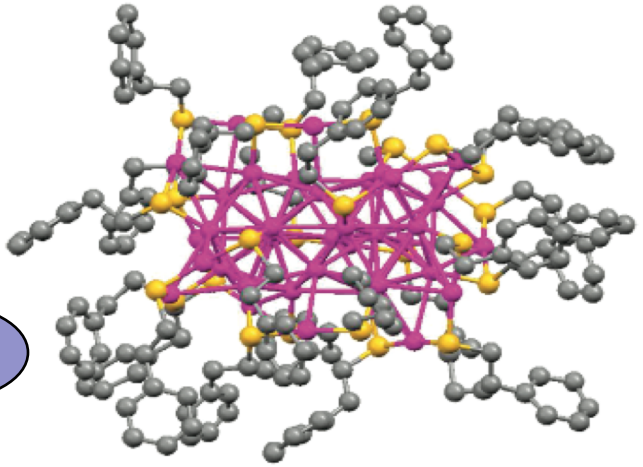
J|A|C|S COMMUNICATIONS

Published on Web 06/01/2010

Total Structure Determination of Thiolate-Protected Au_{38} Nanoparticles

Huifeng Qian,† William T. Eckenhoff,‡ Yan Zhu,† Tomislav Pintauer,‡ and Rongchao Jin*,†

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 and Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania 15282



38

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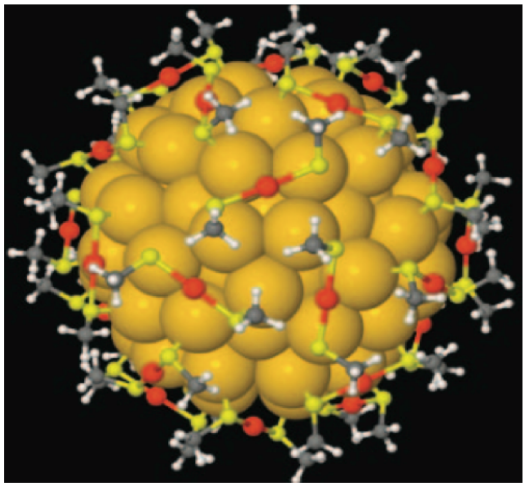
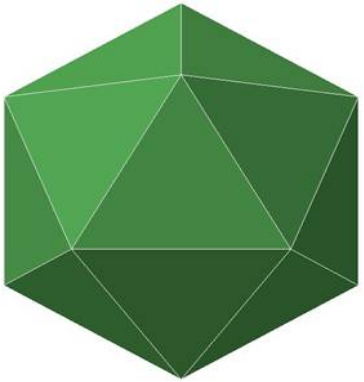
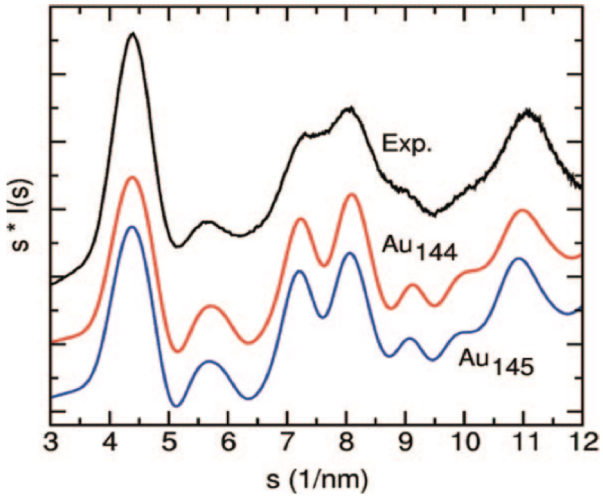
DFT study of Au_{144} structure







Icosahedral core

Au/S surface structure with ligand attachment

THE JOURNAL OF PHYSICAL CHEMISTRY C LETTERS

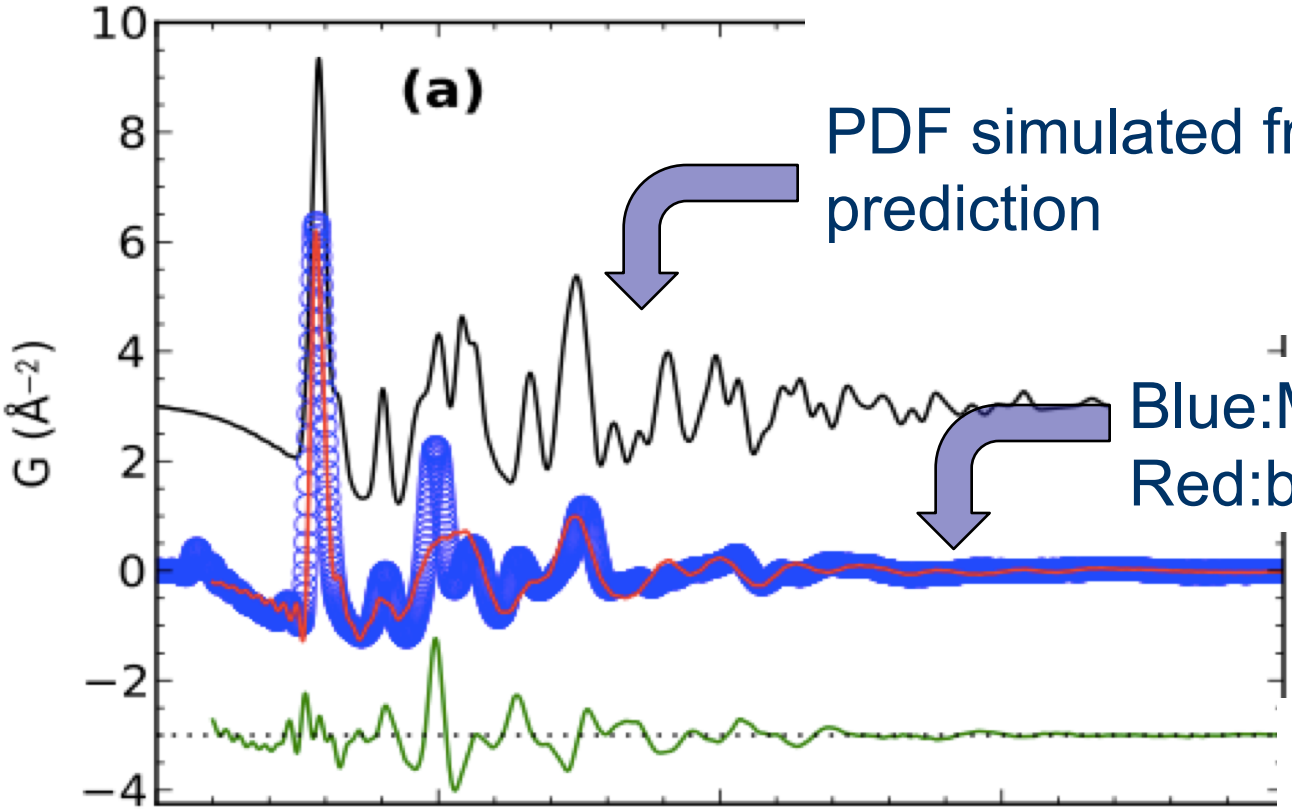
2009, *113*, 5035–5038
Published on Web 01/16/2009

Structure and Bonding in the Ubiquitous Icosahedral Metallic Gold Cluster $Au_{144}(SR)_{60}$

Olga Lopez-Acevedo,[†] Jaakko Akola,[†] Robert L. Whetten,[‡] Henrik Grönbeck,[§] and Hannu Häkkinen*,[†,||]

Validate this prediction:

Measure X-ray diffraction data (in the form of an atomic pair distribution function (PDF))



PDF simulated from DFT prediction

Blue:Measured PDF
Red:best fit of DFT model

Refinement:
Expansion factor
Thermal parameters for core
Thermal parameters for surface
Correlated motion

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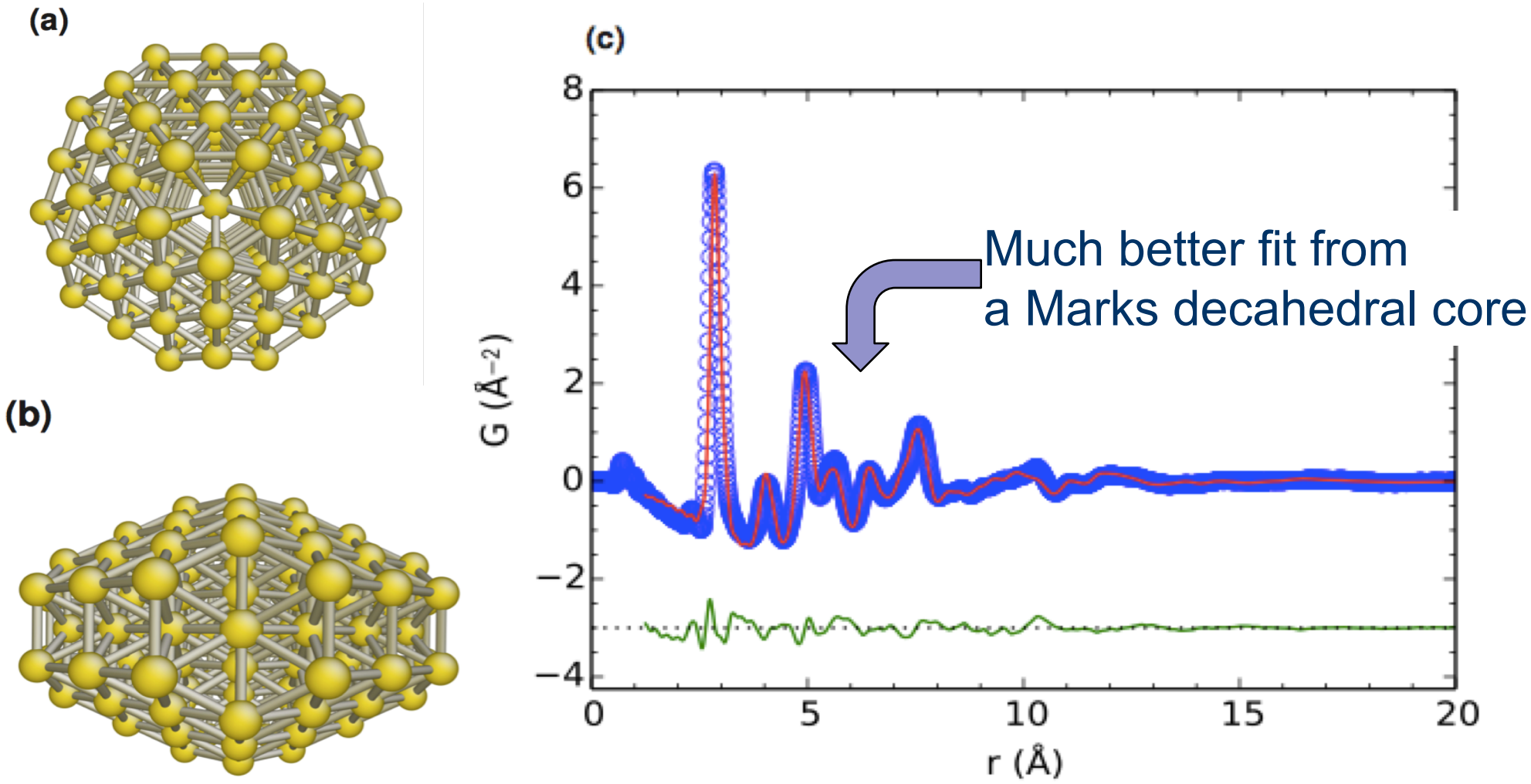
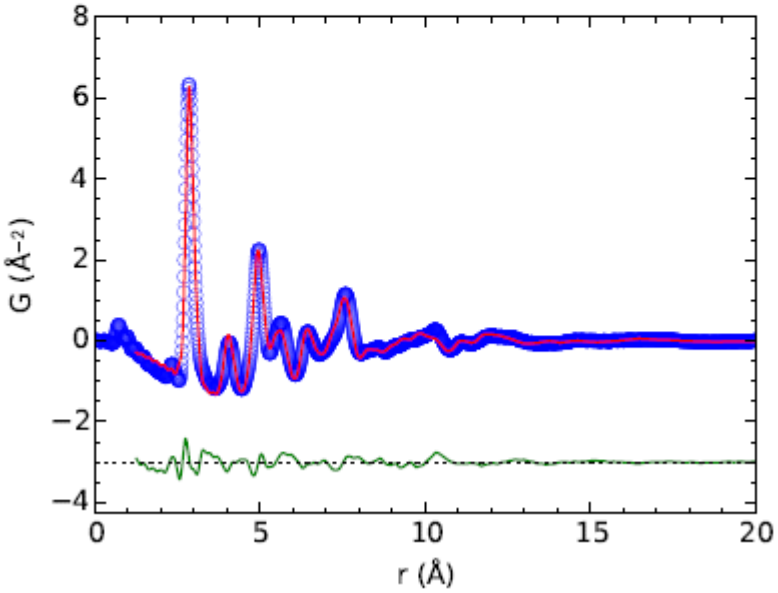
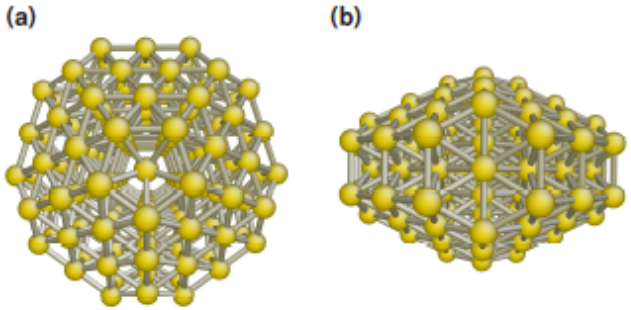
The MD6441 structure: 144 gold atoms



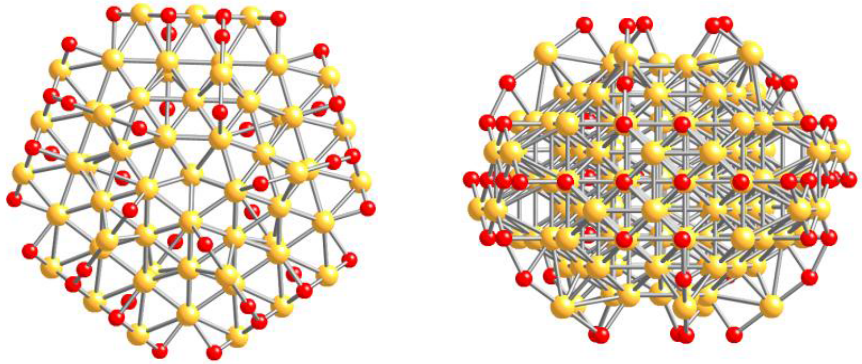
From Pavol Juhas

Gold Au144



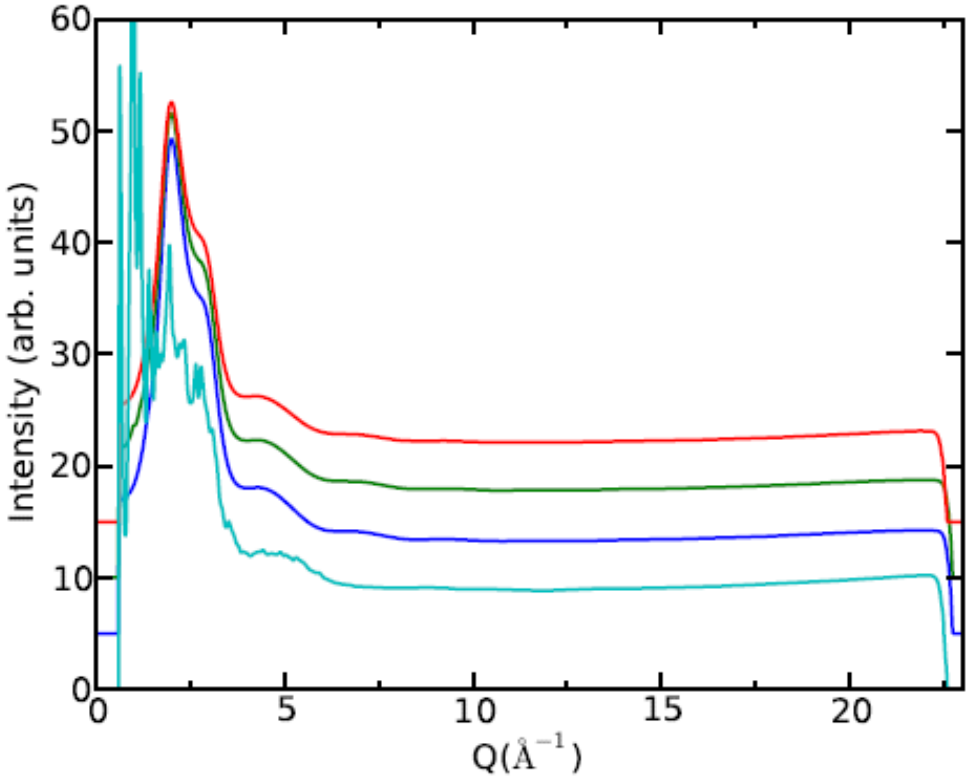


- Proper data validation illustrated theoretical limitation
- But our DFT colleagues told us the structural model also had to be incorrect: no low energy Au-thiol staples on the surface
- Better (correct?) model had a MD core and staples



Sensitivity: Dilute systems

Quantifying amorphous API contents in the presence of crystalline material



- Collaboration with Matthew Johnson, Senior Investigator, GlaxoSmithKline, thanks for help from Marco di Michiel
- Data ID15, ESRF
- Maxwell W. Terban, Matthew Johnson, Marco DiMichiel and Simon J. L. Billinge, *Nanoscale* **7**, 5480-5487 (2015).

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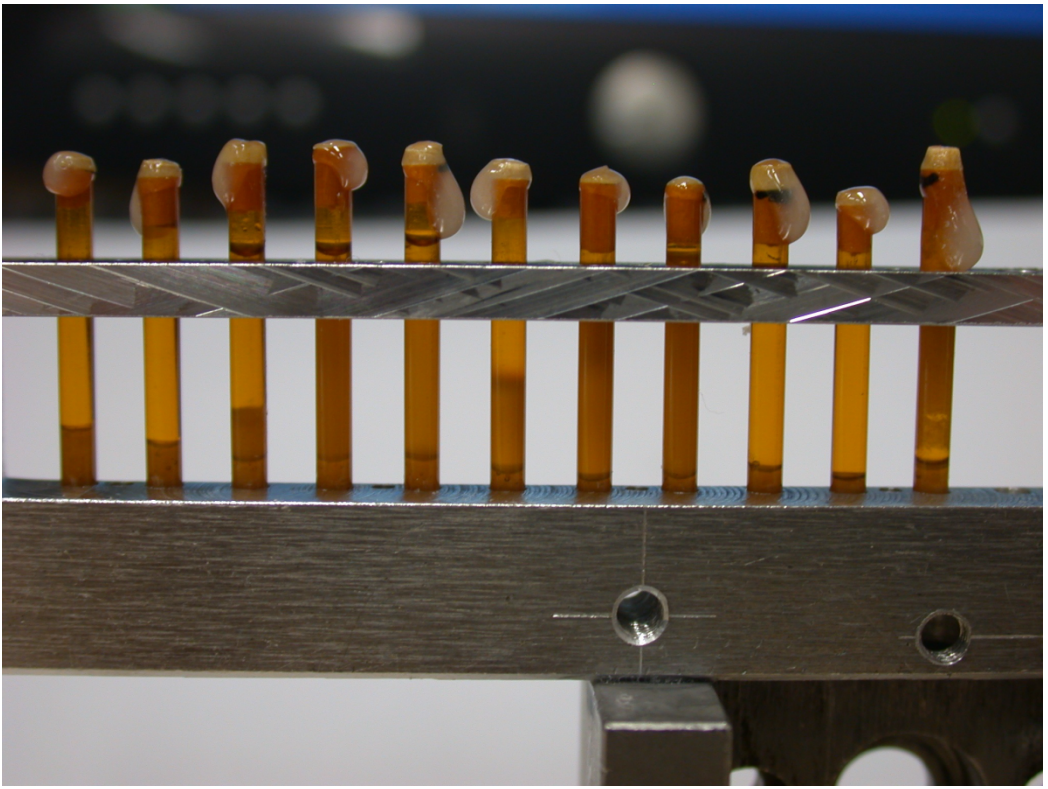
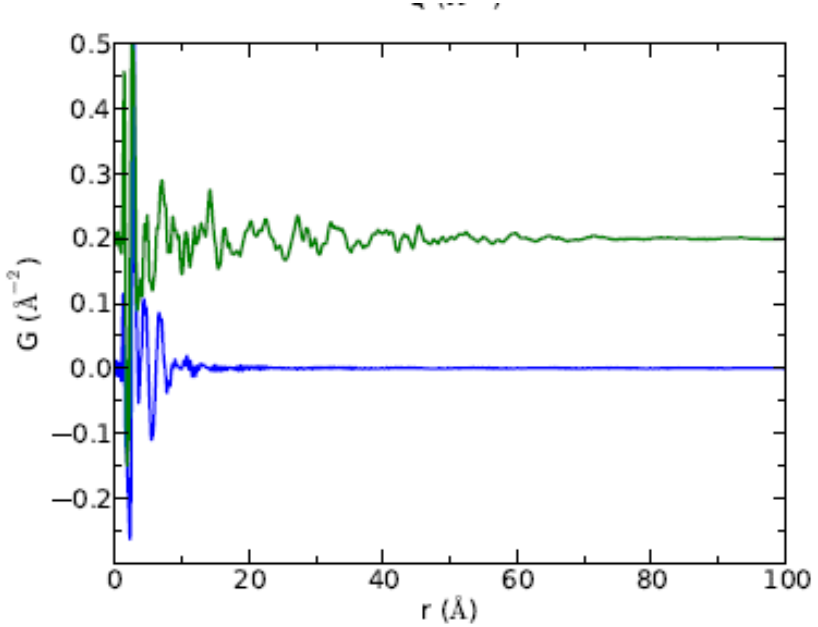
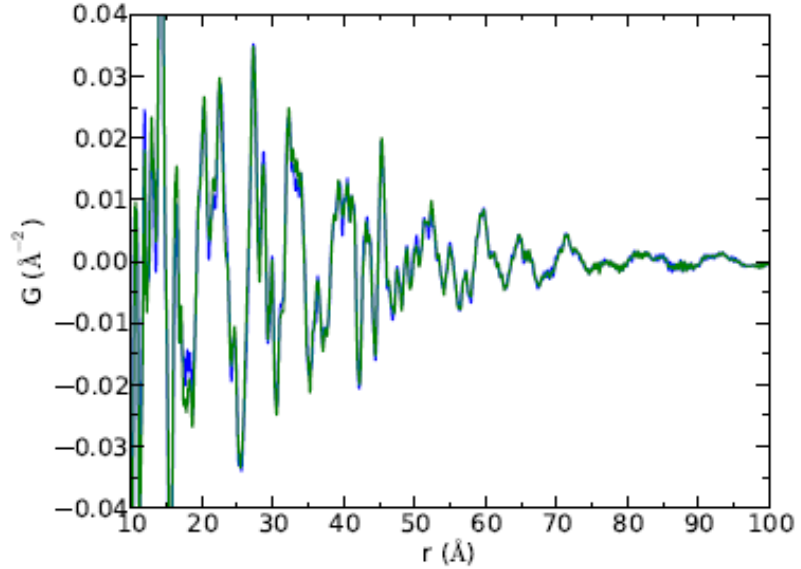
Characterizing nanoparticles of APIs in suspension



- Samples were API particles of various sizes and in various concentrations in aqueous suspension
- These are drugs for nebulizer applications
- The goal was to characterize the structure and nanoparticle size in the different suspensions.

Characterizing nanoparticles of APIs in suspension

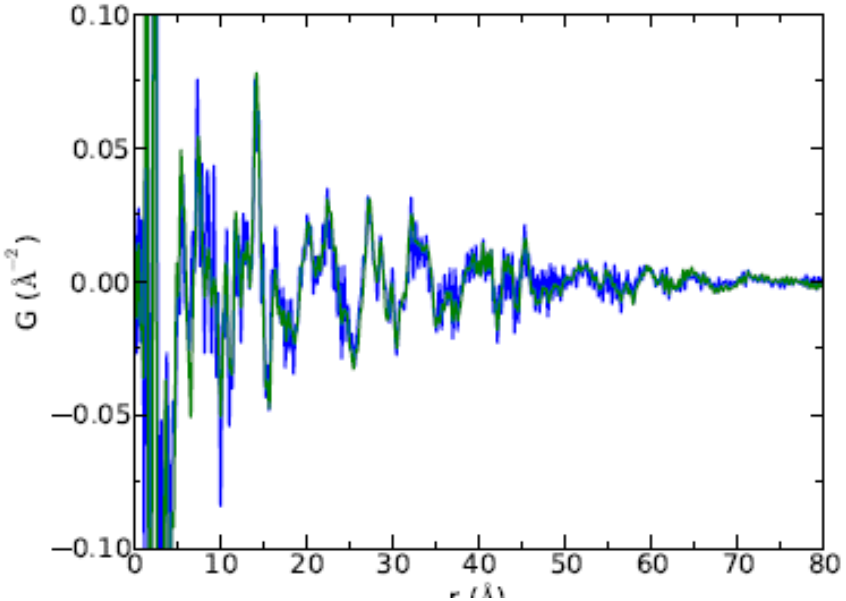


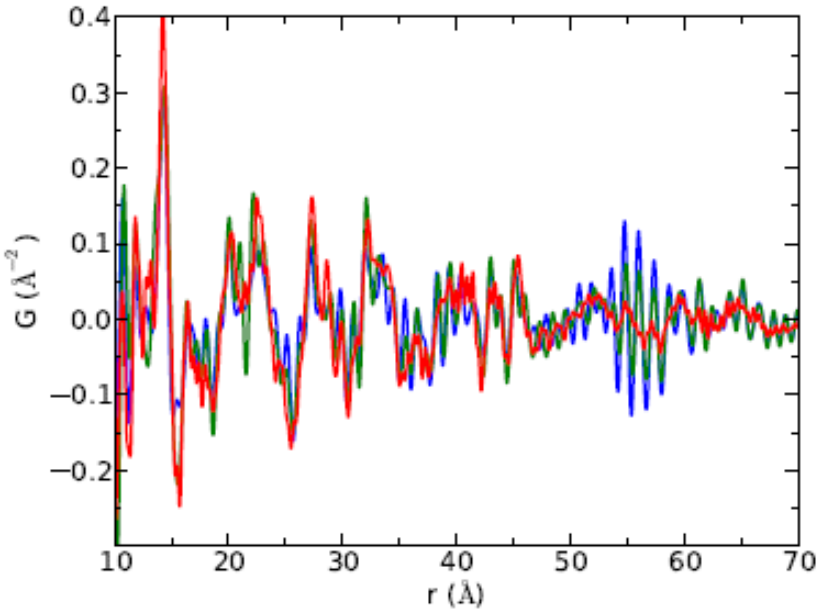


- Green: PDF of the crystalline control sample
- Blue: PDF of the aqueous solvent

- Reproducibility!
- High-r region from the crystalline control and sediment from a high concentration suspension

Characterizing nanoparticles of APIs in suspension





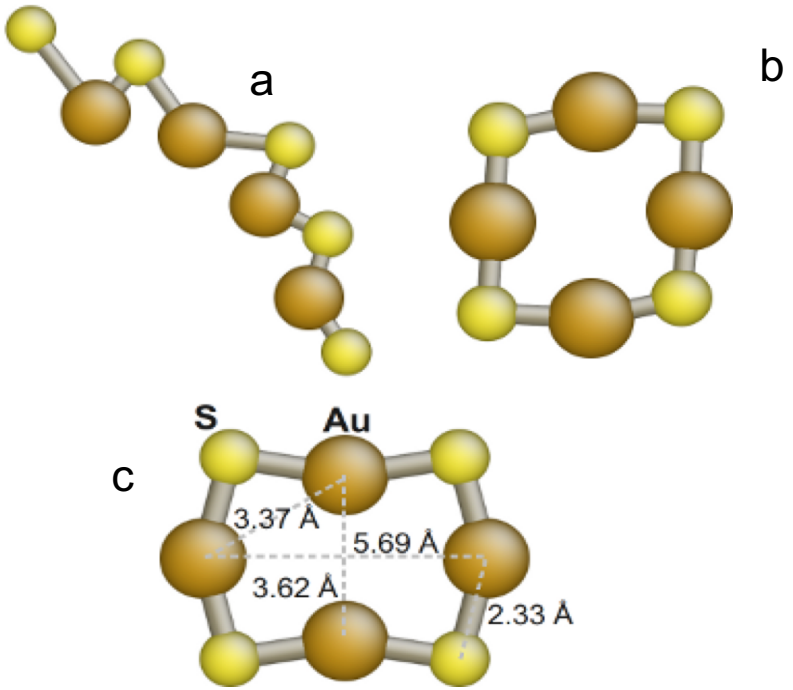
- Green: difference PDF (dPDF => solvent subtracted) from a suspension of 5wt% API in aqueous solvent
- Blue: PDF of the crystalline API

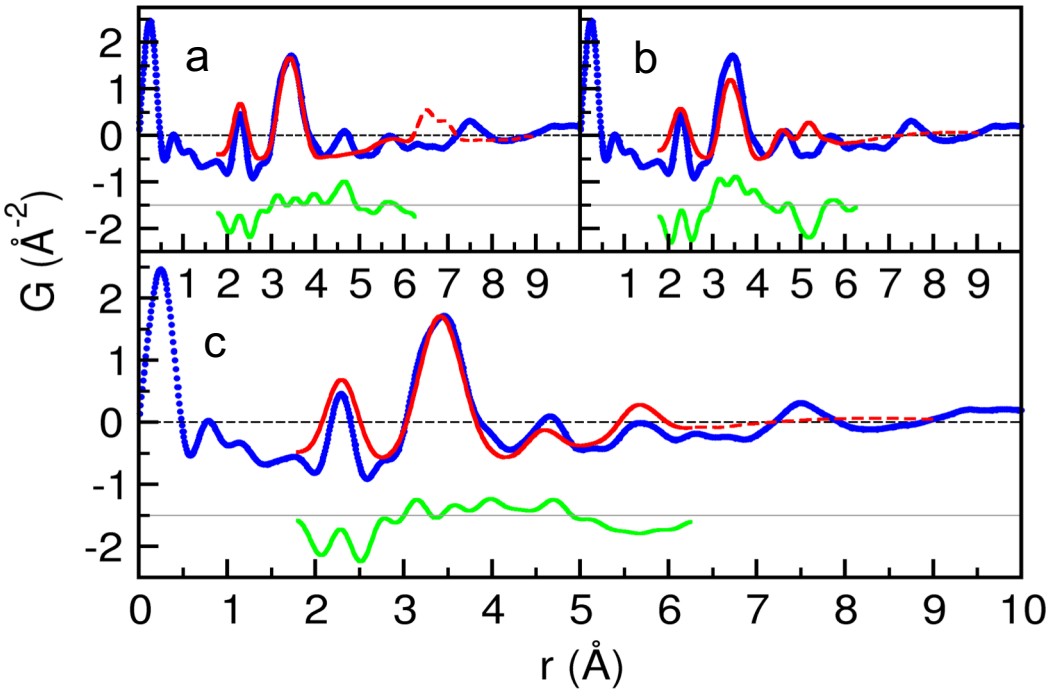
Sensitivity!

  - Blue: 0.25wt% API
  - Green: 0.66wt% API
  - Red: 5% API

- Can see nanocrystalline API even at the 0.25wt% level
- Maxwell W. Terban, Matthew Johnson, Marco DiMichiel and Simon J. L. Billinge, *Nanoscale* **7**, 5480-5487 (2015).

Applications: Molecular Precursors of Gold Nanoparticles





PDF used to investigate non-crystallized precursors in gold nanoparticle synthesis. Novel modeling of bond lengths and angles verifies planar 8-member ring structure. Collaboration with David Cliffel, Vanderbilt

C. A. Simpson, SJLB et al., *Inorg. Chem.* **49**, 10858 - 10866 (2010)

Watching nanoparticle synthesis in-situ

- We can see precursor species in solution
- We can measure Nanoparticle structural parameters
- High energy x-rays can penetrate relatively thick walled vessels

=> Let's do in-situ studies of synthesis

- Rich collaboration with the group of Bo Iversen (Aarhus)

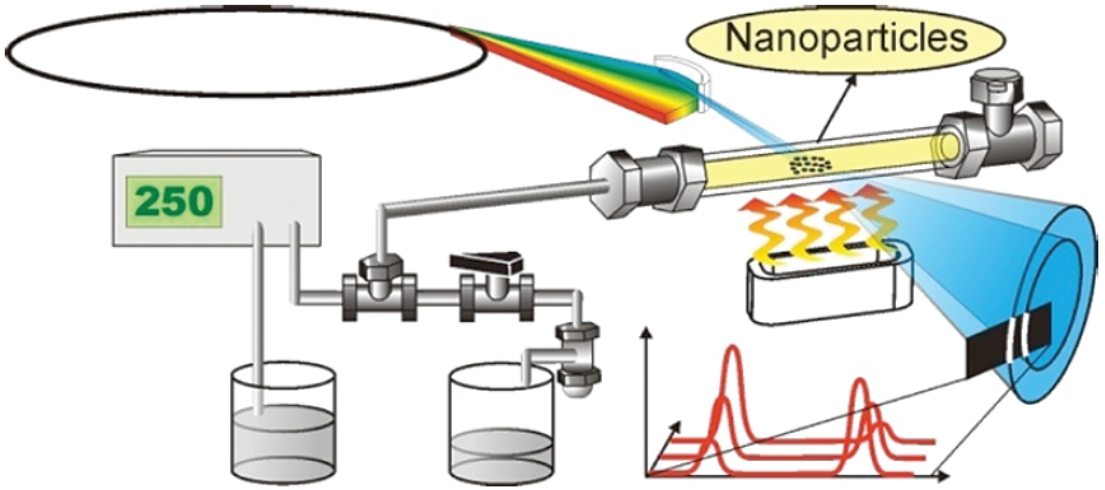


Image credit
Christoffer Tyrsted

It works!

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

J. Am. Chem. Soc. **134**, 6785 (2012)

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*[,†]

Angewandte Communications

Angew. Chem. Int. Edit. **51**, 9030 (2012)

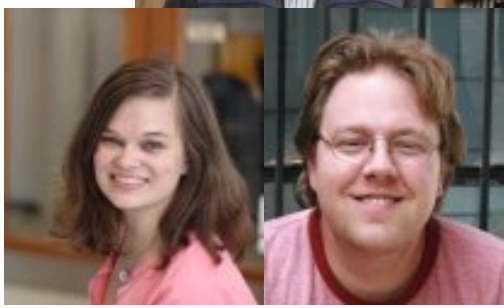
DOI: 10.1002/anie.201204747

Crystal Growth

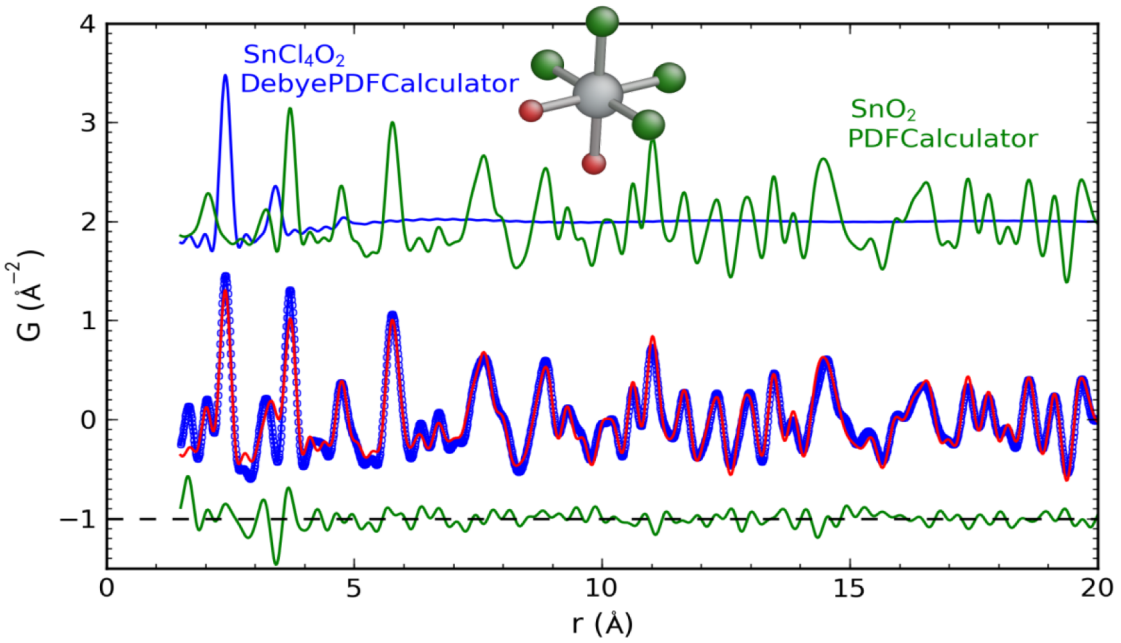
Understanding the Formation and Evolution of Ceria Nanoparticles Under Hydrothermal Conditions**

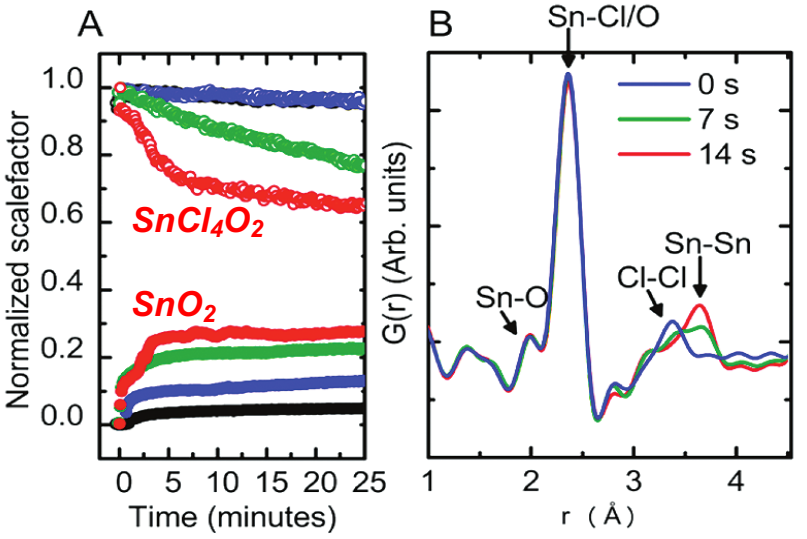
*Christoffer Tyrsted, Kirsten Marie Ørnsbjerg Jensen, Espen Drath Bøjesen, Nina Lock, Mogens Christensen, Simon J. L. Billinge, and Bo Brummerstedt Iversen**

PDF analysis of in situ SnO_2 formation



- in-situ studies of SnO_2 formation during hydrothermal synthesis,
- PDF measured every 7 seconds at an synchrotron x-ray source
- measured PDFs were fitted as a two-phase mixture of $SnCl_4.2H_2O$ molecules and SnO_2 crystallites
- time dependence of the precursor-target ratios and the crystallite size





K. M. Jensen, et al., J. Am. Chem. Soc., 134, 6785 (2012)

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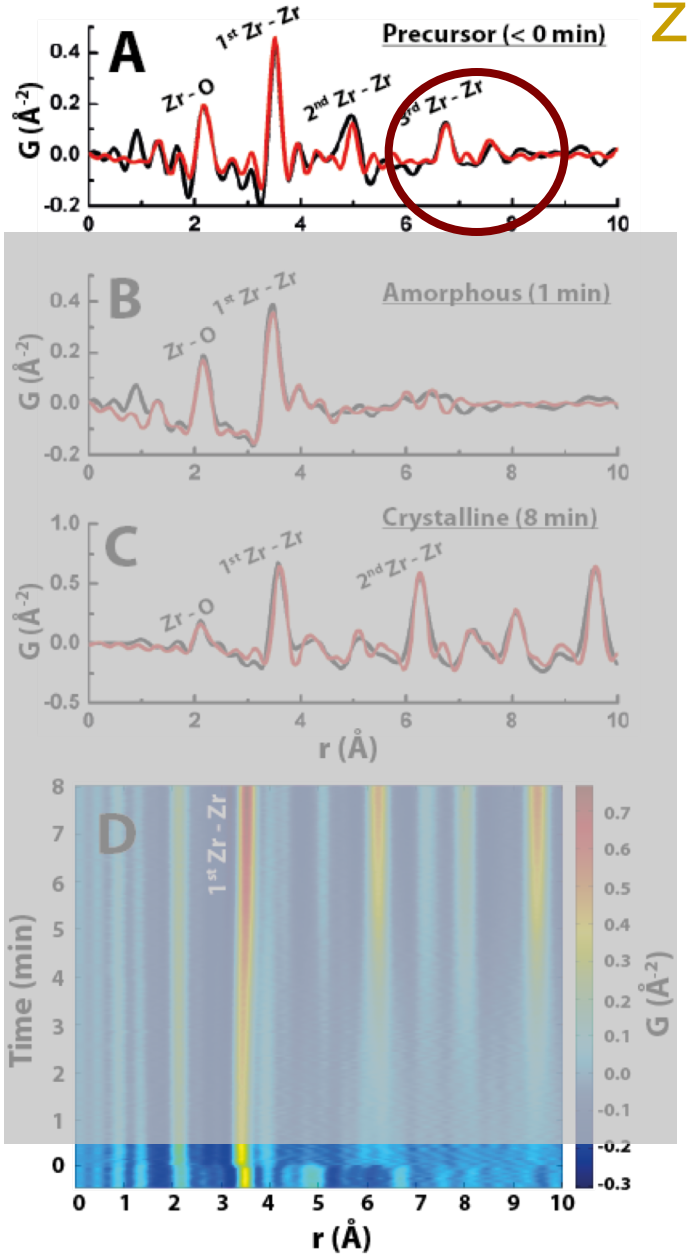
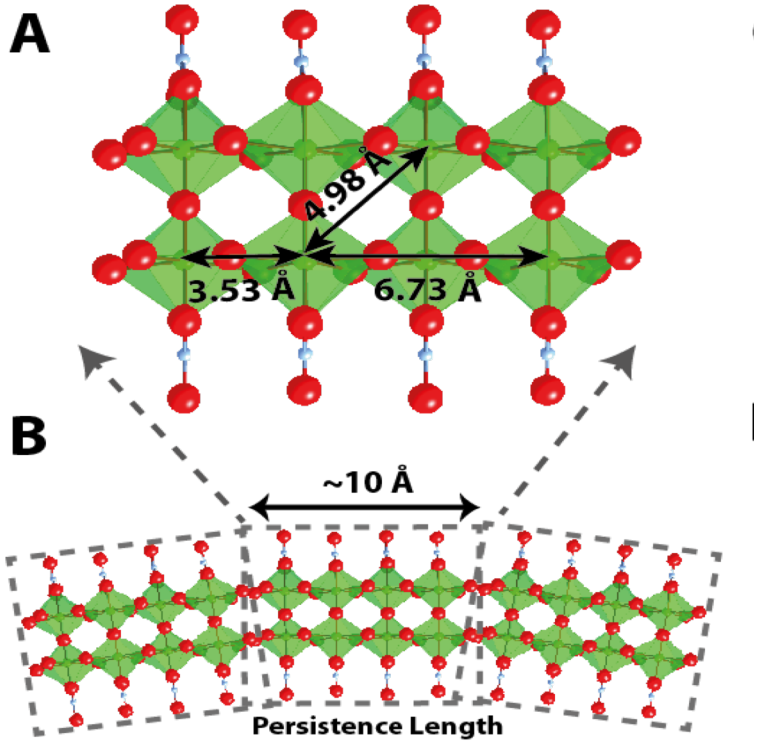
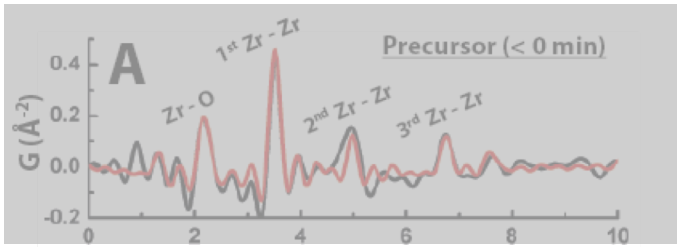
In-situ study of hydrothermal synthesis of yttria-stabilized zirconia nanoparticles

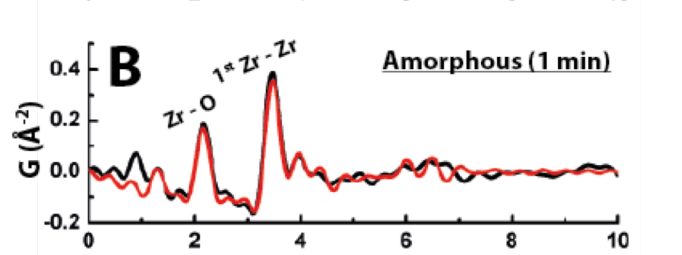


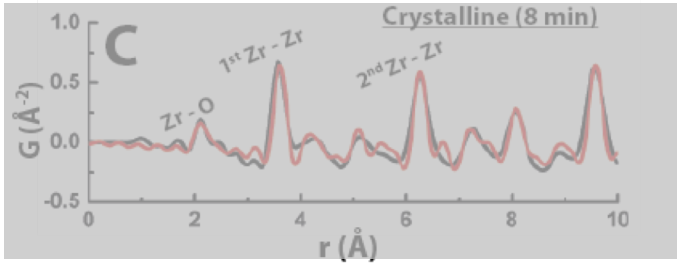
- Christoffer Tyrsted, Nina Lock, Kirsten M. \O. Jensen, Mogens Christensen, Espen D. Bøjesen, Hermann Emerich, Gavin Vaughan, Simon J. L. Billinge and Bo B. Iversen, *IUCrJ.* **1**, 165-171 (2014)
- Precursor

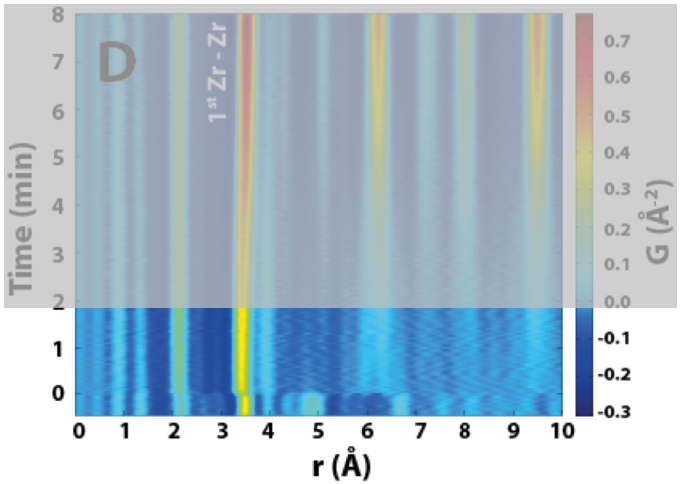


In-situ study of hydrothermal synthesis of yttria-stabilized zirconia nanoparticles

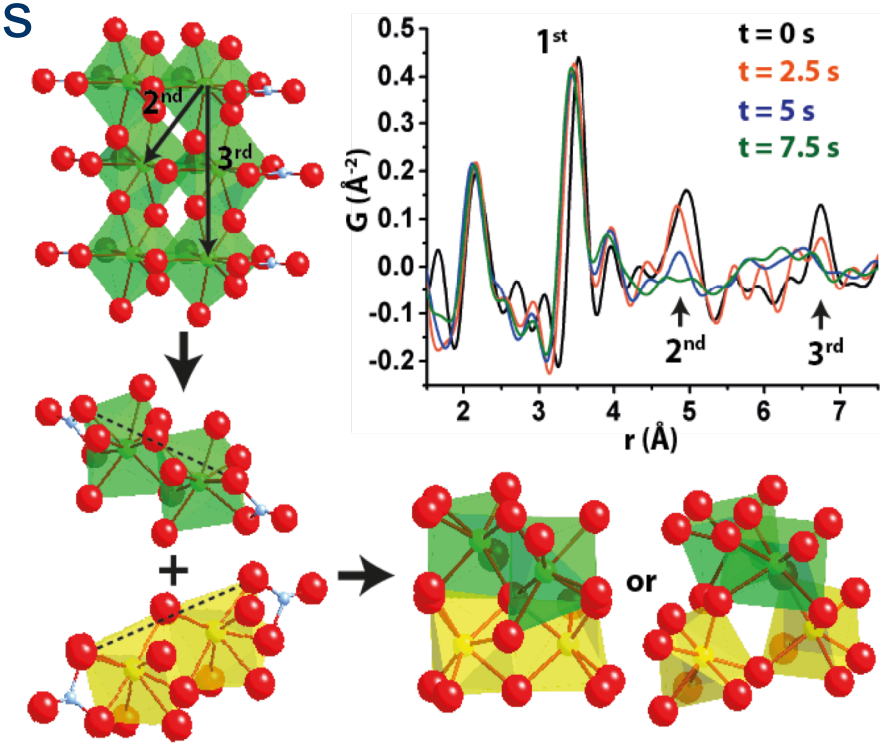




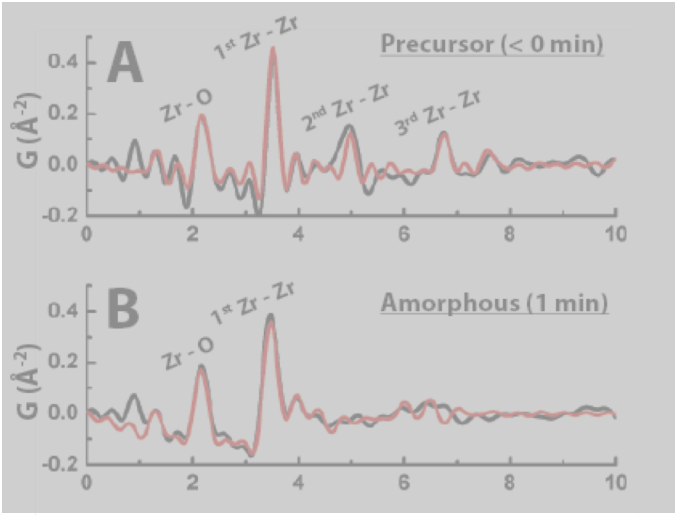




- Christoffer Tyrsted, Nina Lock, Kirsten M. \O. Jensen, Mogens Christensen, Espen D. Bøjesen, Hermann Emerich, Gavin Vaughan, Simon J. L. Billinge and Bo B. Iversen, *IUCrJ.* **1**, 165-171 (2014)
- Amorphous intermdiate

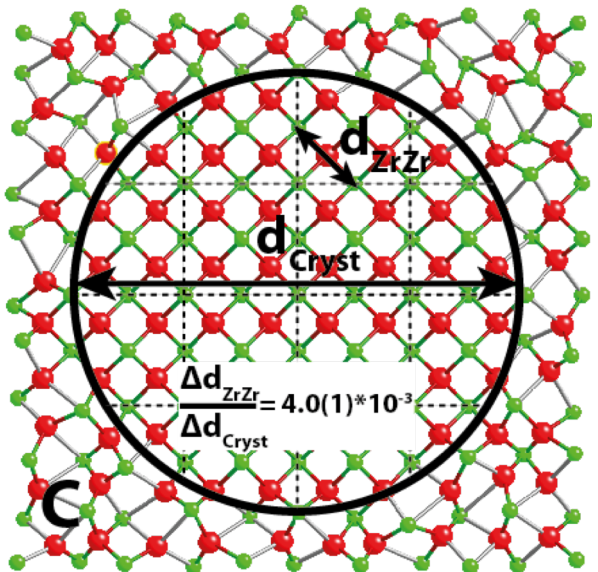


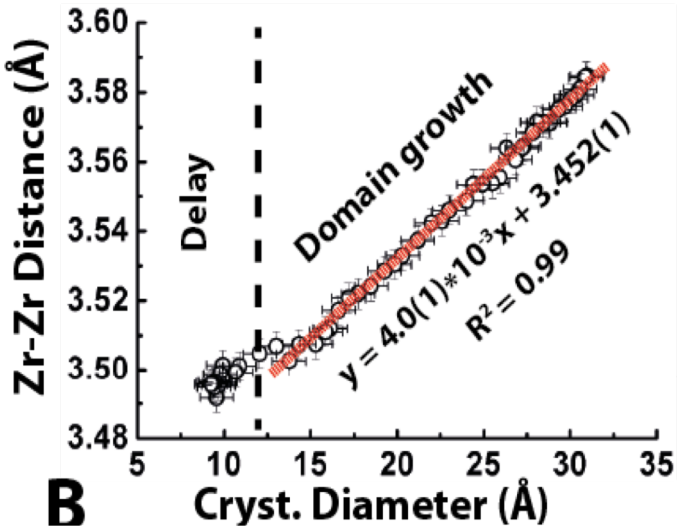
In-situ study of hydrothermal synthesis of yttria-stabilized zirconia nanoparticles



- Christoffer Tyrsted, Nina Lock, Kirsten M. \O. Jensen, Mogens Christensen, Espen D. Bøjesen, Hermann Emerich, Gavin Vaughan, Simon J. L. Billinge and Bo B. Iversen, , *IUCrJ.* **1**, 165-171 (2014)
- Nanocrystalline

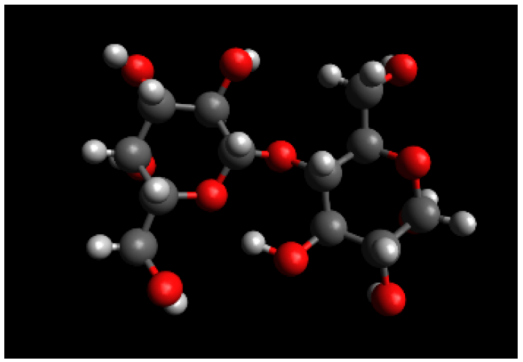
final product

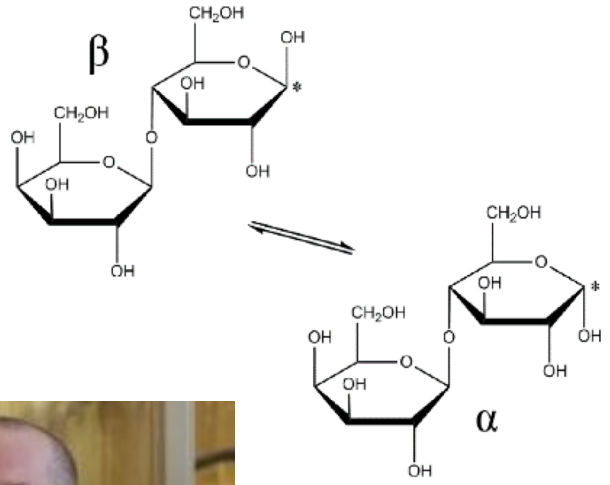


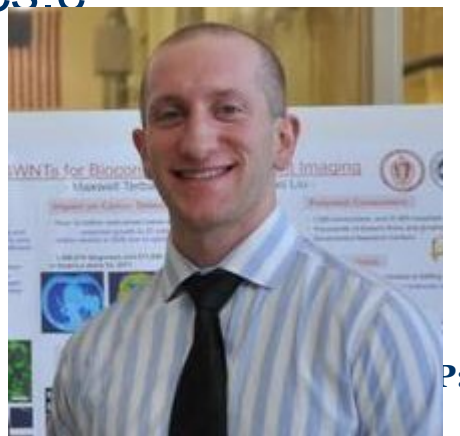


Recrystallization from the amorphous state: Lactose

- Lactose is a common excipient for pharmaceutical tableting
- Commercially available in crystalline or amorphous forms
- A-form can be prepared from α-Monohydrate crystals by spray-drying, melt quenching, and lyophilization
- Maxwell W. Terban, Eugene Y. Cheung, Paul Krolikowski and Simon J. L. Billinge, *Cryst. Growth Des.* , Doi: http://pubs.acs.org/doi/full/10.1021/acs.cgd.5b01100 (2015)





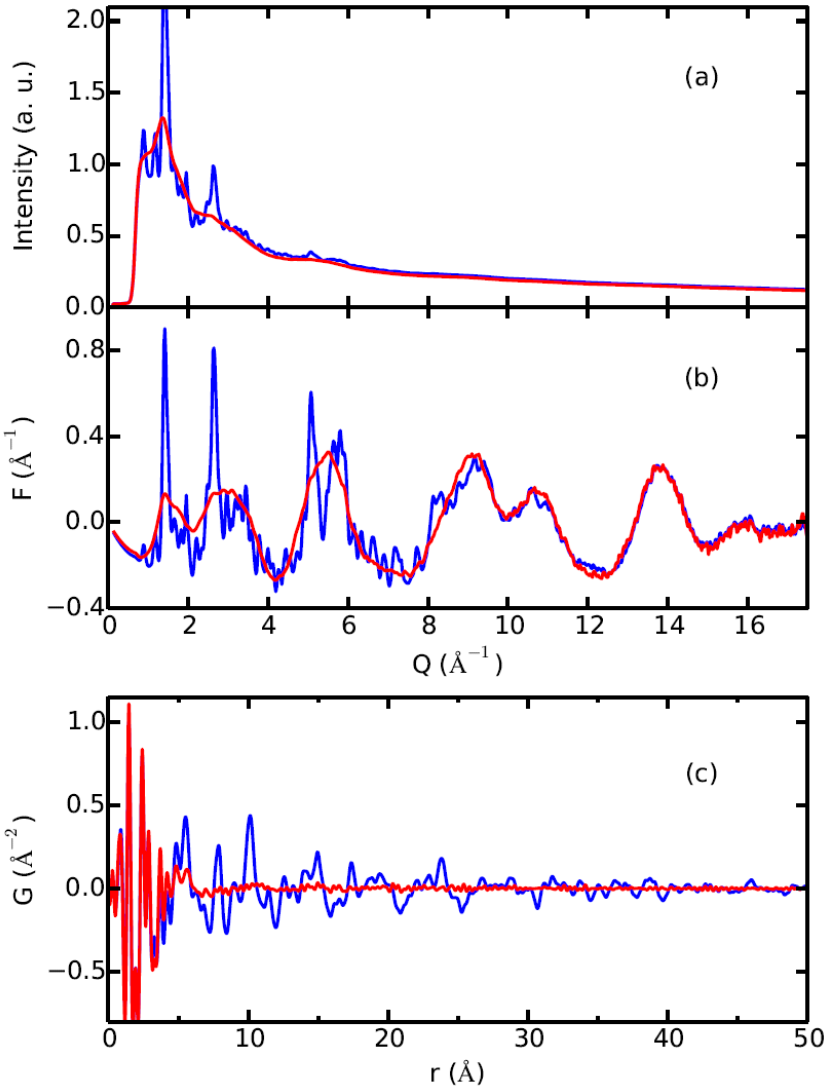


Lactose

- Raw data
- F(Q)
- TSPDF

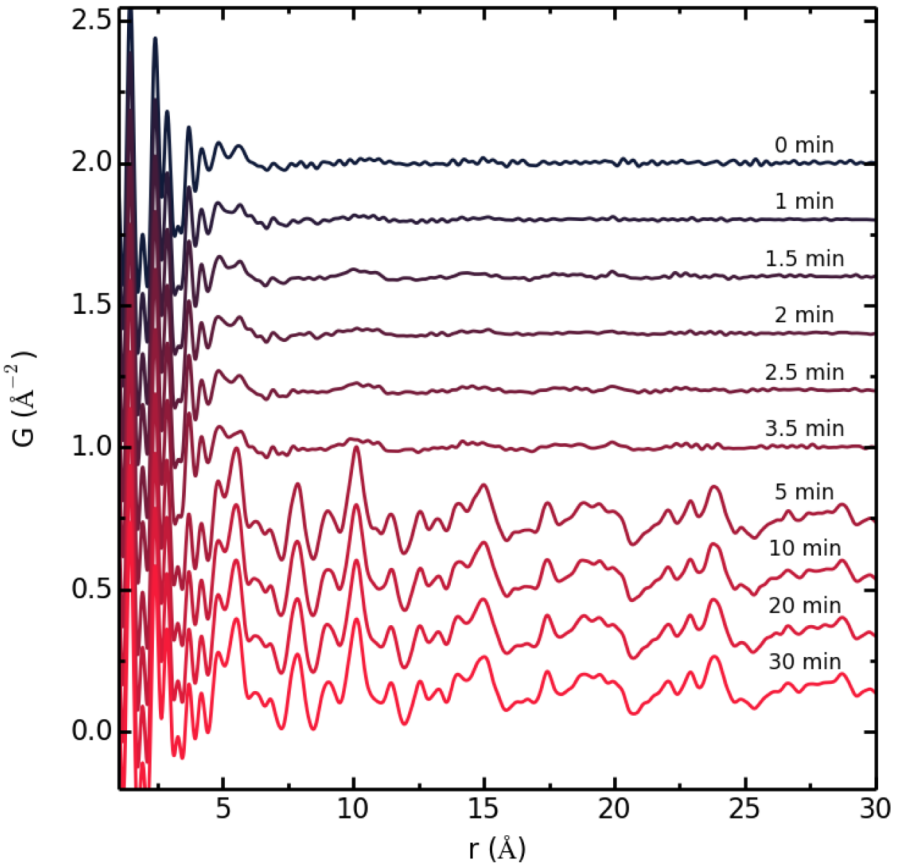
- Of A-form (red) and crystalline (blue) lactose

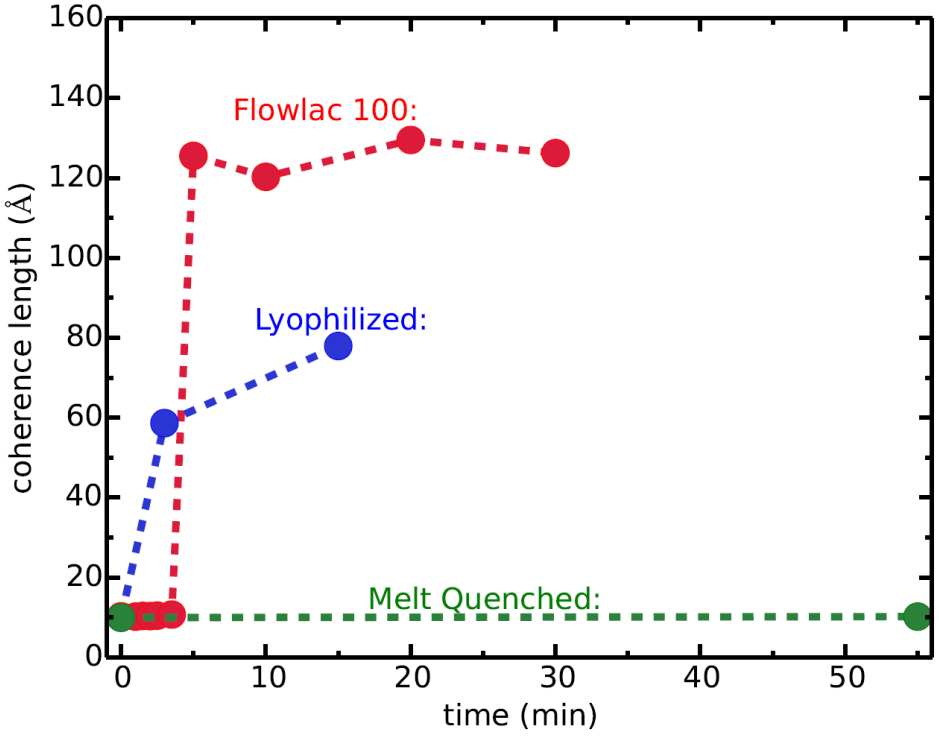
- TSPDF data collected at X17A@NSLS



Time dependent studies

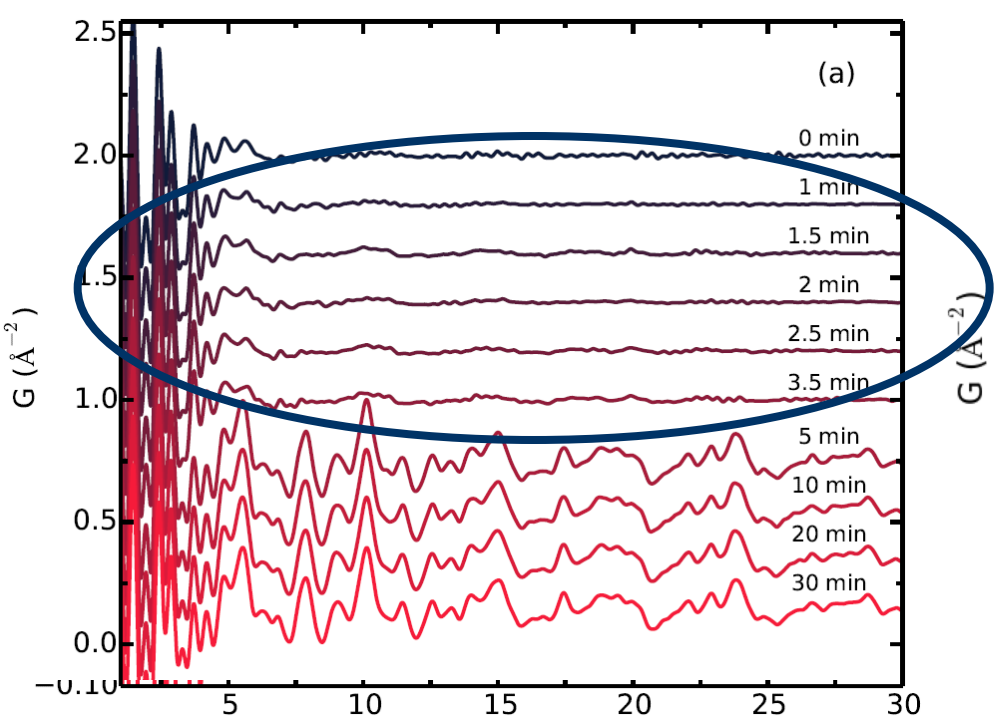
- Various A-form samples aged at, 40°C/75% RH

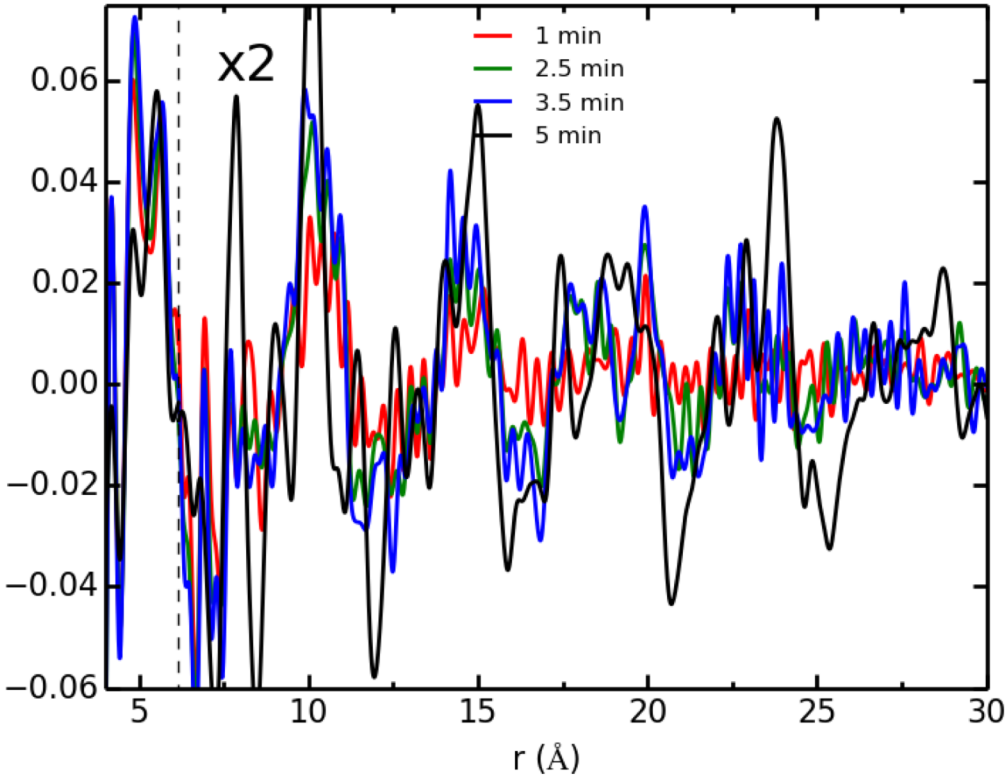




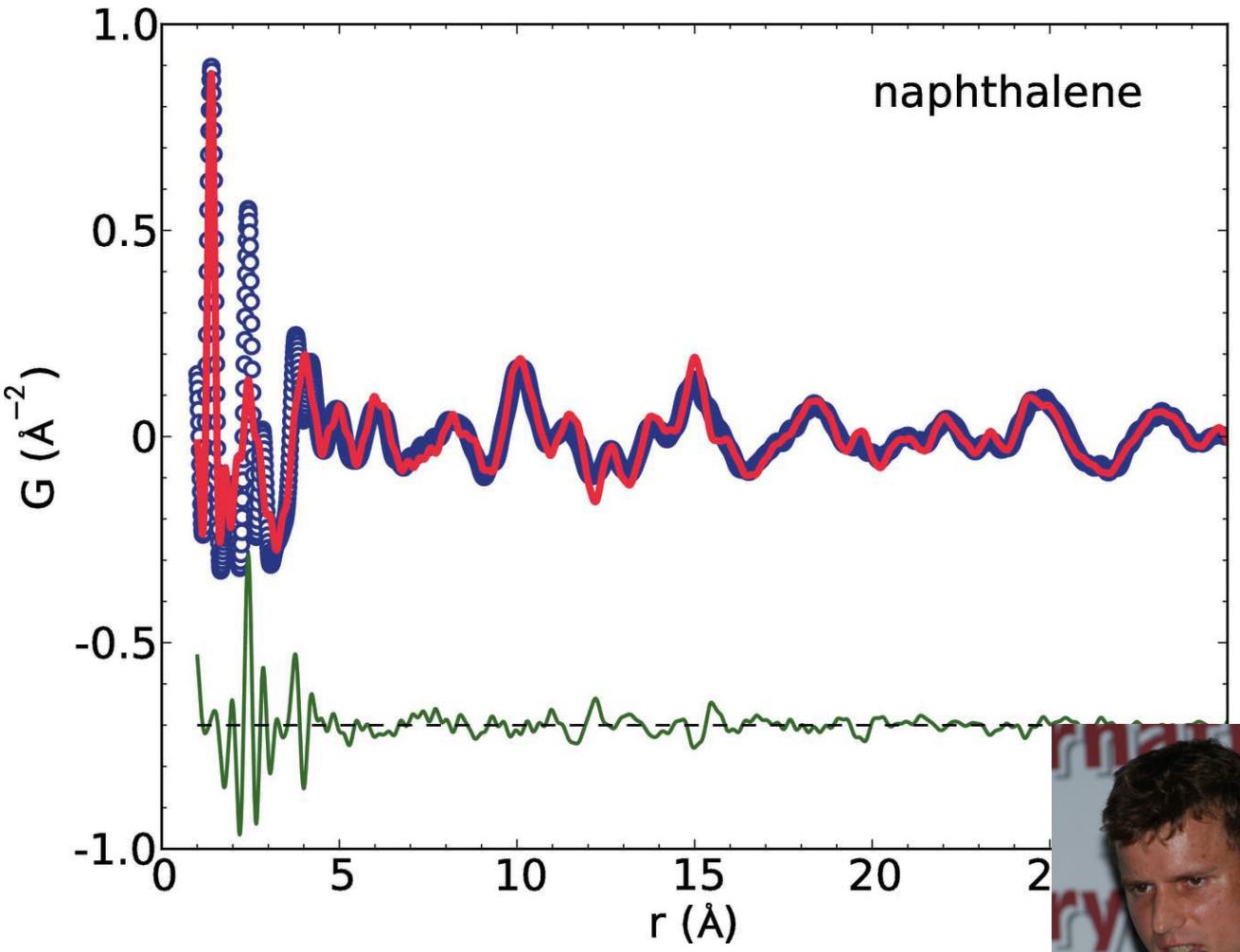
Time dependent studies

- How does the crystallinity grow in?





Solving structure of nanoparticles and molecular solids



- Regular PDFgui fit gives peaks too sharp in high-r, too broad at low-r
- With Dragica Prill, Martin Schmidt and Juhas,
- Prill, Juhás, Schmidt and S.J.L.B., *J. Appl. Crystallogr.* **48**, 171-178 (2015)

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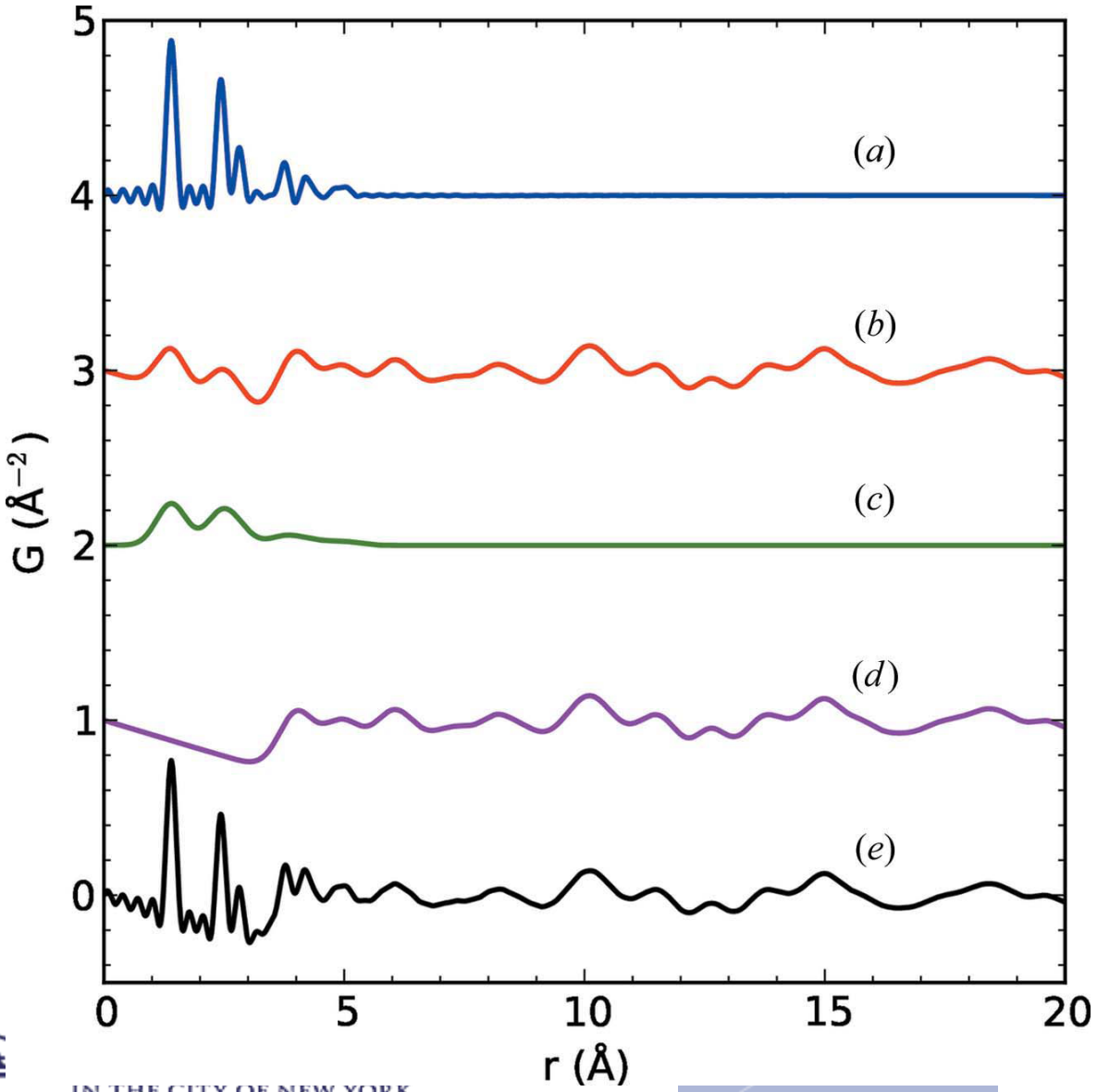
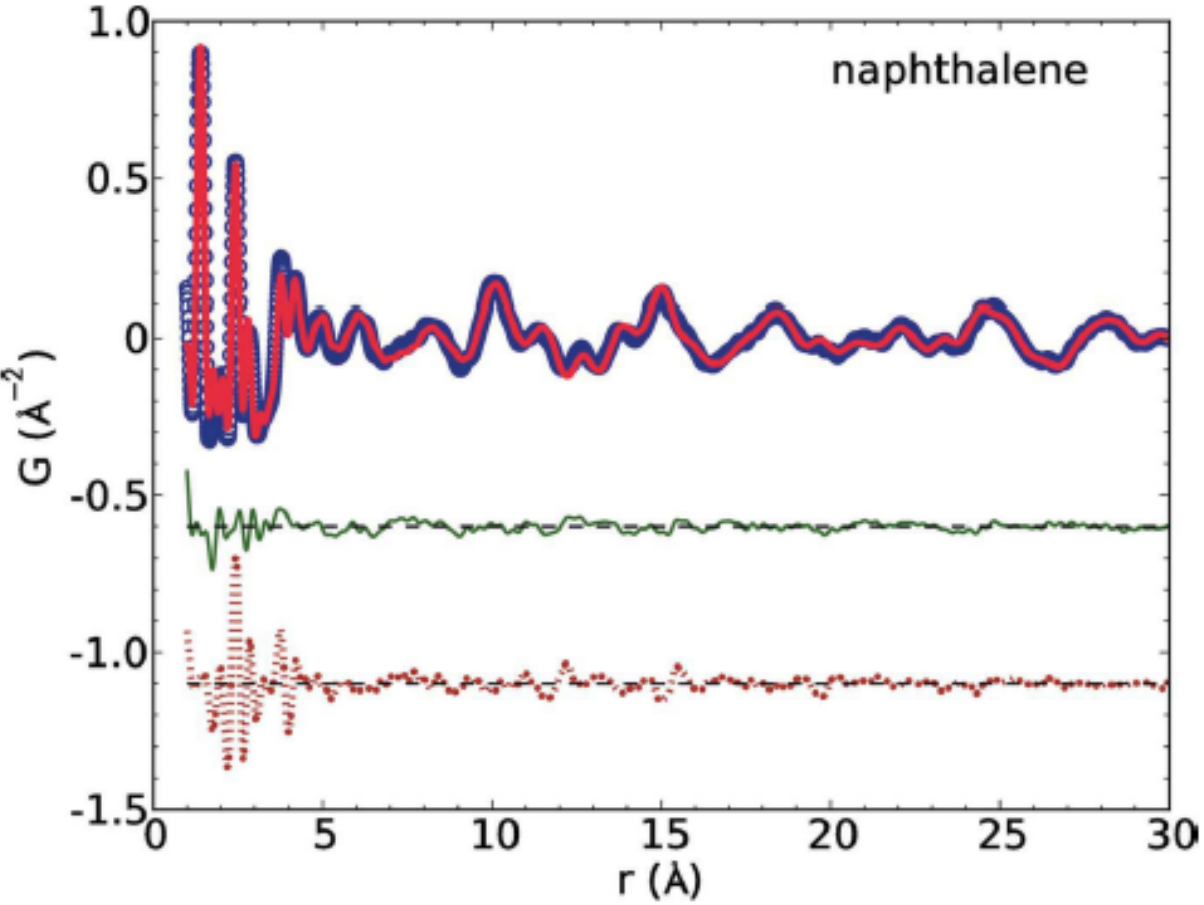
Refinement of molecular PDFs



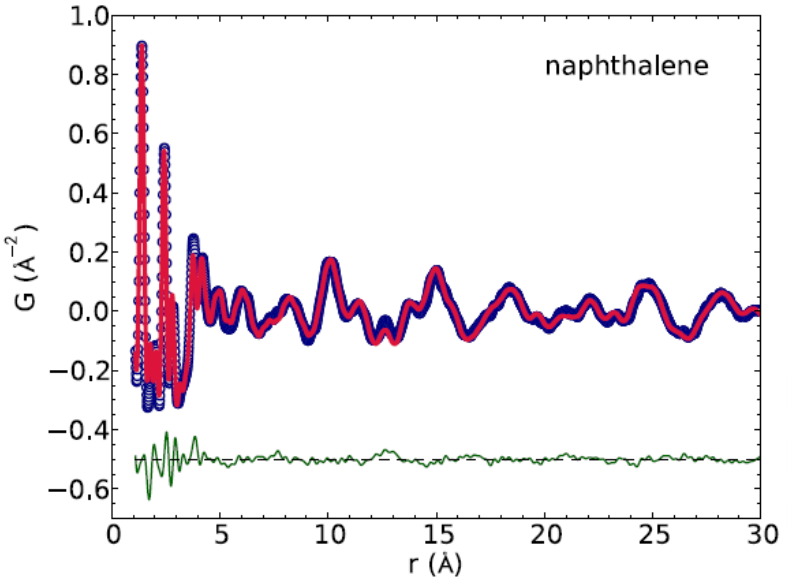
Workaround using DSE + RSC

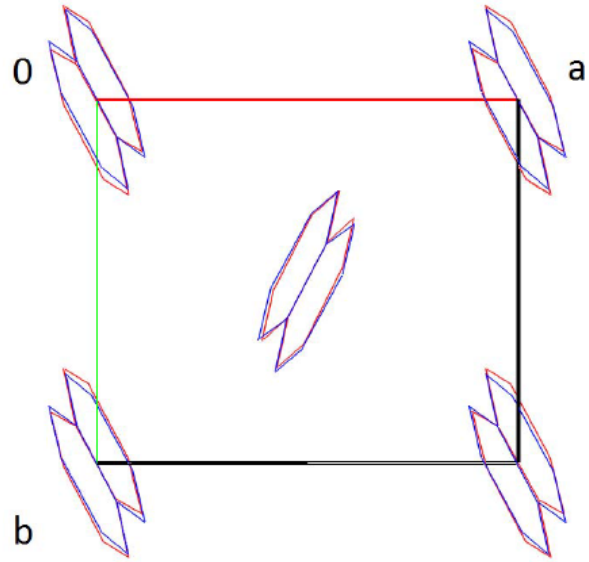
1. Calculate molecule PDF using DSE (a)
2. Calculate crystal structure using RSC (b)
3. Calculate molecule using DSE but with crystal structure ADPs (c)
4. Determine inter-molecular correlation from (b)-(c)
5. Add (a) and (d) to get full pattern (e)



- Result is excellent fit over whole range
- Dragica Prill, Pavol Juhás, Martin U. Schmidt and SJLB *J. Appl. Crystallogr.* **48**, 171-178 (2015)

Update: Structure solution of molecular materials now possible

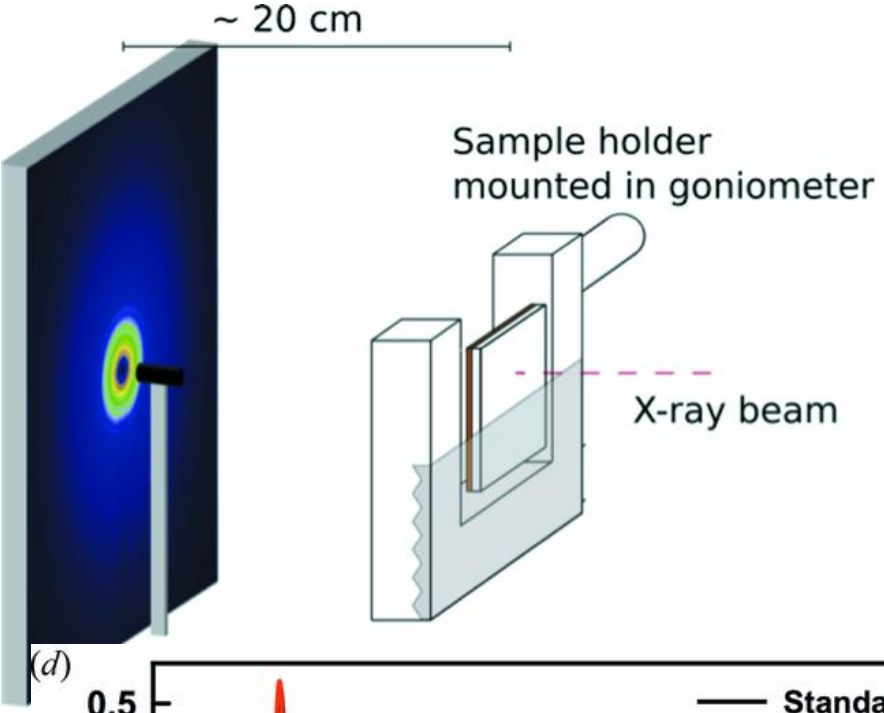




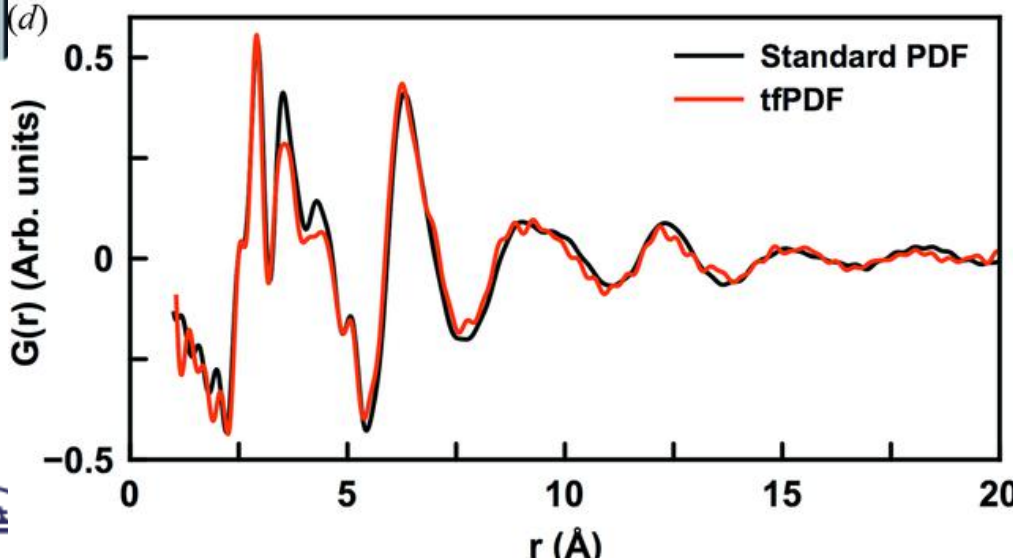
- pyobjcryst wraps functionality from ObjCryst++ (Favre-Nicolin and Cerny)
- Rigid body constraints and quaternions to describe spatial orientations of molecules
- Napthalene, P1, Z=2
- Blue is single crystal structure, red is PDF derived structure
- Dragica Prill, Pavol Juhás, S. J. L. Billinge and Martin U. Schmidt, *Acta Crystallogr. A* **72**, 62-72 (2016)

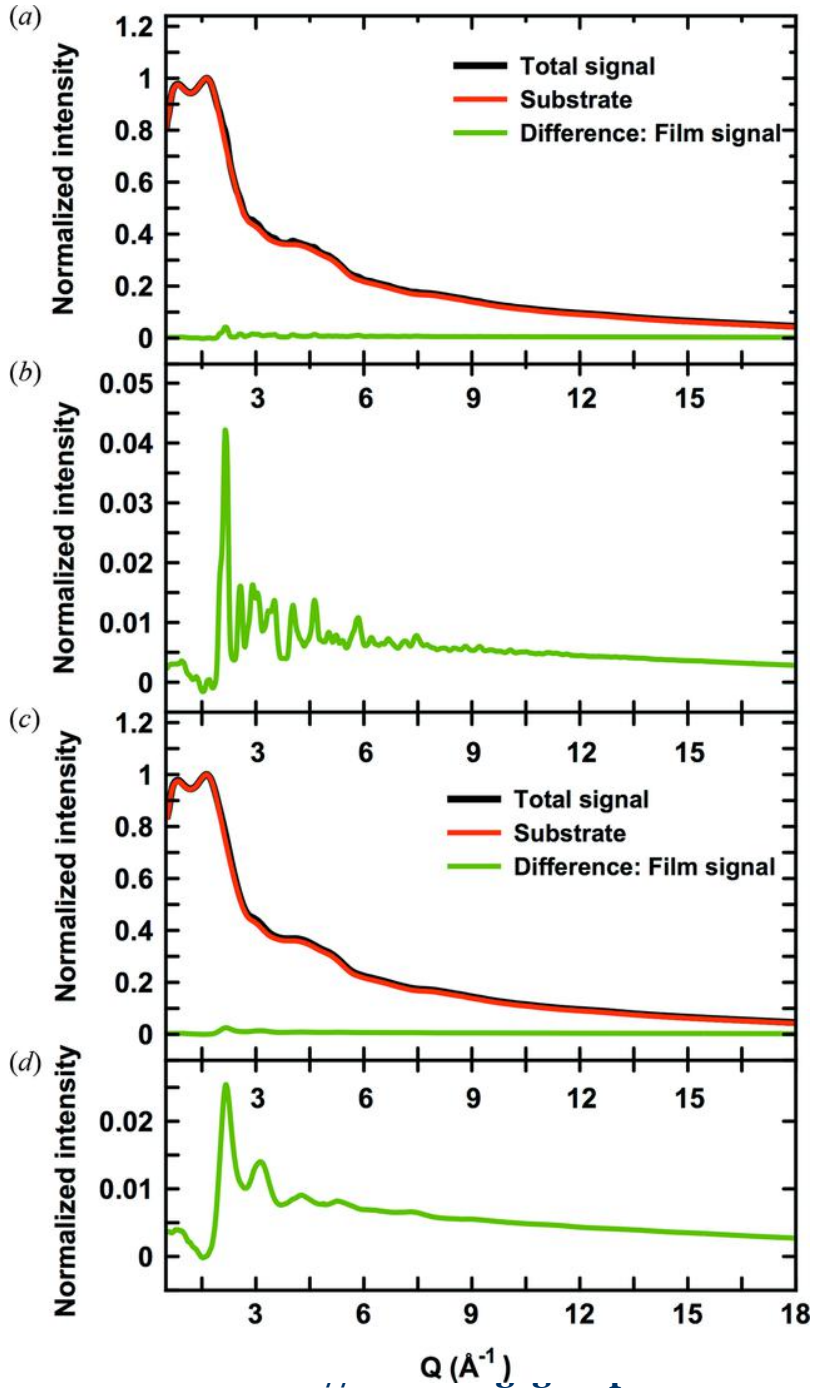
HTTP://thebillingegroup.com

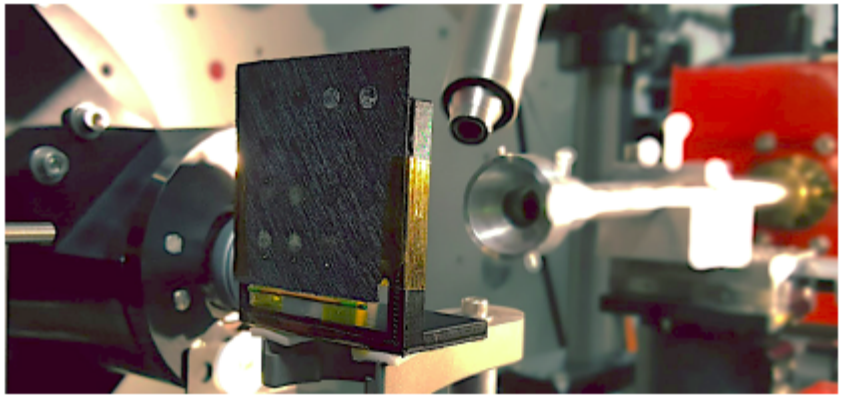
Thin film PDF at normal incidence



Jensen, Iversen, Johnson, Dooryhee SJLB et al. *IUCrJ* 2015

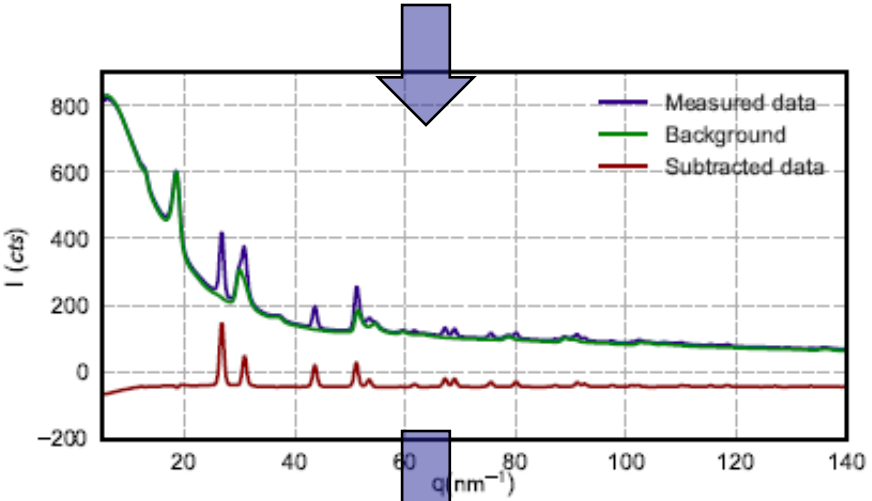


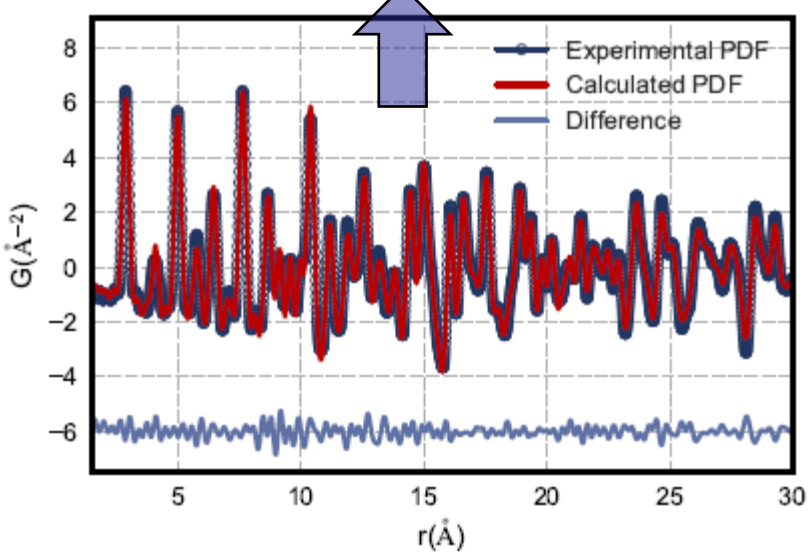




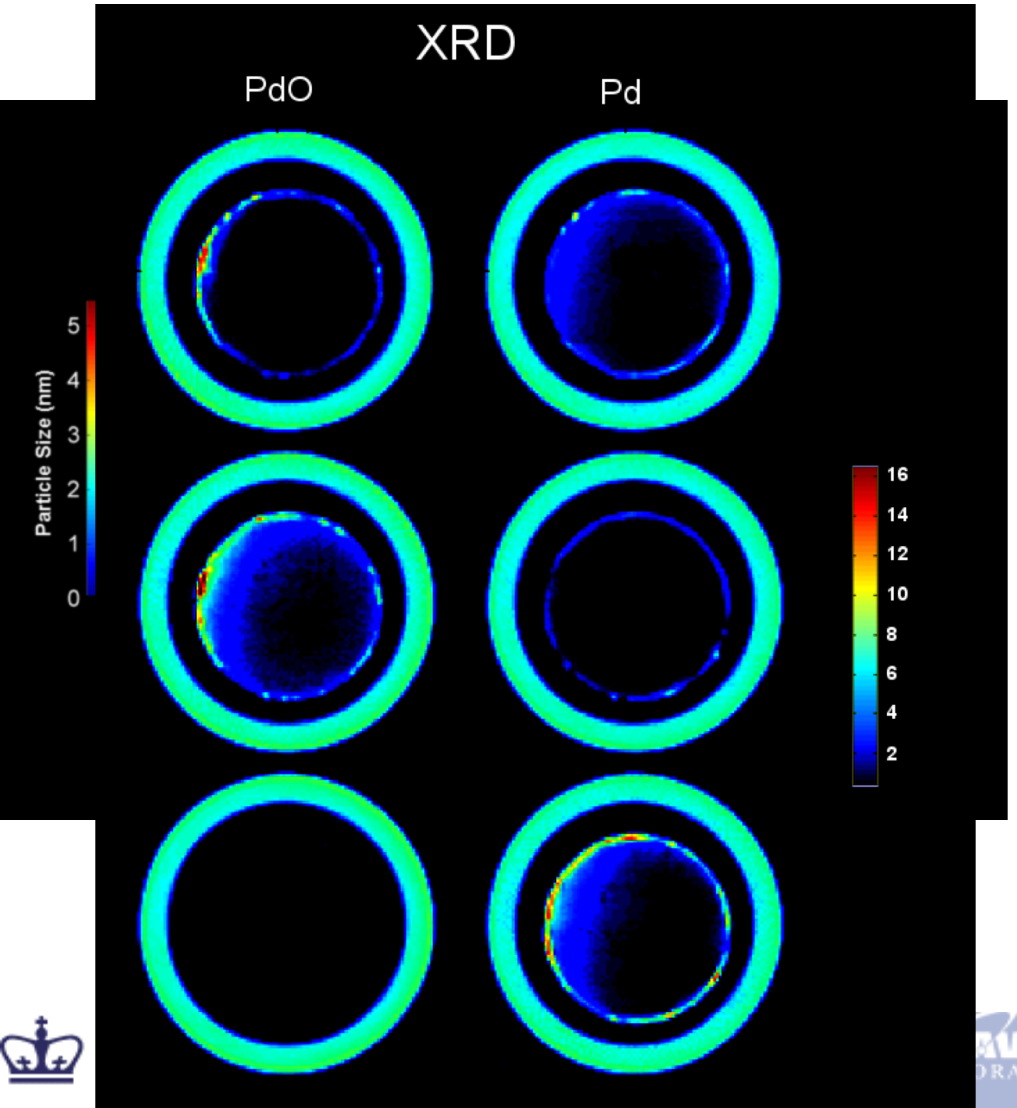
Spatially Resolve PDFs

- Anton Kovyakh, Soham Banerjee, Chia Hao Liu



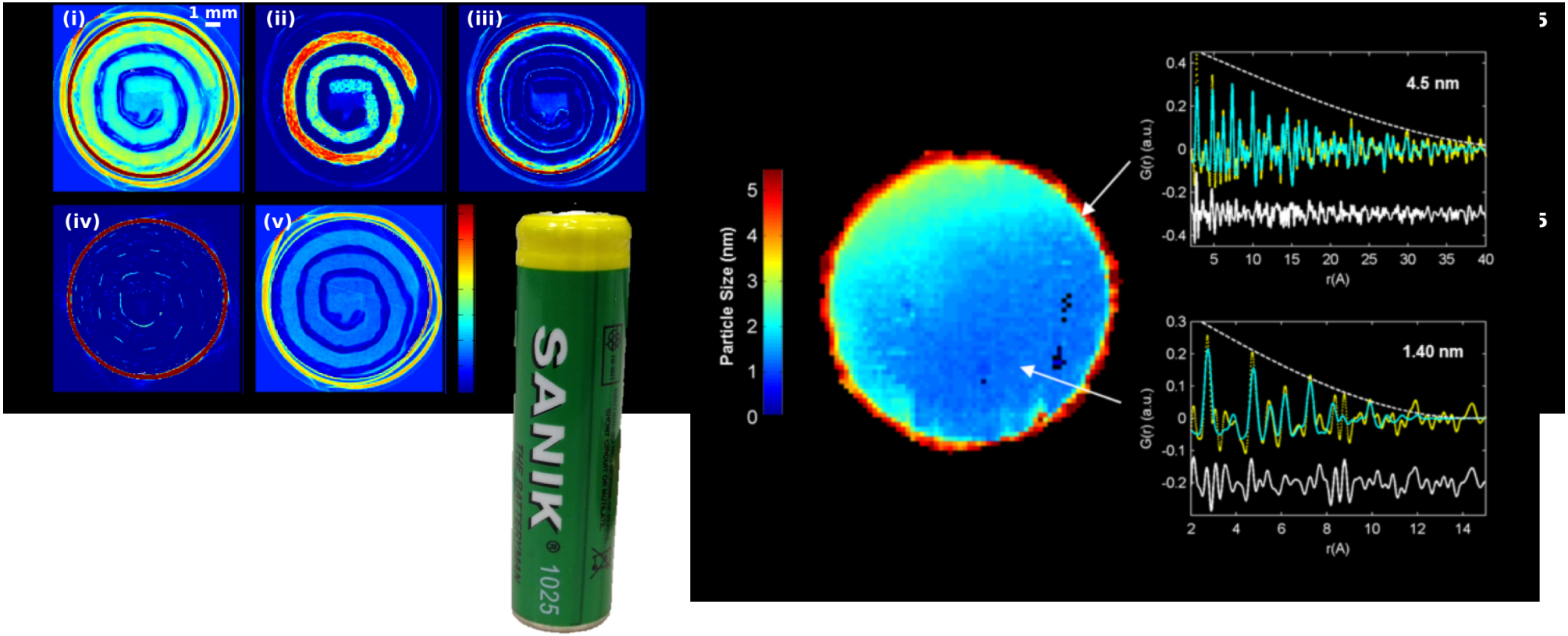


High throughput allows spatially resolved tomographic imaging



- Experiments on ID15 at ESRF
- Pt/PtO nanoparticle catalyst on a γ-alumina support in a flow rig
- Have a fully refinable PDF in every pixel of the image
- Large particle size in a shell around the rim, small particle size and much lower density in the middle
- => Spatially resolved, time resolved nanostructure studies
- S. D. M. Jacques, Di Michiel, SJLB et al. *Nat. Commun.* **4**, 2536 (2013)

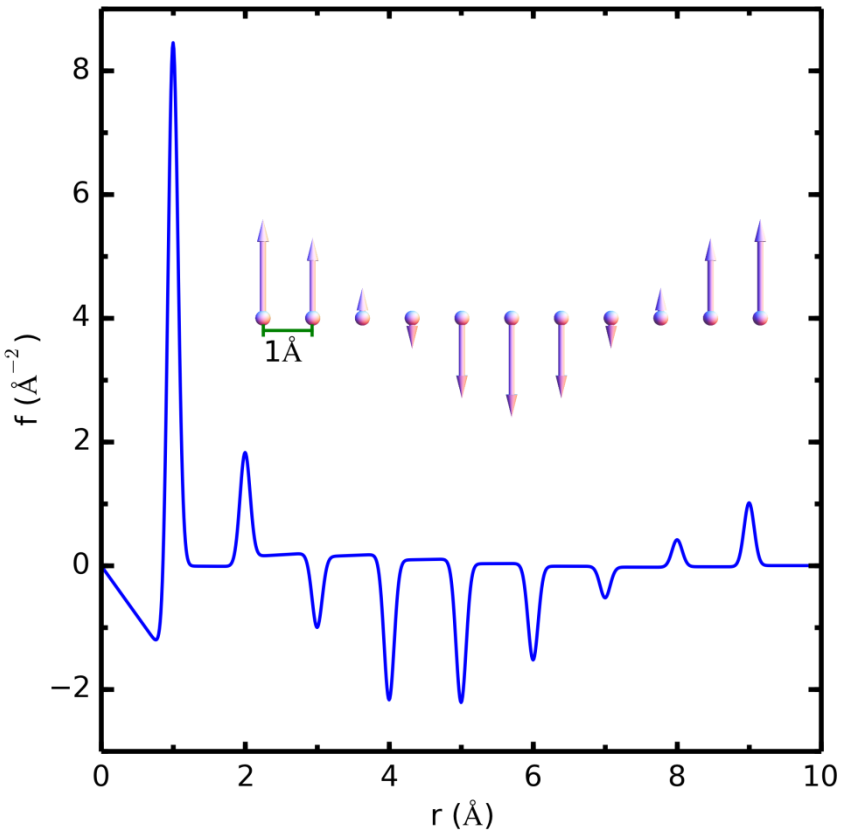
Batteries

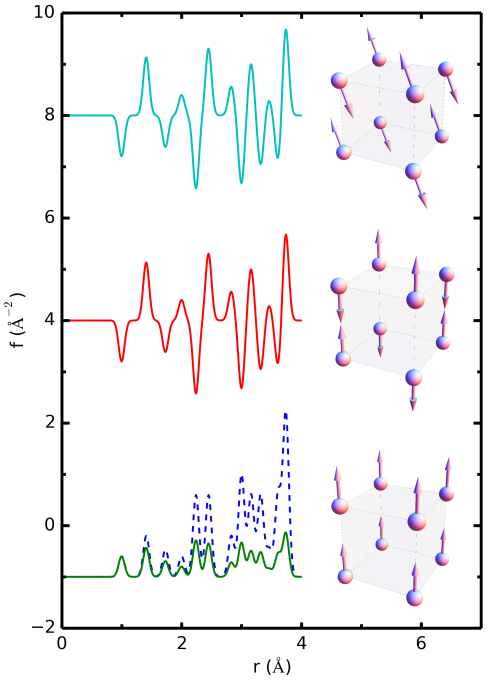


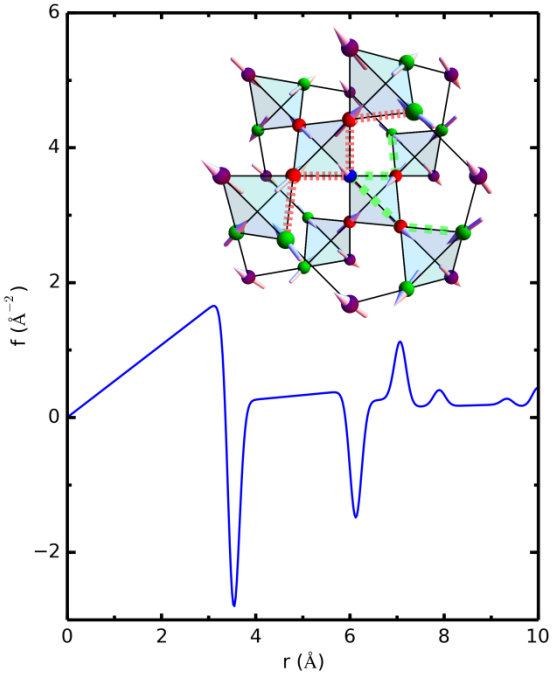
10,000 2D datasets per image, 30 mins per image
~10Tb/day

Jensen, Corr, Di Michiel, SJLB et al., *J. Electrochem. Soc*. (2015)

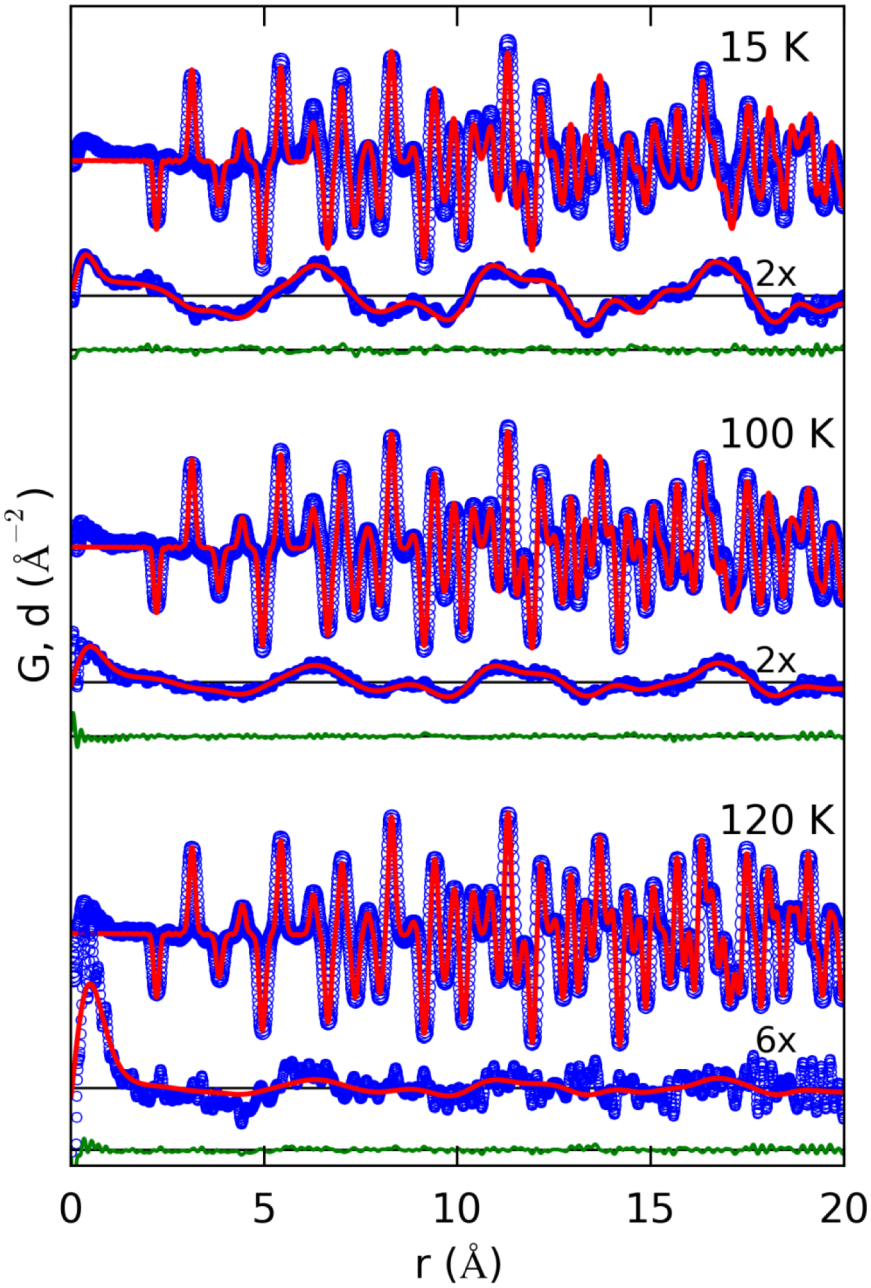
mPDF: PDF of short-range magnetic correlations







- Benjamin A. Frandsen, Xiaohao Yang and Simon J.L. Billinge, *Acta Crystallogr. A* **70**, 3-11 (2014).



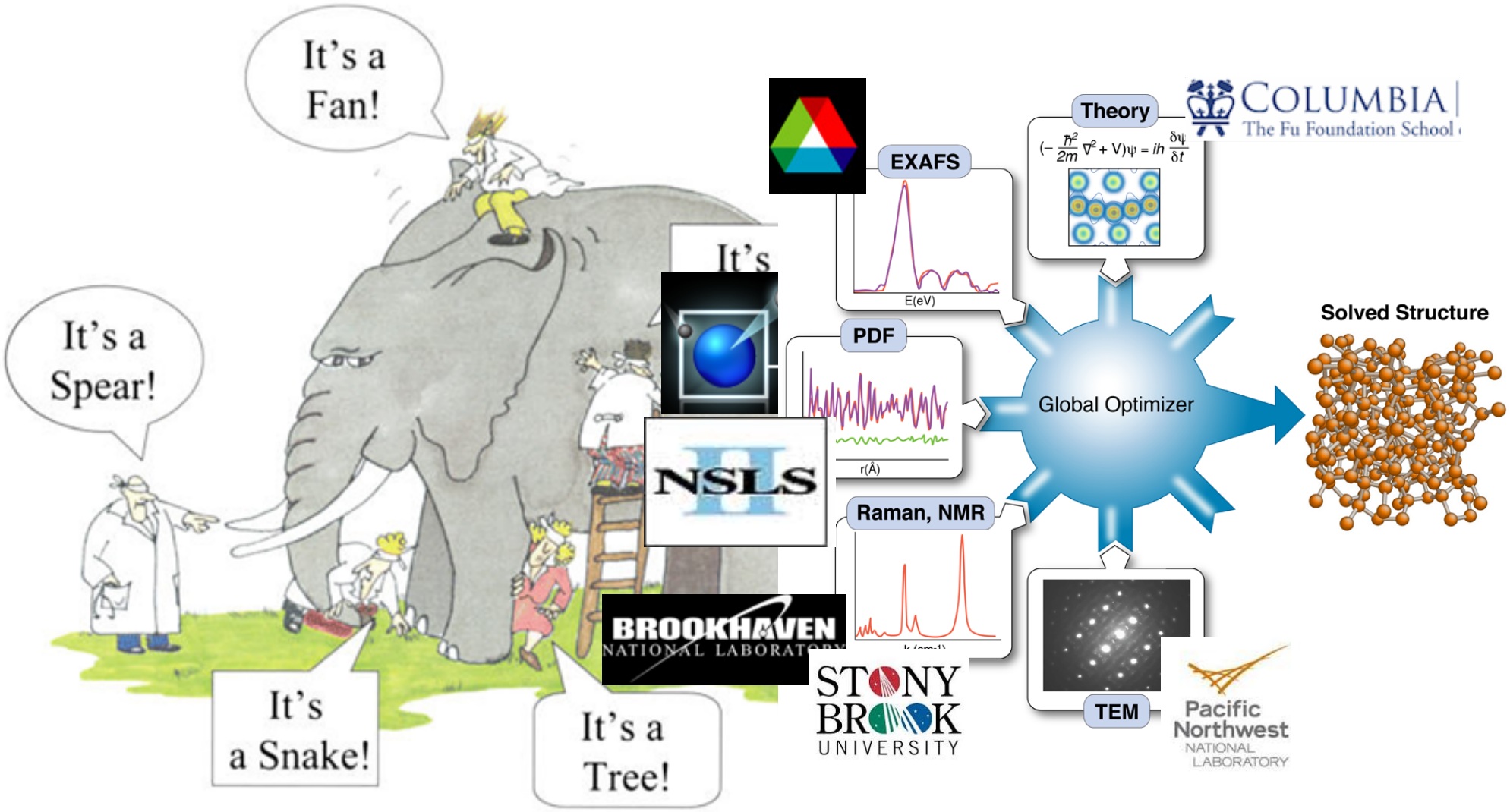
MnO

Top: *Blue*: measured nPDF signal
Red (top) calculated structural PDF
Btm: *Blue*: difference between nPDFsignal and calculated structural PDF
Red: calculated mPDF for AF MnO

Benjamin A. Frandsen, M. Brunelli, K. Page, Y. J. Uemura, Julie B. Staunton, SJLB, arXiv:1512.06270.

Frandsen, SJLB, Acta Crystallogr. A 71, 325-334 (2015)

Summary


It's a Fan!
It's a Spear!
It's a Snake!
It's a Tree!
It's
NSLS
BROOKHAVEN NATIONAL LABORATORY
STONY BROOK UNIVERSITY
EXAFS
E(eV)
PDF
r(Å)
Raman, NMR
TEM
Theory
COLUMBIA
The Fu Foundation School
Global Optimizer
Solved Structure
Pacific Northwest NATIONAL LABORATORY

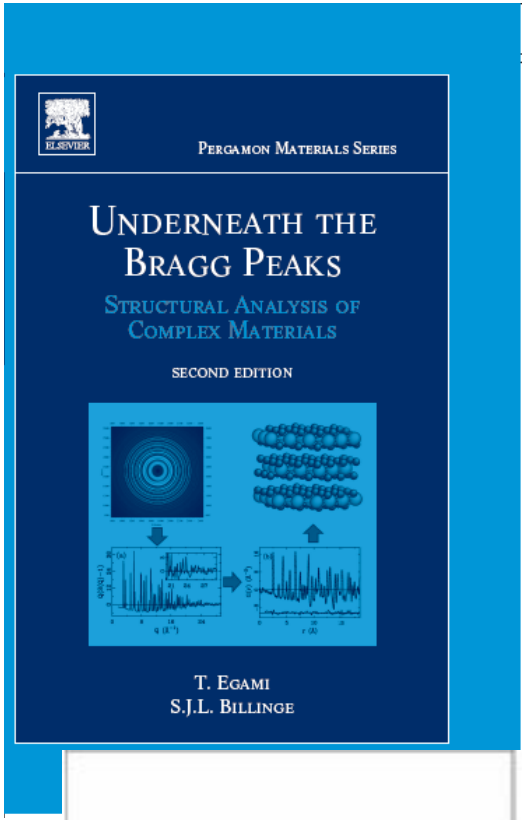
2015

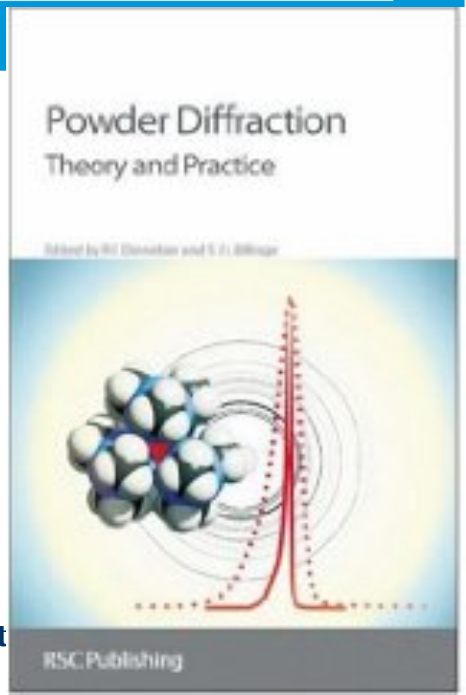
After 100 years of materials revolution…

Hipster

Summary

- Many of society's toughest challenges require complex materials.
- Complex materials characterization present some of our toughest experimental and theoretical challenges
- In general, complex modeling solutions (combining multiple diverse information sources in a structure solution) will be needed to solve these problems





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Also my many wonderful collaborators, mentioned during the talk

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- MLNSC, ISIS, IPNS (and people therein)

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