Structure of nanomaterials: PDF and total scattering analysis

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July 27, 2025

Columbia University in the City of New York



Columbia University in the City of New York



Columbia University, Brookhaven and Oak Ridge National Laboratories





National Synchrotron Light Souce-II (NSLS-II) =>

- XPD/PDF beamlines



Spallation Neutron Source (SNS)

- NOMAD
- POWGEN
- ARCS
- CORELLI

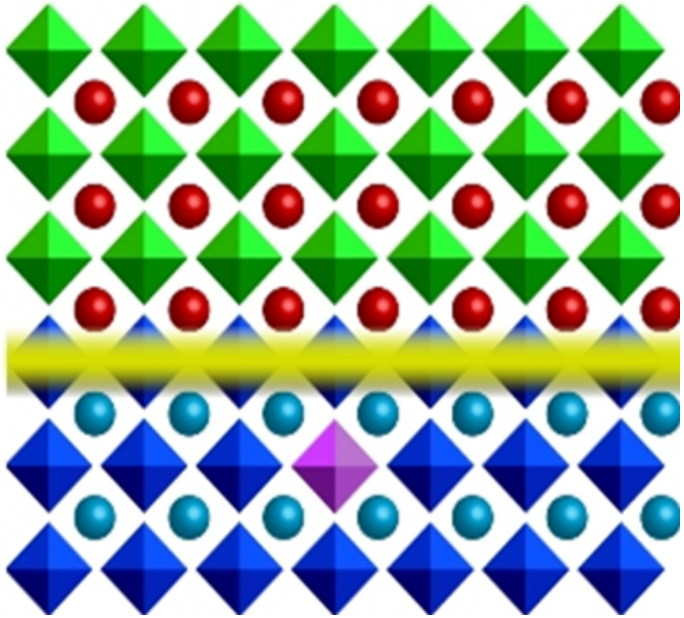
Real Materials

- Crystal structure (if there is one)
- Morphology (could be nano)
- Surface reconstruction
- Surface termination/dressing (ligands etc.)
- Interfaces
- Heterogeneities, phase separation
- Point defects
- Extended defects
- Chemical short-range order
- Distortive short-range order
- ...

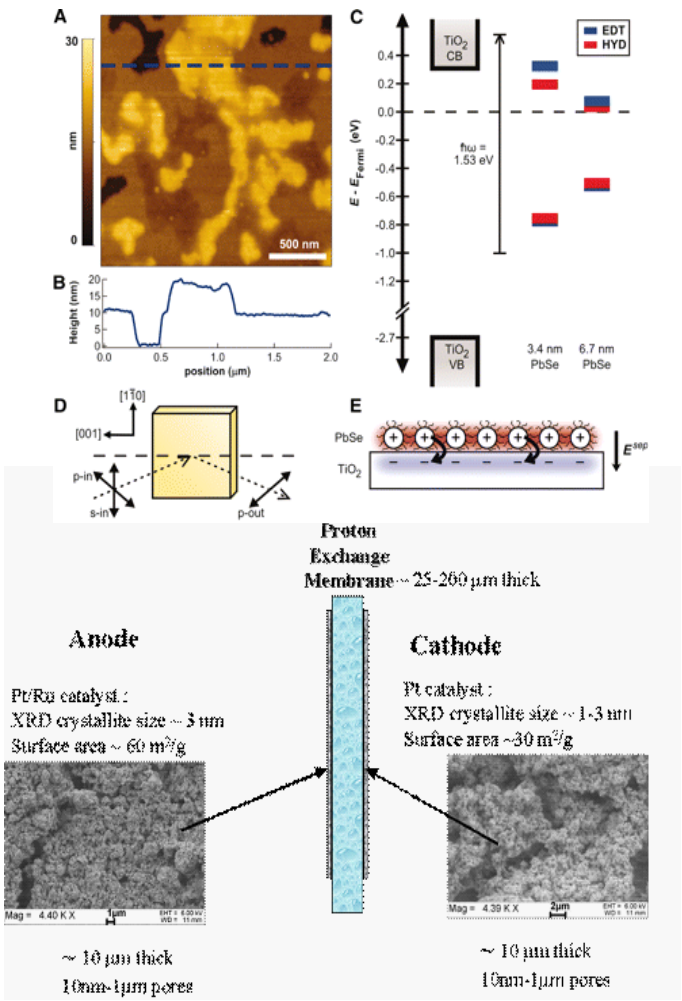
Real material properties depend sensitively on crystalline imperfections

Real Materials

- Optical properties of quantum dots depend on presence or absence of surface trap states
- Photovoltaic performance depends on charge transfer and charge extraction
- Catalysis depends on surface structure
- Battery electrodes depend on access of lithium
- Broken symmetry states in the PG phase of HTSCs
- Place two insulators together and get superconductivity in the interface

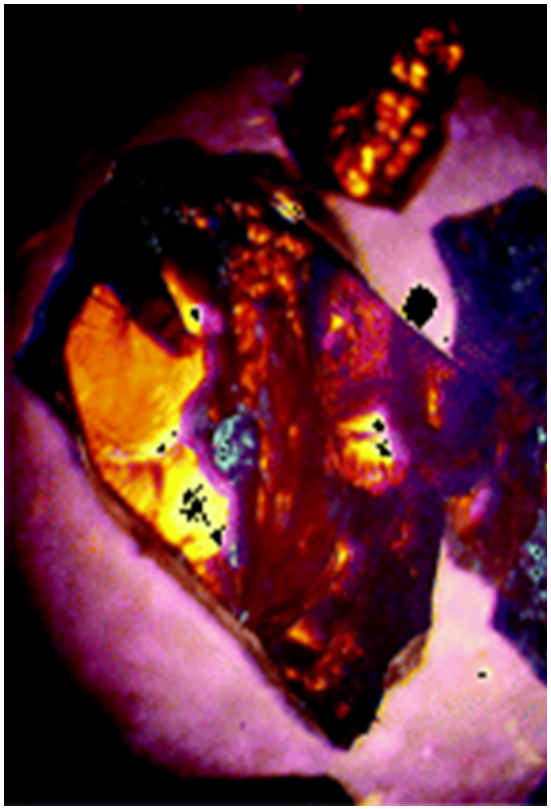


Real Materials



- 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

The crystal structure problem



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 student
2. She puts it on the x-ray machine
3. . . . Pushes the button
   1. Machine tells you the structure
   2. Or Machine gets
      1. Throw away the crystal
      2. Make it the subject of her thesis

This is the characteristic of a solved problem

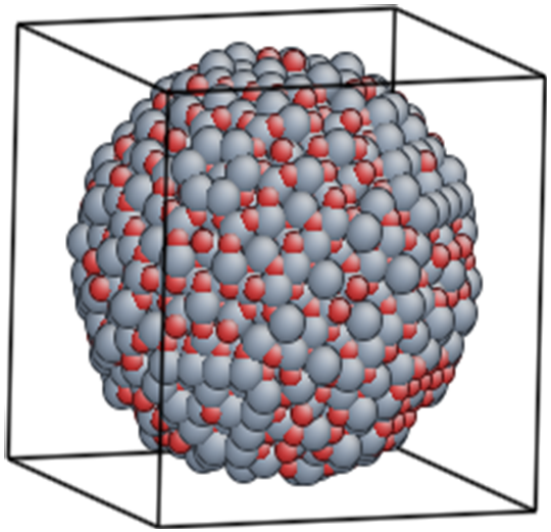
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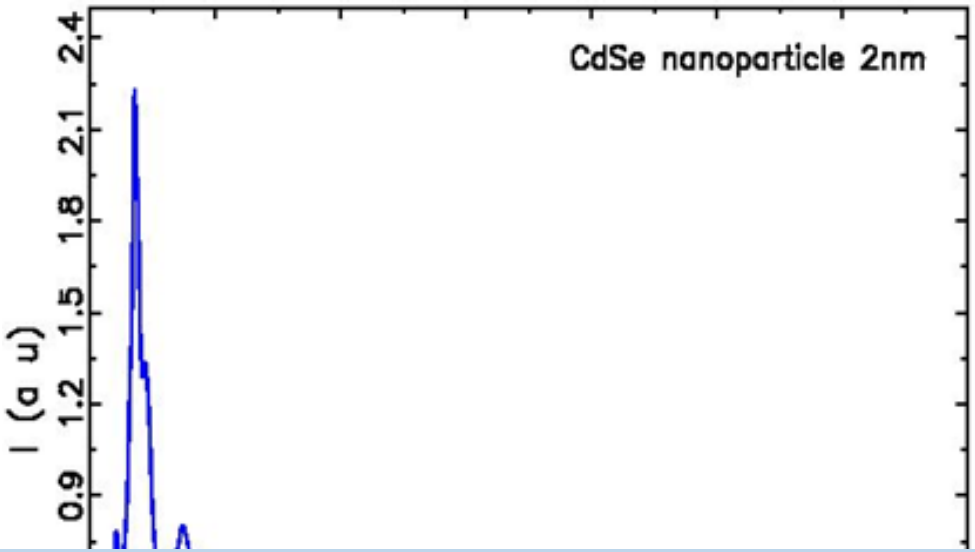
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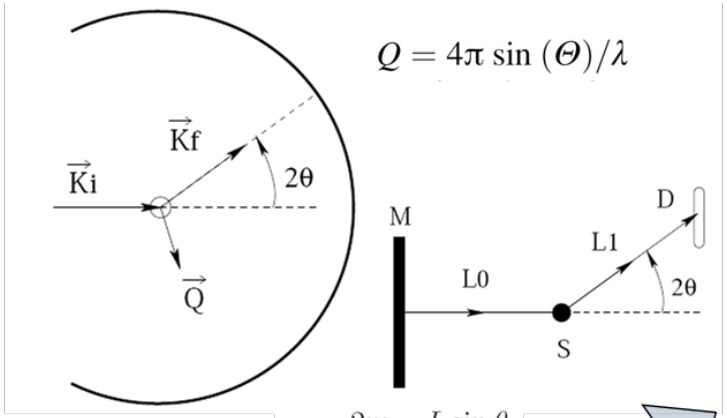
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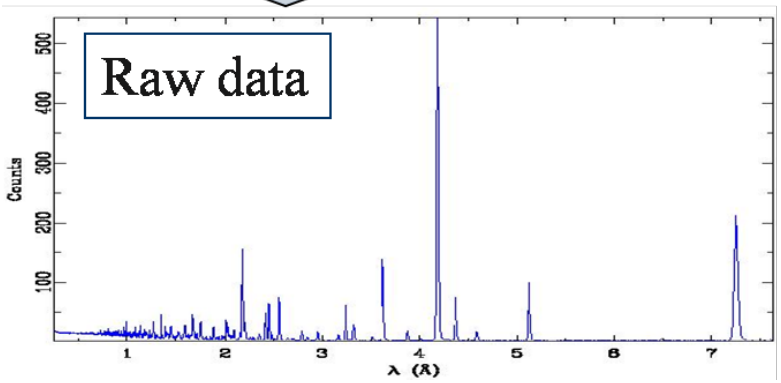


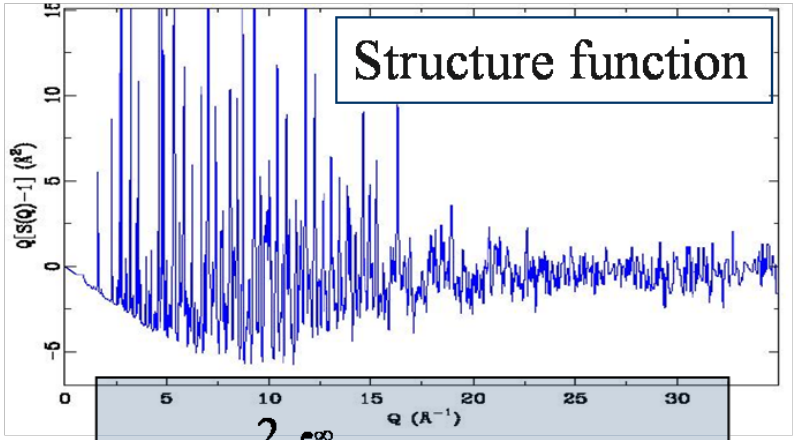


Getting the PDF from data

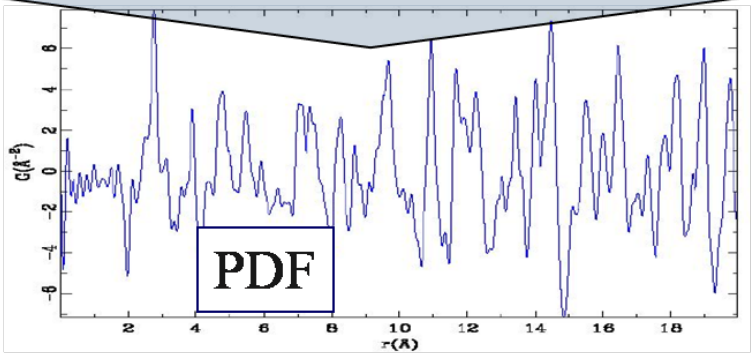


$$Q = \frac{2m_N}{\hbar}\frac{L\sin\theta}{t}$$



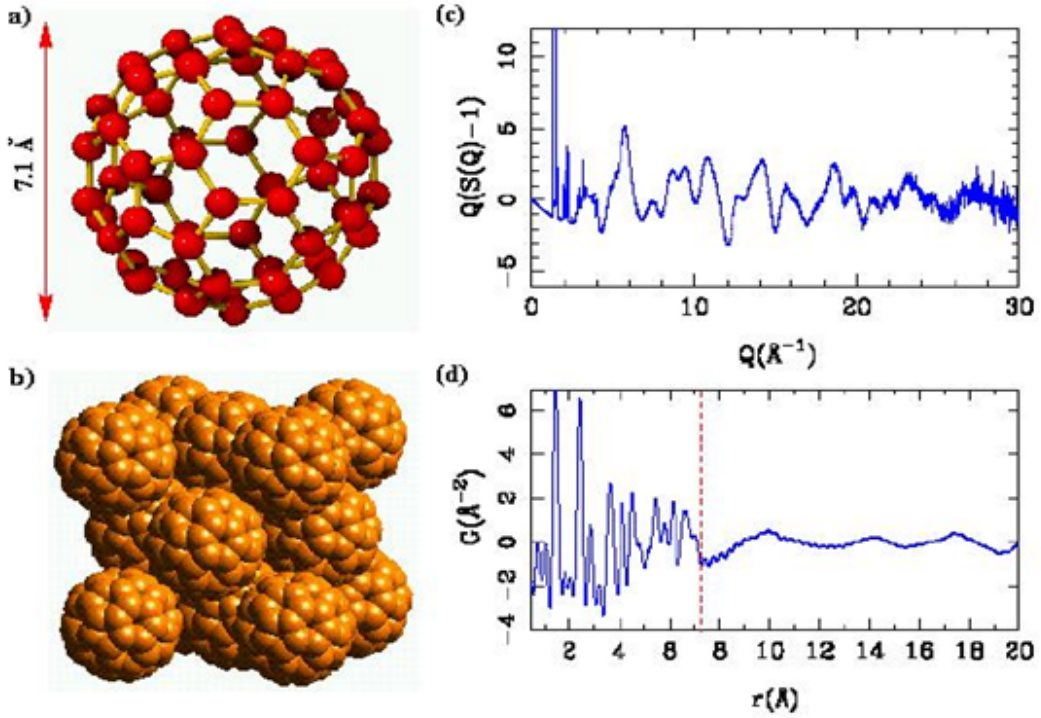


$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin QrdQ$$

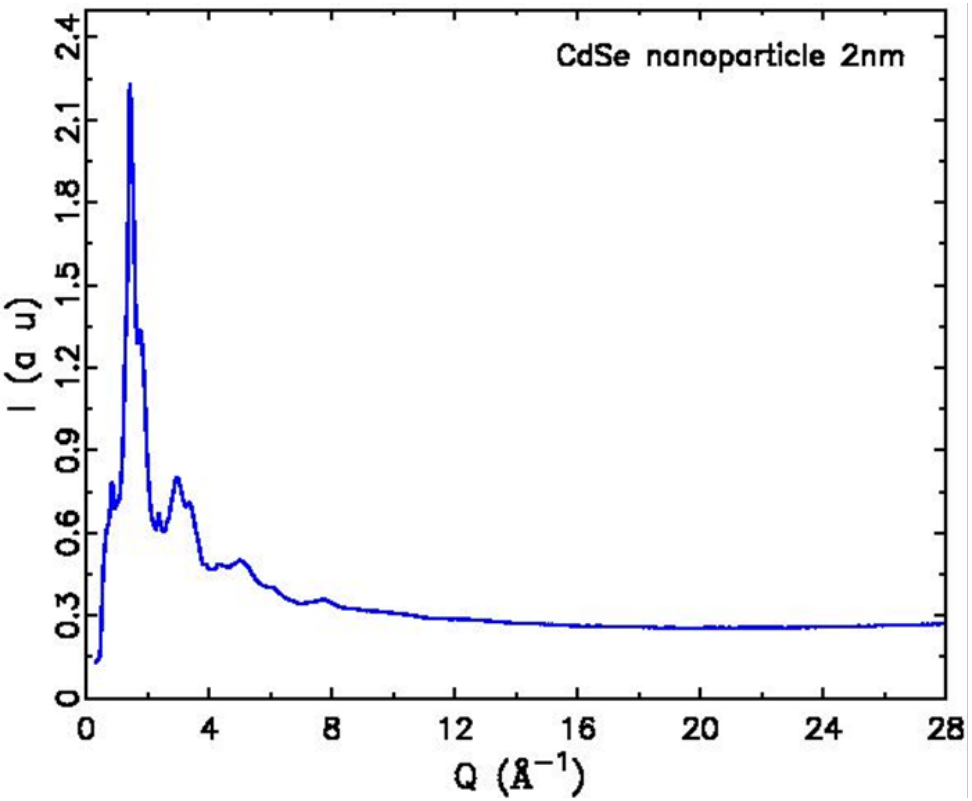


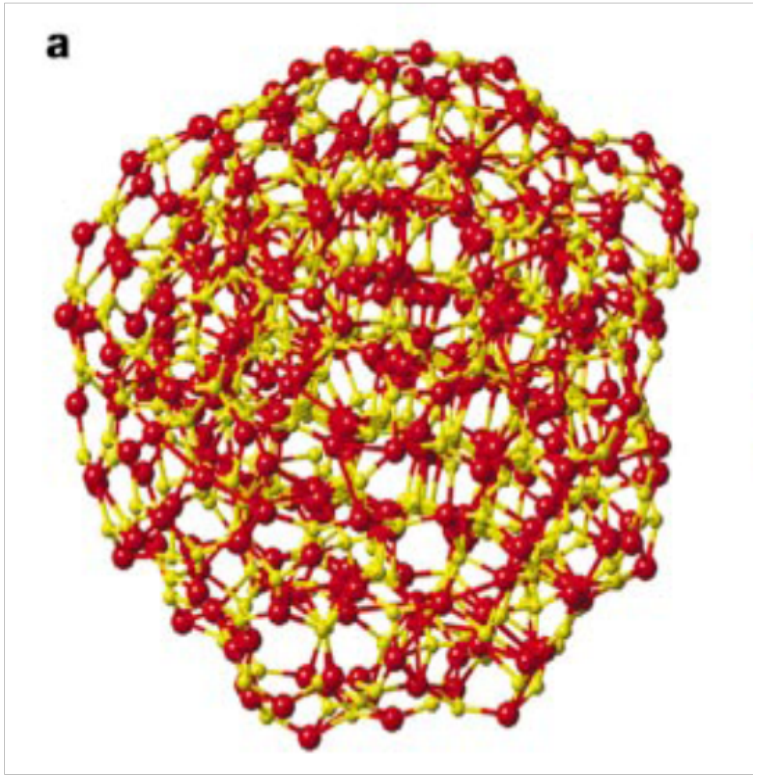
PDF intuition

- 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

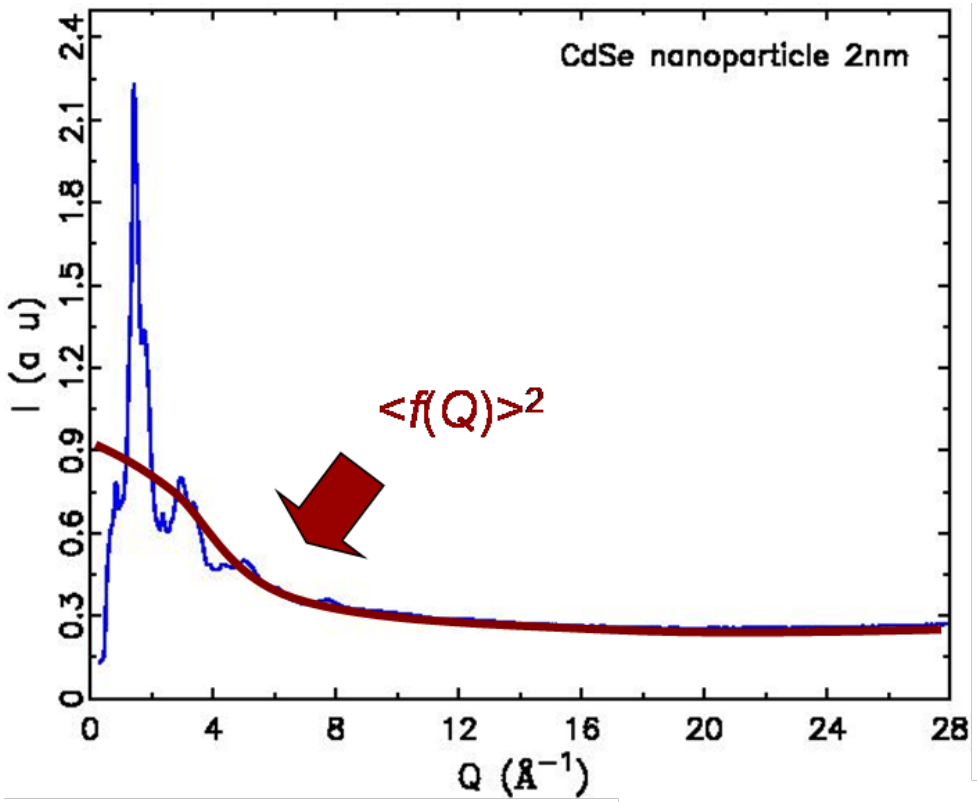


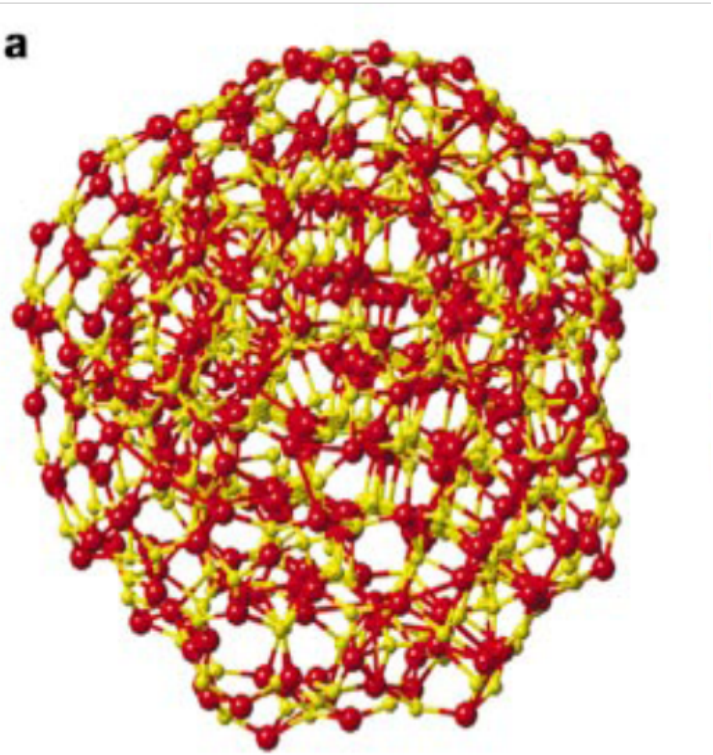
But there is no info at high-Q?





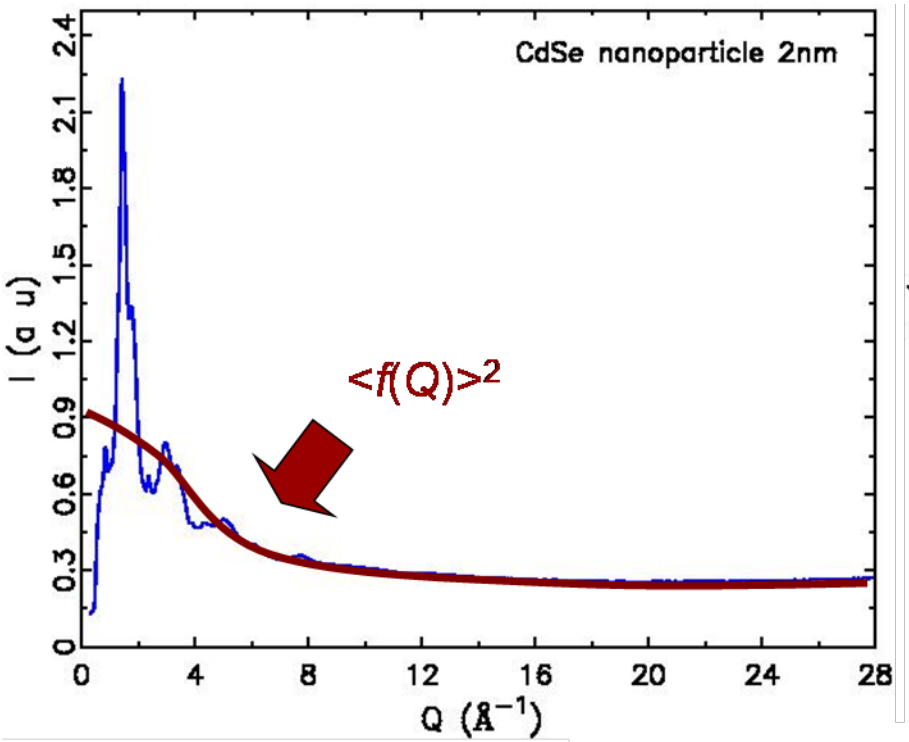
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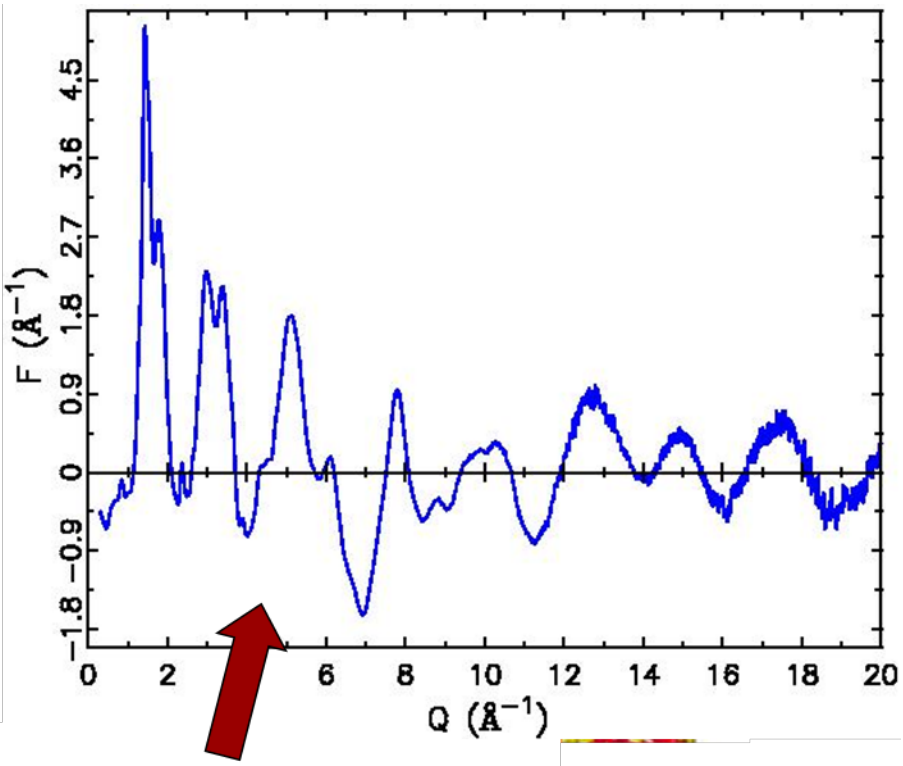




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But there is no info at high-Q?





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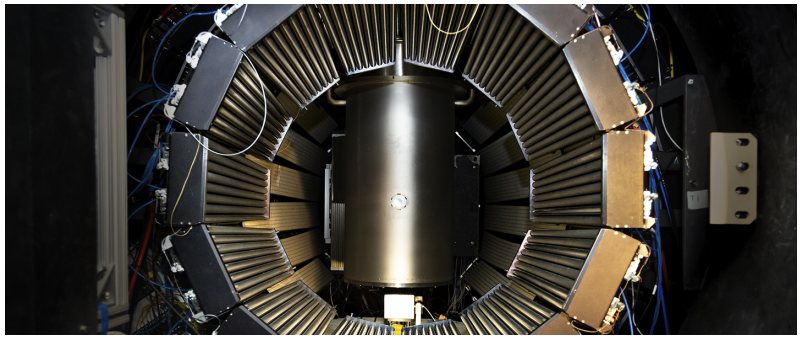
Dedicated x-ray PDF beamlines

- NSLS-II @ Brookhaven National Laboratory
  - XPD, PDF (28-ID-2/1)
- APS @ Argonne National Laboratory
  - 11IDB, 11IDC, 6IDD
- CHESS @ Cornell University
  - A2
- ESRF, Grenoble, France
  - ID15, ID11, ID22
- Spring 8, Japan
  - various
- DESY, Hamburg, Germany
  - P07, P2.1
- Diamond, Harwell Lab, UK
  - XPDF

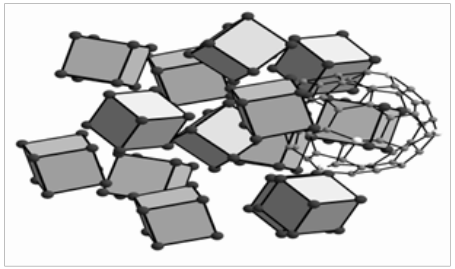


Dedicated neutron PDF beamlines

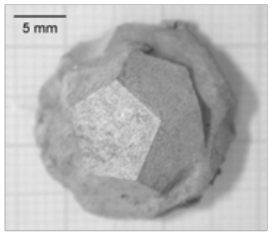
- SNS @ Oak Ridge National Laboratory
  - NOMAD
- CHESS @ Cornell University
  - A2
- ILL, Grenoble, France
  - D4
- JAERI, Japan
  - various
- ISIS, Harwell Lab, UK
  - GEM, POLARIS, NIMROD



Your own PDF beamline in the lab

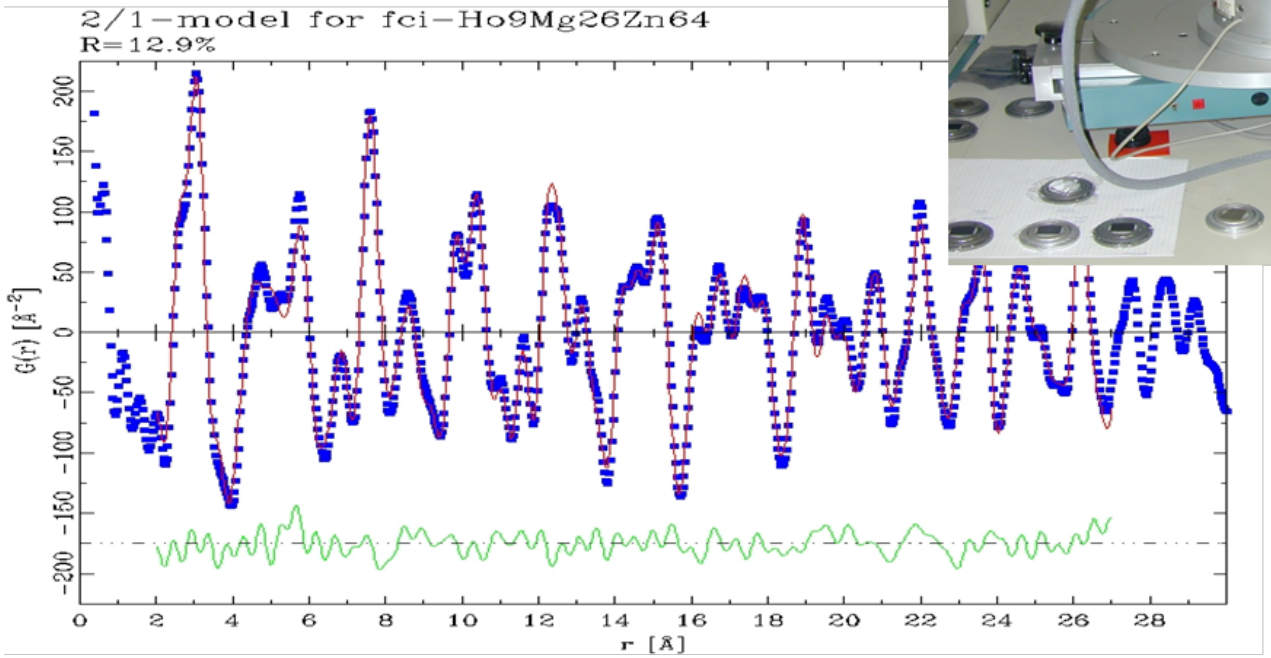


fci-Ho-Mg-Zn



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

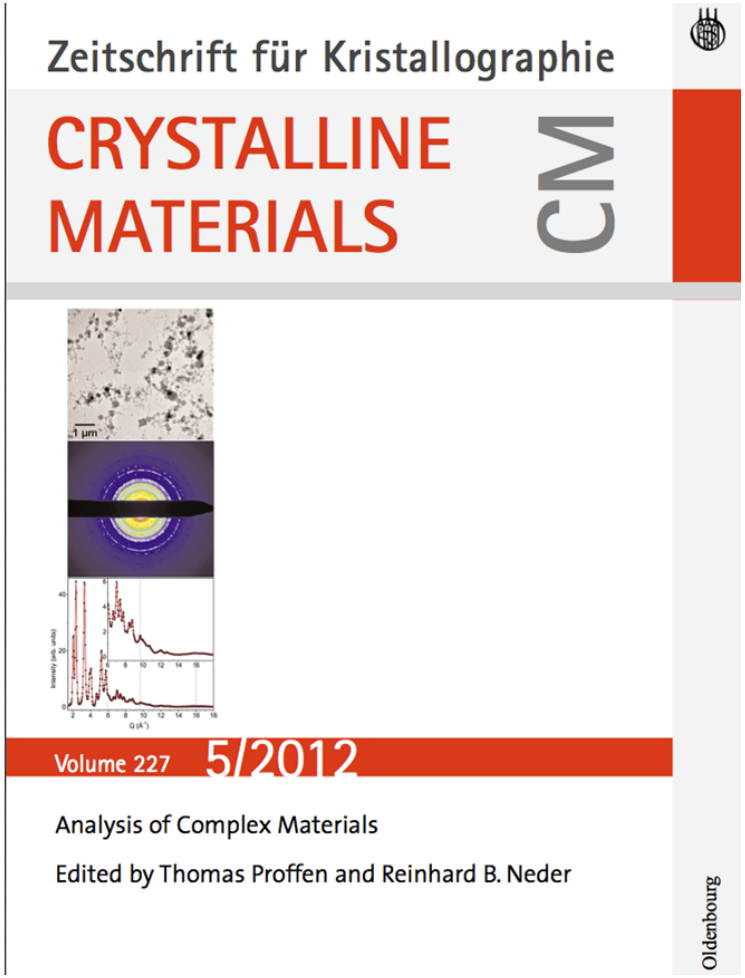




Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

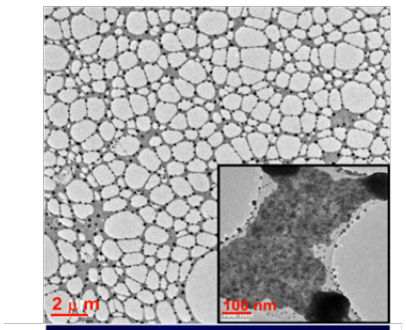
PDFs from laboratory microscopes

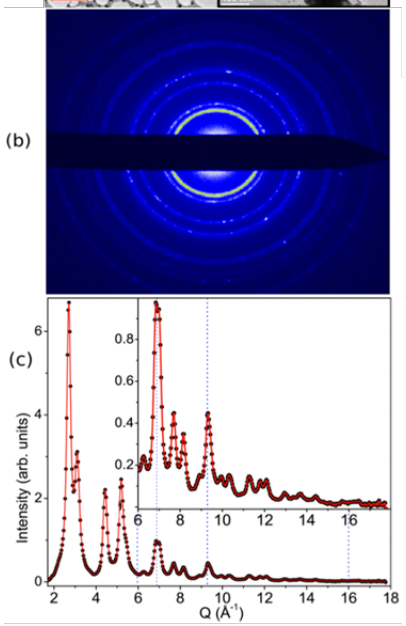




PDFs from laboratory microscopes

Au (1000) Å particles

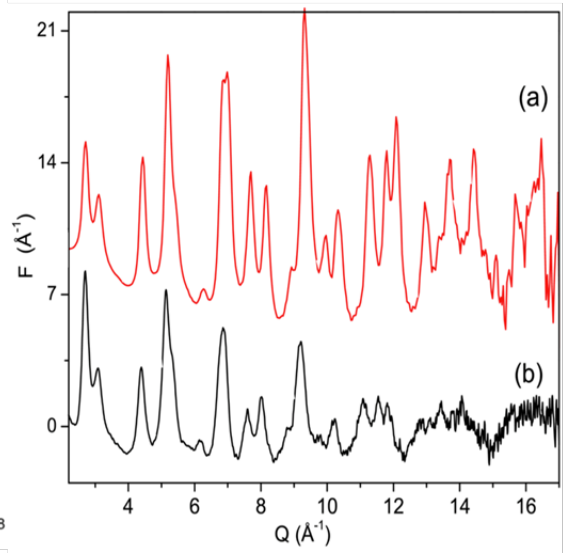


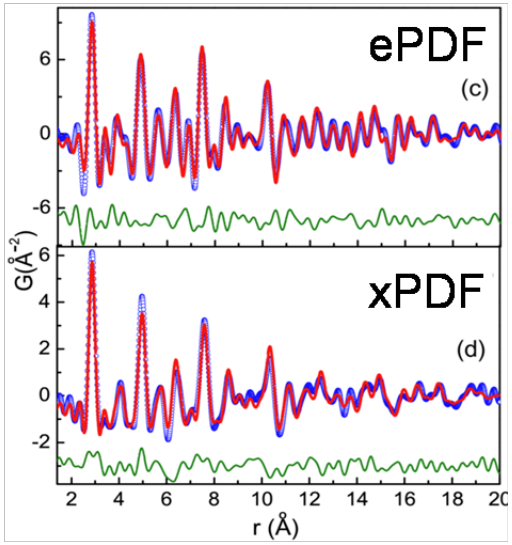


	ePDF (film)	ePDF (NP)	xPDF
Q_{max} (Å^{-1})	15.25	15.25	15.25
Fit range (Å)	1–20	1–20	1–20
Cell parameter (Å)	4.075(3)	4.076(2)	4.058(1)
U_{iso} (Å^2)	0.033(4)	0.006 (3)	0.014(1)
Diameter (Å)	~27[a]	~1000[b]	24.51(9)
Q-damp (Å^{-1})	0.095(5)	0.095(5)	0.047(2)
Rw (%)	17	24	20

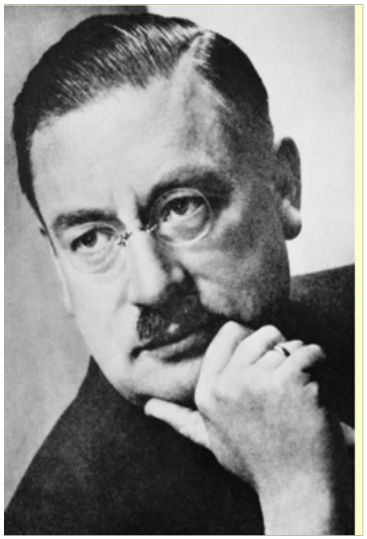
a: film thickness measured during deposition
b: NP diameter estimated directly from the TEM image

ePDFsuite software. Ask for details





Some History - Equations derived



- Pieter Debye, 1915:

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



- Fritz Zernike and Jon Prins, 1927:

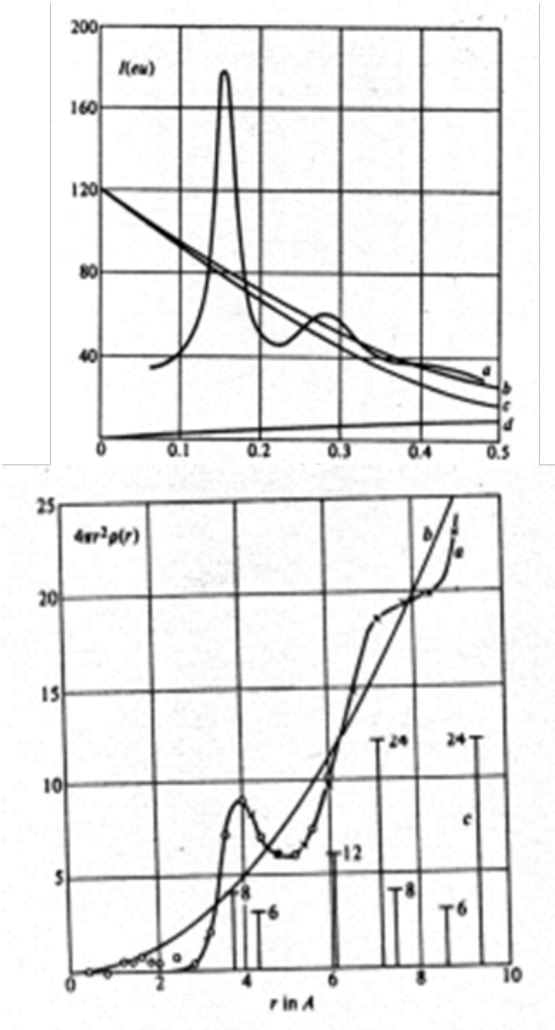
$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi} \int_0^\infty qi(q) \sin qr dq$$



Some History - Early experiments

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



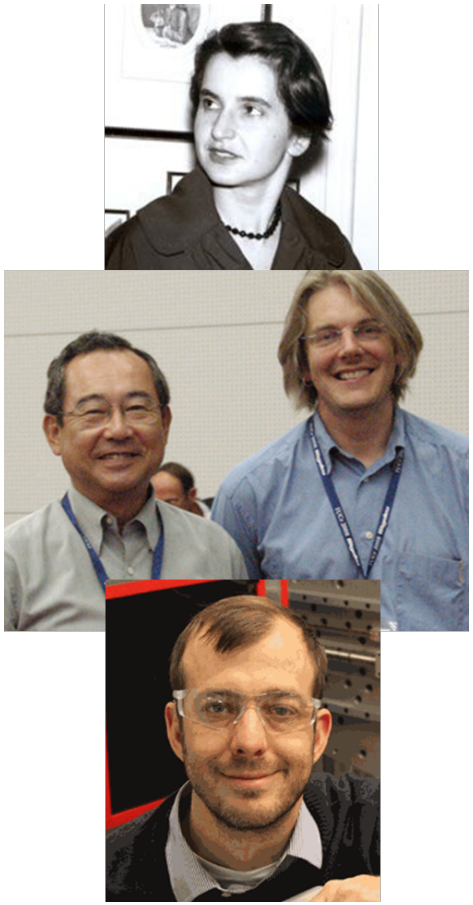


Studying (nano)crystalline materials with PDF



- 1950's Rosalind Franklin: Carbon black, disordered carbon materials
- 1960's Kaplow, Strong and Averbach: Simple metals, e.g., Lead. Interested in using them as models for liquid and glassy metals
- 1990's Takeshi Egami (and me!): Use of the newly available pulsed neutron source IPNS for quasicrystals then high temperature superconductors
- Mid-late 1990's:
  - Discovery of polarons in manganites
  - High resolution x-ray PDFs of semiconductor alloys from CHESS
- January 2000: National Nanotechnology initiative announced By Pres. Clinton
- 2003: Rapid acquisition x-ray PDF method

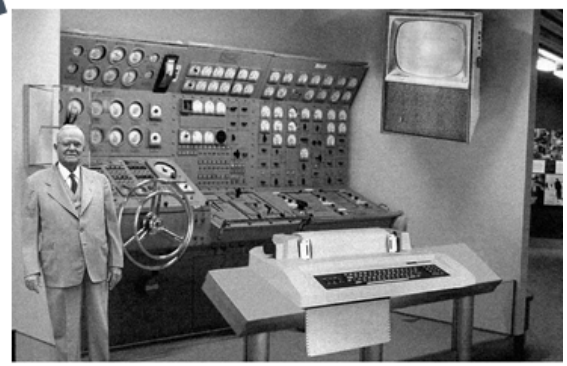
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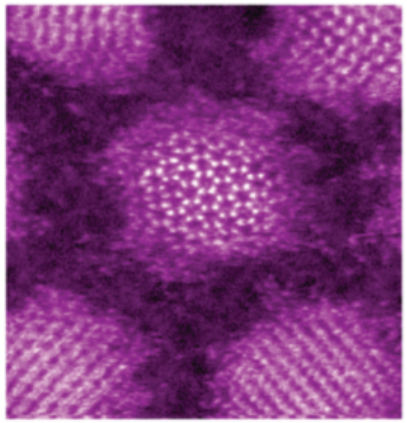


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The Perfect Storm is Now



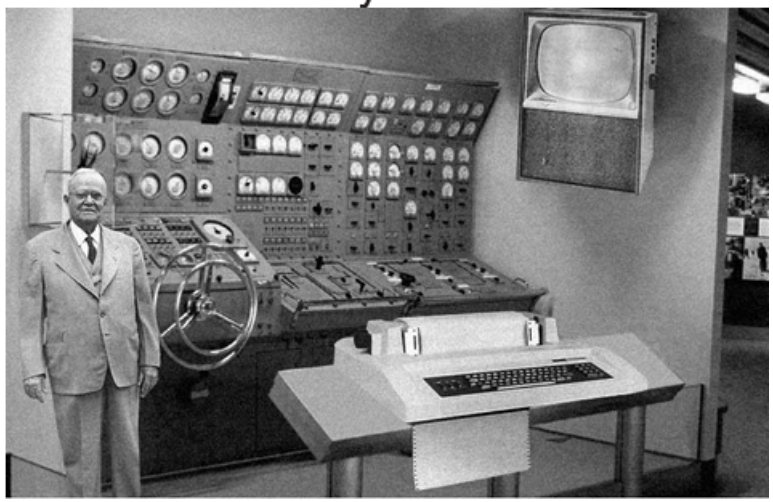




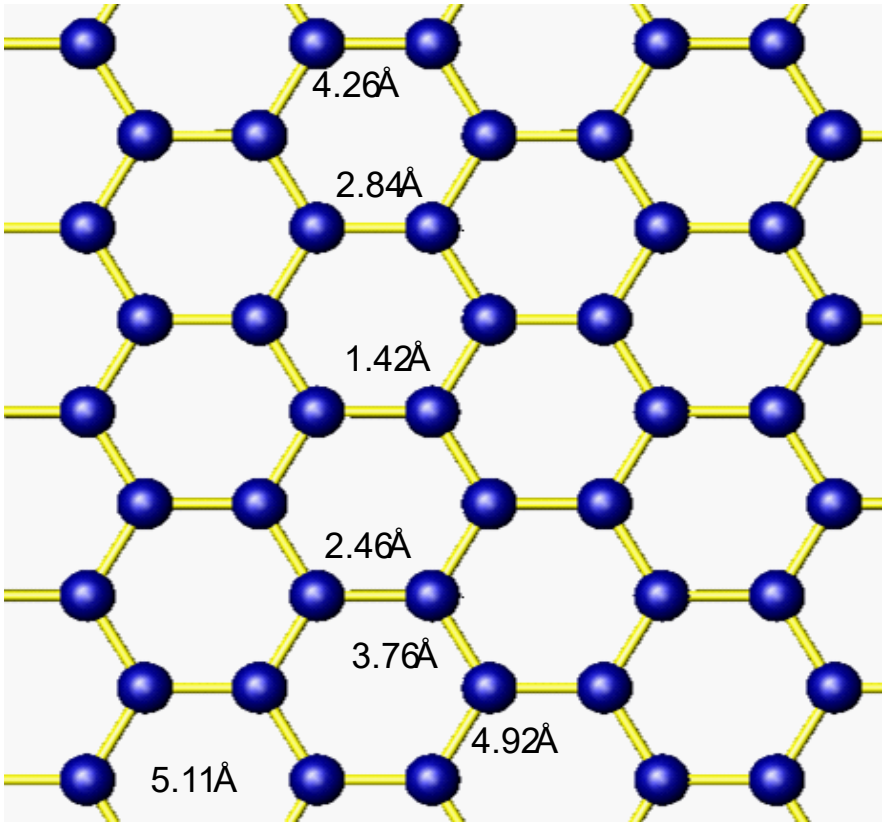
Sources/detectors + computing + nanoscience

Home Computing circa 1950

Scientists from RAND Corporation have created this model to illustrate how a "home computer" could look in the year 2004. However the needed technology will not be economically feasible for the average home. Also the scientists readily admit that the computer will require not yet invented technology to actually work, but 50 years from now scientific progress is expected to solve these problems. With teletype interface and the Fortran language, the computer will be easy to use.

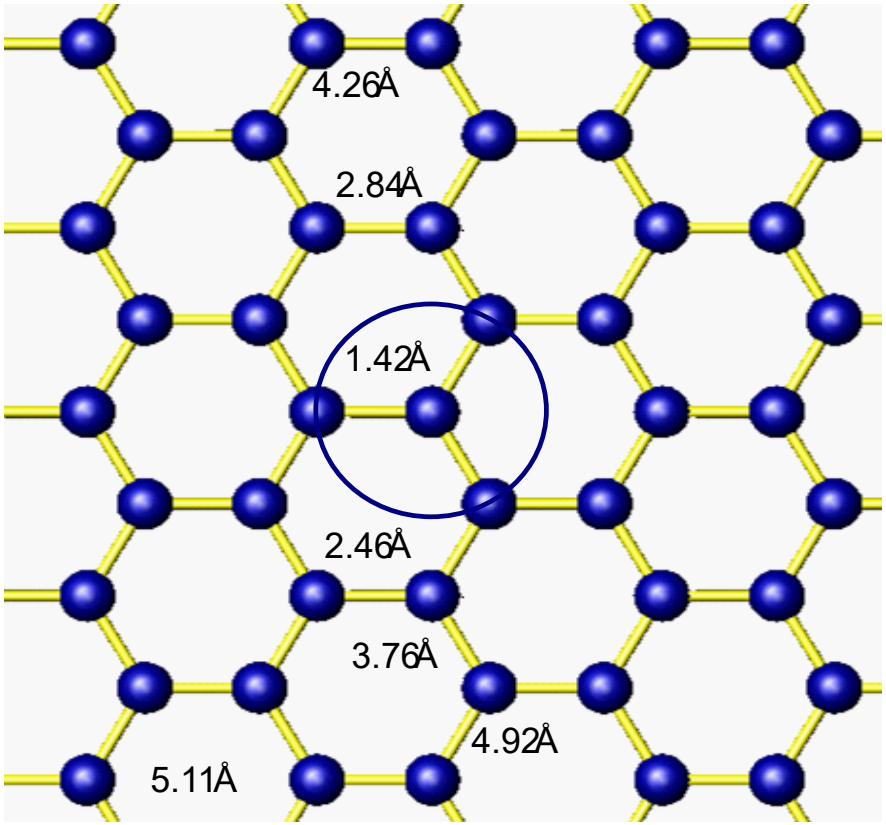


Getting the PDF from a model

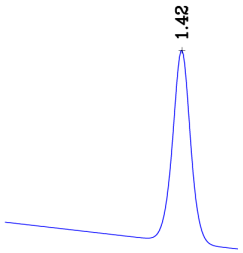


Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.

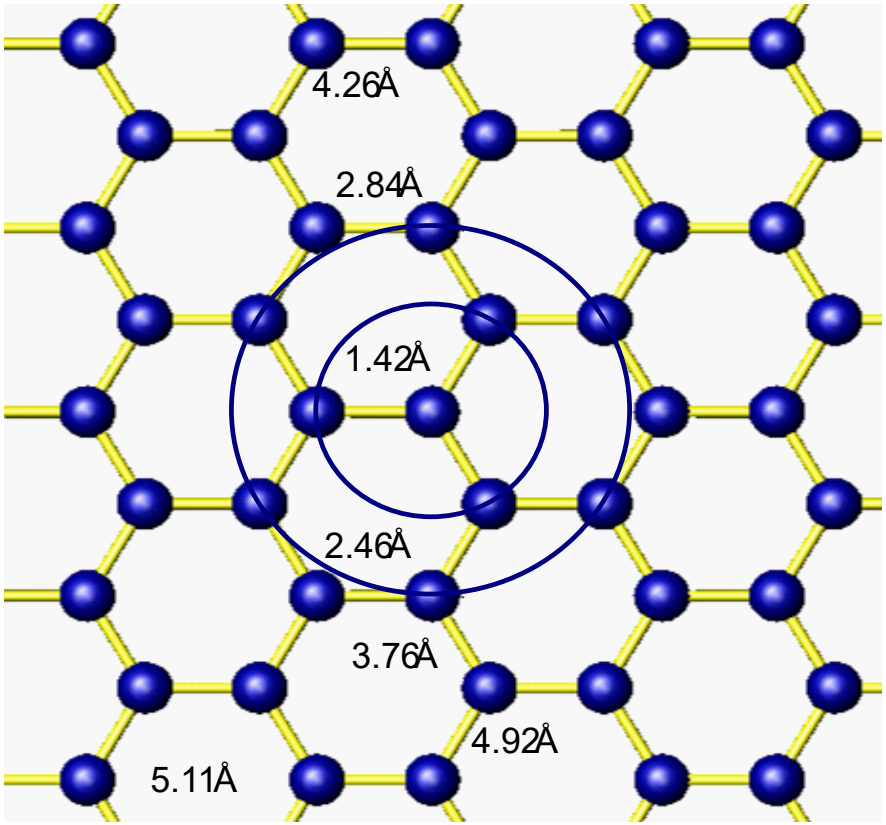
Getting the PDF from a model



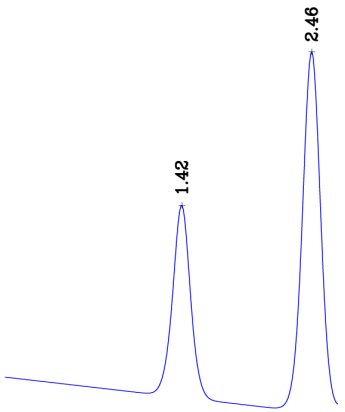
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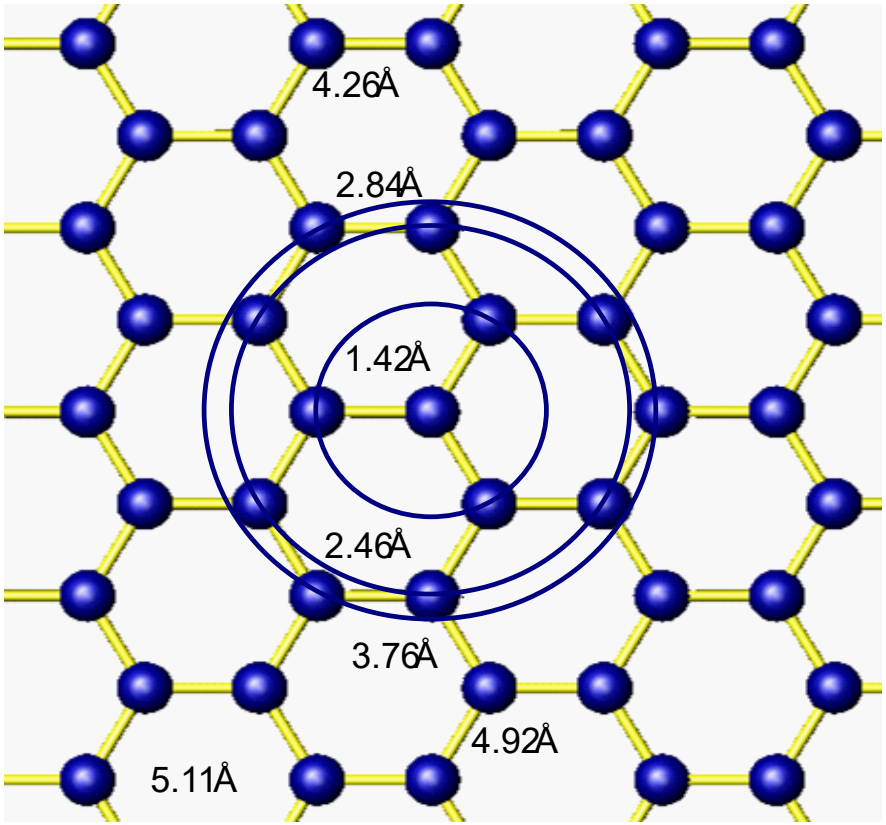
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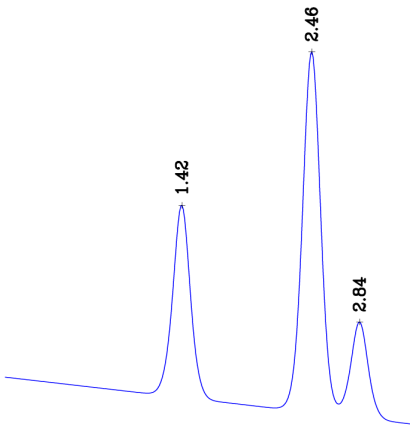
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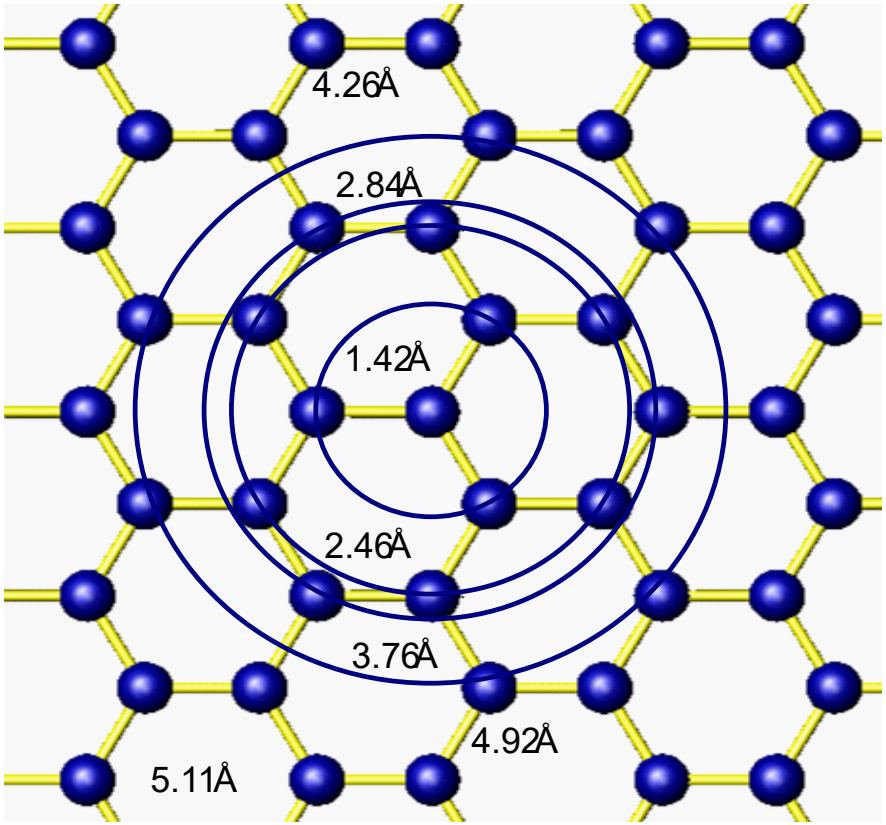
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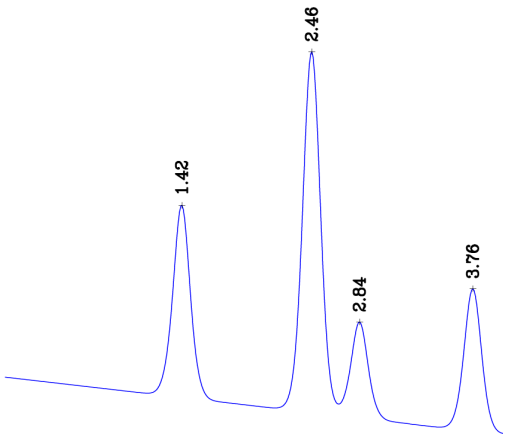
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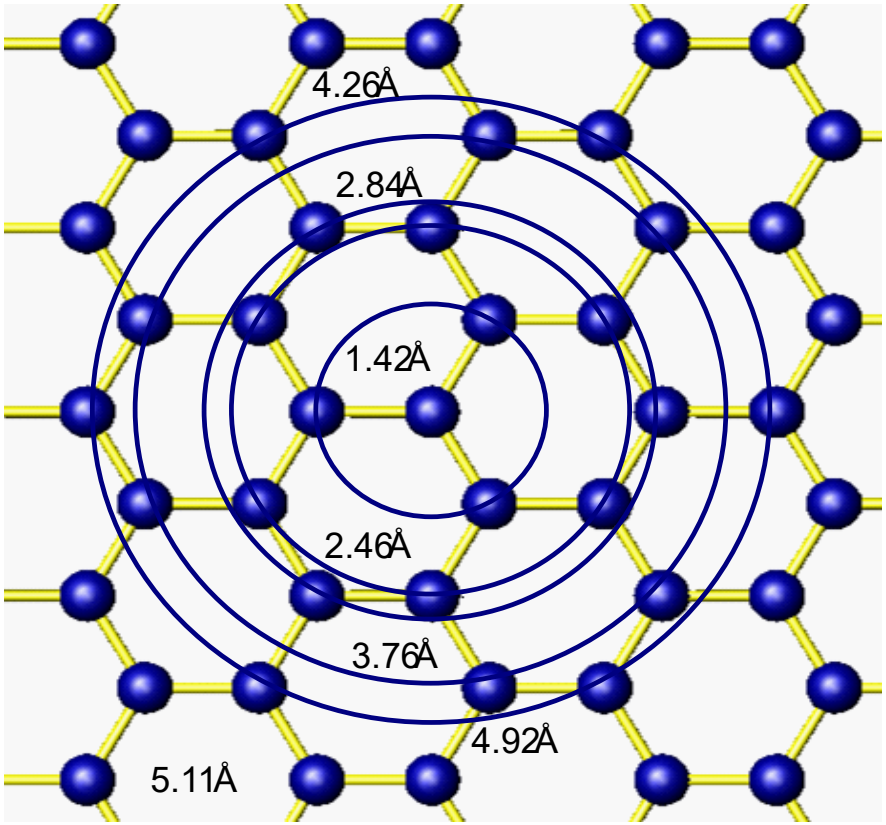
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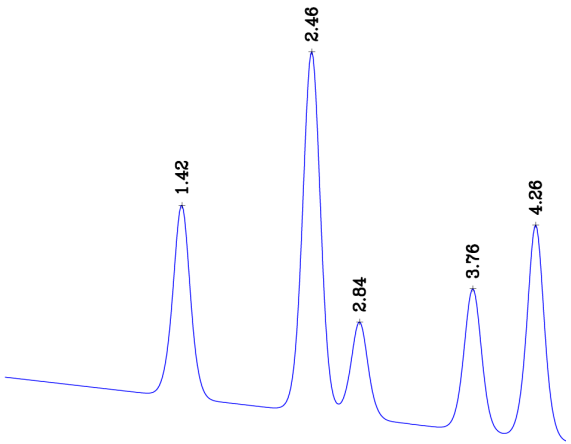
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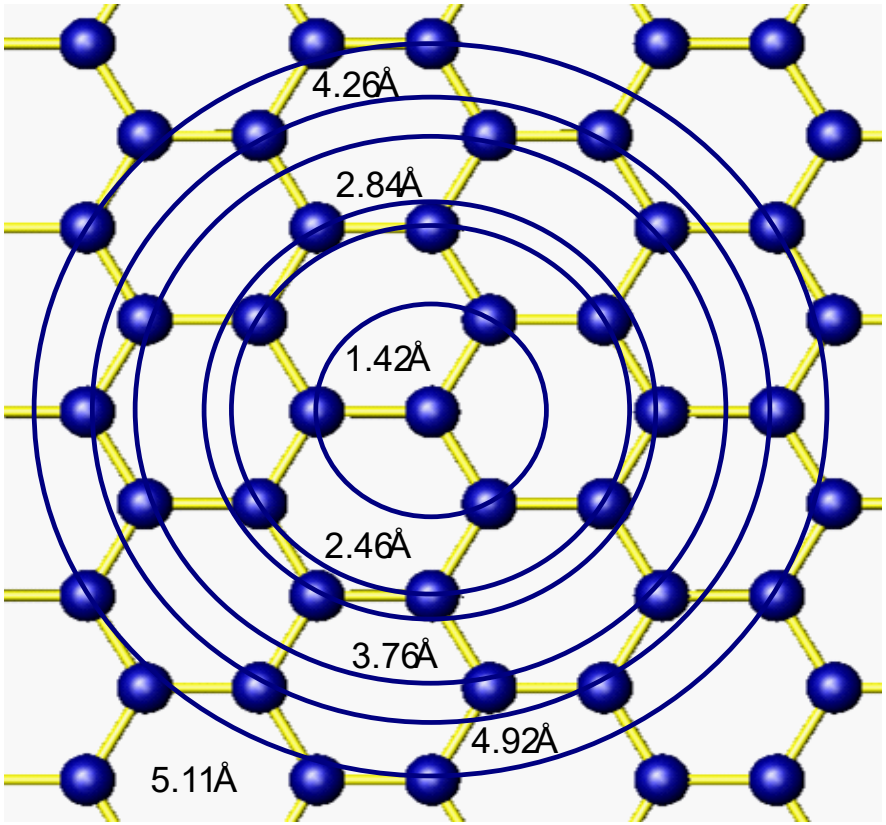
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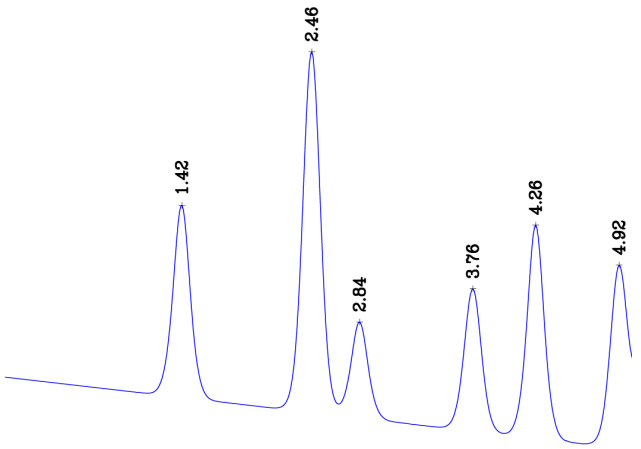
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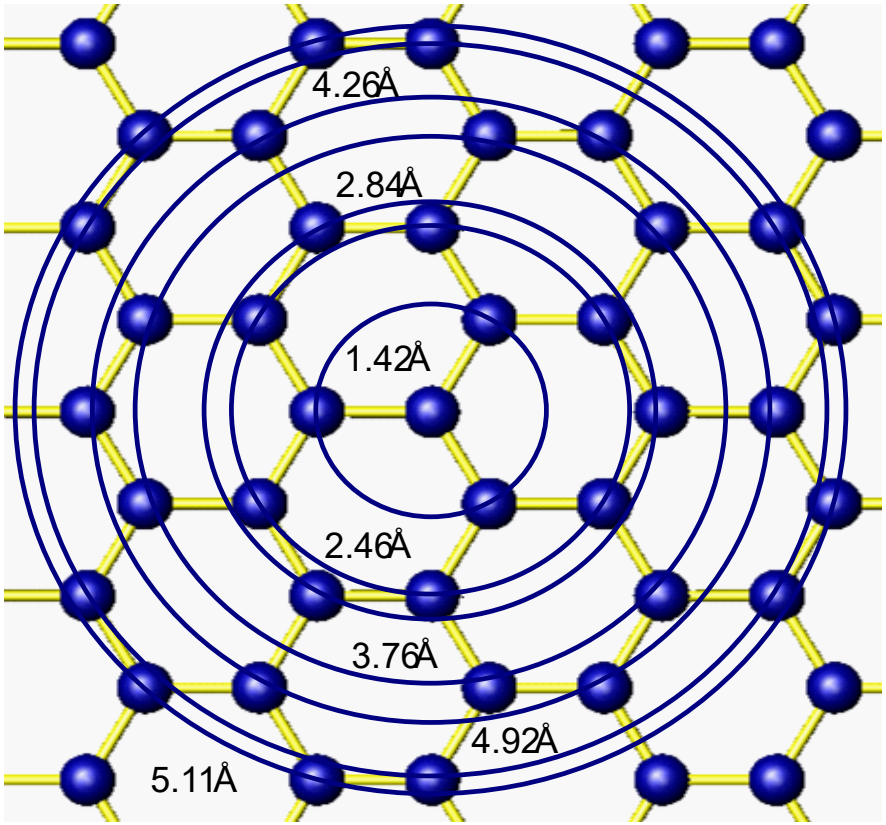
Getting the PDF from a model



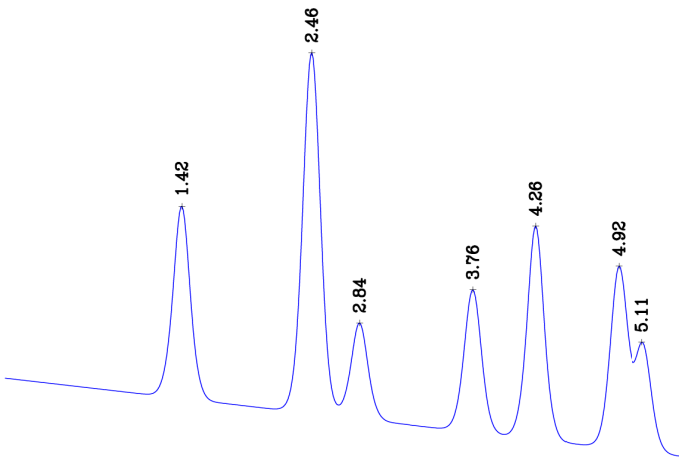
Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.



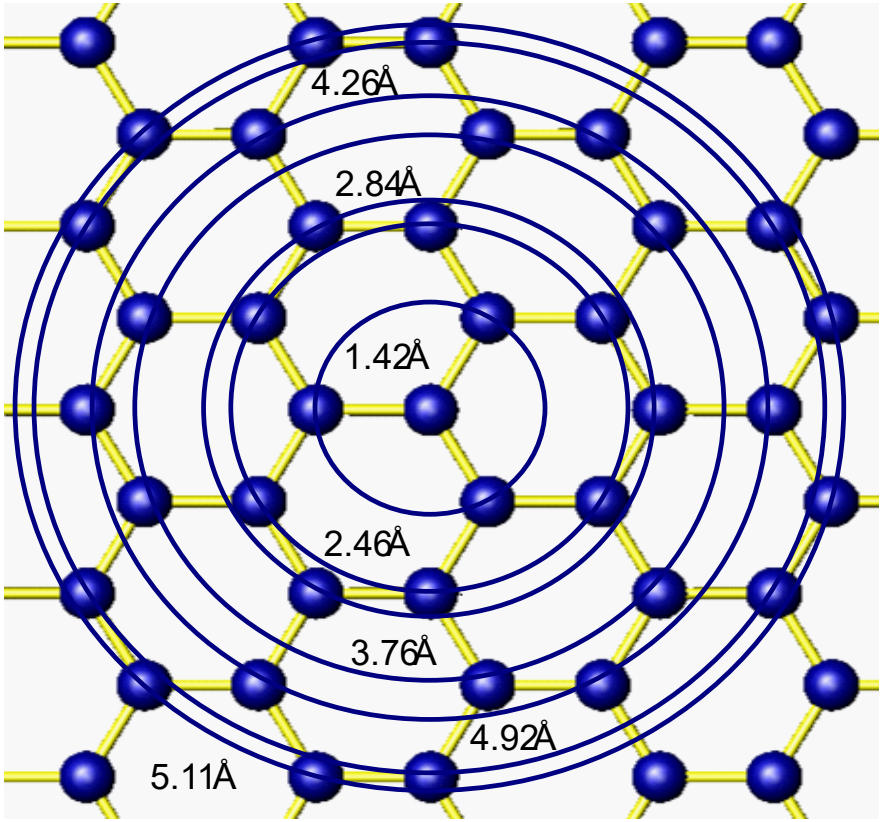
Getting the PDF from a model



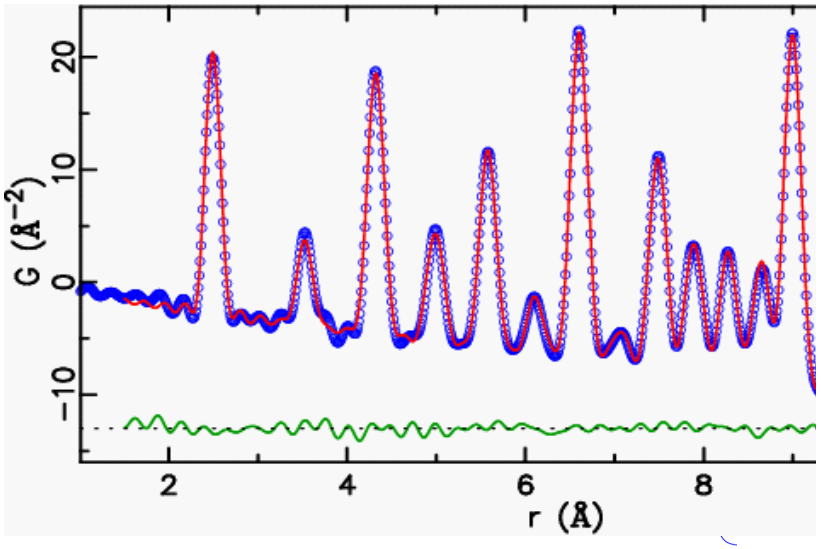
Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.



Getting the PDF from a model

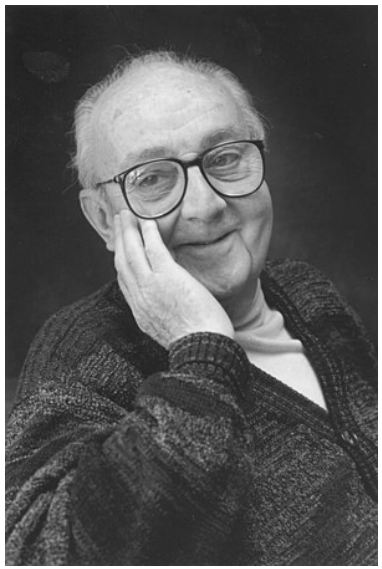


Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.



Modelling Strategies

- Small Box modeling:
  - Similar to Rietveld refinement
  - Small number of parameters, highly constrained fits
  - Danger of model bias, difficult to find distorts.
  - Exemplars: PDFgui
- Large Box modeling:
  - Large number of atoms allowed to move around
  - Small number of constraints, exploratory unbiased fitting. Good at finding distorted solutions
  - Danger of overfitting and degenerate solutions. Difficult to assess uncertainties
  - Exemplars: RMCprofile, DISCUS, EPSR (hybrid method)
- George Box modeling:
  - All models are wrong some; models are useful.
  - George E. P. Box, William Hunter and Stuart Hunter, Statistics for Experimenters, second edition, 2005.



DiffPy Community Publications Products Search

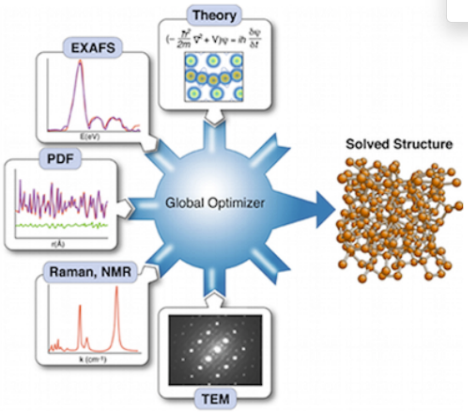
Please update your PDFgui to PDFgui v2.0, the fi ... 10, 2023)

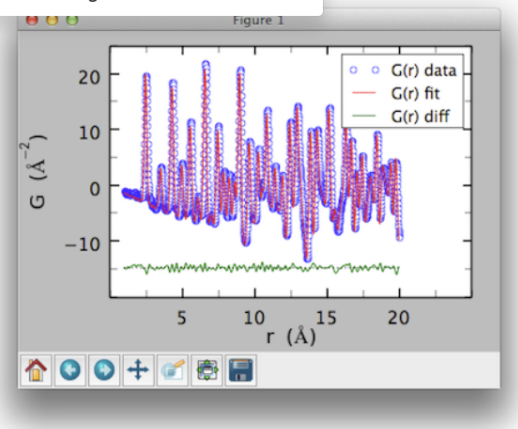
Get PDFgui v2.0 Credits

- DiffPy-CMI
- xPDFsuite
- PDFgetX3, PDFgetN3 and PDFgetS3
- PDFgui
- SrMise
- mPDF
- xINTERPDF
- Python Packages

DiffPy - Atomic Struc ... Python

A free and open source software project to provide p ... e study of the atomic structure of materials.

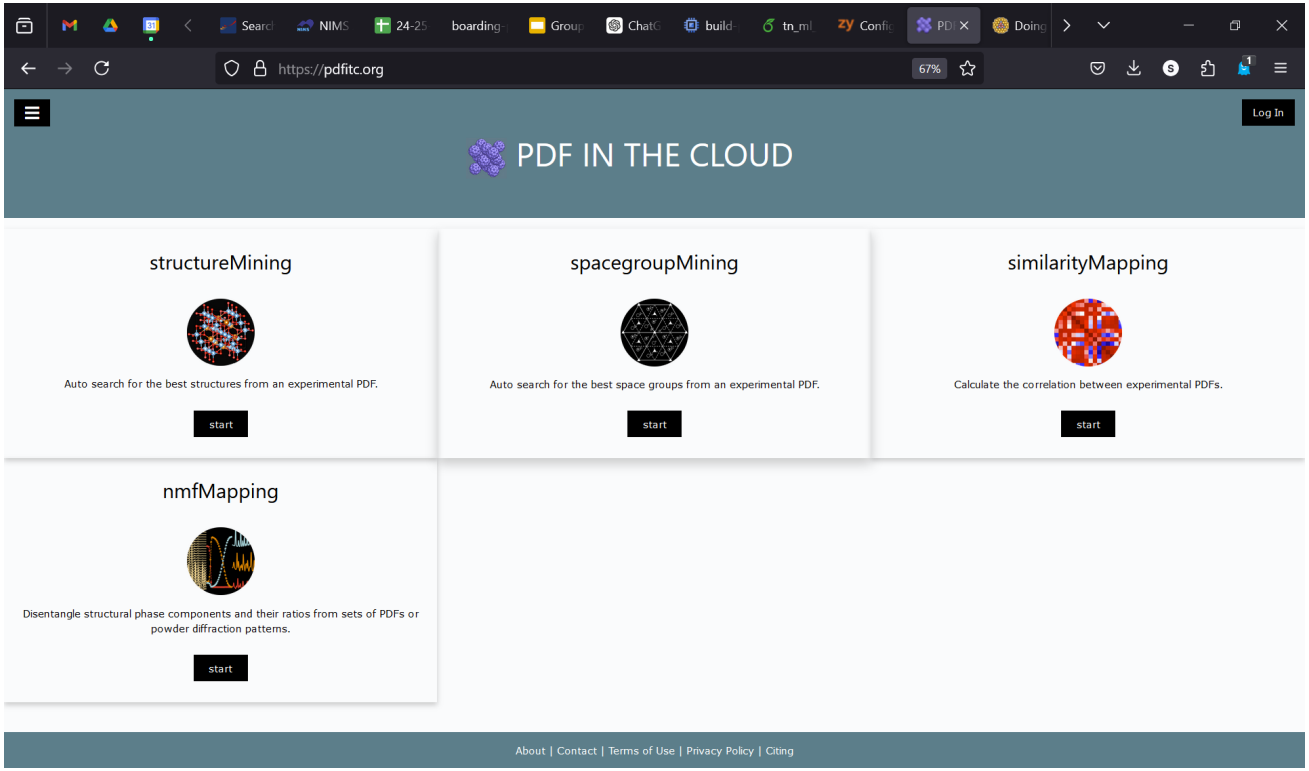




DiffPy is the home of the DiffPy-CMI Complex Modeling framework, a modular software framework for robust and extensible modeling of diffraction data. We welcome contributions to this project from the community.

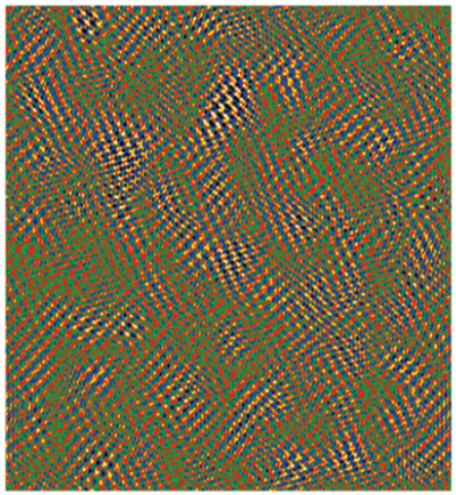
https://diffpy.org - home of Billinge-group software

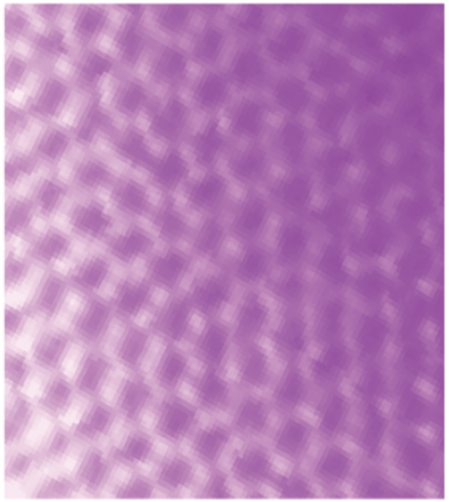
Deploying ML models in production

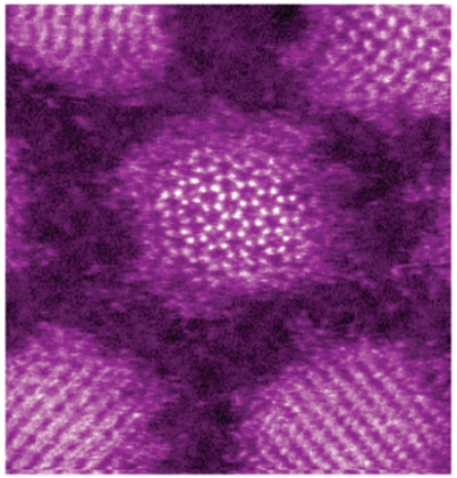


https://pdfitc.org

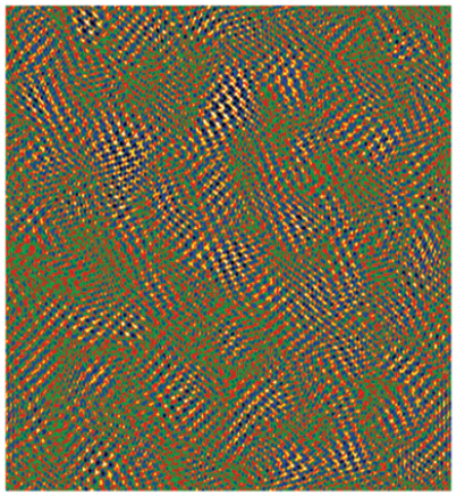
Types of nanostructure

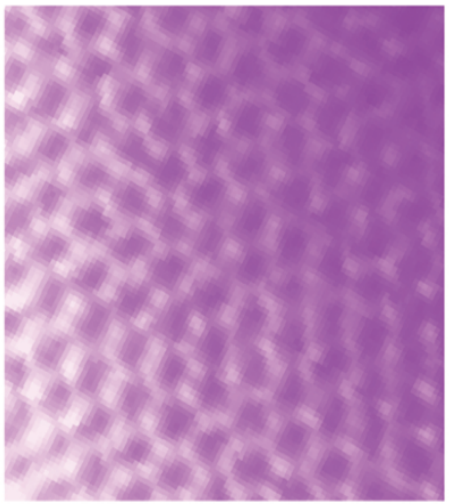


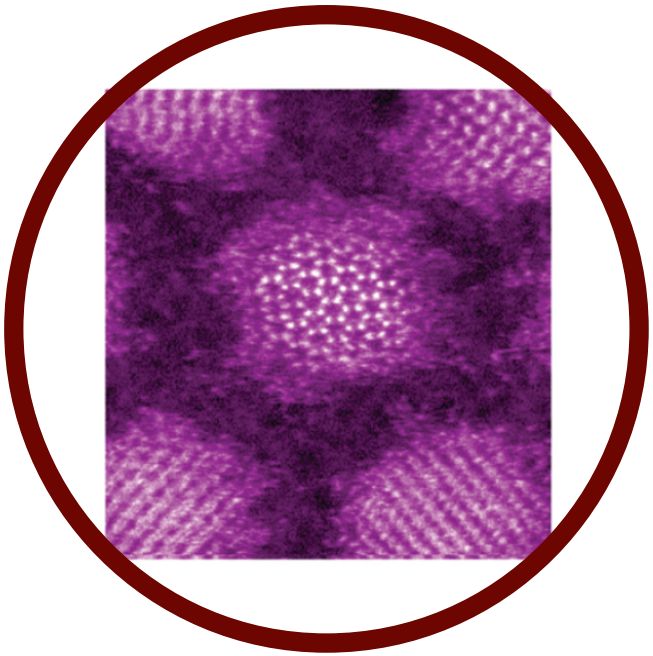




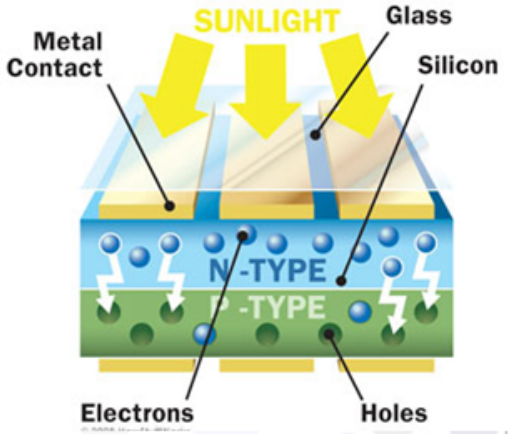
Types of nanostructure

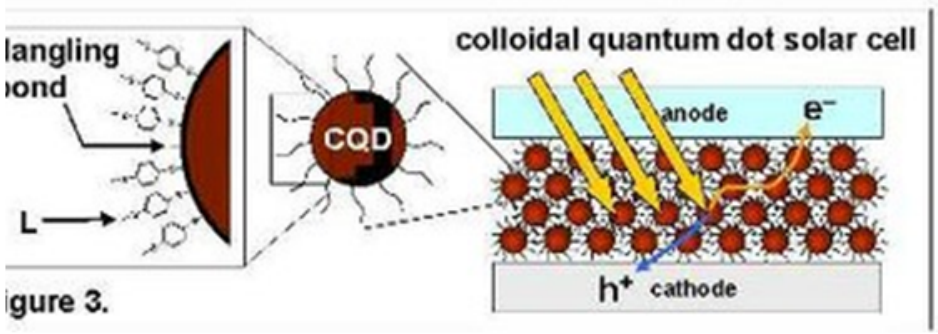


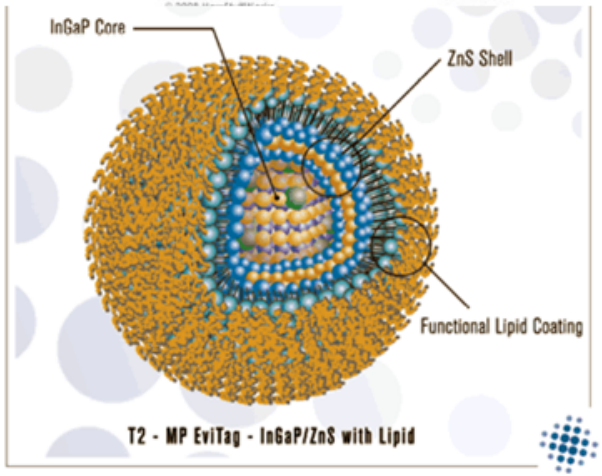




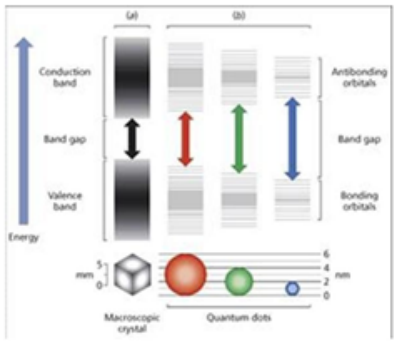
Semiconductor Quantum Dots



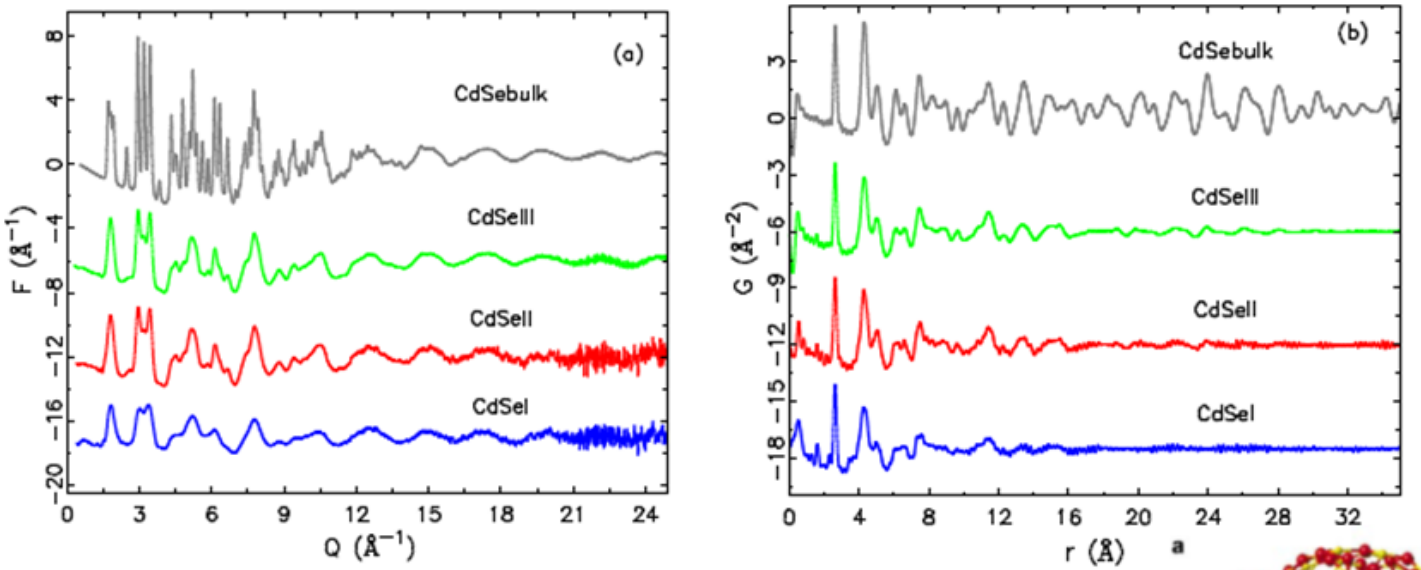




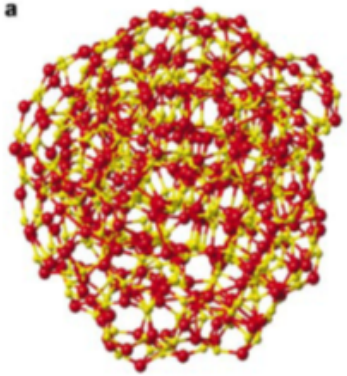




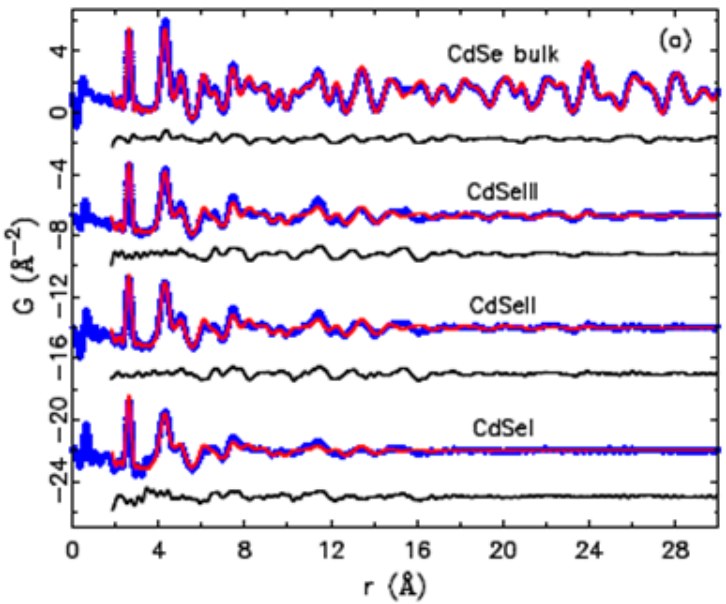
CdSe Quantum Dots

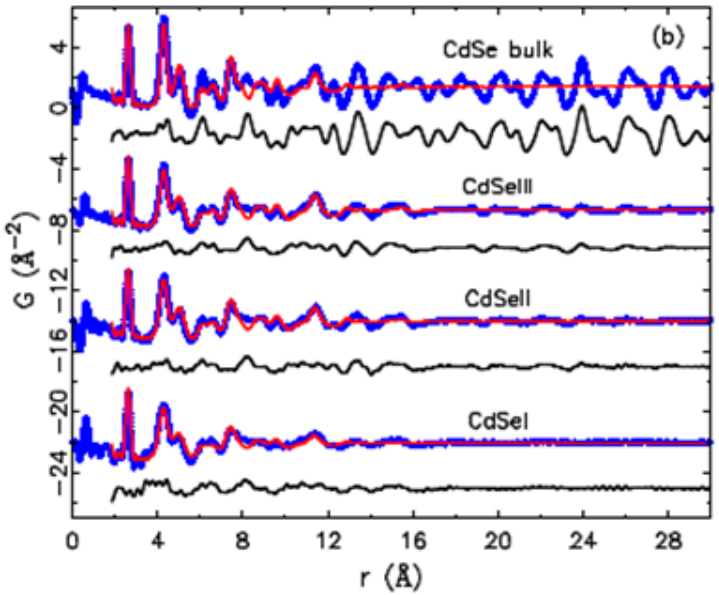


- RAPDF experiments at APS, Sector 6
- Work of grad student Ahmad Masadeh
- Masadeh, SJB *et al.* PRB **76**, 115413 (2007)

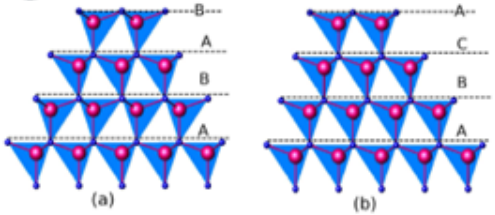


What is the structure of their core?

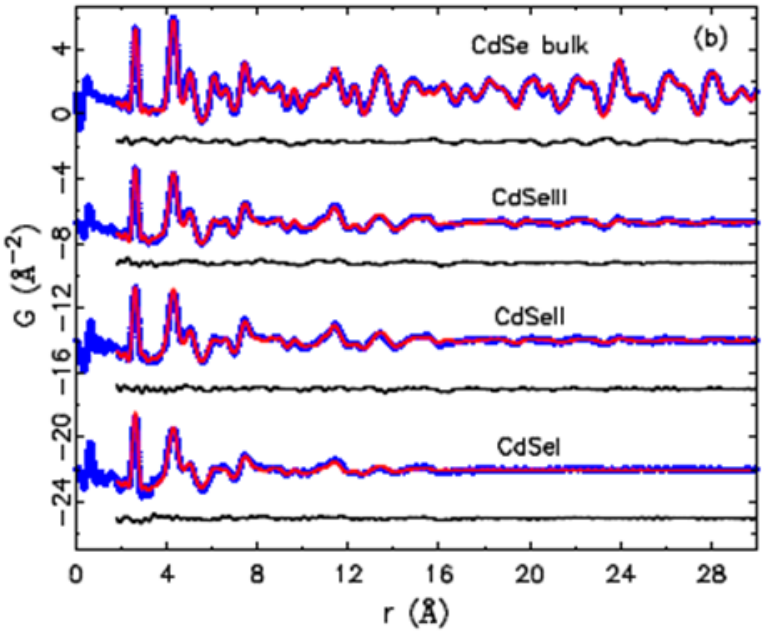




- Wurtzite structure
- Zinc blende structure



What is the structure of their core?

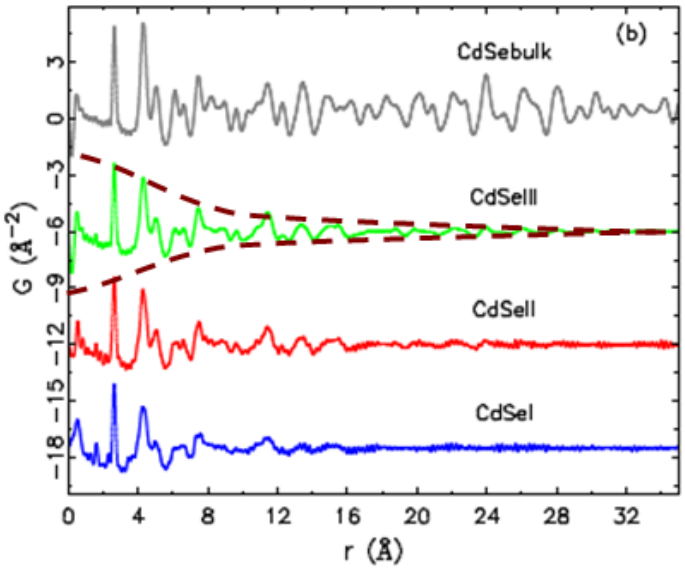


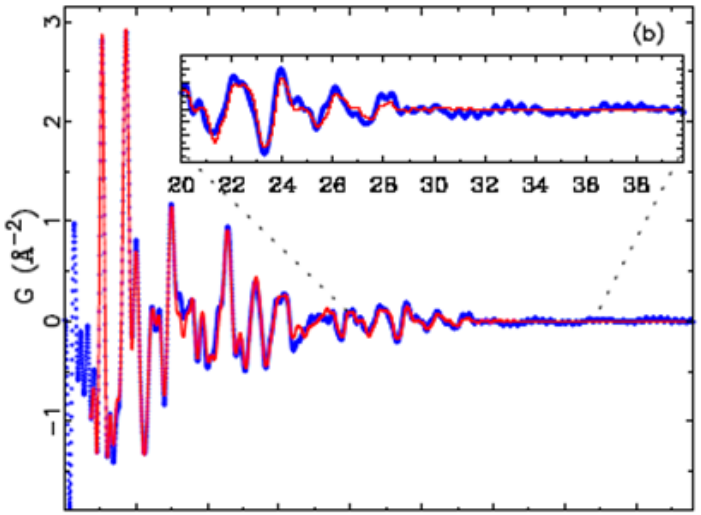
Masadeh, SJB *et al.* PRB **76**, 115413 (2007)

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-fmc.*	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

What is the size of their core?





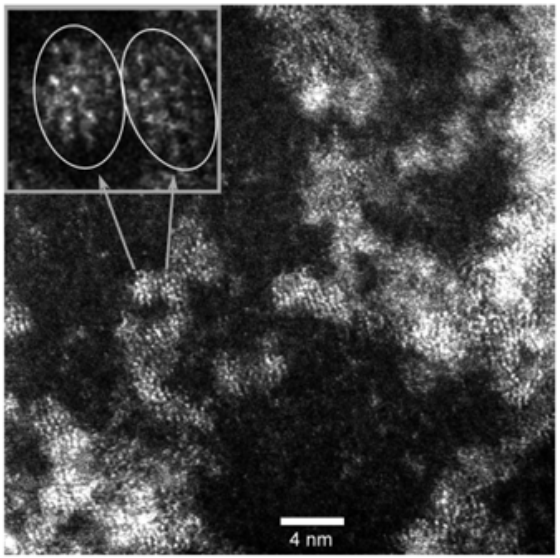
$$f(r,d) = \left[1 - \frac{3r}{2d} + \frac{1}{2}\left(\frac{r}{d}\right)^3\right]\Theta(d-r),$$

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

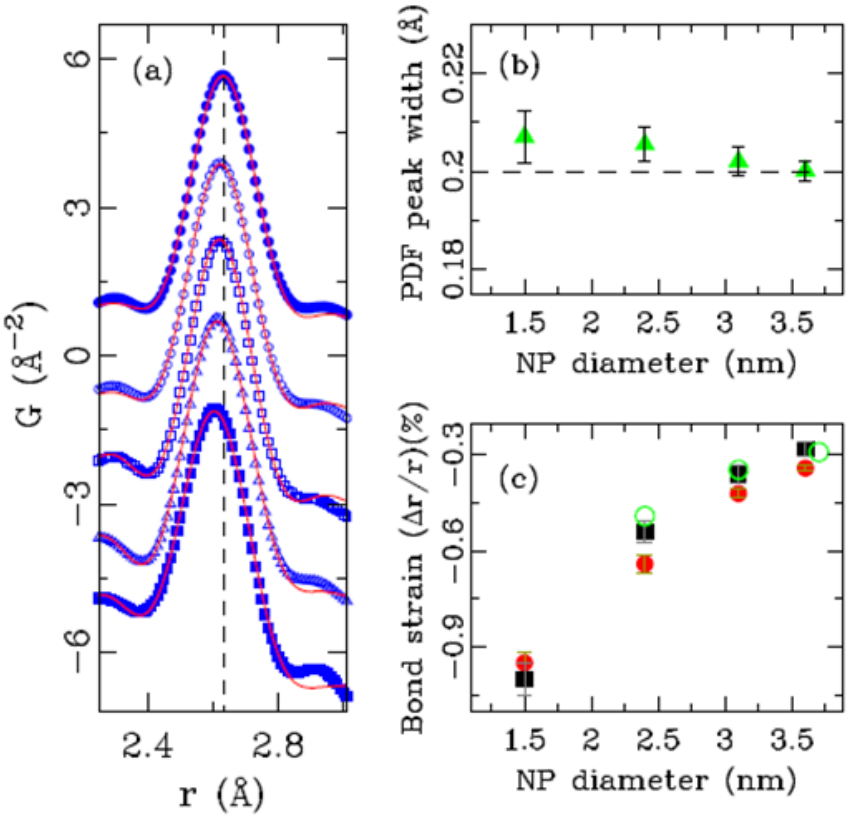
TABLE I: CdSe nanoparticle diameter as determined using various methods.

	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)

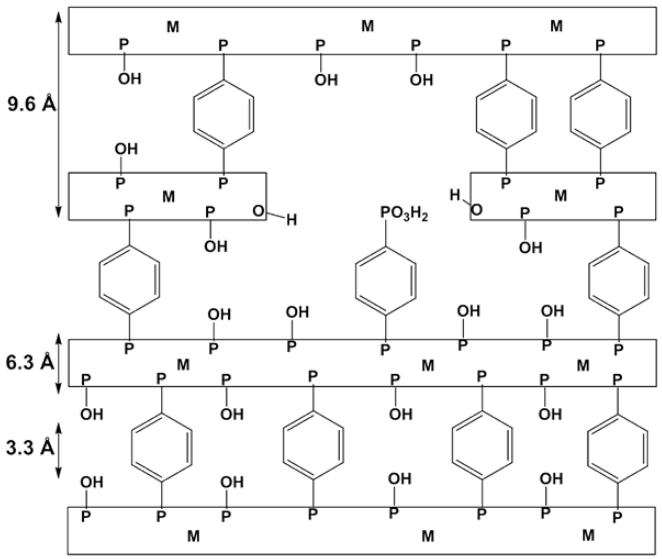
Do they have a size-dependent strain?

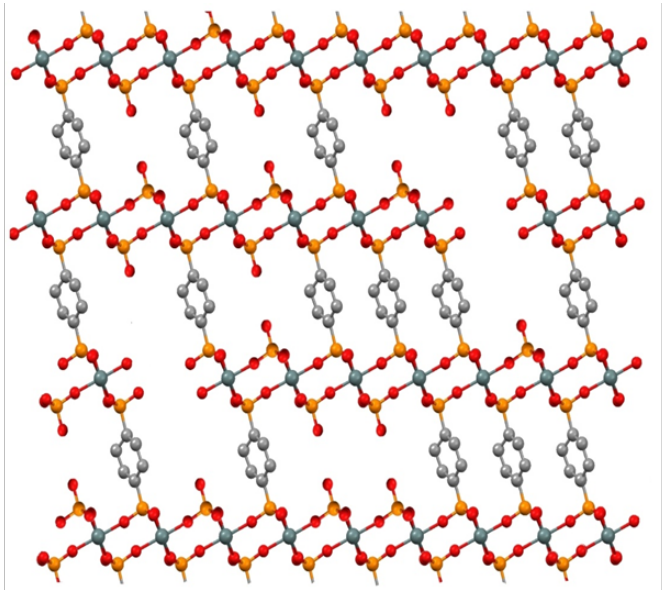


- Xiaohao Yang, Masadeh, McBride, Bozin, Rosenthal and SJLB, *Phys. Chem. Chem. Phys.* **15**, 8480-8486 (2013)



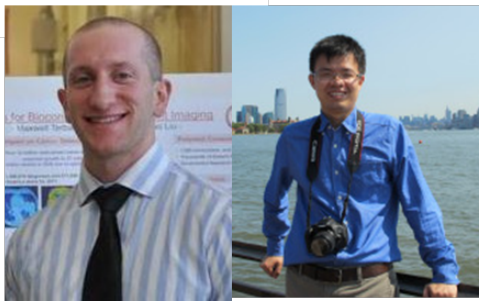
Zr/Sn phenyl phosphate, unconventional MOFs





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

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



Structure of small gold clusters

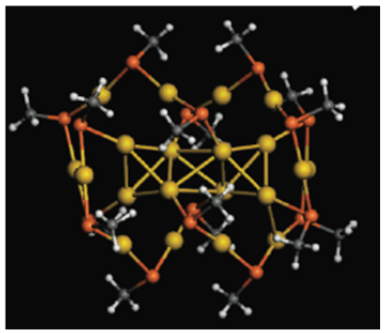
J|A|C|S COMMUNICATIONS

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



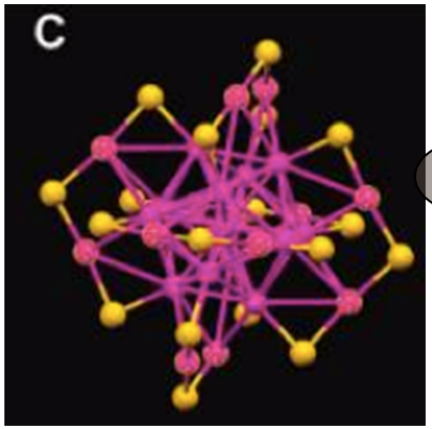
20

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

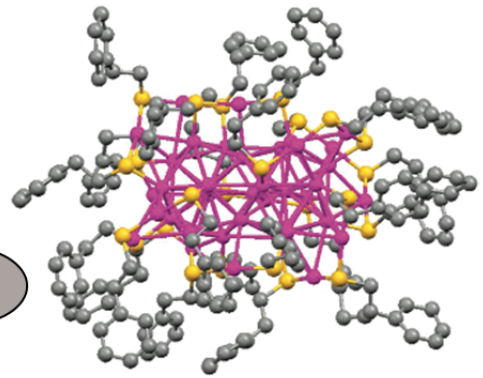
J|A|C|S COMMUNICATIONS

Published on Web 06/01/2010

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

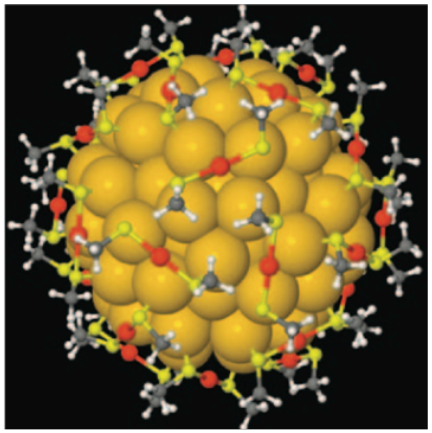
Huifeng Qian,† William T. Eckenhoff,‡ Yan Zhu,† Tomislav Pintauer,‡ and Rongchao Jin*,†

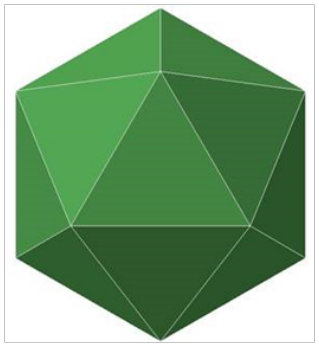
Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 and Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania 15282

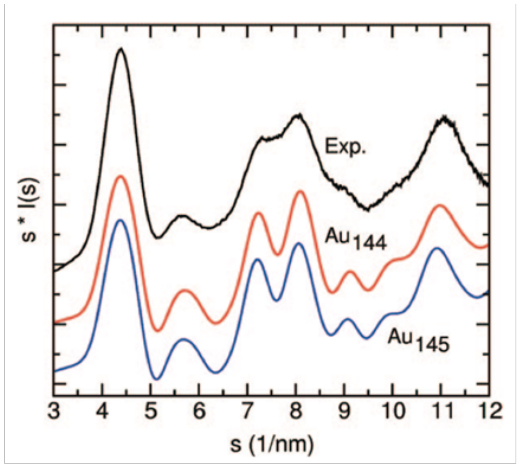


38

DFT study of Au144 structure







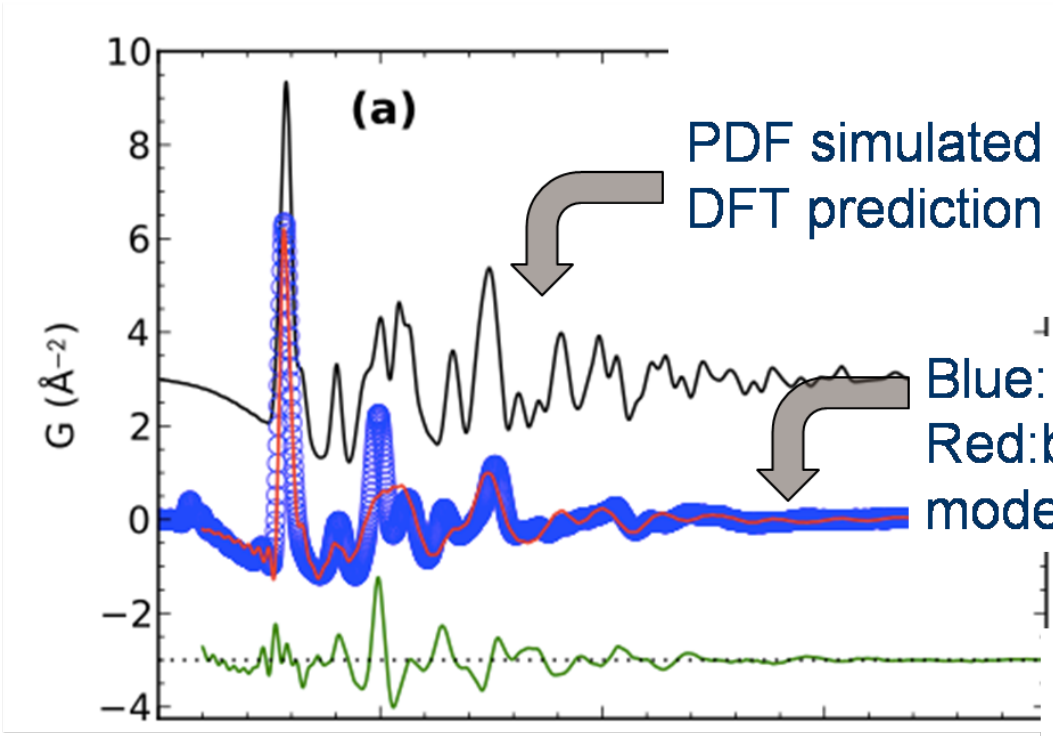
Icosahedral core

Au/S surface structure with ligand attachment

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

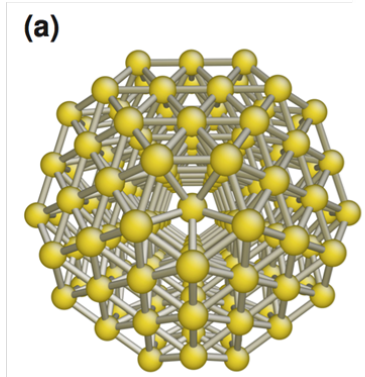
Olga Lopez-Acevedo,[†] Jaakko Akola,[†] Robert L. Whetten,[‡] Henrik Grönbeck,[§] and Hannu Häkkinen*,[†,∥]

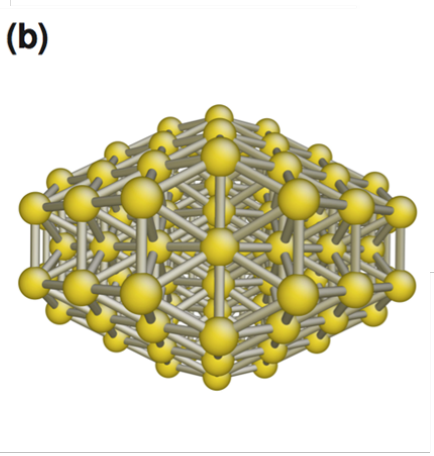
Structure of small gold clusters

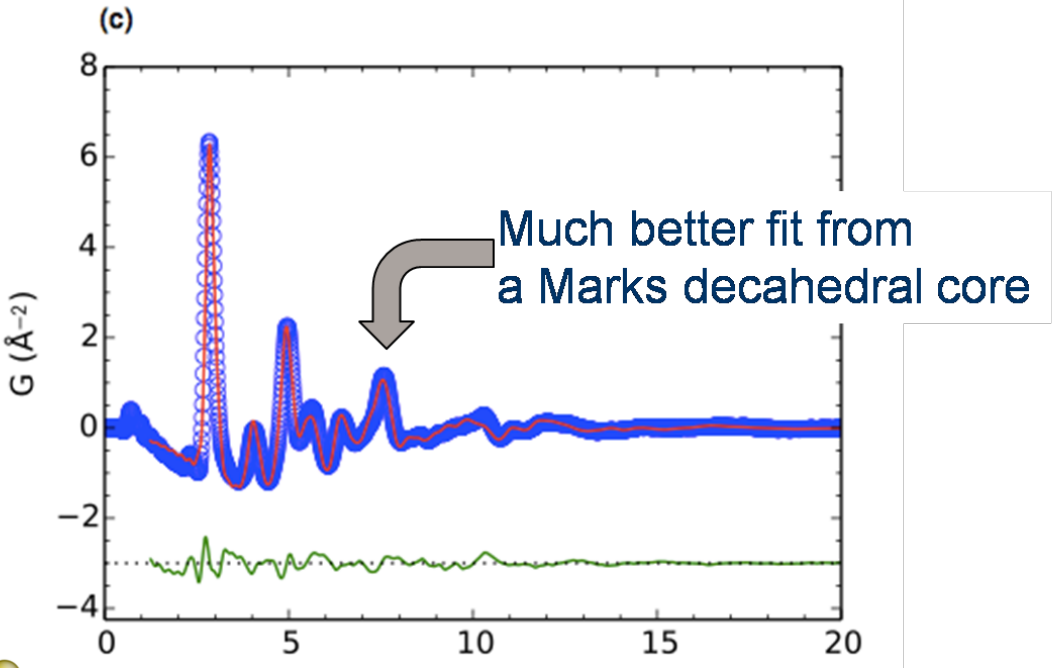


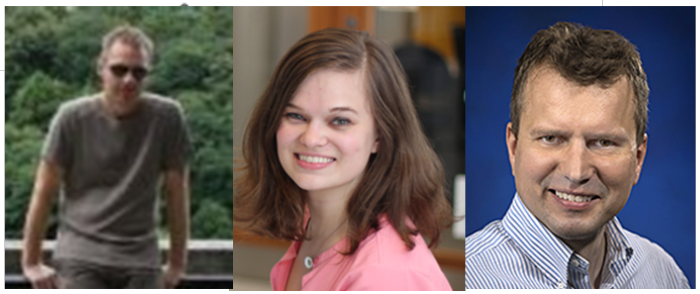
Refinement:
Expansion factor
Thermal parameters for core
Thermal parameters for surface
Correlated motion

The MD6441 structure: 144 gold atoms







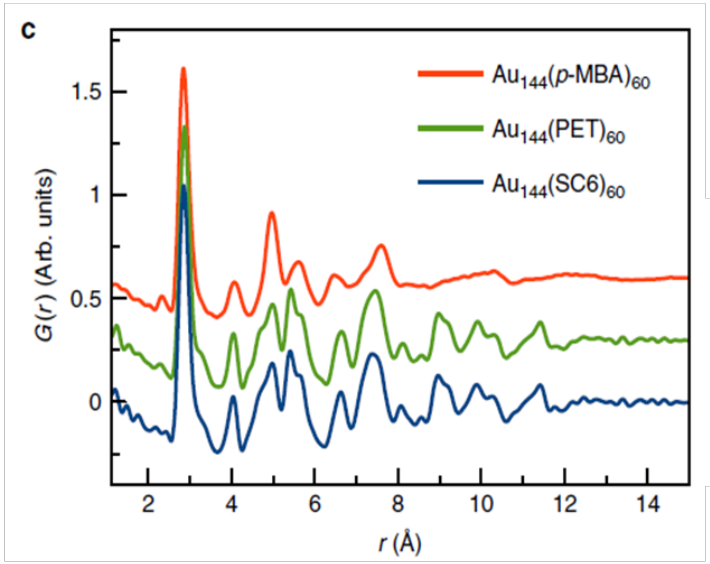


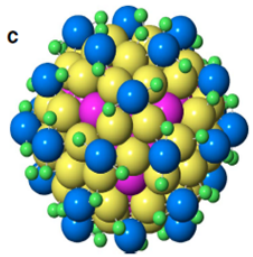
Structure of small gold clusters

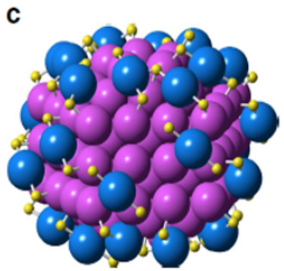
NATURE COMMUNICATIONS | 7:11859 | DOI: 10.1038/ncomms11859
ARTICLE
Received 22 Aug 2015 | Accepted 6 May 2016 | Published 14 Jun 2016
DOI: 10.1038/ncomms11859 OPEN

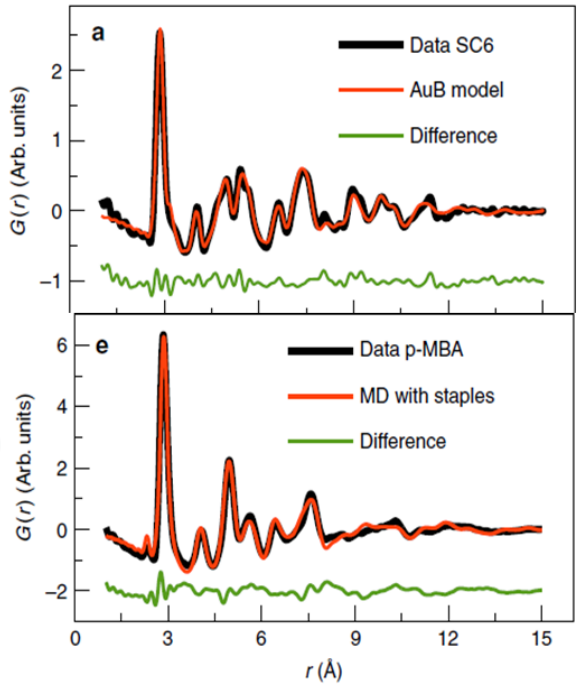
Polymorphism in magic-sized $Au_{144}(SR)_{60}$ clusters

Kirsten M.Ø. Jensen[1,*], Pavol Juhas[2,*], Marcus A. Tofanelli[3], Christine L. Heinecke[3], Gavin Vaughan[4], Christopher J. Ackerson[3] & Simon J.L. Billinge[1,2]

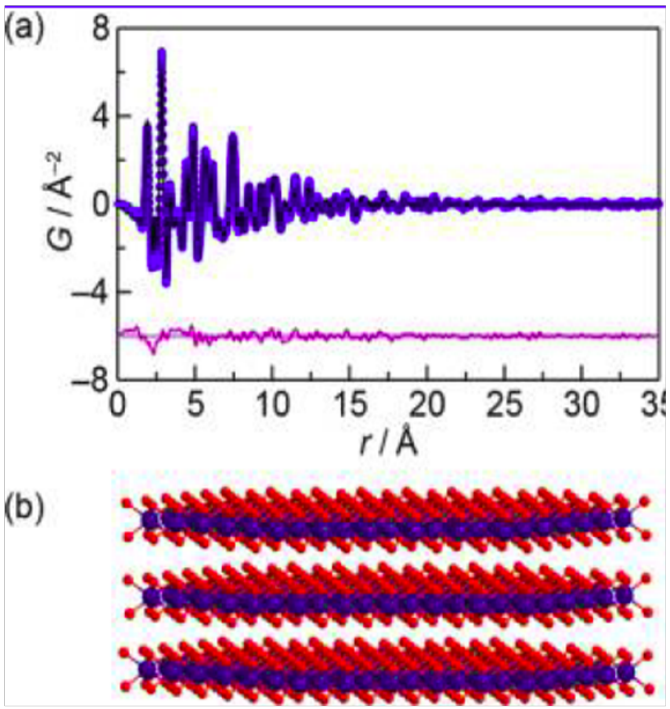


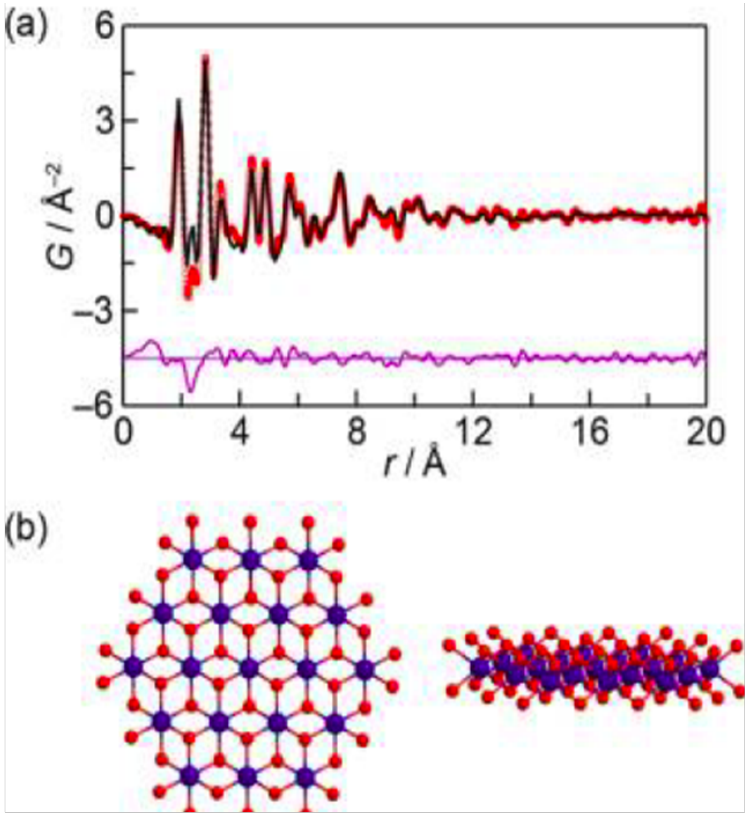






CoO catalysts for the OER (oxygen evolution reaction)

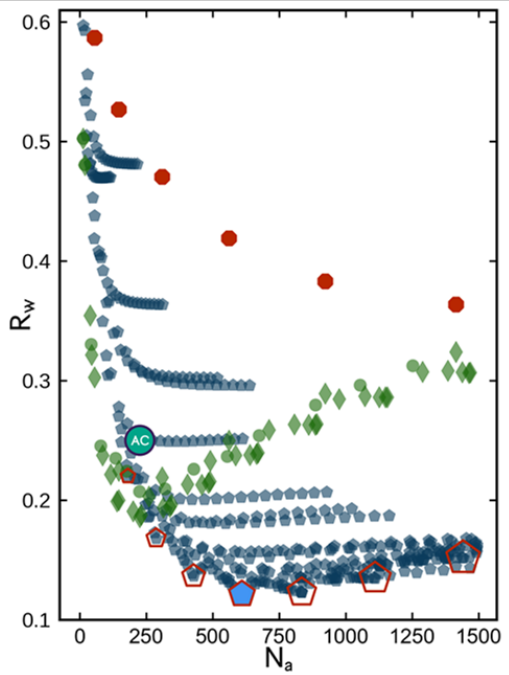


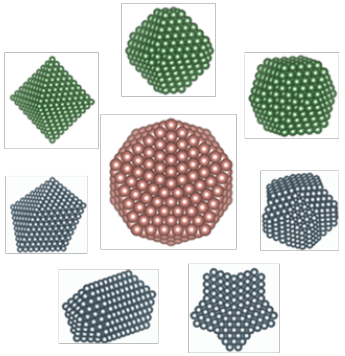


C. L. Farrow, SJB, Dan Nocera et al. *J. Am. Chem. Soc.* **135**, 6403 (2013).

Clustermining

- Build cluster families and variants algorithmically
- Test them against the provided data in a "screening" approach
- Brute force method finds good solutions but is slow







Banerjee, SJLB, et al. "Cluster-mining: An approach for determining core structures of metallic nanoparticles from atomic pair distribution function data". In: Acta Crystallogr. A 76.1 (2020), pp. 24–31. doi: 10.1107/S2053273319013214.

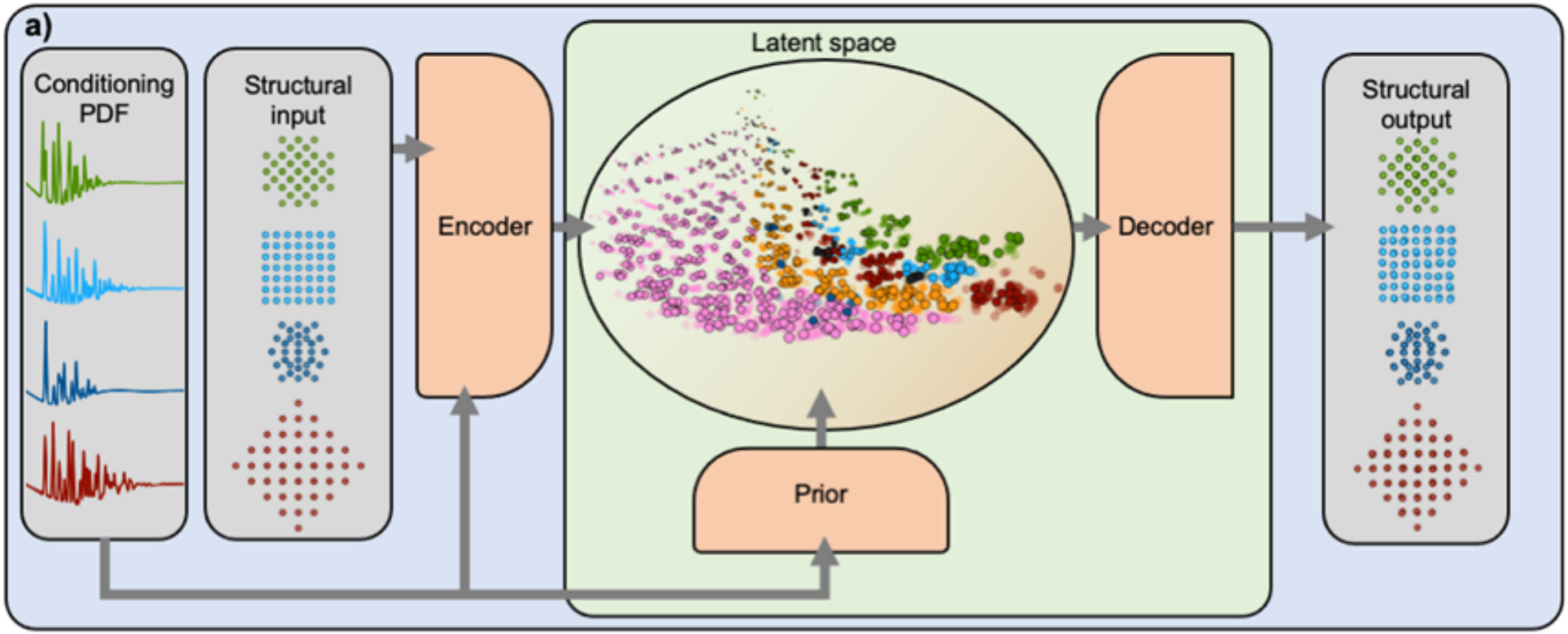
Case 1: close packed structures

Let's do close-packed structures that interpolate

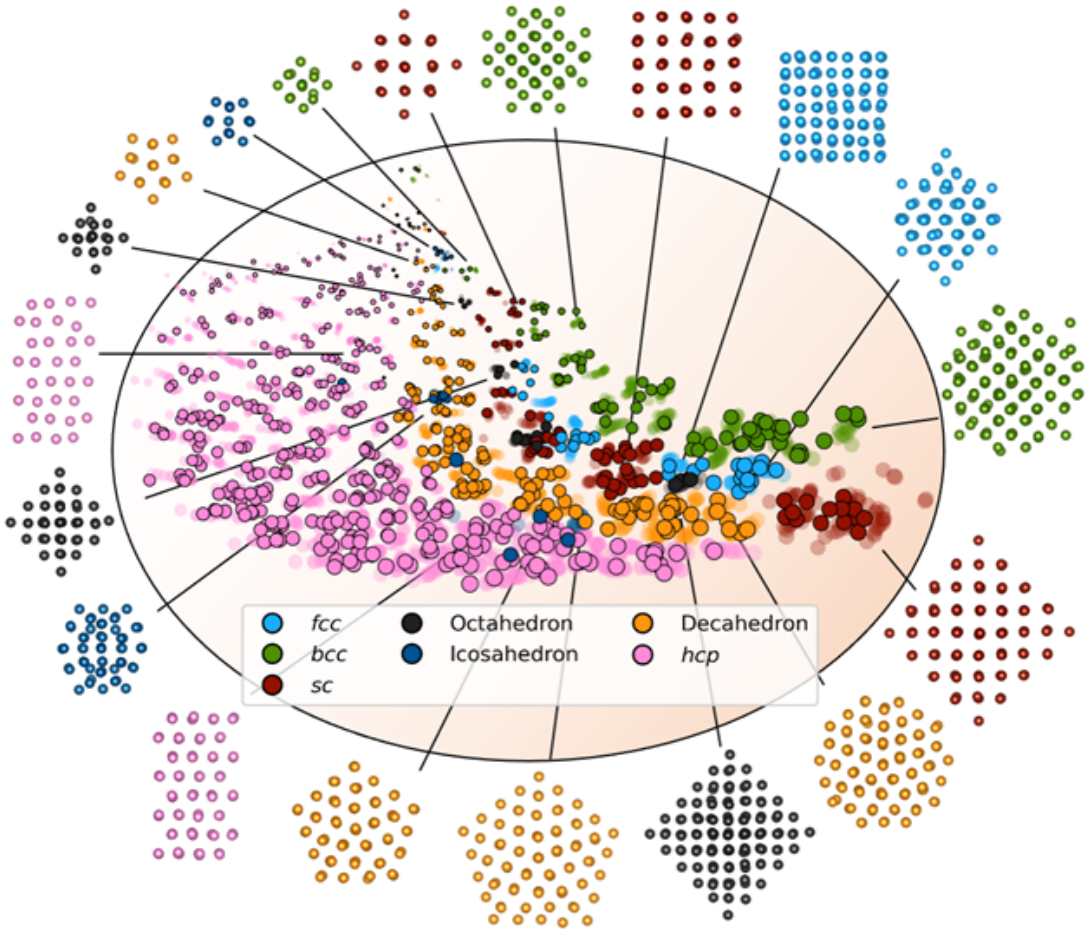
- Graph Convolutional Variational Autoencoder (CVAE)
- Collaboration with Kirsten Jensen, Raghav Selvan, U. Copenhagen
- Work of students Emil Kjaer and Andy Anker
- Kjaer, Anker, et al., Digital Discovery (2023), 10.1039/D2DD00086E

Structure solution using Neural Nets

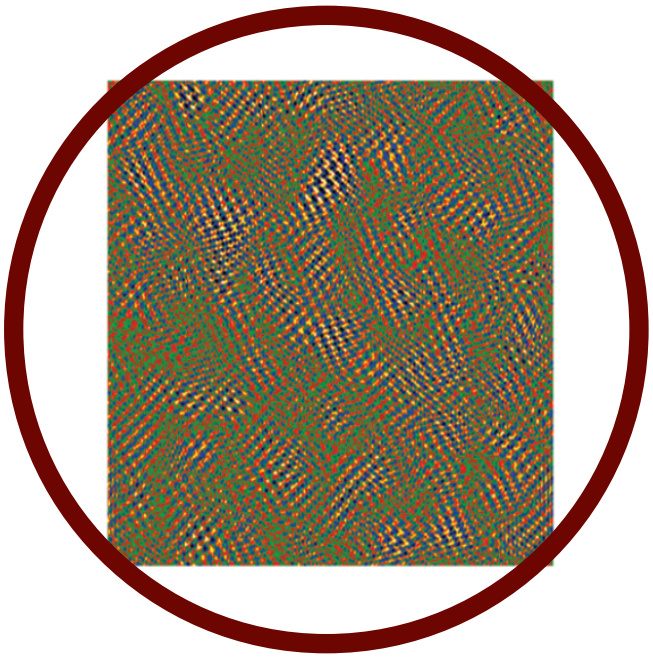
Deepstruc: close packed nanoparticles with a CVAE

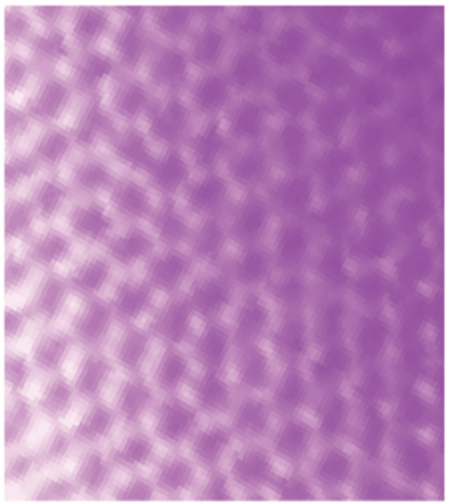


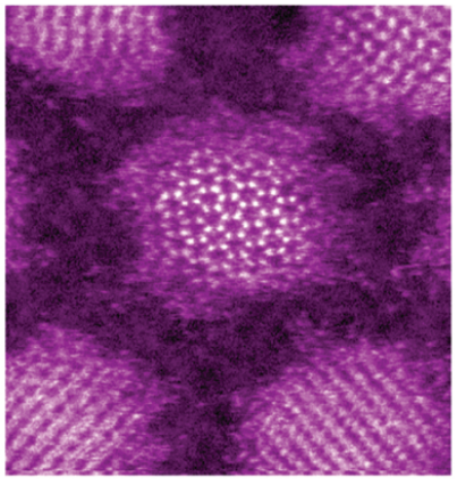
Deepstruc: close packed nanoparticles with a CVAE



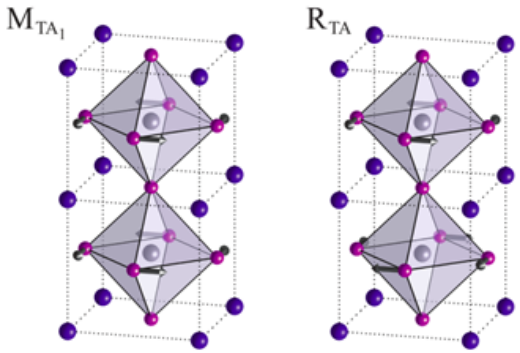
Types of nanostructure

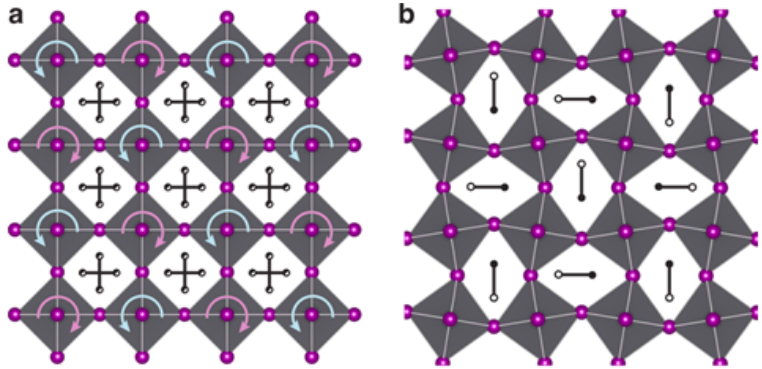


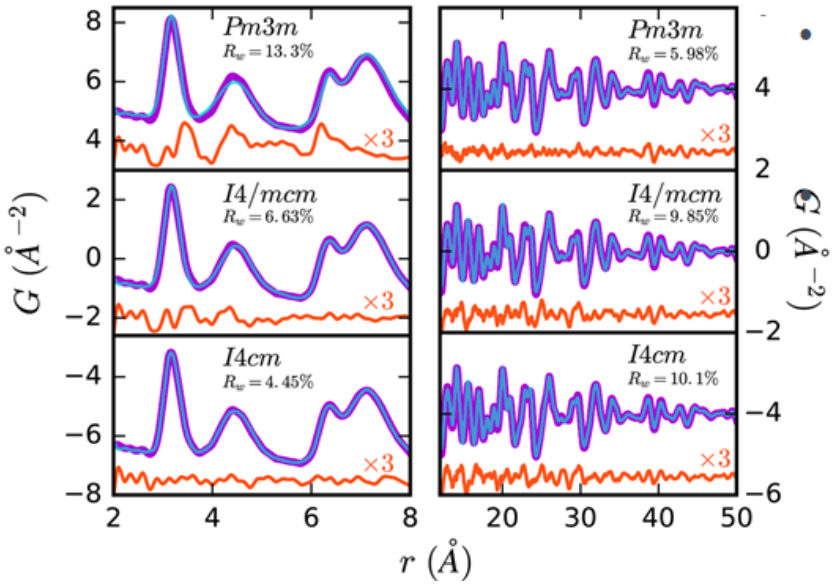




Dynamics of Soft-Hard Materials







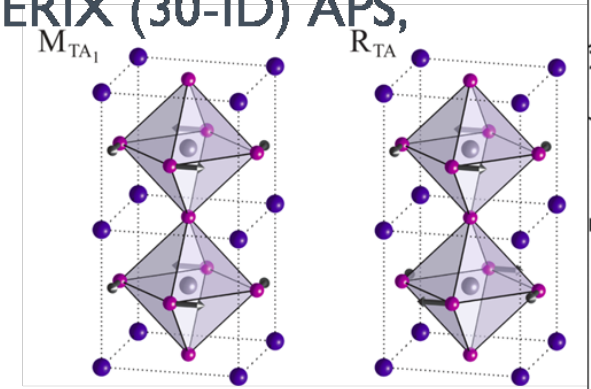
- PDF + inelastic x-ray scattering shows dynamic distortions in the local structure

Beecher/Semonin, SJLB, et al., ACS Energy (2016)

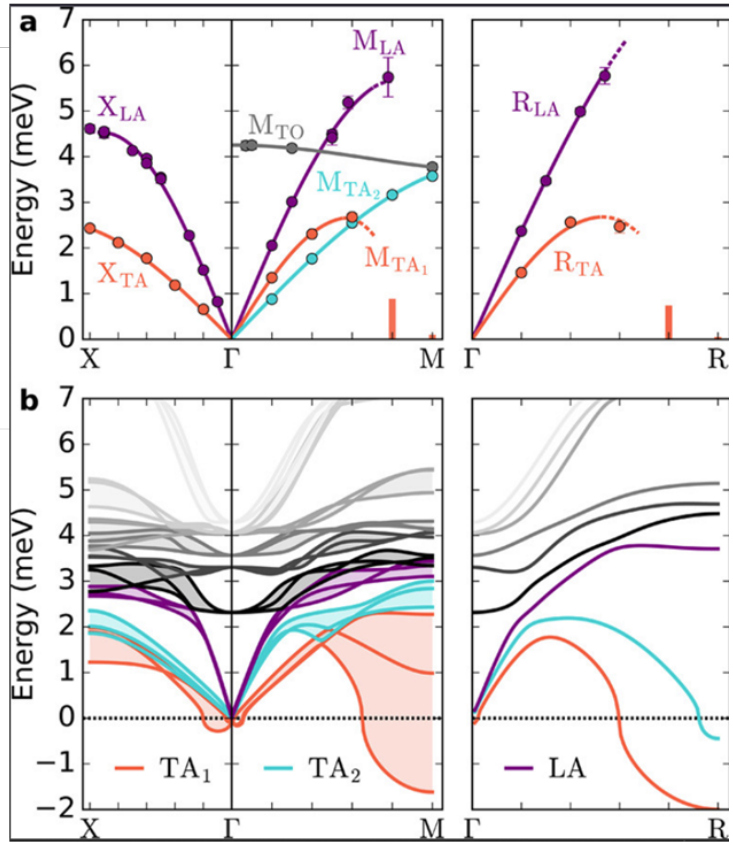


Inelastic x-ray scattering, APS, Chicago

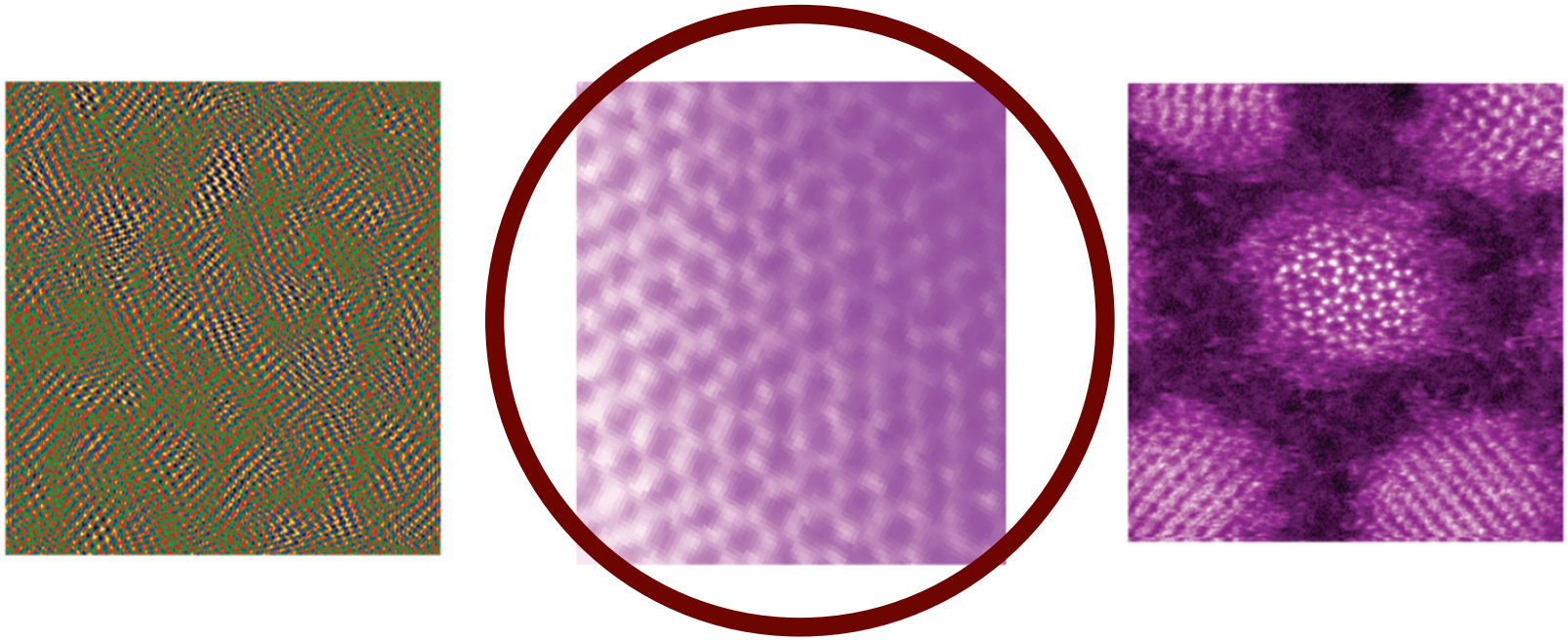
- IXS at HERIX (30-ID) APS, Argonne





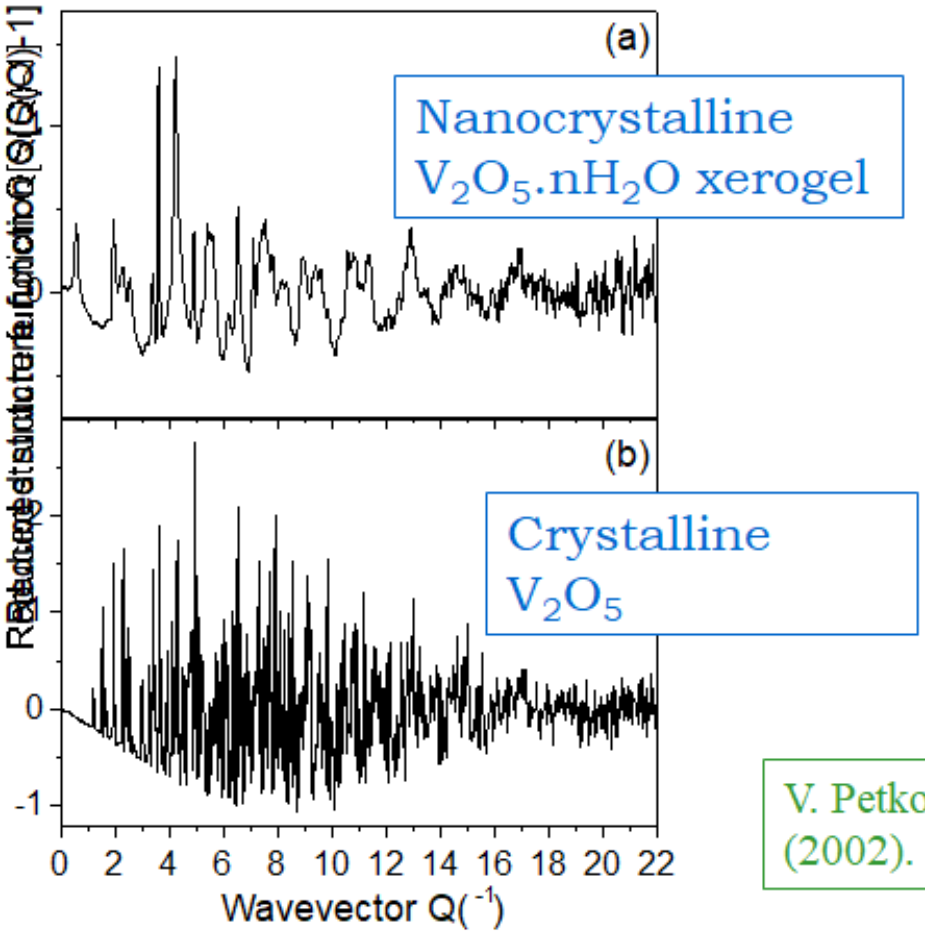


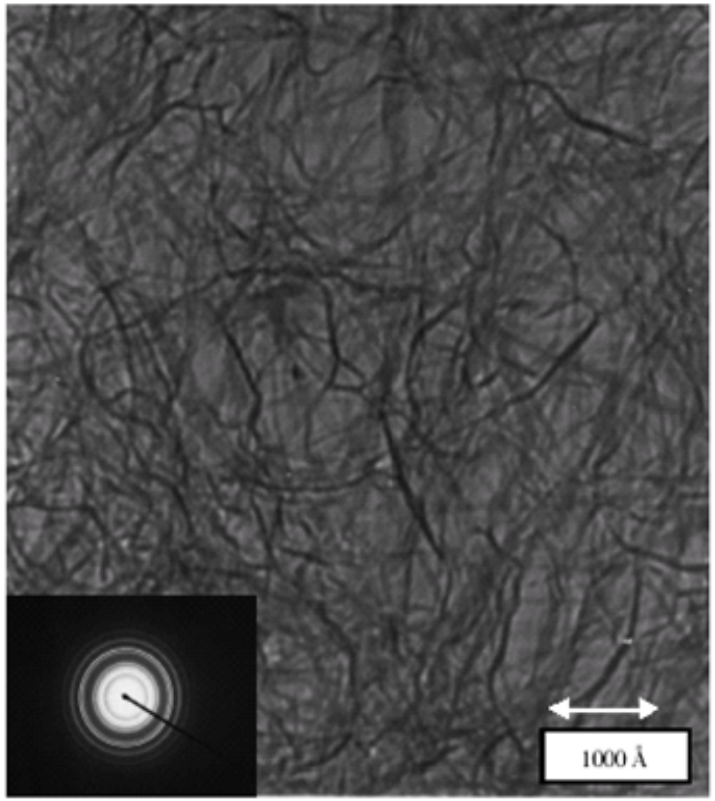
Types of nanostructure



Dynamics of Soft-Hard Materials

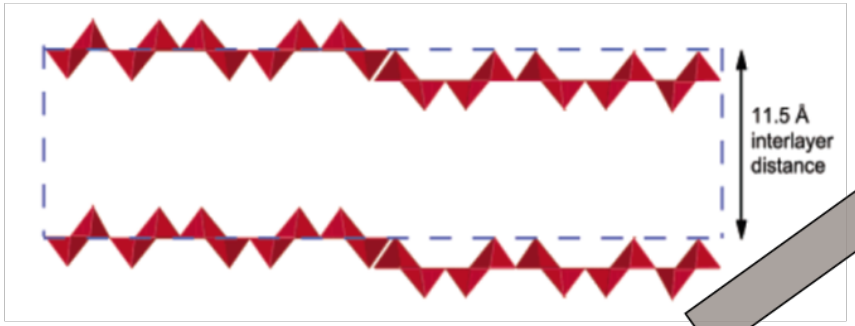
- Crystallography fails in nanocrystalline materials:





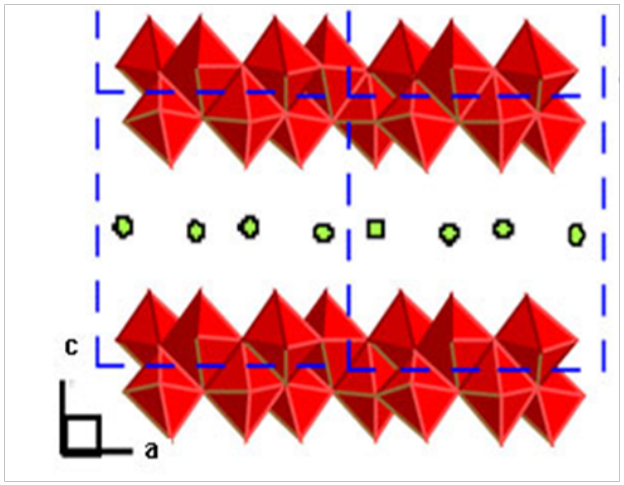
V. Petkov, SJB et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

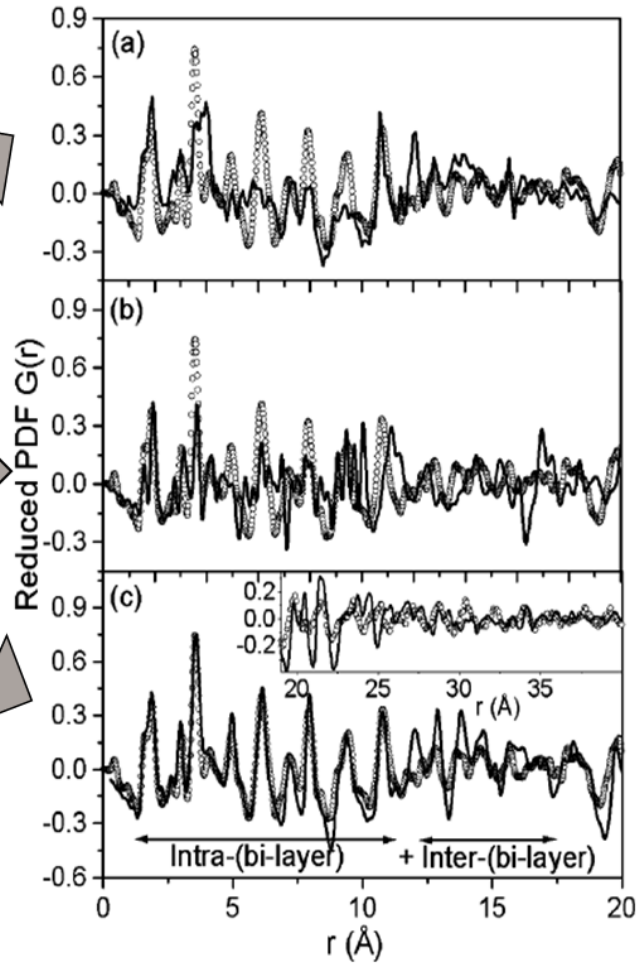
Dynamics of Soft-Hard Materials



Structure proposed by

- Livage et al. J. Chem Mater. 1991
- Petkov et al. J. Appl. Crystallogr. 1998
- Oka et al. J. Mater. Chem. 1992

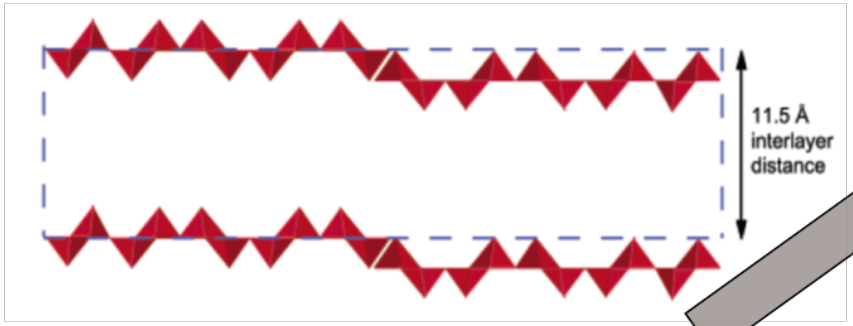




V. Petkov, SJB et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

Dynamics of Soft-Hard Materials

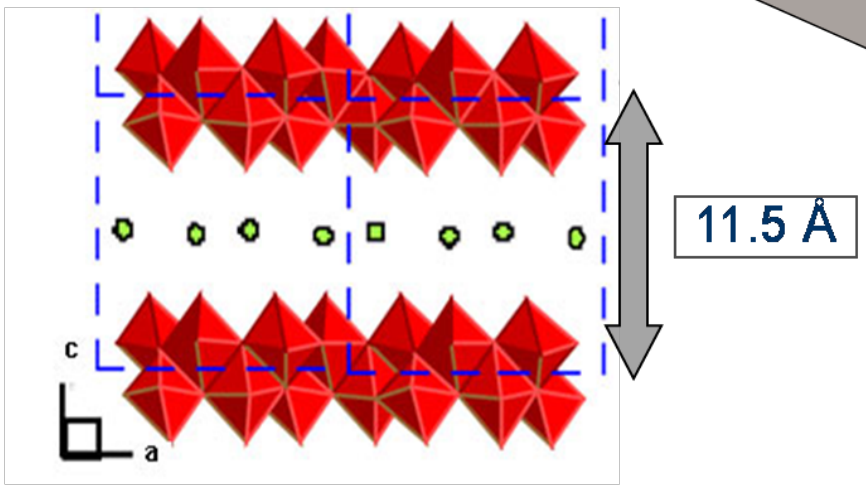
(a)

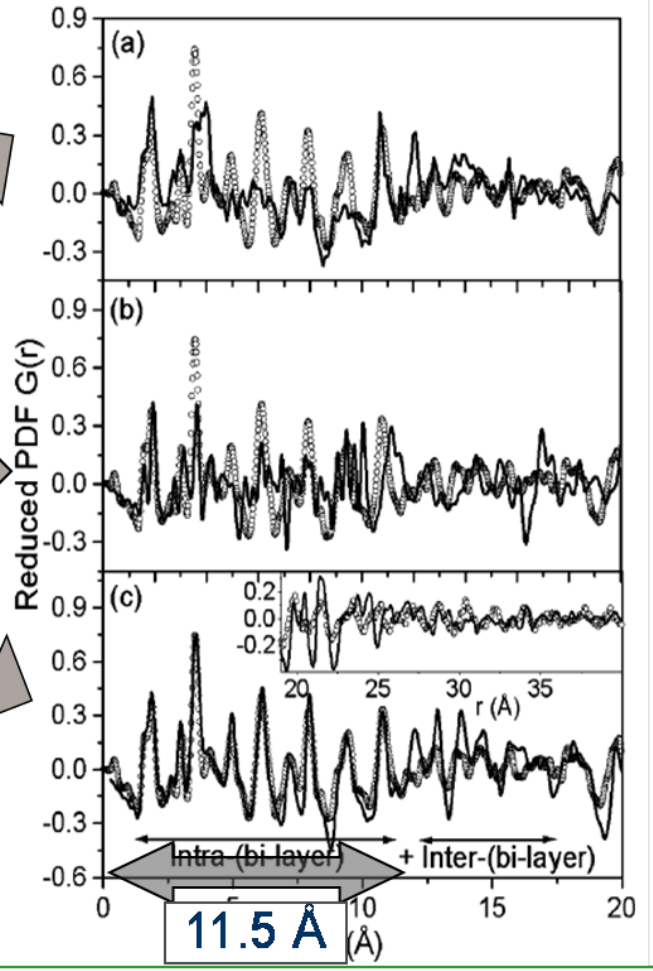


Structure proposed by

- Livage et al. J. Chem Mater. 1991
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- Oka et al. J. Mater. Chem. 1992

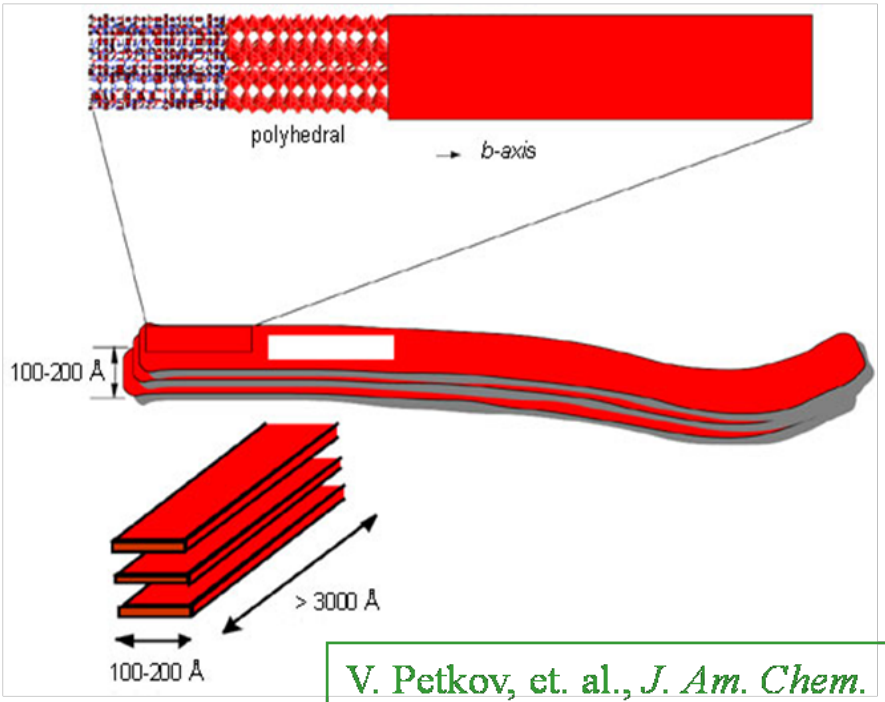
(c)



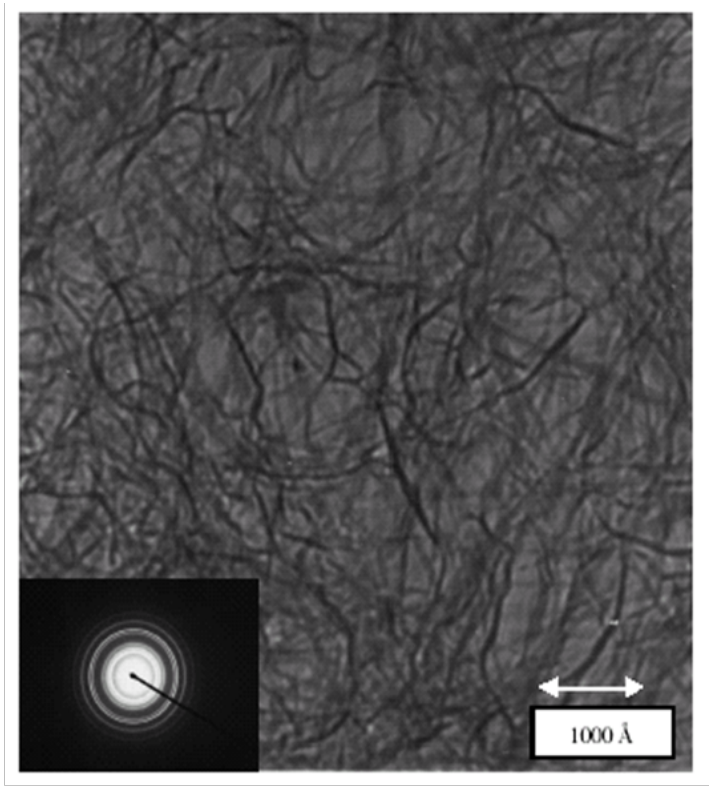


V. Petkov, SJB et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

Dynamics of Soft-Hard Materials

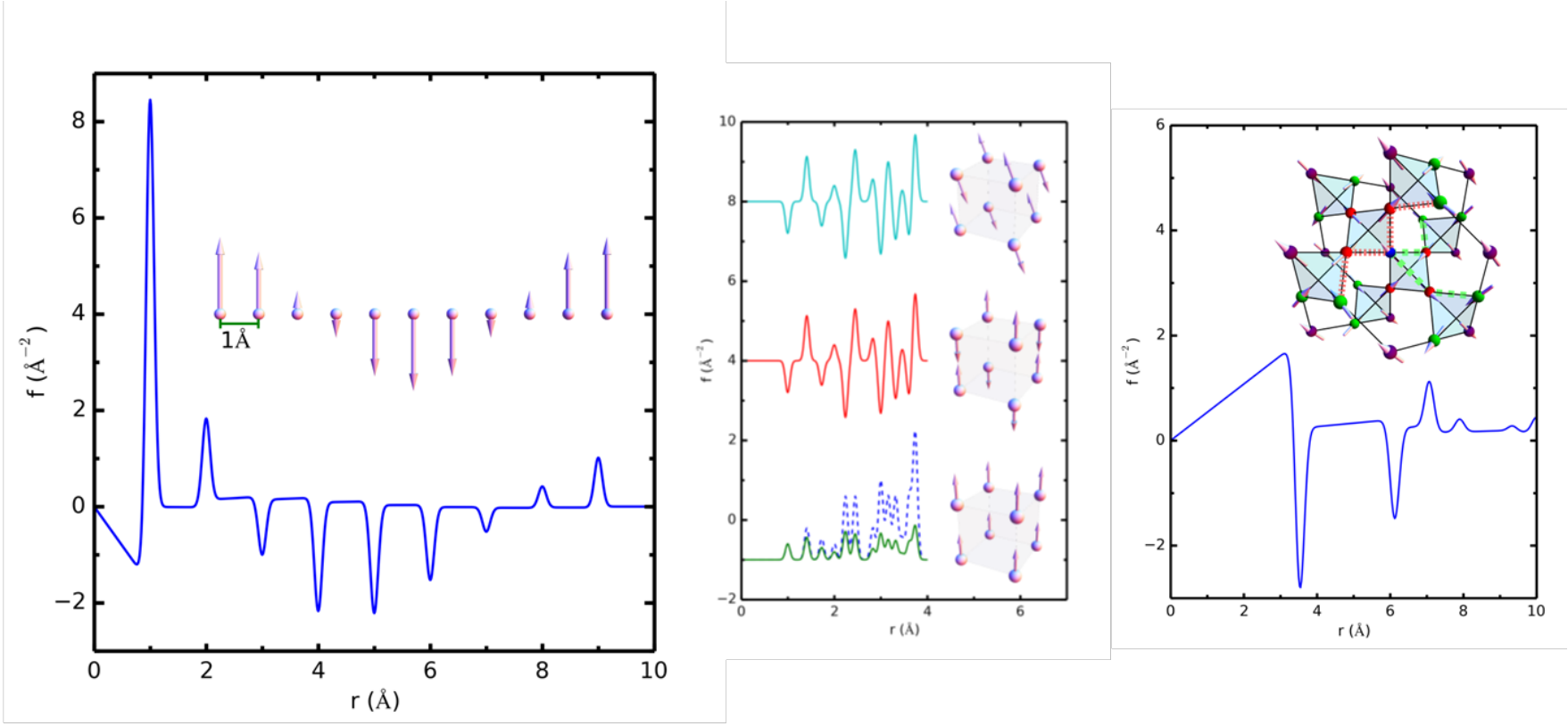


V. Petkov, et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).



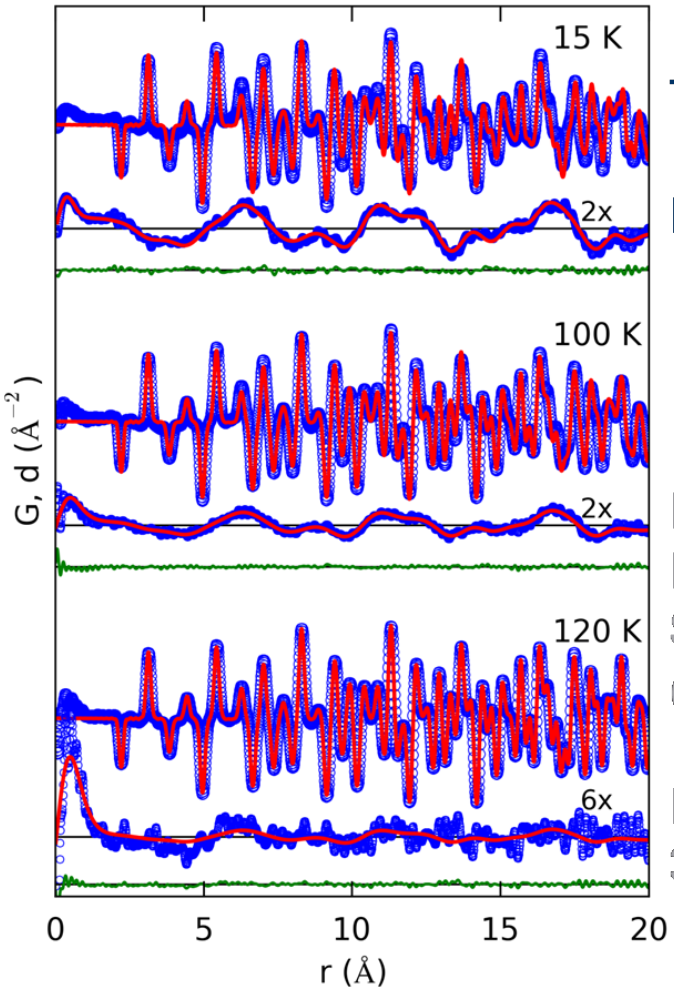
- Turbostratic disorder seen in the PDF consistent with bent and tangled fibres

Magnetic PDF



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

Magnetic PDF of MnO

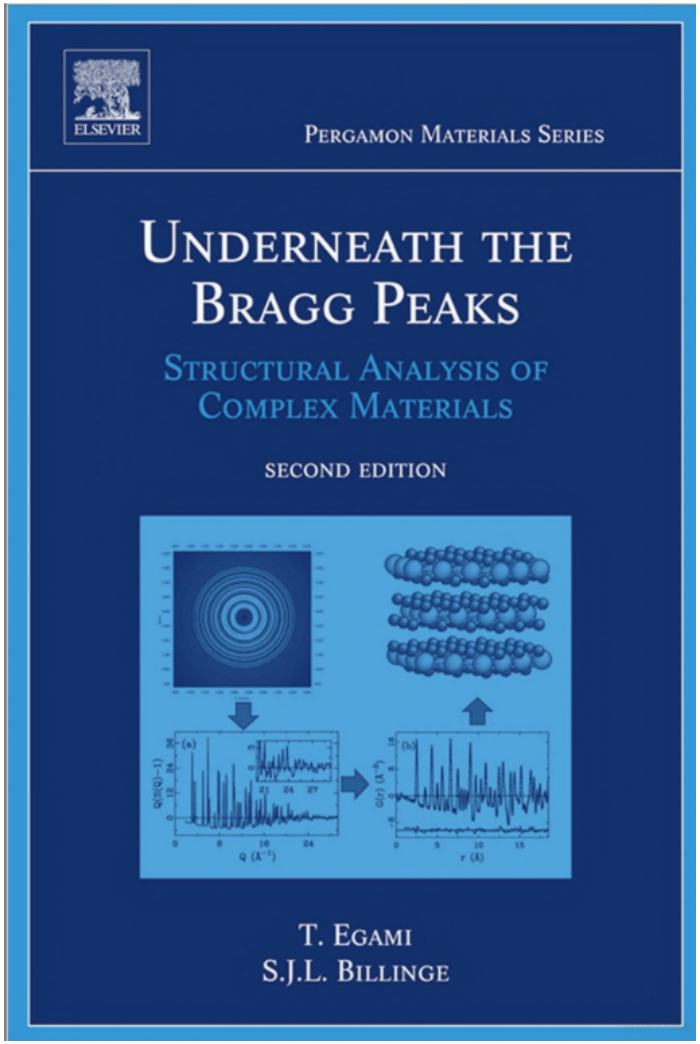


Top: *Blue*: measured nPDF signal
Red (top) calculated structural PDF
Btm: *Blue*: difference between nPDFsignal and calculated structural PDF
Red: calculated mPDF for AF MnO

Benjamin A. Frandsen, M. Brunelli, K. Page, Y. J. Uemura, Julie B. Staunton, SJLB, Phys. Rev. Lett. 116, 197204 (2016)

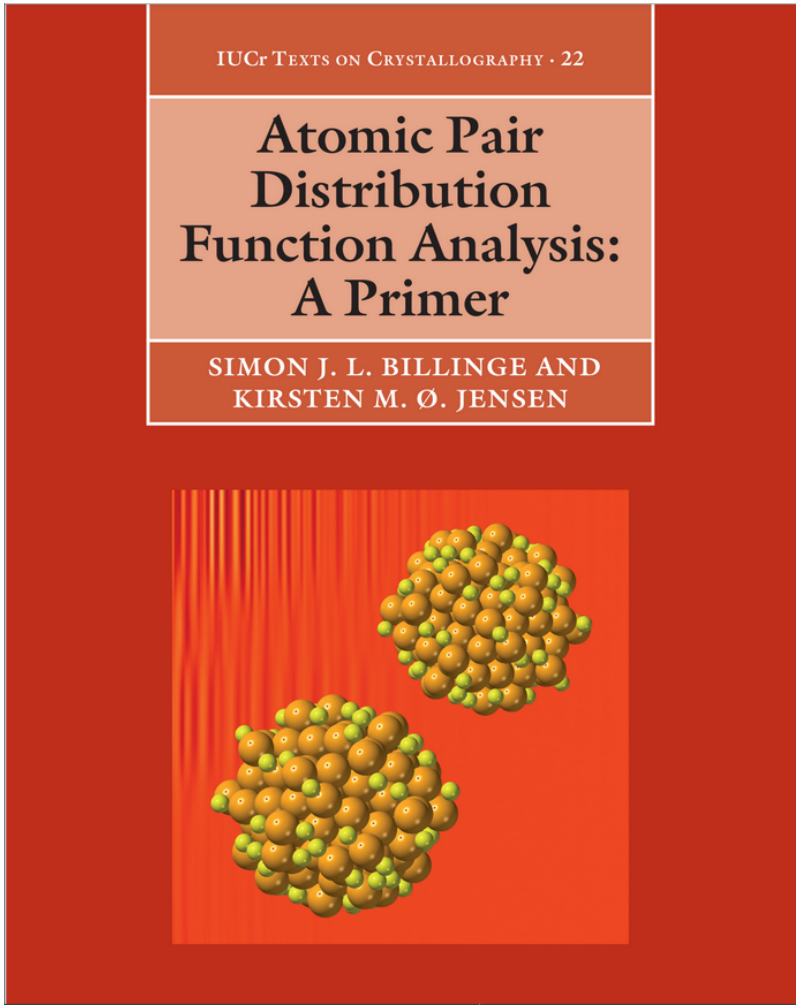
Frandsen, SJLB, Acta Crystallogr. A 71, 325-334 (2015)

Underneath the Bragg peaks



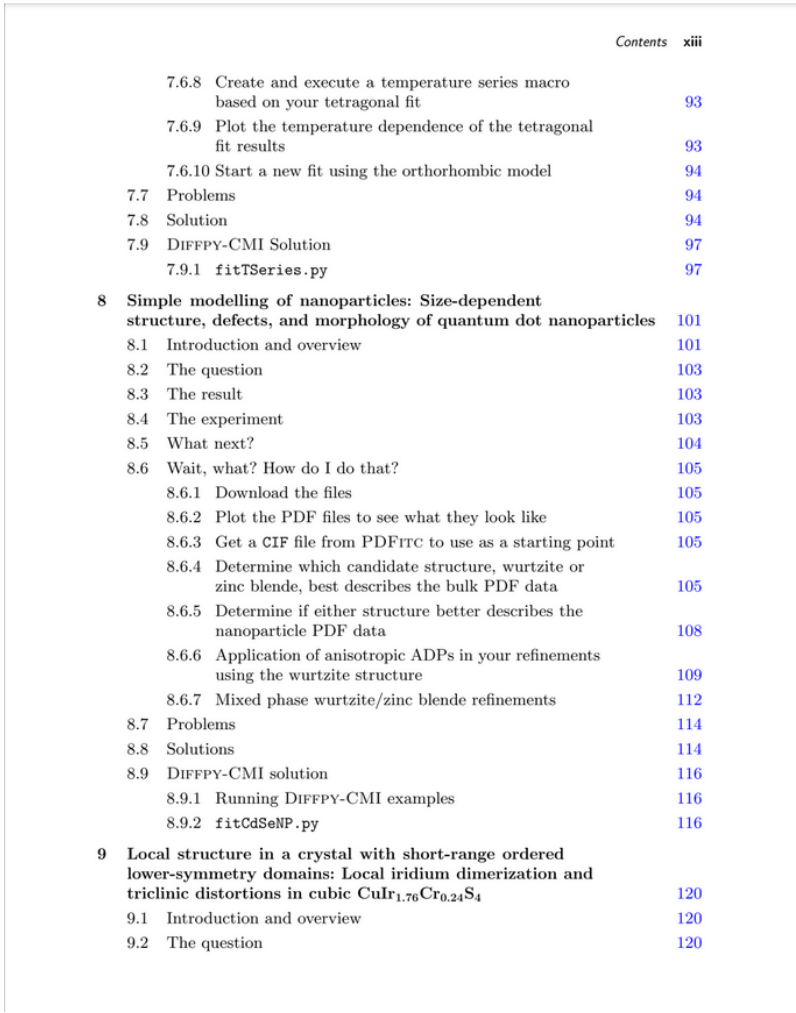
- Takeshi Egami
- me

PDF to the People



- Max Terban
- Emil Bozin
- Soham Banerjee
- Ben Frandsen
- Robert Koch

PDF to the People



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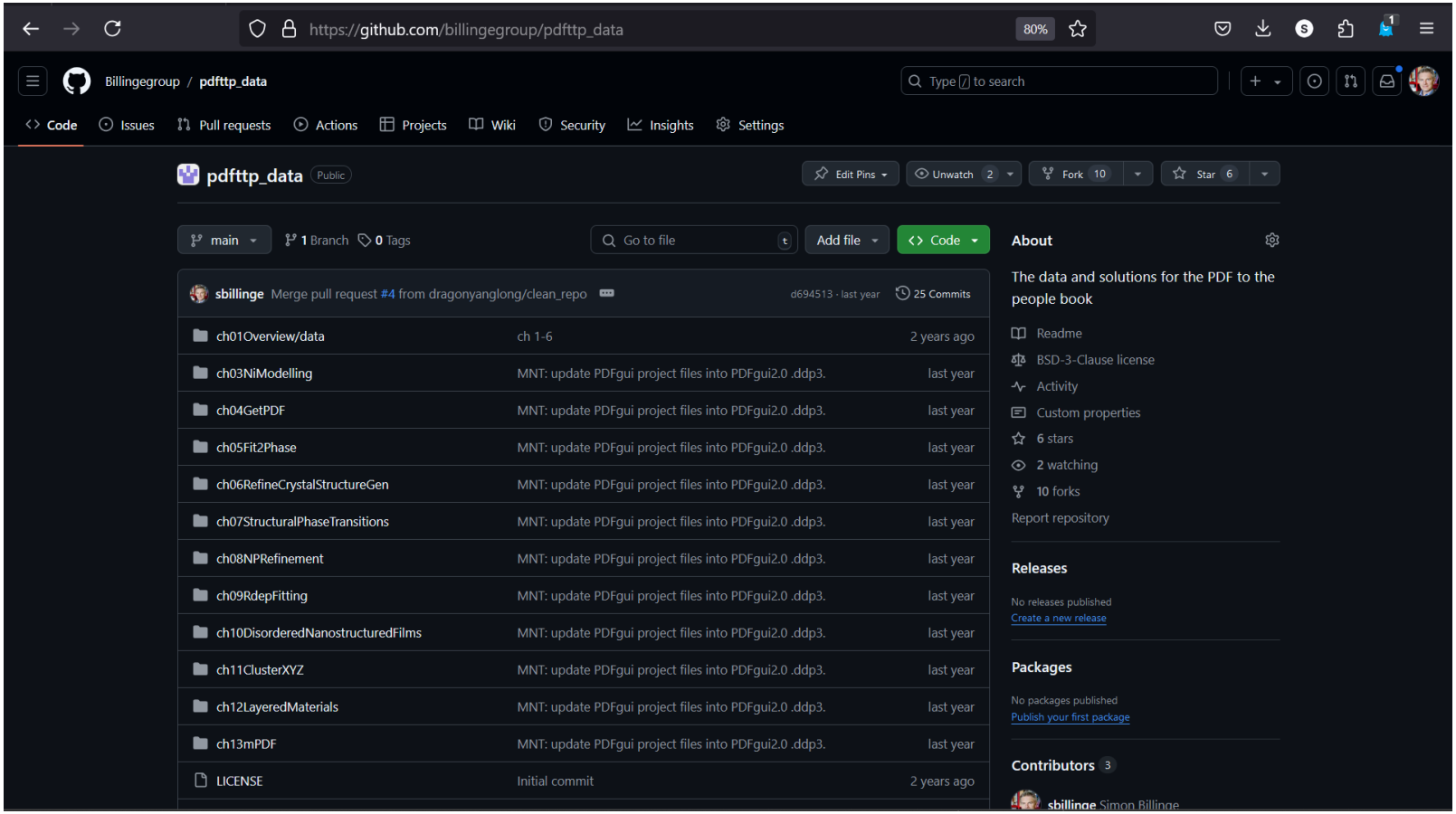
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- Worked examples of how to get from an experimental PDF to a scientific result
- Different levels of scaffolding. Start out with more hand-holding, later try by yourself
- All solutions are give in PDFgui (where possible) and also diffpy-cmi
- A great way to learn diffpy-cmi and have starting scripts

The data for PDF to the People



https://github.com/billingegroup/pdfttp_data

Acknowledgements



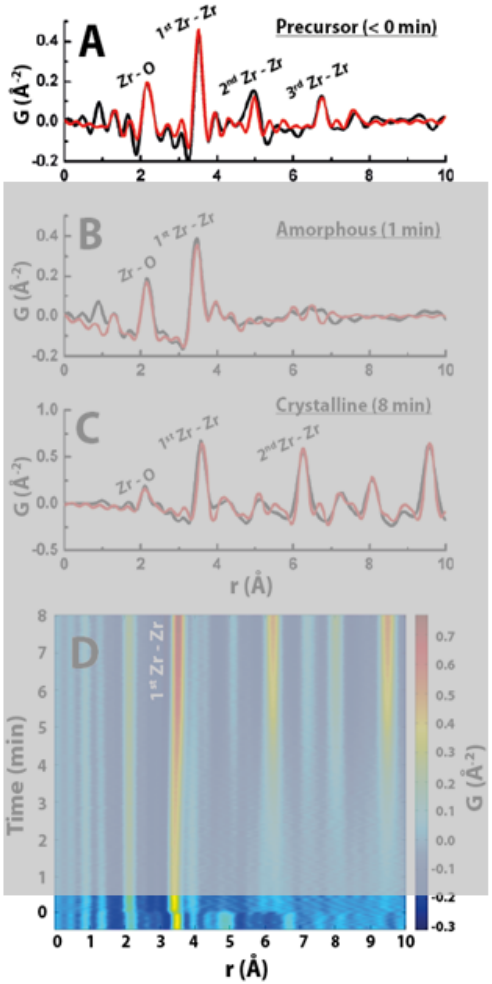
- My current and former students and post-docs
- Beamline and software teams
- Collaborators

- Funding (DOE-BES, NSF-DMR, TRI, Columbia-DSI)
- The Facilities!

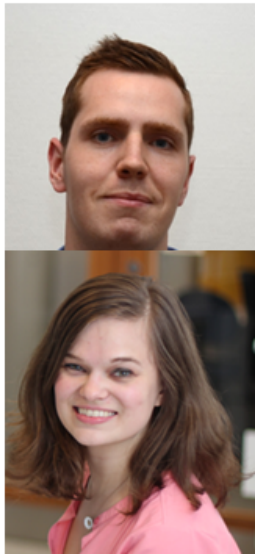
Where is PDF going?

- Time resolved measurements
  - In situ
  - Operando
  - ufPDF
- Spatially resolved
  - X-ray mapping (SNXM)
  - Electron PDF mapping (SNEM)
  - Computed tomography PDF (ctPDF)
- Autonomated

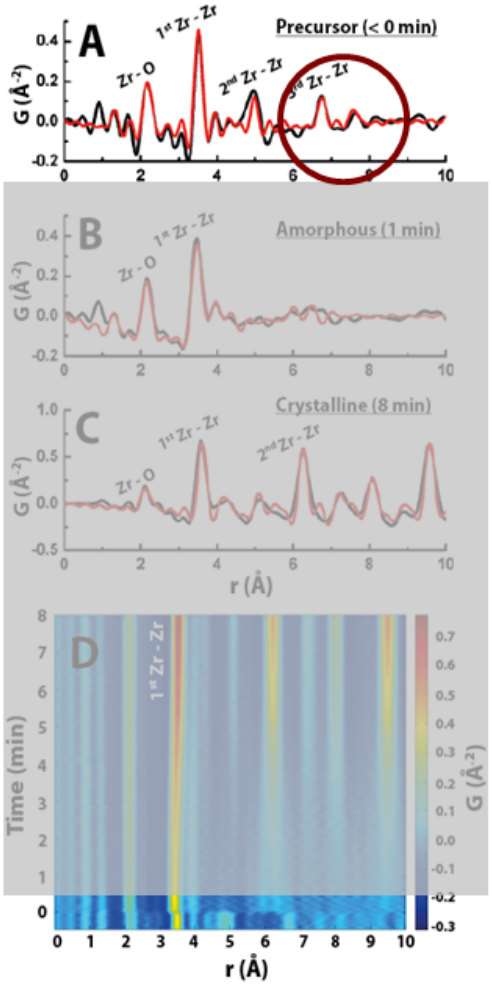
In situ hydrothermal synthesis of yttria-stabilized zirconia nanoparticles



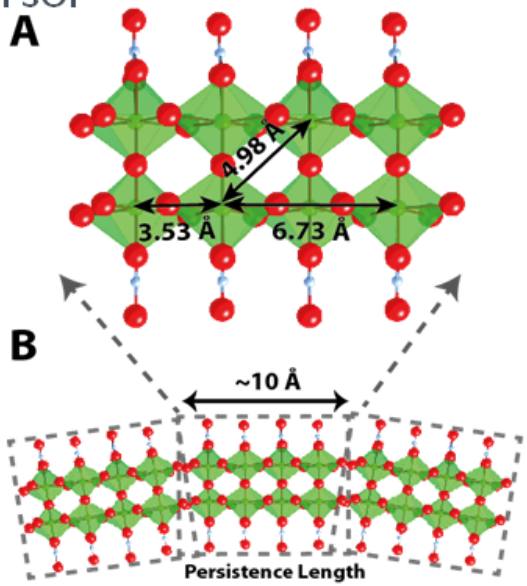
- Christoffer Tyrsted, Nina Lock, Kirsten M. \O. Jensen, Mogens Christensen, Espen D. Bøjesen, Hermann Emerich, Gavin Vaughan, Simon J. L. Billinge and Bo B. Iversen, *IUCrJ.* **1**, 165-171 (2014)
- Precursor

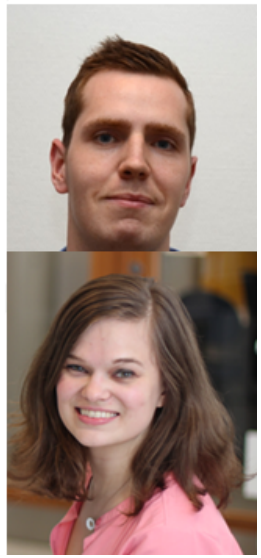


In situ hydrothermal synthesis of yttria-stabilized zirconia nanoparticles

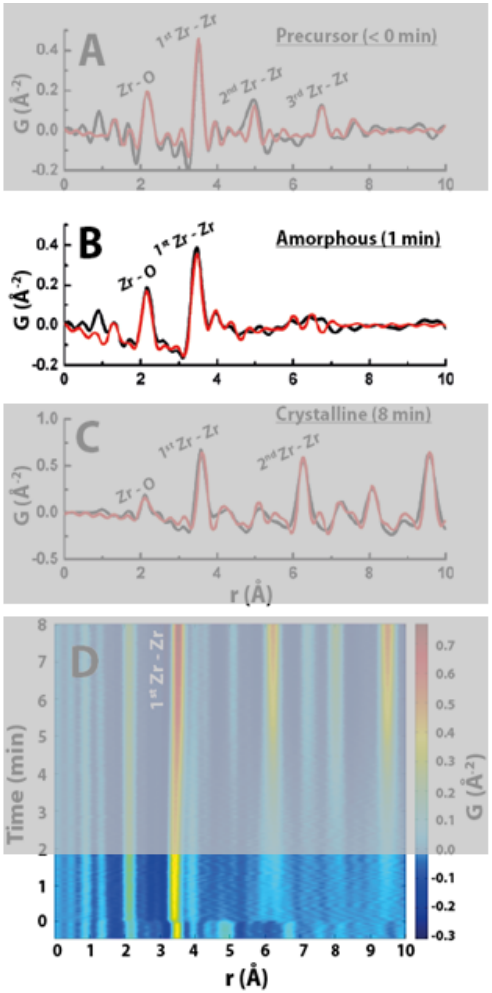


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- Precursor





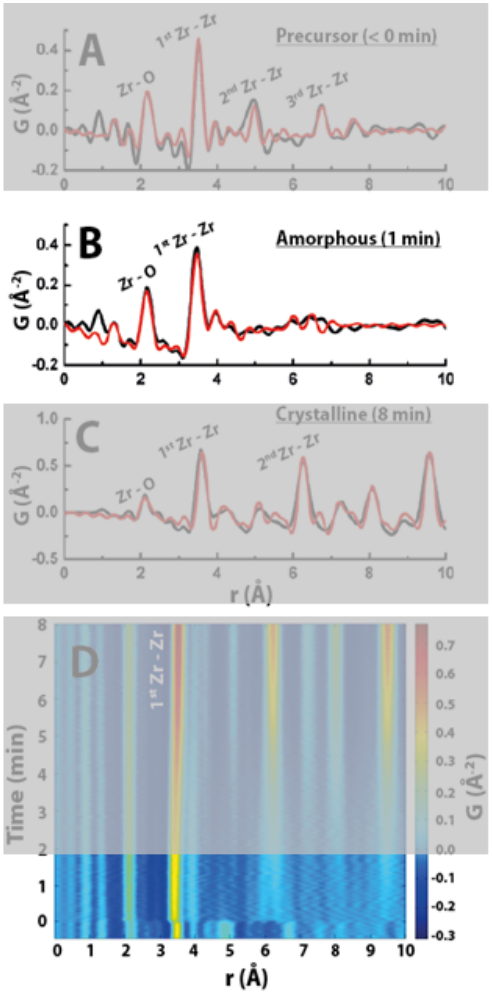
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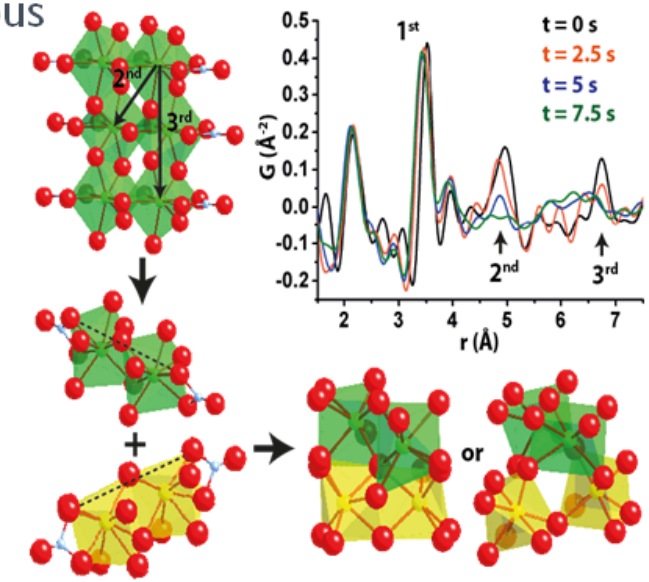
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- Amorphous

intermdiate

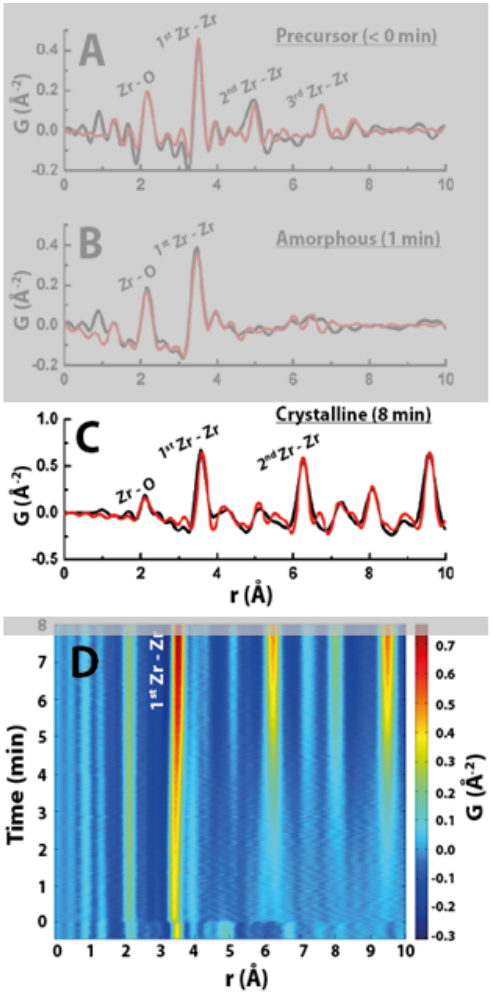
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- Amorphous intermdiate

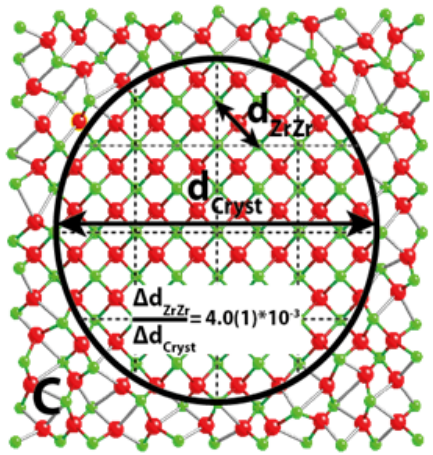


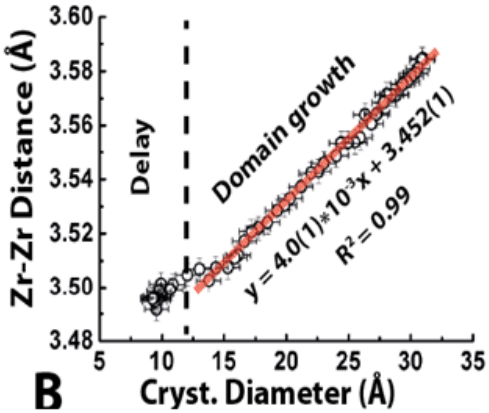
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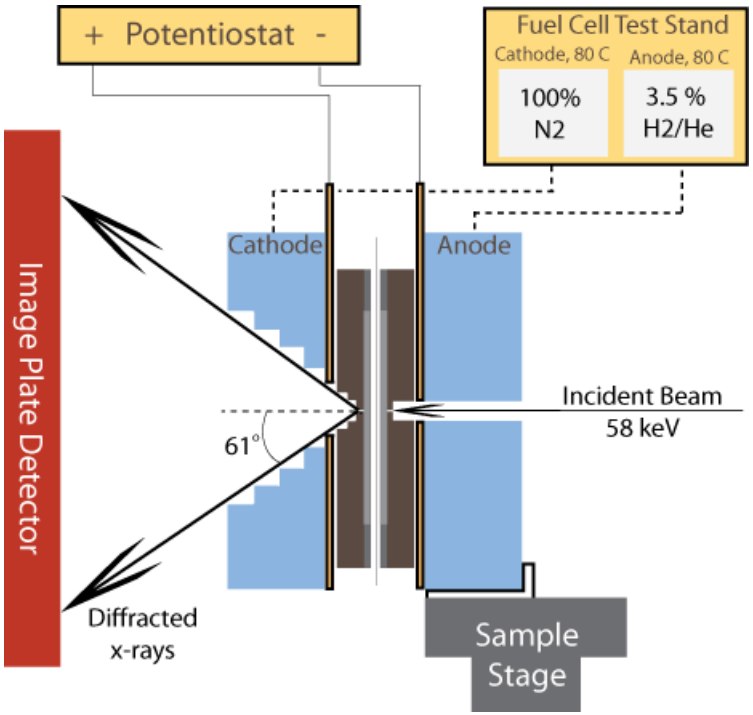
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- Nanocrystalline

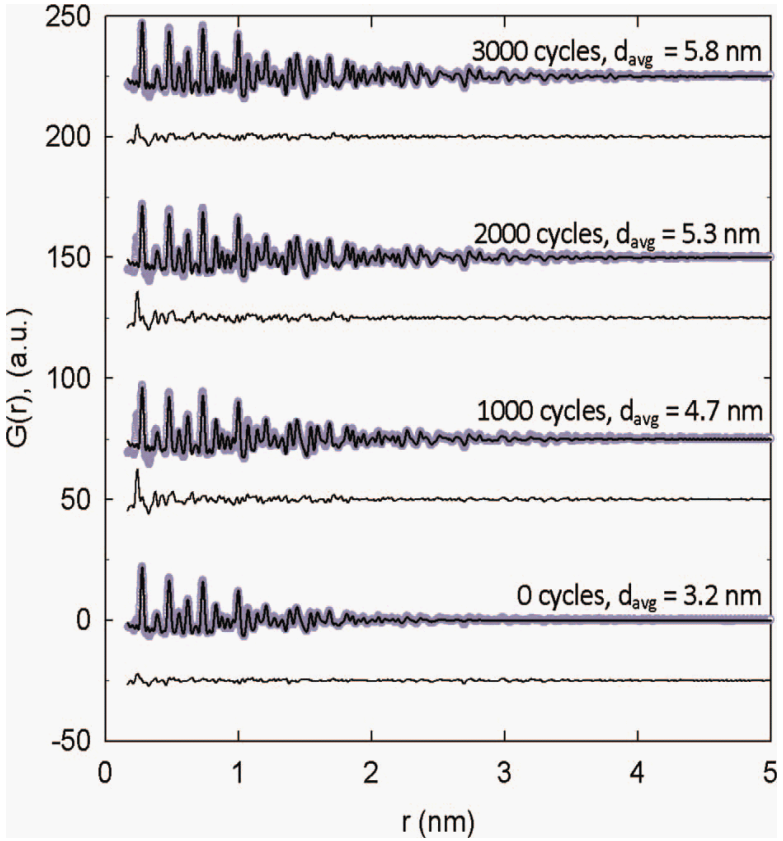
final product





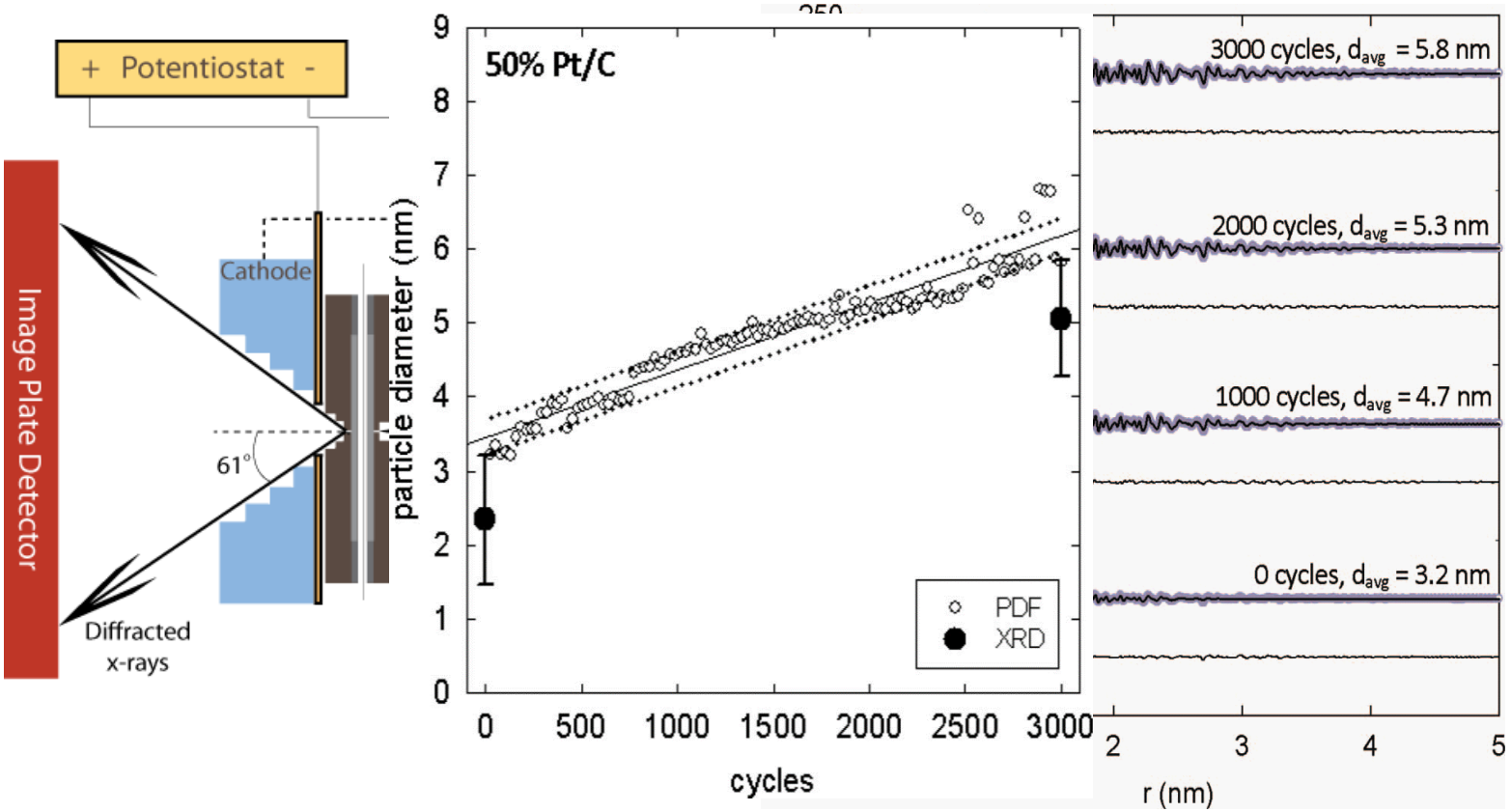
Real materials in action: operando measurements





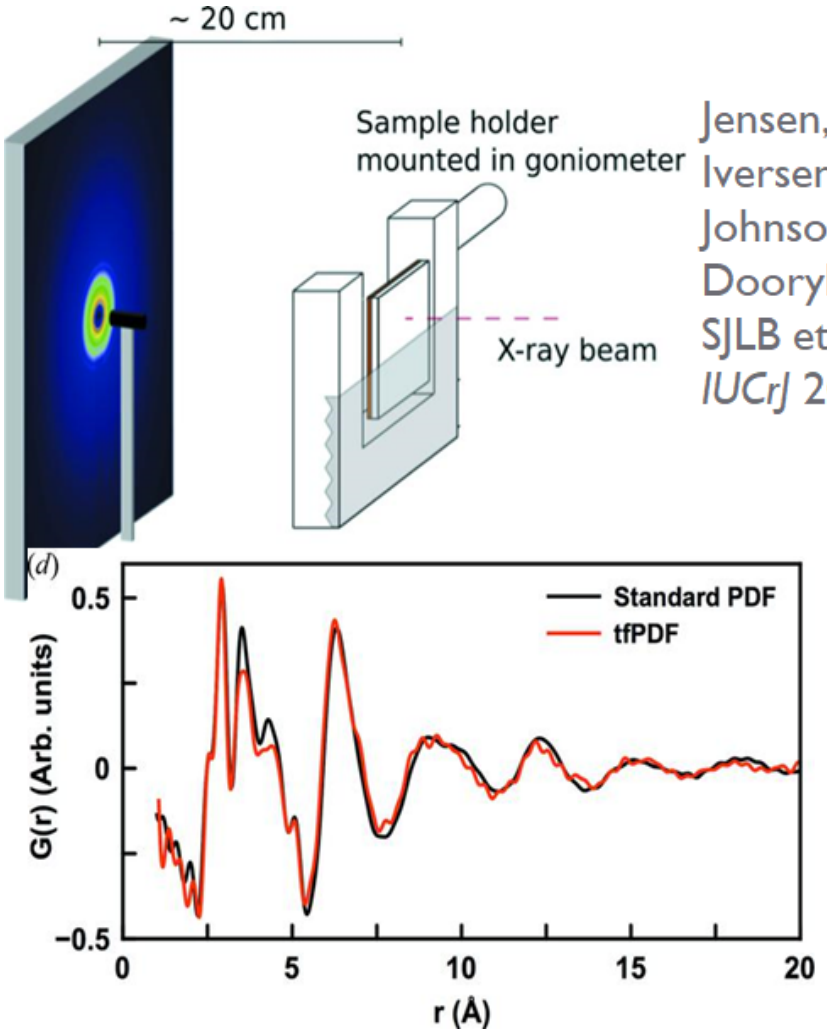
Redmond, et al., Electrochem. Solid St., 15 (5), B72-B74.

Real materials in action: operando measurements

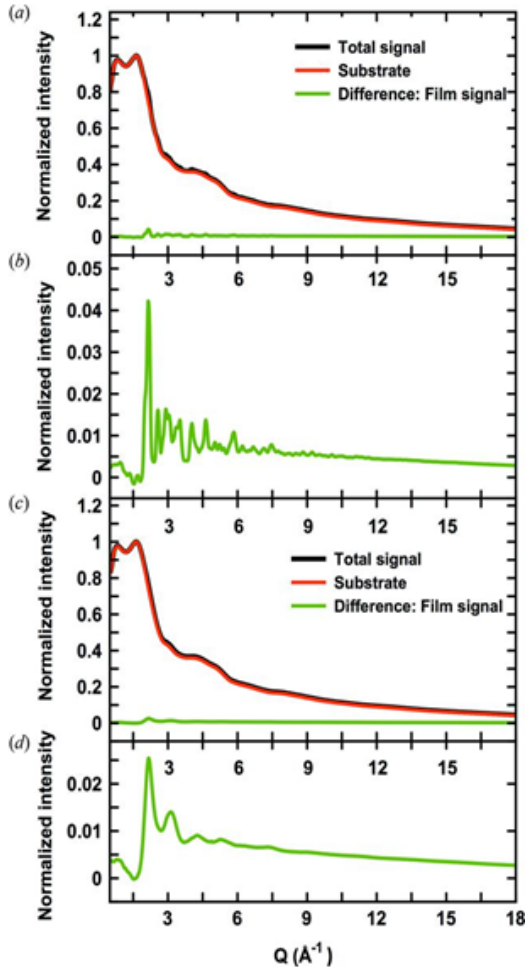


Redmond, et al., Electrochem. Solid St., 15 (5), B72-B74.

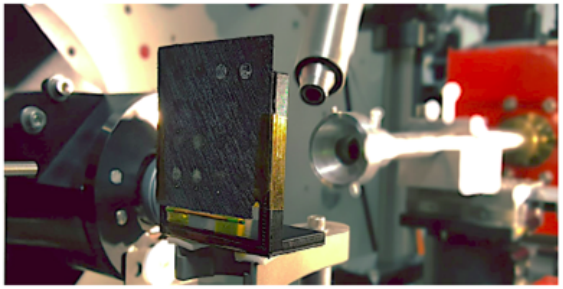
Thin film PDF (at normal incidence) tfPDF



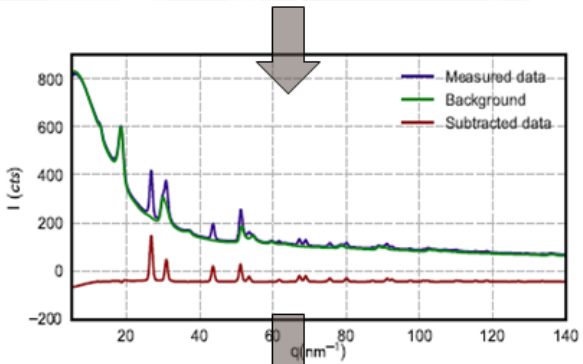
Jensen, Iversen, Johnson, Dooryhee SJLB et al. *IUCrJ* 2015

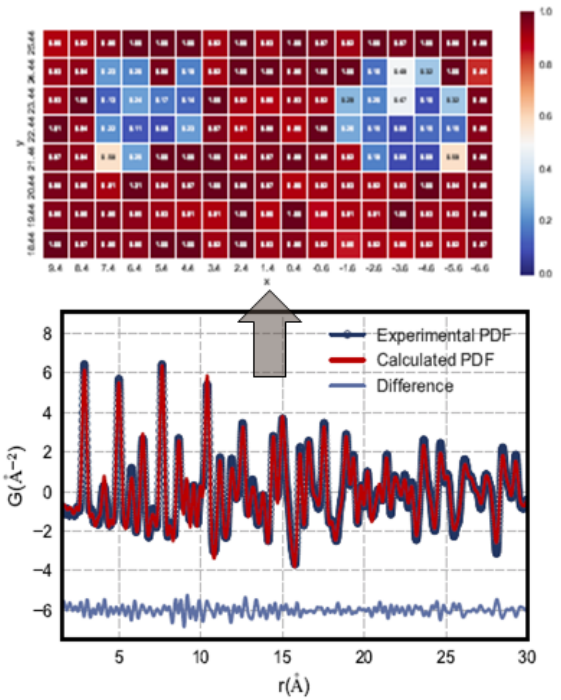


Spatially Resolved PDFs (Lab on a Chip)

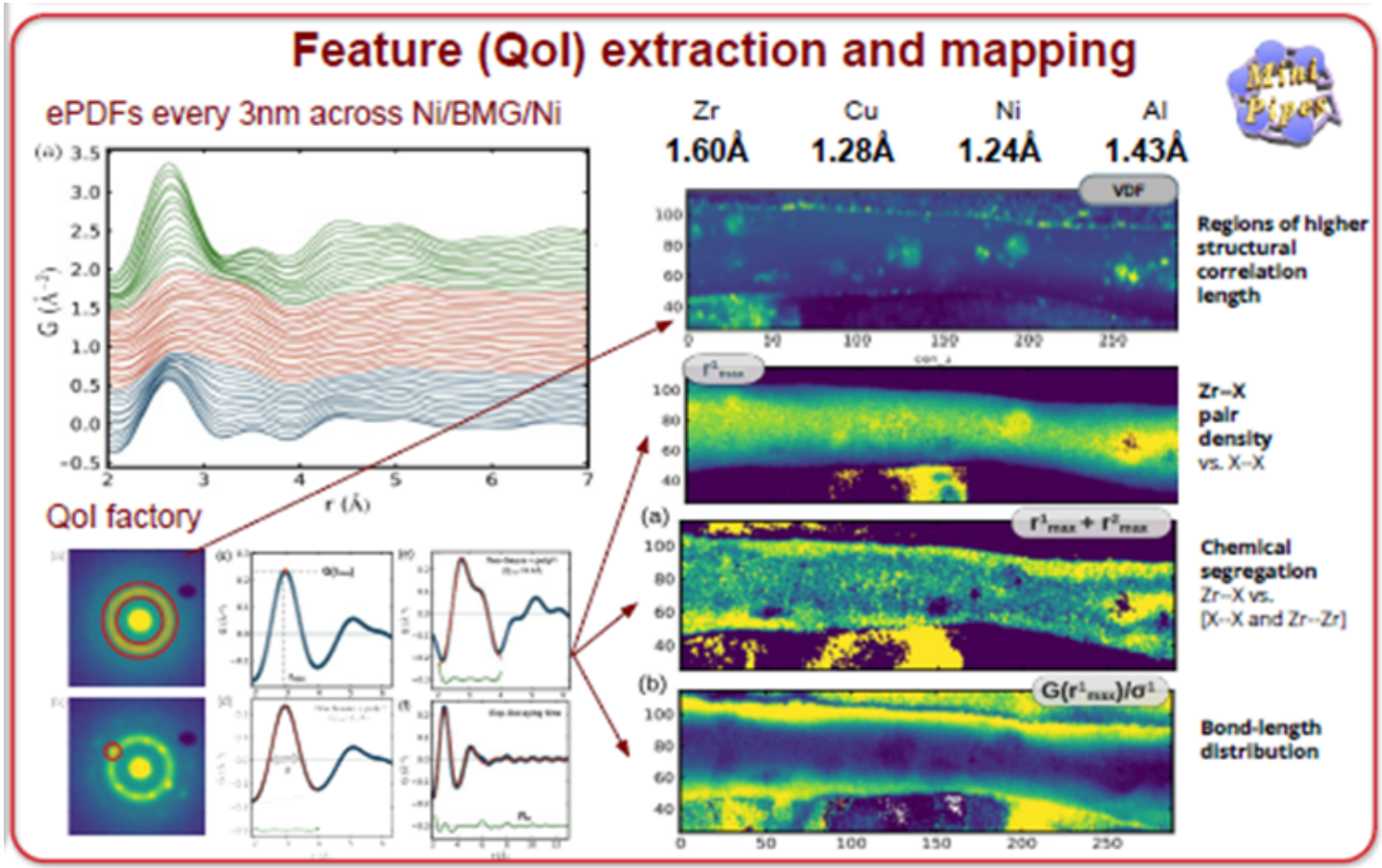


- Kovyakh, Banerjee, Liu, et al., arXiv:2110.01656 [cond-mat]
- Evey pixel contains a complete PDF



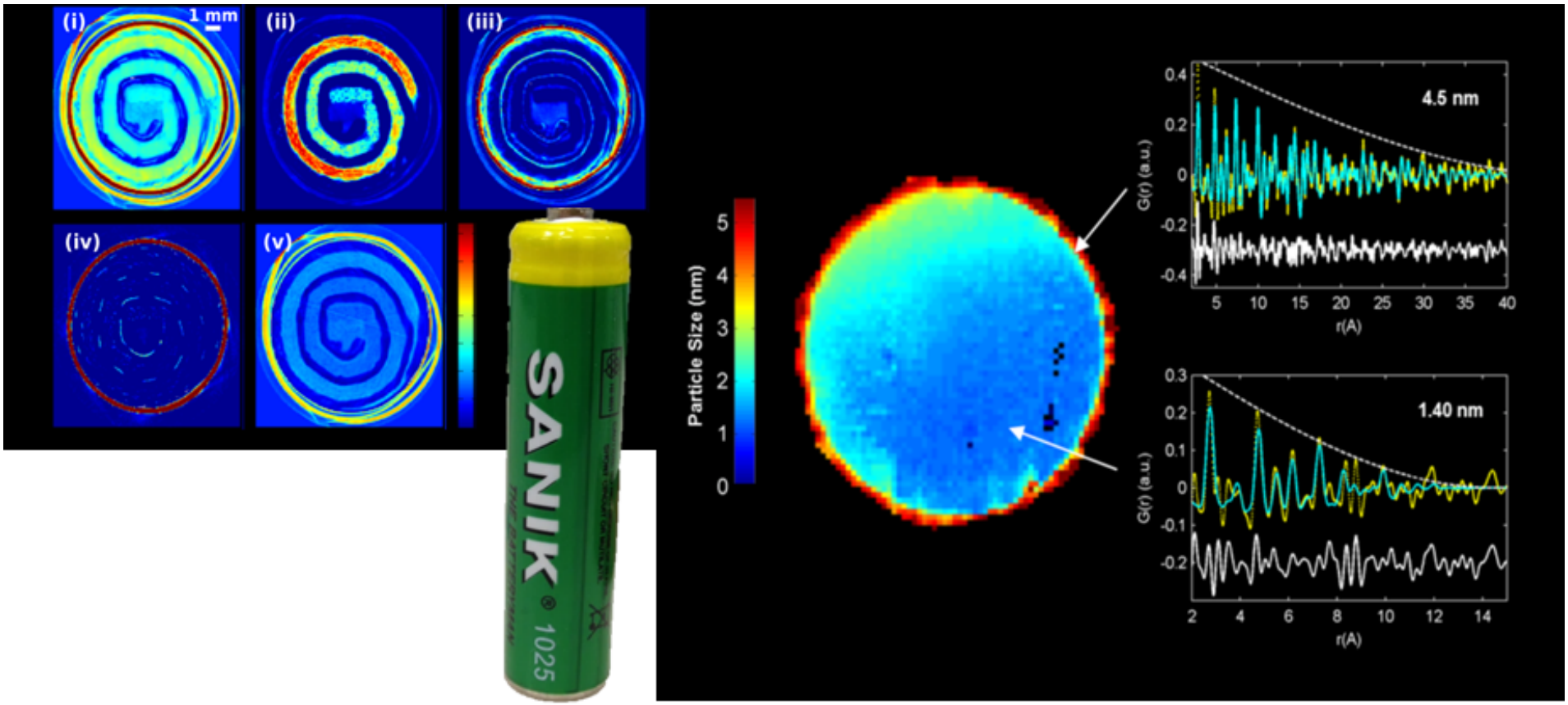


Scanning Nanostructure EM (SNEM)



Rakita, et al. Acta Materiala 242 (2023), 118426. 10.1016/j.actamat.2022.118426

Computed Tomography PDF (ctPDF)



Jacques et al., Nature Communications 4, 2536. 10.1038/ncomms3536 Jensen et al., J. Electrochem. Soc. 162, A1310-A1314. 10.1149/2.0771507jes

Dynamics of Soft-Hard Materials

nature materials

Letter

https://doi.org/10.1038/s41563-023-01483-7

Dynamic crystallography reveals spontaneous anisotropy in cubic GeTe

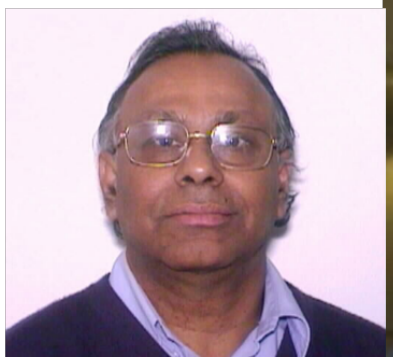
Received: 24 May 2021

Accepted: 19 January 2023

Published online: 20 February 2023

Check for updates

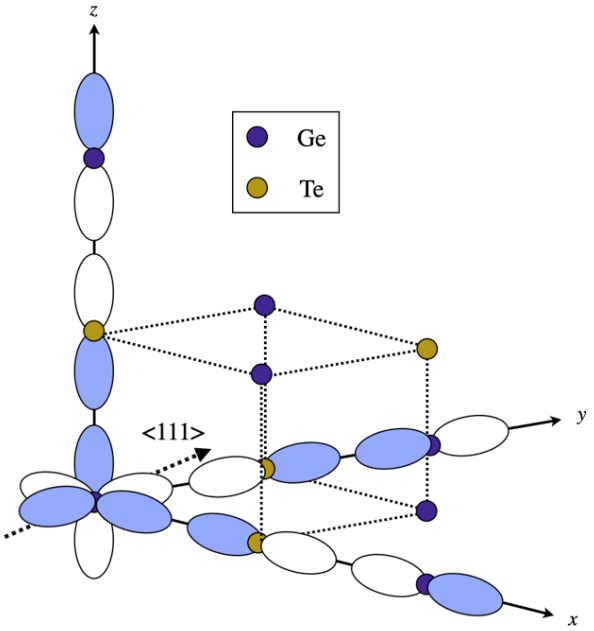
Simon A. J. Kimber[1], Jiayong Zhang[2], Charles H. Liang[3,4], Gian G. Guzmán-Verri[5,6], Peter B. Littlewood[3,7], Yongqiang Cheng[2], Douglas L. Abernathy[2], Jessica M. Hudspeth[8], Zhong-Zhen Luo[9], Mercouri G. Kanatzidis[9], Tapan Chatterji[10], Anibal J. Ramirez-Cuesta[2] & Simon J. L. Billinge[11,12]

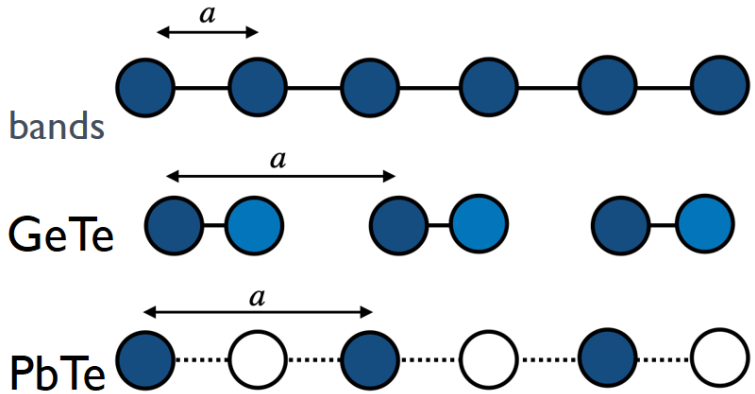


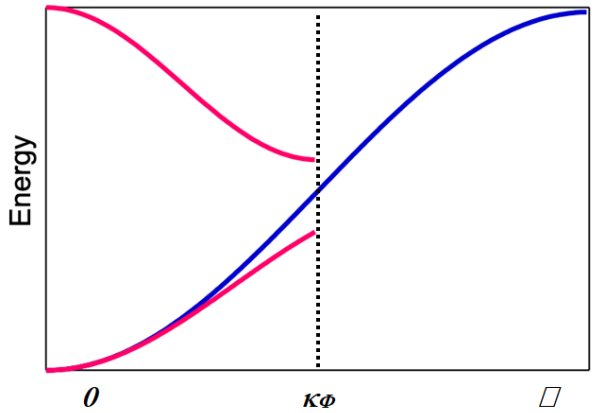


Germanium Telluride

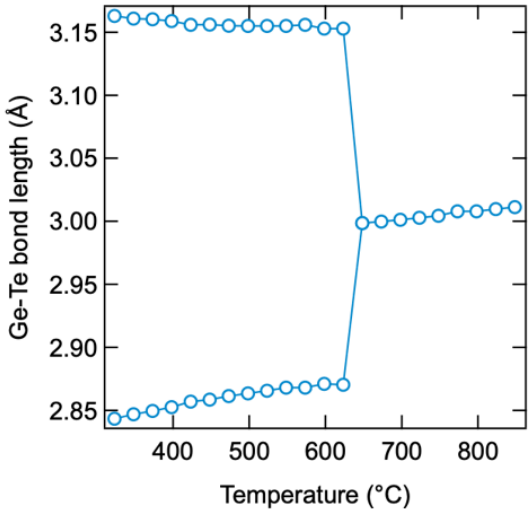
- Rhombohedral groud state
- Minimal model' is a Peierls distortion
- One p-electron per bond => half-filled bands



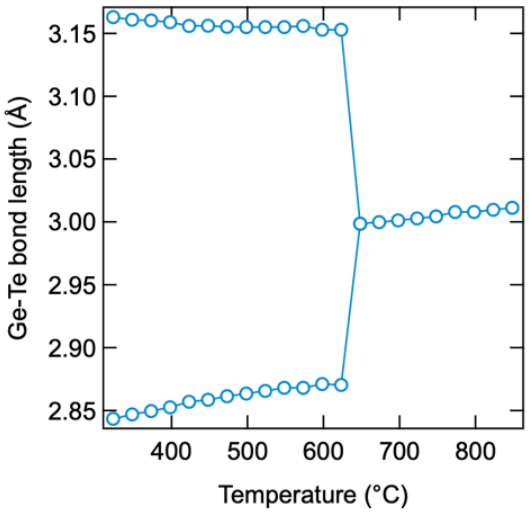


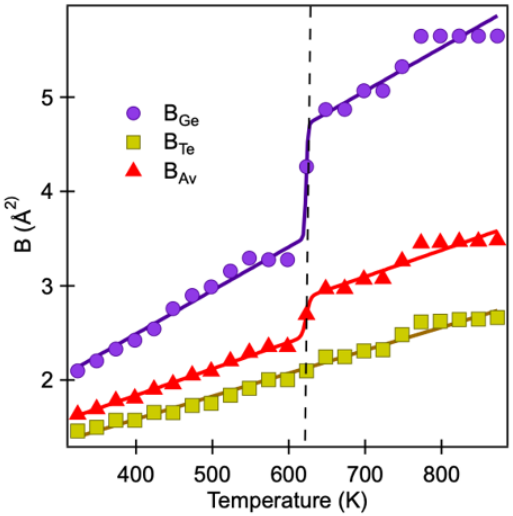


Germanium Telluride

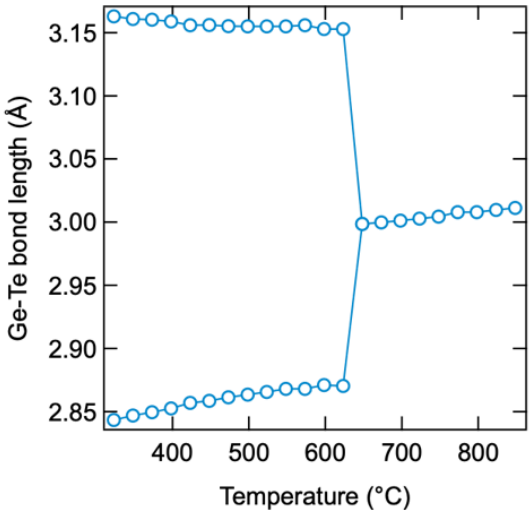


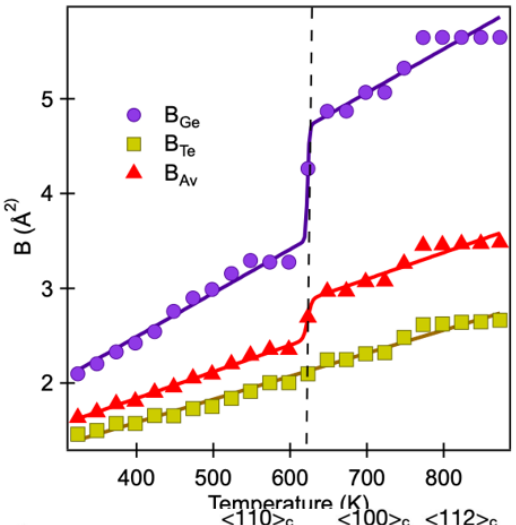
Germanium Telluride

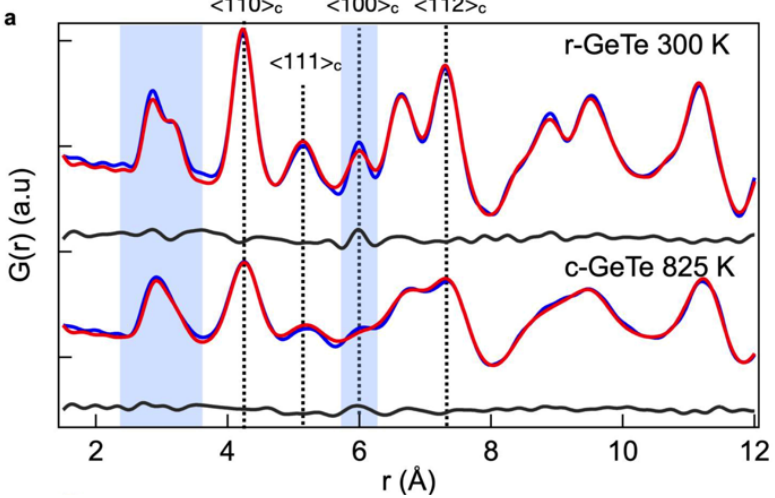




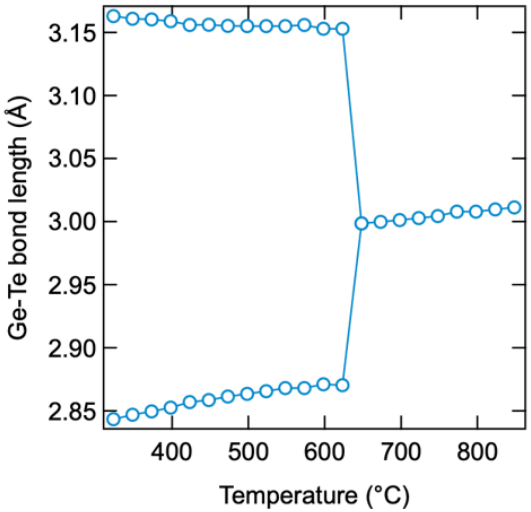
Germanium Telluride

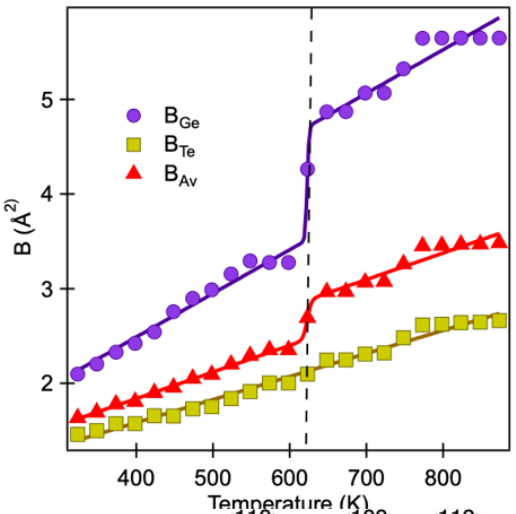


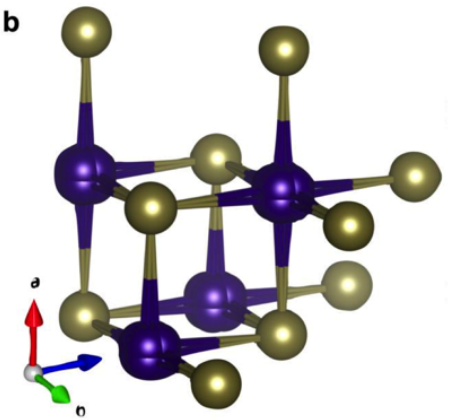


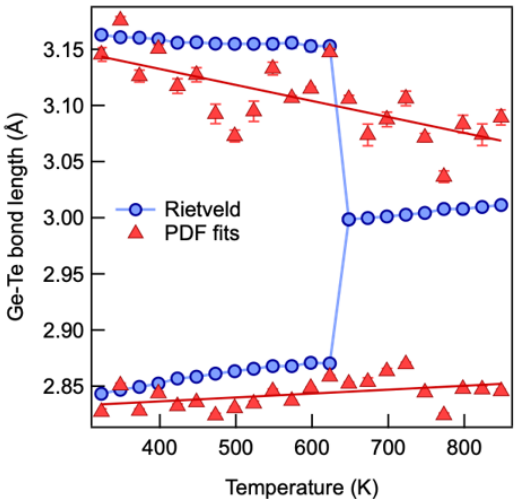


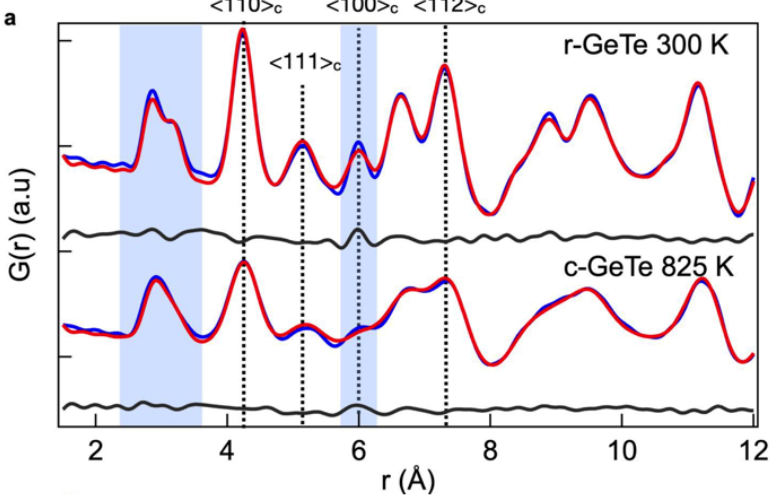
Germanium Telluride











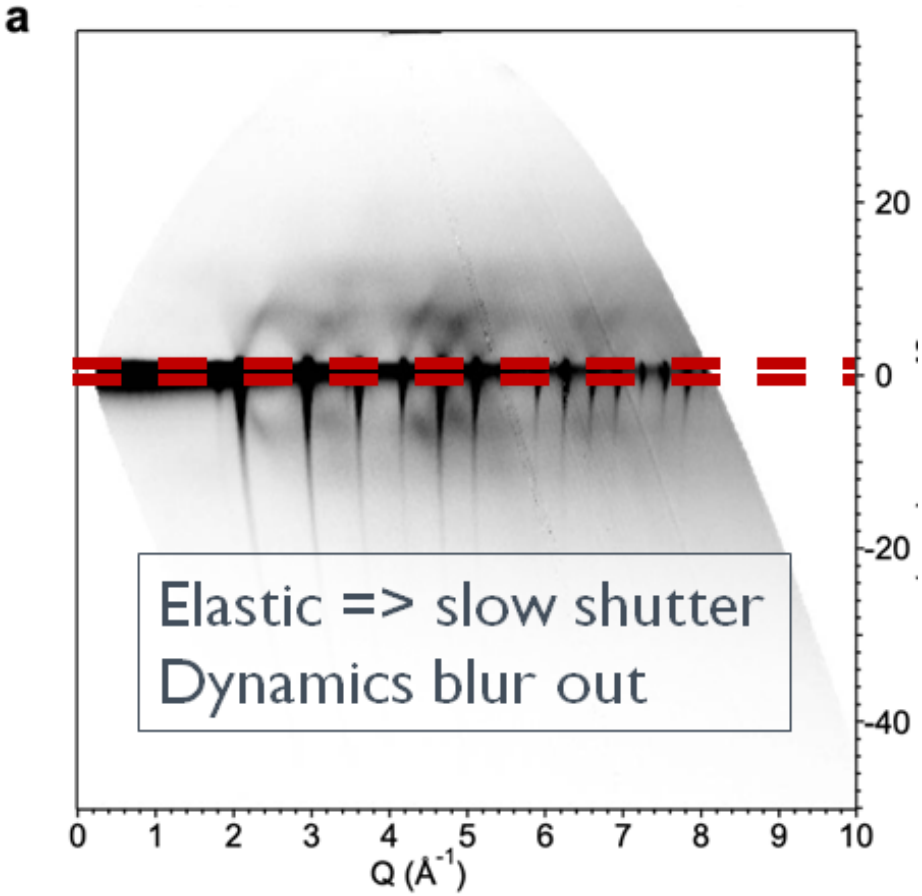
Local symmetry breaking: is it dynamic or not?

- Take a picture with a camera with a slow shutter
- Moving objects will blur out, stationary objects won't



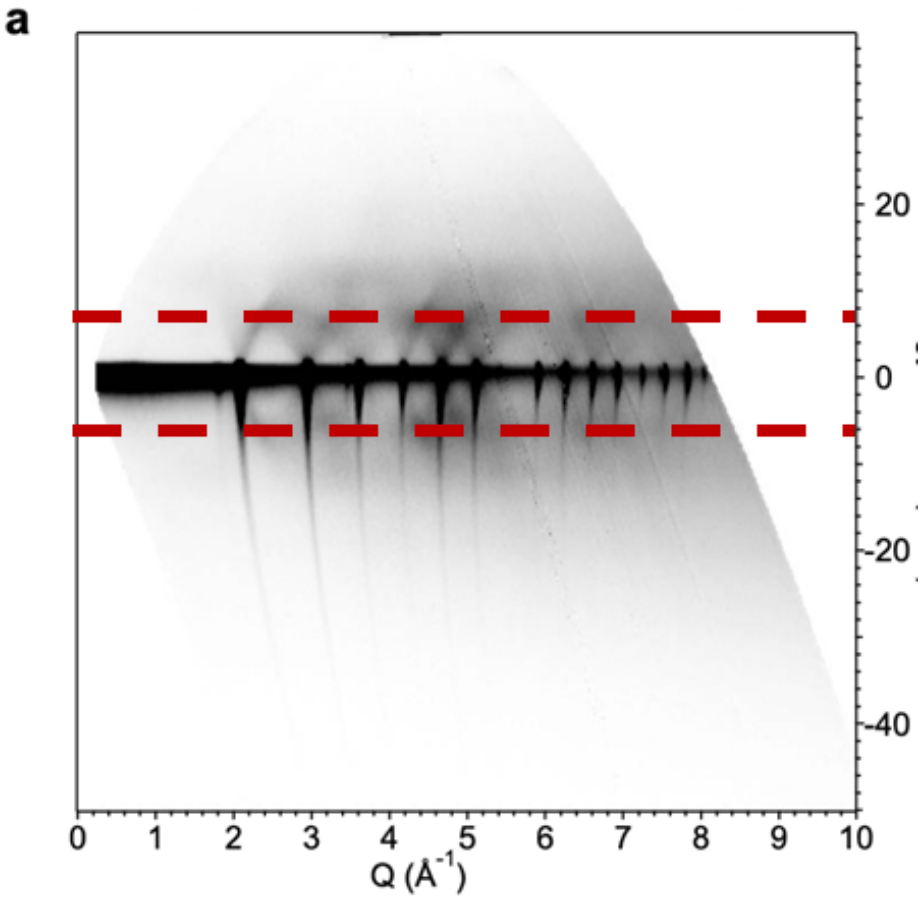
Changing the shutter speed with neutrons

- Vary the energy window (elastic line is always included)
- Extrapolates between $G(r, \tau = \infty)$ and $G(r, \tau = 0)$
- Infinite time correlations are blurred out $\Rightarrow$ average structure
- instantaneous correlations show all the ugly details



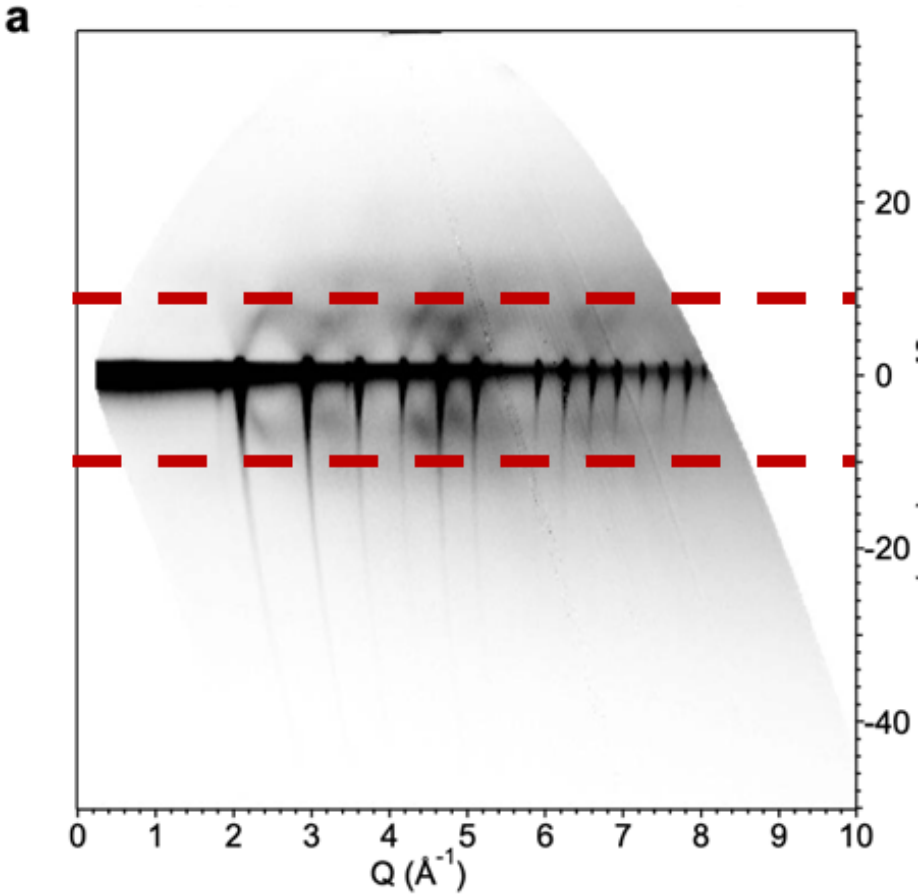
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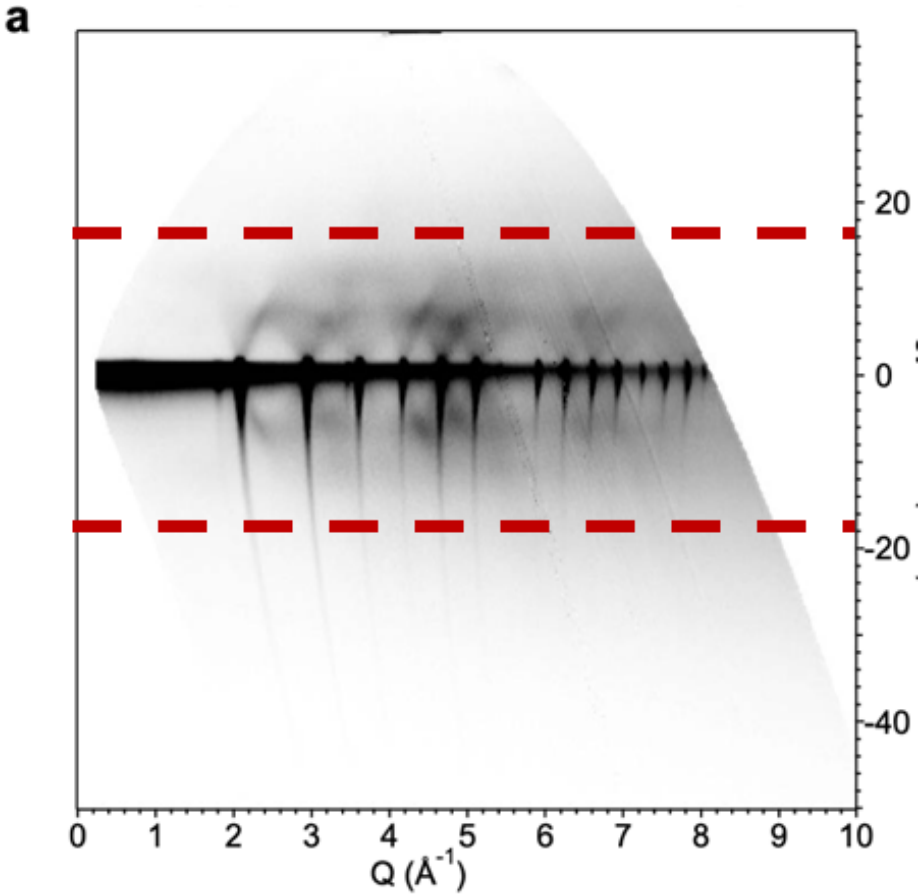
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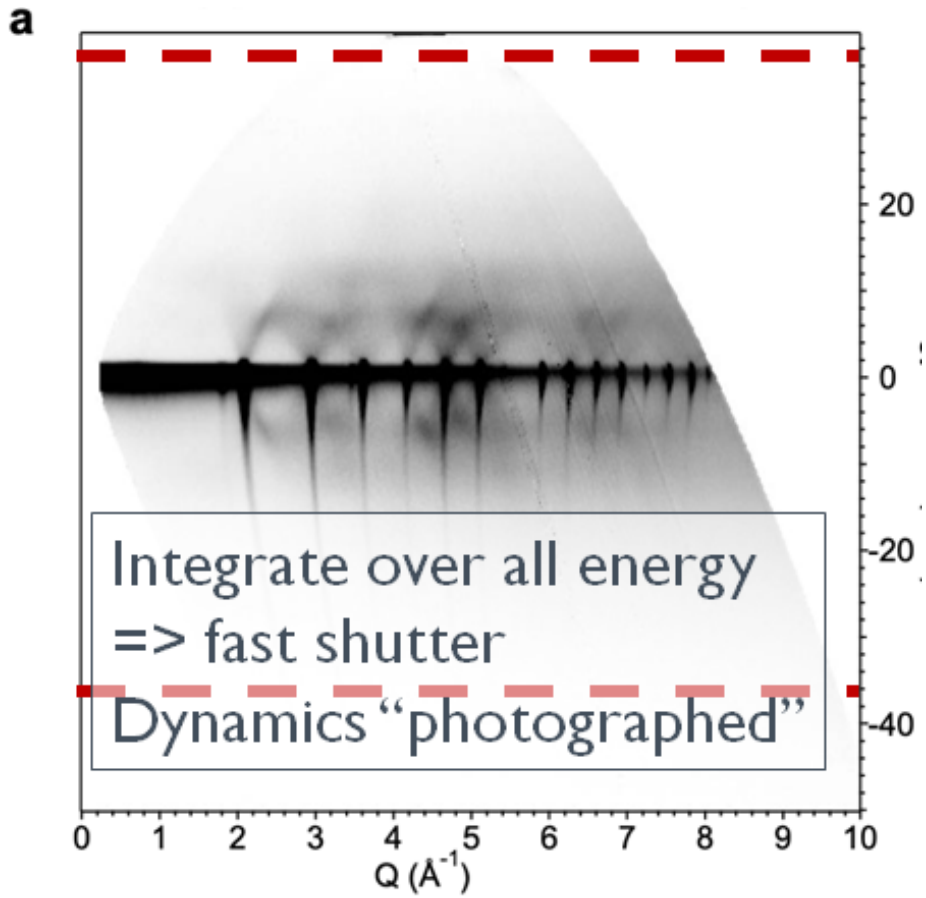
Changing the shutter speed with neutrons

- Vary the energy window (elastic line is always included)
- Extrapolates between $G(r, \tau = \infty)$ and $G(r, \tau = 0)$
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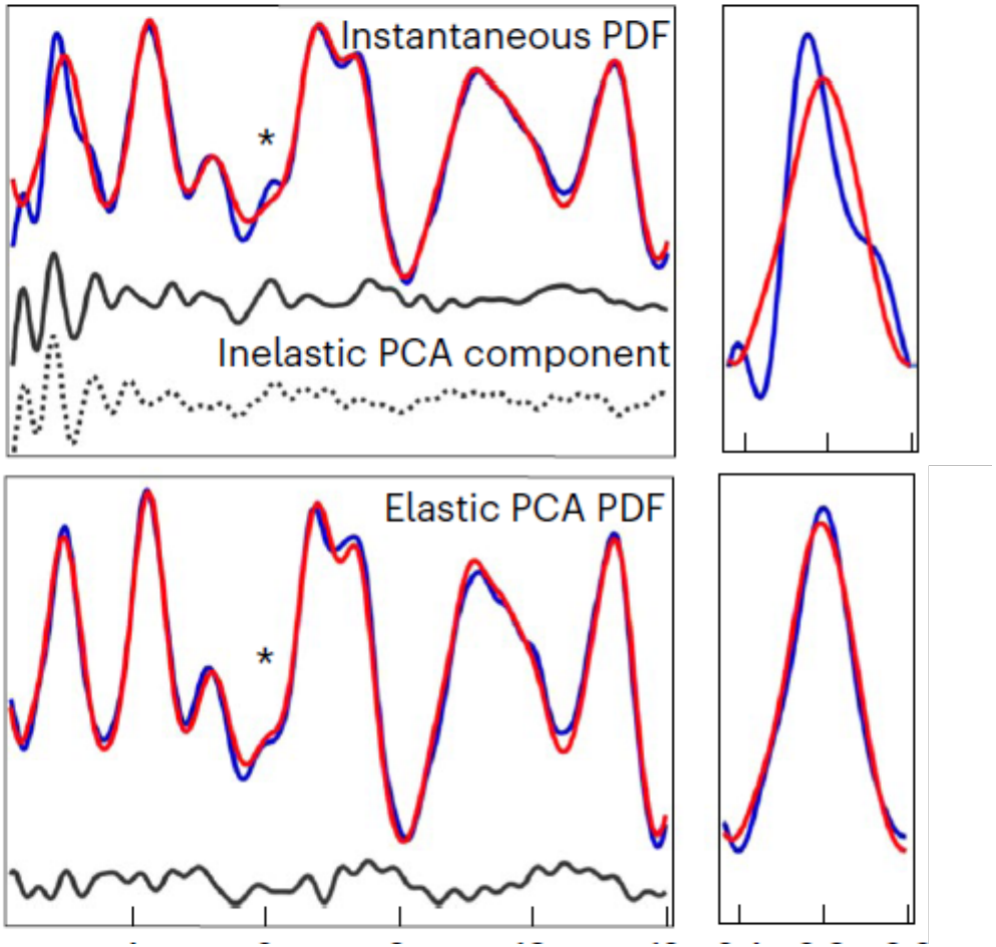
Changing the shutter speed with neutrons

- Vary the energy window (elastic line is always included)
- Extrapolates between $G(r, \tau = \infty)$ and $G(r, \tau = 0)$
- Infinite time correlations are blurred out $\Rightarrow$ average structure
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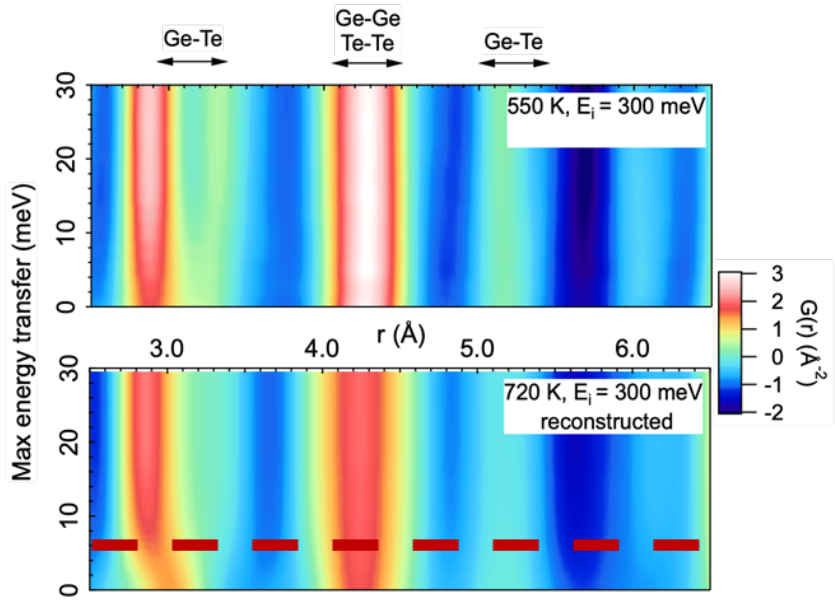
Fast shutter, Slow shutter

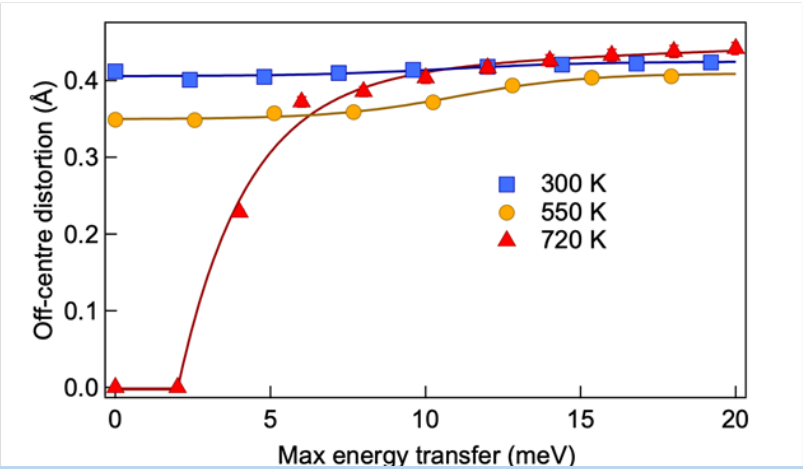
- Measured fast shutter vs cubic model
- Measured slow shutter PDF vs cubic model



Variable shuttering

- Crossover happens at 6 meV in the cubic phase
- No Crossover in the R phase (unsurprisingly)



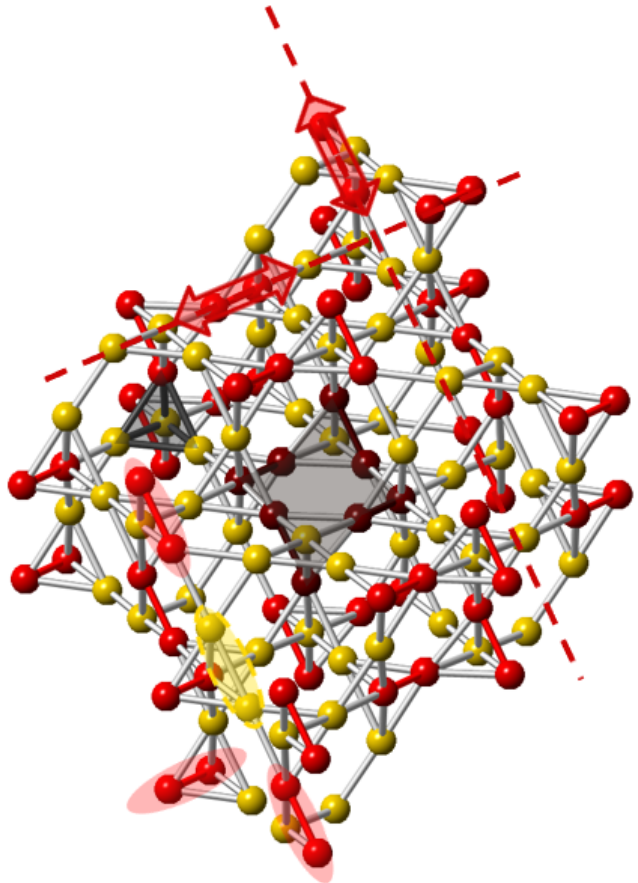


ODL and the Metal-Insulator Transition in $CuIr_2S_4$

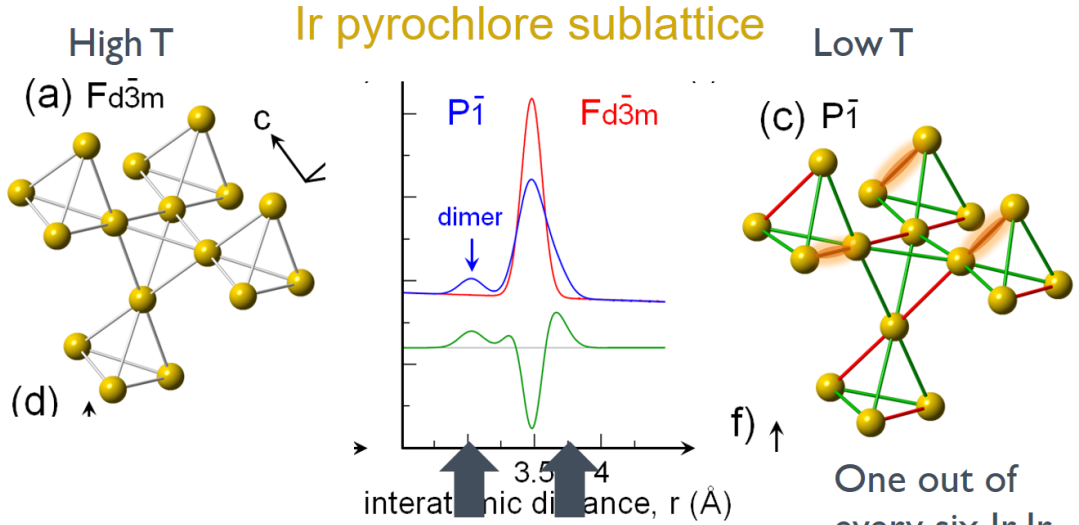
Emil Bozin
w/ JF Mitchell, ANL
M. Abeykoon, BNL

Data from 28-ID-2 NSLS-II

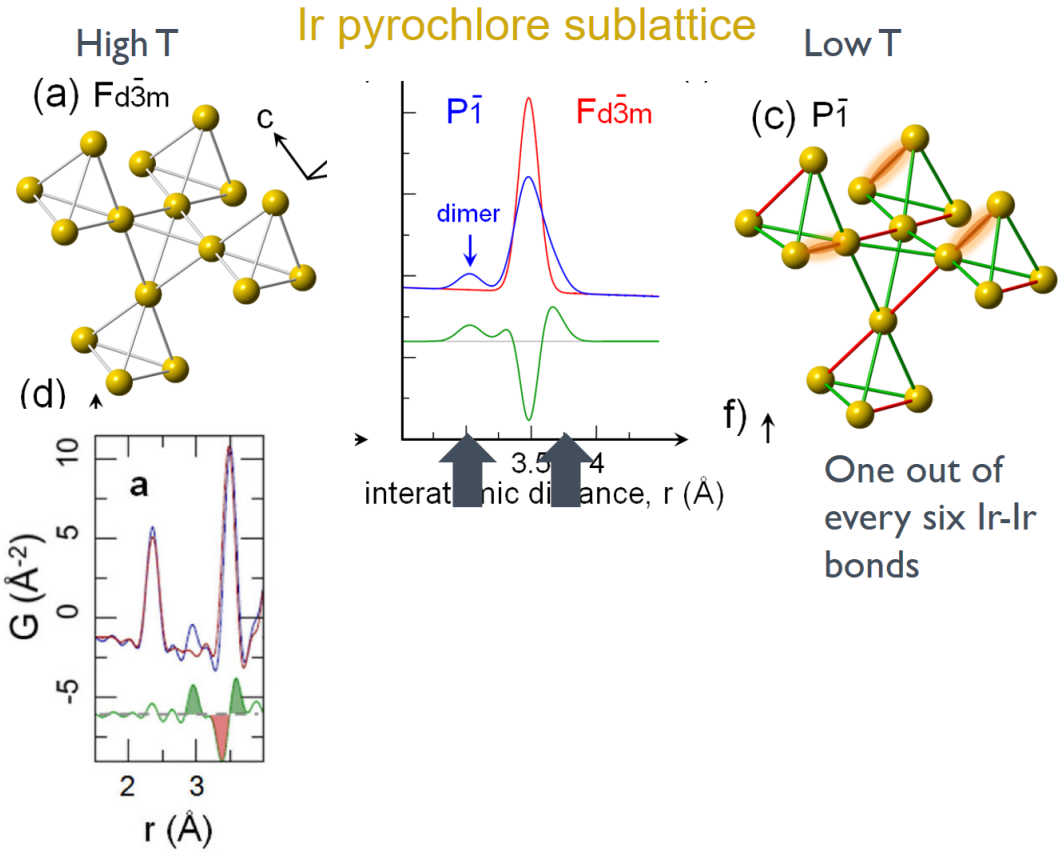




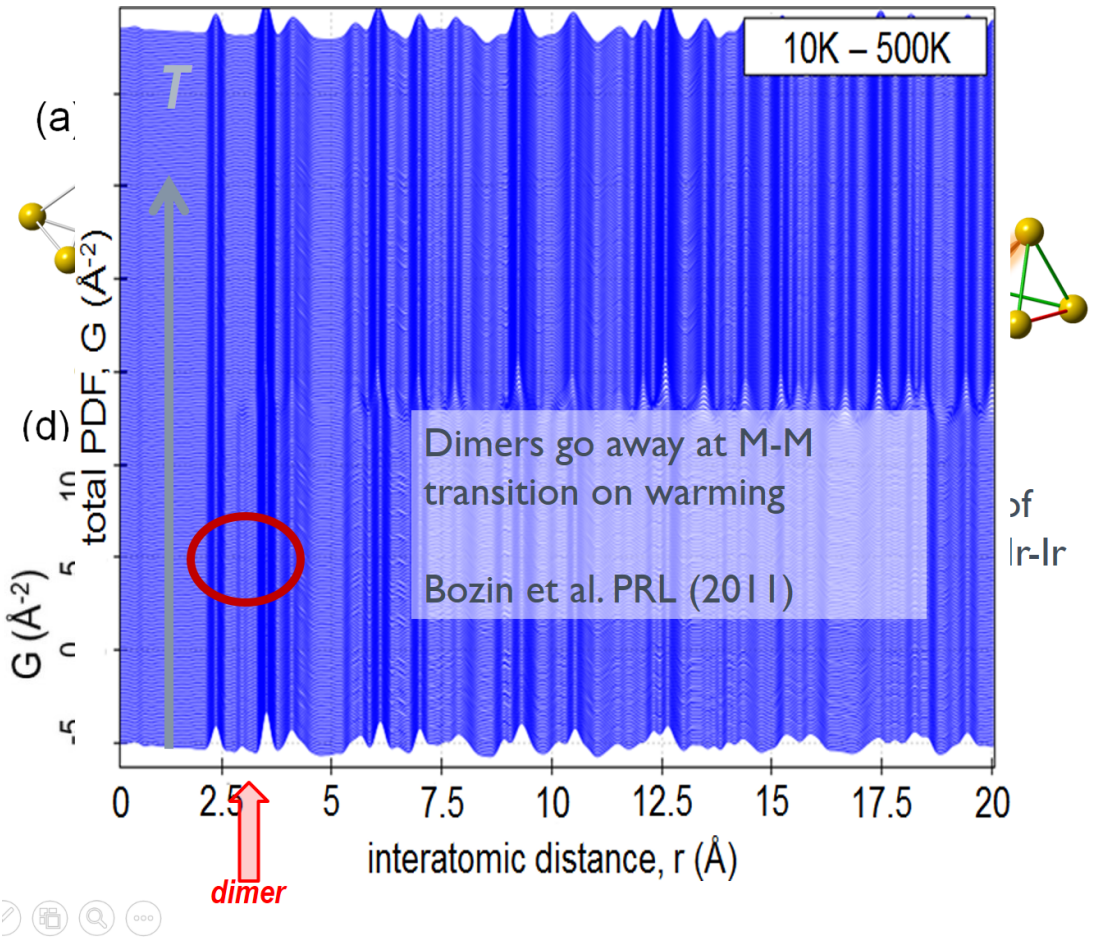
ODL and the Metal-Insulator Transition in $CuIr_2S_4$



ODL and the Metal-Insulator Transition in $CuIr_2S_4$

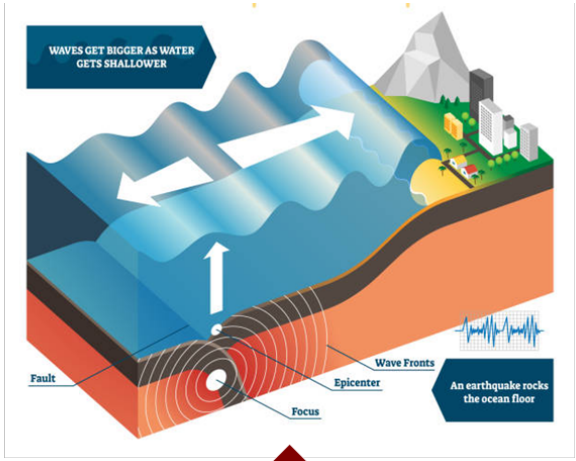


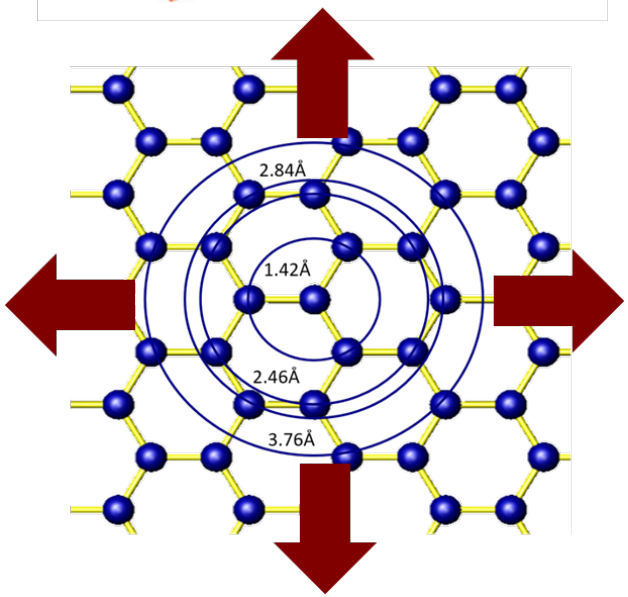
ODL and the Metal-Insulator Transition in $CuIr_2S_4$



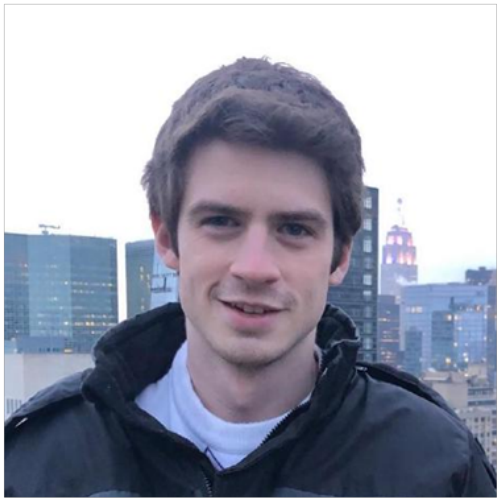
Goal of the Experiment

- Cool sample so it is in the dimer state
- Photo-excite with fs laser pulse to "excite" the system
- Does the dimer go away?
- What is the resulting state?
- How quickly is the dimer state destroyed?
- How does the effect propagate through the lattice



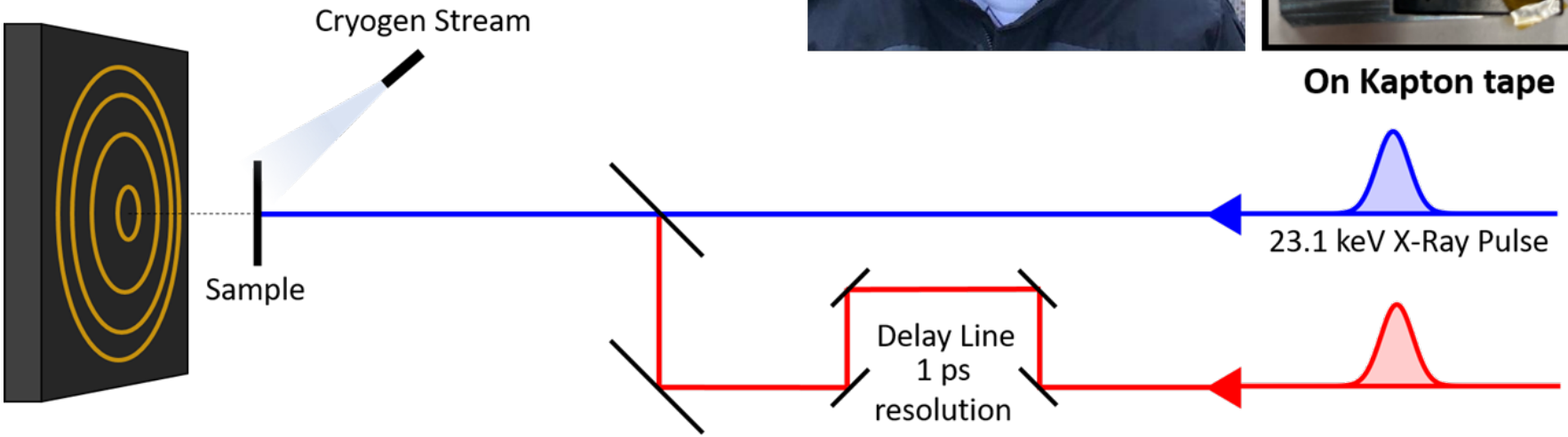


Experimental Setup

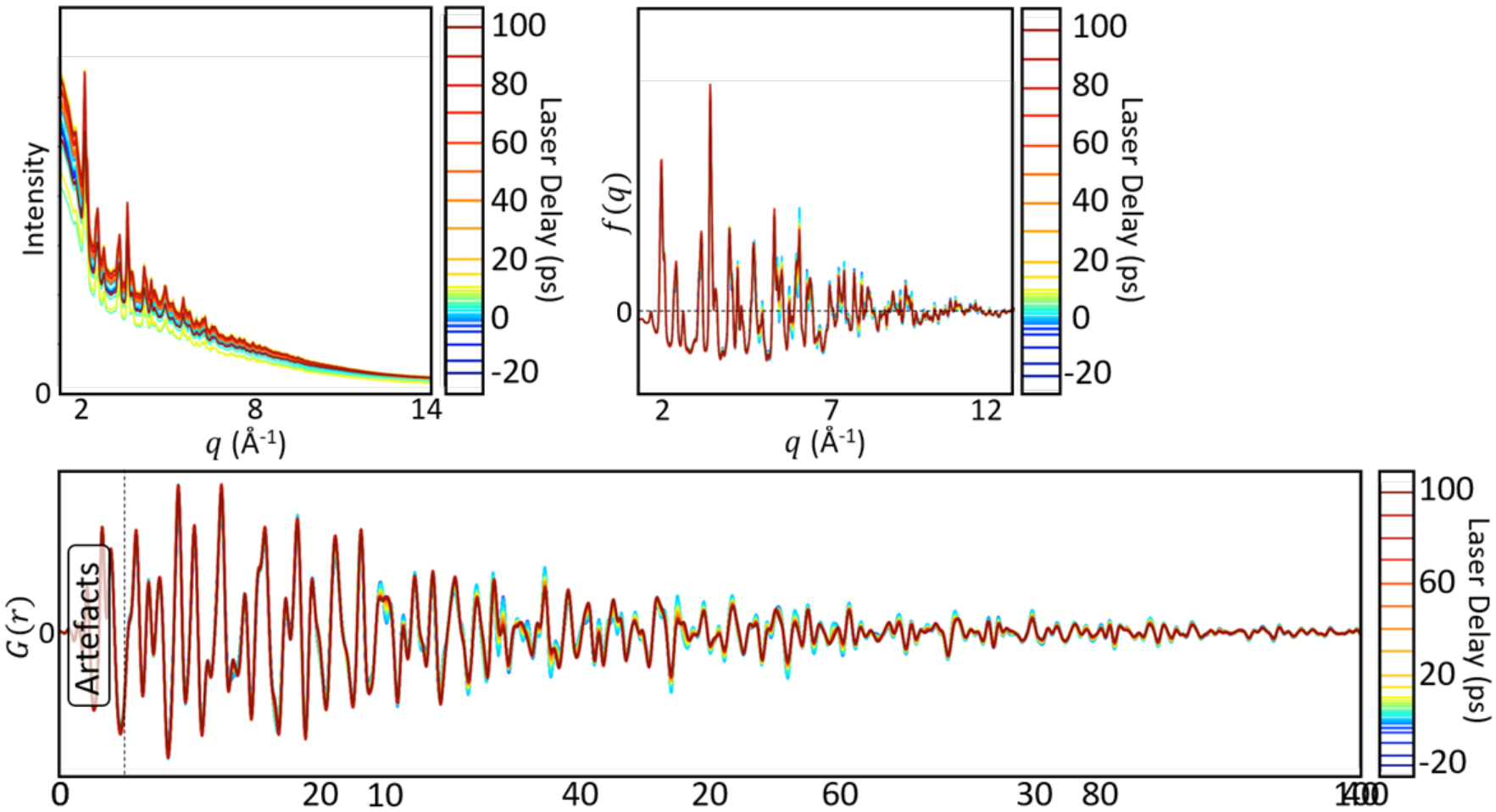




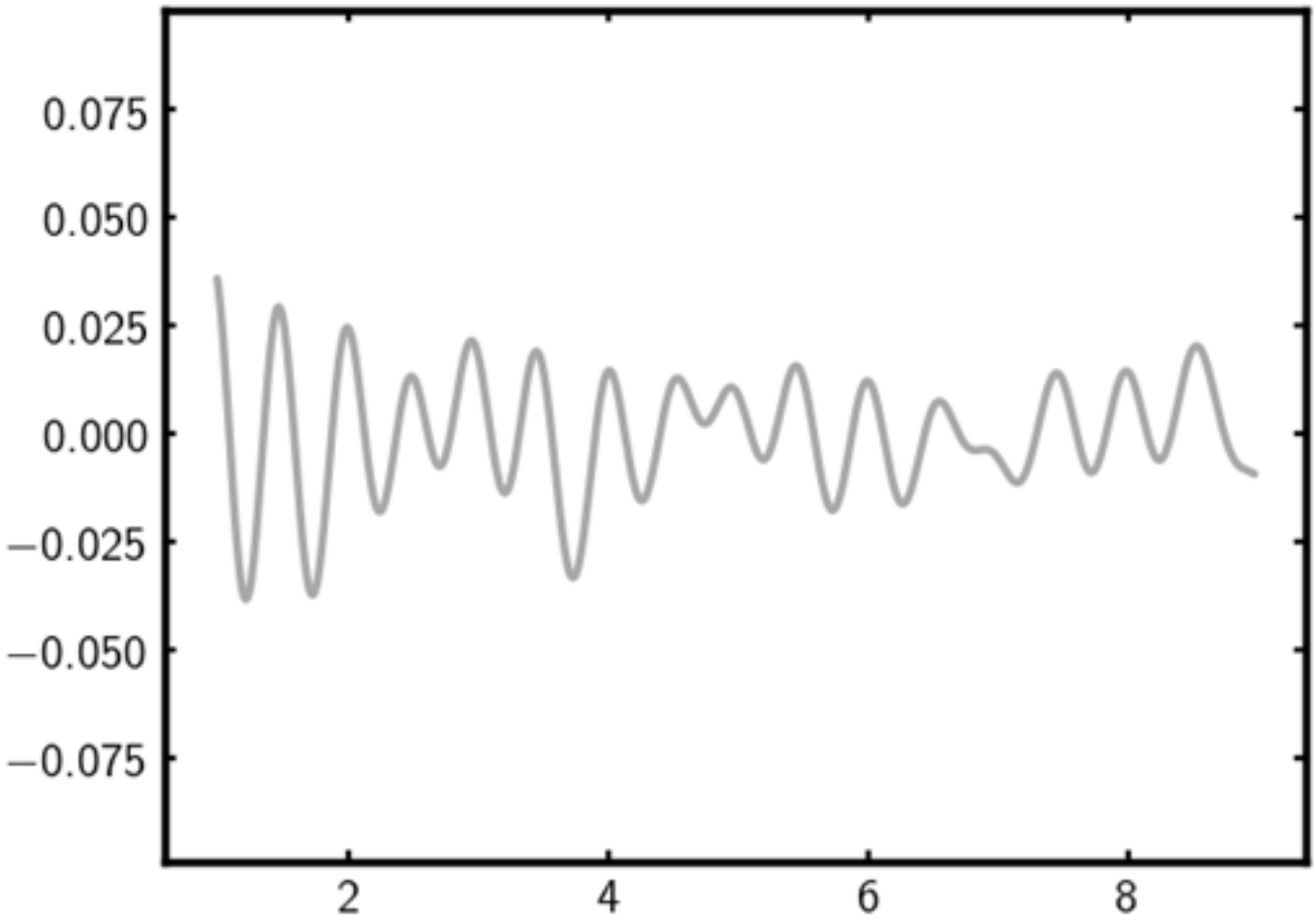
On Kapton tape



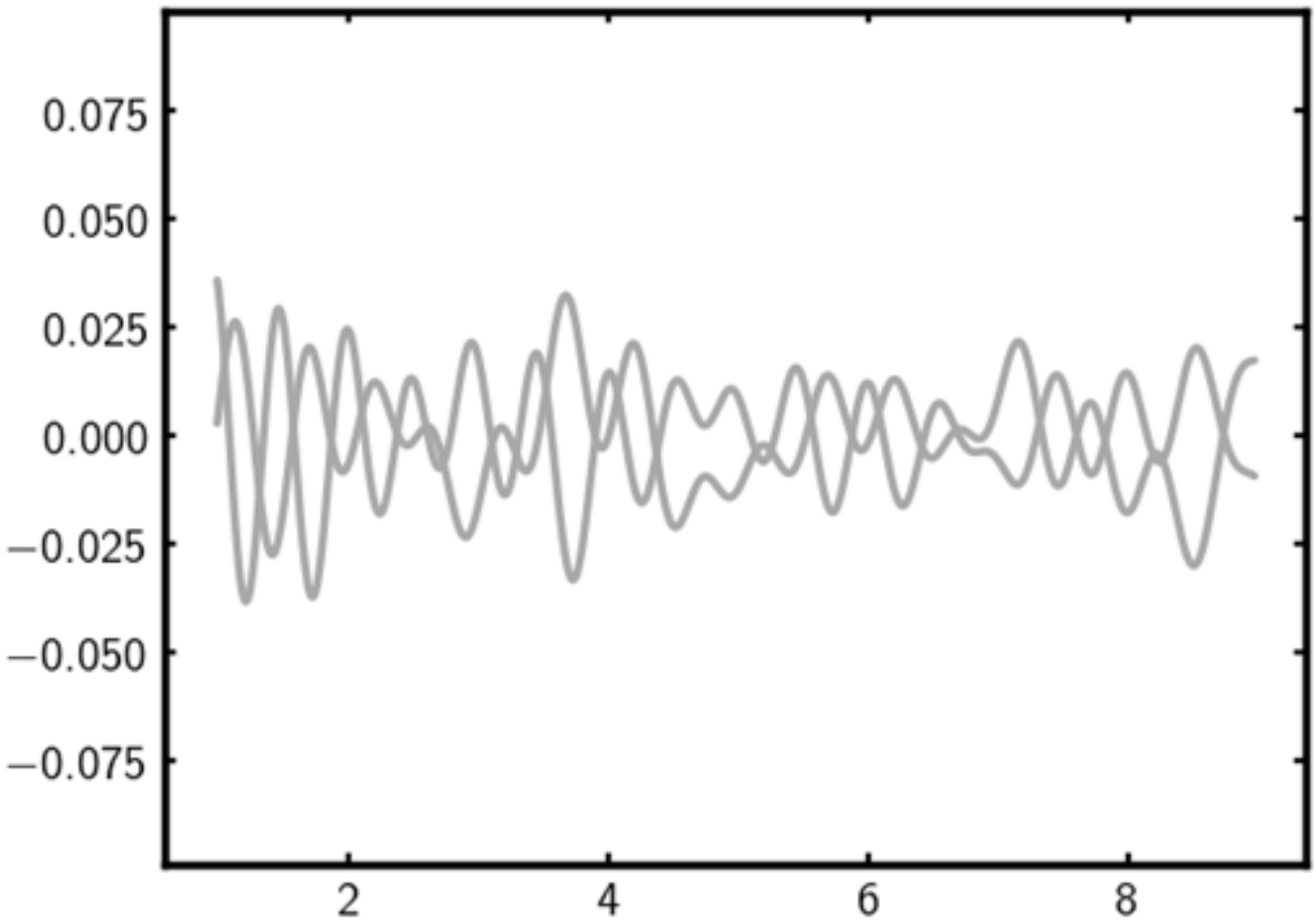
Data Reduction



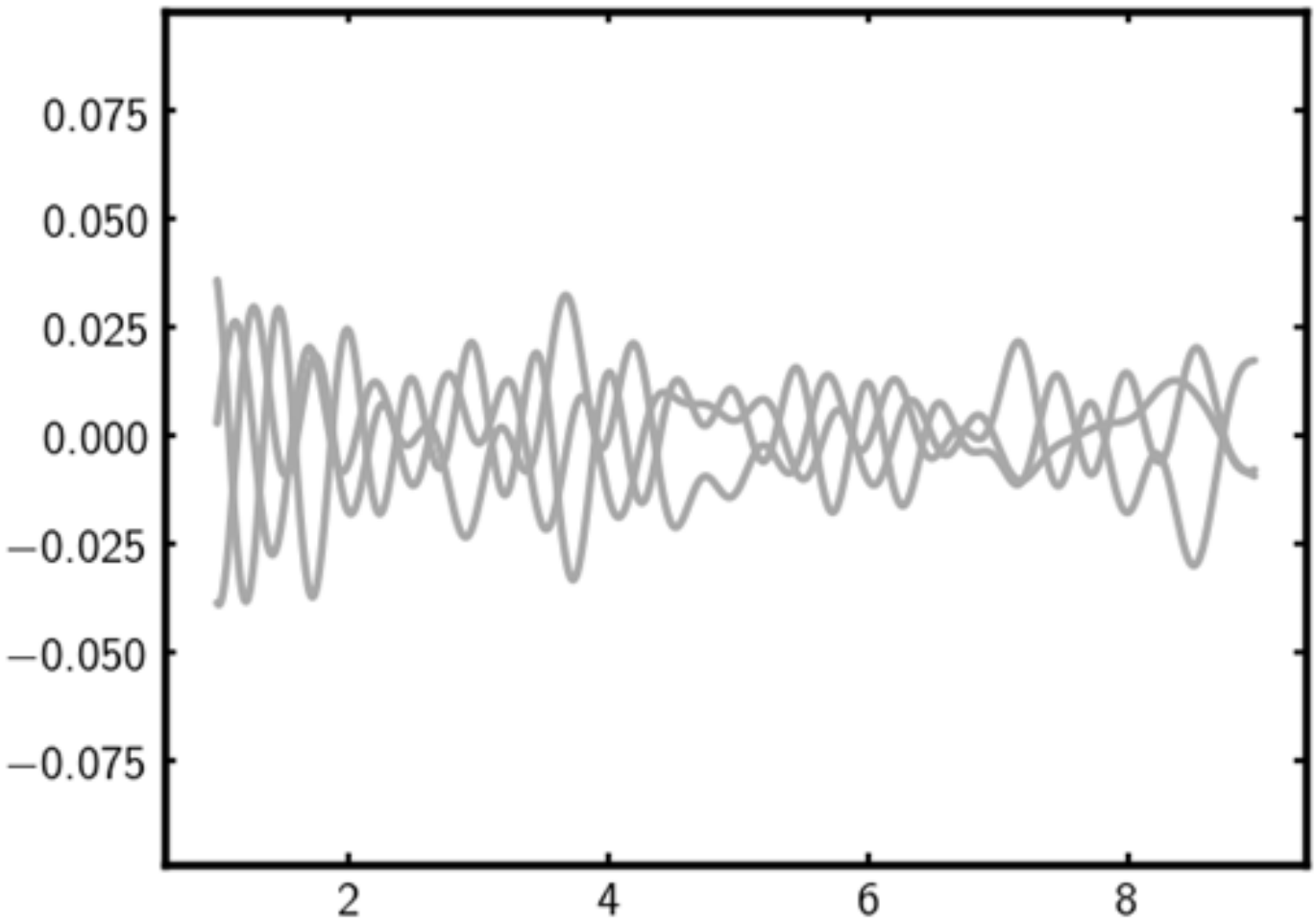
$$\Delta G = G(t = -20\text{ps}) - \langle G(t < 0) \rangle$$



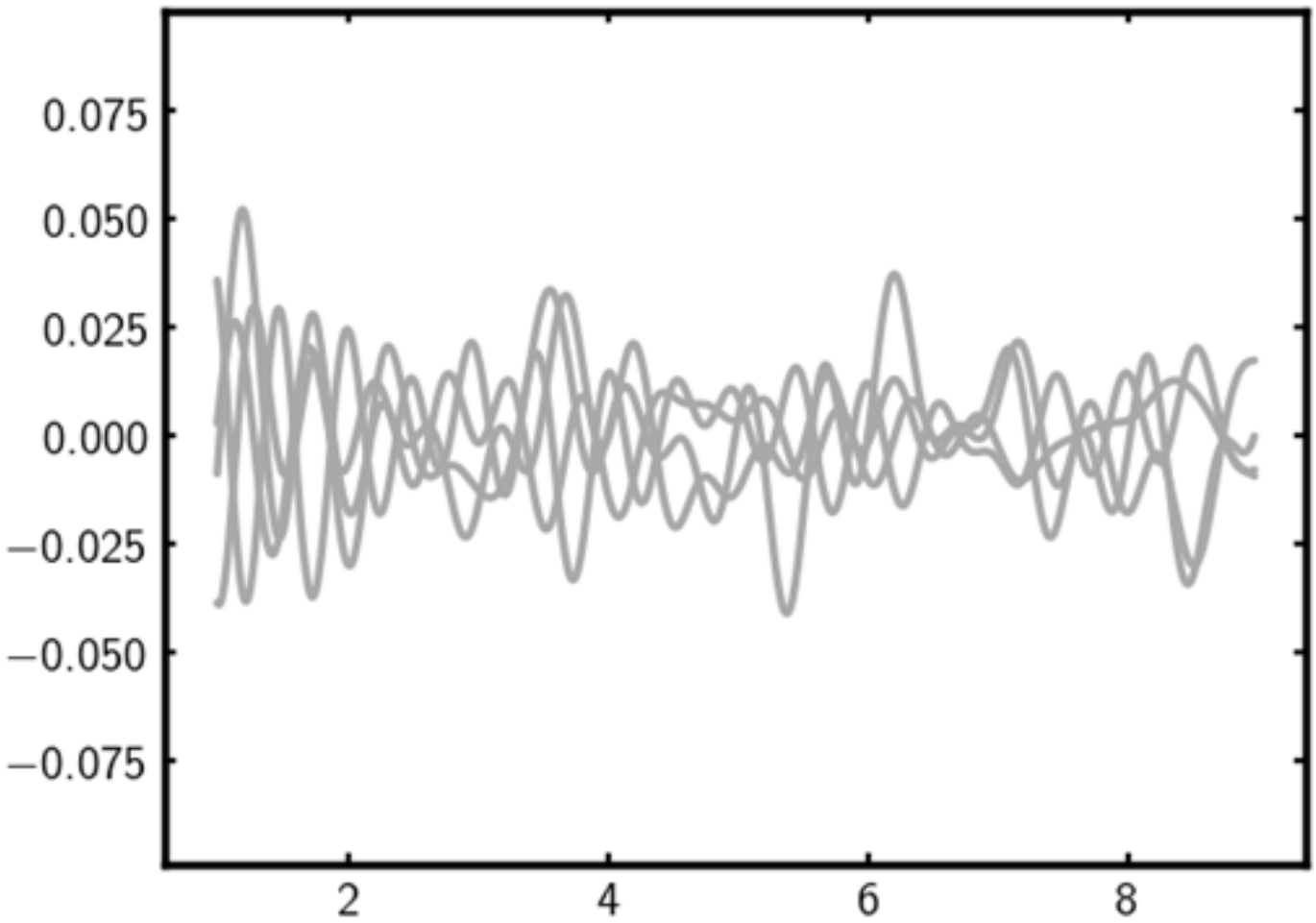
$$\Delta G = G(t = -15\text{ps}) - \langle G(t < 0) \rangle$$



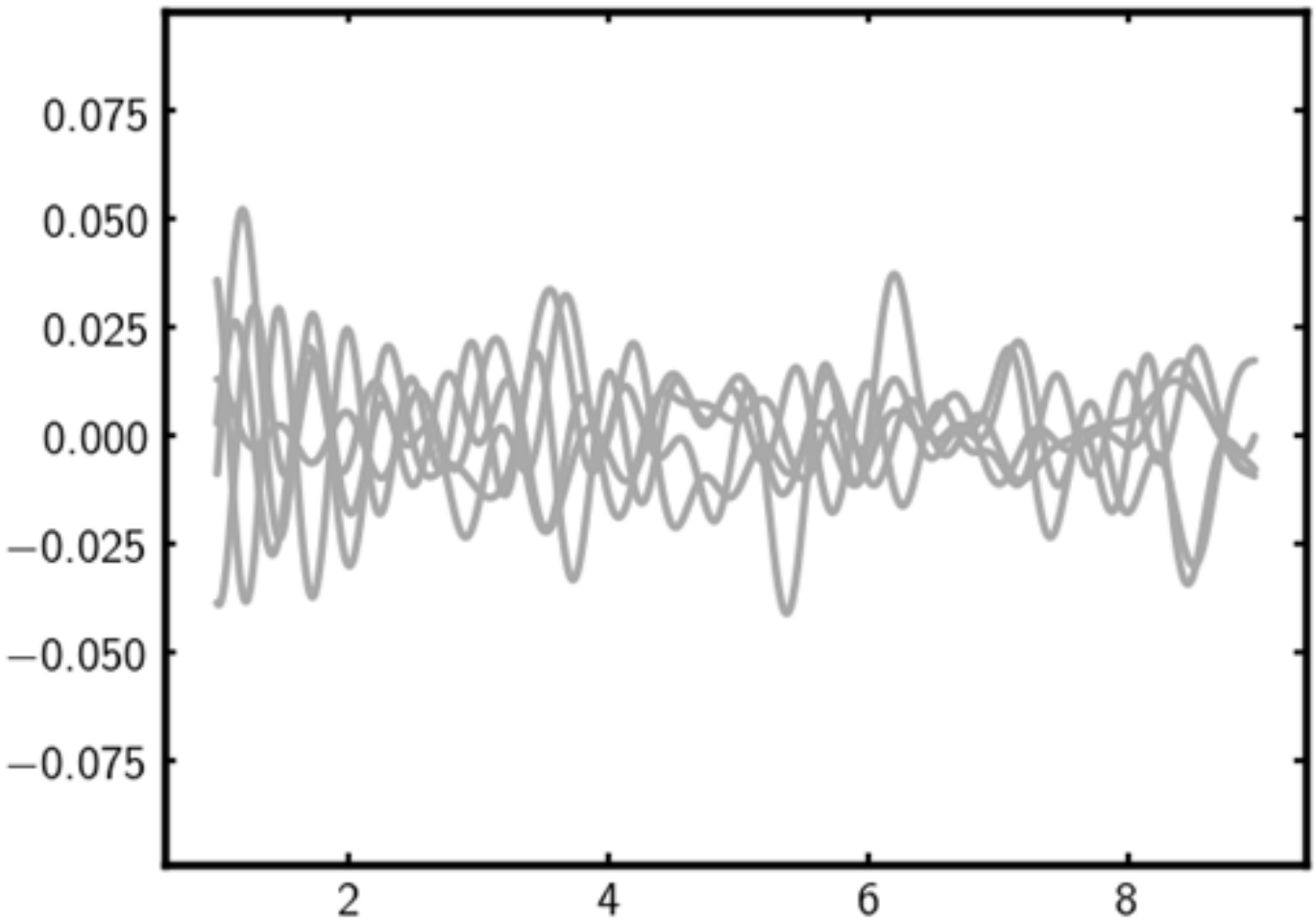
$$\Delta G = G(t = -10\text{ps}) - \langle G(t < 0) \rangle$$



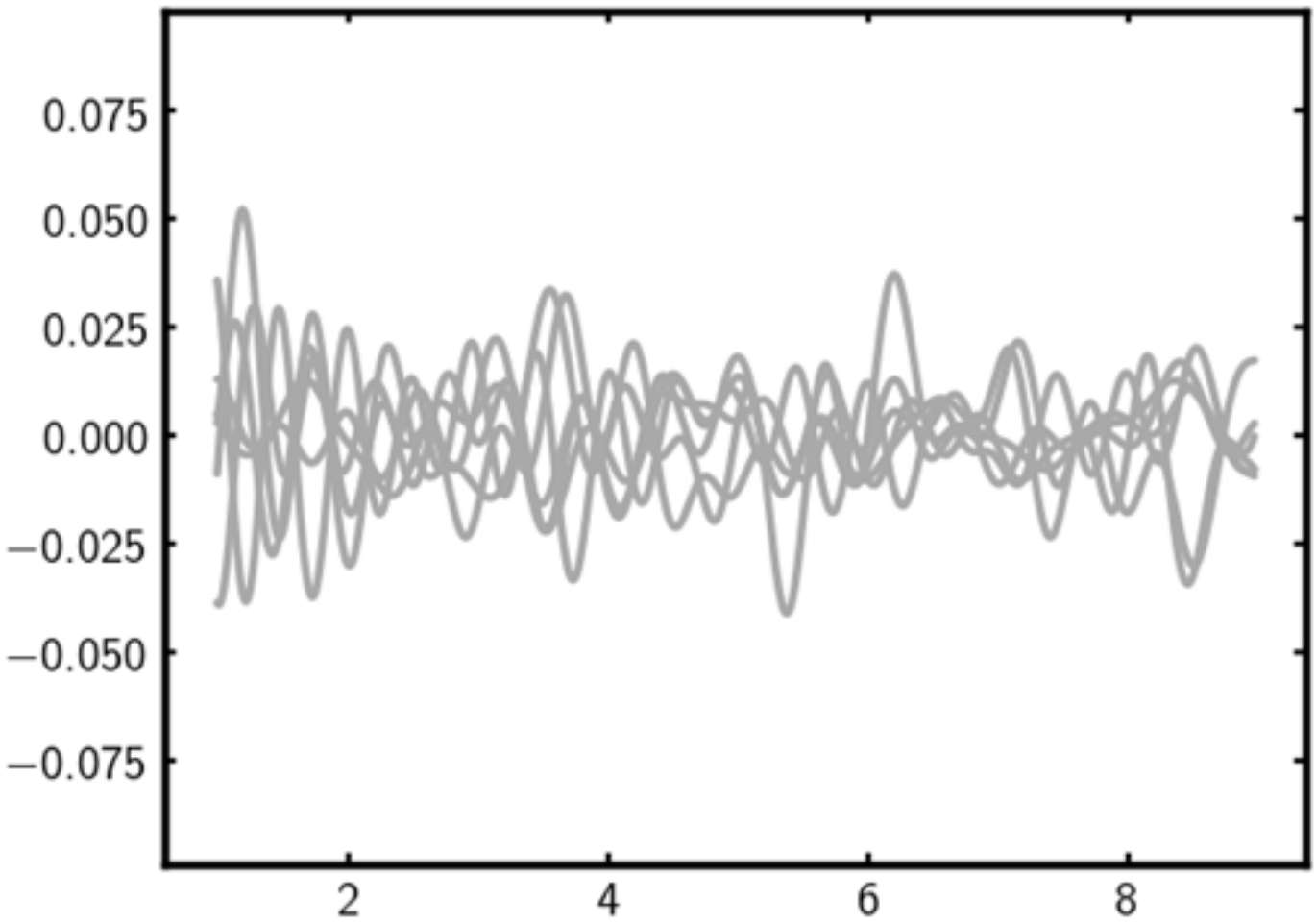
$$\Delta G = G(t = -5\text{ps}) - \langle G(t < 0) \rangle$$



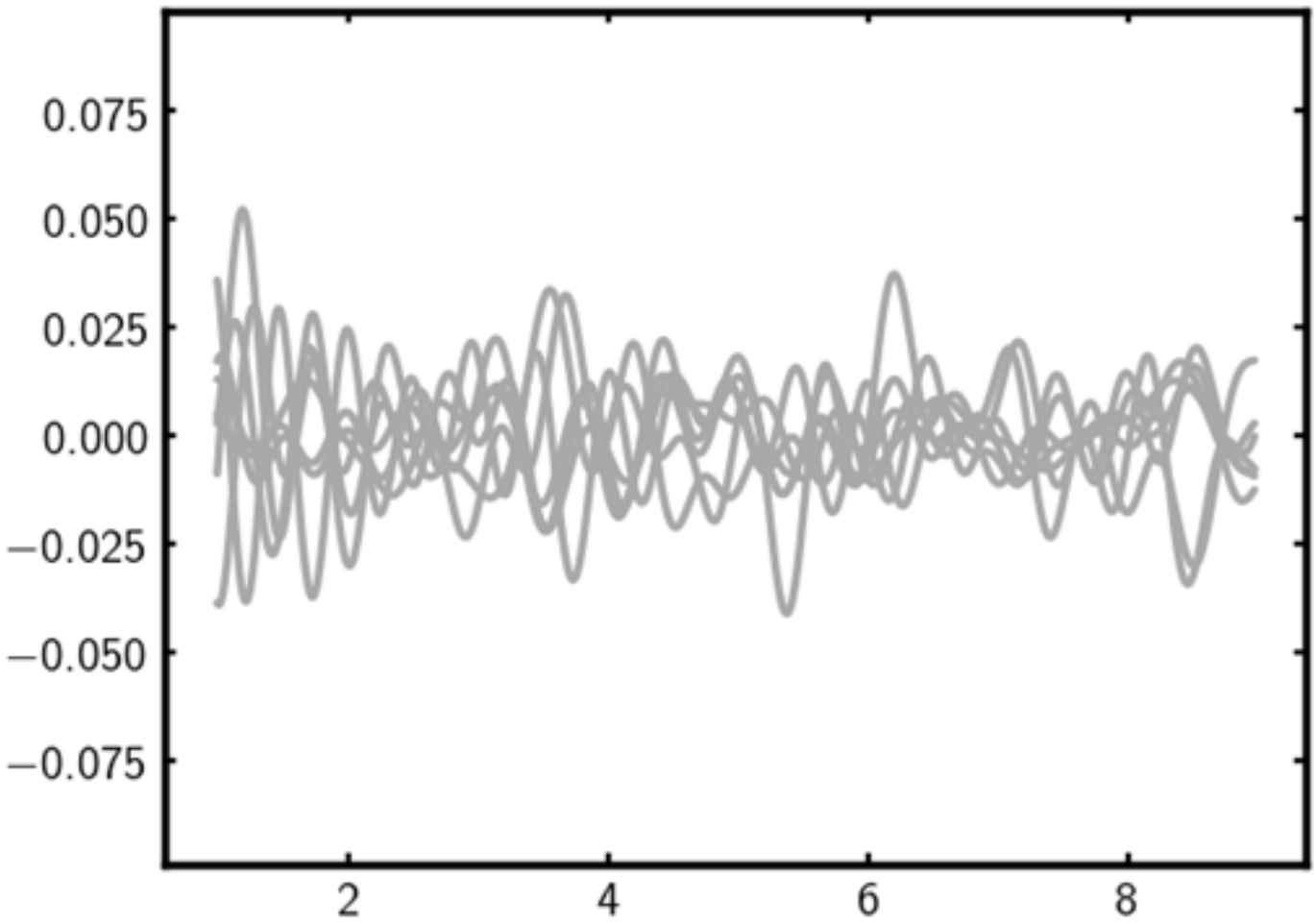
$$\Delta G = G(t = -3\text{ps}) - \langle G(t < 0) \rangle$$



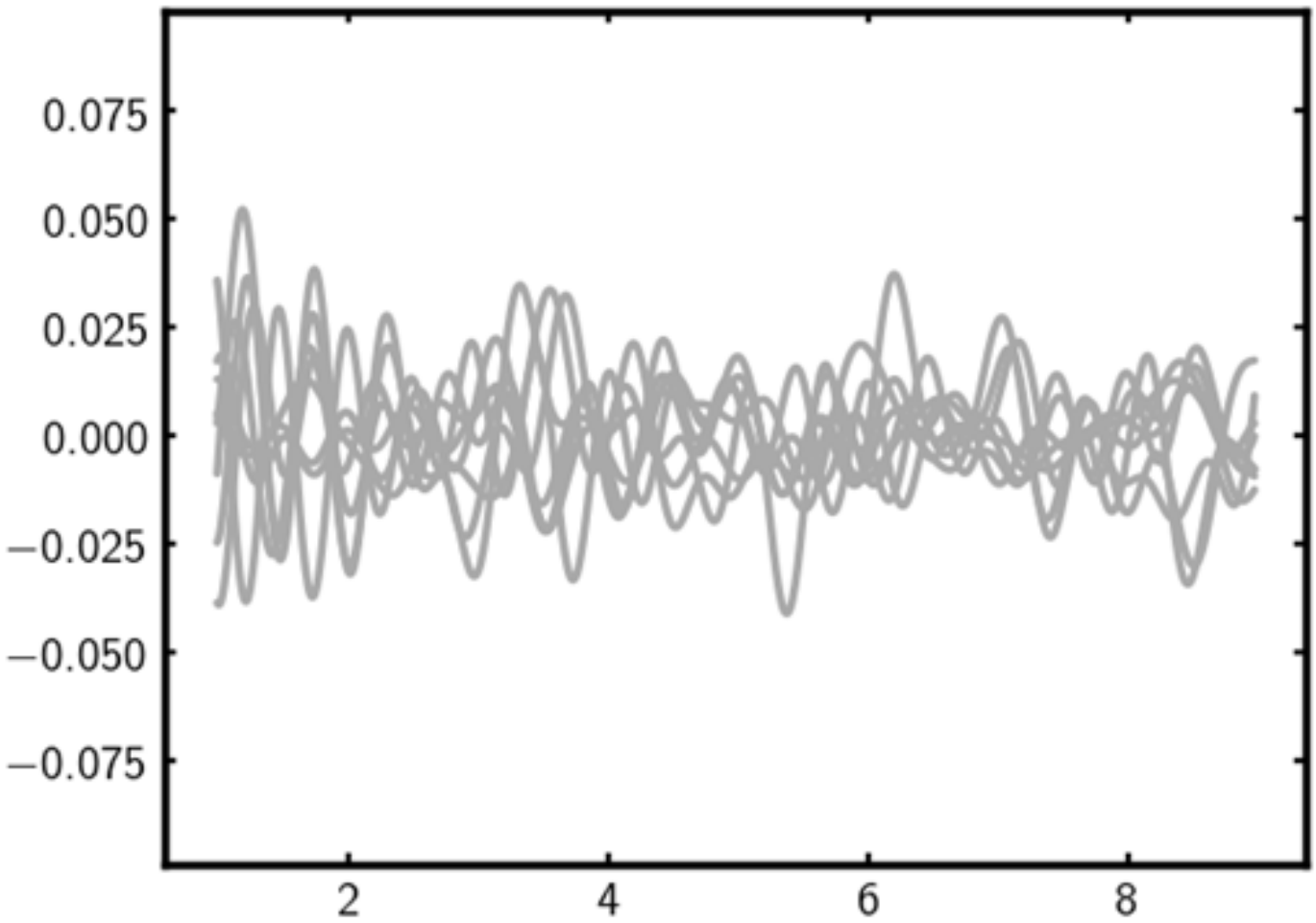
$$\Delta G = G(t = -2\text{ps}) - \langle G(t < 0) \rangle$$



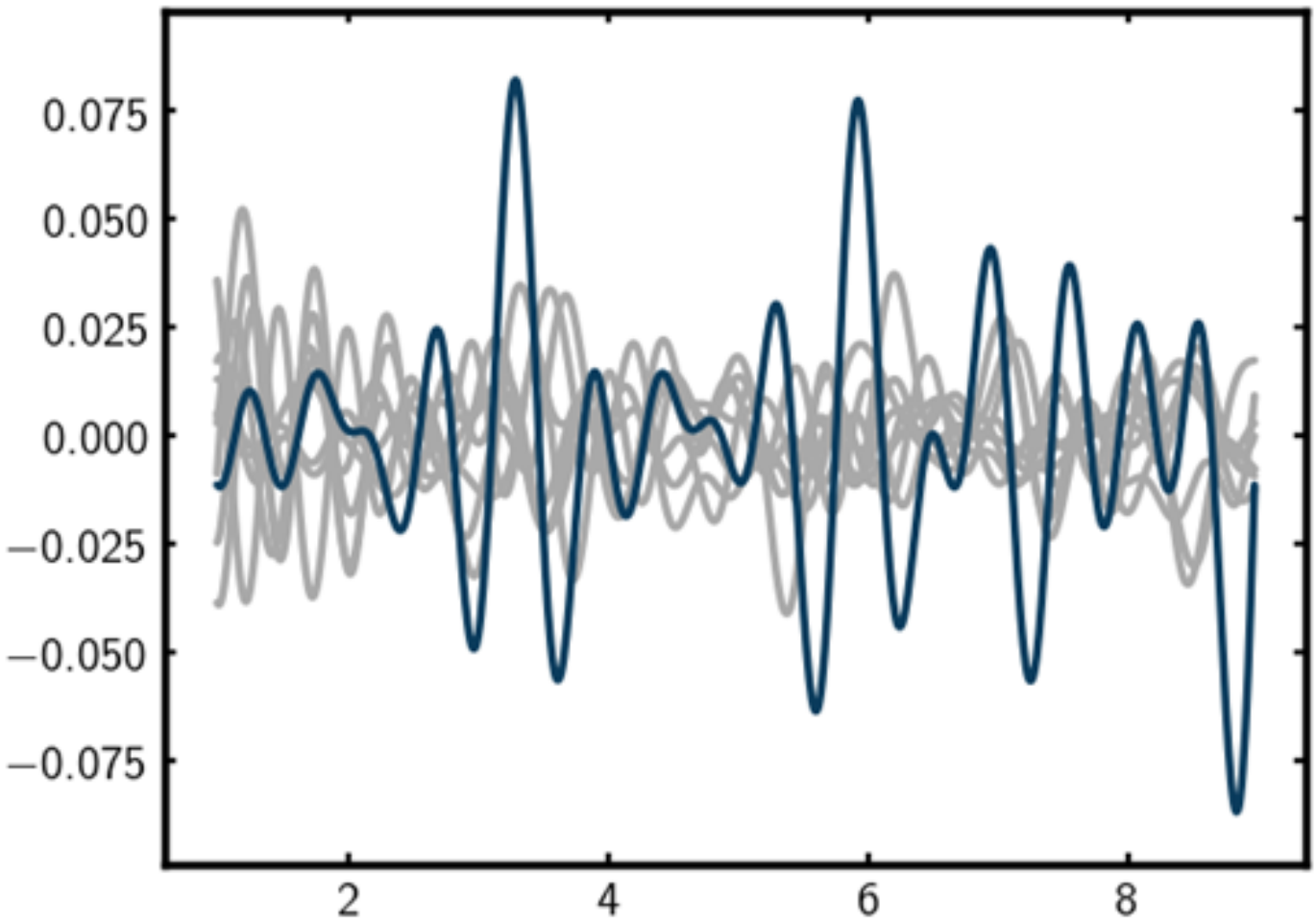
$$\Delta G = G(t = -1\text{ps}) - \langle G(t < 0) \rangle$$



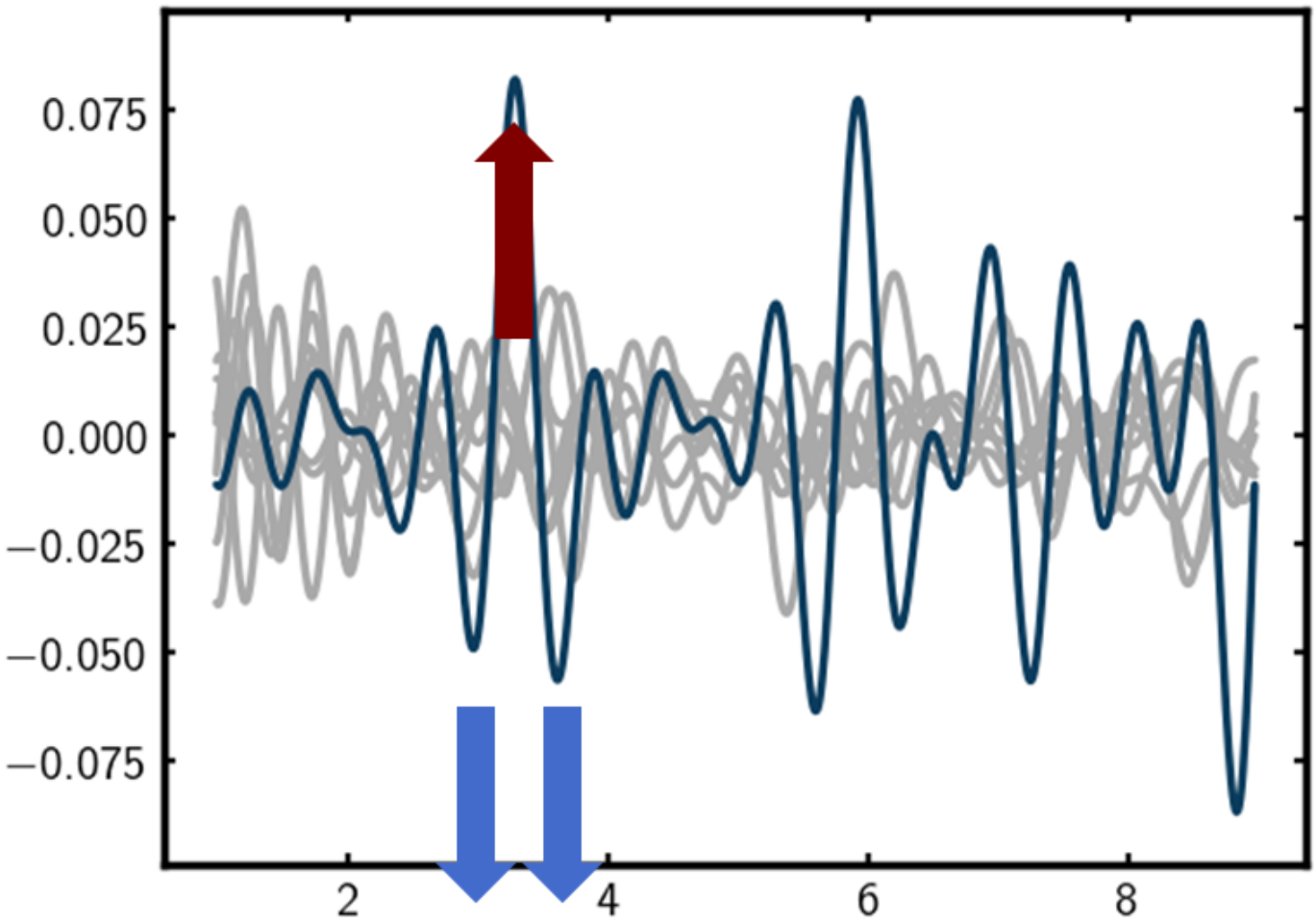
$$\Delta G = G(t = -0\text{ps}) - \langle G(t < 0) \rangle$$



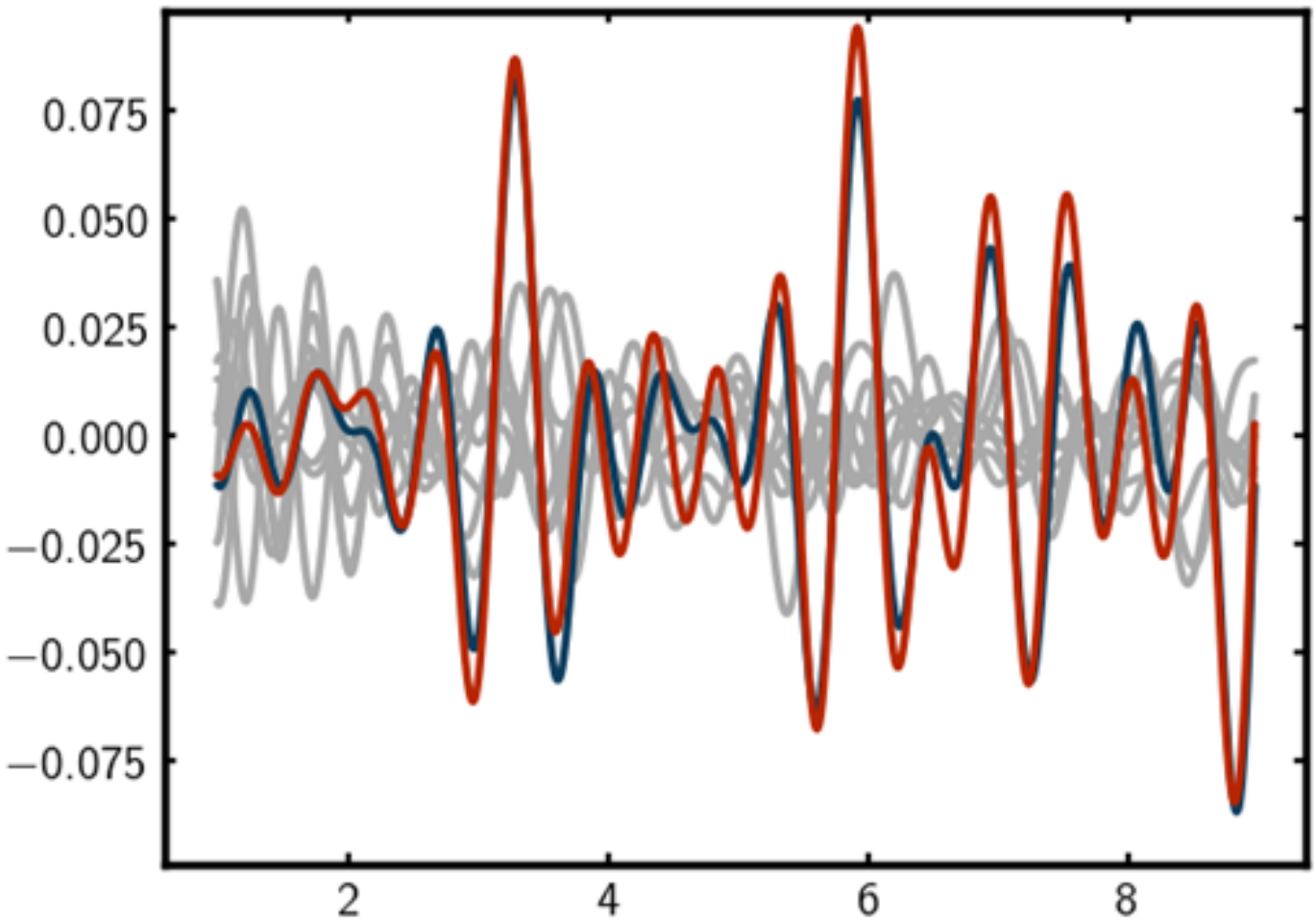
$$\Delta G = G(t = +1\text{ps}) - \langle G(t < 0) \rangle$$



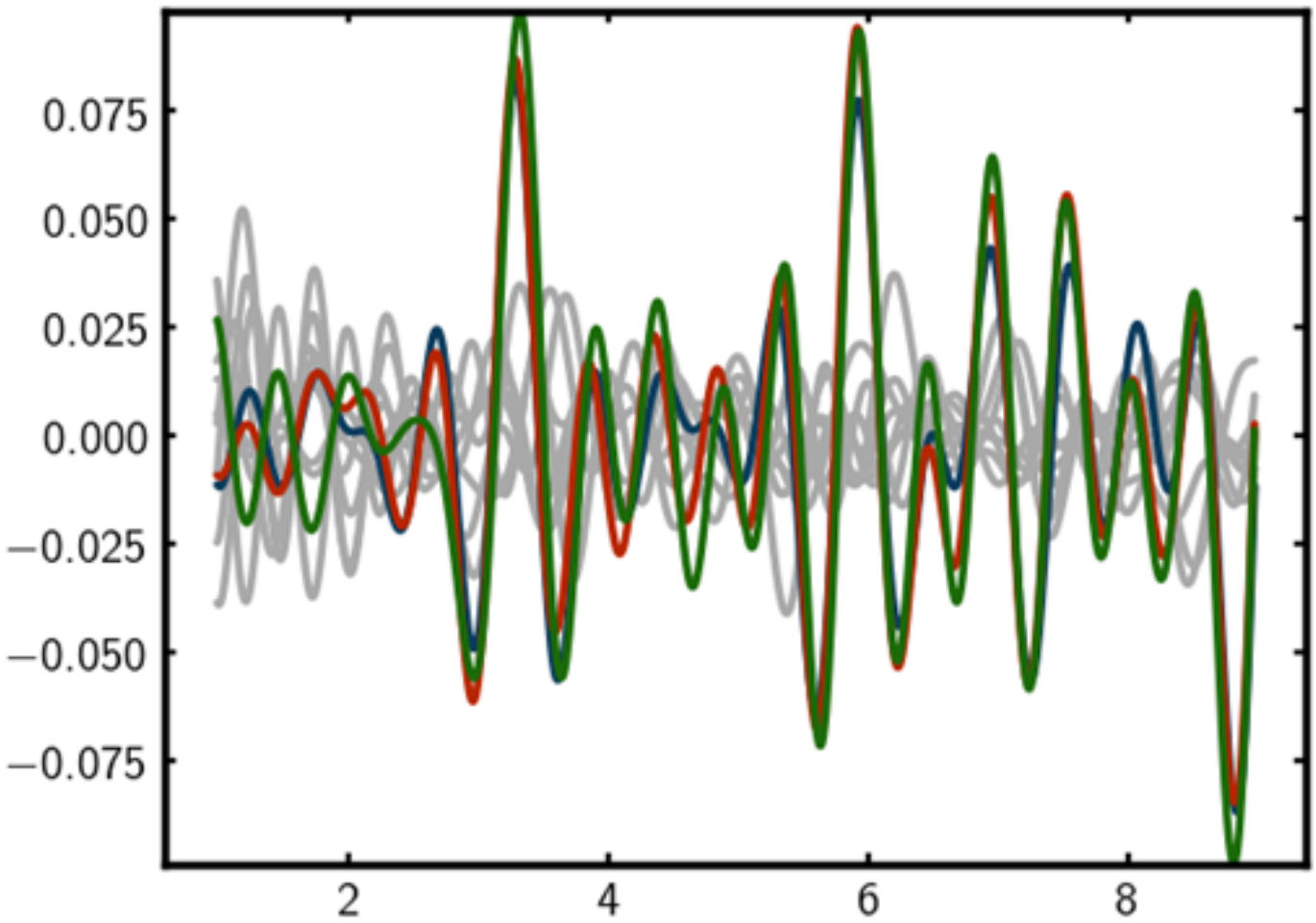
$$\Delta G = G(t = +1\text{ps}) - \langle G(t < 0) \rangle$$



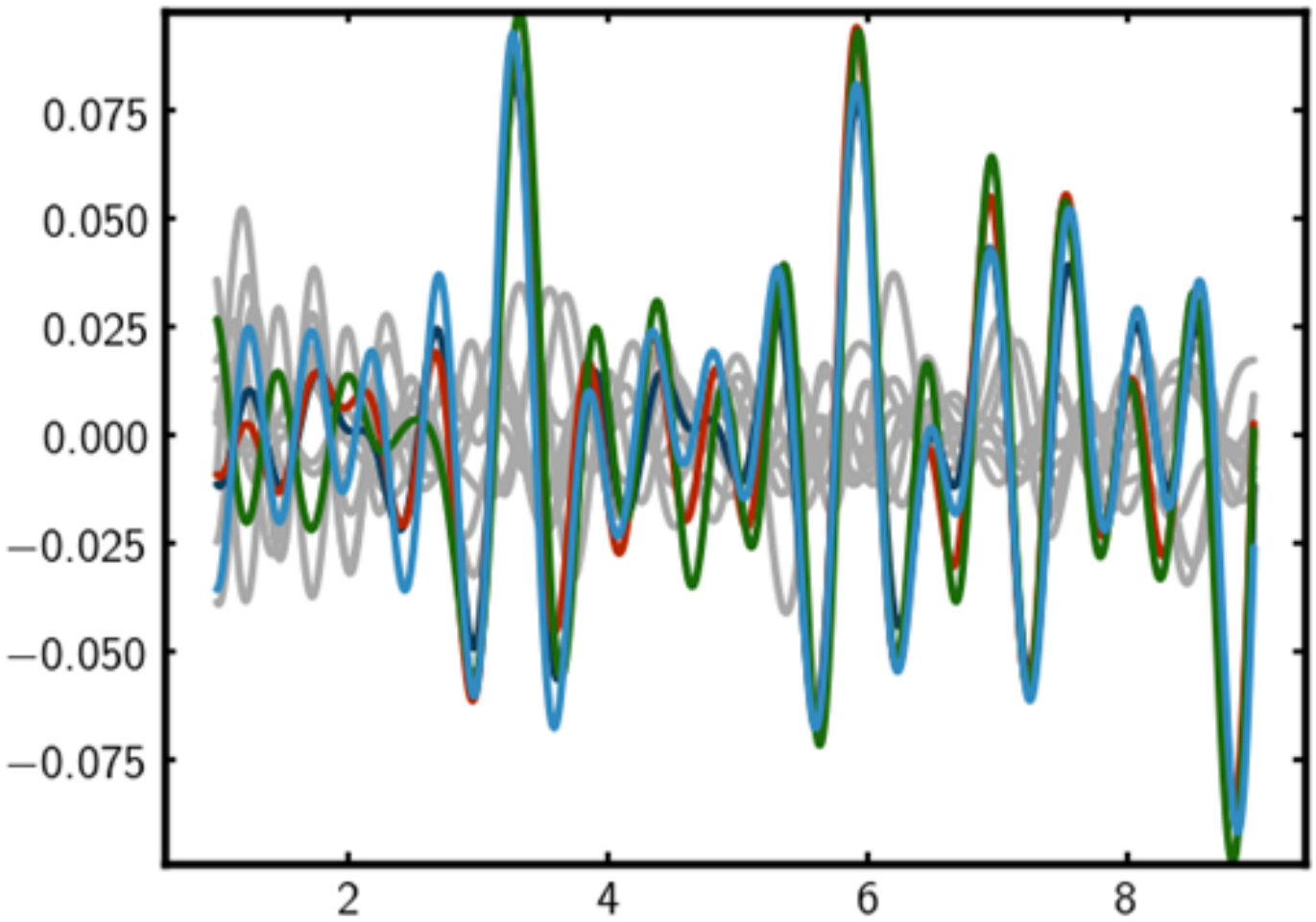
$$\Delta G = G(t = +2\text{ps}) - \langle G(t < 0) \rangle$$



$$\Delta G = G(t = +3\text{ps}) - \langle G(t < 0) \rangle$$

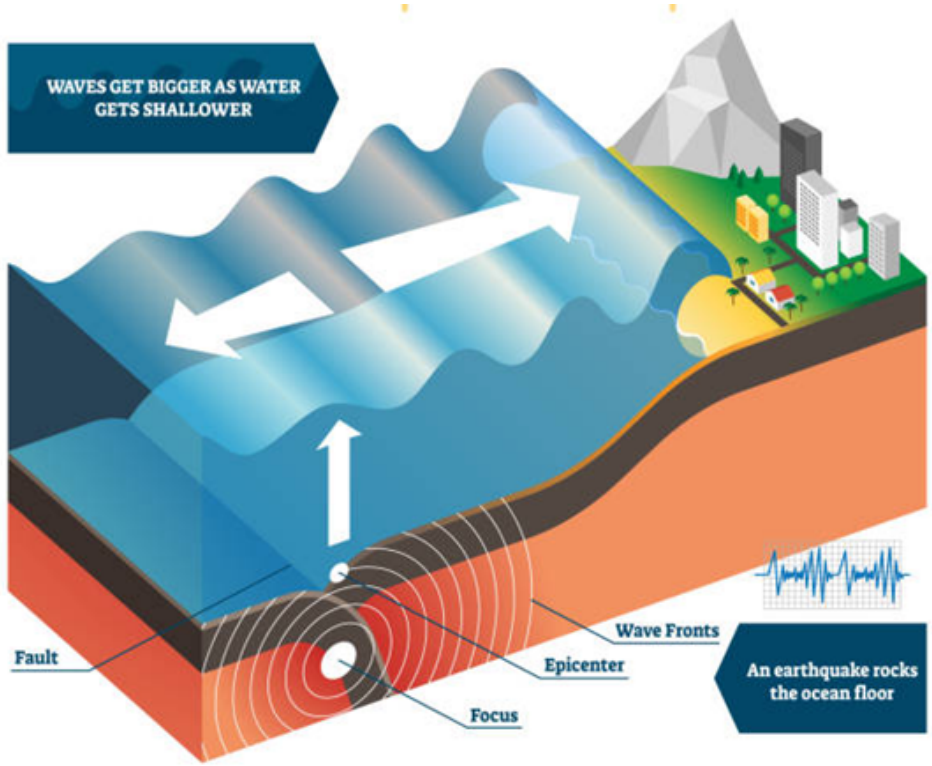


$$\Delta G = G(t = +4\text{ps}) - \langle G(t < 0) \rangle$$

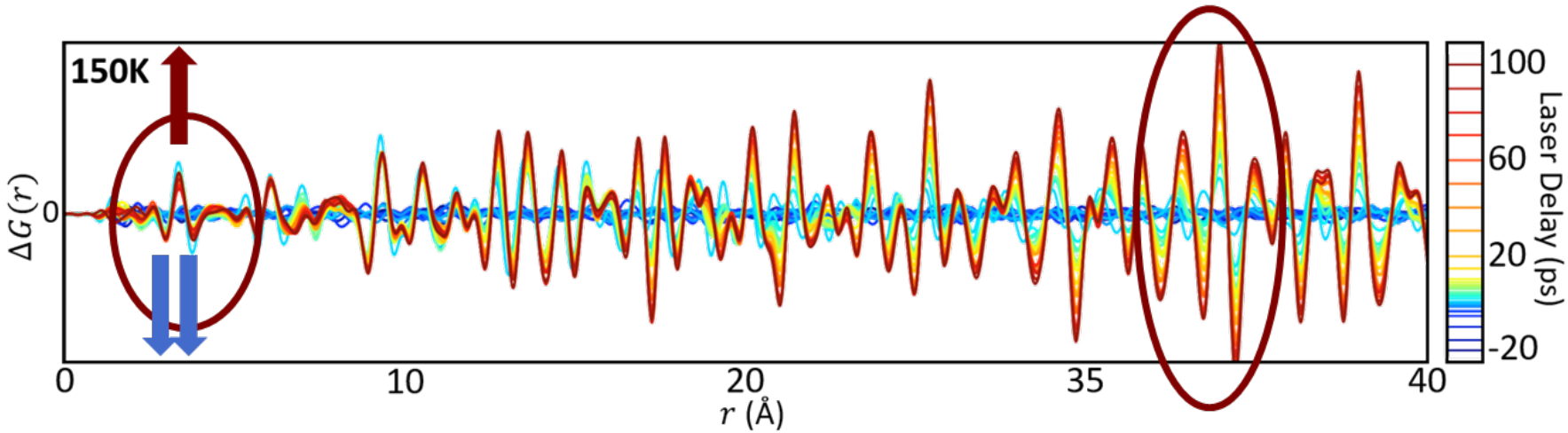


What about the Tsunami model?

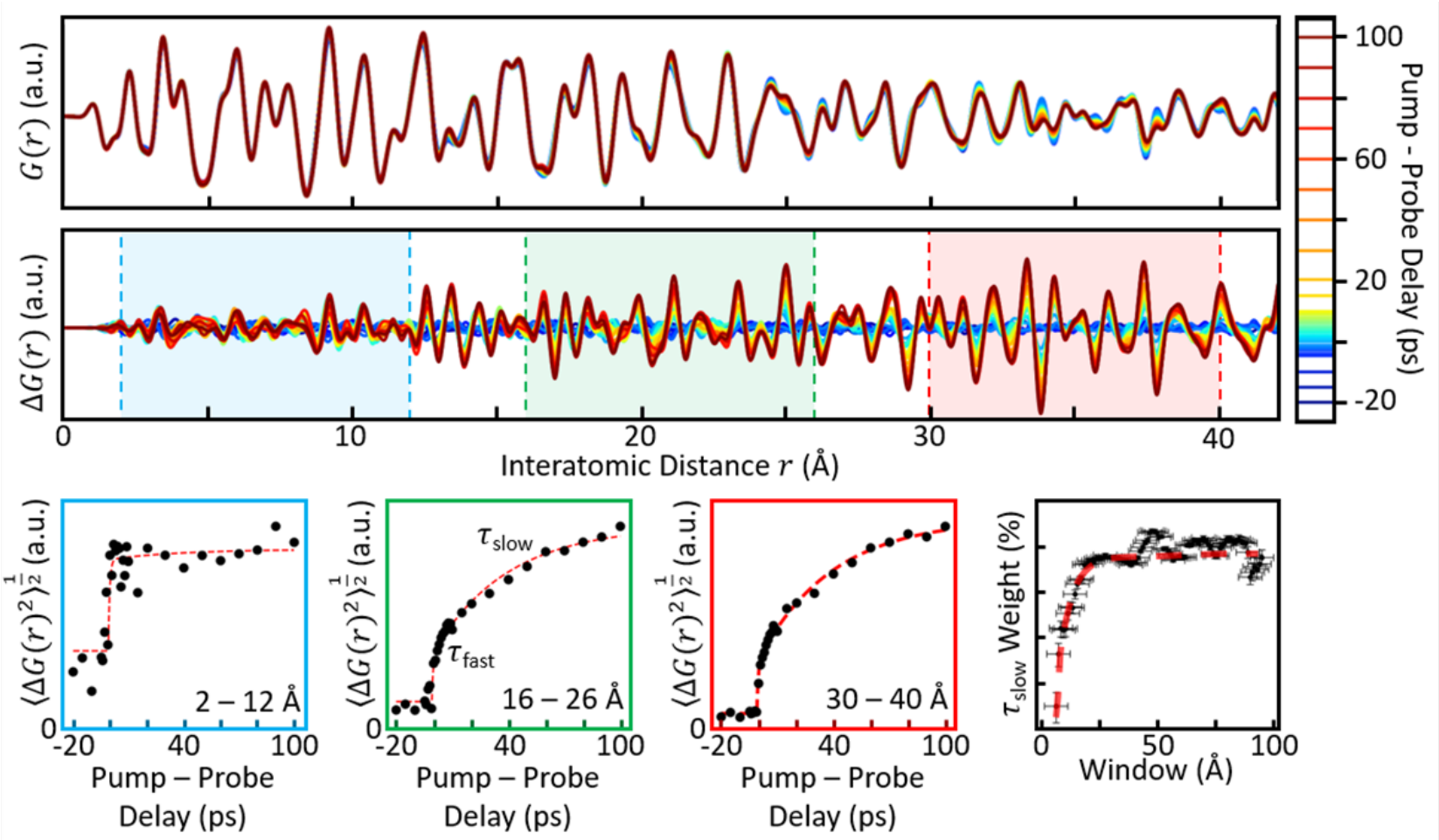
- Object destroyed/excited locally but...
- How do the effects propagate out through the lattice?



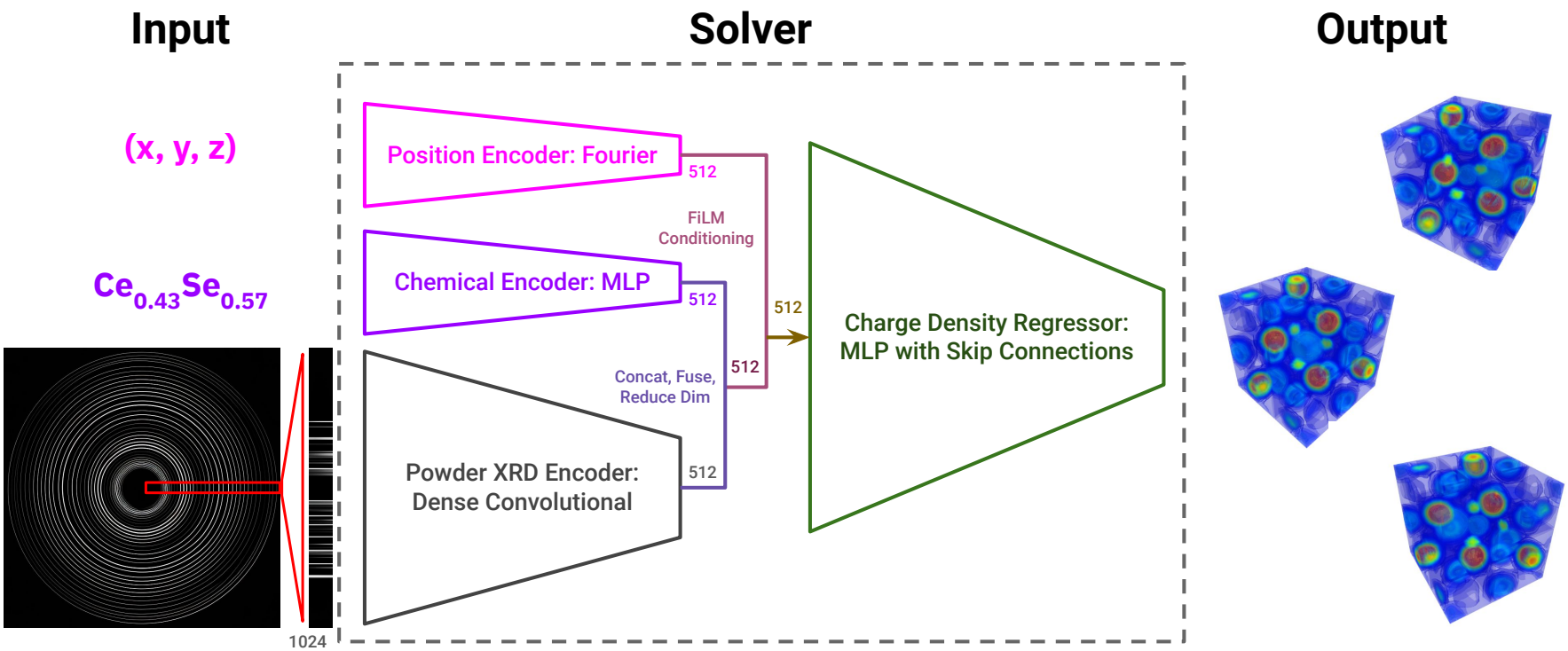
R-DEPENDENT RESPONSE



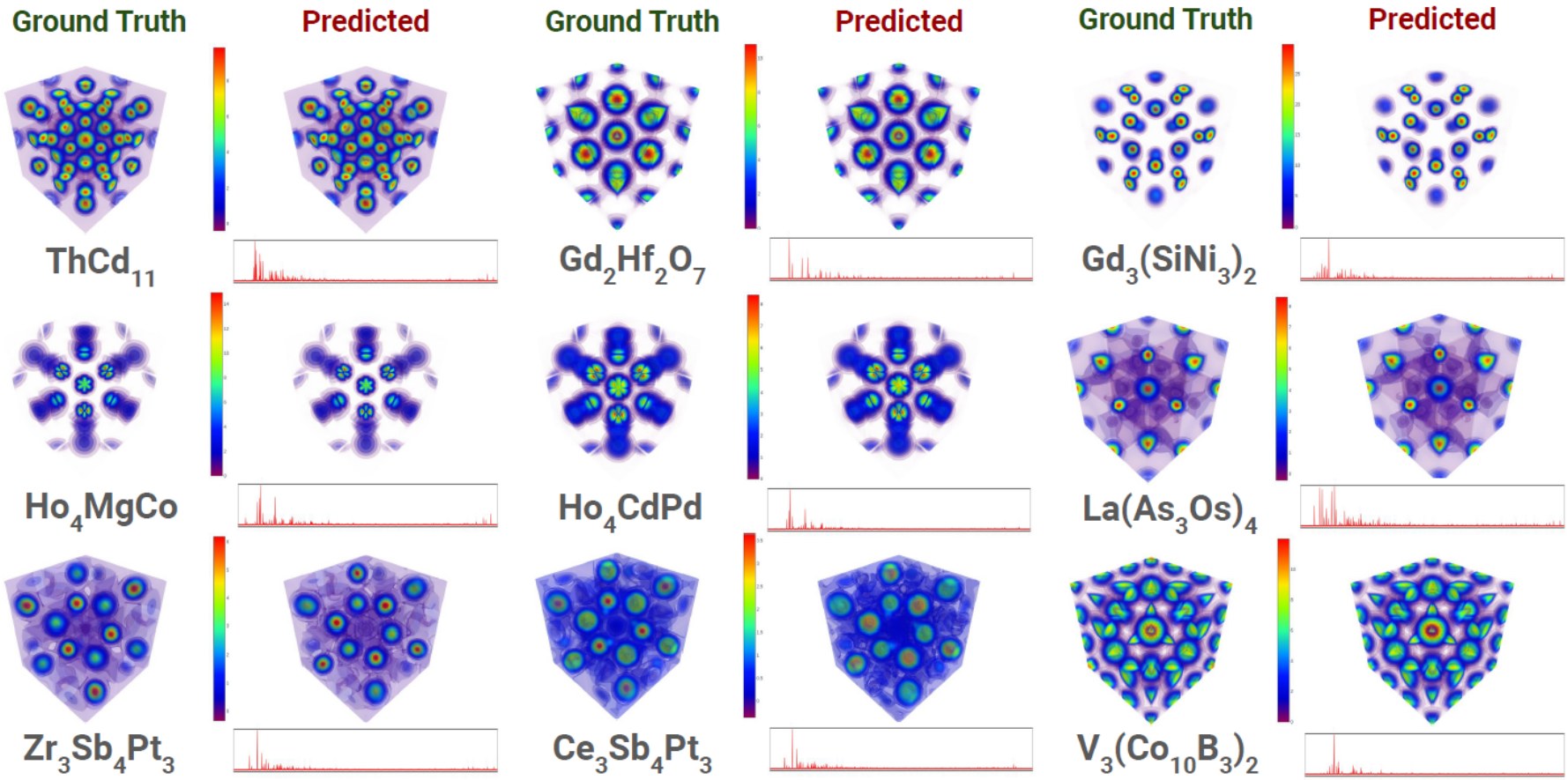
R-DEPENDENT RESPONSE



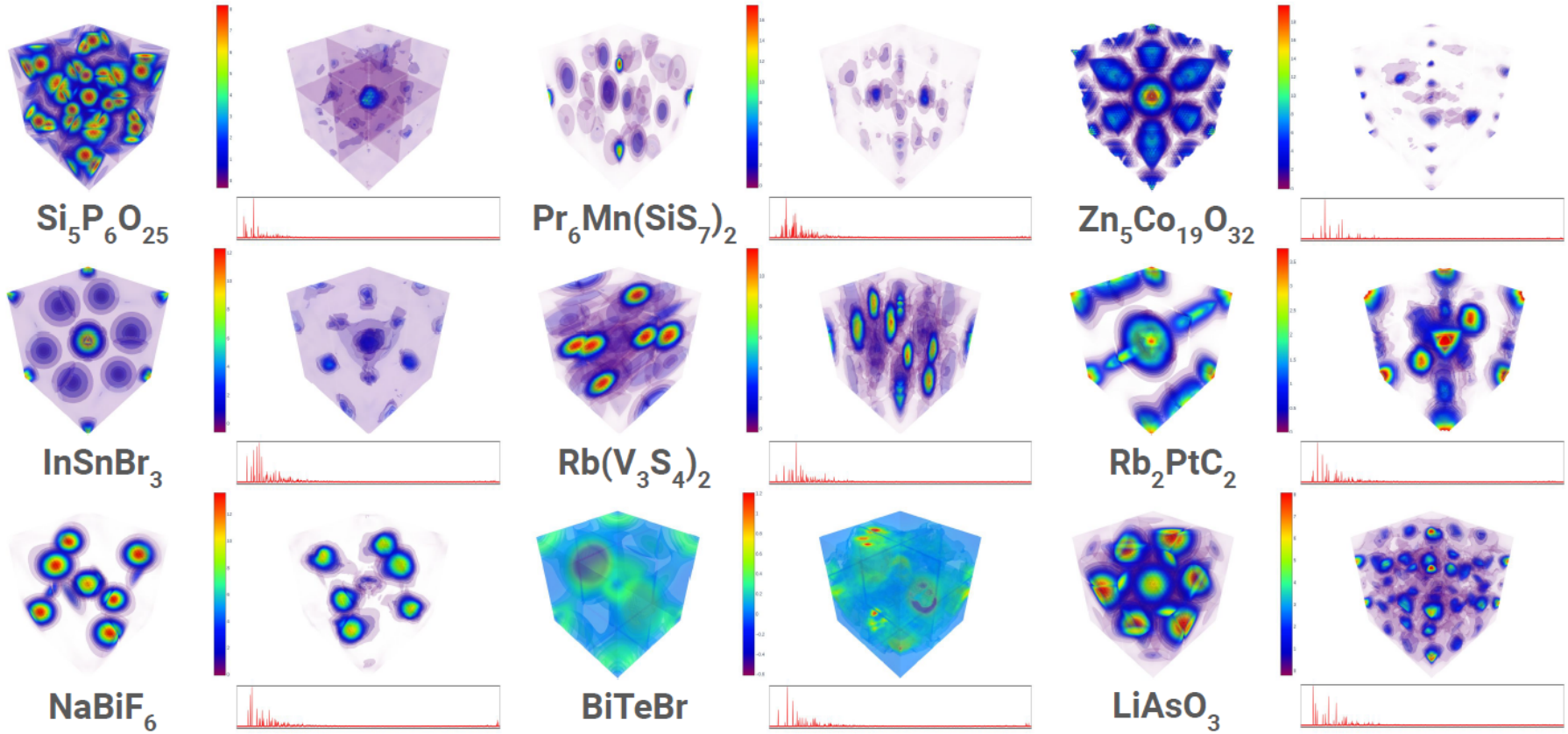
CrystalNet: Electron density reconstruction with CVAE



CrystalNet: Electron density reconstruction with CVAE



CrystalNet: Electron density reconstruction with CVAE



Case 3: structure solution of nanoparticles

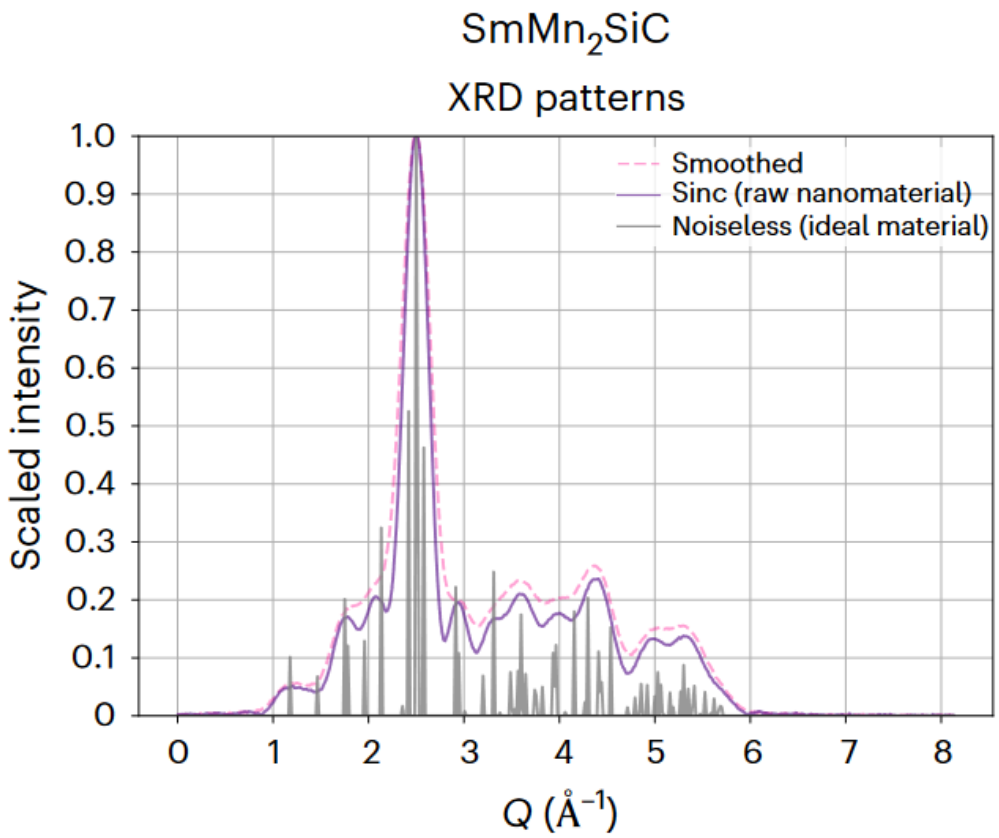
The magic of diffusion models

- Collaboration with Hod Lipson (Columbia University)
- Work of students Gabriel Guo and Tristan Saidi
- G. Guo et al., Nature Materials, (2025) https://doi.org/10.1038/s41563-025-02220-y
- input: nanostructure powder diffraction pattern and composition
- output: "structure": unit cell, coordinates and coloring

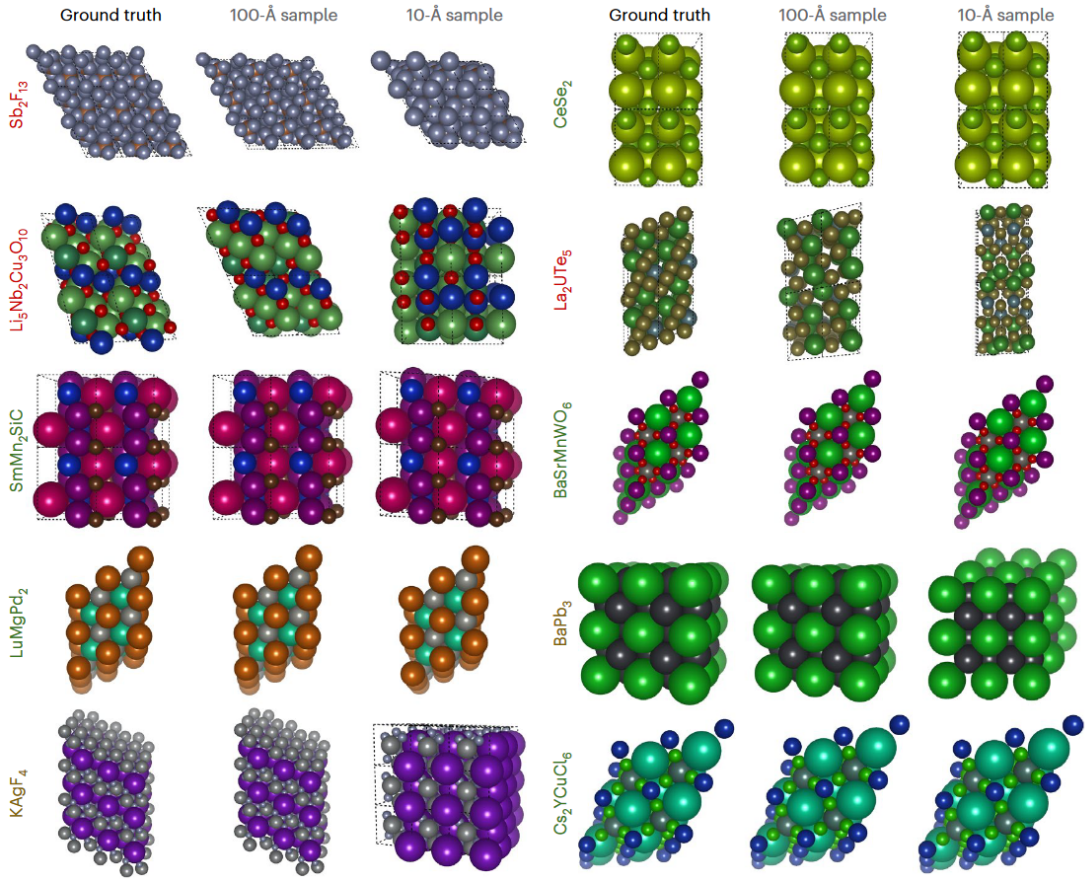
PXRDNet: structure solution with diffusion model

PXRDNet

- 100 Å or 10 Å NP powder data. Low information content!
- Based on CDVAE (T. Xie, Proc. International Conference on Learning Representations (2022).
- SE(3) equivariant graph NN autoencoder for composition, lattice parameters and number of atoms.
- Denoising diffusion via noise-conditioned score networks for the atomic coordinates



PXRDNet: structure solution with diffusion model



Acknowledgements



- My current and former students and post-docs
- Beamline and software teams
- Collaborators

- Funding (DOE-BES, NSF-DMR, TRI, Columbia-DSI)
- The Facilities!

Temporary page!

LaTeX was unable to guess the total number of pages correctly. A
there was some unprocessed data that should have been added
the final page this extra page has been added to receive it.
If you rerun the document (without altering it) this surplus page
will go away, because LaTeX now knows how many pages to expe
for this document.