Nanostructure and Diffraction of Heterogeneous Materials with Nanobeams

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Materials Science with Coherent Nanobeams at the Edge of Feasibility

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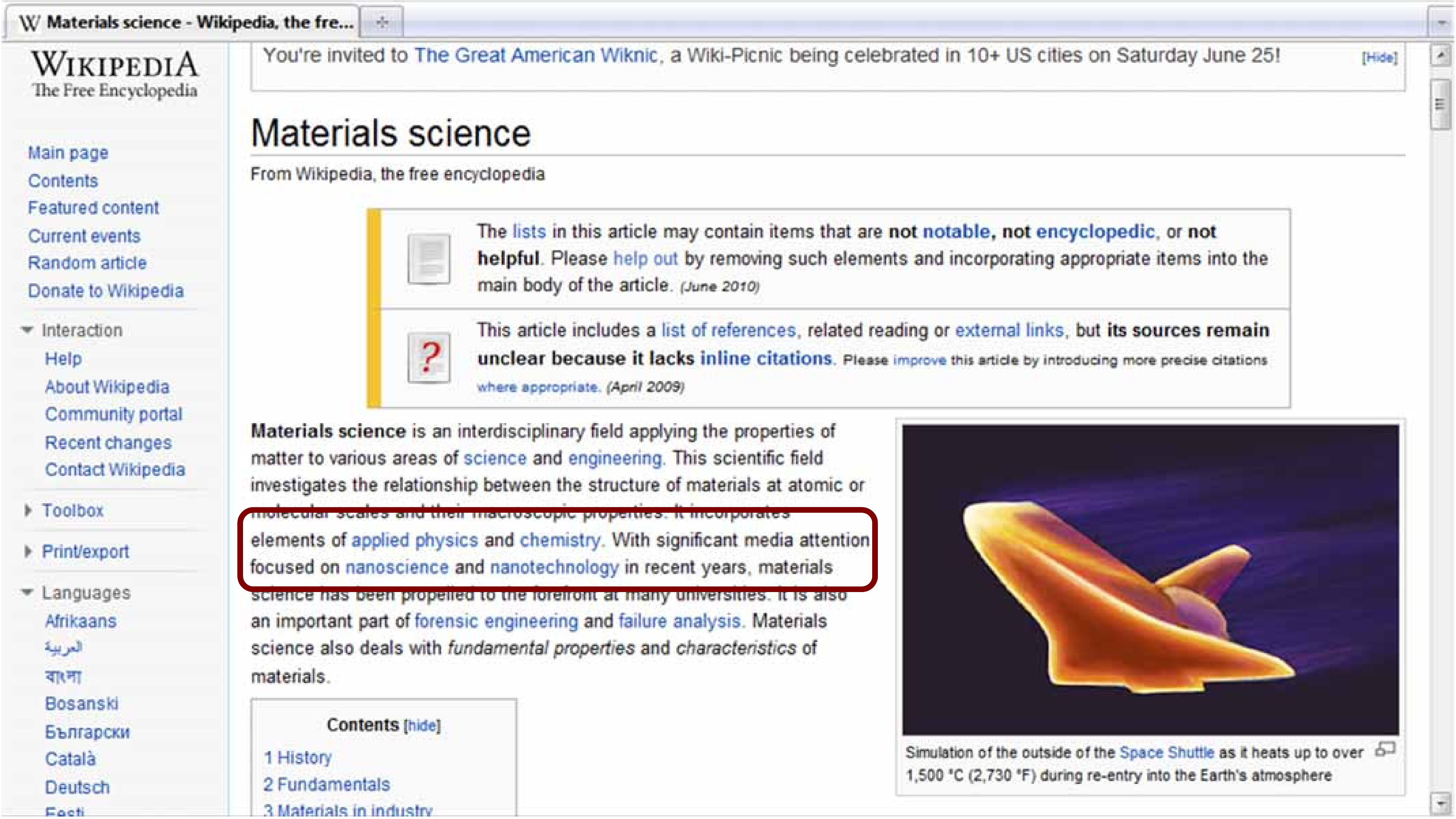

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Materials science

From Wikipedia, the free encyclopedia

The lists in this article may contain items that are **not notable, not encyclopedic**, or **not helpful**. Please help out by removing such elements and incorporating appropriate items into the main body of the article. *(June 2010)*

This article includes a list of references, related reading or external links, but **its sources remain unclear because it lacks inline citations.** Please improve this article by introducing more precise citations where appropriate. *(April 2009)*

Materials science is an interdisciplinary field applying the properties of matter to various areas of science and engineering. This scientific field investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. It incorporates elements of applied physics and chemistry. With significant media attention focused on nanoscience and nanotechnology in recent years, materials science has been propelled to the forefront at many universities. It is also an important part of forensic engineering and failure analysis. Materials science also deals with *fundamental properties* and *characteristics* of materials.

Simulation of the outside of the Space Shuttle as it heats up to over 1,500 °C (2,730 °F) during re-entry into the Earth's atmosphere

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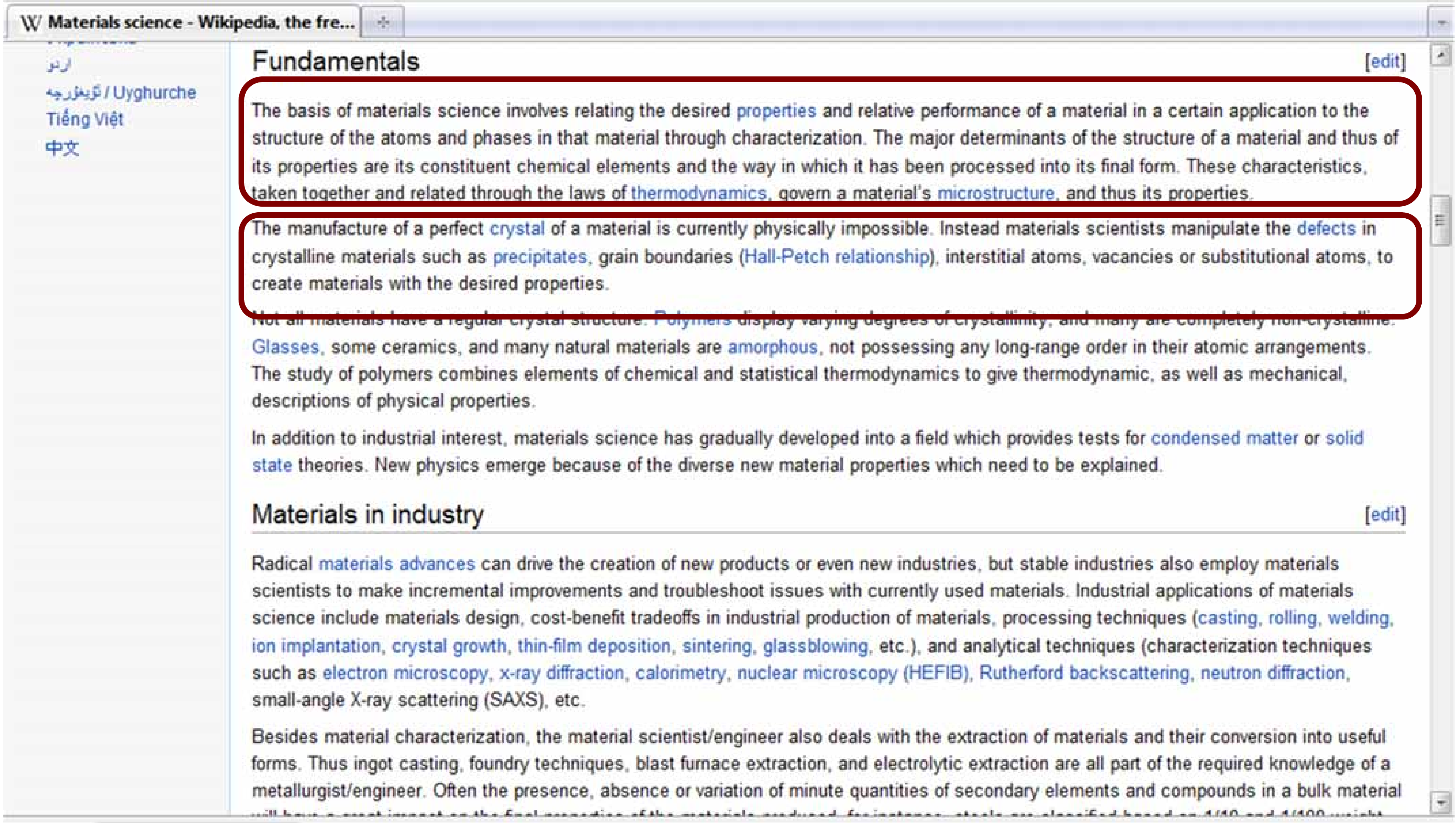
1 History
2 Fundamentals
3 Materials in industry



Fundamentals

The basis of materials science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through characterization. The major determinants of the structure of a material and thus of its properties are its constituent chemical elements and the way in which it has been processed into its final form. These characteristics, taken together and related through the laws of thermodynamics, govern a material's microstructure, and thus its properties.

The manufacture of a perfect crystal of a material is currently physically impossible. Instead materials scientists manipulate the defects in crystalline materials such as precipitates, grain boundaries (Hall-Petch relationship), interstitial atoms, vacancies or substitutional atoms, to create materials with the desired properties.

Not all materials have a regular crystal structure. Polymers display varying degrees of crystallinity, and many are completely non-crystalline. Glasses, some ceramics, and many natural materials are amorphous, not possessing any long-range order in their atomic arrangements. The study of polymers combines elements of chemical and statistical thermodynamics to give thermodynamic, as well as mechanical, descriptions of physical properties.

In addition to industrial interest, materials science has gradually developed into a field which provides tests for condensed matter or solid state theories. New physics emerge because of the diverse new material properties which need to be explained.

Materials in industry

Radical materials advances can drive the creation of new products or even new industries, but stable industries also employ materials scientists to make incremental improvements and troubleshoot issues with currently used materials. Industrial applications of materials science include materials design, cost-benefit tradeoffs in industrial production of materials, processing techniques (casting, rolling, welding, ion implantation, crystal growth, thin-film deposition, sintering, glassblowing, etc.), and analytical techniques (characterization techniques such as electron microscopy, x-ray diffraction, calorimetry, nuclear microscopy (HEFIB), Rutherford backscattering, neutron diffraction, small-angle X-ray scattering (SAXS), etc.

Besides material characterization, the material scientist/engineer also deals with the extraction of materials and their conversion into useful forms. Thus ingot casting, foundry techniques, blast furnace extraction, and electrolytic extraction are all part of the required knowledge of a metallurgist/engineer. Often the presence, absence or variation of minute quantities of secondary elements and compounds in a bulk material

Summary

- We desire non-destructive tools that can characterize material structure/property relationships on multiple length-scales down to the nano and atomic scales.
- In situ/in operando studies of functioning materials
  - Structure
  - Microstructure
  - Defects
- Structures in equilibrium, but also “close to equilibrium”, i.e., time resolved studies under “load”.

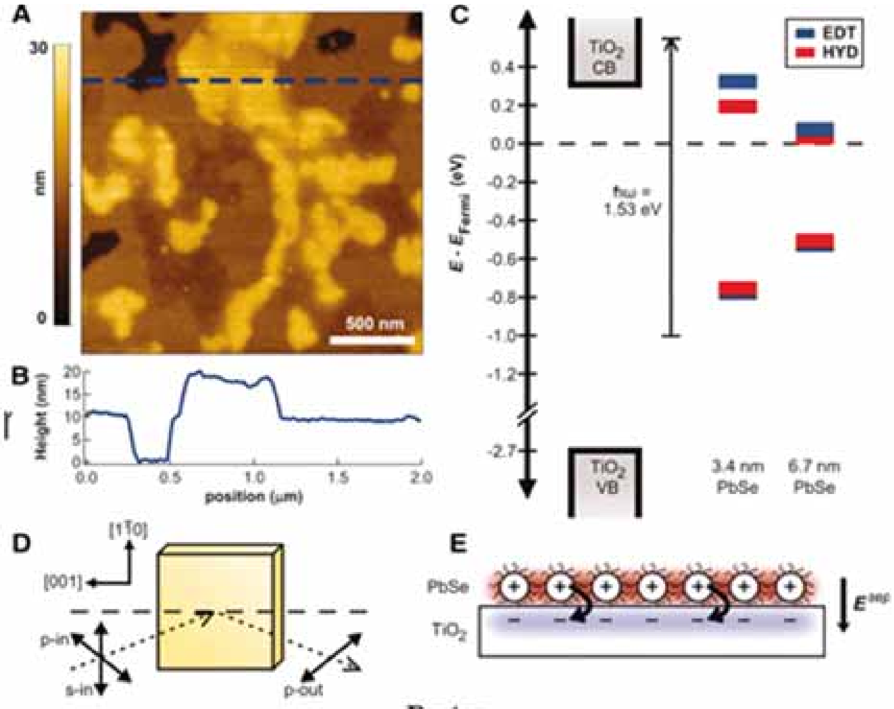
The Complexity frontier

Complex materials will lie at the heart of the solutions to many of society’s most pressing problems

- Sustainable Energy
- Environmental remediation
- Health

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



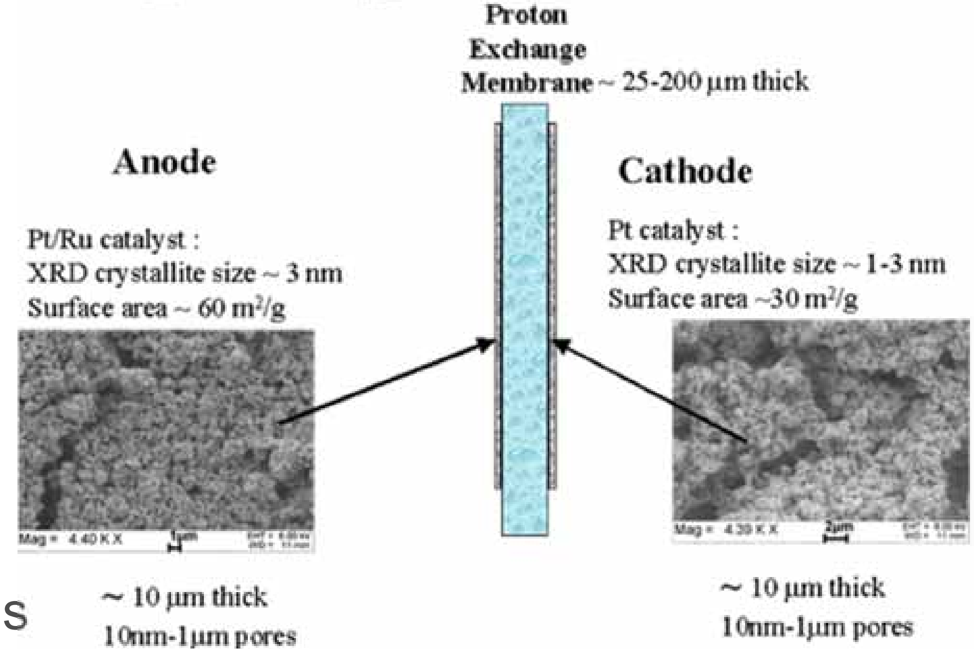


Image credits: 10.1126/science.1185509
U. Uppsala

Recurring themes in Complex Materials:

They have

- Structure at the nanoscale
  - E.g., just about everything

- Complicated structures, large unit cells, multiple elements
  - E.g., thermoelectrics, next generation battery materials, etc..

- Sub-micron heterogeneities
  - E.g., core-shell nanoparticles, supported catalysts, real devices

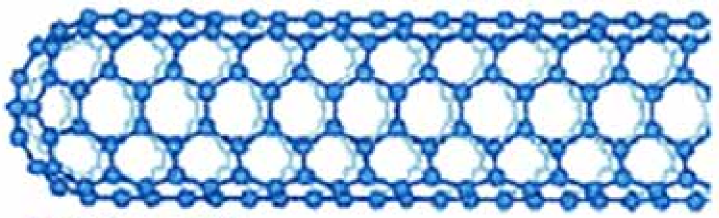
Enormous experimental and theoretical challenges in Complex Materials

Properties depend sensitively on structure

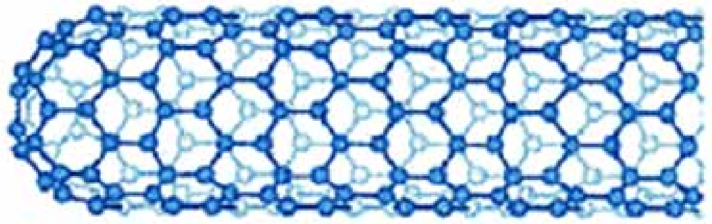
- Semiconductor -> metal depending on chirality of nanotube
- Metal -> insulator for Mn-O bond-length change of ~0.05Å in manganites (JT effect)
- CDW induced loss in conductivity with bond-length change ~0.02Å in CeTe$_3$
- …

Need to know structural parameters

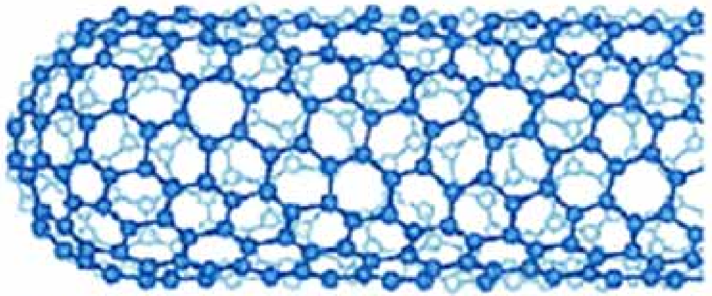
Accurately, quantitatively



Armchair ($\alpha = 30^\circ$)



Zigzag ($\alpha = 0^\circ$)



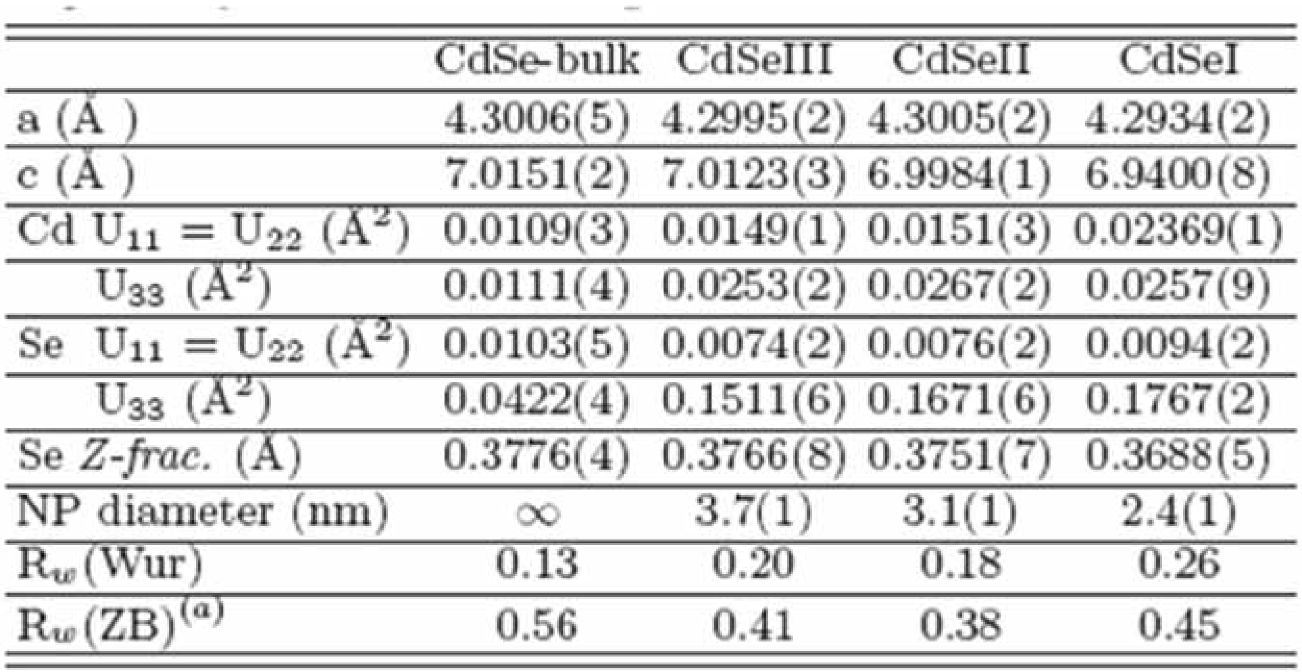
Intermediate ($0 < \alpha < 30^\circ$)

Complex Nanostructured materials

Nanostr

bulk

s



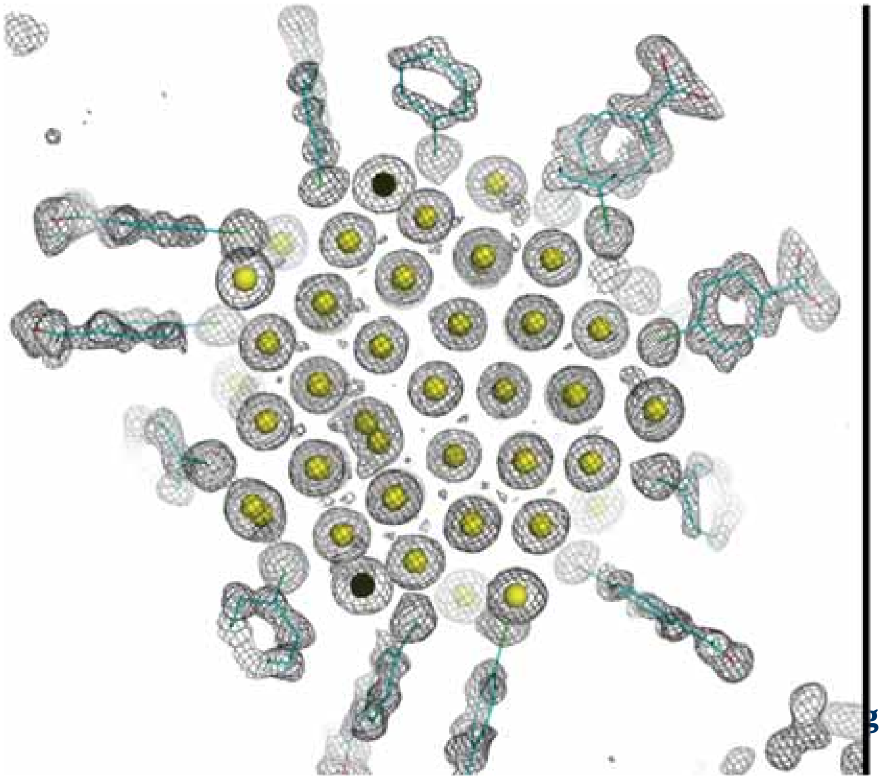
	CdSe-bulk	CdSeIII	CdSeII	CdSeI
a (Å)	4.3006(5)	4.2995(2)	4.3005(2)	4.2934(2)
c (Å)	7.0151(2)	7.0123(3)	6.9984(1)	6.9400(8)
Cd $U_{11} = U_{22}$ (Å^2)	0.0109(3)	0.0149(1)	0.0151(3)	0.02369(1)
U_{33} (Å^2)	0.0111(4)	0.0253(2)	0.0267(2)	0.0257(9)
Se $U_{11} = U_{22}$ (Å^2)	0.0103(5)	0.0074(2)	0.0076(2)	0.0094(2)
U_{33} (Å^2)	0.0422(4)	0.1511(6)	0.1671(6)	0.1767(2)
Se *Z-frac.* (Å)	0.3776(4)	0.3766(8)	0.3751(7)	0.3688(5)
NP diameter (nm)	∞	3.7(1)	3.1(1)	2.4(1)
R_w(Wur)	0.13	0.20	0.18	0.26
R_w(ZB)$^{(a)}$	0.56	0.41	0.38	0.45

- Image credits: Igor Levin/Tom Pinnavaia/Sandra Rosenthal
- Old English-language saying: a picture is worth 1000 words
- But: a table is worth 1000 pictures

Do nanoparticles have a unique structure?

1. Make a periodic, orientationally ordered, array of the nanoparticles and solve it using crystallographic methods
    - Suitable for identical small NPs that will crystallize!

- Work of Kornberg group at Stanford, Science 2007
- 102 atom gold cluster passivated by organic molecules



Quiz

Question:

- What do electron microscopists do when they want an atomic resolution, 3D image of an object?

Answer:

- Crystallography

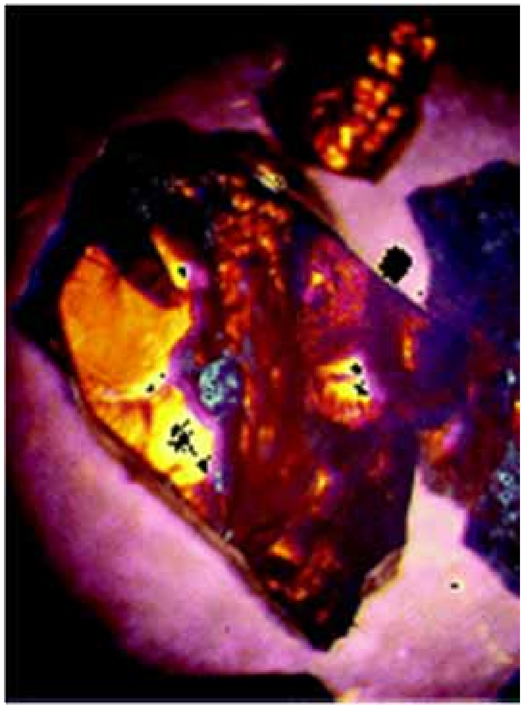
Nano

- 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)

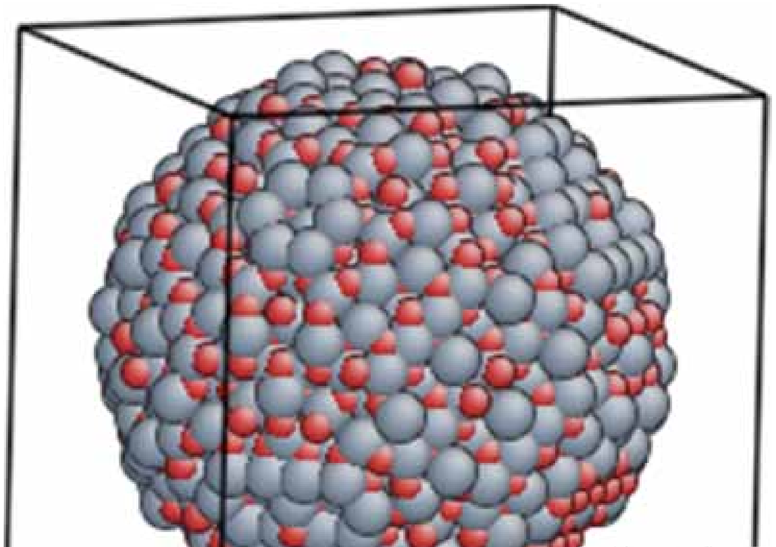
- Problem:
  - Here is a crystal, what is its structure?
- Solution:

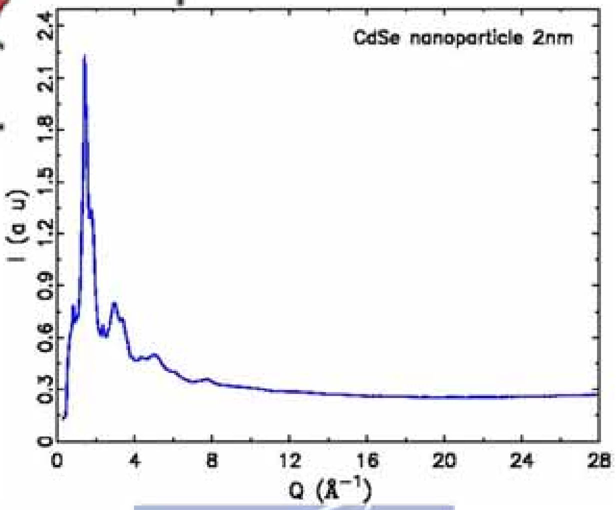
1. Give it to your grad student
2. She puts it on the x-ray machine
3. …Pushes the button
   1. Machine tells you the structure
   2. Or Machine gets stuck
      1. Throw away the crystal
      2. Make it the subject of her thesis

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

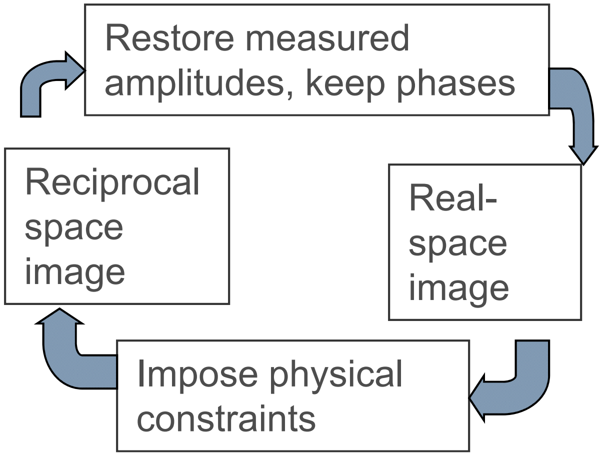




Single Crystal Nanocrystallography

Solve the structure of a single nanoparticles by atomic resolution lenseless (diffraction) imaging.

- Electrons have been used for simple structures



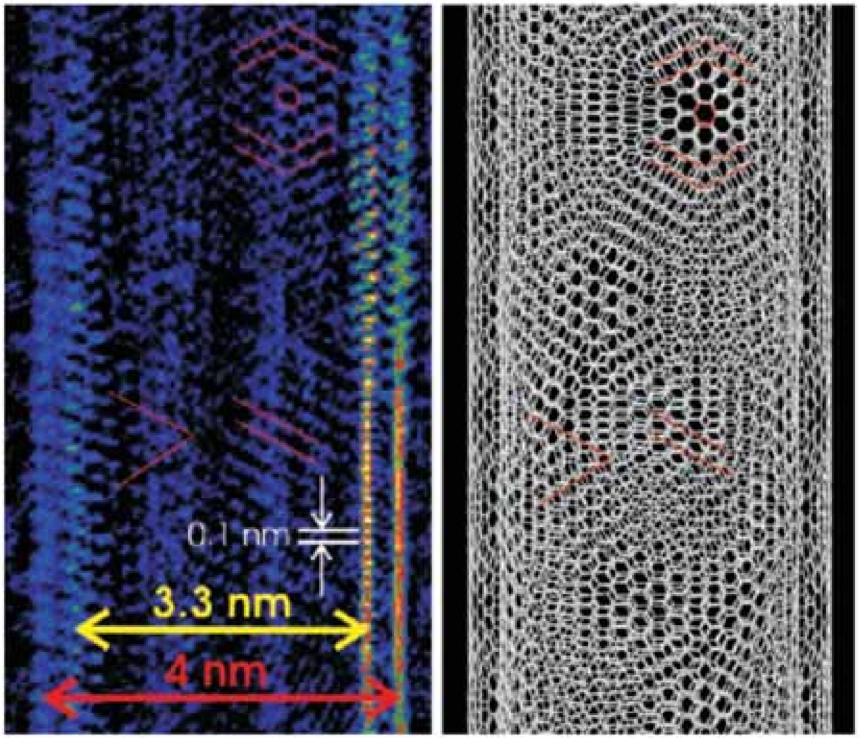
Restore measured amplitudes, keep phases

Real-space image

Impose physical constraints

Reciprocal space image

- Atomic resolution image obtained from electron diffraction by iterative phase retrieval and compared to calculated structures
- Zuo et al, Science 2003



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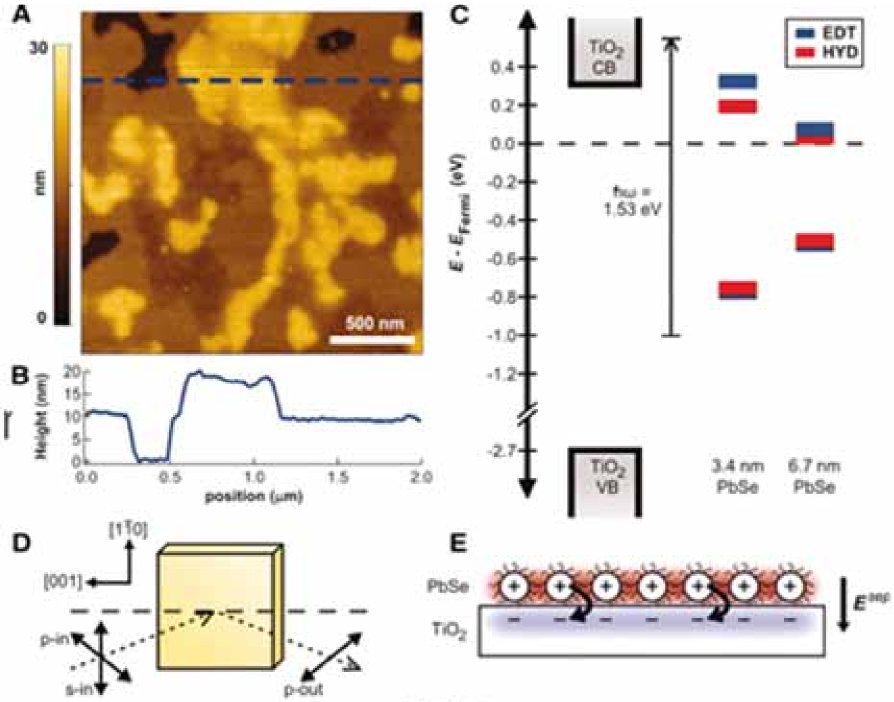
Complex materials

- 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



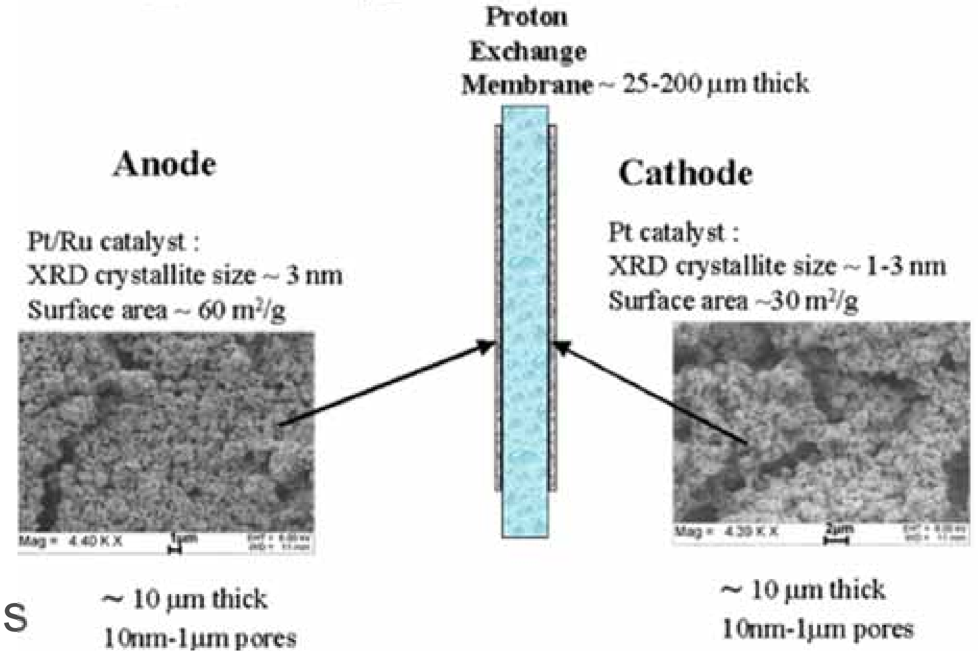


Image credits: 10.1126/science.1185509
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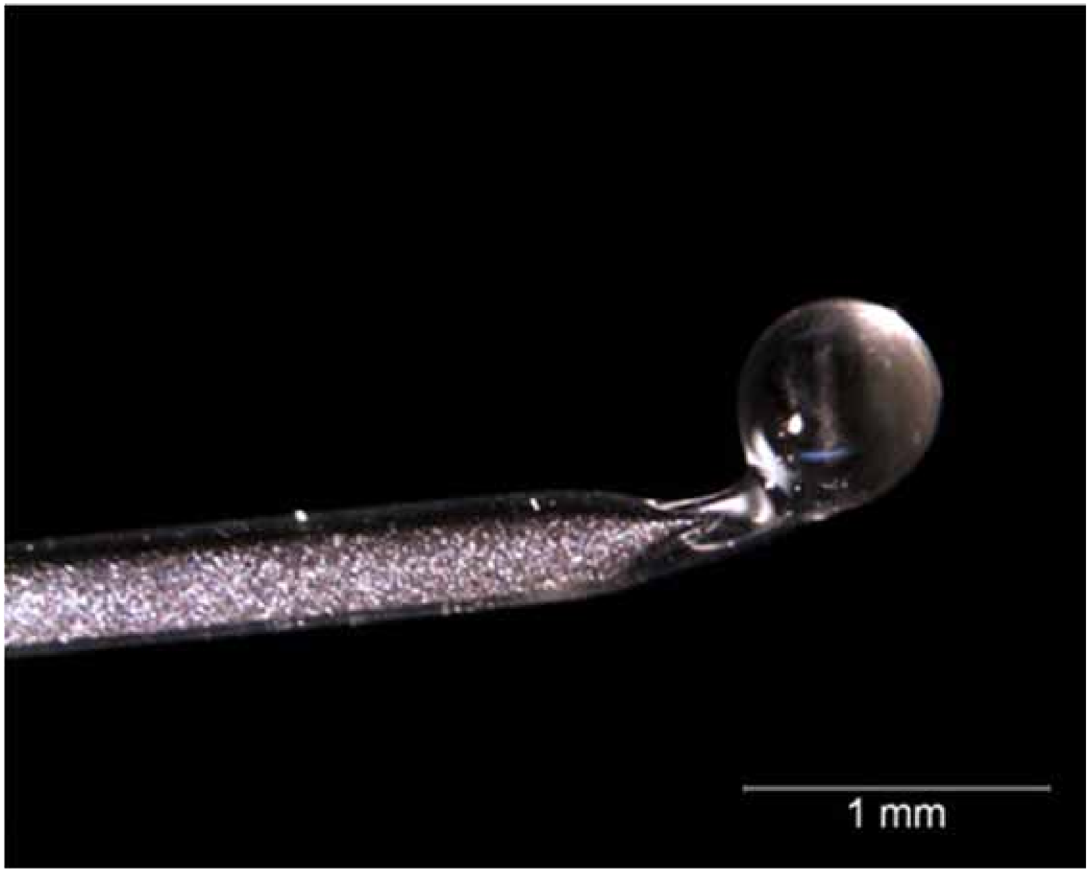
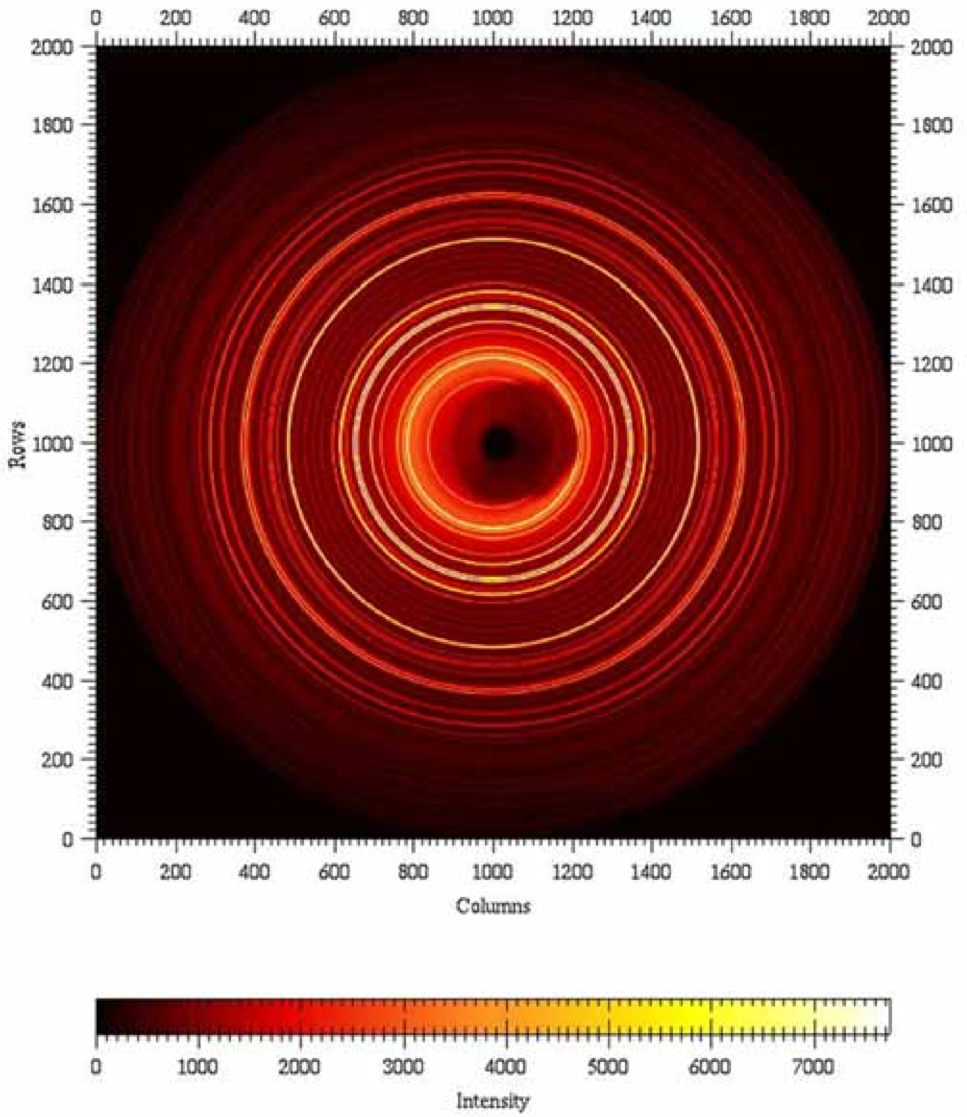
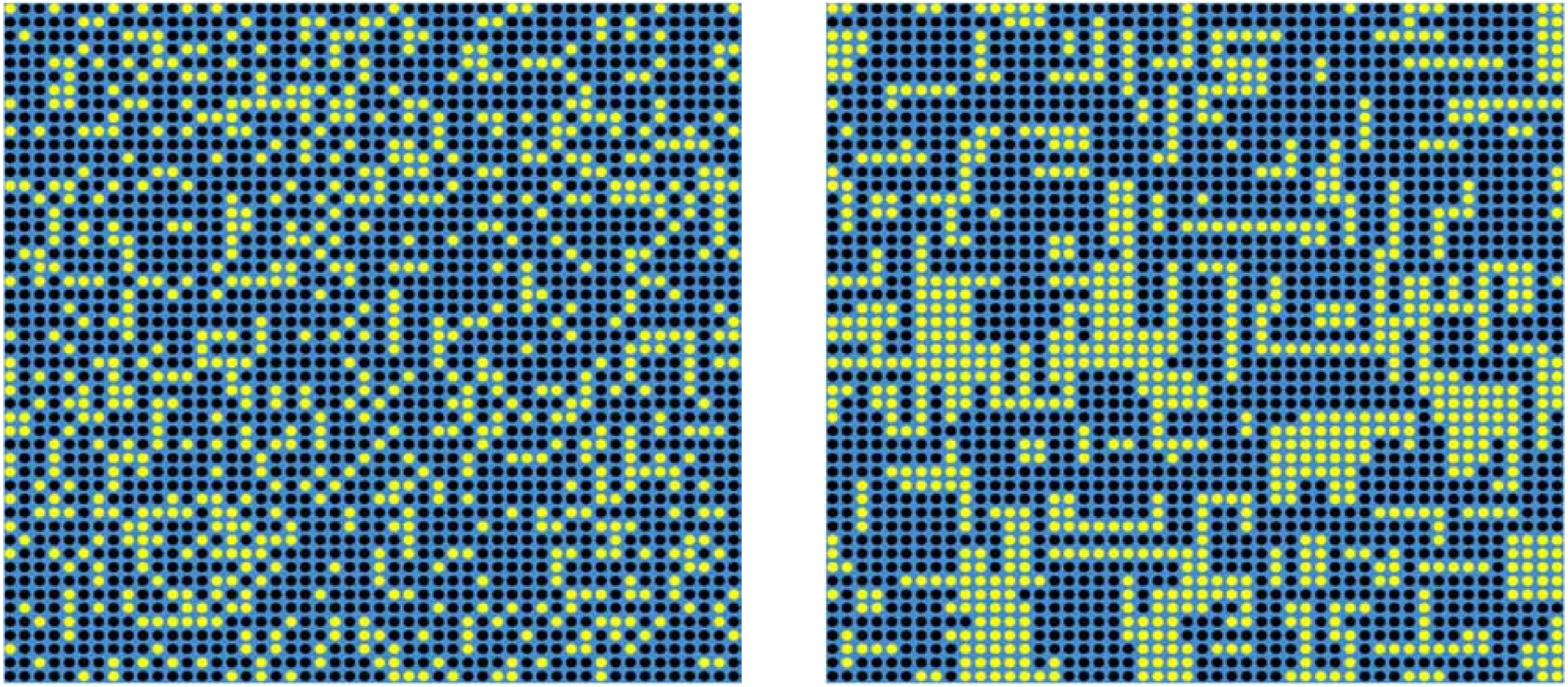
Powder Nanocrystallography

- Good signal, but loss of information due to orientational averaging. Can we recover?





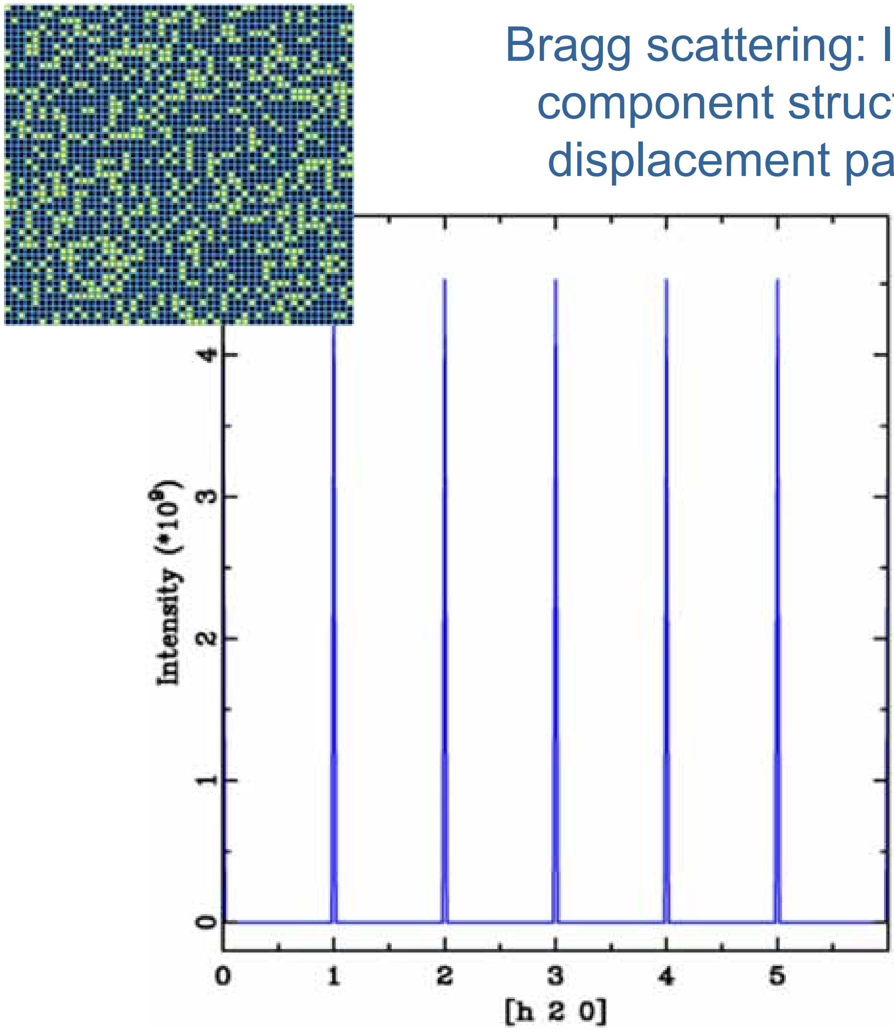
Why is diffuse scattering important?

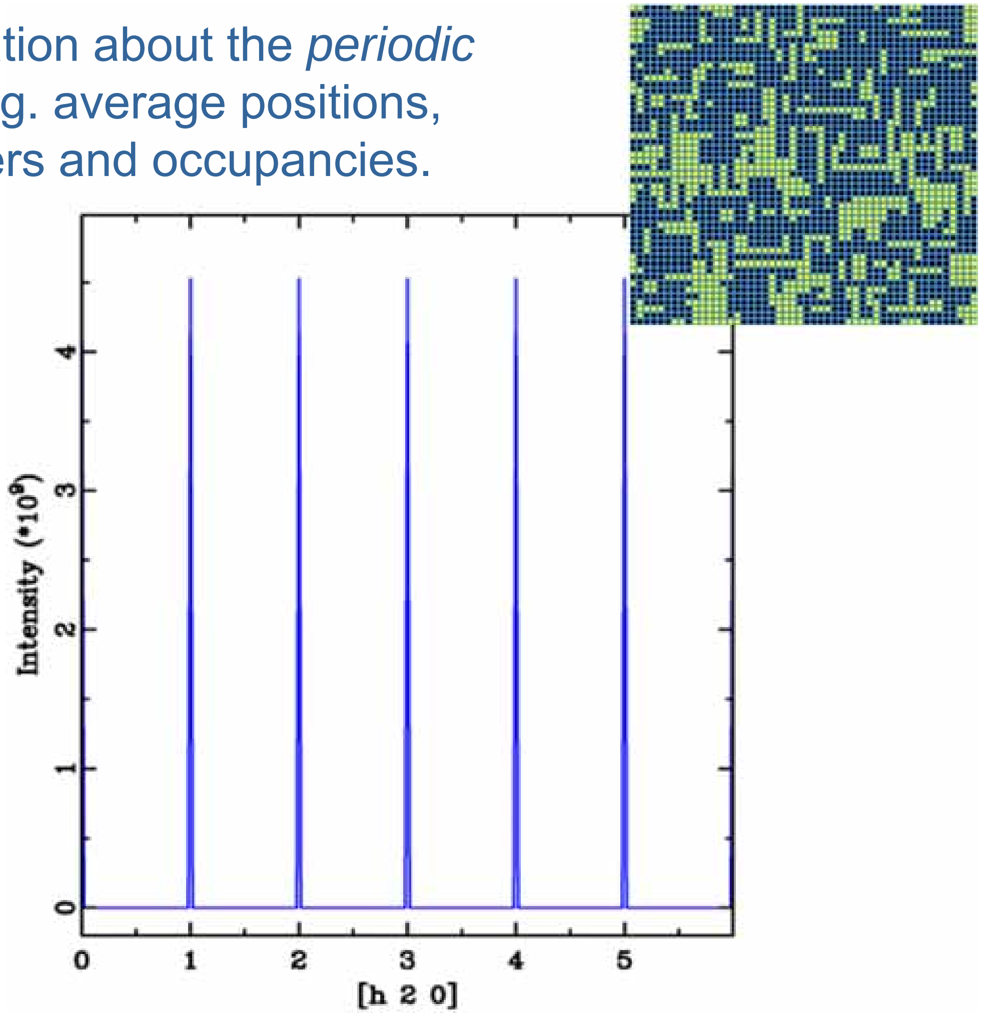


Cross section of 50 x 50 x 50 unit cell model crystal with 70% black atoms and 30% yellow, Simulation using DISCUS courtesy of Thomas Proffen

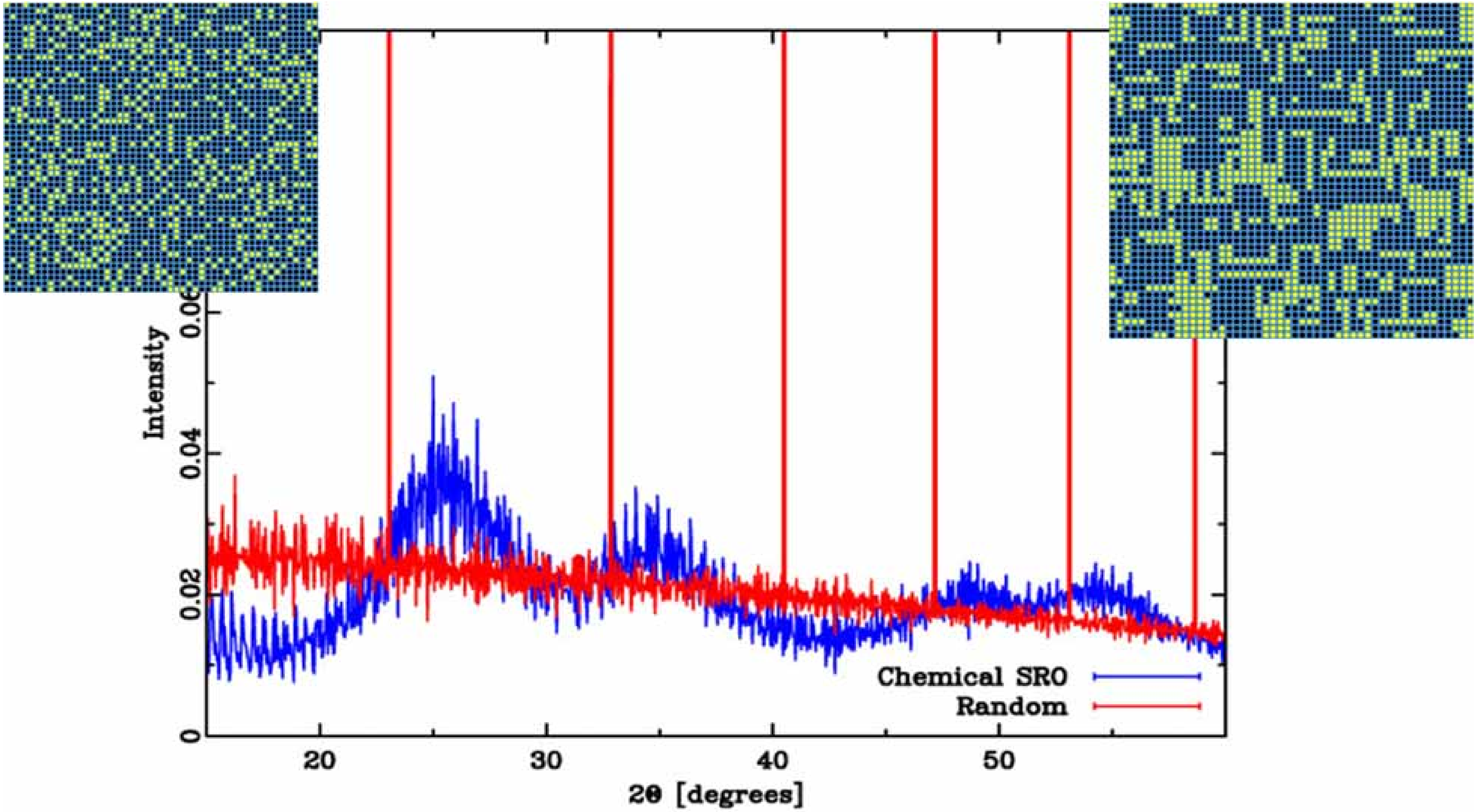
Bragg peaks are blind to the nanoscale order

Bragg scattering: Information about the *periodic* component structure, e.g. average positions, displacement parameters and occupancies.

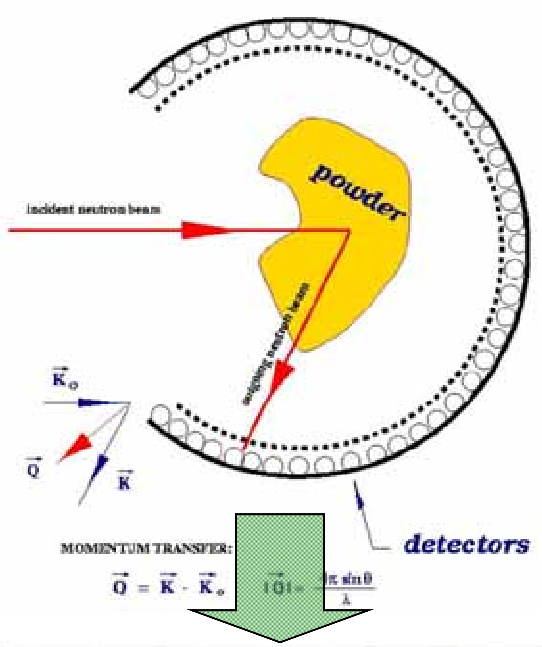


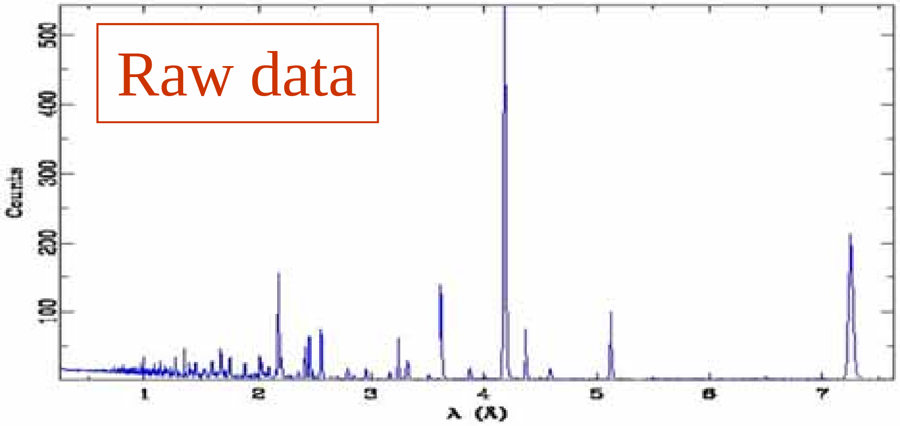


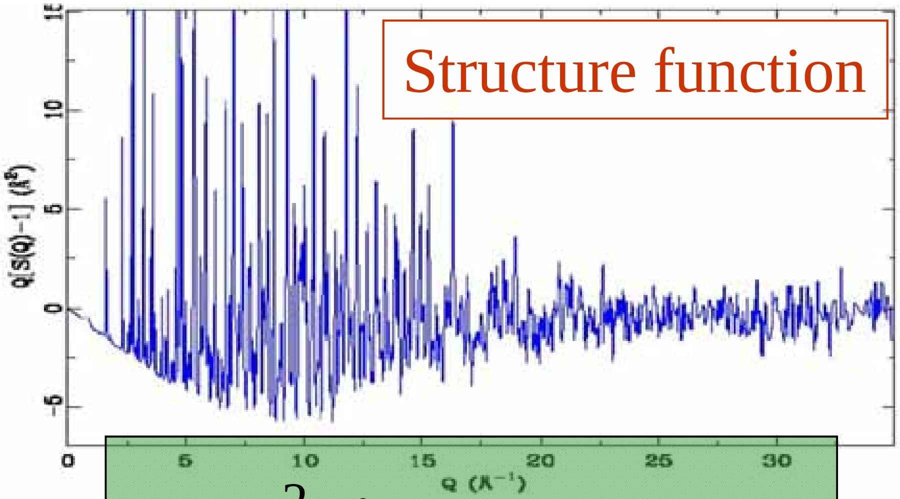
Diffuse scattering: Underneath the Bragg-peaks
Total Scattering: Bragg + diffuse



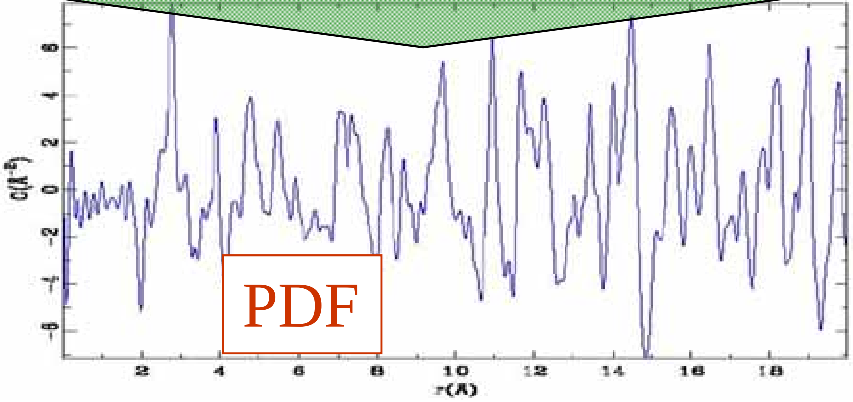
Obtaining the PDF




Raw data


Structure function

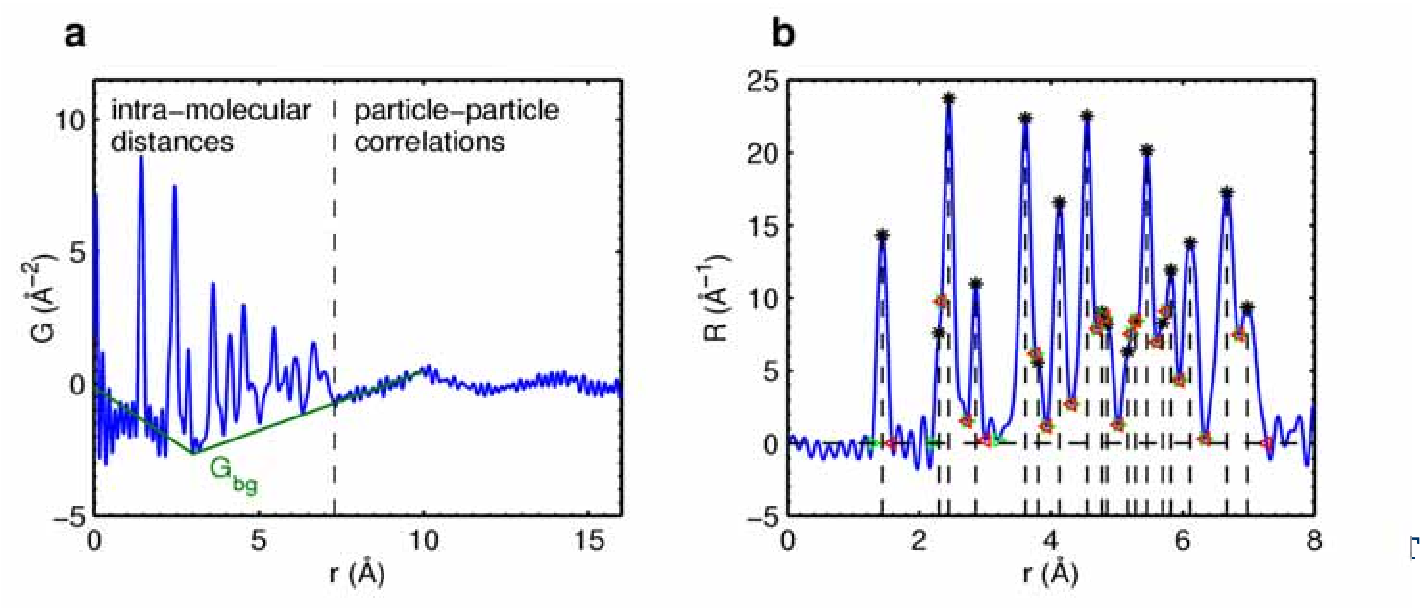
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr\,dQ$$


PDF

Is there enough information for an ab-initio structure solution?

Example: C60

- 60 atoms => n(n-1)/2 = 1770 pair-vectors
- We know the lengths (not the directions) of ~18 unique distances
- We have an imperfect measure of the multiplicities of those distances
- We don't have any symmetry information to help us



Is the problem well conditioned or ill conditioned?

Is there a unique solution?

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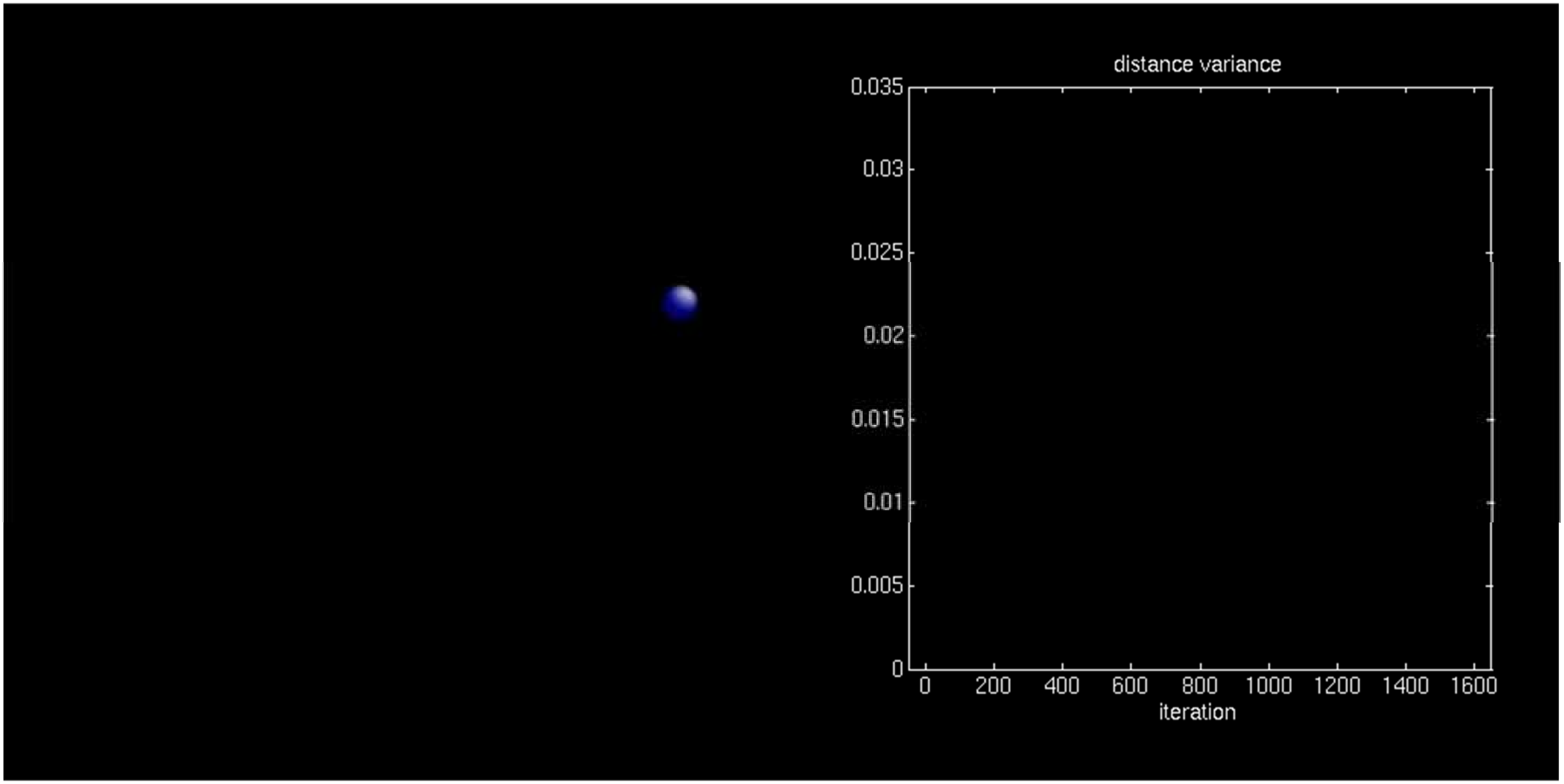
ab-initio structure solution directly from PDF data



Frontiers in complex materials structure solution

As materials get more complex

- the information needed to constrain a unique solution goes up
  - Larger “unit cells”
  - More structural degrees of freedom
- The information content in the data goes down
  - Peaks broaden and overlap or become pure diffuse scattering
  - Information becomes polluted by larger backgrounds from host materials or supports (often the interesting signal is the minority component)

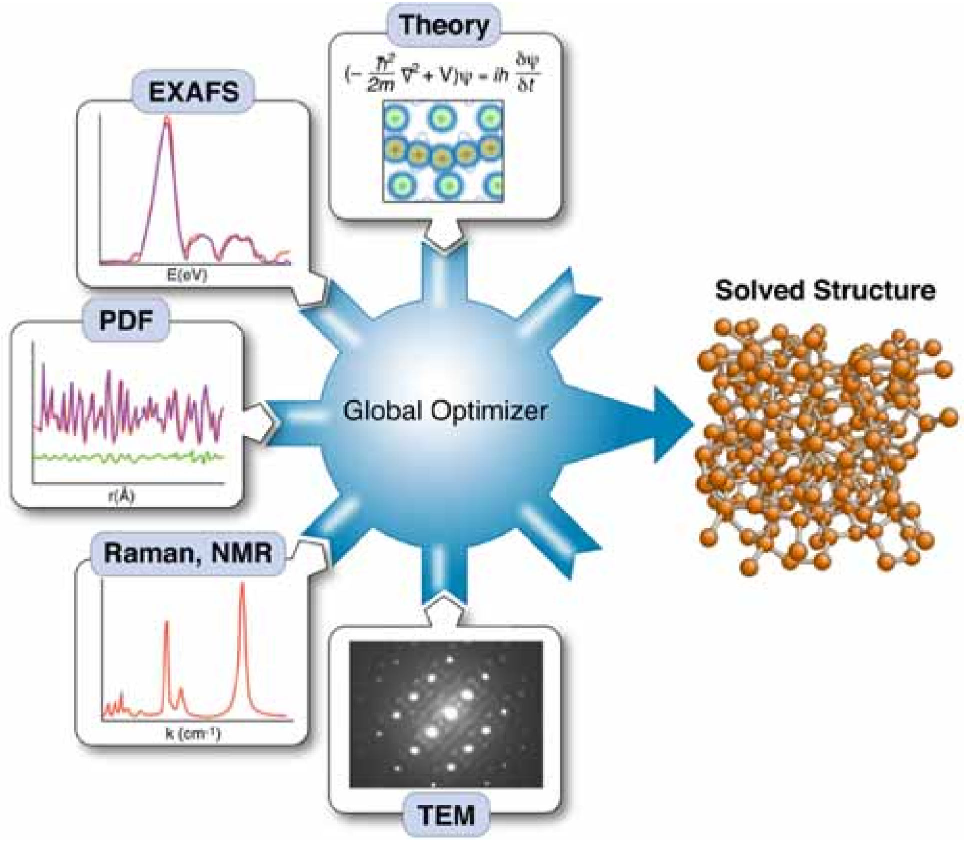
Complex Modeling

- S. J. L. Billinge and I. Levin, **The problem with determining atomic structure at the nanoscale**, *Science* **316**, 561-565 (2007).
- Simon J. L. Billinge, **The nanostructure problem**, *Physics* **3**, 25 (2010).

Complex Modeling

- c = a + ib – complex number mixes real and imaginary parts
- m = e + it – complex modeling mixes experiment and theory in a coherent computational framework

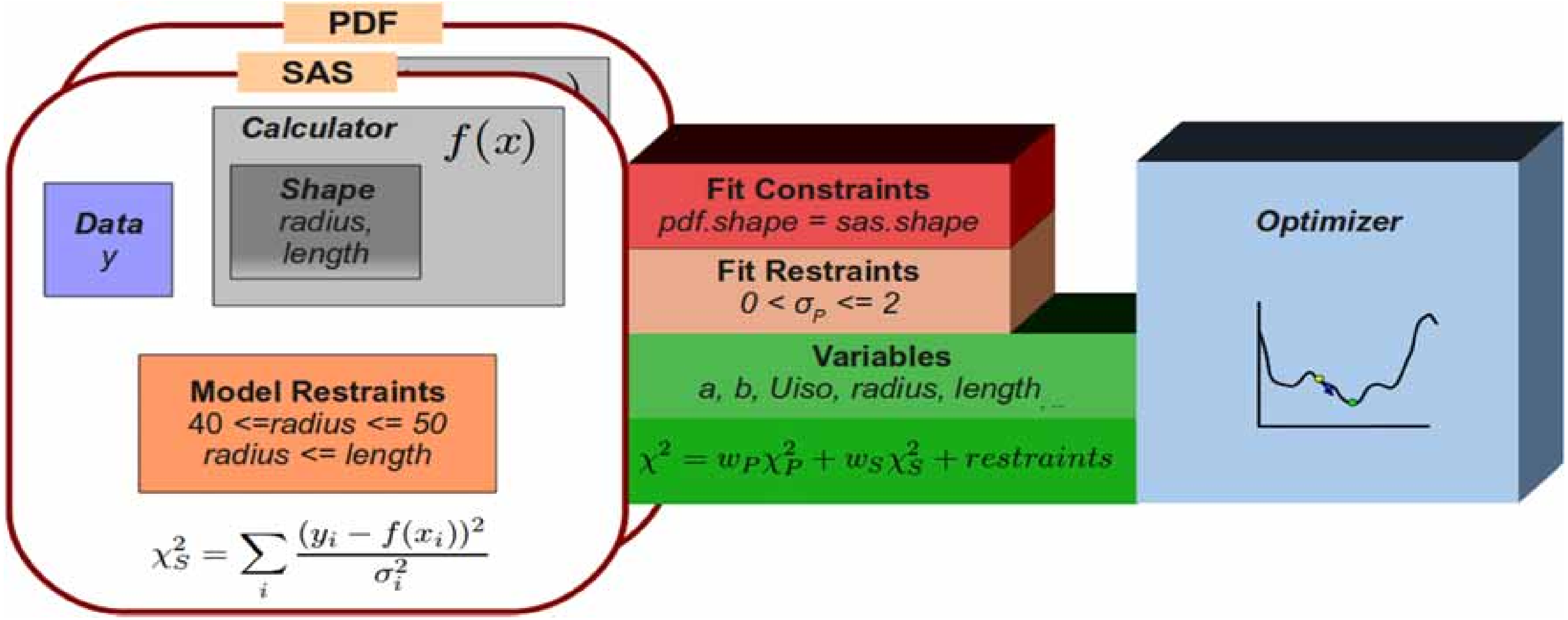
- Billinge and Levin, Science 2007



Complex Modeling - SrFit

- Python framework for Complex Modeling
  - Build a cost function from available forward calculators and data
- Each “page” a separate cost function
- Pages tied together with common variables and a unified cost function

- Interfaces with existing software
  - DANSE diffraction for PDF
  - DANSE SANS for SAS
- Developed by Chris Farrow and Pavol Juhas



PDF

SAS

Calculator $f(x)$

Shape
radius,
length

Data
y

Model Restraints
40 <=radius <= 50
radius <= length

$$\chi_S^2 = \sum_i \frac{(y_i - f(x_i))^2}{\sigma_i^2}$$

Fit Constraints
pdf.shape = sas.shape

Fit Restraints
$0 < \sigma_P <= 2$

Variables
a, b, Uiso, radius, length

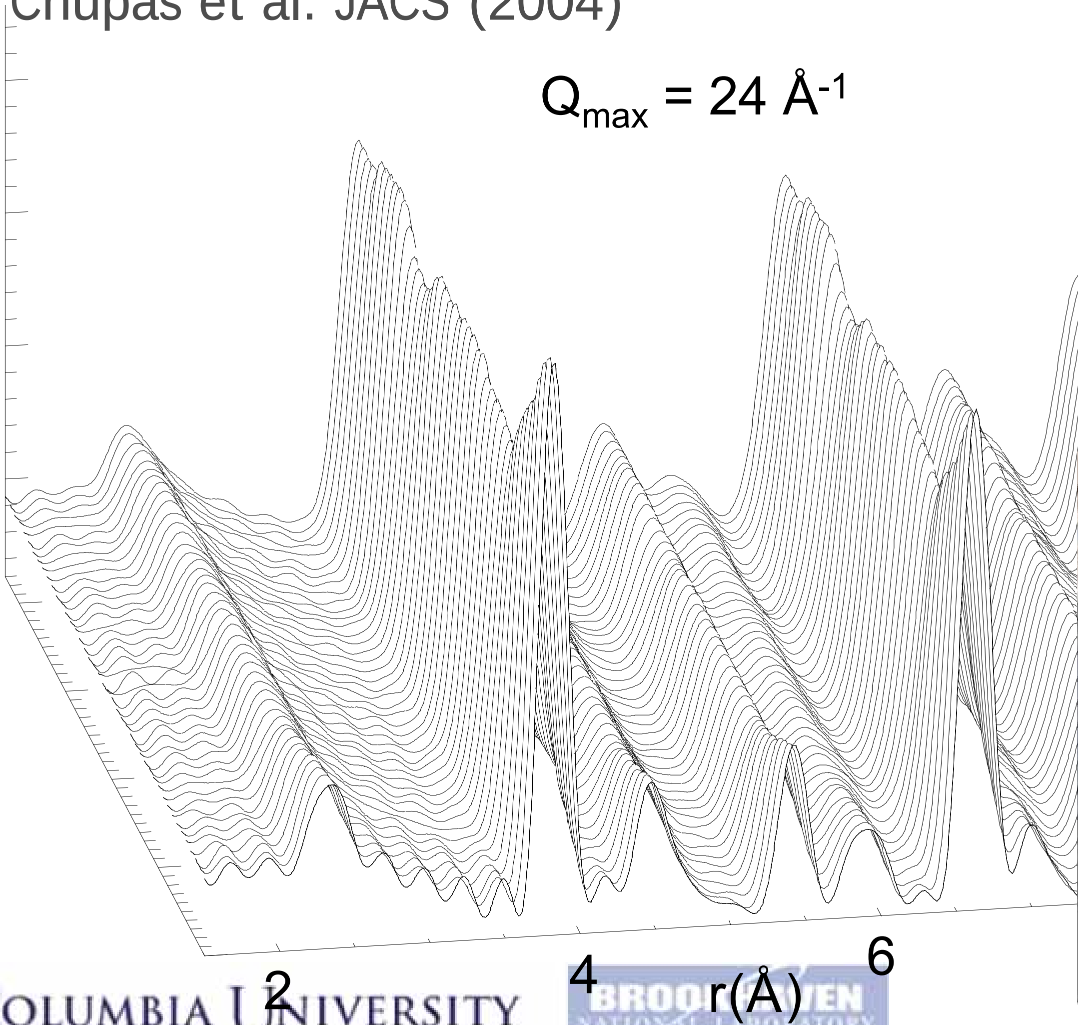
$$\chi^2 = w_P\chi_P^2 + w_S\chi_S^2 + restraints$$

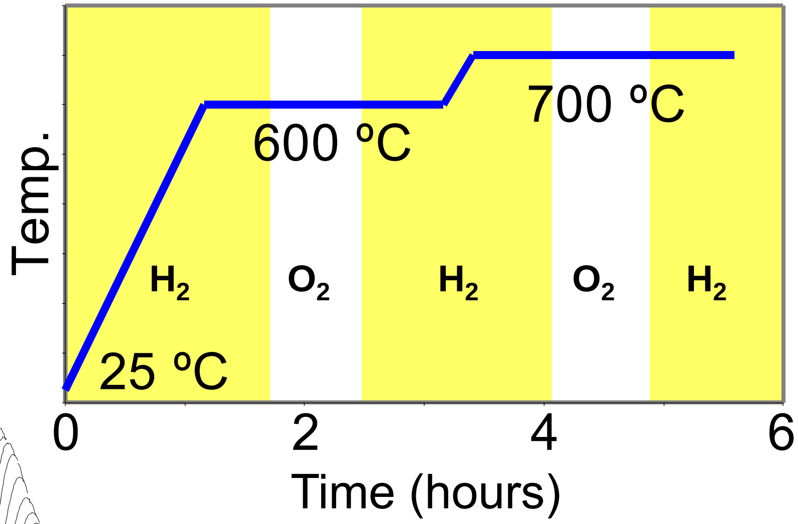
Optimizer

In-Situ Reduction and Oxidation

Study of nano-ceria demonstrated by Pete Chupas, Clare Grey and Jon Hanson

Chupas et al. JACS (2004)





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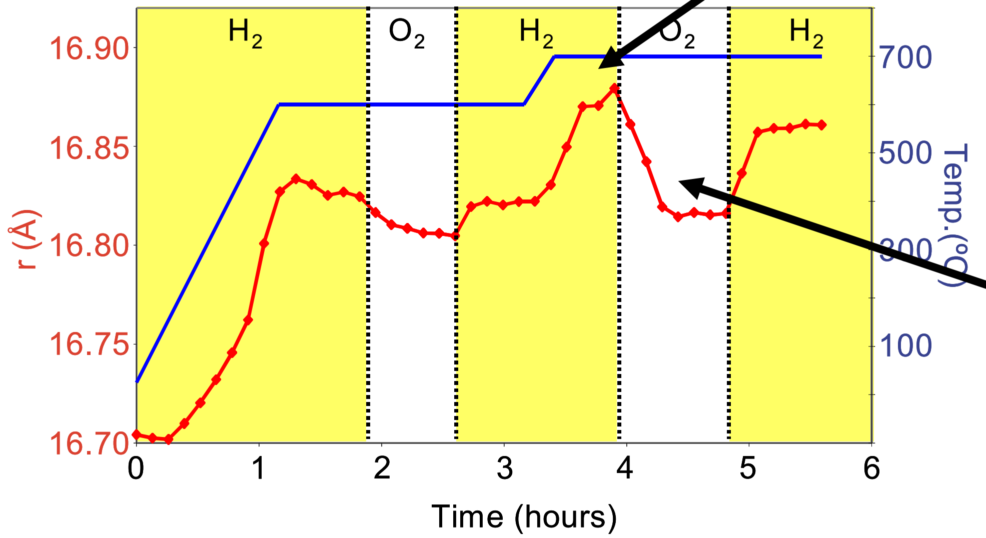
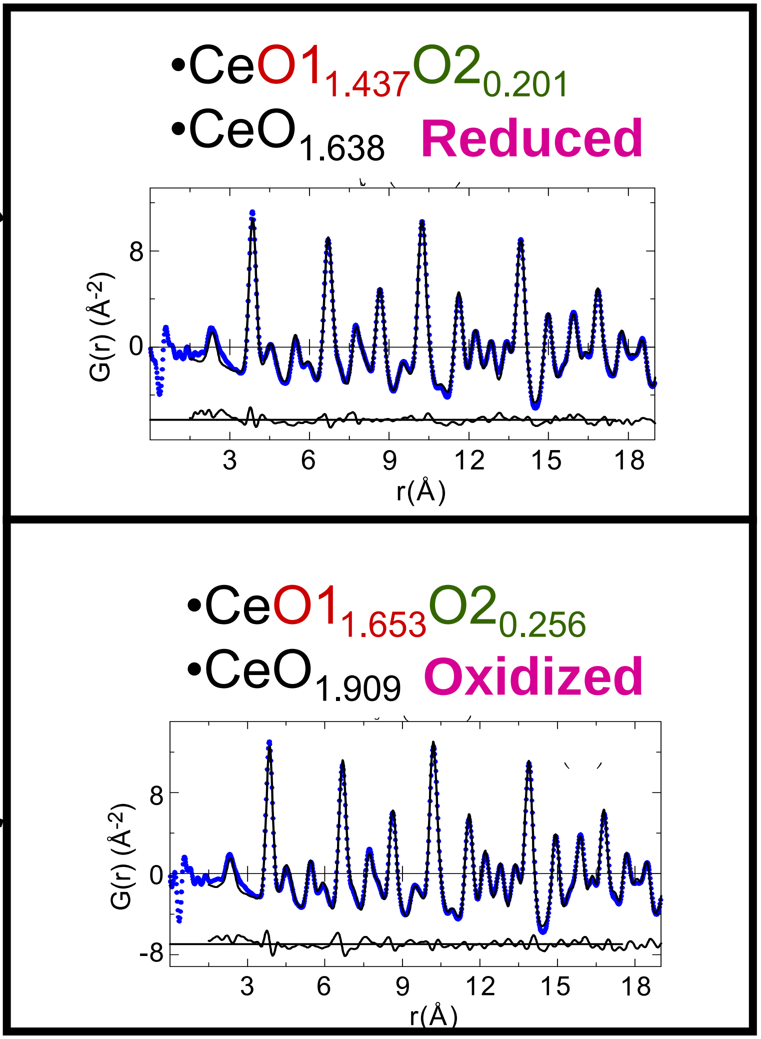
Reduced vs. Oxidized Structure

- It is possible to see oxygen move in and out of the structure
- Are there cooperative effects between the defect site and tetrahedral O site?
- Chupas et al JACS 2004





- $CeO1_{1.437}O2_{0.201}$
- $CeO_{1.638}$ **Reduced**

- $CeO1_{1.653}O2_{0.256}$
- $CeO_{1.909}$ **Oxidized**

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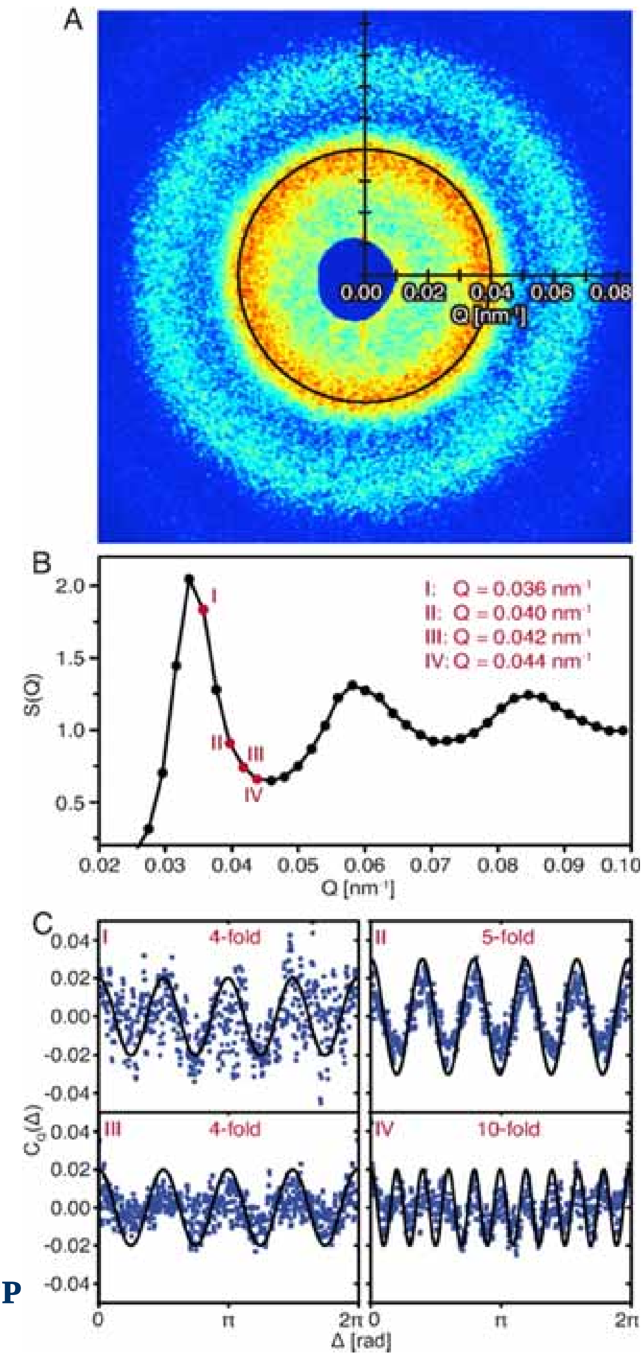
What can’t we do currently with powder PDF methods?

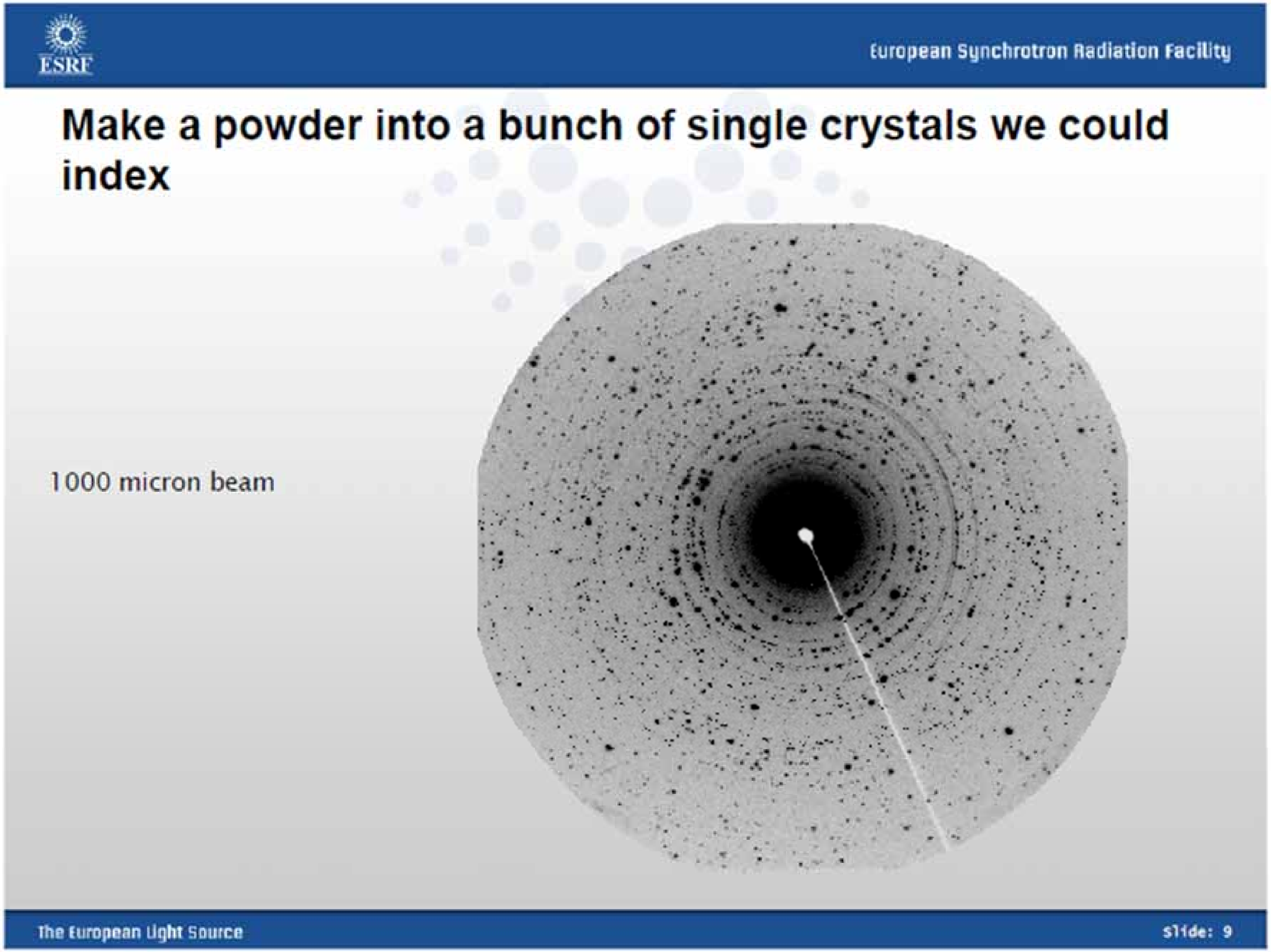
- Thin films and special geometries
- Very small sample volumes
- Buried interfaces, embedded particles/membranes
- Powders that are not powders: going beyond the powder average
  - Need to do a much better job of exploiting speckle, e.g., angular correlation analysis
  - Higher than second order correlation functions
- Special environments/high throughput for parametric studies
- Non destructive tickle and probe, i.e., close to equilibrium studies
  - But: beam damage will be a big issue



Wochner et al. PNAS **106** No 28, 11511-11514 (2009):

HTTP

Gavin Vaughn, ESRF



ESRF

European Synchrotron Radiation Facility

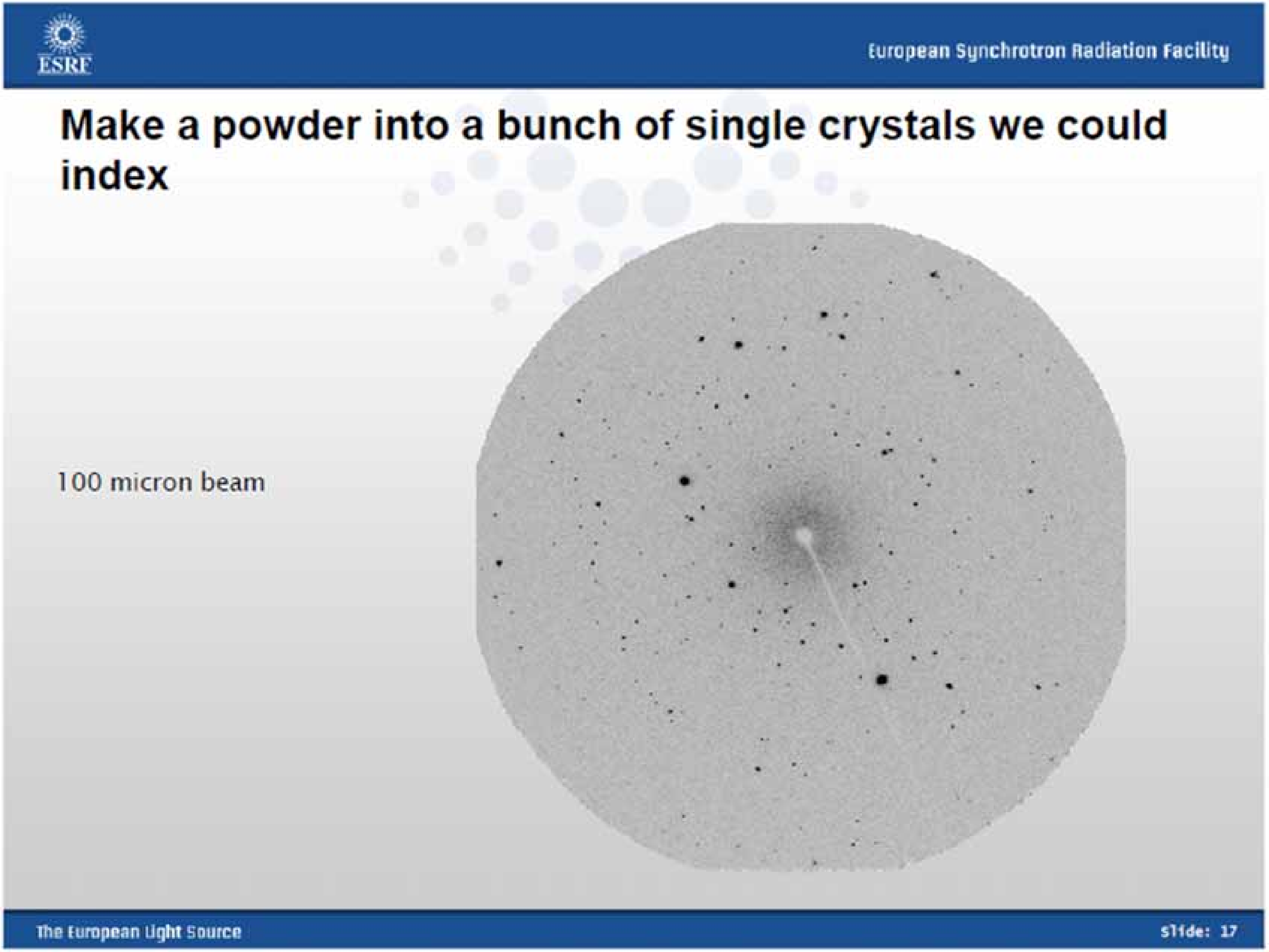
Make a powder into a bunch of single crystals we could index

1000 micron beam

The European Light Source

slide: 9

Gavin Vaughn, ESRF



Make a powder into a bunch of single crystals we could index

100 micron beam