Today's outline - October 14, 2021

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- Powder diffraction

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Reading Assignment: Chapter 6.1-6.2

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Reading Assignment: Chapter 6.1-6.2

Homework Assignment #04:
Chapter 4: 2,4,6,7.10
due Tuesday, October 19, 2021

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- Powder diffraction
- Pair distribution function
- Bragg & Laue geometries

Reading Assignment: Chapter 6.1-6.2

Homework Assignment #04:
Chapter 4: 2,4,6,7.10
due Tuesday, October 19, 2021

Homework Assignment #05:
Chapter 5: 1,3,7,9,10
due Tuesday, November 02, 2021

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})}\right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

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The second term is the Thermal Diffuse Scattering and actually increases with mean squared displacement.

Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

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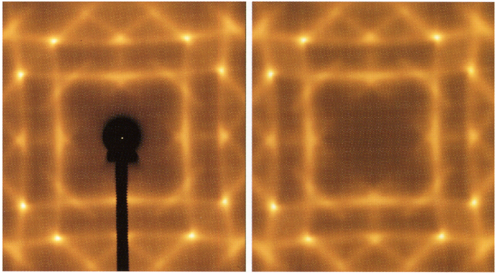

incident beam along (100)

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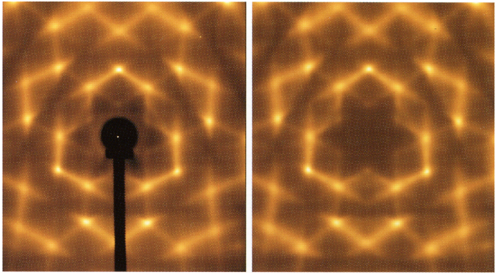

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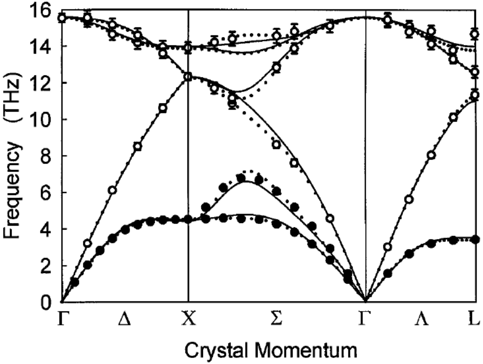

dotted line from this measurement

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Properties of the Debye-Waller Factor

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In general, Debye-Waller factors can be anisotropic

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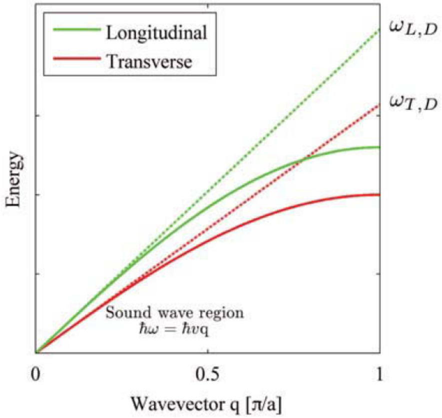

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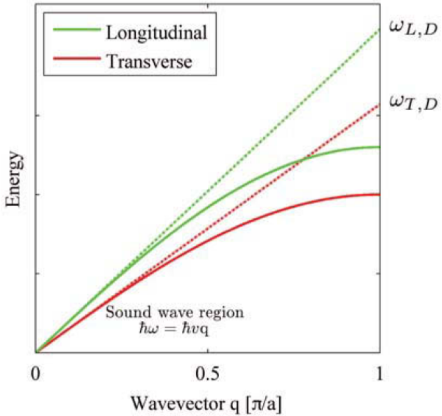

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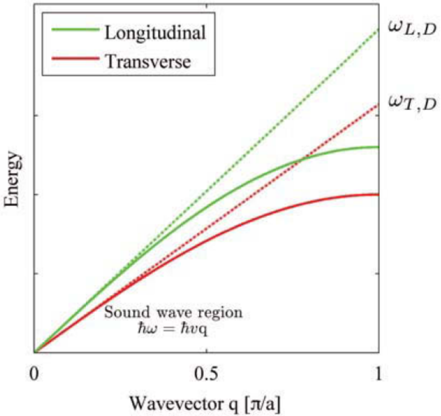

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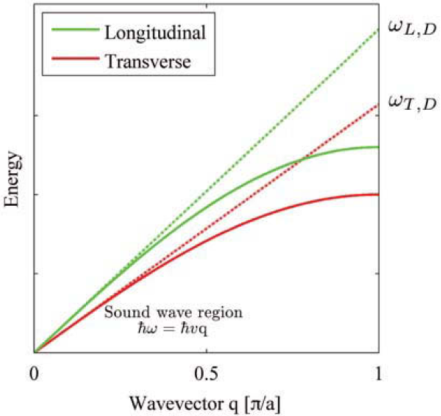

$$B_T[\text{Å}^2] = \frac{11492\text{T[K]}}{\text{A}\Theta^2[\text{K}^2]}\phi(\Theta/\text{T}) + \frac{2873}{\text{A}\Theta[\text{K}]}$$

Debye Temperatures

	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
C*	12	2230	0.11	0.11	0.12
Al	27	428	0.25	0.30	0.72
Cu	63.5	343	0.13	0.17	0.47

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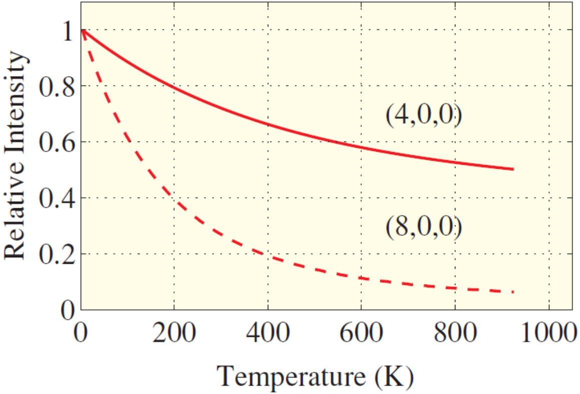

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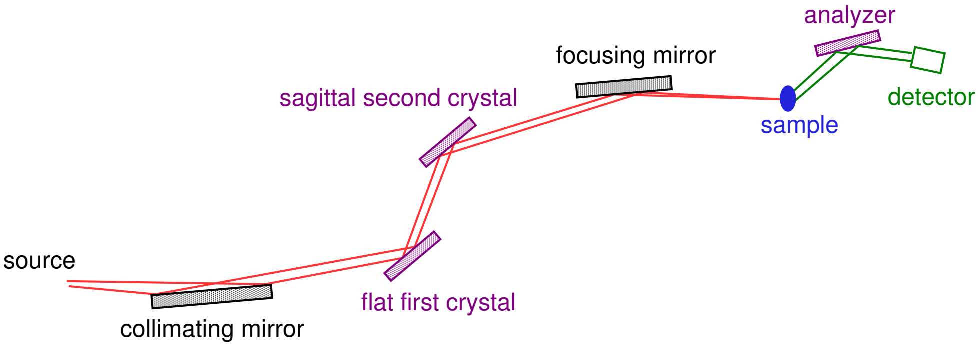
Beamline 11BM at the APS



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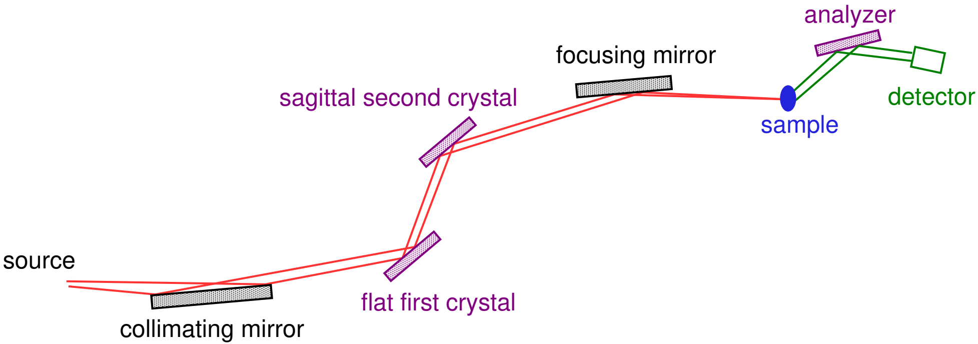

2D detectors have limited angular resolution, for high resolution routine powder diffraction, beamlines such as 11BM are ideal

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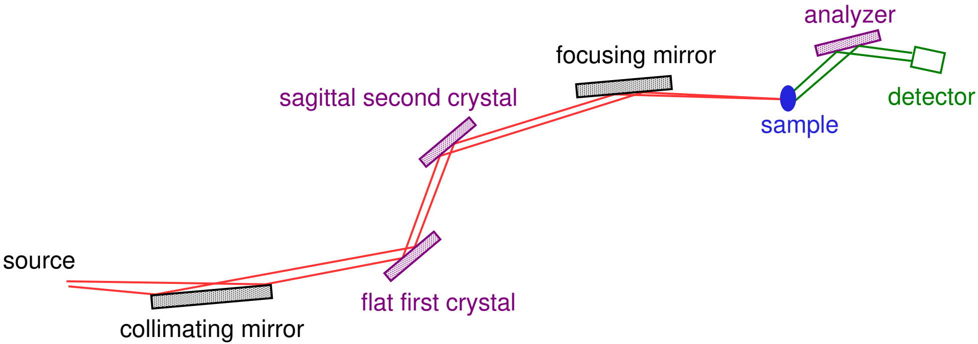

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The initial collimating mirror makes the beam more parallel and then it is focused horizontally and vertically to the sample

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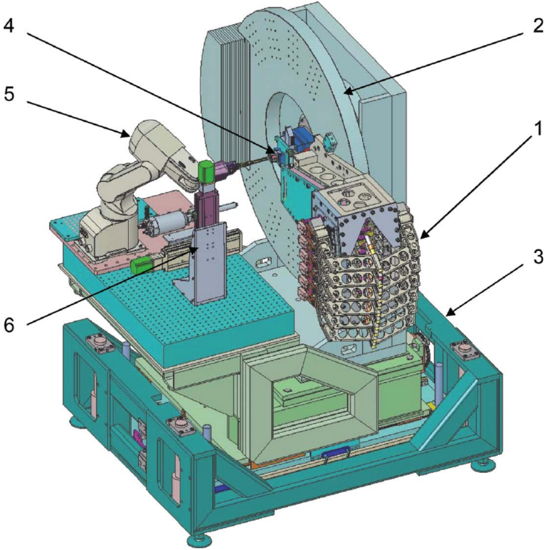
The high resolution analyzer



"A twelve-analyzer detector system for high resolution powder diffraction," P.L. Lee et al. *J. Synch. Rad.* **15**, 427-432

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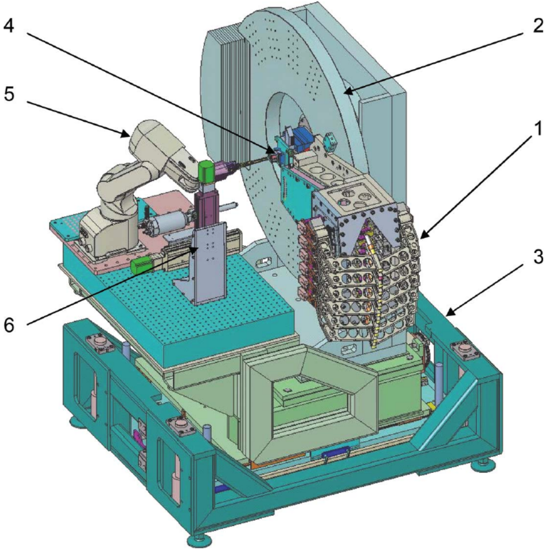

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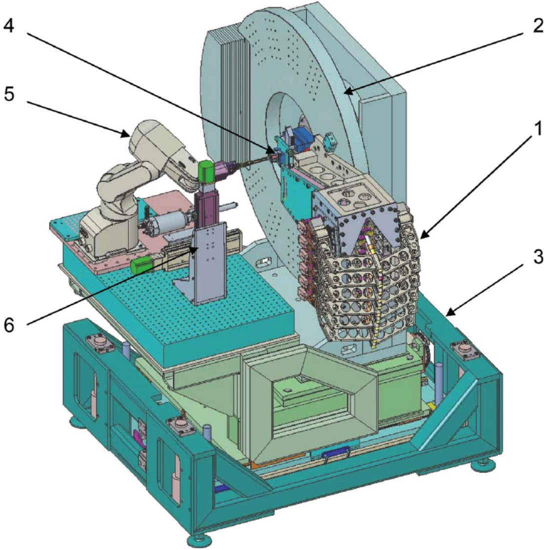

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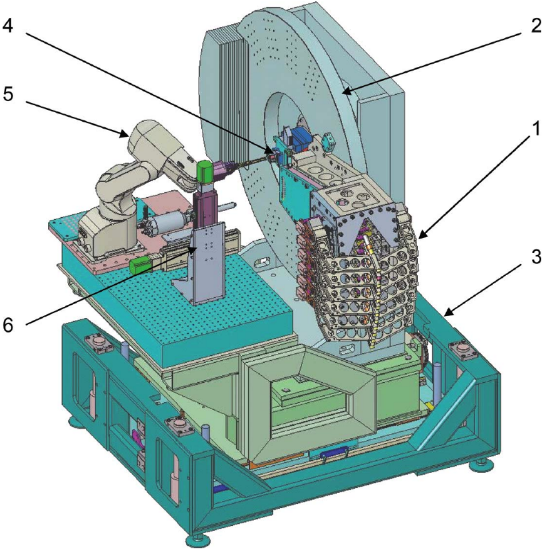

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High resolution is achieved with a 12 crystal analyzer system which is rotated on the main circle of the goniometer

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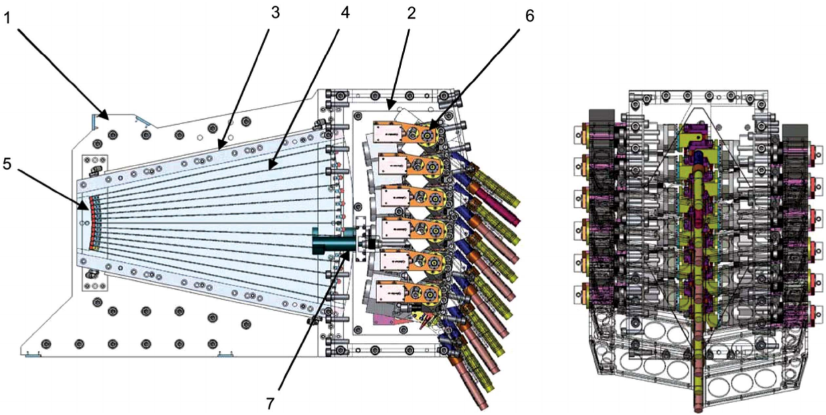
The high resolution analyzer



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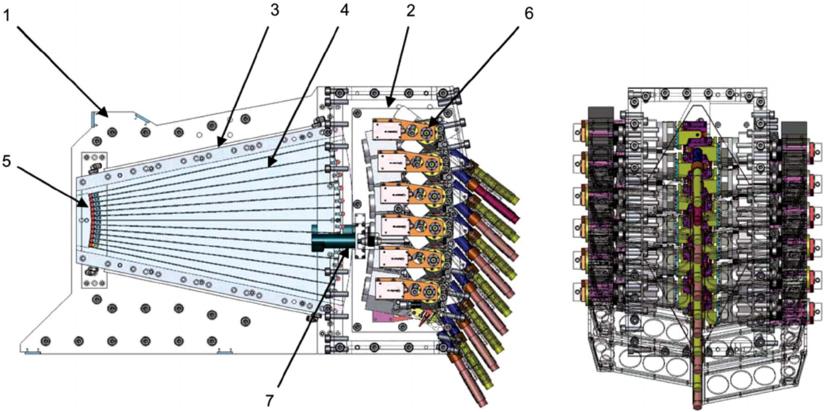

Each of the 12 analyzer crystals is tuned to the desired scattering energy and as the entire assembly is scanned, all twelve banks are collecting data and then are merged

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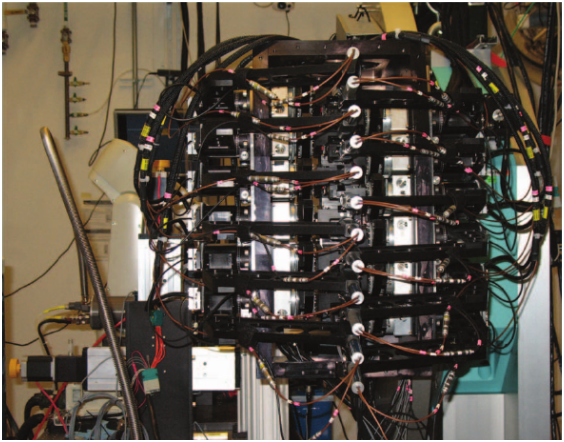
The analyzer and robot arm



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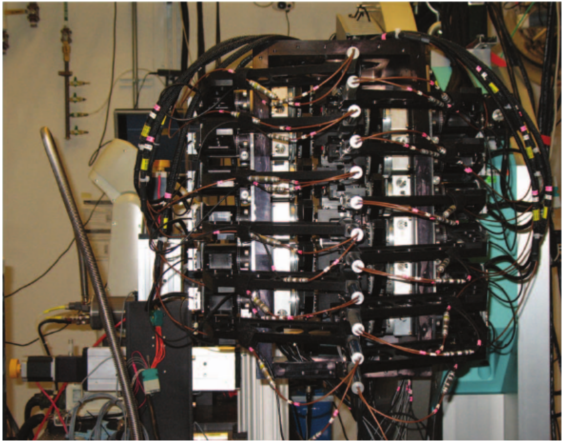

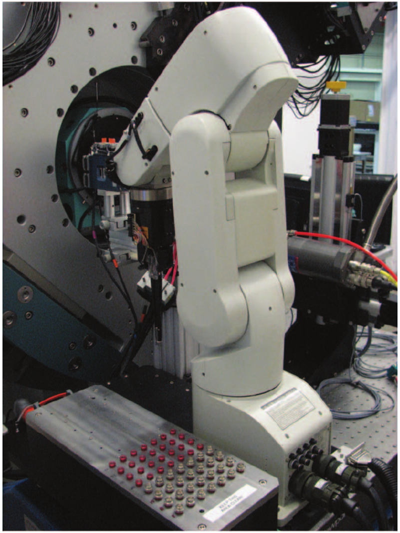

Samples are in Kapton capillaries and magnetic bases for remote mounting

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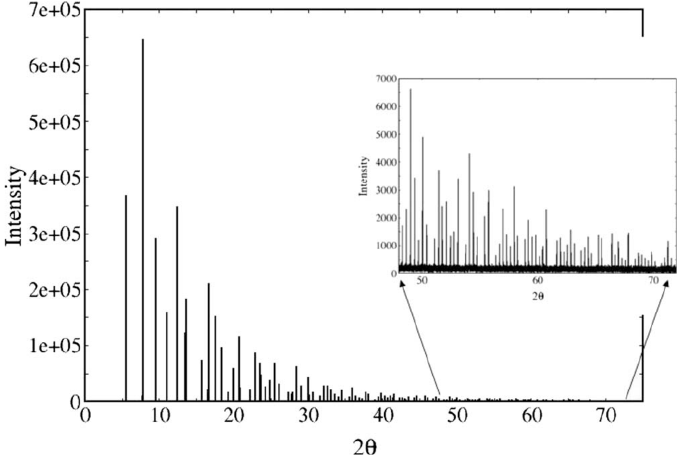
Data from high resolution LaB_6 standard



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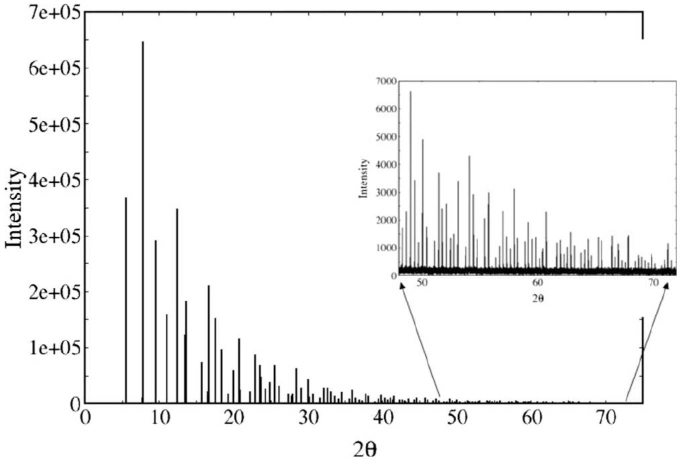

High resolution data with high count rates can be obtained out to very high angles with a wavelength of $\lambda \approx 0.5$Å.

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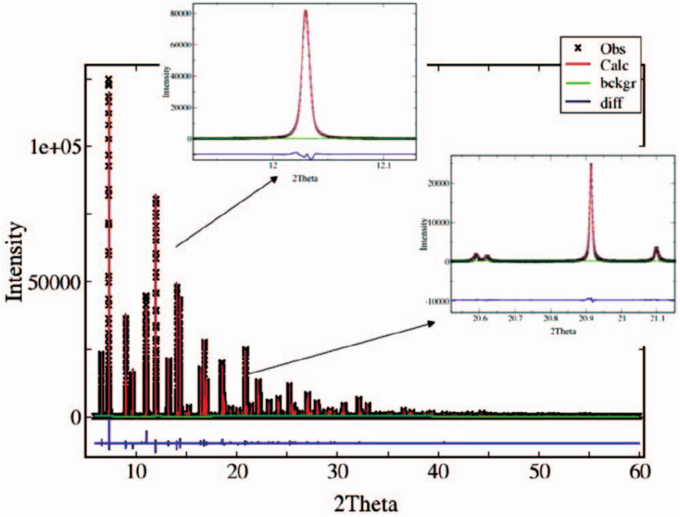
Refinement of SiO_2 and Al_2O_3



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CaO-CaO_2 reaction kinetics

CaO is a possible material to be used for carbon sequestration

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Rietveld refinement was used to measure the lattice parameters, crystallite sizes and phase fractions during carbonation and calcination cycles

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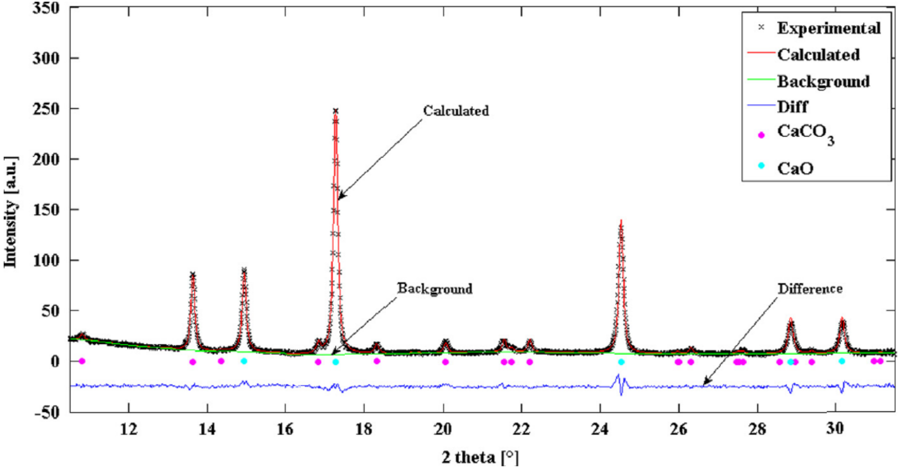
Typical diffraction pattern



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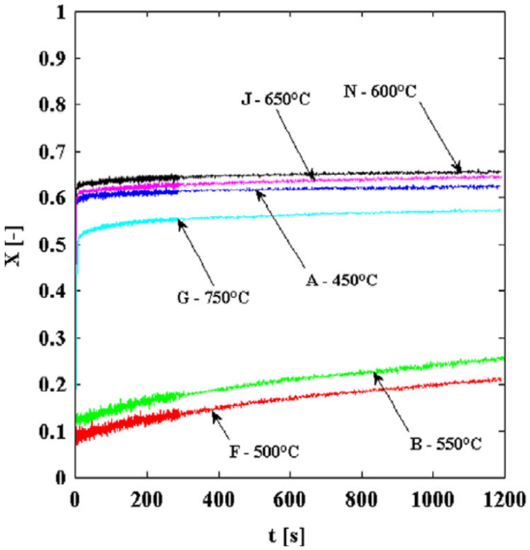

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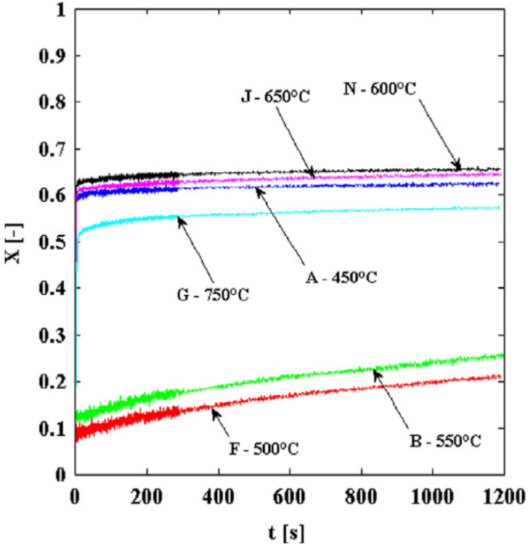

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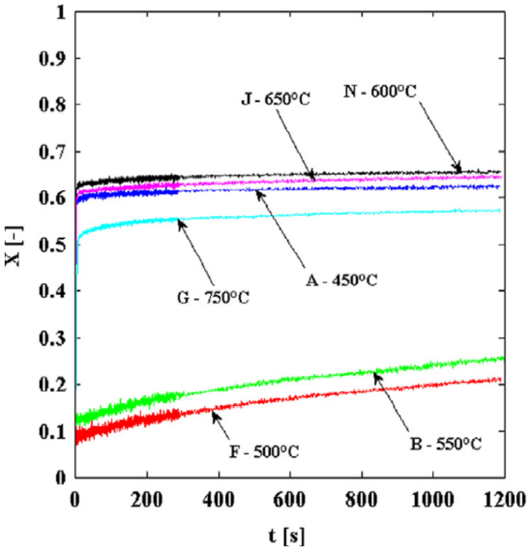

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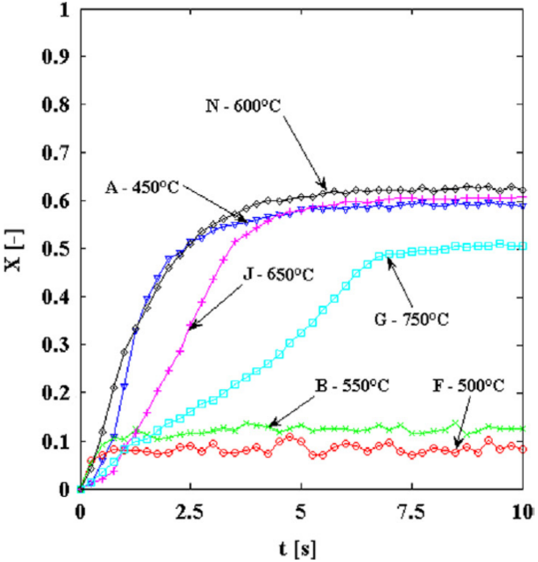

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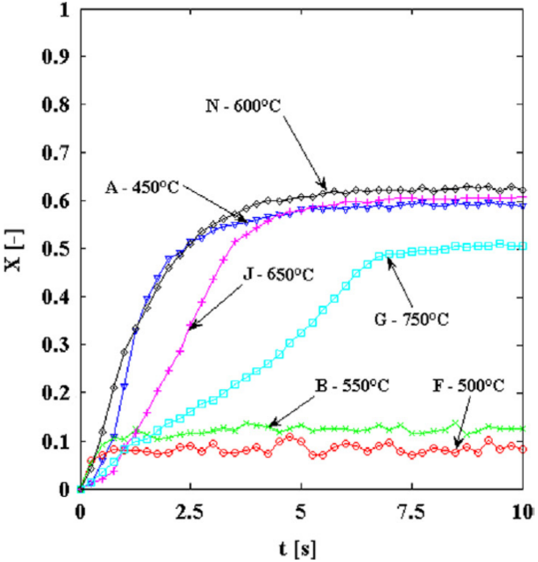

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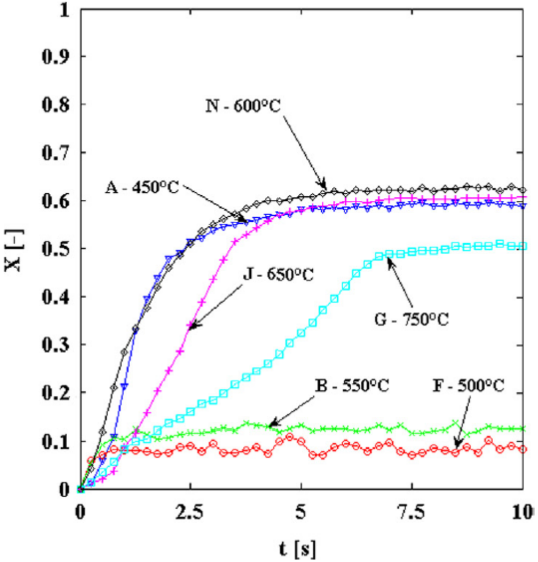

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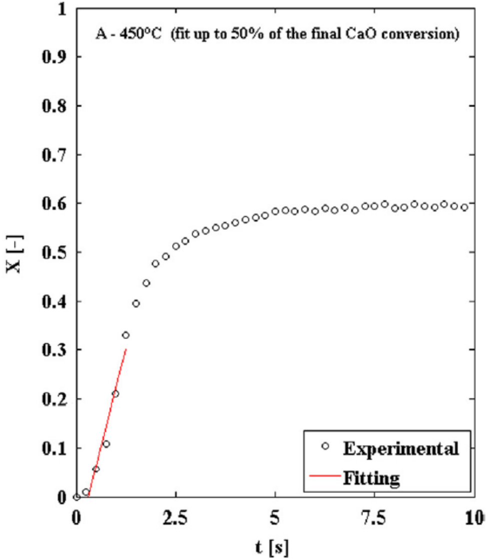

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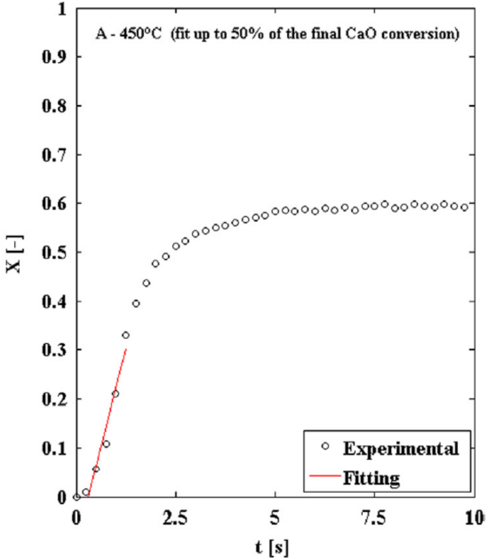

The rates of conversion are determined by fitting the initial (up to 50%) slope of the phase fraction as a function of time with a straight line

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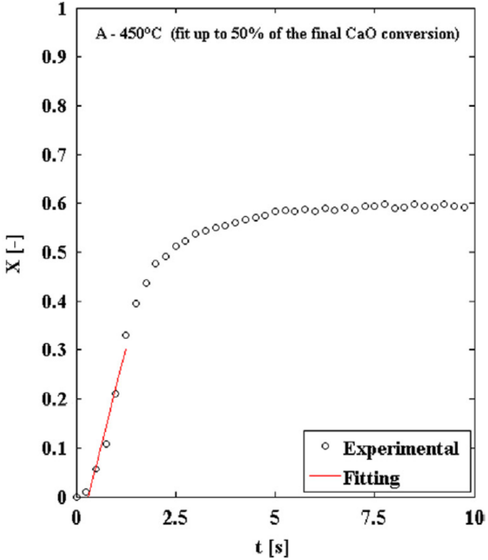

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These data are then plotted versus the initial CaO crystallite size as determined by Rietveld refinements

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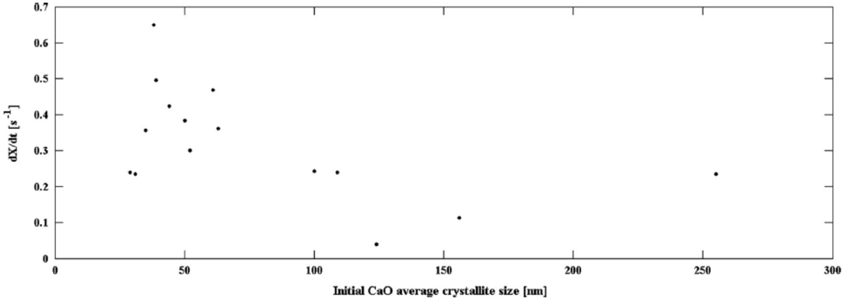

Initial crystallite size is one of the determining factors in inital rate of conversion and fraction converted.

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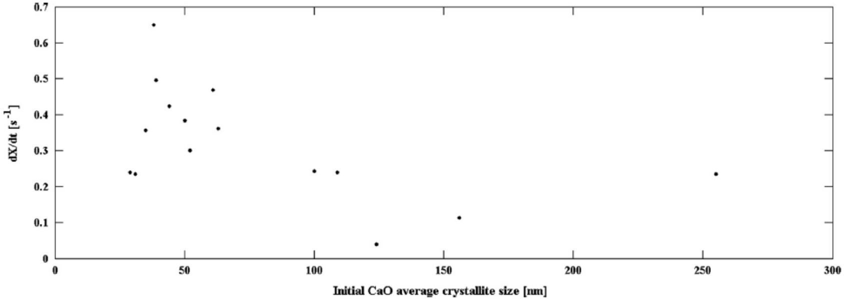

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CaO crystallite size can be related to porosity which is key to the conversion process.

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Pair distribution function

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$$G(r) = 4\pi r[\rho(r) - \rho_0], \qquad \rho(r) = \frac{1}{4\pi r^2 N\langle f\rangle^2} \sum_{n,m\neq n} Z_m Z_n \delta(r - r_{mn})$$

PDF modeling

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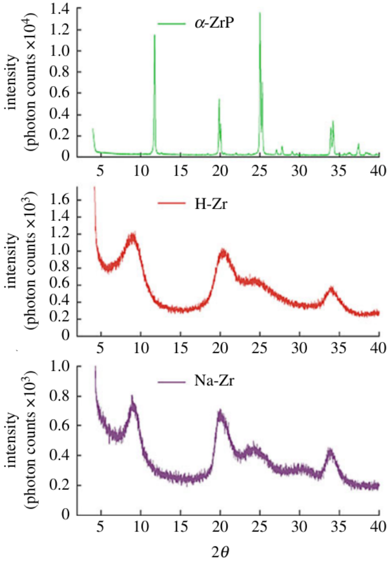
So what does the pair distribution function look like in practice?

PDF processing: $F(Q)$ and $G(r)$



"Local environment of terbium(III) ions in layered nanocrystalline zirconium(IV) phosphate – phosphate ion exchange materials," M.W. Terban, et al. *Inorg. Chem.* **56**, 8837-8846 (2017).

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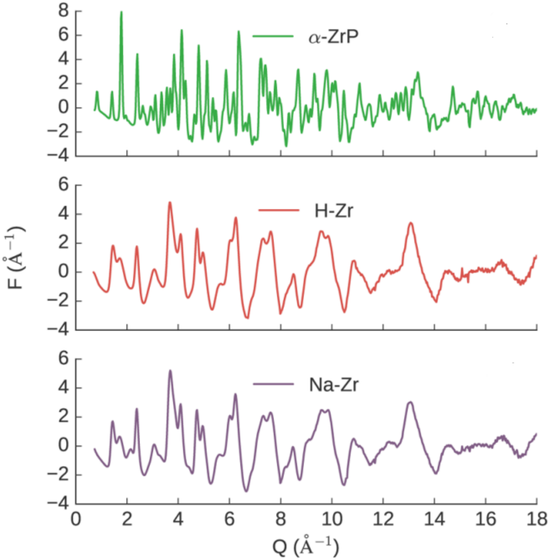

The broad peaks of nanoparticle systems still contains information once processed into the reduced total scattering function

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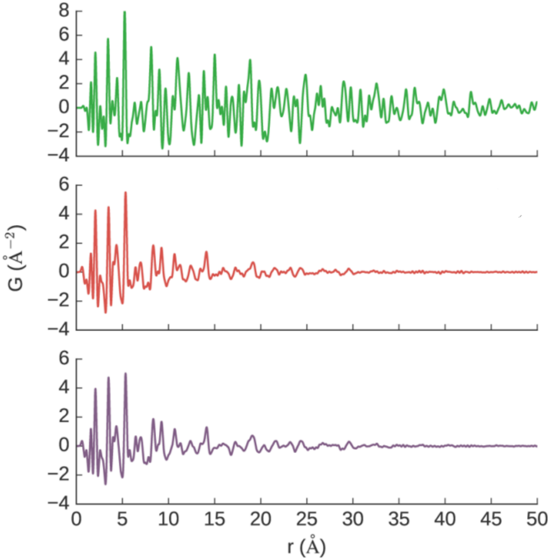

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When Fourier transformed, the significant differences in crystalline and nanoparticulate samples are obvious

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PDF structure of CdSe nanoparticles

The goal of this study was to compare the PDF structures of CdSe nanoparticles of various sizes with the results obtained from traditional analysis of optical data and electron microscopy

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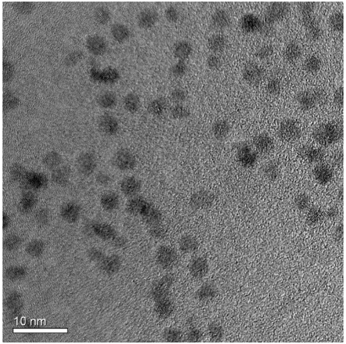

Nanoparticles of of three different sizes were obtained by changing the nucleation time from 1200 s (left)

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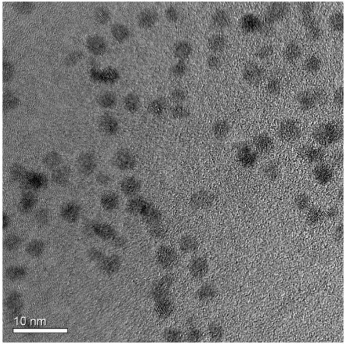
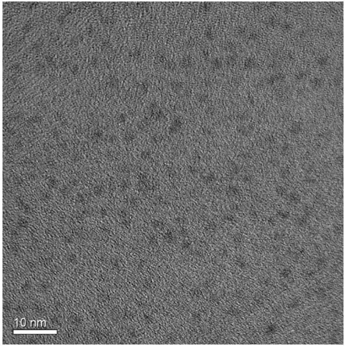


Nanoparticles of of three different sizes were obtained by changing the nucleation time from 1200 s (left) to 15 s (right) during synthesis



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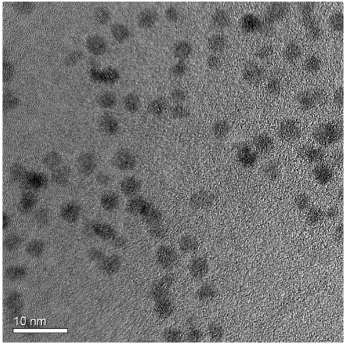

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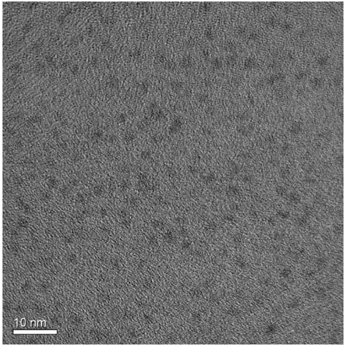

Optical absorbance and fluorescence indicates particle sizes ranging from 3.5 nm to 2.0 nm

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PDF data collection

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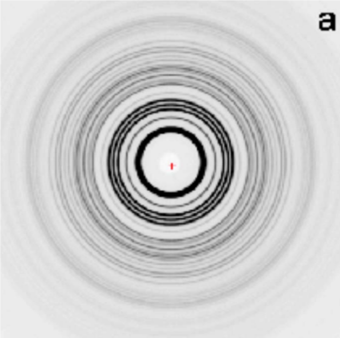

Data were collected on bulk CdSe (left)

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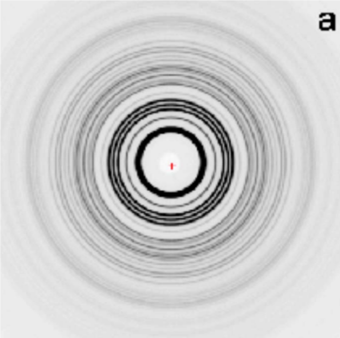
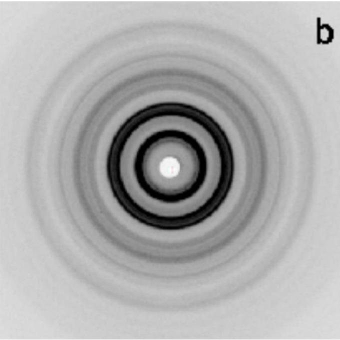


Data were collected on bulk CdSe (left) and the CdSe nanoparticles (right) then azimuthally integrated to get the powder pattern



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$F(Q)$ and $G(r)$

The data for bulk and nanoparticle samples was processed to obtain $F(Q)$ and $G(r)$ in preparation for structural modeling

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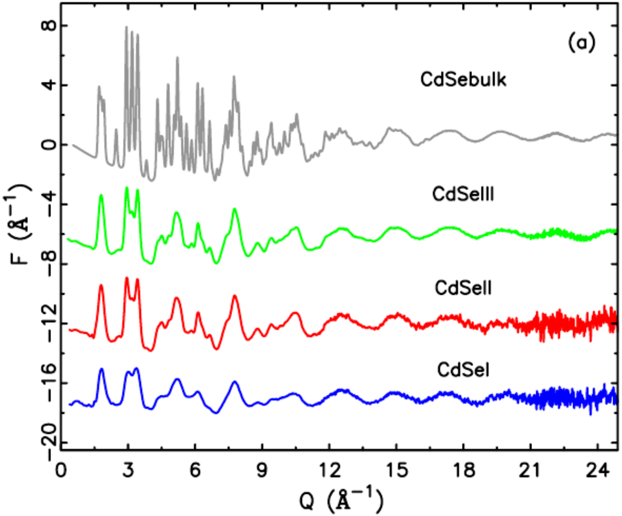

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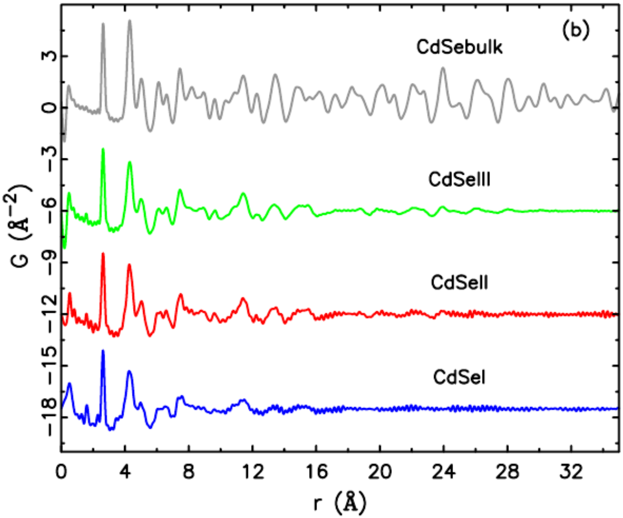

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The particle size progression shows in the range over which the $G(r)$ has distinct peak structure

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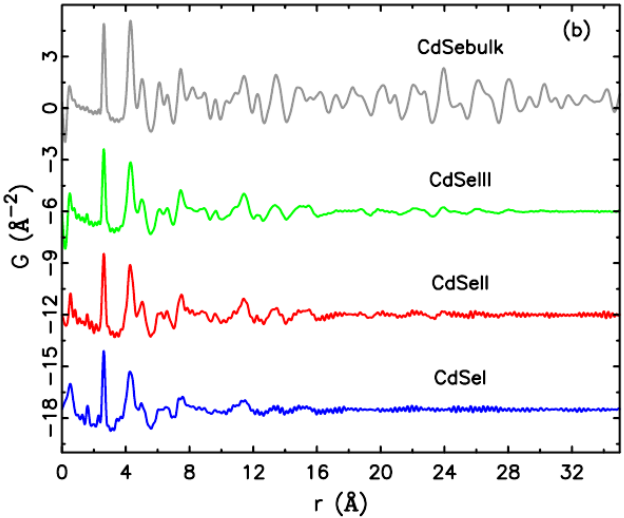
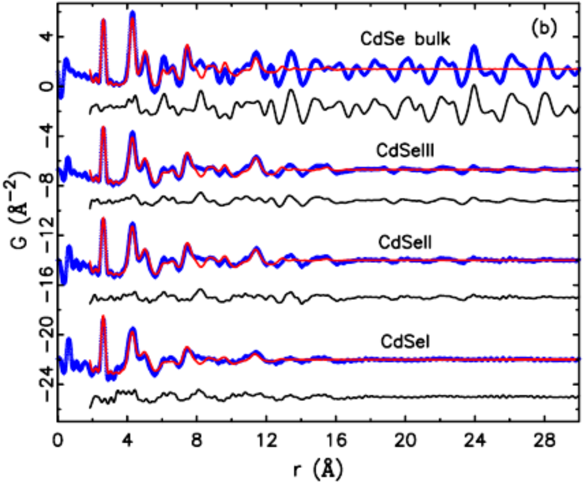


Initial modeling



The first fit to the data uses the wurtzite structure which has ABAB stacking of hexagonal planes

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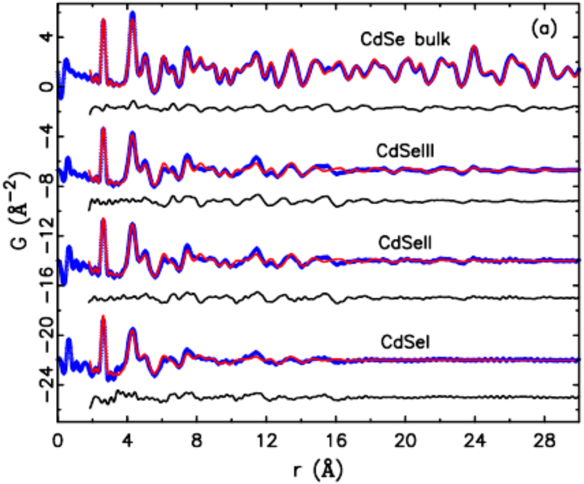

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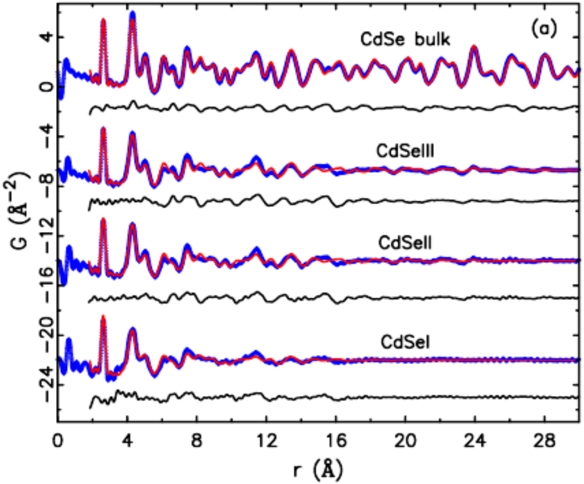

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While the zinc blende does slightly better at fitting the experimental data, it is clear that neither is perfect for the bulk or the nanoparticles

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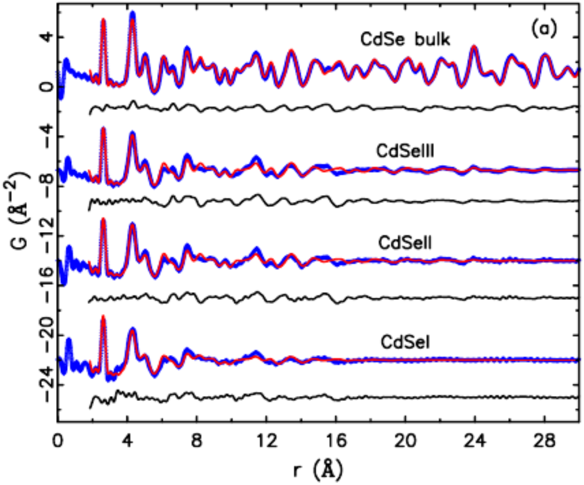

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It is likely that a better fit can be obtained using a mixture of the two stacking arrangements

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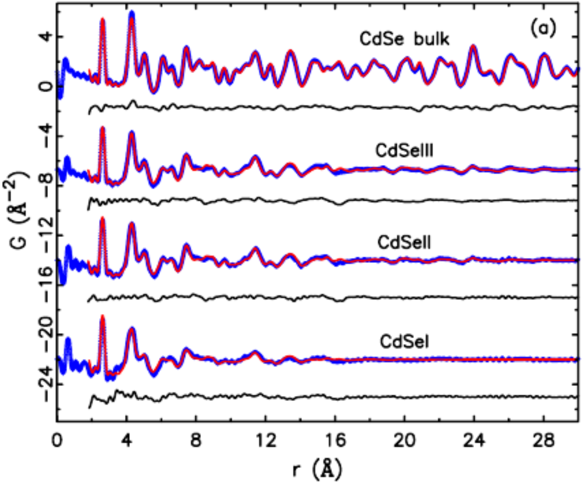
Final structural models



A fit using both wurtzite and zinc blende fits much better for all particles

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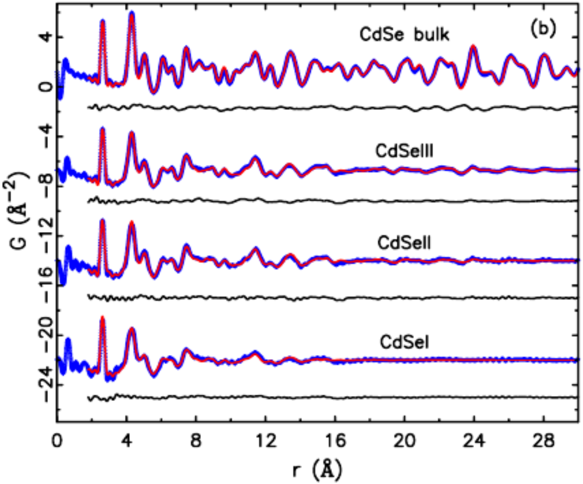

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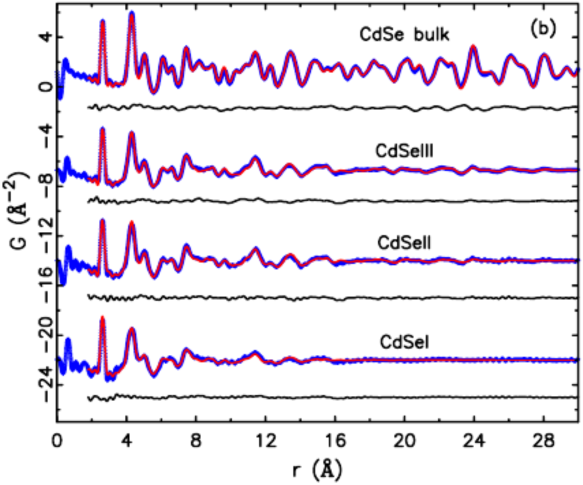

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The final values obtained in the fitting give particle sizes consistent with TEM and optical measurements. The fits also show that the bulk sample has only about 33% stacking faults while the nanoparticles have 50%

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