
Atomic-scale structure of materials with intrinsic disorder by the atomic pair distribution function technique and high energy x-ray diffraction

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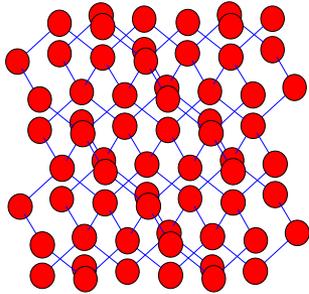
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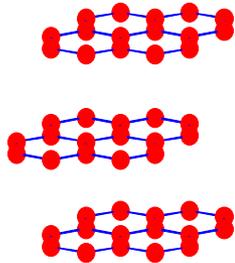
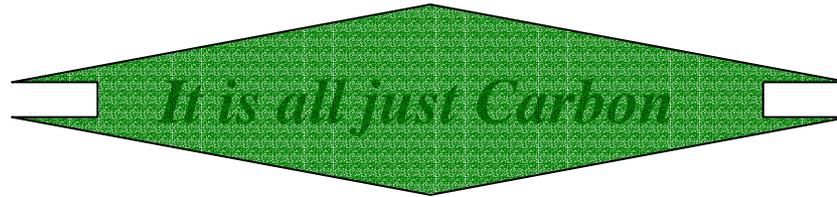
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Why do materials behave as they do ? It has a lot to do with their structure, i.e. how the atoms arrange themselves in space.



Diamond - hard, transparent, insulating and expensive.



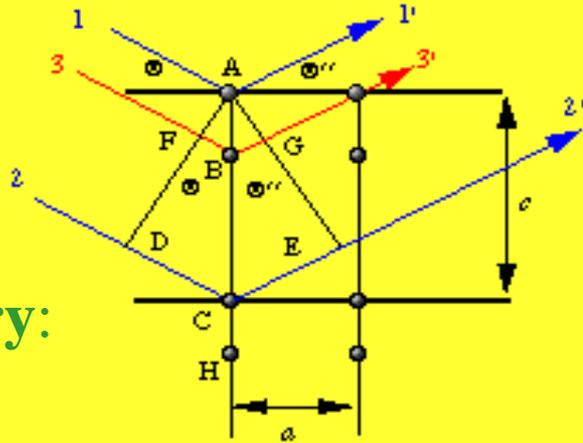
Graphite - soft, black, conducts heat and electricity and cheap.



And now we have nanotubes...

Structure: How it is determined ?

Theory:



For the above diagram Bragg conditions are met when $DC = CE$ and $\theta = \theta''$.

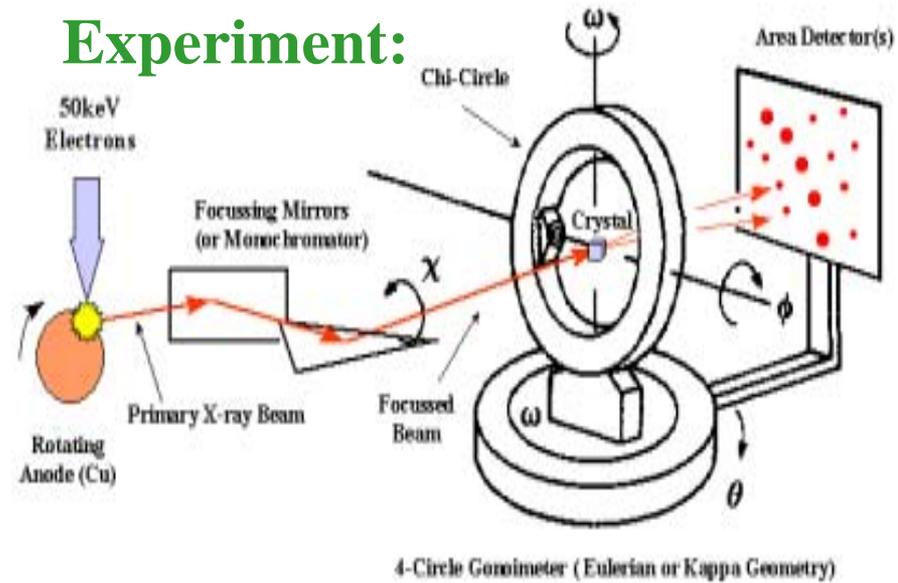
Therefore, $AC \sin \theta = DC$ and $AC \sin \theta''$ or $2AC \sin \theta = DC + CE$

Let: $d = AC$ and $DC + CE = n\lambda$

Then :

$$2d \sin \theta = n\lambda$$

Experiment:

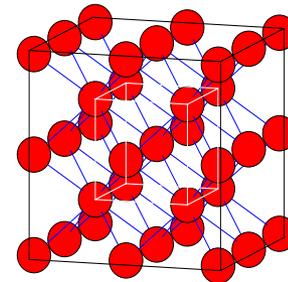


What do we actually learn & use:

Lattice parameters: $a, b, c, \alpha, \beta, \gamma$,

Symmetry: S.G.

Atomic positions: (x, y, z) and $B(\text{\AA}^2)$



Diffraction patterns from materials with different degrees of structural coherence

No disorder

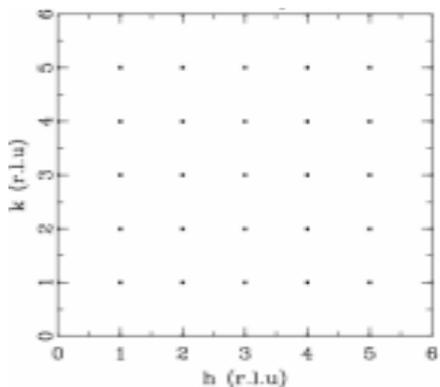
Moderate disorder

A great deal of disorder

Ideal crystals

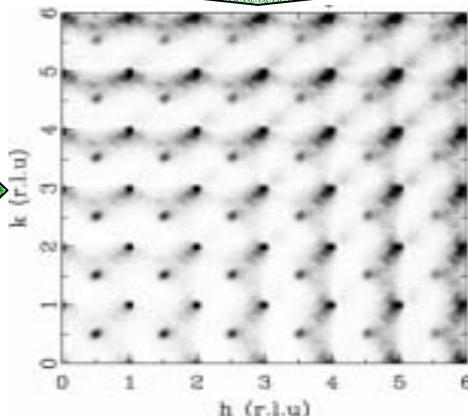
Imperfect crystals

Glass



Simulated

2d patterns



Simulated

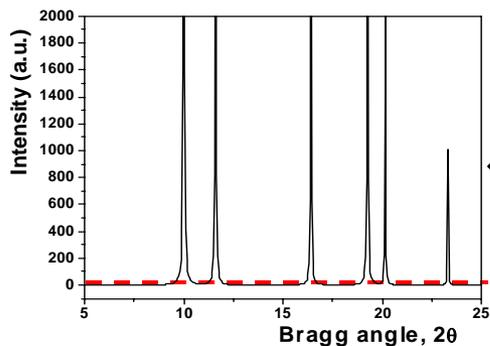
2d patterns



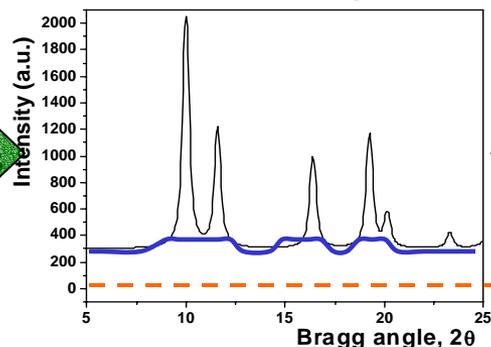
Bragg peaks only

Both Bragg peaks and diffuse scattering

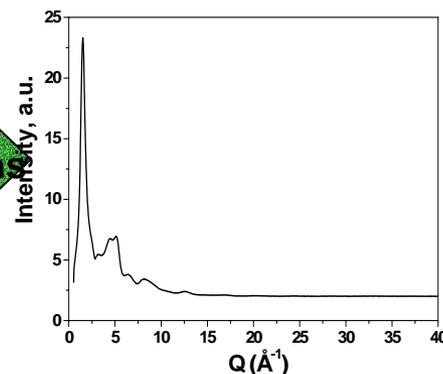
Diffuse scattering only



1d patterns

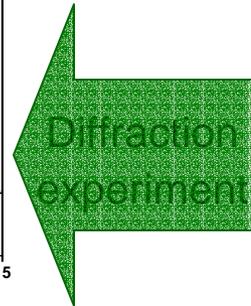
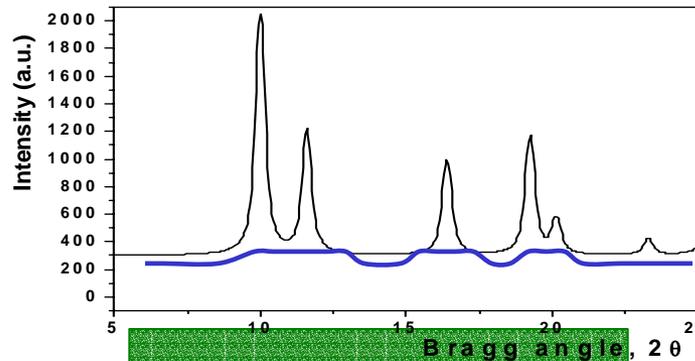
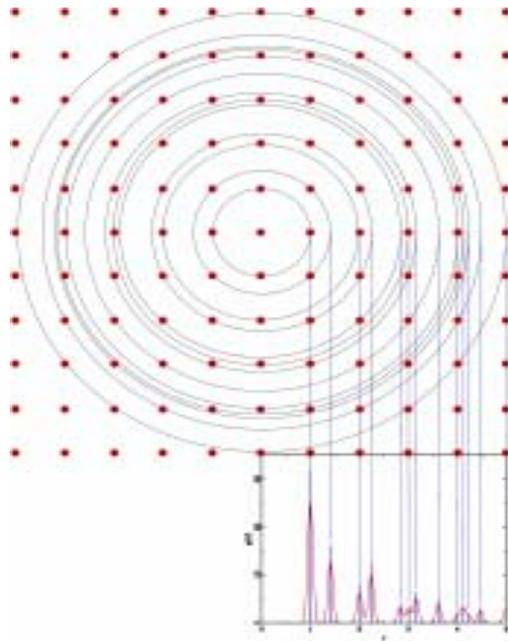


1d patterns



Diffraction patterns of perfect crystals show Bragg peaks only. Diffraction patterns of materials of limited structural coherence contain a diffuse component which is of low intensity and is widely spread in reciprocal space. All components of the diffraction patterns have to be accounted for in the atomic structure determination.

The Atomic Pair Distribution Function Technique



$$S(Q) = 1 + \frac{[I^{el.}(Q) - \sum c_i f_i^2(Q)]}{[\sum c_i f_i(Q)]^2}$$

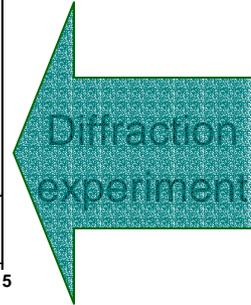
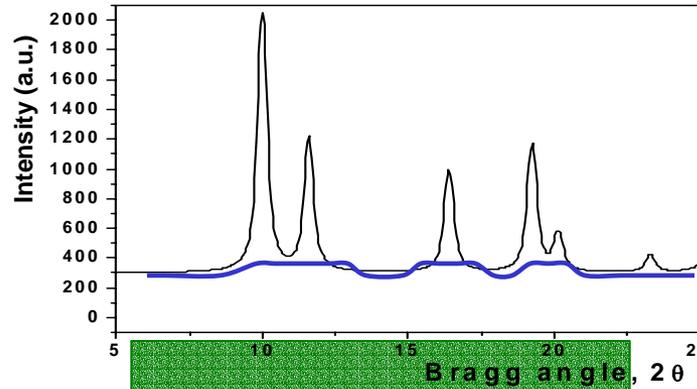
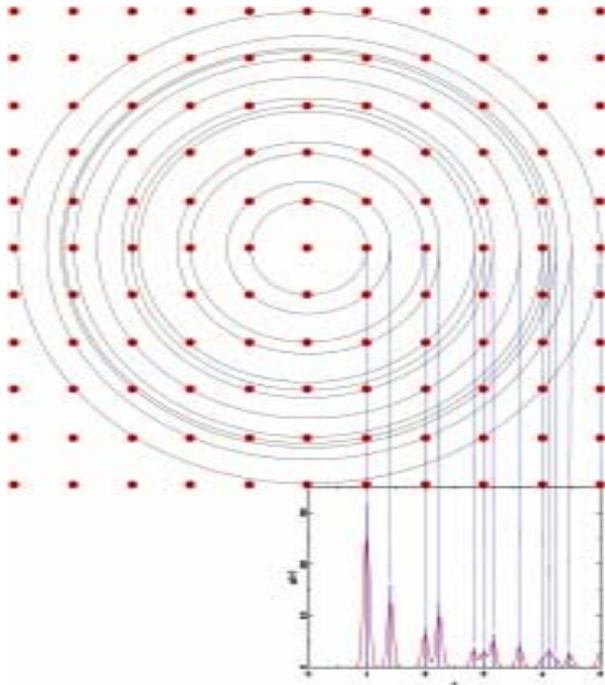
$$G(r) = \frac{2}{\pi} \int_{Q=0}^{Q_{max}} Q [S(Q) - 1] \sin(Qr) dQ,$$

$$Q = 4\pi \sin(\theta) / \lambda = 1.0135 \sin(\theta) E[\text{keV}]$$

$G(r) = 4\pi[\rho(r) - \rho_0]$
 $\rho(r)$ is the local and
 ρ_0 the average atomic density

The atomic PDF, $G(r)$, peaks at characteristic interatomic distances and thus reflects the structure of materials. It is the Fourier sine transform of the experimentally observable structure factor $S(Q)$ which is related to the elastic part of the **total diffracted intensity** $I^{el.}(Q)$. Since both the sharp **Bragg peaks** and the **diffuse components** of the diffraction spectrum contribute to $G(r)$ it reflects **both the average, long-range structure and the local structural imperfections**. The PDF is barely influenced by diffraction optics and experimental factors. Also, high-resolution $G(r)$'s can be obtained by accessing high values of Q . This can be done by using high energy x-rays.

The Atomic PDF function ~ Patterson function



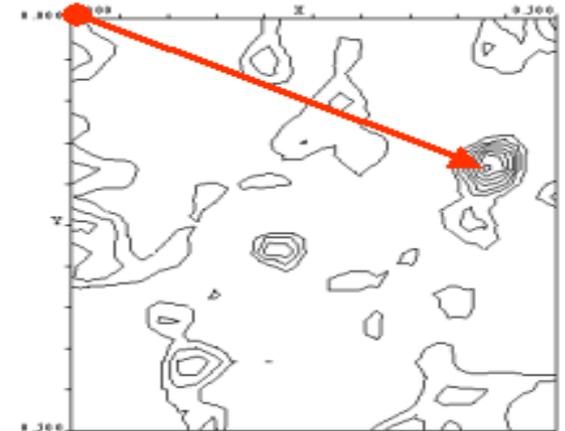
$$S(Q) = 1 + \frac{I^{el.}(Q) - \sum c_i f_i^2(Q)}{[\sum c_i f_i(Q)]^2}$$

$$G(r) = (2/\pi) \int_{Q=0}^{Q_{max}} Q [S(Q) - 1] \sin(Qr) dQ,$$

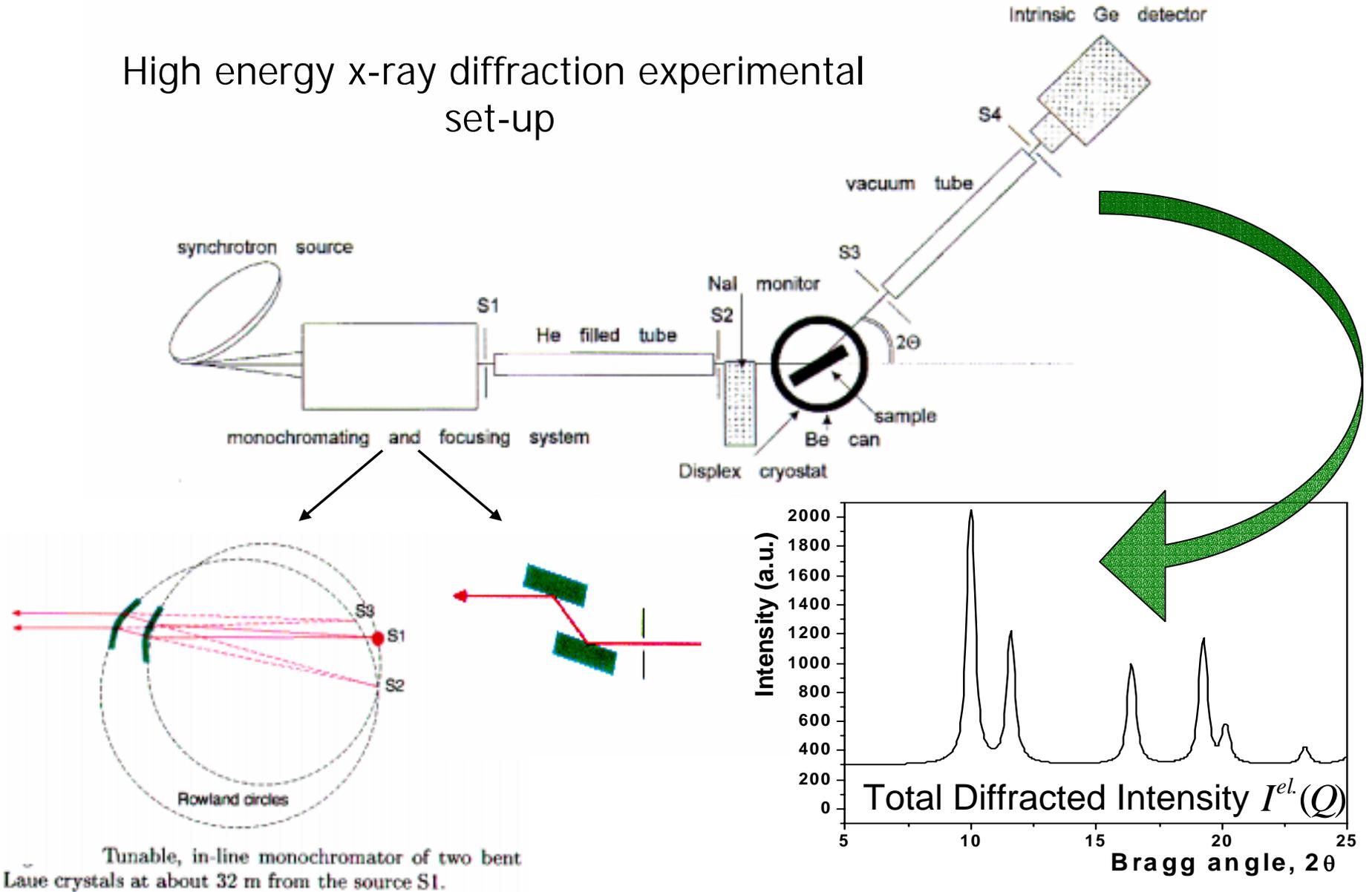
Total scattering → atomic PDF: 1-D map of all interatomic distances

Bragg peaks → Patterson function: map of interatomic distances in the unit cell

$$P_{(u)} = \frac{1}{a} \sum_h |F_h|^2 \cos(2\pi hu)$$



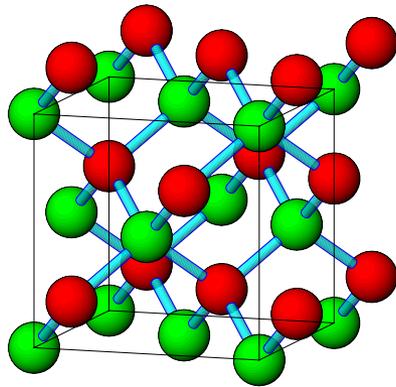
High energy x-ray diffraction experimental set-up



Examples of recent structure studies on materials with intrinsic disorder:

1. In-Ga-As semiconductor alloys
 2. V_2O_5 nanotubes
 3. Dendritic and hyper-branched macromolecules
 4. Ca/Al silicate glasses
 5. Gold nanoparticles
-

Local structure of $\text{In}_x\text{Ga}_{1-x}\text{As}$ semiconductor alloys



Zinc-blende type structure:

$$a(\text{GaAs}) = 5.653 \text{ \AA}$$

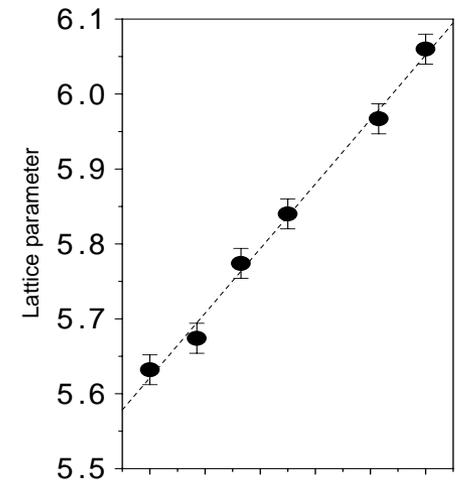
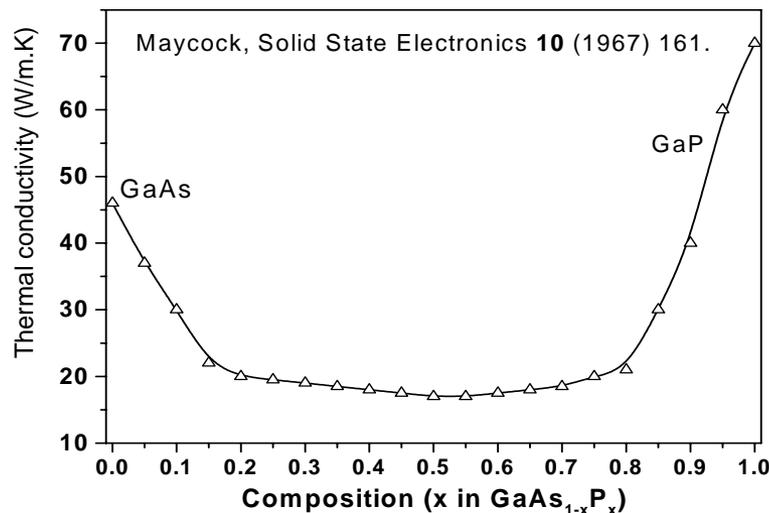
$$a(\text{InAs}) = 6.038 \text{ \AA}$$

● - In, Ga (0,0,0)

● - As (1/4, 1/4, 1/4)

However,

Properties show nonlinear dependence on concentration, x .



From Vegard's law:

$$NN[(\text{In};\text{Ga})\text{-As}] = 2.447 \text{ \AA}; x=0$$

$$NN[(\text{In};\text{Ga})\text{-As}] = 2.615 \text{ \AA}; x=1$$

EXAFS

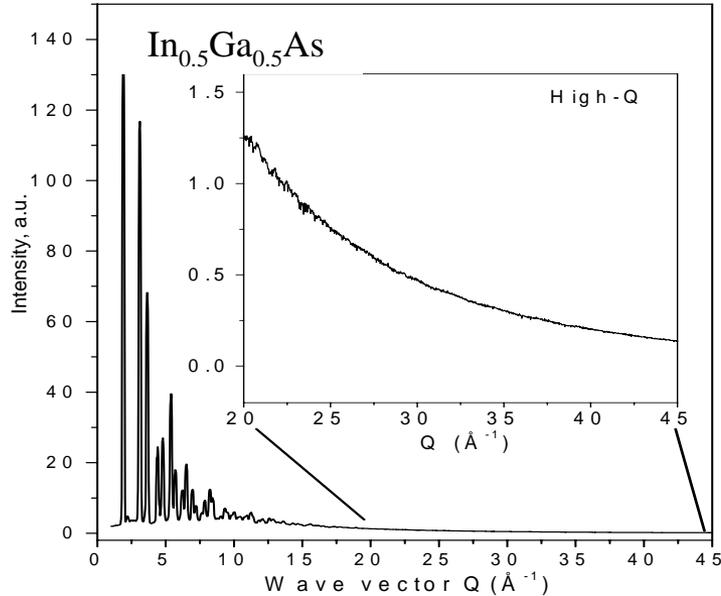
Mikkelsen et al. PRL **49** (1982) p. 1412

$$NN(\text{Ga-As}) = 2.45 \text{ \AA}$$

$$NN(\text{In-As}) = 2.61 \text{ \AA}, \text{ for any } x$$

E = 60 keV,
A2, CHESS

Consider the total scattering:

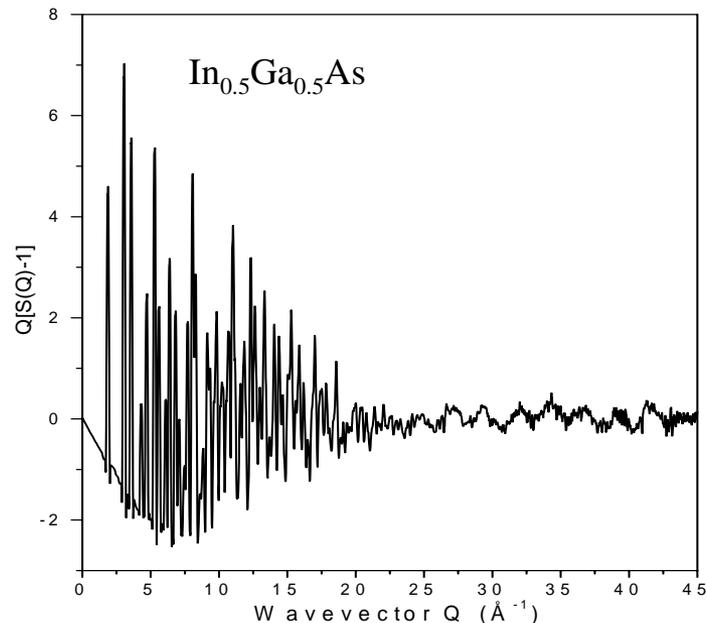


High energy x-ray data from
 $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$

Very little structure is evident in
the raw data at high-Q (inset to
top panel)

However, significant diffuse scattering
is present in the total scattering
function $S(Q)$ from the same data

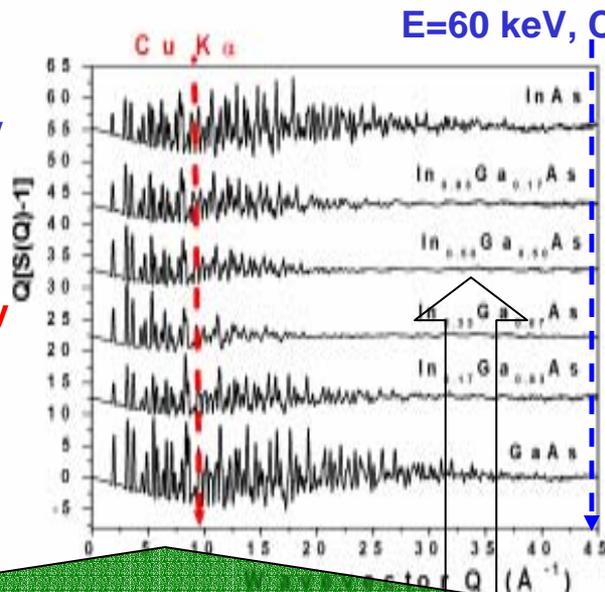
It becomes evident by dividing the raw
data to $\langle f(Q) \rangle^2$ and multiplying by Q .



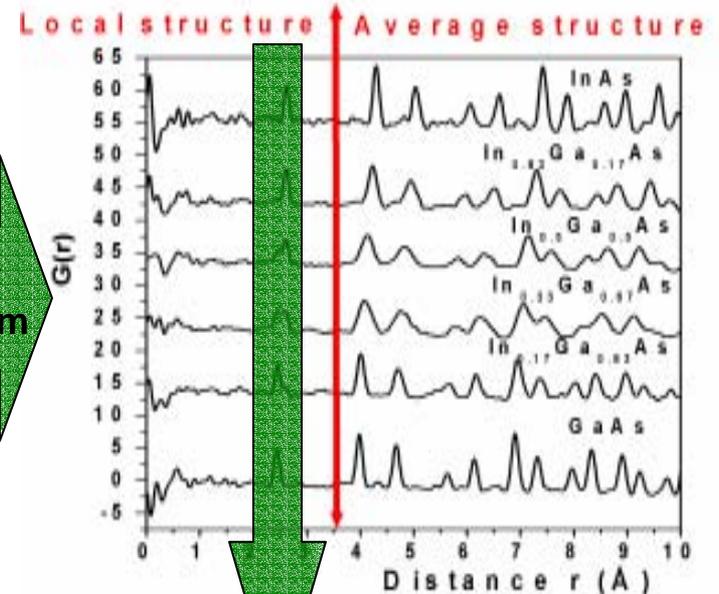
The structural information is there
if we measure carefully enough

Local structural disorder In-Ga-As alloys - experimental data

With $E = 60 \text{ keV}$
 $Q_{\text{max}} = 45 \text{ \AA}^{-1}$
 With $E = 8 \text{ keV}$
 (i.e. $\text{Cu K}\alpha$)
 $Q_{\text{max}} = 8 \text{ \AA}^{-1}$ only



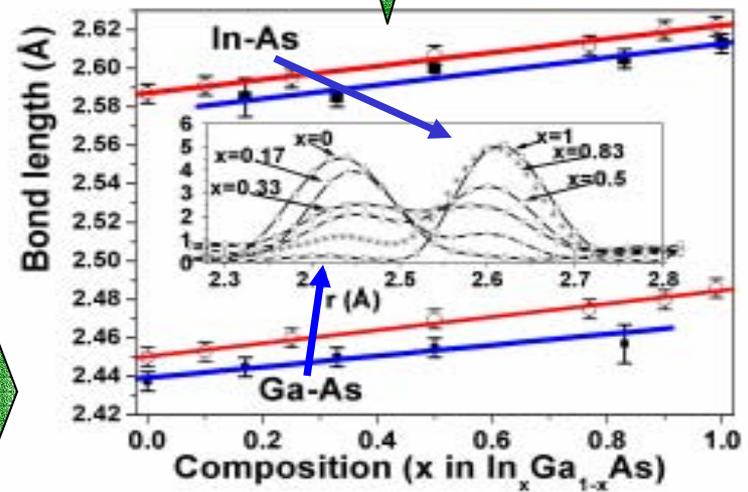
Fourier Transform



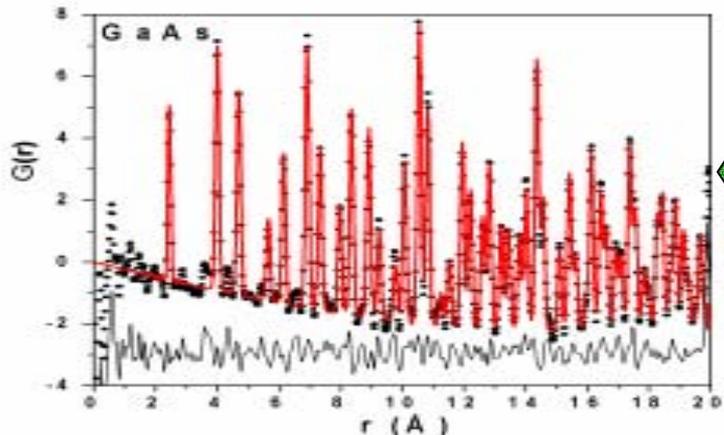
Significant Bragg scattering is present in the $S(Q)$ s of the end members GaAs and InAs. The materials are perfectly crystalline. The

Bragg peaks disappear at much lower Q values in the alloys. At high Q values, only oscillating diffuse scattering is present. The

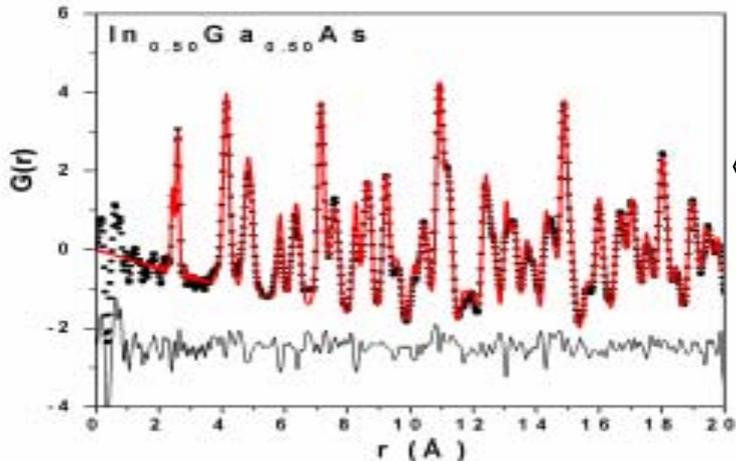
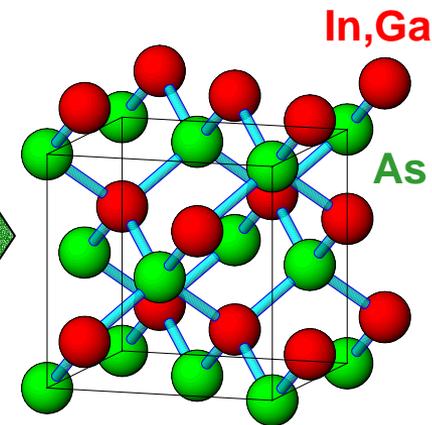
alloys exhibit significant local positional disorder due to the presence of two distinct bond lengths - Ga-As and In-As. These bonds are seen as a split first peak in the experimental PDFs.



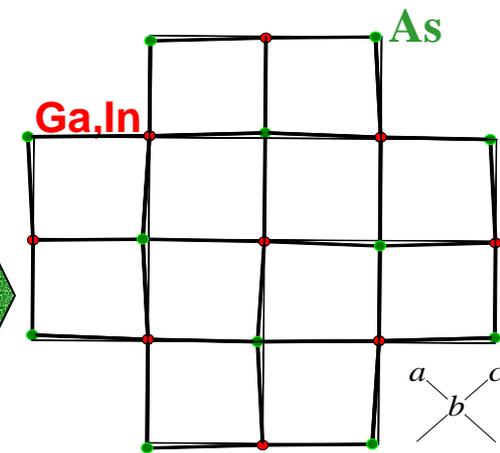
In-Ga-As alloys - average & local crystal structure refinement by a PDF full profile fitting.



The experimental PDFs of the end members can be fit well with a structure model based on the perfect zinc-blende lattice



The experimental PDFs of the alloys can be fit only if both As and metal (In,Ga) atoms are allowed to be statically displaced from their positions in the ideal zinc-blende lattice.

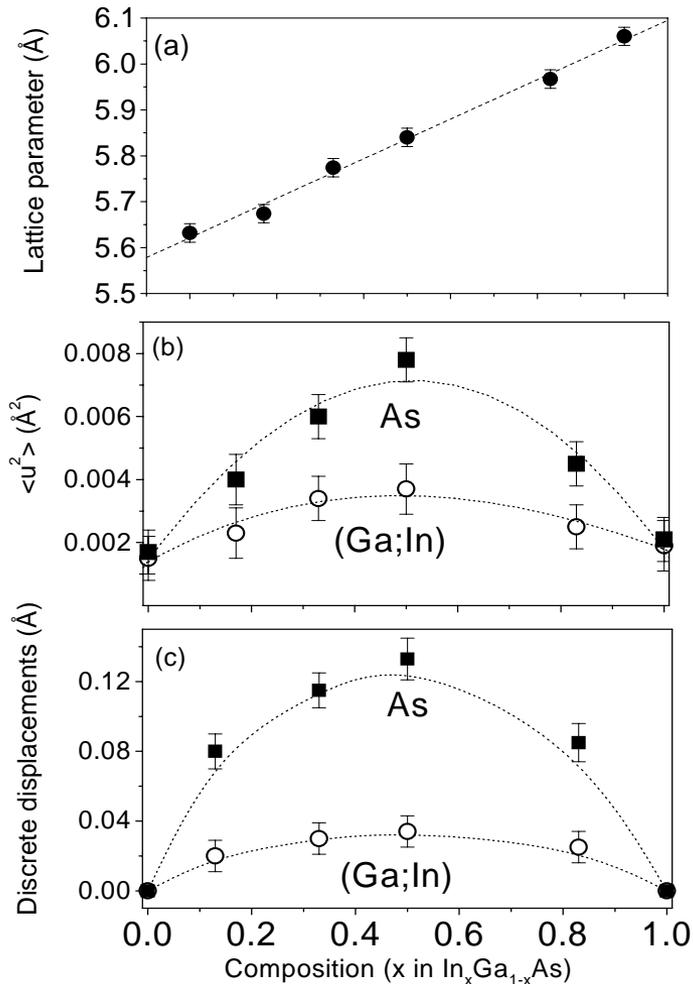


Exp. Data - symbols
Fits - red line

Schematics of the discrete atomic displacements in In-Ga-As alloys. The ideal lattice (thin line) can be compared with the distorted lattice (thick line).

Here is **how** the zinc-blende lattice distorts locally to accommodate the two distinct Ga-As and In-As bonds present of In-Ga-As alloys.

Petkov and Billinge, J. Phys.: Cond. Matter (2001)



The average structure preserves its cubic symmetry

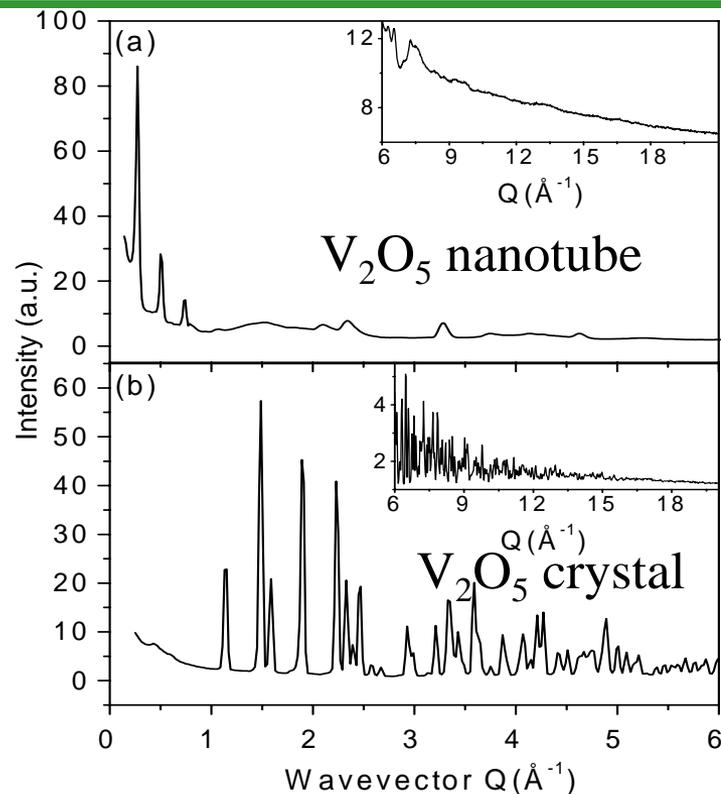
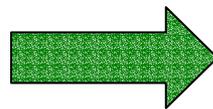
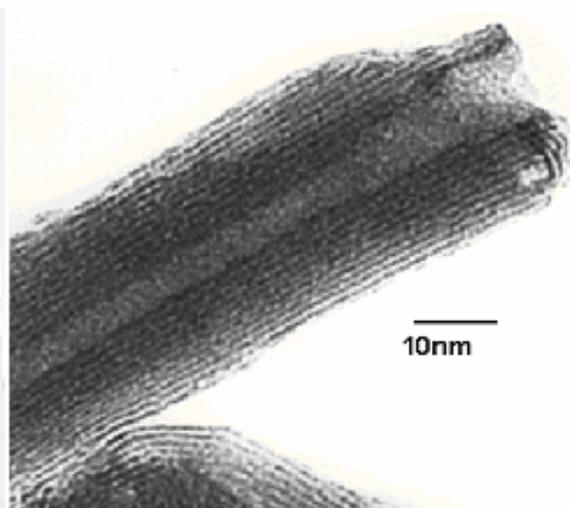
The rms deviations (effective thermal factors) of both As and metal (In,Ga) atoms increase

Both As and metal (In,Ga) atoms are displaced from their positions in the ideal zinc-blende lattice.

The lattice distortions are more pronounced on the As than on the metal (In,Ga) sites.

Results from the crystal structure refinements based on the experimental PDFs

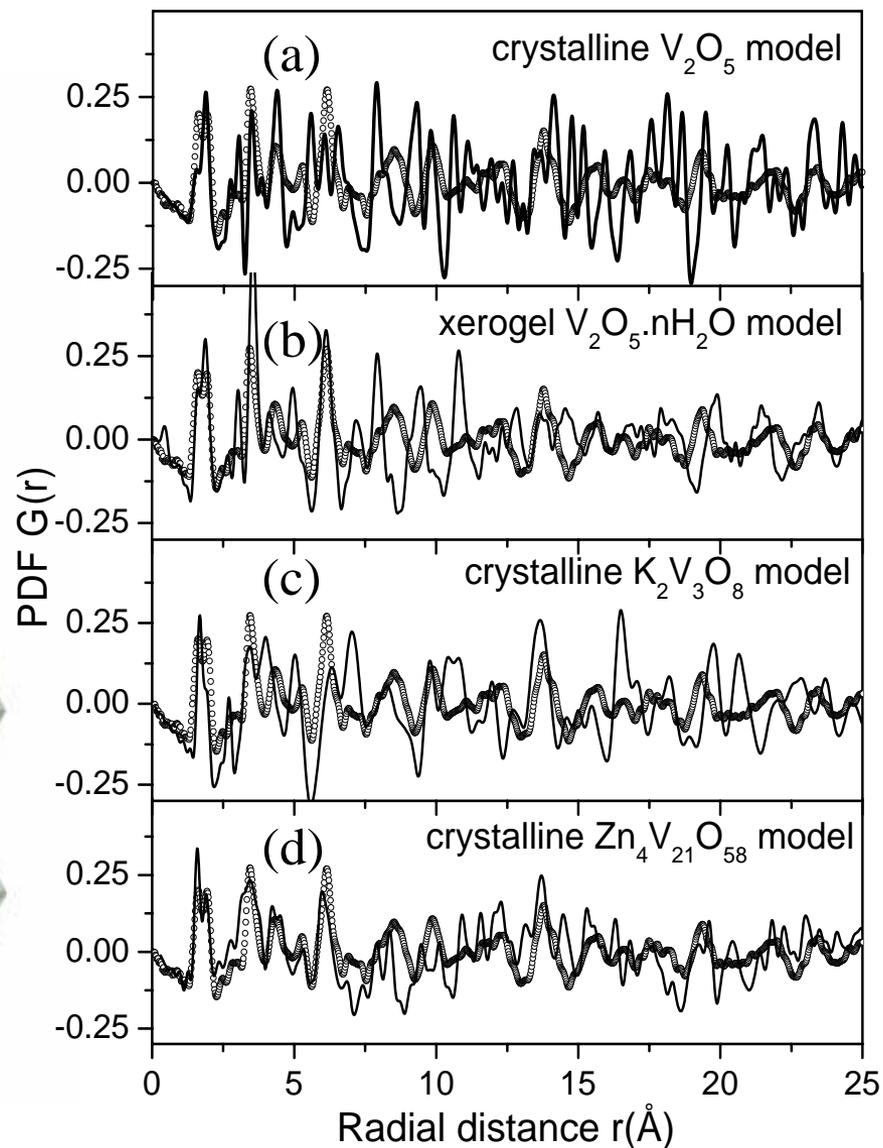
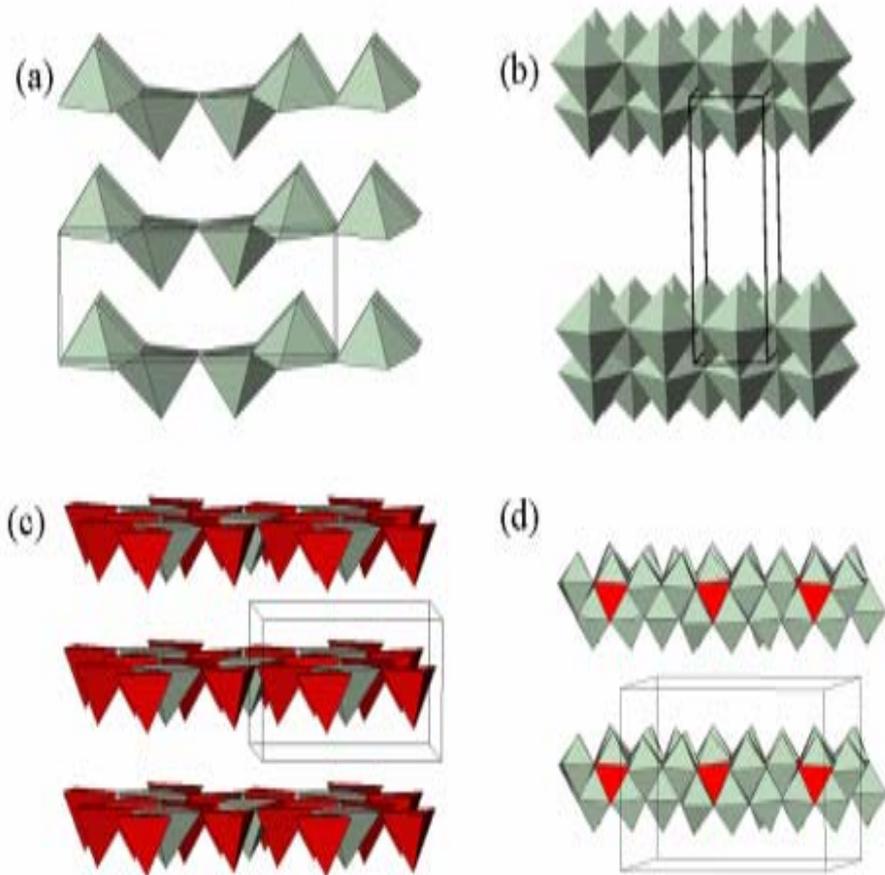
Structure study on V_2O_5 nanotubes



Crystalline V_2O_5 is widely used in application as chemical sensors, catalysts and solid state batteries. The material possesses an outstanding structural versatility and can be manufactured into nanotubes that have many of the useful properties of the parent crystal significantly enhanced.

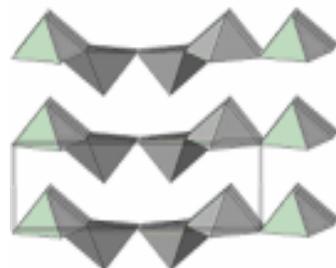
The lack of long range order due to the curvature of the tube walls has a profound effect on the diffraction patterns. That of the crystal shows sharp Bragg peaks. The diffraction pattern of the nanotubes has a pronounced diffuse component rendering the traditional techniques for structure determination impossible.

V_2O_5 nanotubes - search for a structure model

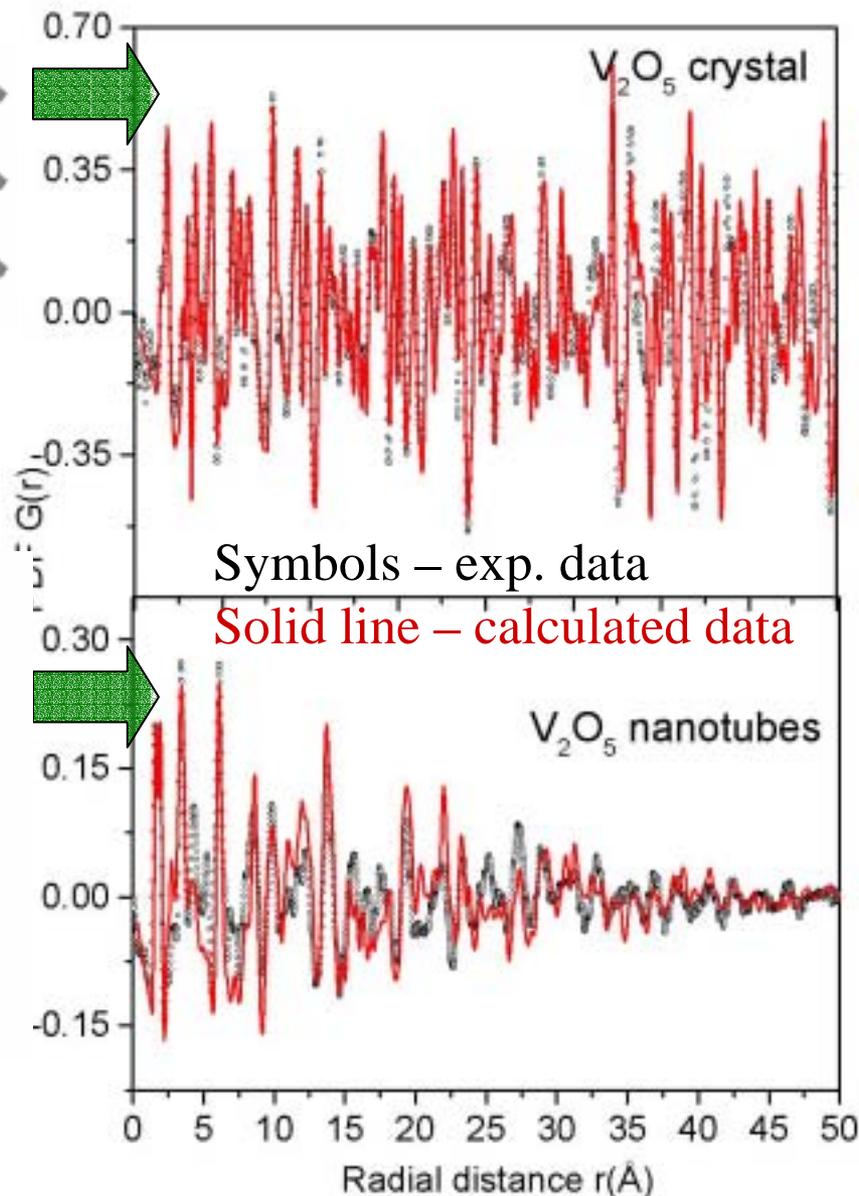
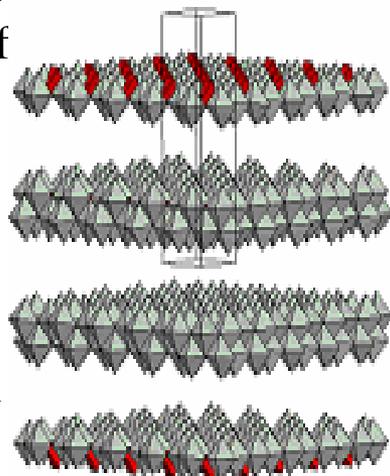


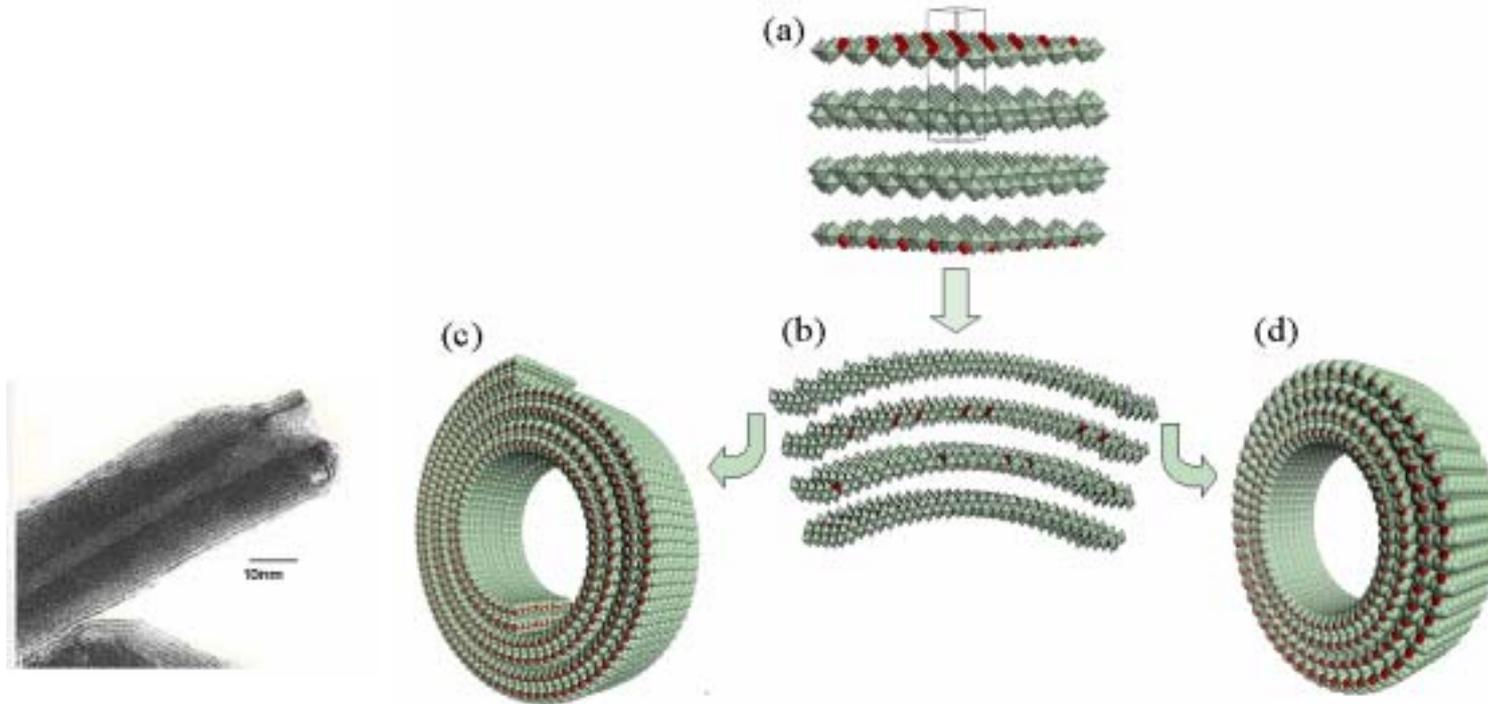
Exp. Data – symbols
Model data – solid line

The well known 16-atom unit cell of crystalline V_2O_5 (S.G. $Pm\bar{m}n$) fits the experimental data well. The agreement documents the fact the atomic PDF provides a reliable basis for structure determination.



Best fit to the experimental PDF data for the nanotube was achieved on a basis of a 46-atom unit cell (S.G. $P\bar{1}$). Even a nanocrystal with the complex morphology of V_2O_5 nanotubes possesses an atomic structure very well defined on the nanometer length scale and well described in terms of a unit cell and symmetry.



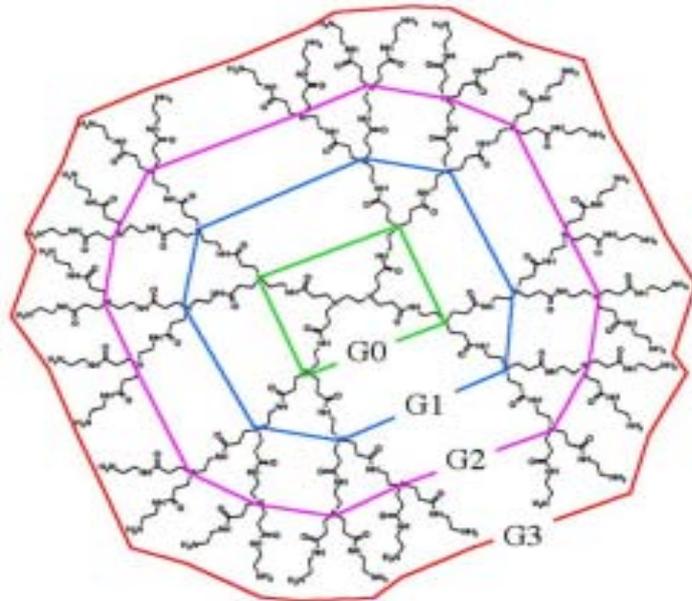
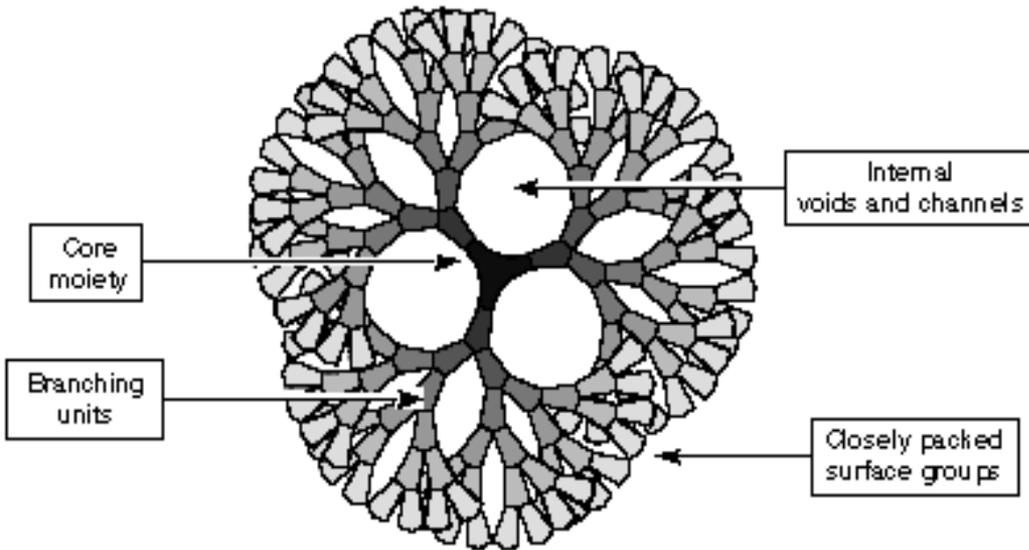


Structure description of V_2O_5 nanotubes: Double layers of $V-O_6$ octahedral (green) and $V-O_4$ tetrahedral (red) units are undistorted and stacked in perfect registry with the crystal (a). When bent (b) such layers may form nanoscrolls (c) or closed nanotubes (d).

Double layers of such complexity may sustain only a limited deformation. As a result, V_2O_5 nanotubes occur with inner diameters not less than 5 nm. The real-size models shown in (c) and (d) have an inner diameter of approx. 10 nm and involve 33,000 atoms. The bending of vanadium oxide layers into nanotubes can be explained by the presence of an anisotropy in the distribution of vanadium 4+ and 5+ ions.

More details in Petkov et al Phys. Rev. B 69 (2004) 085410.

Polymer nanoscience



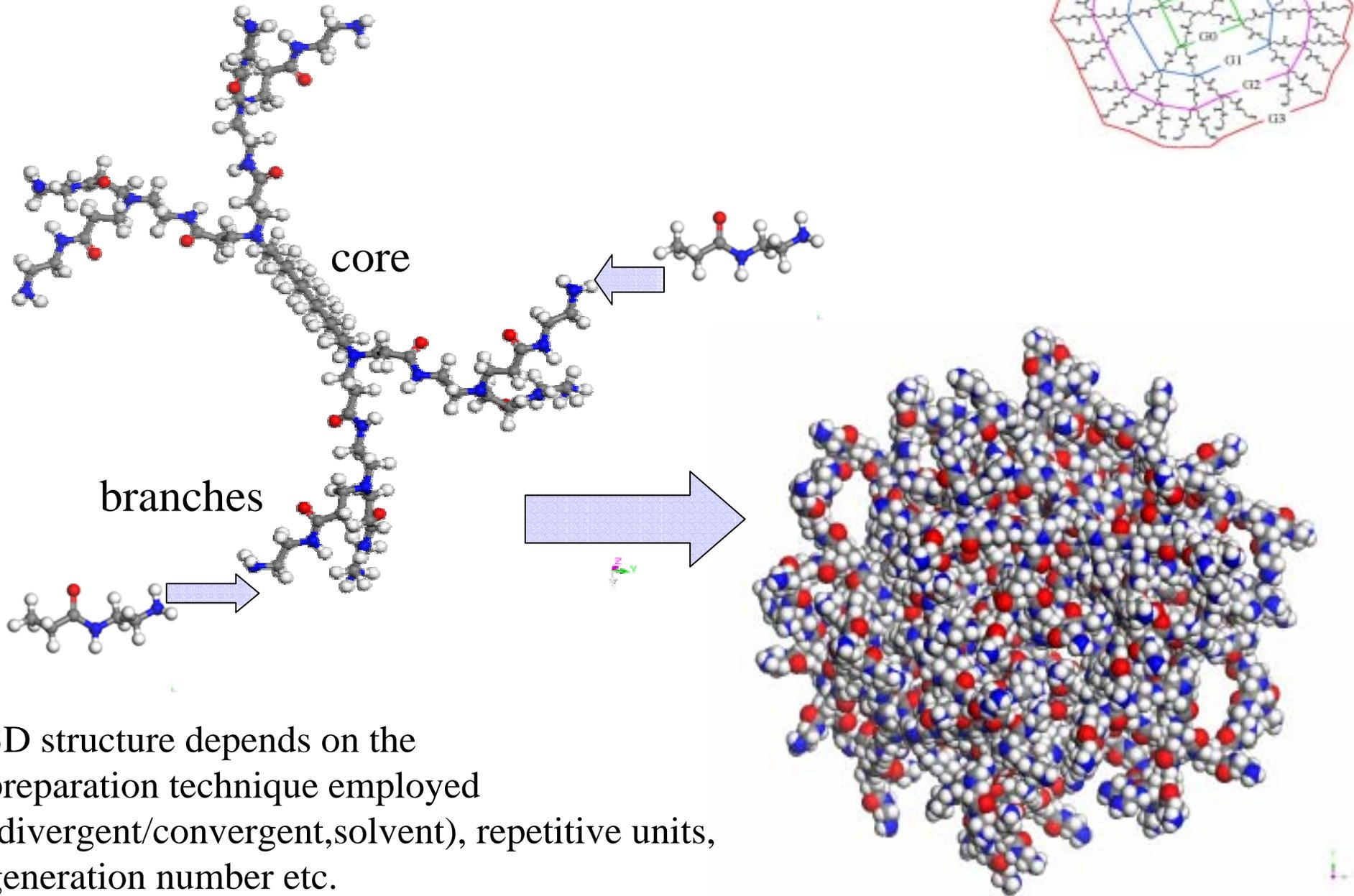
Dendrimers: consist of a series of chemical shells built on a small core molecule. Can be designed with a variety of organic and inorganic cores and branches, with tunable branch length, multiplicity and surface functionality:

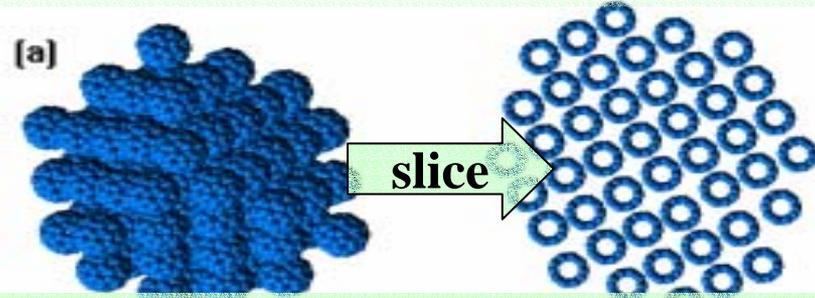
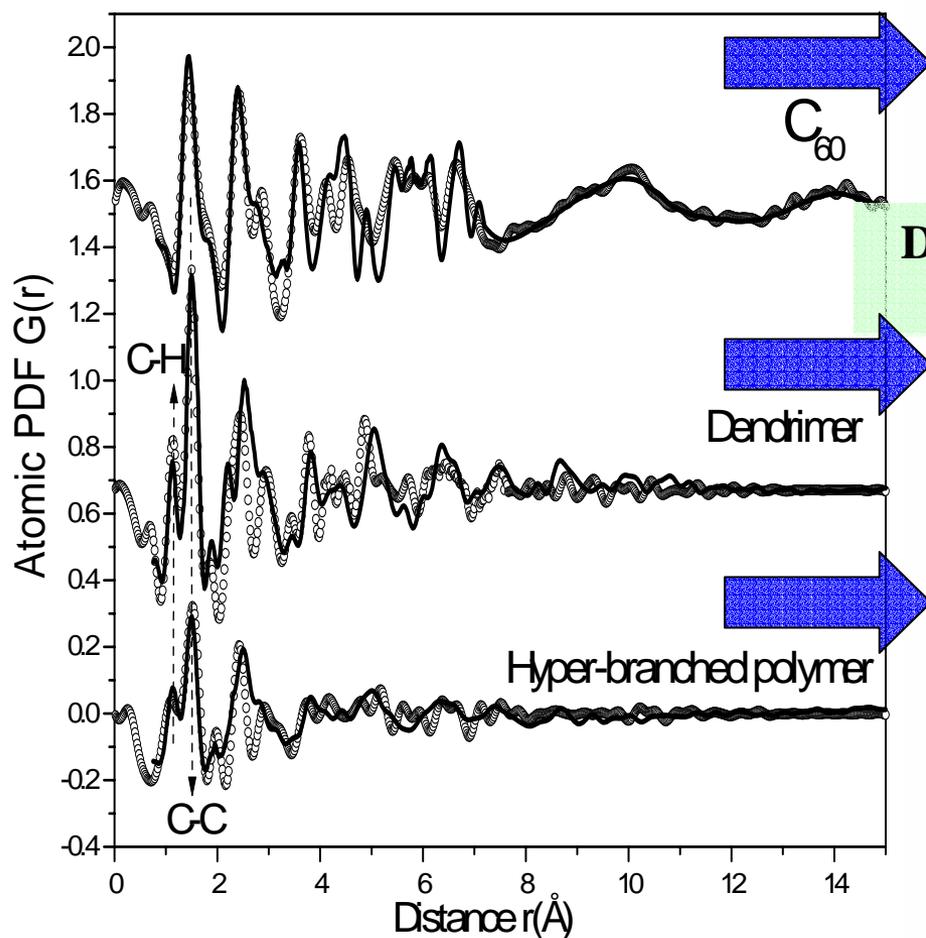
Applications:

Polymer mimics of globular proteins
Building blocks of multifunctional nanocomposites
Hosts of guests molecules and nanoparticles

Questions: Is the interior hollow ?
How big is the free volume, if any ?

Synthesis of PAMAM dendrimers

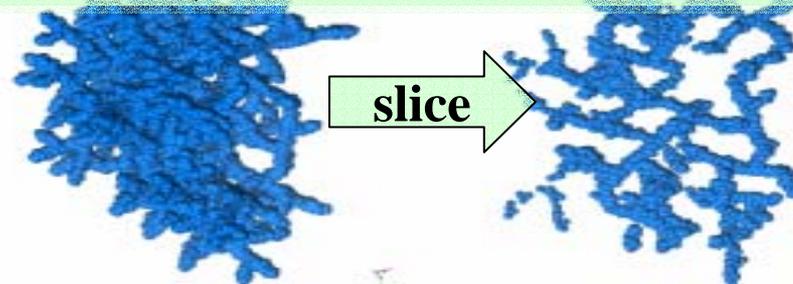




Dendrimers – semi regular network with open interior; narrow distribution of cavities



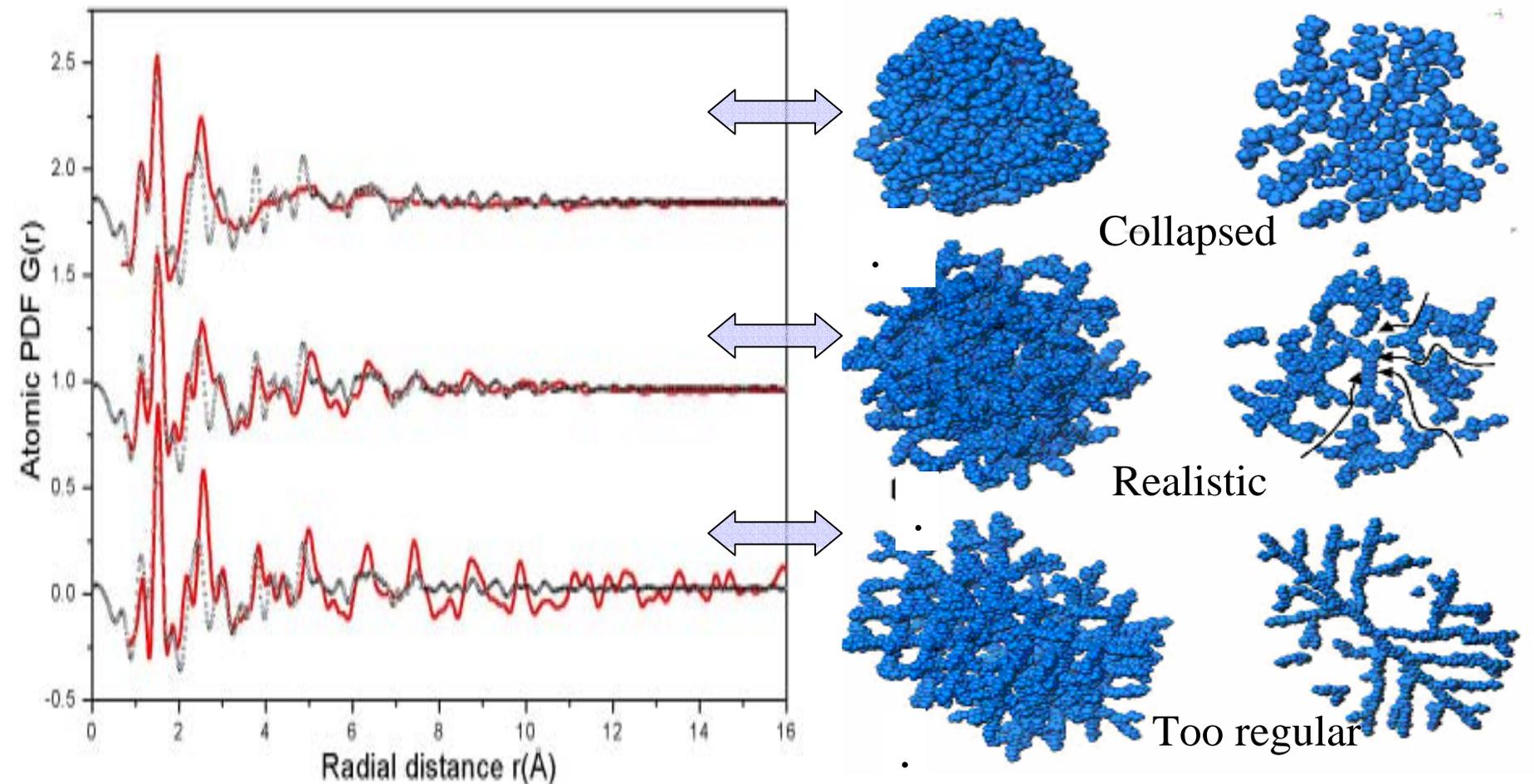
Hyper-branched: less regular but still open network; wide distribution of cavities



Experimental(dots) and model(line) atomic PDFs for fullerene, PAMAM dendrimers and hyper-branched polymers

Fragments of structure models for fullerene, PAMAM dendrimers and hyper-branched polymers

PDF study of dendrimers

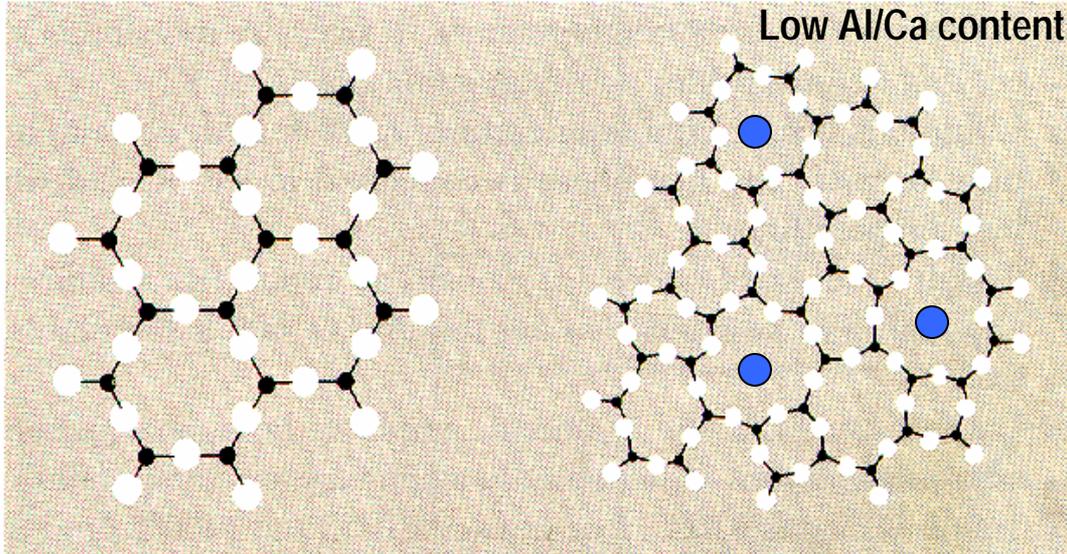


Exp. data – symbols

Model data – **line in red**

3D models of PAMAM dendrimers

What do we know about the atomic ordering in network calcium aluminosilicate glasses ?



$\text{Si}^{4+}\text{-O}$ (tetrahedral) $\sim 1.6 \text{ \AA}$



$\text{Al}^{3+}\text{-O}$ (tetrahedral) $\sim 1.75 \text{ \AA}$

$\text{Al}^{3+}\text{-O}$ (octahedral) $\sim 1.85 \text{ \AA}$

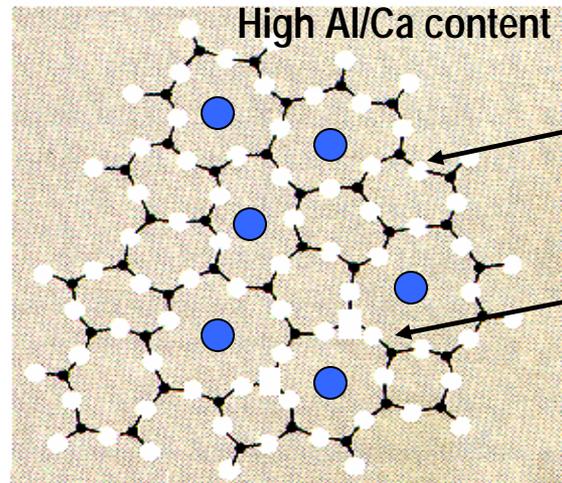
$\text{Ca}^{2+}\text{-O}$ $\sim 2.32 \text{ \AA}$

Questions:

What is Al-O coordination ?

What is Ca-O coordination ?

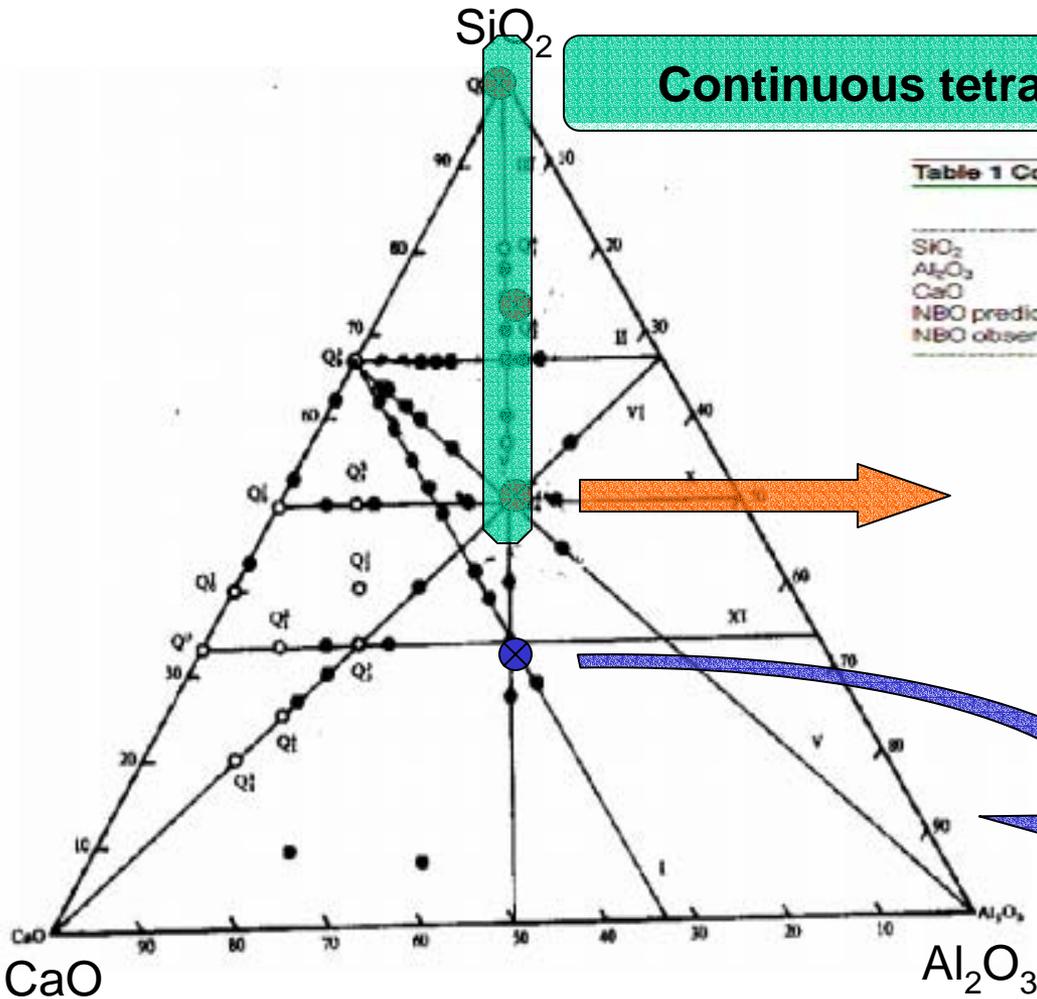
Where are the NBO's ?



Bridging oxygens (BO)

Non-bridging oxygens (NBO)

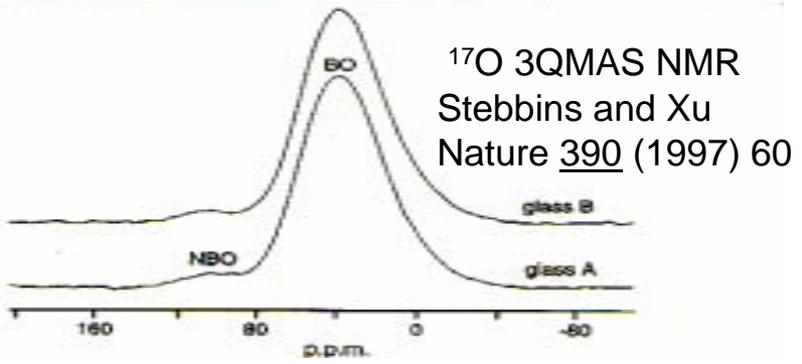
Samples: $\text{Ca}_{x/2}\text{Al}_x\text{Si}_{1-x}\text{O}_2$ glasses ($x=0,0.25,0.5,0.67$)



Continuous tetrahedral network

Table 1 Composition (in mol%) of glass samples similar to $\text{CaAl}_2\text{Si}_2\text{O}_8$

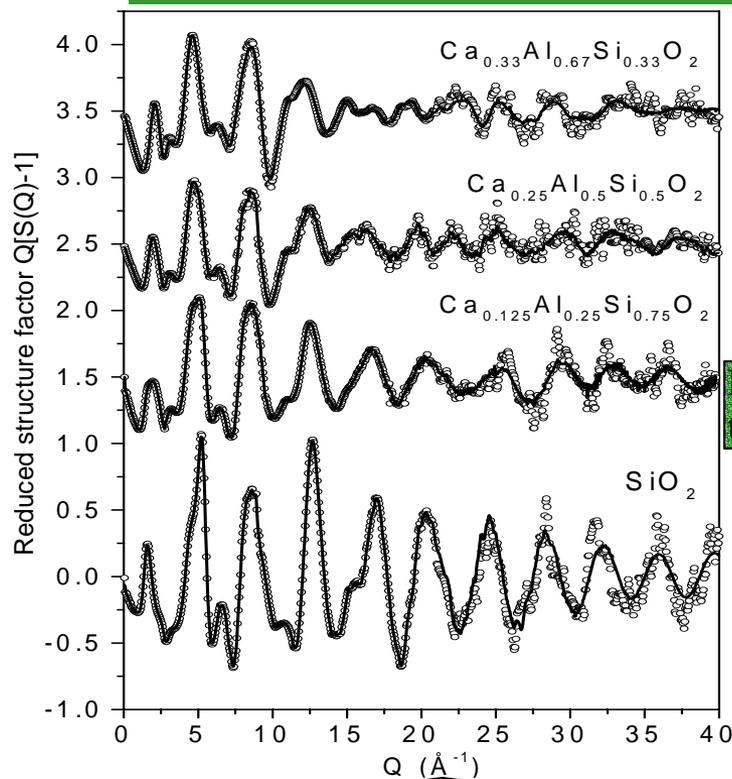
	Glass A	Glass B
SiO_2	49.6 ± 0.1	49.4
Al_2O_3	25.0 ± 0.2	25.2
CaO	25.5 ± 0.1	25.3
NBO predicted	0.5 ± 0.2	0.1
NBO observed	5 ± 1	4



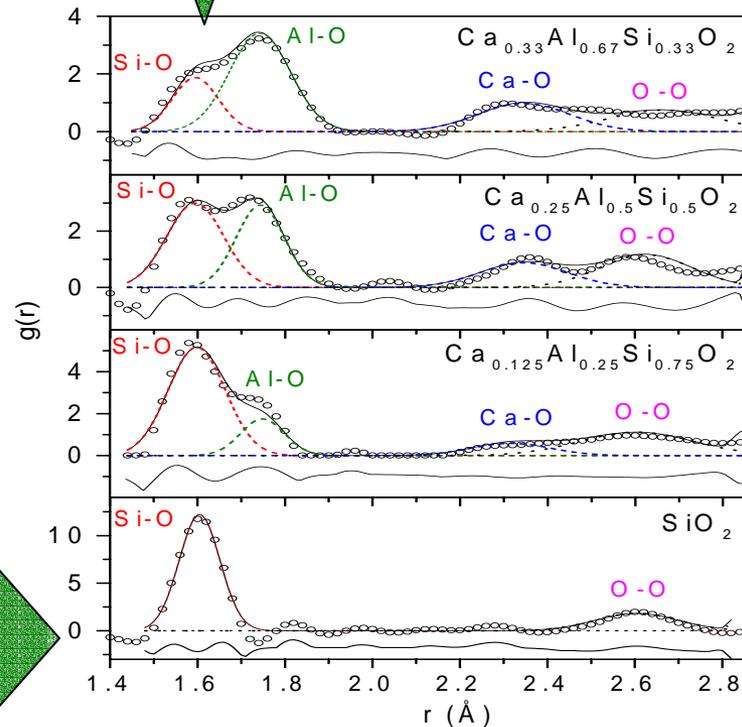
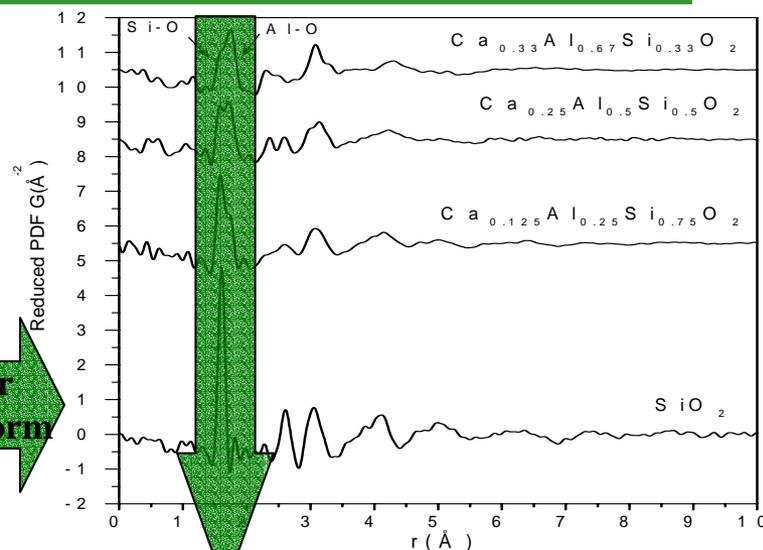
Partially disintegrated tetrahedral network

^{29}Si & ^{27}Al NMR
Engelhardt, Phys. Chem. Glasses 5 (1985) 157

Calcium aluminosilicate glasses. Experimental results:



Fourier transform



Advanced Photon Source,
beamline 1-ID, $E = 80.6 \text{ keV}$

By employing high-energy x-ray diffraction structure factors extended to at least 40 Å^{-1} can be obtained even for materials composed

of weakly scattering, light atomic species. This allows structural features differing in as little as 0.15 Å to be clearly resolved.

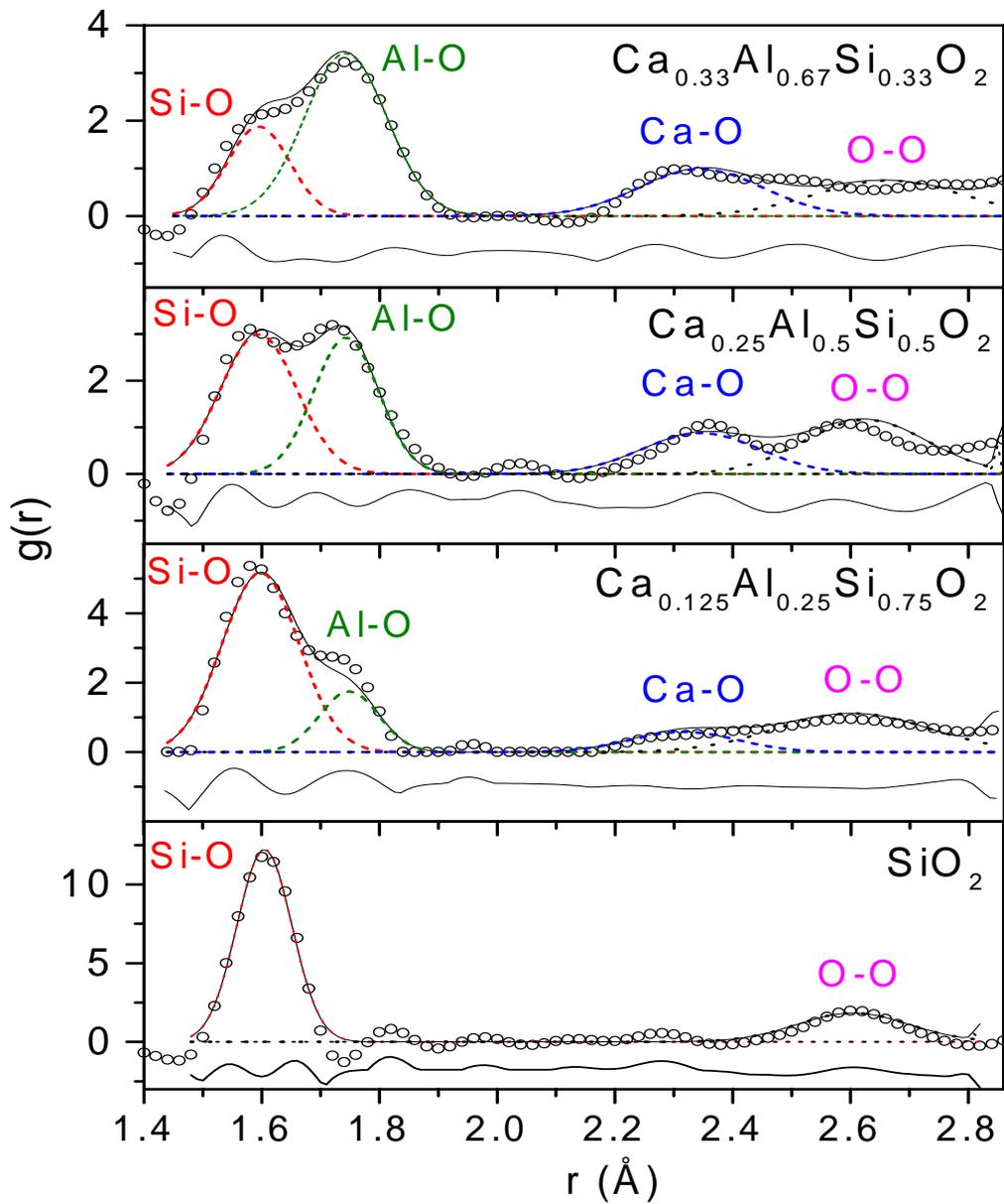
Gaussian fit to the peaks in the experimental PDFs:

Si-O ~ 1.60(1) Å

Al-O ~ 1.75(1) Å

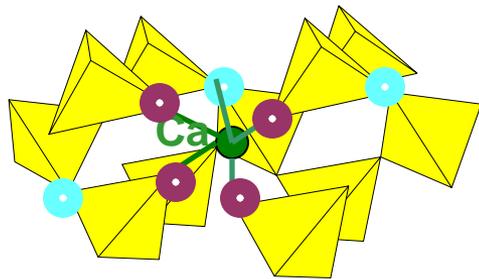
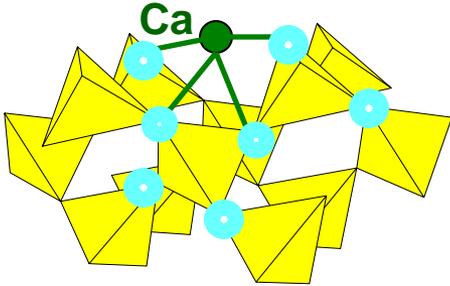
Ca-O ~ 2.35(1) Å

O-O ~ $\sqrt{8/3}(\text{Si,Al})\text{-O}$
2.61- 2.85 Å



Coordination polyhedra and connectivity in $\text{Ca}_{x/2}\text{Al}_x\text{Si}_{1-x}\text{O}_2$ glasses. Answers:

Continuous network ($x=0,0.25$):
Only **BO's** are present and the *average* coordination numbers of both Si and Al are 4.



Disrupted network ($x=0.5,0.67$):
Both **BO's** and **NBO's** are present. The emerging of NBO's effectively removes Si-O bonds and the *average* Si-O coordination number drops below 4 without necessarily creating oxygen vacancies.

First neighbour Si-O, Al-O, Ca-O and O-O **distances** and **average coordination numbers** in $\text{Ca}_{x/2}\text{Al}_x\text{Si}_{1-x}\text{O}_2$ glasses ($x=0,0.25,0.5,0.67$) obtained by a Gaussian fit to the corresponding high-resolution PDFs, $g(r) = \rho(r)/\rho_0$.

x	Si-O	Al-O	Ca-O
0	1.61(1) Å / 4.0(1)		
0.25	1.60(1) Å / 3.95(10)	1.75(1) Å / 3.95(10)	2.32(2) Å / 5.3(2)
0.5	1.60(1) Å / 3.85(10)	1.75(1) Å / 4.0(1)	2.36(2) Å / 5.2(2)
0.67	1.60(1) Å / 3.2(1)	1.75(1) Å / 3.95(10)	2.34(2) Å / 5.3(2)

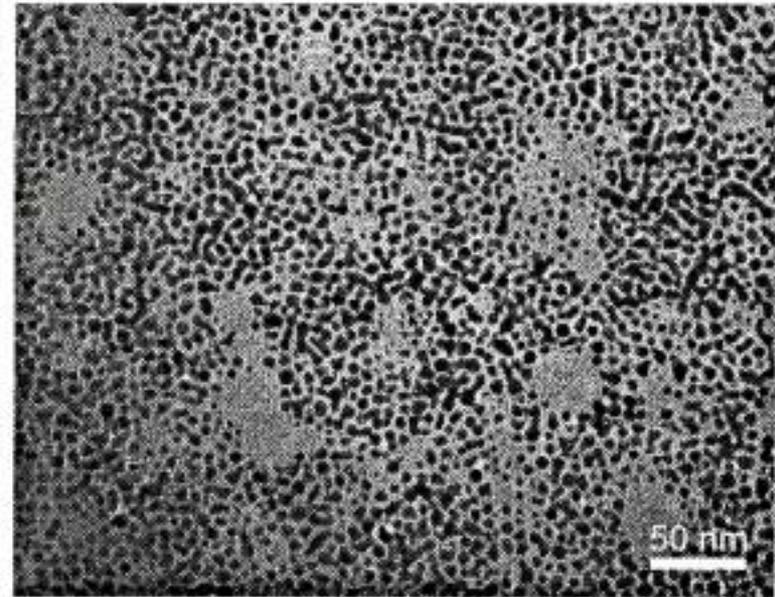
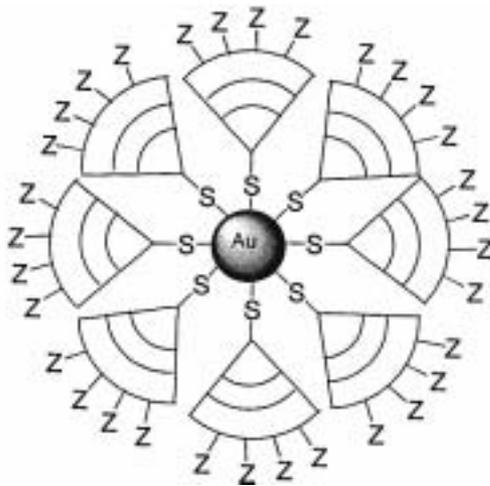
x	Si-O	Al-O	Ca-O
0	tetrahedral / BO's		
0.25	tetrahedral / BO's	tetrahedra / BO's	well defined unit
0.5	tetrahedral / BO's+NBO's	tetrahedral / BO's	well defined unit
0.67	tetrahedral / BO's+NBO's	tetrahedral / BO's	well defined unit

i) $\text{Ca}_{x/2}\text{Al}_x\text{Si}_{1-x}\text{O}_2$ glasses are built up of interconnected Si-O and Al-O tetrahedra with the degree of their connectivity decreasing with increasing x.

ii) the breaking of the network proceeds via the creation of **NBO's** located on Si-O but not Al-O tetrahedra.

iii) Even when two strong network-formers such as Si and Al as well as **NBO's** are present the network-modifier Ca acquires a well-defined and constant coordination sphere and so it is very likely to play a role in the formation of the glass structure.

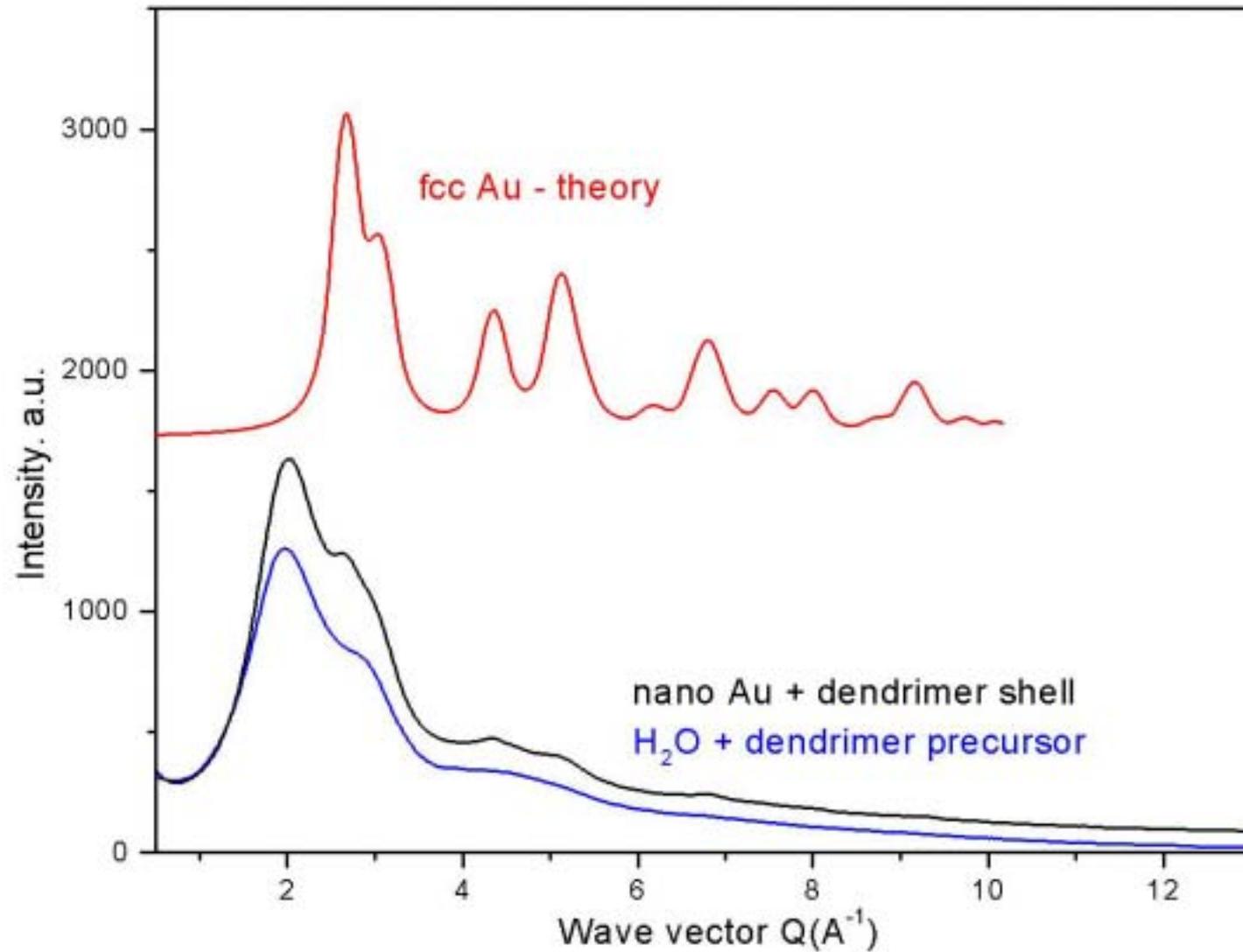
Structure study of dendrimer stabilized Au nanoparticles



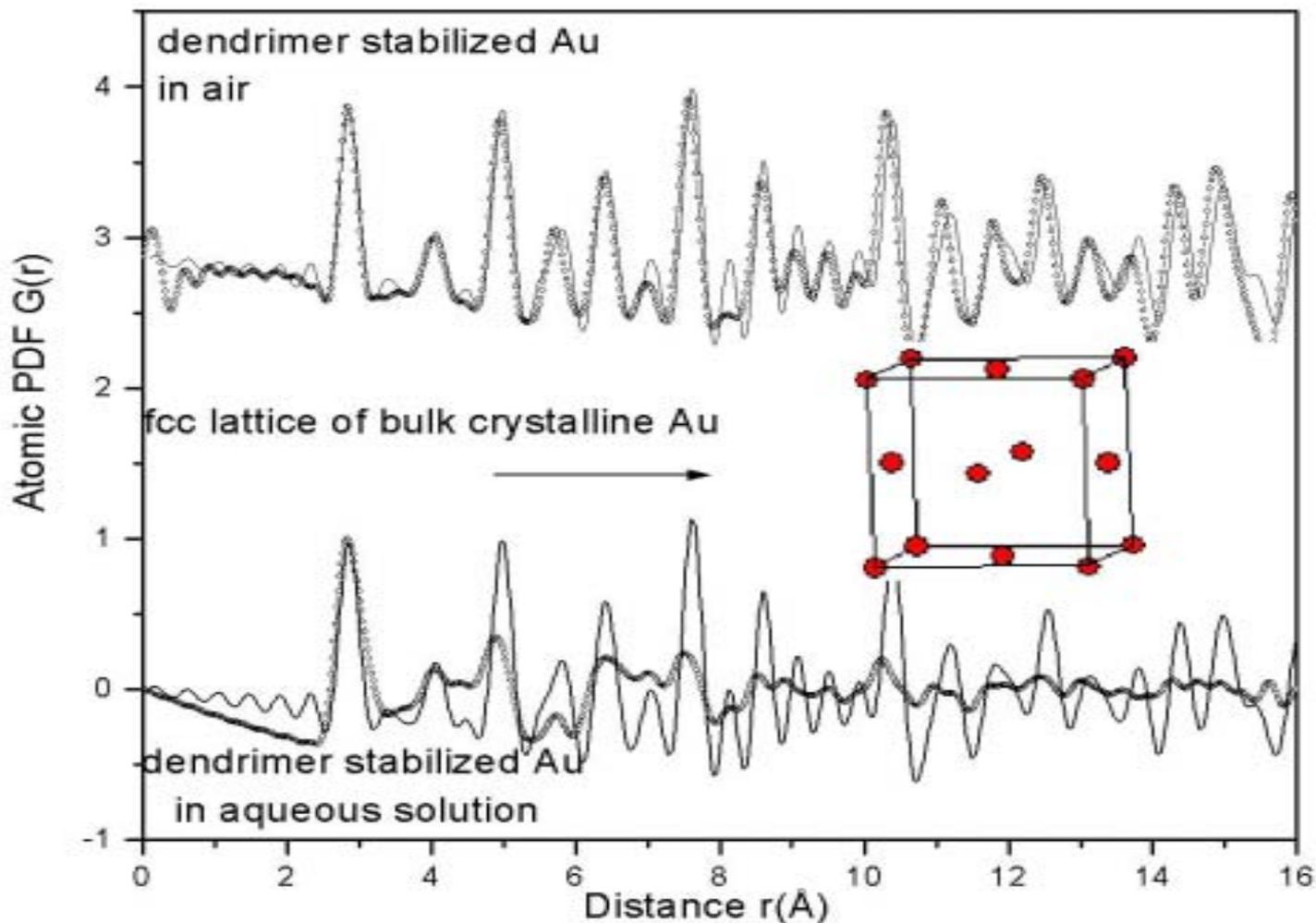
TEM image of Au nanoparticles in water

Collaboration with DNT

Structure study of dendrimer stabilized Au nanoparticles



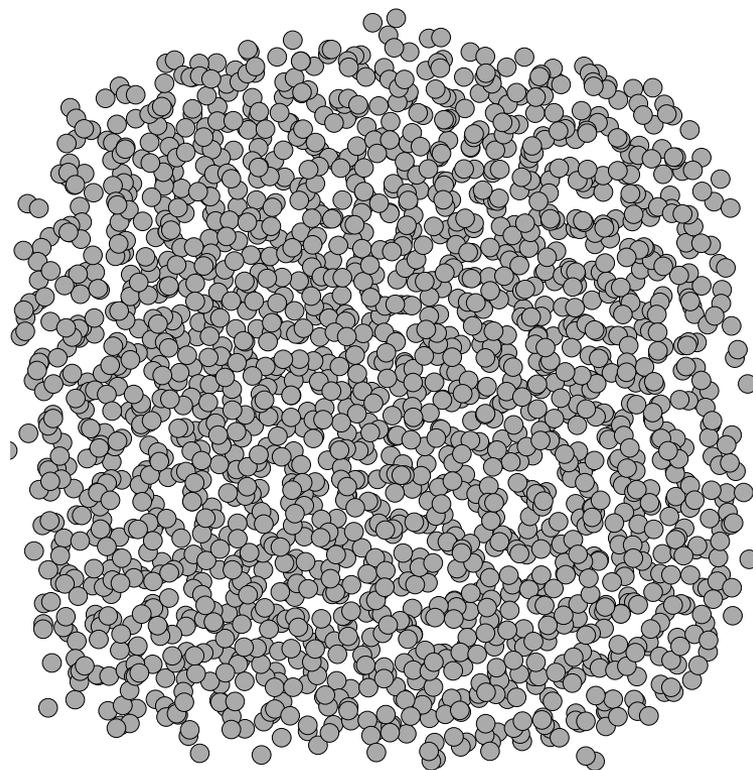
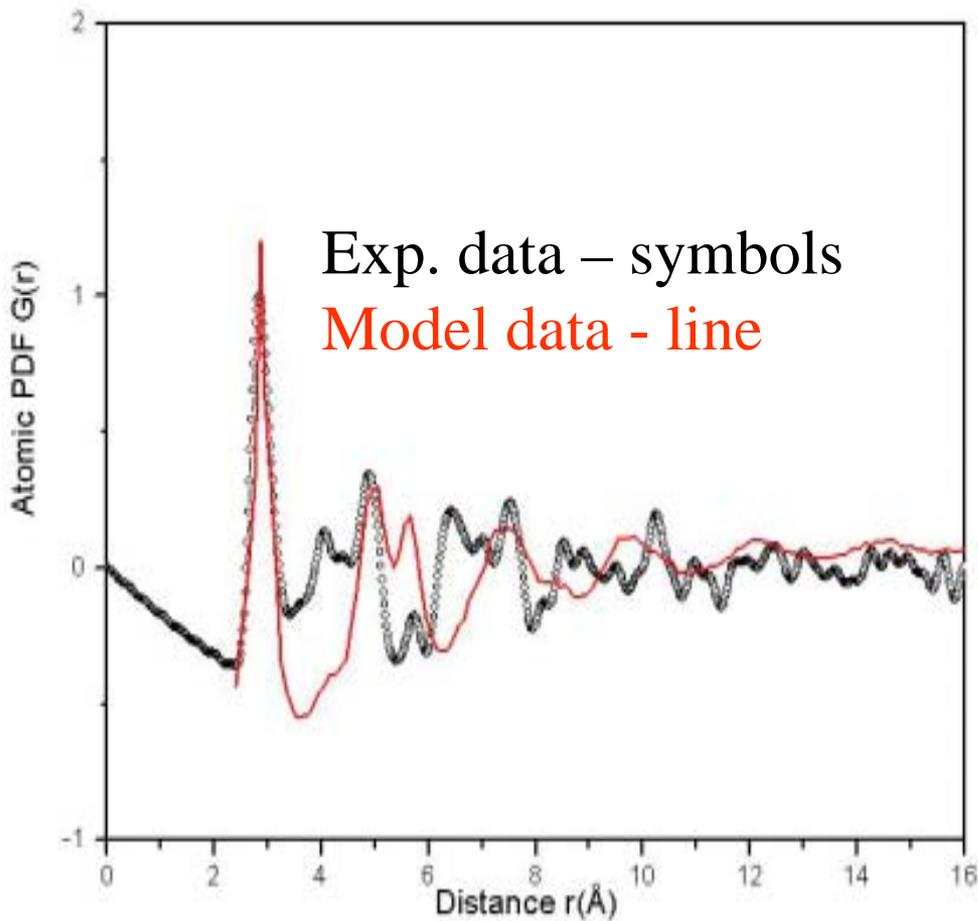
Structure study of dendrimer stabilized Au nanoparticles



Exp. data – symbols

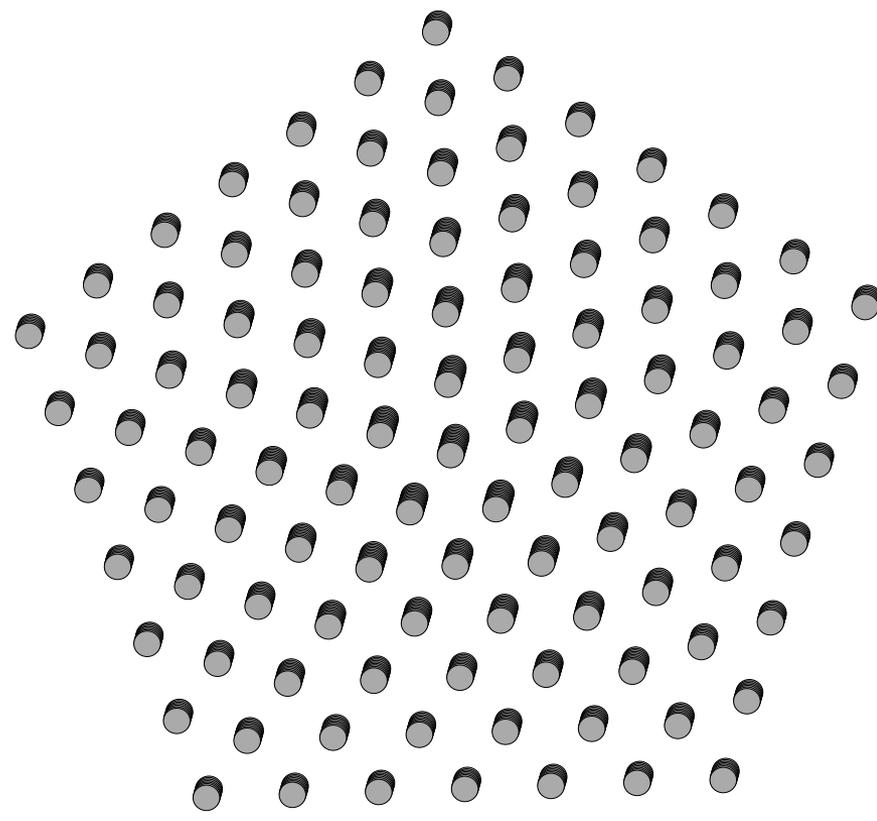
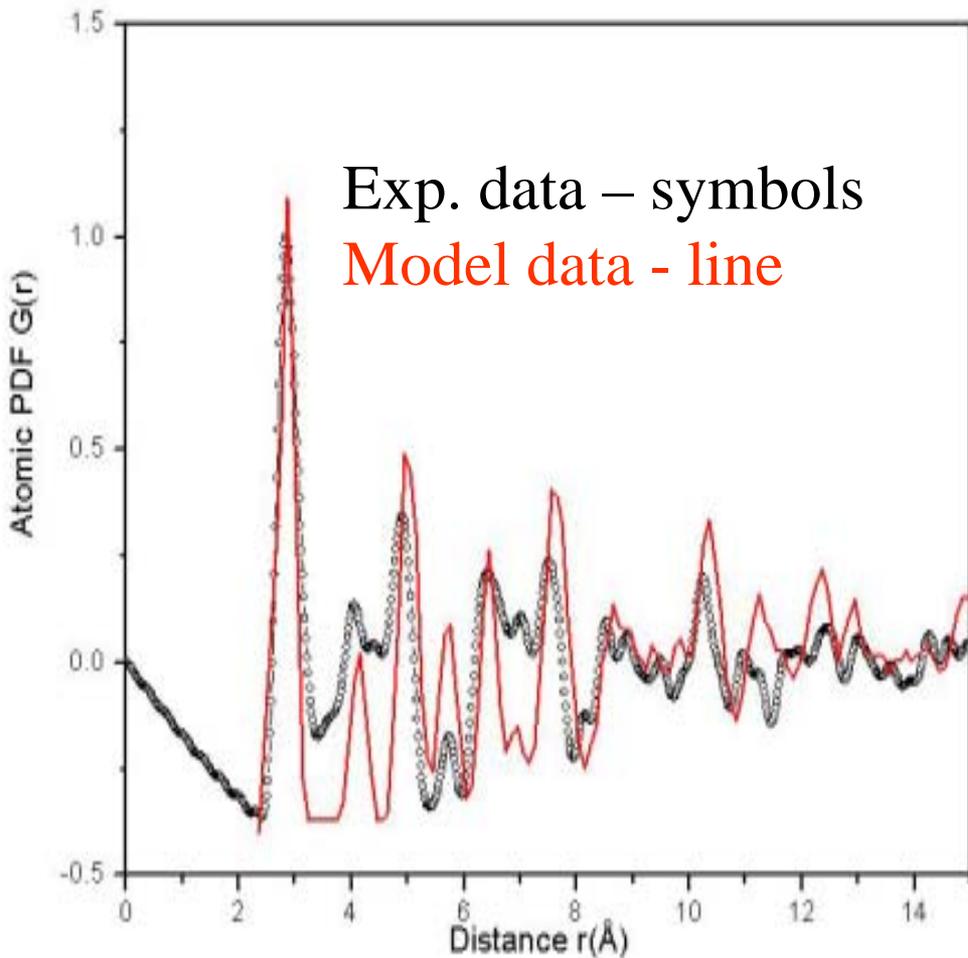
Model data for fcc Au –solid line

Structure study of dendrimer stabilized Au nanoparticles



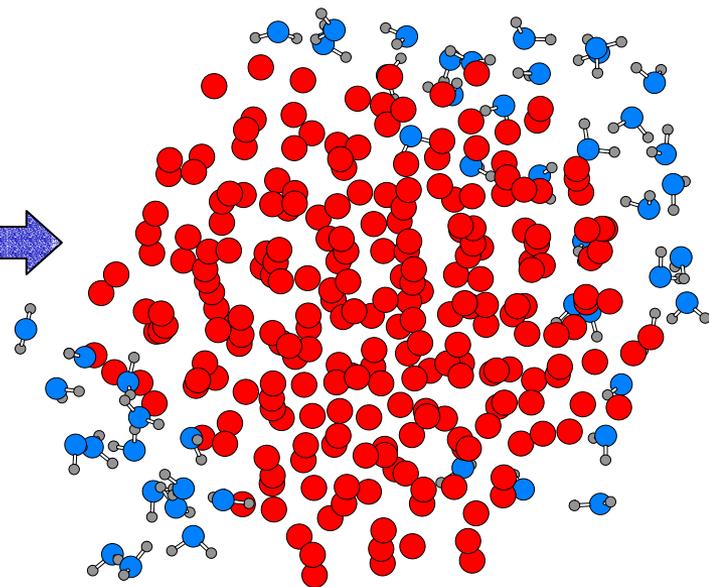
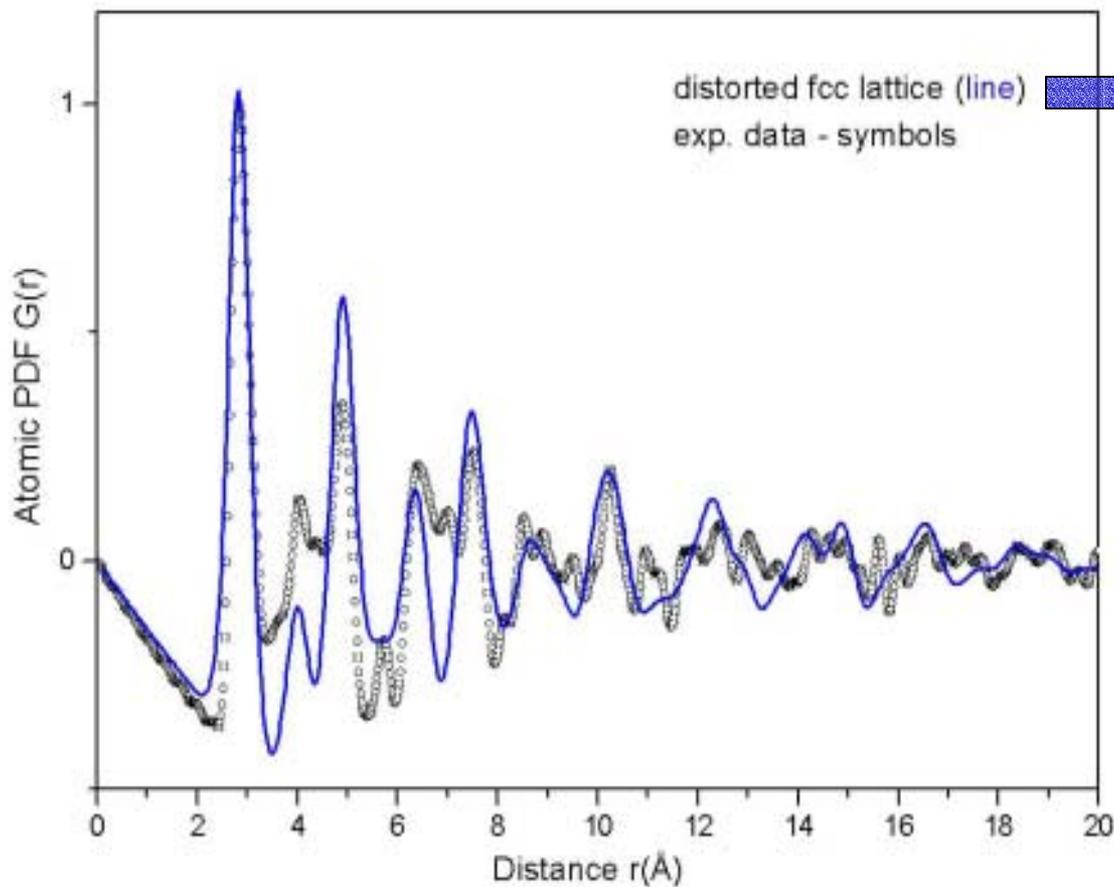
Random model - 5,000 atoms

Structure study of dendrimer stabilized Au nanoparticles



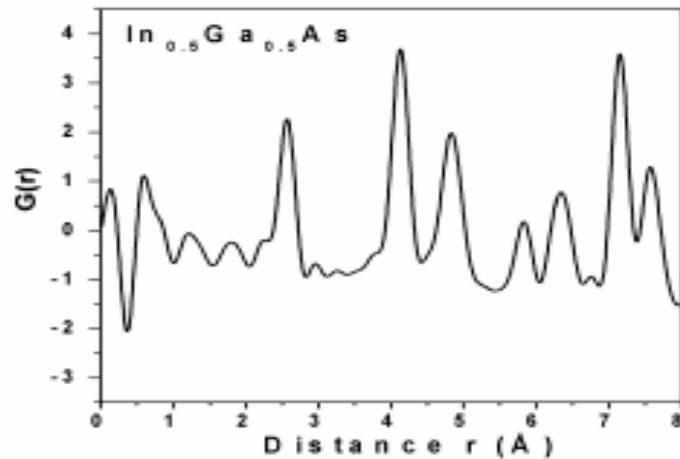
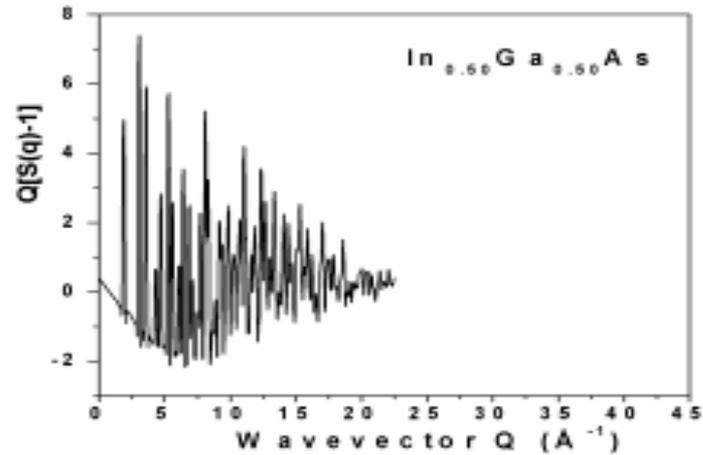
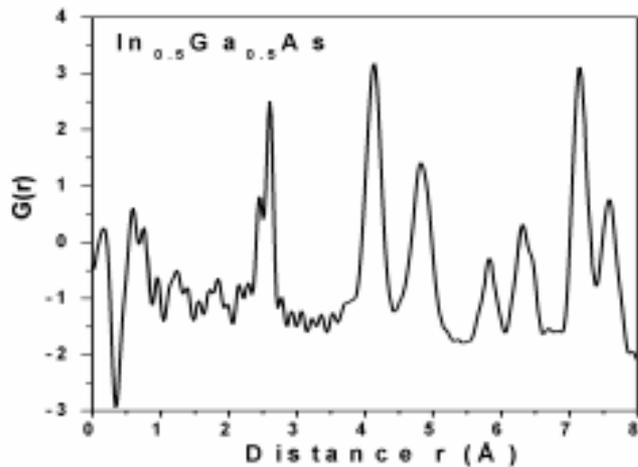
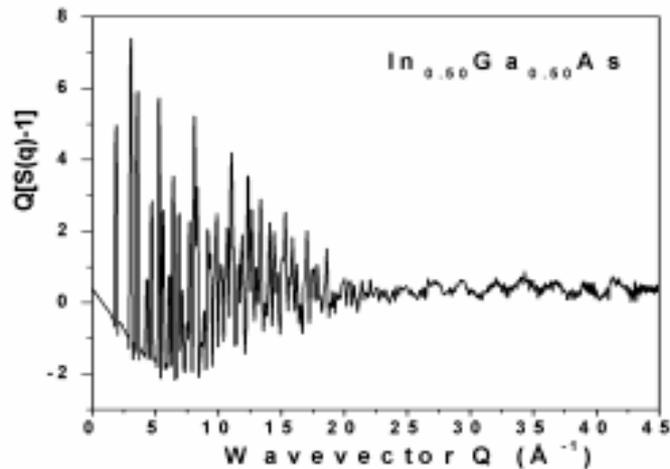
Non-crystallographic
cluster model

Structure study of dendrimer stabilized Au nanoparticles



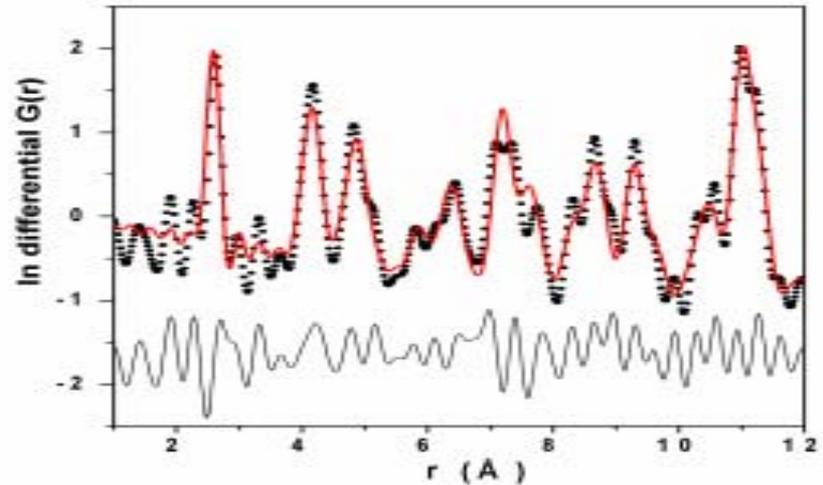
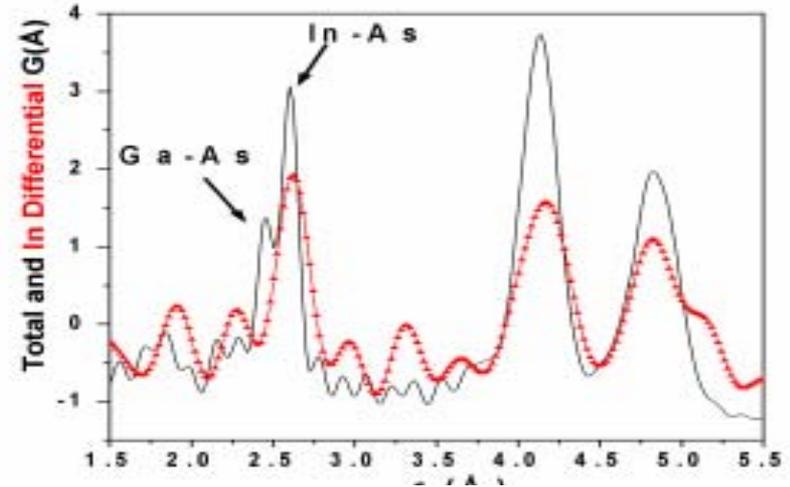
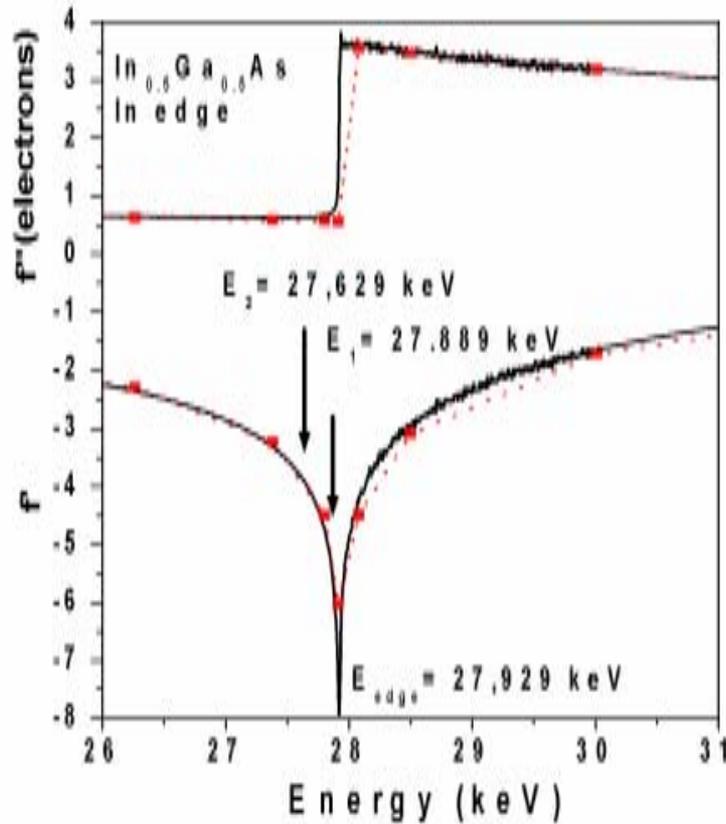
Distorted fcc lattice
~ 300 atoms

High energy/high-Q = High real space resolution



High energy resolution = high sensitivity to chemical species

NLS, X7A



Petkov et al., J. Appl. Phys. 88 (2000) 665

Good Q-space resolution = increased sensitivity to longer-range correlations

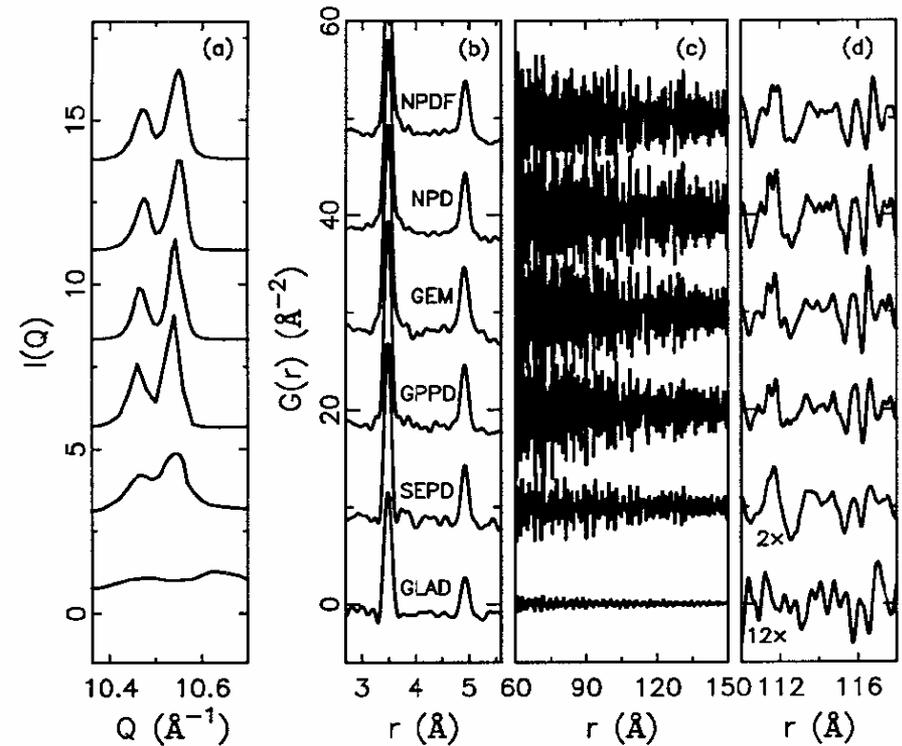
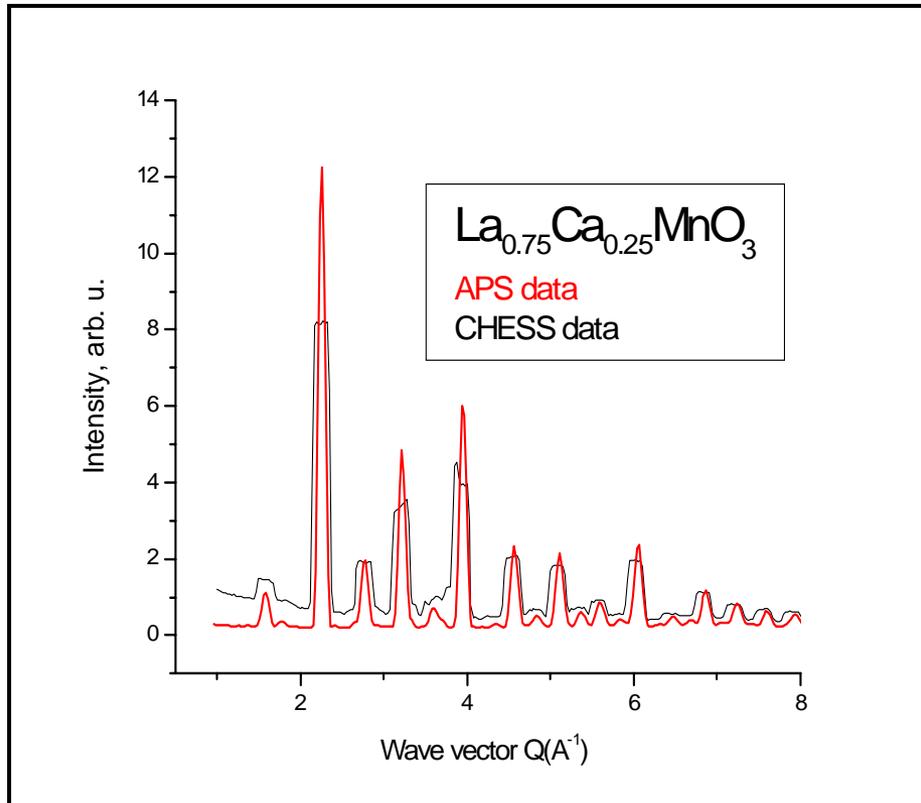
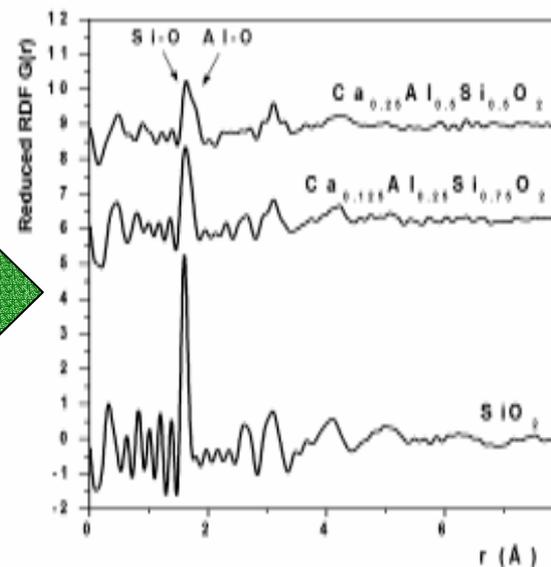
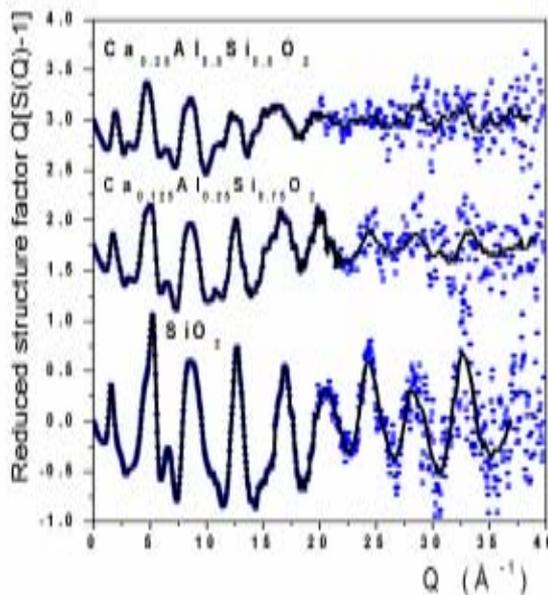


Figure 3

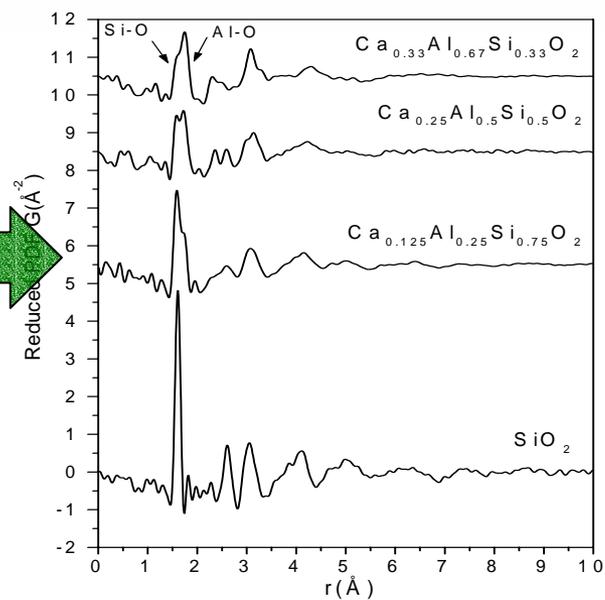
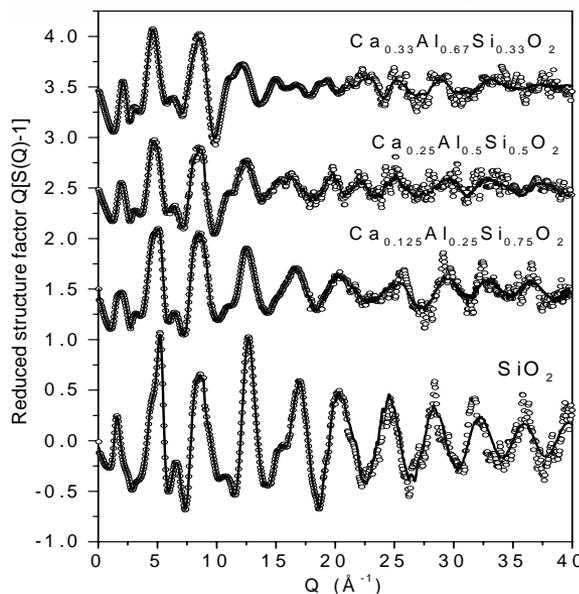
Experimental data shown in all frames are ordered as NPDP, NPD, GEM, PPD, SEPD and GLAD (from top to bottom). GLAD data have Q_{\max} of 32.0 \AA^{-1} , while the others have Q_{\max} of 38.0 \AA^{-1} . (a) A doublet near $Q = 10.50 \text{ \AA}^{-1}$ taken from the diffraction pattern of Pb. (b) Low- r region of experimental Pb PDFs where the differences are very small. (c) High- r region of the experimental Pb PDFs where the differences are rather significant. (d) A focused region of the experimental Pb PDFs. Note that SEPD and GLAD data are amplified by 2 and 12, respectively.

High flux = good statistical accuracy

1-BM, 16h
Bending magnet

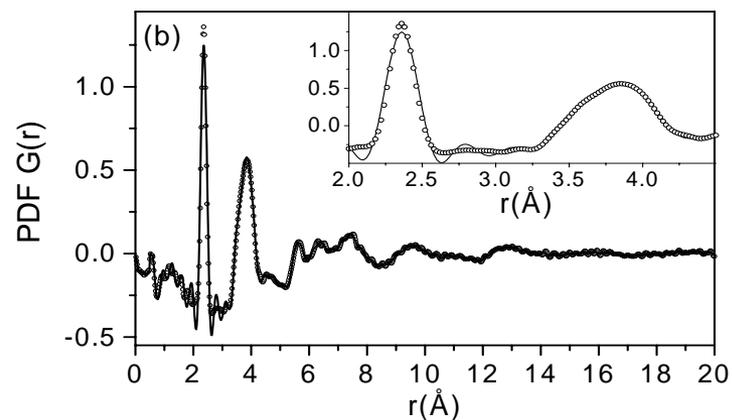
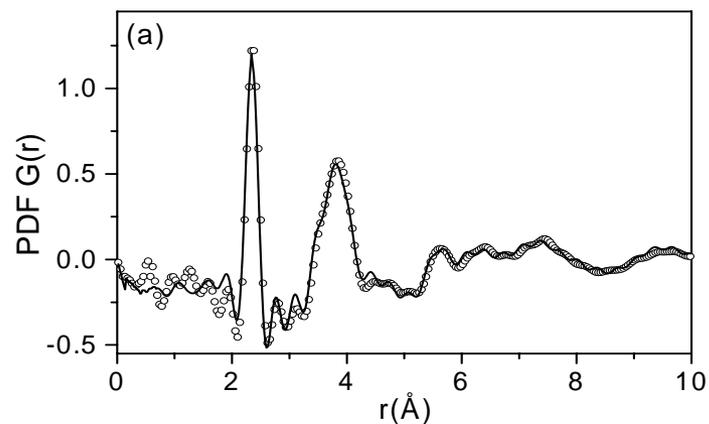
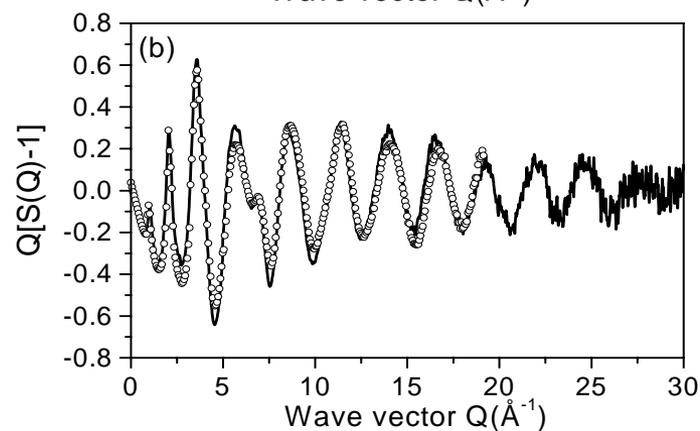
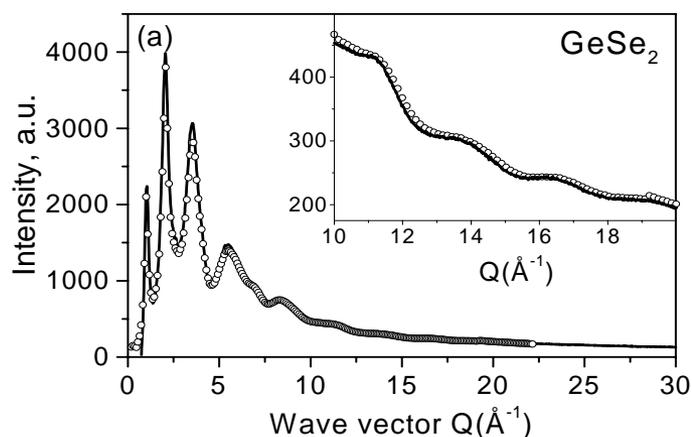
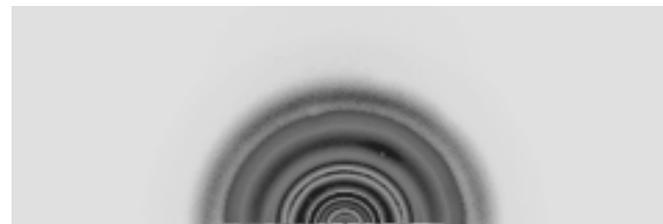


1-ID, 10 h
Undulator



Extended area/fast detectors = fast experiments

Image plates: exposure time – 1 sec.
Point (Ge SSD) detector – 10 hours



Conclusions:

High energy x-ray diffraction and the atomic PDF technique can be confidently employed in structure studies of materials with intrinsic disorder. Key to the success of the approach is that all components of the diffraction data are collected over a wide range of wave vectors and converted into an atomic PDF. Then the 3-D structure is inferred through modeling. The approach can be applied to materials showing any degree of structural coherence. It works with low-Z materials, offers high spatial resolution (~ 0.1 Å) and chemical specificity.

Needs: dedicated instruments and improved software for data reduction and modeling

<http://www.phy.cmich.edu/people/petkov/software.html>

<http://www.phy.cmich.edu/people/petkov/nano.html>

<http://www.pa.msu.edu/cmp/billinge-group/programs/discus/pdfit.html>