Atomic-scale structure of nanosized objects (nanoparticles)

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Mount Pleasant, Michigan

From Wikipedia, the free encyclopedia

Mount Pleasant is a city that serves as the county seat of Isabella County[6] in the U.S. state of Michigan. As of the 2000 census, the city population was 25,946.

Part of the city (with a population of 8,741) is on the Isabella Indian Reservation, site of the Soaring Eagle Casino. The city is also home to the main campus of Central Michigan University. Former Michigan governor John Engler was born in Mount Pleasant.

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4 Local media
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Geography [edit]

According to the United States Census Bureau, the city has a total area of 20.2 km² (7.8 mi²), all land. The Chippewa River runs through the city. Mount Pleasant is located approximately 61 miles north of Lansing, Michigan's state capital, along US 127.

Demographics [edit]

As of the census² of 2000, there were 25,946 people, 8,449 households, and 3,126 families residing in the city. The population density was 1,284.3/km² (3,327.2/mi²). There were 8,878 housing units at an average density of 439.5/km² (1,138.5/mi²). The racial makeup of the city was 89.12% White, 3.67% African American, 1.54% Native American, 2.85% Asian, 0.07% Pacific Islander, 0.93% from other races, and 1.83% from two or more races. Hispanic or Latino of any race were 2.49% of the population.

Mount Pleasant, Michigan

Seal

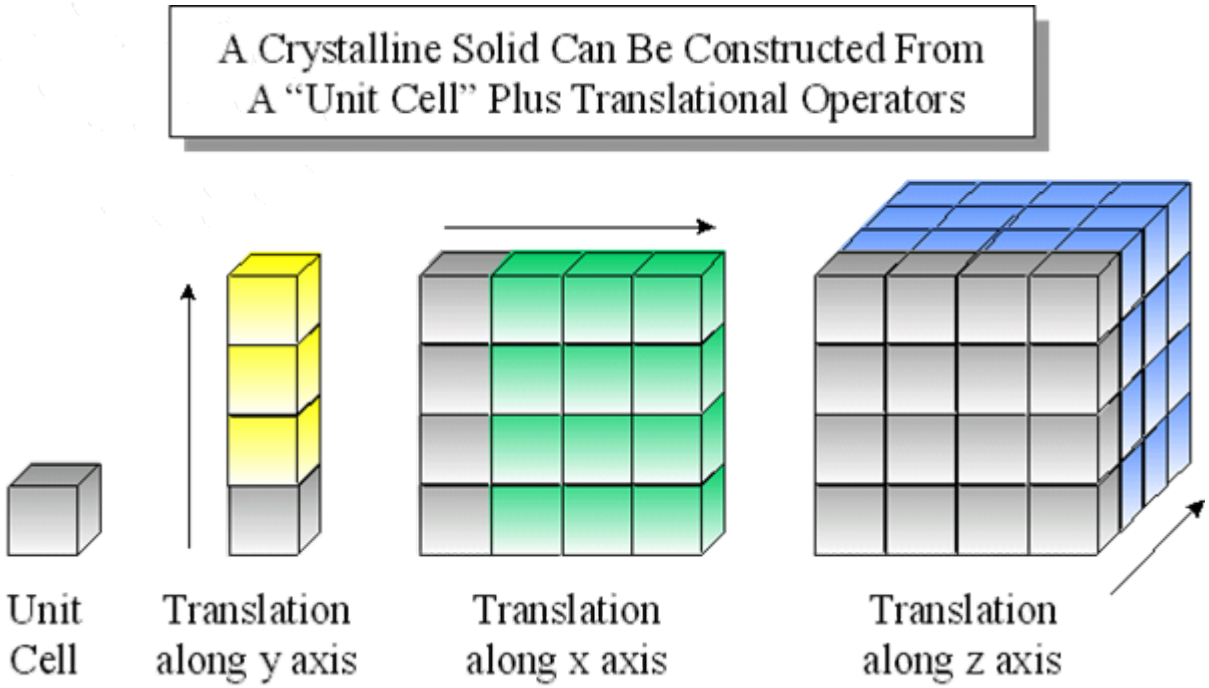
Location in Isabella County the state of Michigan

Coordinates: 43°35'52.71"N 84°46'3.75"W

Country	United States
State	Michigan
County	Isabella County

Structure of bulk objects (crystals)

Atoms in crystals sit on the vertices of 3D periodic lattices...

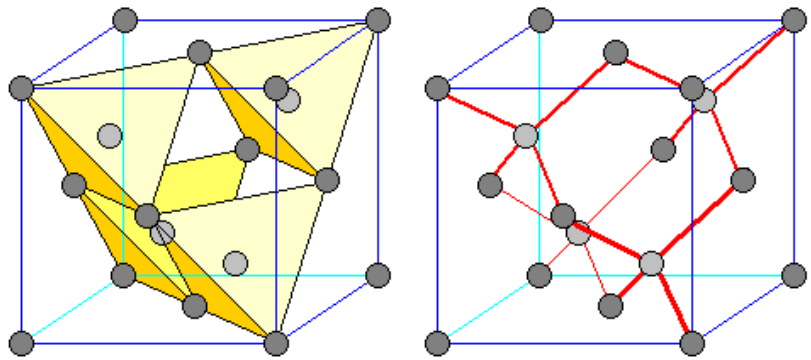


"Crystal Structure" =

Lattice type and symmetry
Unit cell parameters:
a, b, c, α, β, γ
Atomic positions inside the unit cell: (x,y,z).....

Allow to compute and predict properties of crystals..

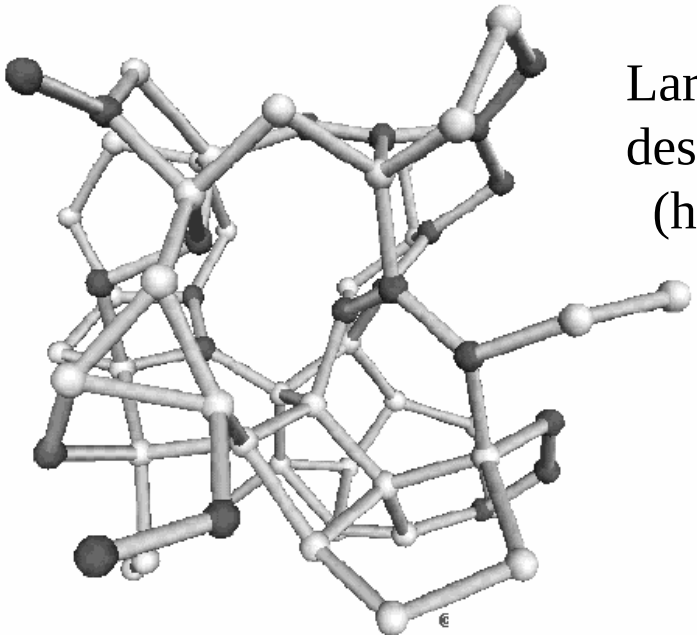
Diamond



How it is characterized ?

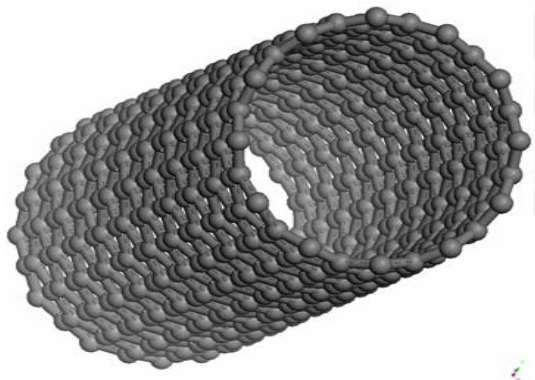
Structure of bulk objects (non crystals)

Atoms in non crystals do not sit on the vertices of 3D periodic lattices...



Large-size, non-periodic models giving a statistical description of the atomic-scale structure..
(here is indeed where atomic PDFs were applied first)

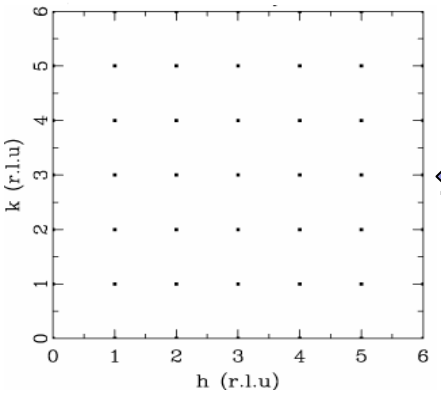
What about nanosized objects ?



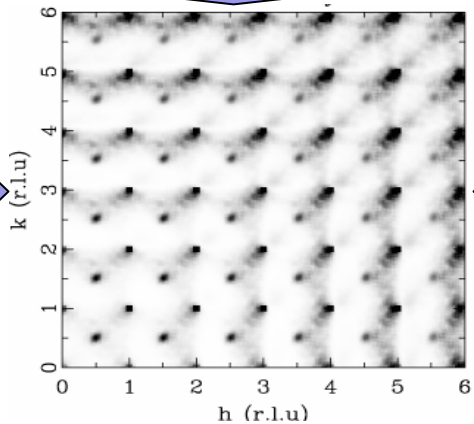
Diffraction patterns from materials with different degrees of structural coherence/size/periodicity

Long-range (~mm), periodic order | **Limited (~ nm) but measurable order** | **Short-range (sub-nano) order only**

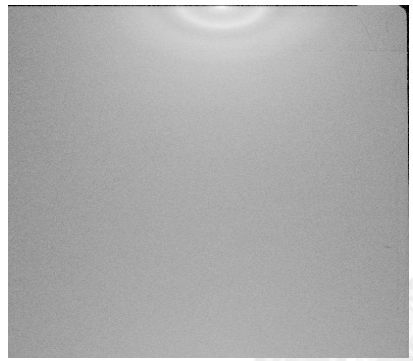
Crystals | Disordered/nanocrystals | Glasses, liquids



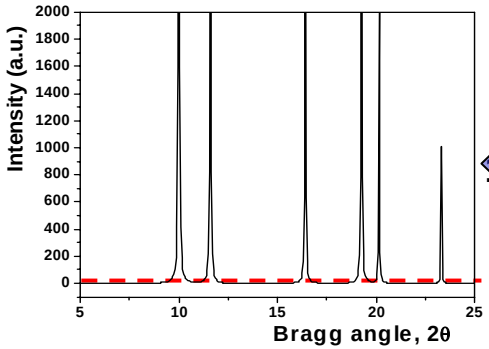
Simulated 2d patterns



Simulated 2d patterns

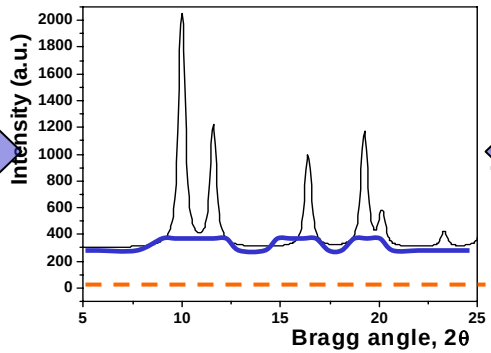


Bragg peaks only



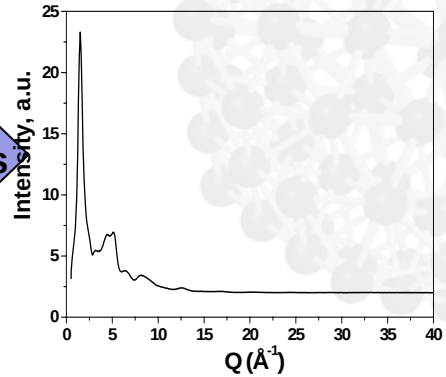
1d patterns

Both Bragg peaks and diffuse scattering



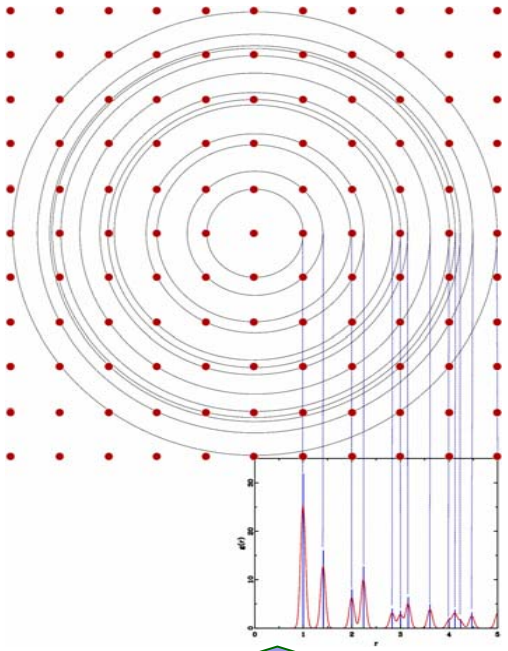
1d patterns

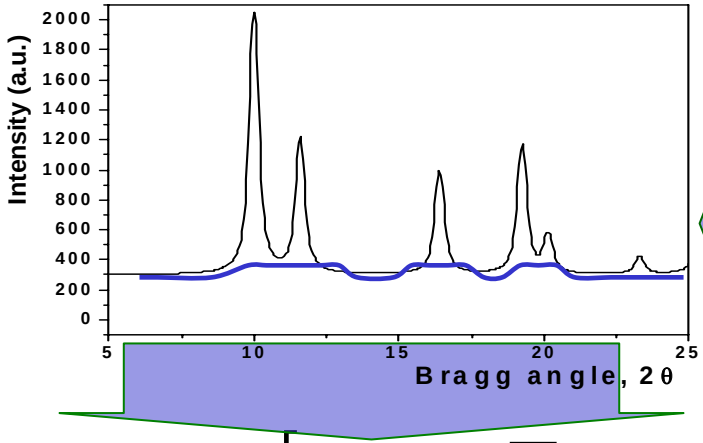
Diffuse scattering only



Diffraction patterns of bulk crystals show many well-defined Bragg peaks.
Diffraction patterns of nanosized objects show both Bragg-like peaks (not so many, not so sharp) and diffuse scattering (that may not be neglected).
Diffraction patterns of bulk non-crystals (glasses, polymers, liquids) show diffuse scattering only.

So, what do we do: **Atomic Pair Distribution Function Analysis (PDF)**





Diffraction experiment

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

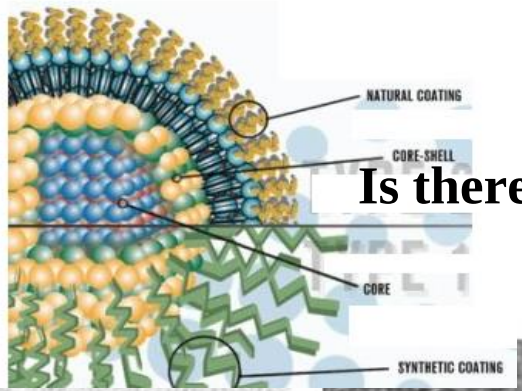
$$G(r) = (2/\pi) \int_{Q=o}^{Q_{max}} Q\,[S(Q) - 1] \sin(Qr)\, dQ ,$$

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

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

The **atomic PDF** peaks at characteristic interatomic distances **reflecting** the **3D structure** of materials. It does not imply **periodicity**.

CdSe and CdTe nanoparticles



Is there a core-shell "sub-structure" ?

Oleic acid-caped CdSe

Thiol-caped CdTe

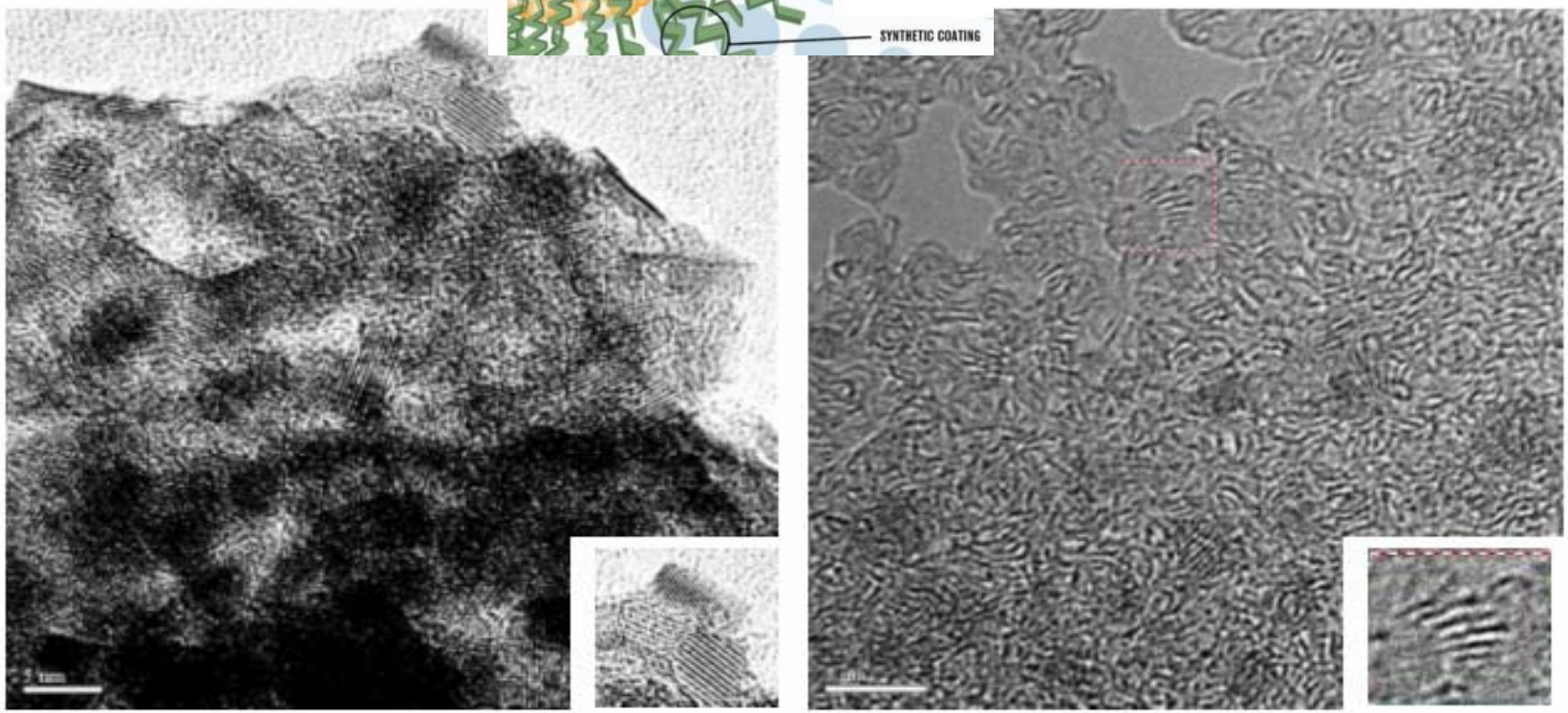


FIG. 1. TEM images of OA-caped CdSe (left) and TGA-caped CdTe (right) NCs. CdSe and CdTe NCs show very good and poor (see the insets) crystallinity, respectively. The length of the bar shown in the images (lower left corner) is 5 nm.

Metallic/semiconductor nanoparticles = Quantum Dots

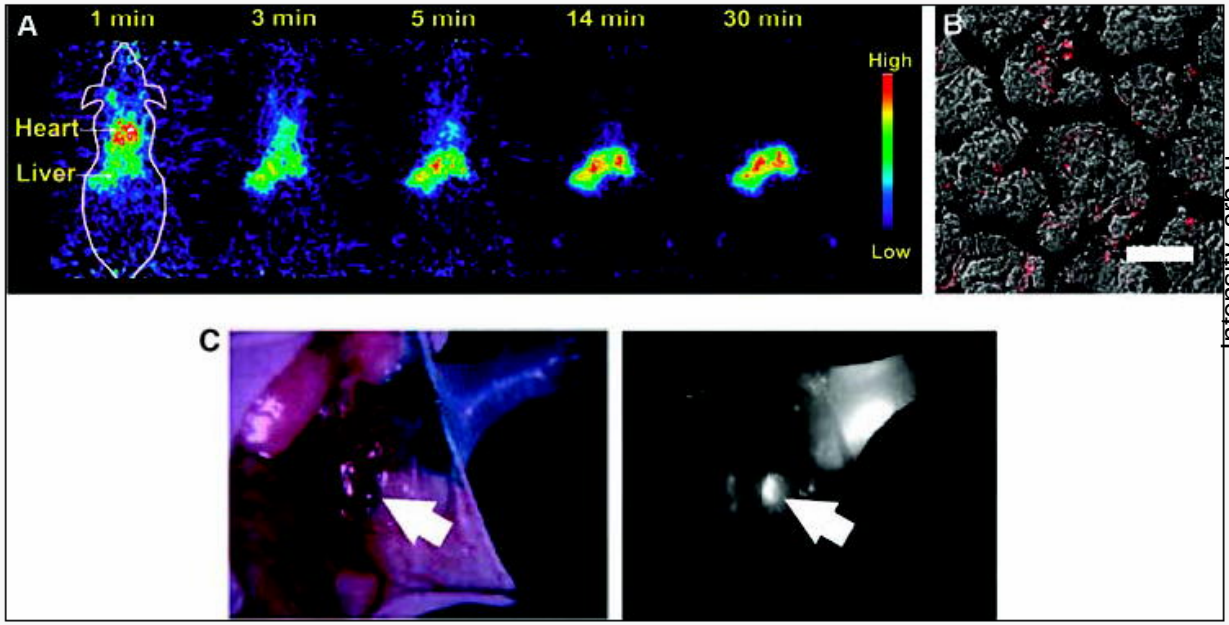
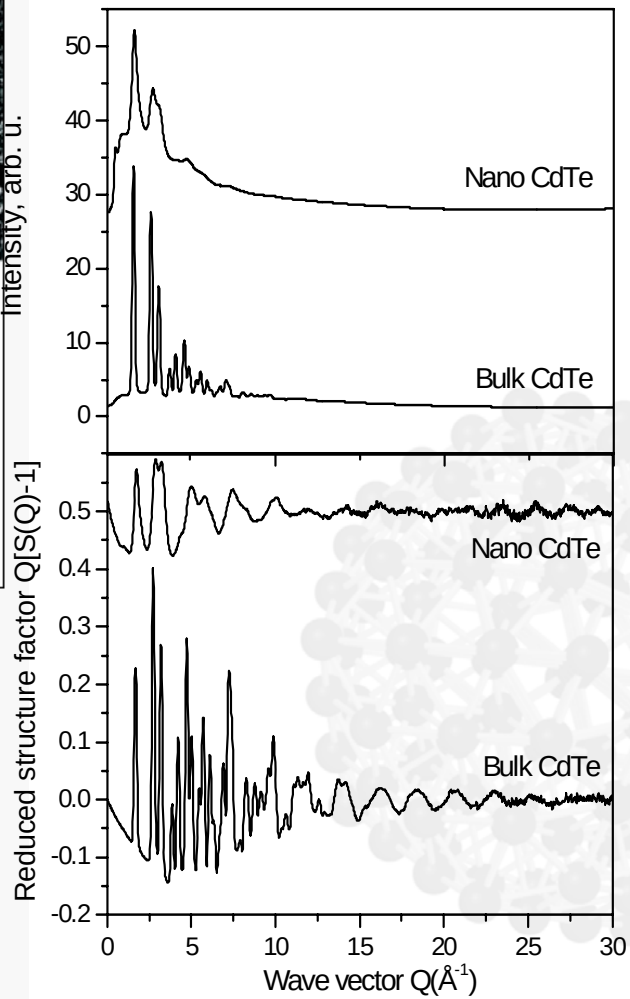


Fig. 4

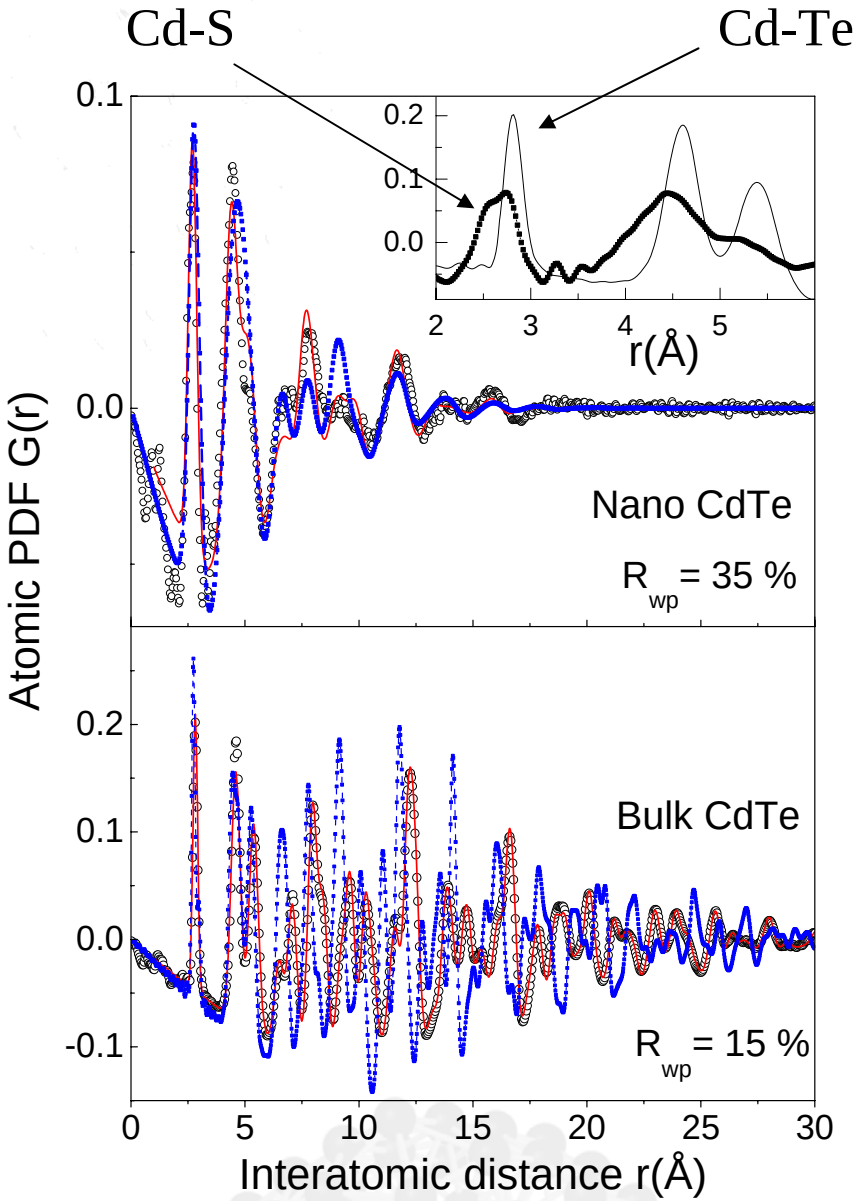
Animal use of qdots. (**A** and **B**) microPET and fluorescence imaging of qdots. Qdots having DOTA (a chelator used for radiolabeling) and 600-dalton PEG on their surface were radiolabeled with ^{64}Cu (positron-emitting isotope with half-life of 12.7 hours). These qdots were then injected via the tail vein into nude mice (~80 μCi per animal) and imaged in a small animal scanner. (A) Rapid and marked accumulation of qdots in the liver quickly follows their intravenous injection in normal adult nude mice. This could be avoided by functionalizing qdots with higher molecular weight PEG chains, as other studies have shown (49). (B) Overlay of DIC and fluorescence images of hepatocytes from a mouse shows the accumulation of qdots within liver cells. Scale bar, 20 μm. A further step could involve TEM imaging of the precise localization of qdots in cells, illustrating the potential of qdots as probes at the macro-, micro-, and nanoscales. (**C**) Surgical use of NIR qdots. A mouse was injected intradermally with 10 pmol of NIR qdots in the left paw, 5 min after reinjection with 1% isosulfan blue and exposure of the actual sentinel lymph node. Left, color video; right, NIR fluorescence image. Isosulfan blue and NIR qdots were localized in the same lymph node (arrows). Copyright 2004 Nature Publishing Group. Reproduced with permission from (60).

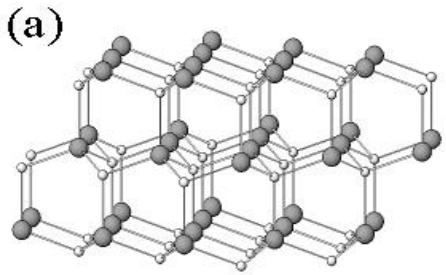
Nice properties….



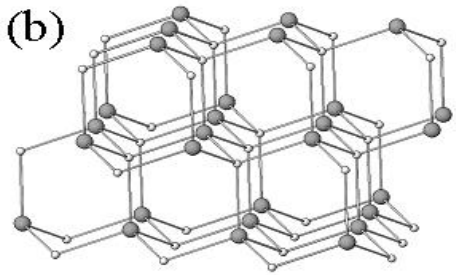
Not so nice XRD patterns…

CdTe and CdSe nanoparticles





Wurtzite



Zinc-blende

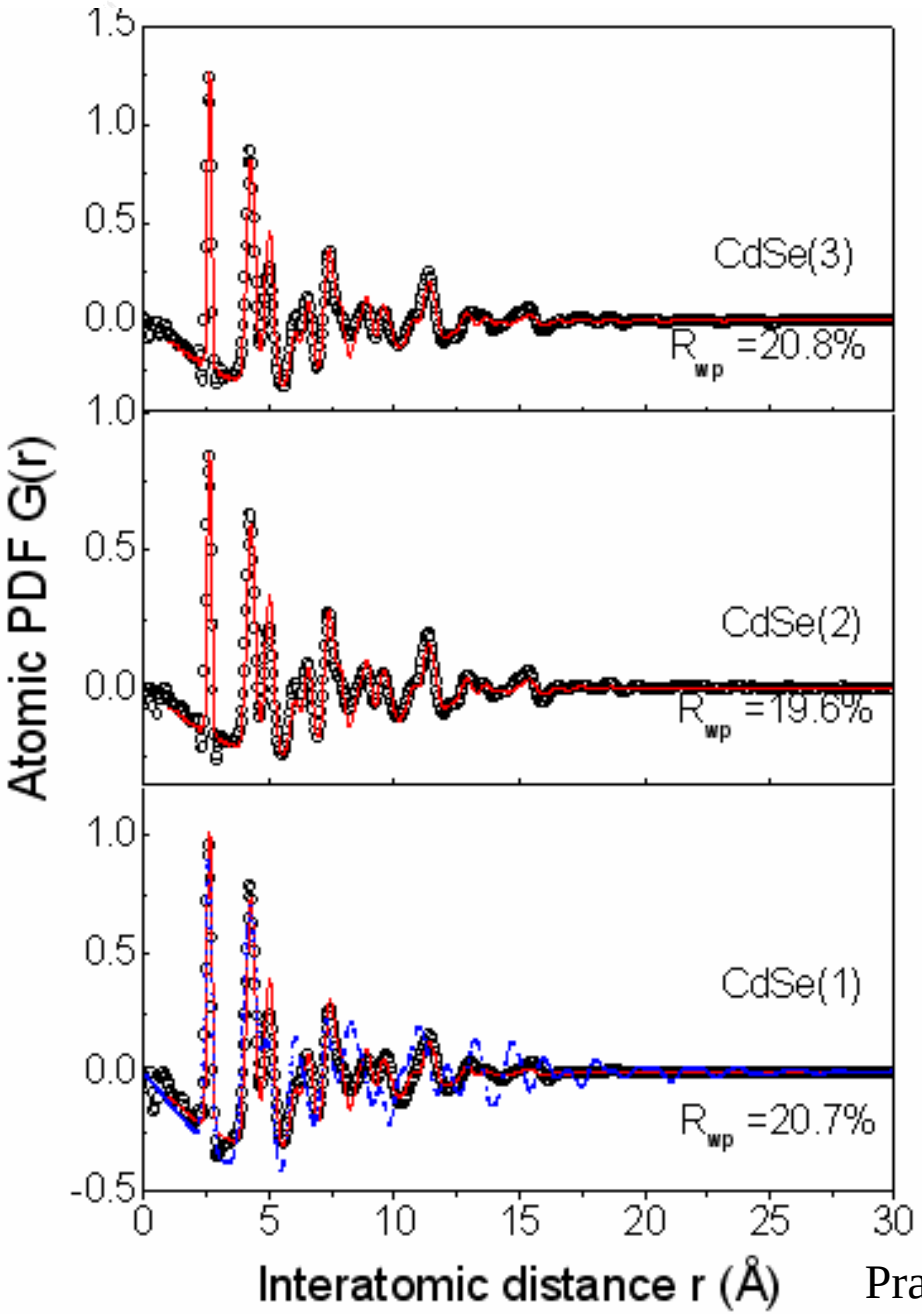
Thiol-caped CdTe quantum dots are:

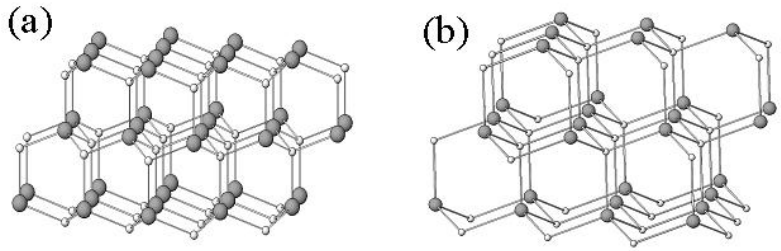
i) of zinc-blende type

ii) core(CdTe)-shell(CdS) sub-structure

Message one: Nanoparticles may be with the periodic structure of their bulk counterpart

CdSe Nanoparticles





Wurtzite Zinc-blende

Acetate-caped CdSe nanopartciles are:
i) of good crystallinity
ii) zinc-blende type structure
ii) note bulk CdSe is of wurtzite type

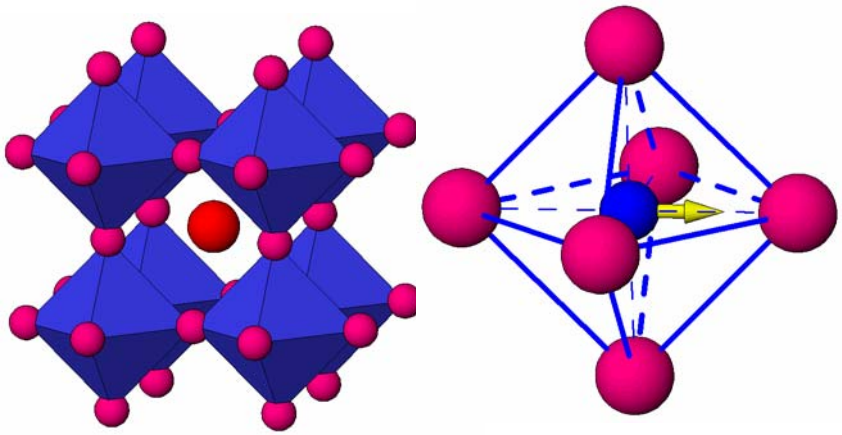
Message two: Nanoparticles may not exhibit the 3D structure of their bulk counterpart but a closely related, still periodic one.

Pradhan et. al; J. Appl. Phys. **102 (2007) 044304.**

$BaTiO_3$

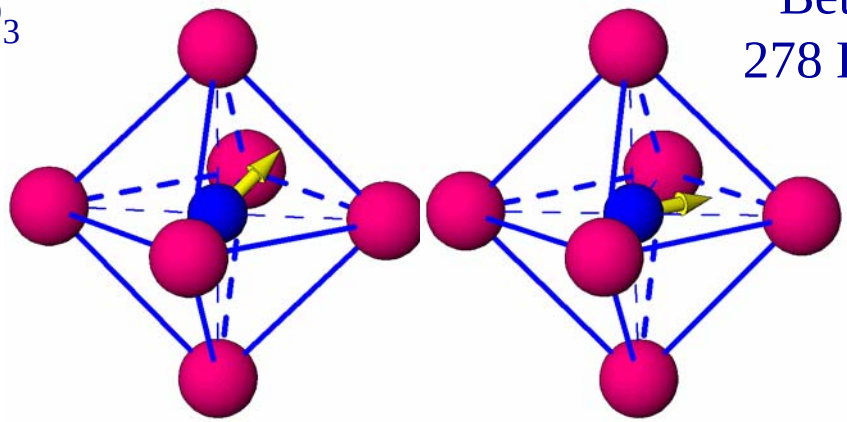
At high temperature $BaTiO_3$ has a centrosymmetric cubic structure and is paraelectric.

When 278K < T < 393K the material possesses a tetragonal-type structure.



Below 183 K $BaTiO_3$ has rhombohedral symmetry.

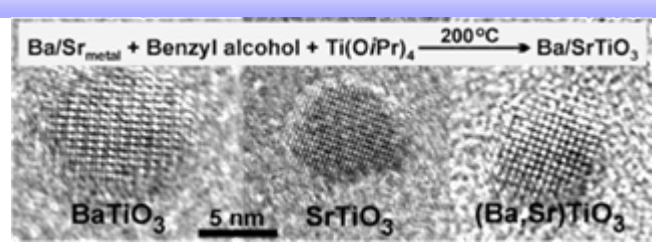
Between 183 K and 278 K the structure is orthorhombic.

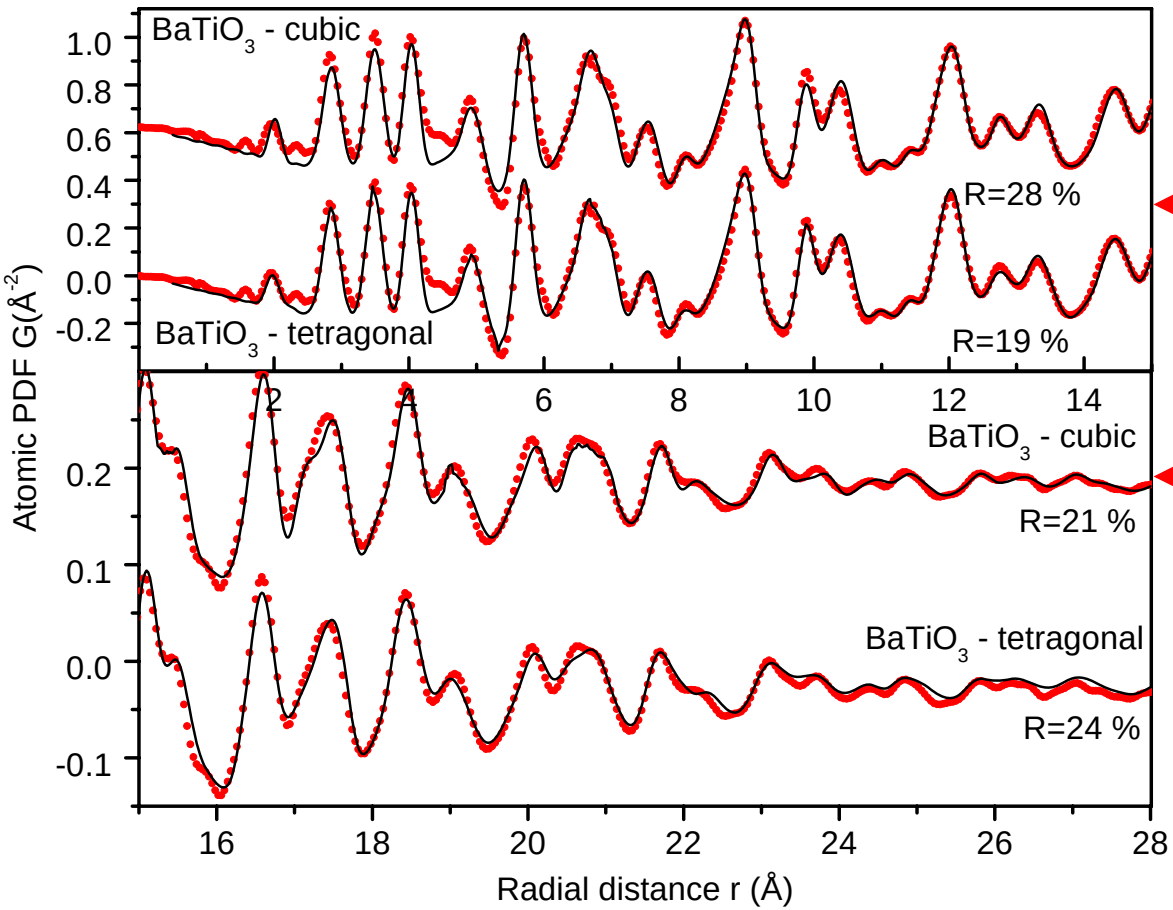


Although the tetragonal polymorph is the thermodynamically stable form at room temperature, most low-temperature synthesis routes often result in the formation of the “cubic” polymorph, and a high-temperature treatment at around 1000 °C followed by cooling is necessary to induce a phase transformation to the tetragonal one.

BaTiO3 nanoparticles

Sr/Ba titanate is virtually the most investigated perovskite material, because of its high dielectric constant and ferroelectric properties making it quite useful in electronics applications





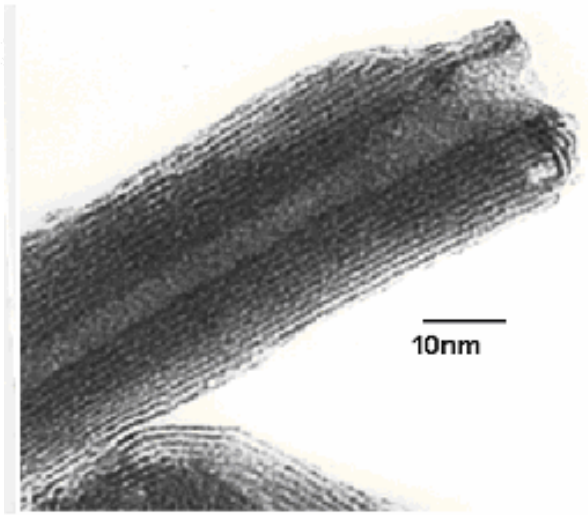
PDF fit in the range 1-14 Å

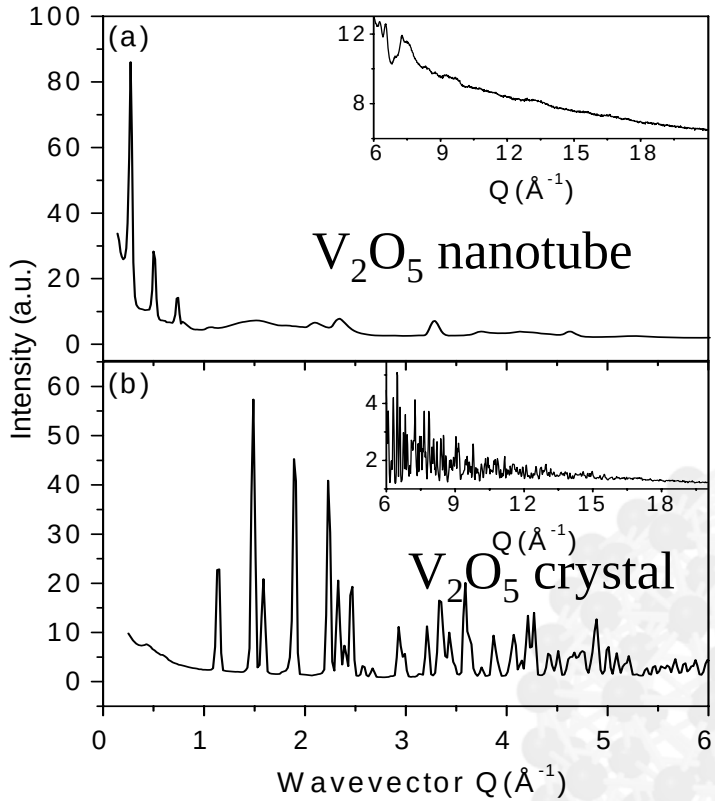
PDF simulation using the parameters obtained from the fit at short distances

Message three: Nanoparticles may show the periodic structure (e.g. cubic) of the bulk material on average but show local deviations (e.g. tetragonal) from it.

More details in V. Petkov et al, ***Chem. Mater.*** **18 (2006) 814.**

Nanosized objects of complex morphology: V_2O_5 tubes

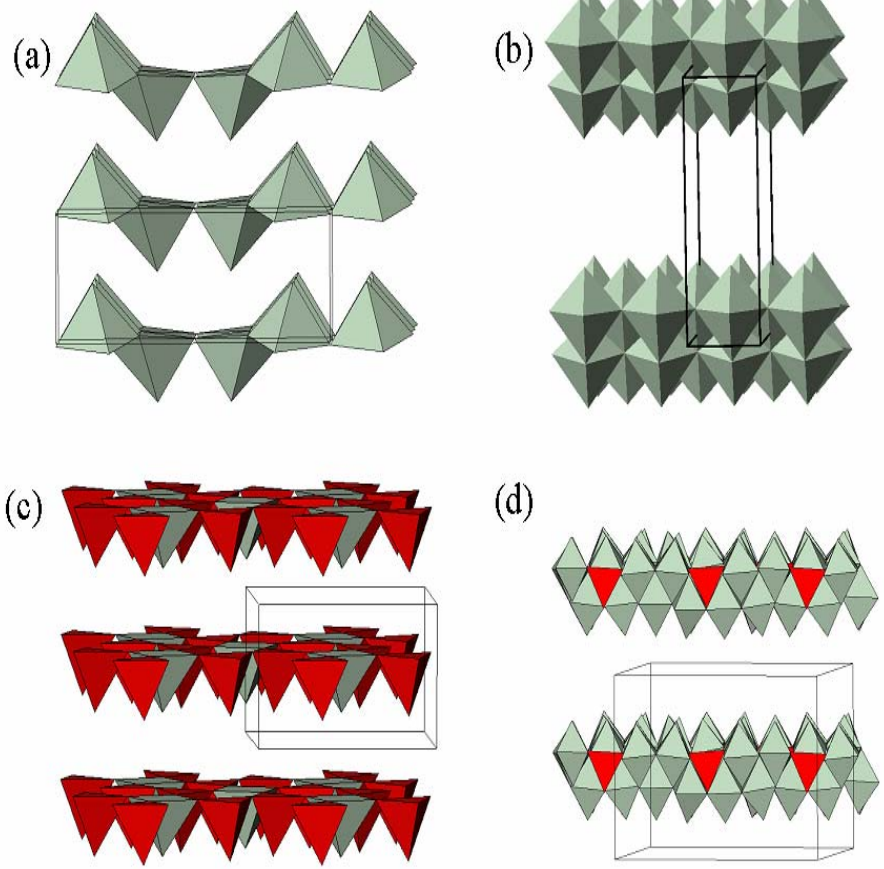


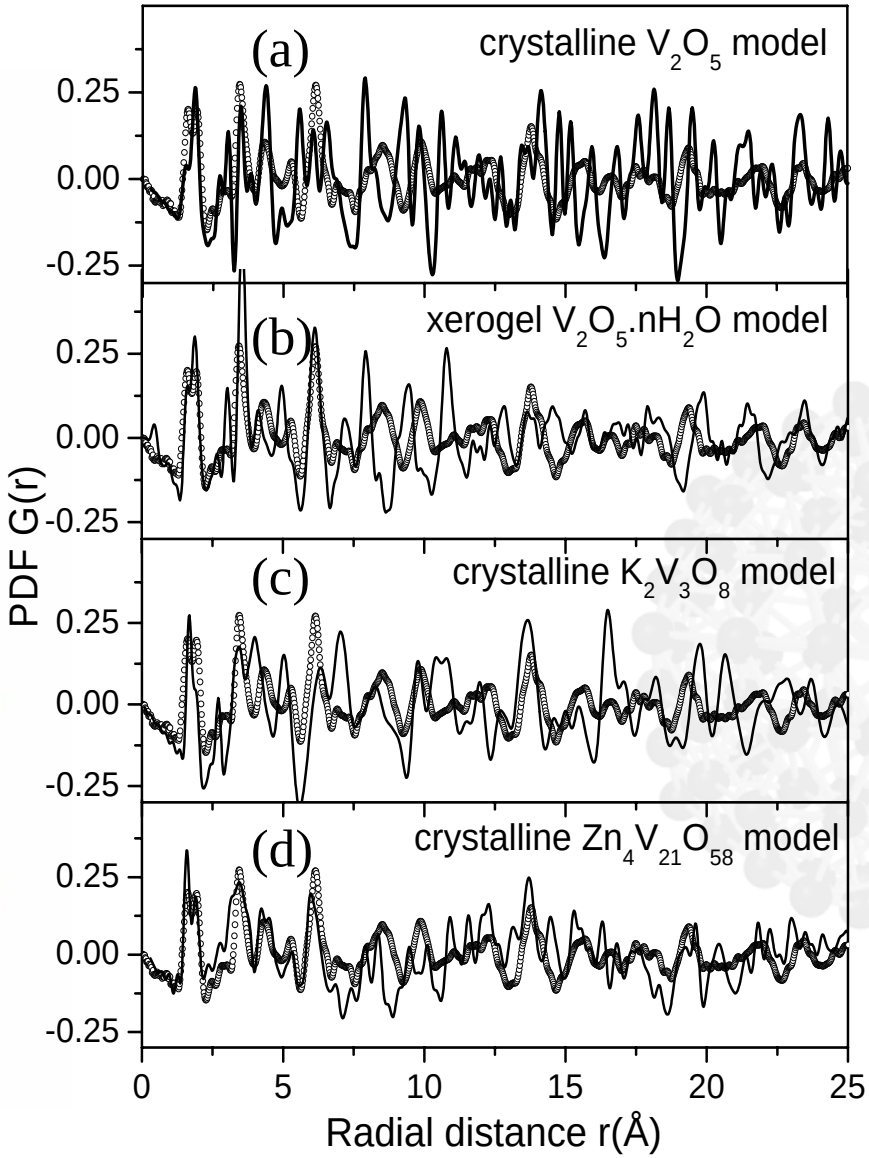


Crystalline V_2O_5 is widely used in application as chemical sensors, catalysts and solid state batteries. The material possesses an outstanding structural versatility and can be manufactured into nanotubes that have many of the useful properties of the parent crystal significantly enhanced.

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

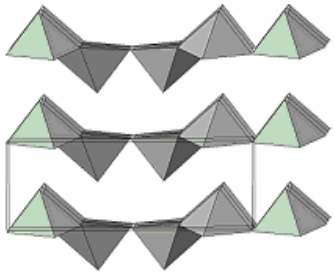




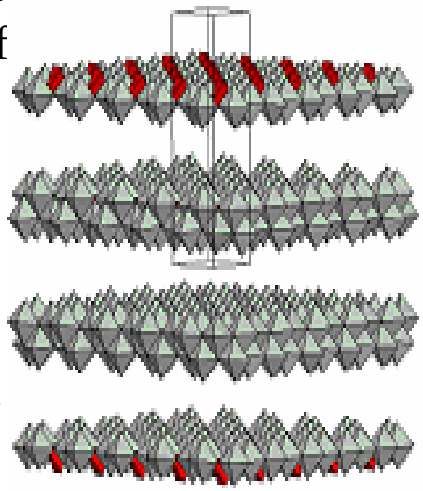
Exp. Data – symbols
Model data – solid line

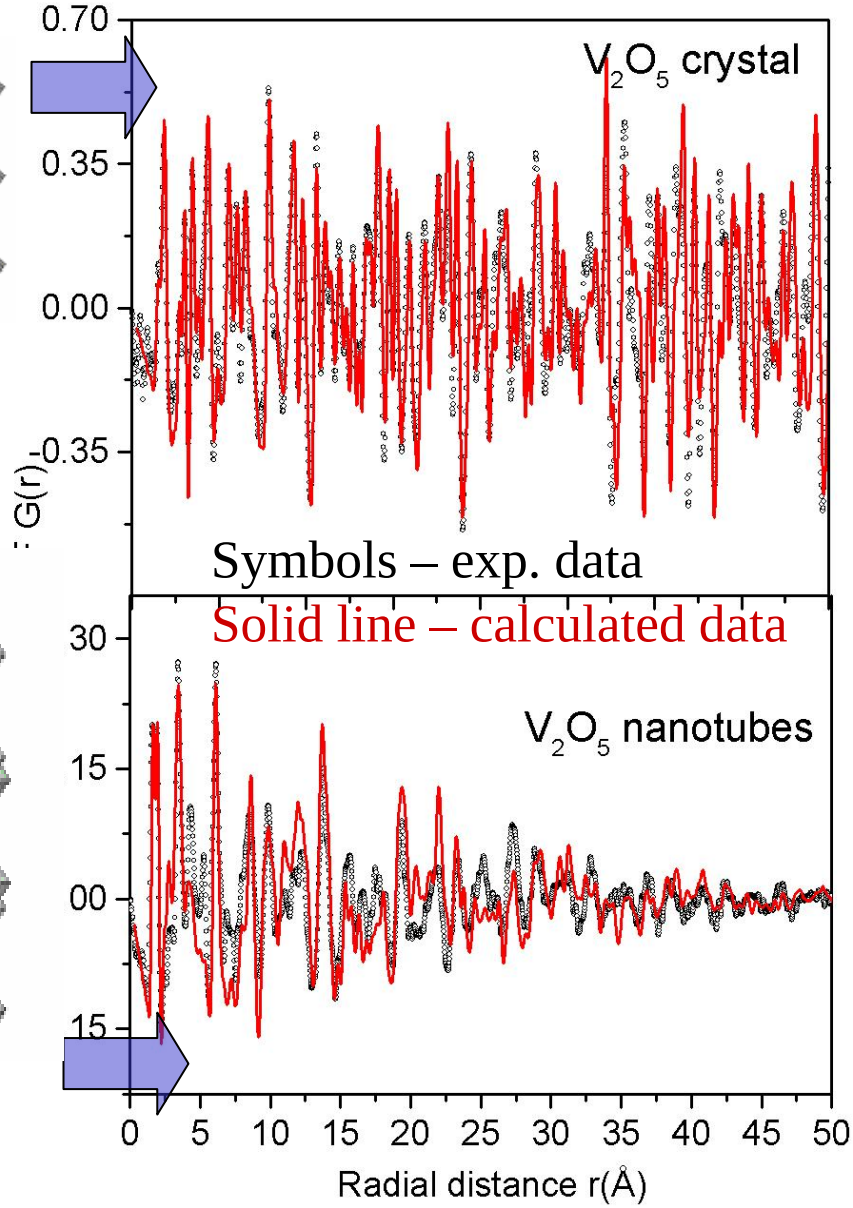
V_2O_5 nanotubes – PDF refinement

The well known 16-atom unit cell of crystalline V_2O_5 (S.G. *Pmmn*) fits the experimental data well. The agreement documents the fact the atomic PDF provides a reliable basis for structure determination.

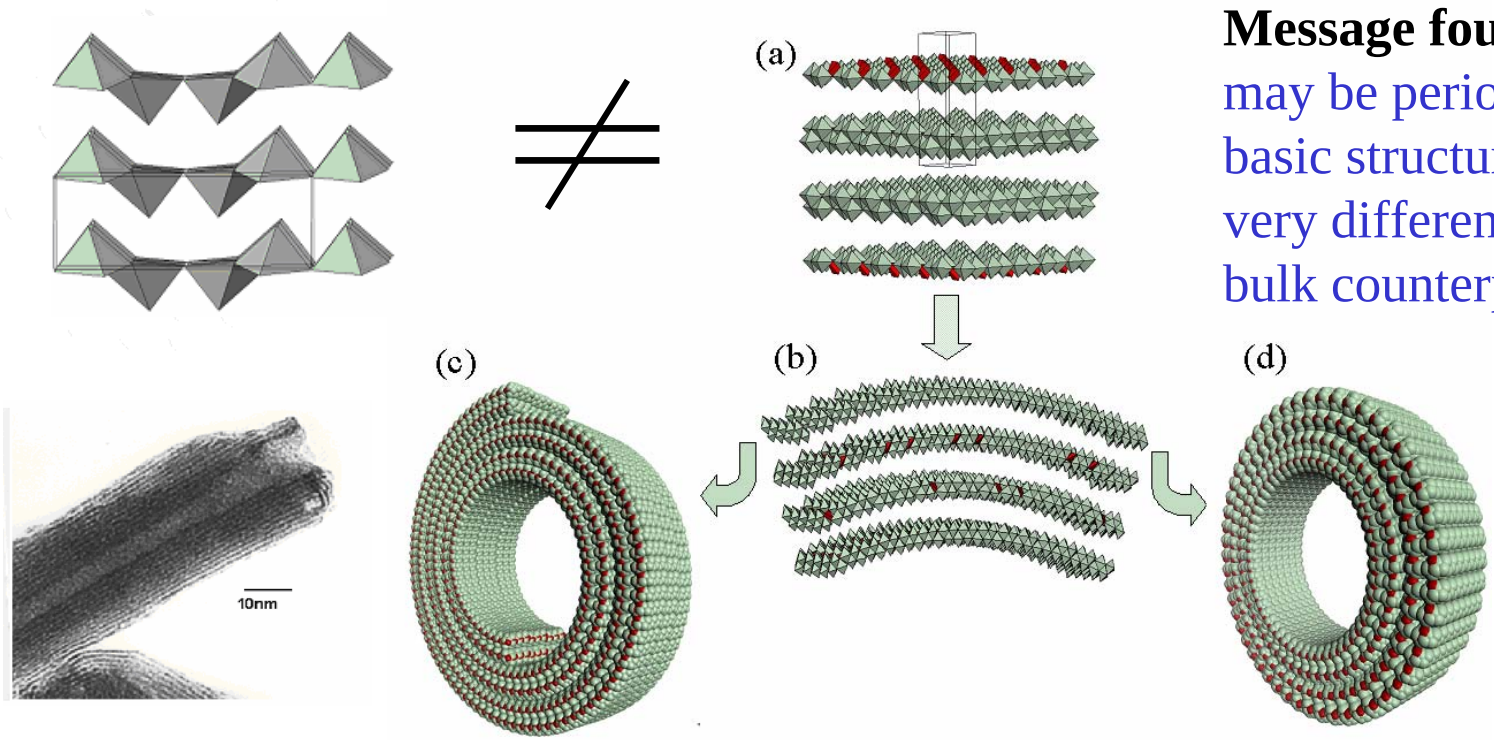


Best fit to the experimental PDF data for the nanotubes was achieved on a basis of a 46-atom unit cell (S.G. $P\ \bar{1}$). Even a nanocrystal with the complex morphology of V_2O_5 nanotubes possesses an atomic structure very well defined on the nanometer length scale and well described in terms of a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





V_2O_5 nanotubes – summary

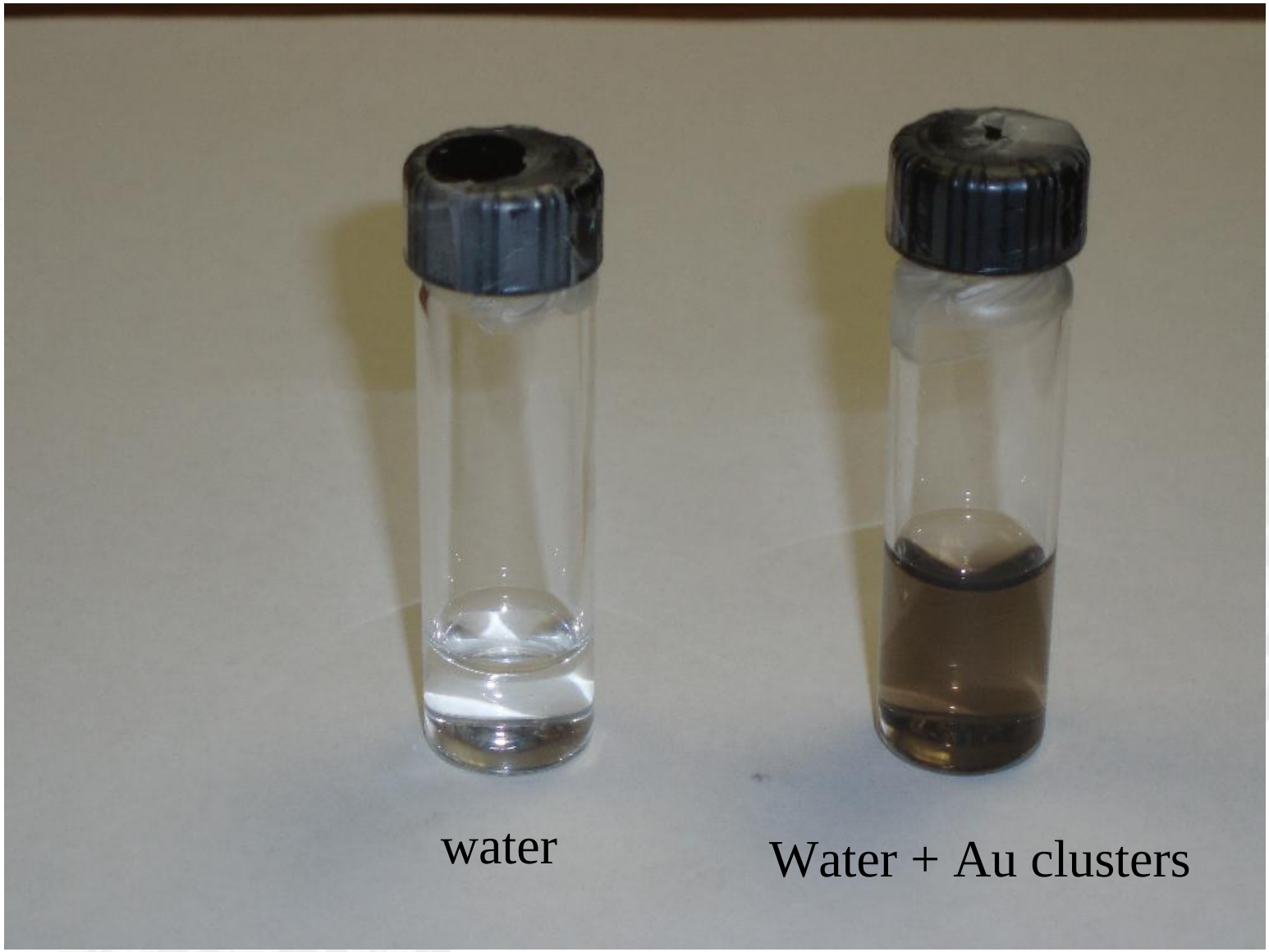


Message four: the structure may be periodic but the basic structural unit may be very different from that of the bulk counterpart…

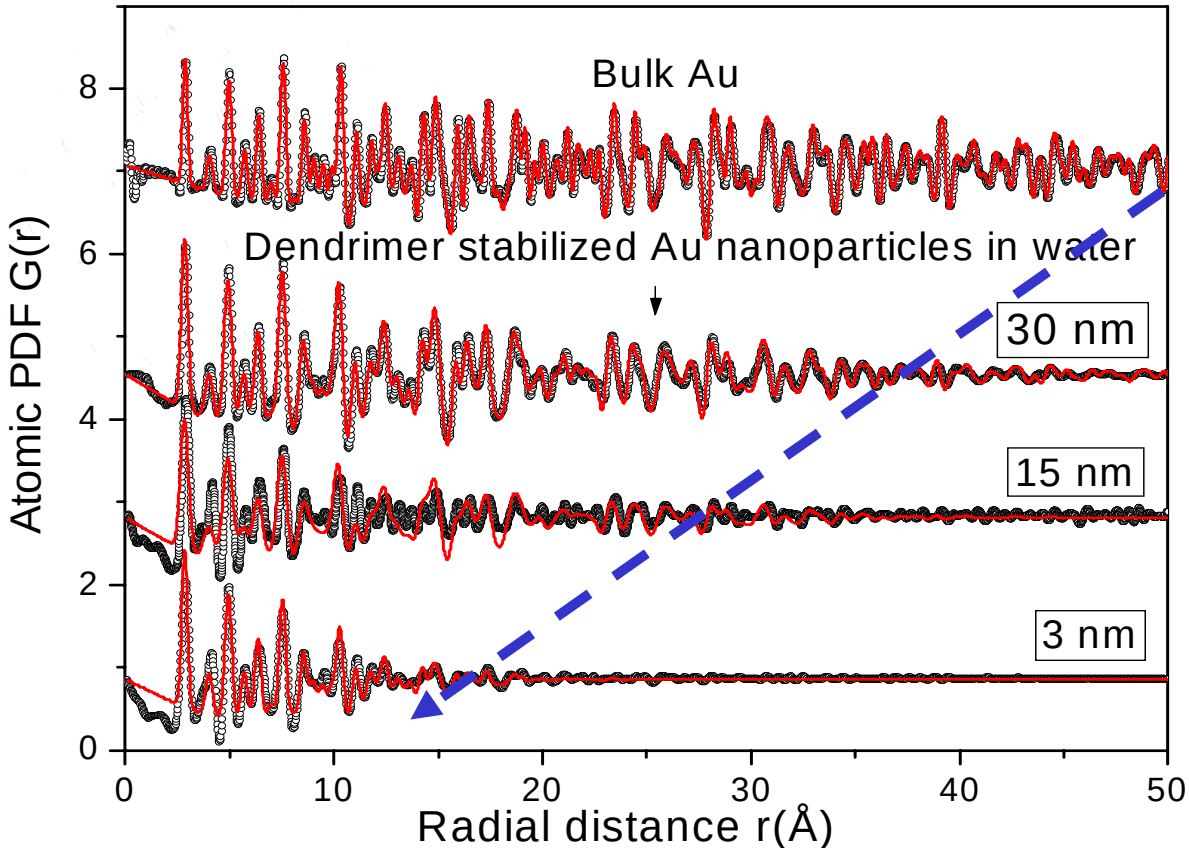
Structure description of V_2O_5 nanotubes: Double layers of V-O_6 octahedral (green) and V-O_4 tetrahedral (red) units are undistorted and stacked in perfect registry with the crystal (a). When bent (b) such layers may form nanoscrolls (c) or closed nanotubes (d). Double layers of such complexity may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

Au nanoparticles

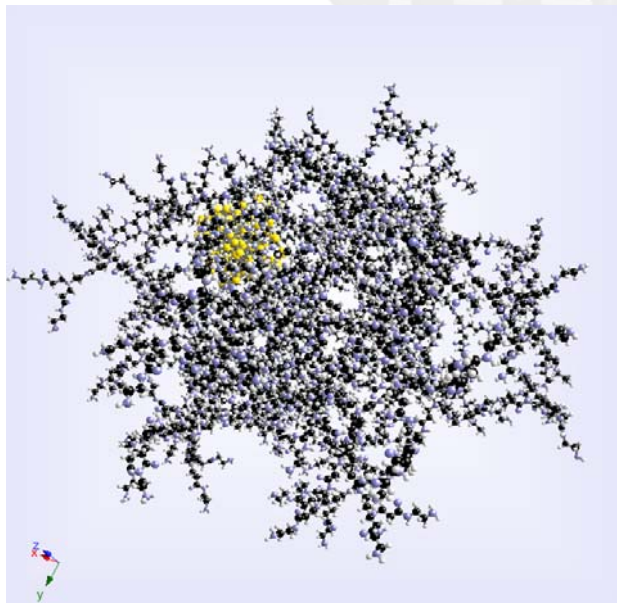


Au nanoparticles



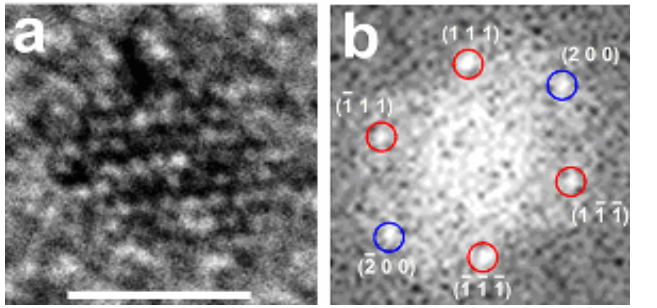
Experimental atomic PDFs (symbols) for Au nanosize particles. The x-ray diffraction experiments were carried out at the beamline 11IDC at the Advanced Photon Source using x-rays of energy 115 keV.

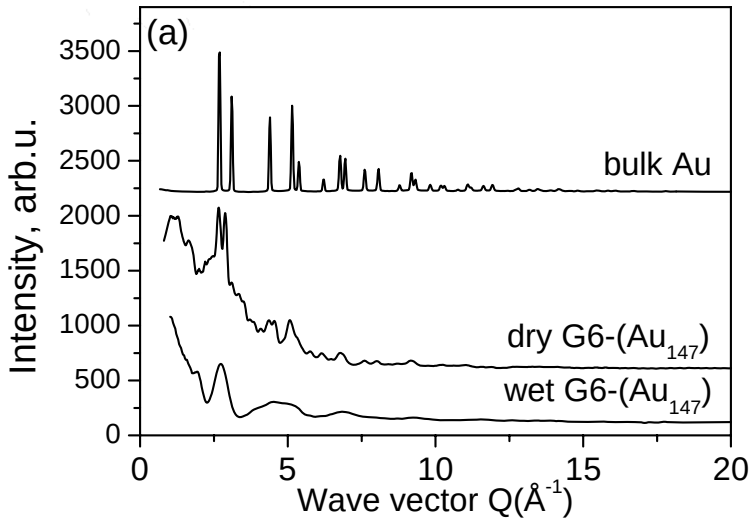
Larger Au nanoparticles exhibit the fcc-type structure (somewhat distorted) of bulk Au.

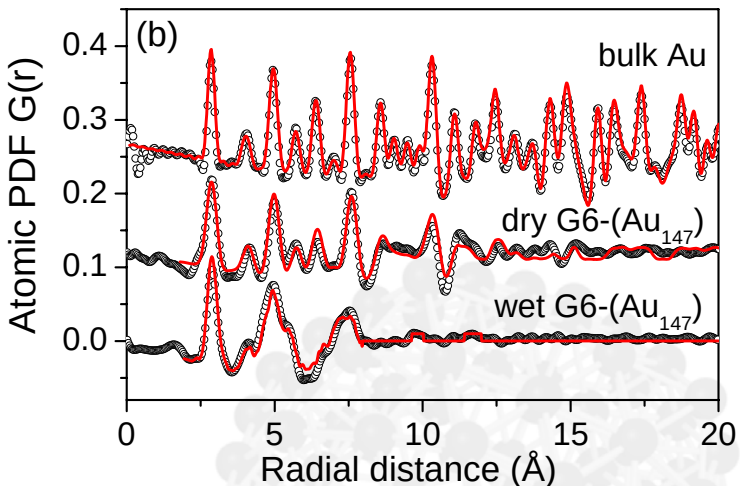


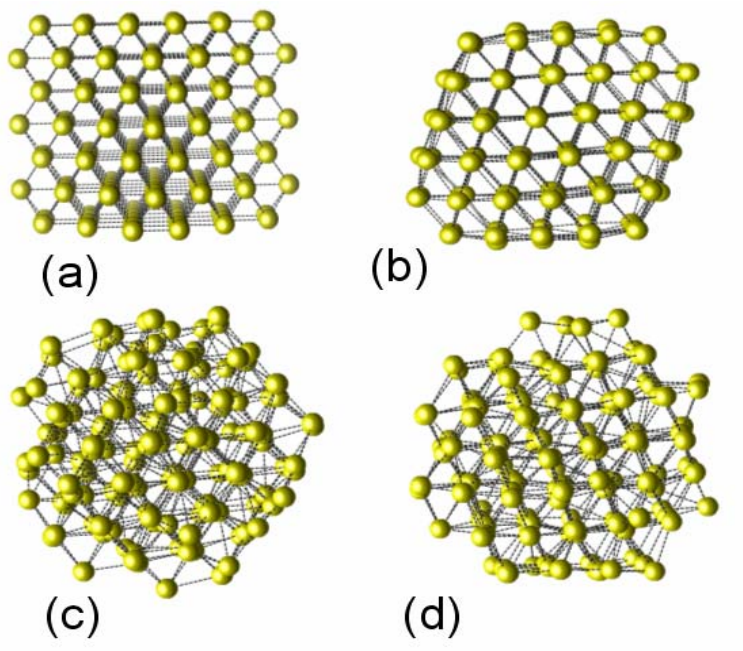
What about smaller sizes ?

Au nanoparticles









Message five:

Nanoparticles (~ 2nm Au/147 atoms) may exhibit a non-periodic atomic ordering that shows some signatures (e.g. the local symmetry) of the 3D structure (fcc–type) of the bulk only.

Conclusions:

i) With new technologies moving quickly toward smaller scales nanosized object (“nanoparticles”) of various shapes are produced in increasing numbers.

ii) Nanoparticles have a well defined structure but the structure is not necessarily that of their bulk counterpart.

iii) That is why the structure of nanoparticles has to be determined with care (and not just assumed).

iv) PDFs seem to do a very good job and, for now, the PDF future looks bright….

What would be helpful (from our point of view) ?

1. **Improved instrumentation**, including in-house

For now we have:

i) Mo/Ag Ka, convenient to use at home but it is very time consuming (there are no detectors optimized for Mo or Ag radiation..). **XRD equipment makers: where are you ?**

(ii) Synchrotron with IPs. Fast but energy not sensitive (more difficult data corrections)

iii) Synchrotron with SSD, energy sensitive but is not very fast (easier data corrections)

Could we combine the best of (ii) and (iii) ?

2. There is no **software** to handle models of finite objects (i.e. nanoparticles with free surface). Even RMC assumes bulk-like models with a cell-type periodicity….

Scientific software developers: any ideas/developments ?