How can we describe a crystal?

Crystal structure = lattice + basis

A lattice

A basis
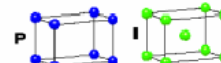
A crystal structure
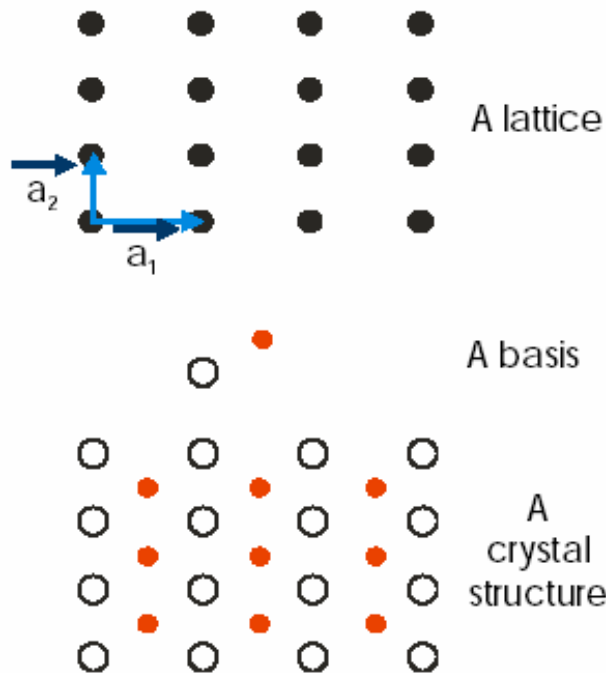
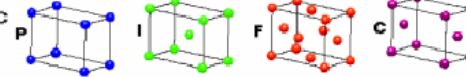The 14 Bravais lattices in 3D

CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$
P   I   F
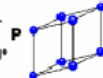
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
P   I

ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
P   I   F   C
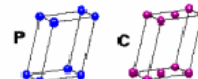
HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

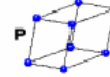TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
P

MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$
P   C

TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$
P

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

- Notice that we know have different lattice types:
- P = primitive (1 lattice point)
- I = Body-centred (2 lattice pts)
- F = Face- centred (4 lattice pts)
- C = Side-Centred (2 lattice pts)
- In this course, we will concentrate upon only a few of these types

Examples of common structures:
(1) The Sodium Chloride (NaCl) Structure
### (LiH, MgO, MnO, AgBr, PbS, KCl, KBr)

- The NaCl structure is FCC
- The basis consists of one Na atom and one Cl atom, separated by one-half of the body diagonal of a unit cube
- There are four units of NaCl in each unit cube
- Atom positions:
- Cl : 000 ; ½½0; ½0½; 0½½
 Na: ½½½; 00½; 0½0; ½00
- Each atom has 6 nearest neighbours of the opposite kind
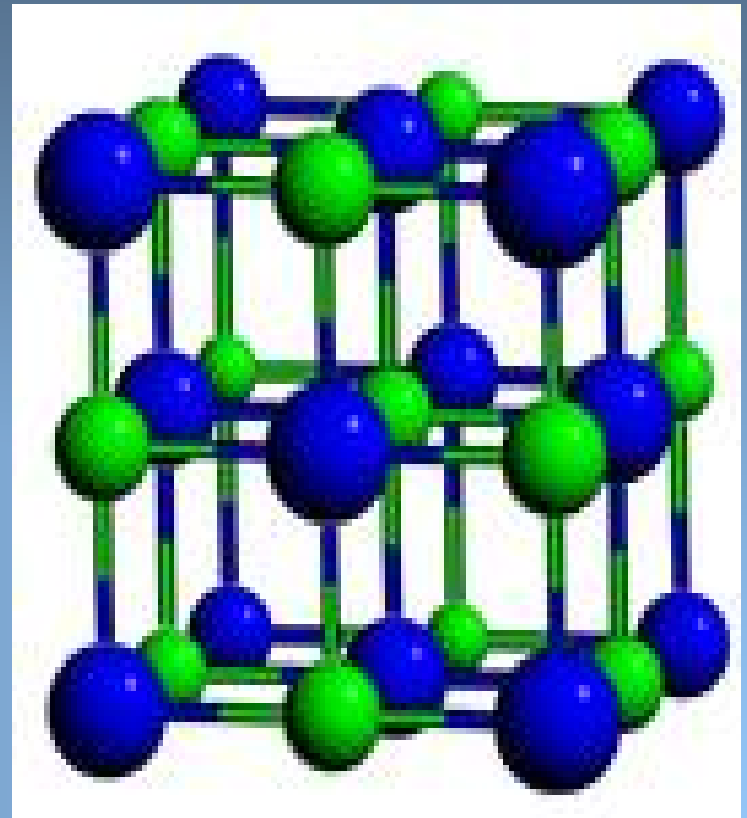
Often described as 2 interpenetrating FCC lattices

(1) NaCl structure

| Crystal	a
LiH	4.08 Å
MgO	4.20
MnO	4.43
NaCl	5.63
AgBr	5.77
PbS	5.92
KCl	6.29
KBr	6.59
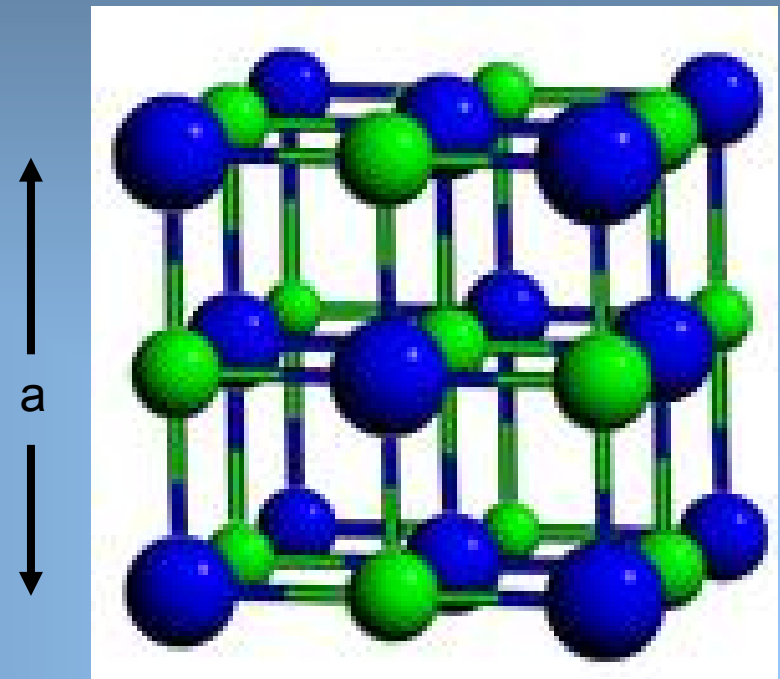
(2) CsCl structure

(CsBr, CsI, RbCl, AlCo, AgZn, BeCu, MgCe, RuAl, SrTl)

- The CsCl structure is BCC
- The basis consists of one Cs atom and one Cl atom, with each atom at the center of a cube of atoms of the opposite kind
- There is on unit of CsCl in each unit cube
- Atom positions:
- Cs : 000
- Cl : ½½½ (or vice-versa)
- Each atom has 8 nearest neighbours of the opposite kind
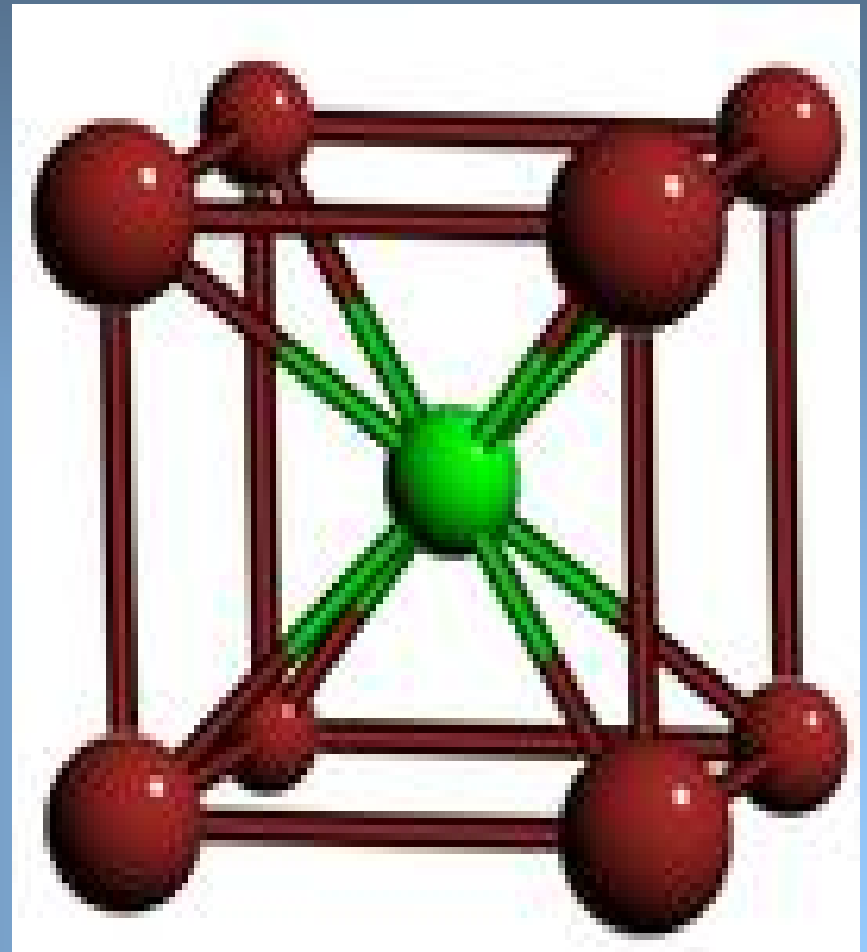
Closed-packed structures

- There are an infinite number of ways to organize spheres to <u>maximize</u> the packing fraction.
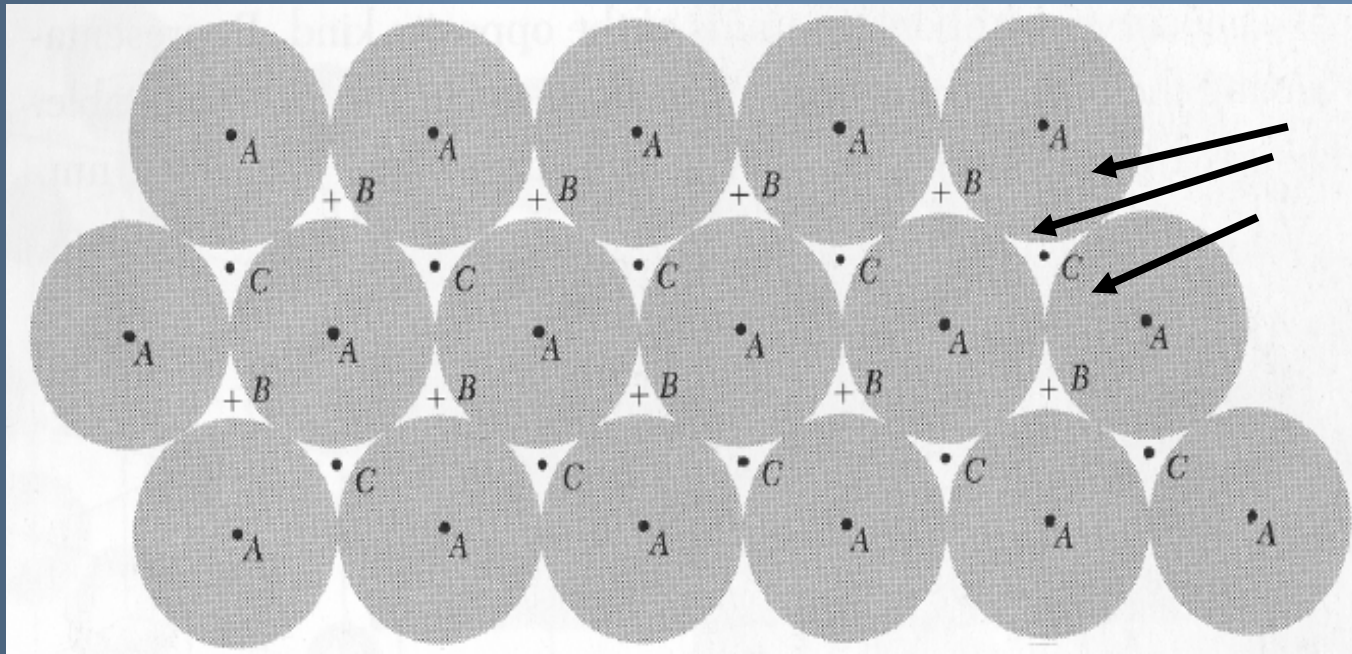

The centres of spheres at A, B, and C positions (from Kittel)

There are different ways you can pack spheres together. This shows two ways, one by putting the spheres in an ABAB… arrangement, the other with ACAC…. (or any combination of the two works)
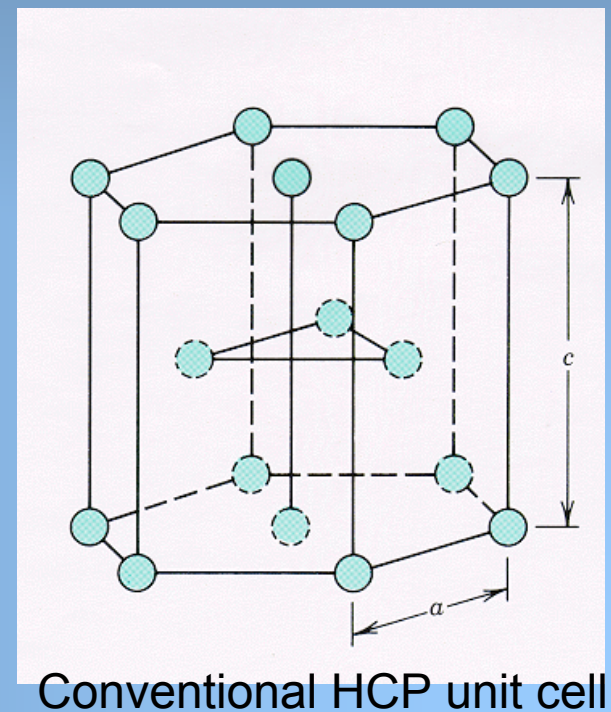
(3) The Hexagonal Closed-packed (HCP) structure

Be, Sc, Te, Co, Zn, Y, Zr, Tc, Ru, Gd,Tb, Py, Ho, Er, Tm, Lu, Hf, Re, Os, Tl

- The HCP structure is made up of stacking spheres in a ABABAB… configuration
- The HCP structure has the primitive cell of the hexagonal lattice, with a basis of two identical atoms
- Atom positions: 000, 2/3 1/3 ½ (remember, the unit axes are <u>not</u> all perpendicular)
- The number of nearest-neighbours is 12.
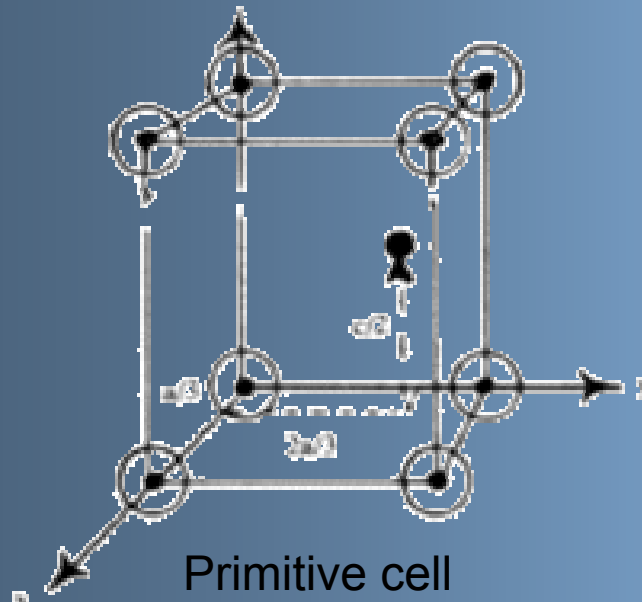
Rotate three times
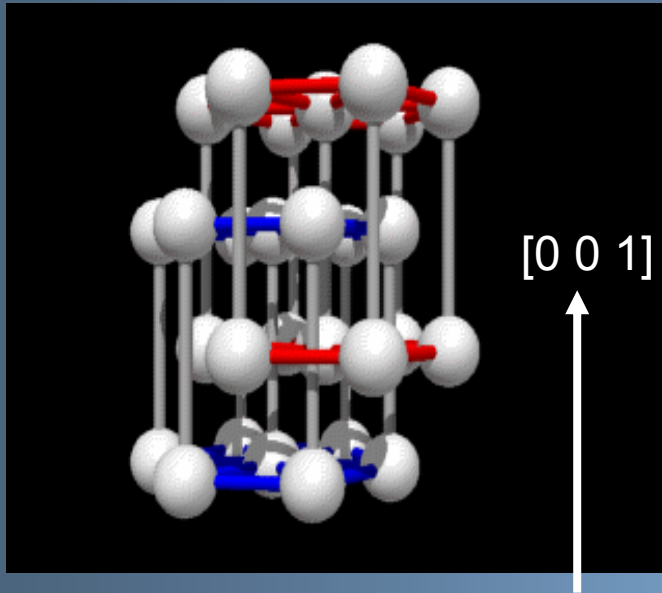
To get the full structure

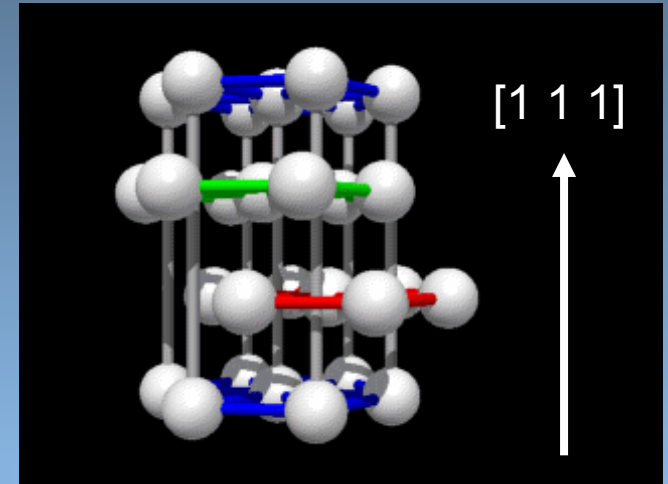Primitive cell

Conventional HCP unit cell

The FCC and hexagonal closed-packed structures (HCP) are formed from packing in different ways. FCC (sometimes called the cubic closed-packed structure, or CCP) has the stacking arrangement of ABCABCABC… HCP has the arrangement ABABAB….
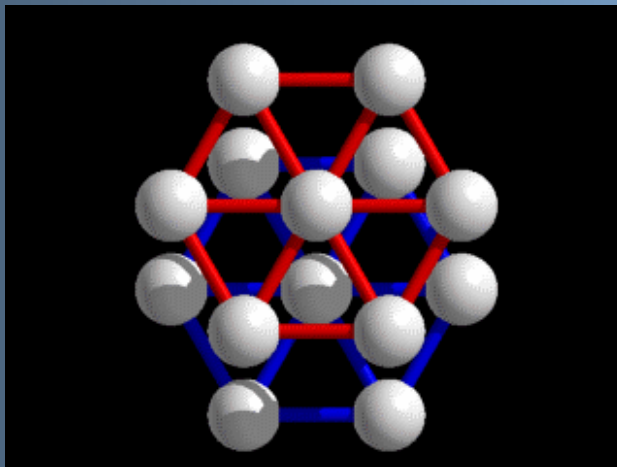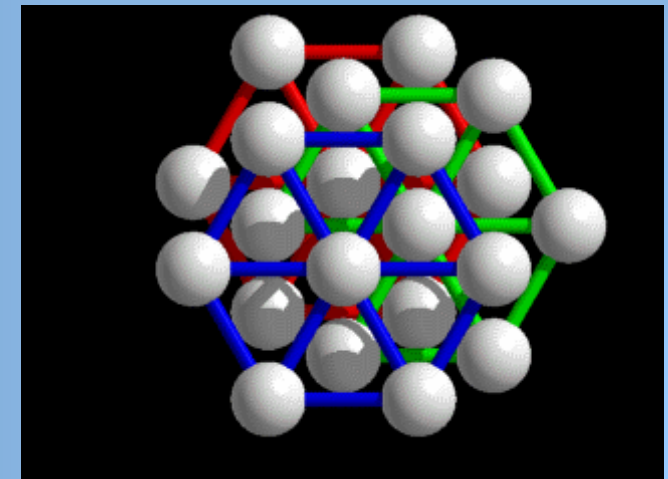
HCP

[0 0 1]

FCC
(CCP)
(looking along
[111] direction

[1 1 1]

ABAB
sequence

ABCABC
sequence

Indexing system for crystal planes

- Since crystal structures are obtained from diffraction experiments (in which particles diffract from planes of atoms), it is useful to develop a system for indexing lattice planes.

- We can use the lattice constants a_1, a_2, a_3, but it turns out to be more useful to use what are called Miller Indices.

Index
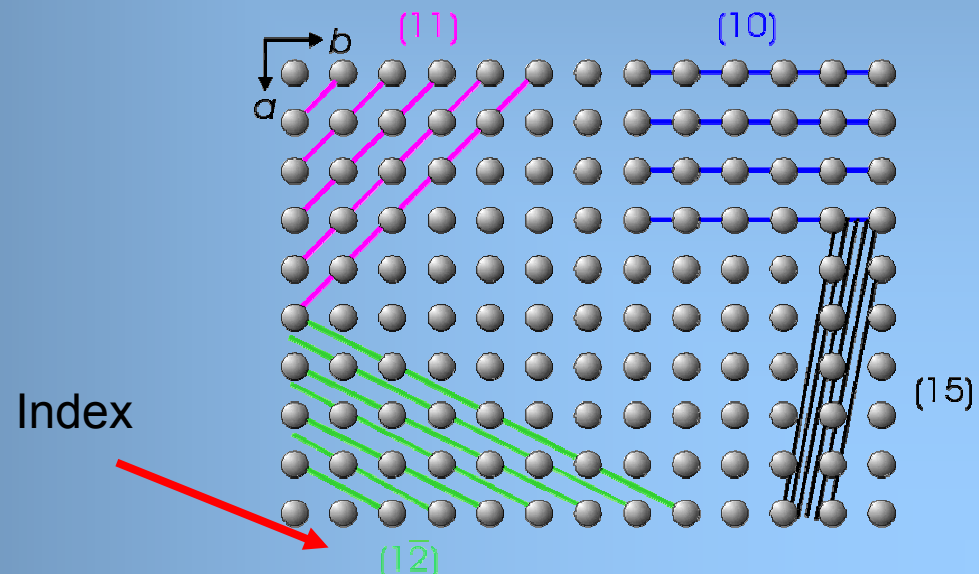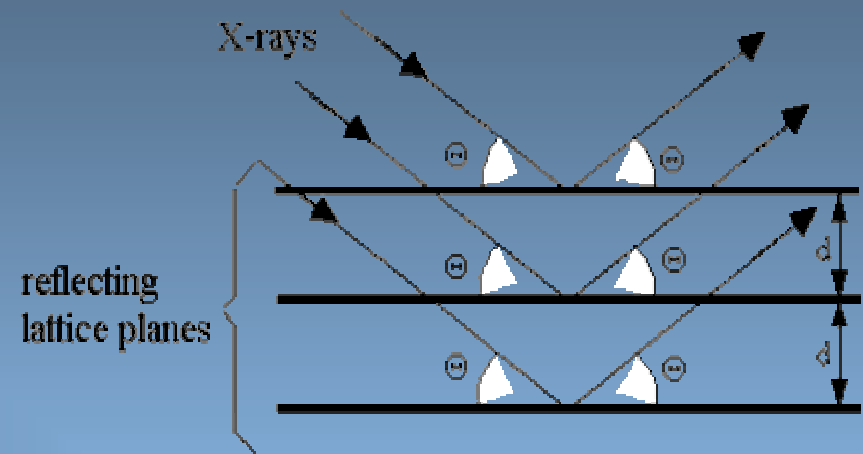
Rules for determining Miller Indices

- (1) Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3.
- (2) Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest of the three integers. The result, listed as (*hkl*), is called the index of the plane.
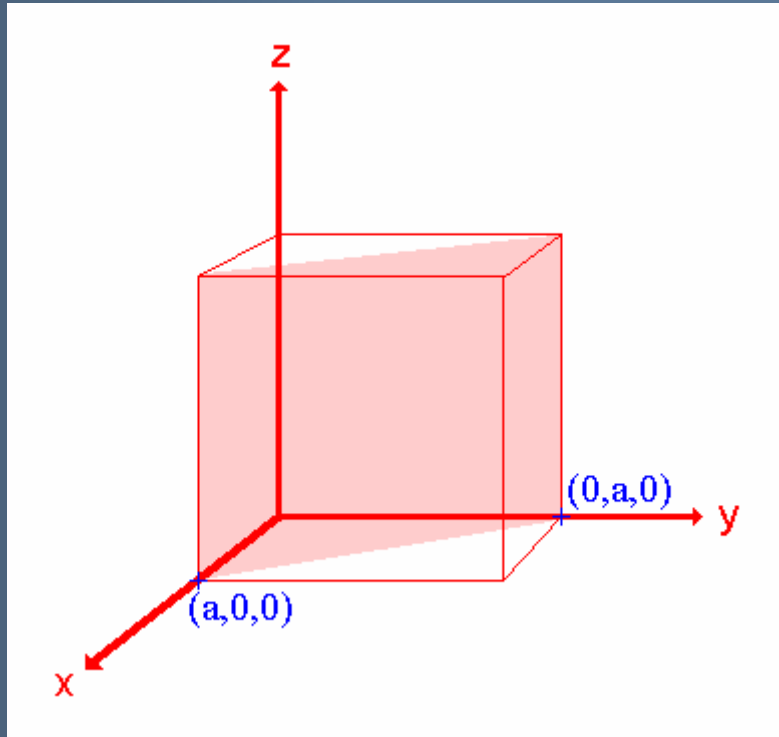
An example:
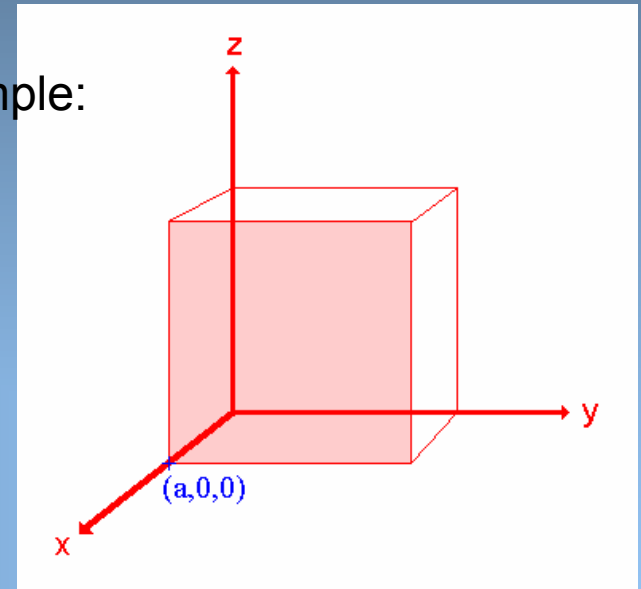
Intercepts: a, ∞, ∞
Reciprocals: a/a, a/∞, a/∞
= 1, 0, 0
Miller index for this plane : (1 0 0)
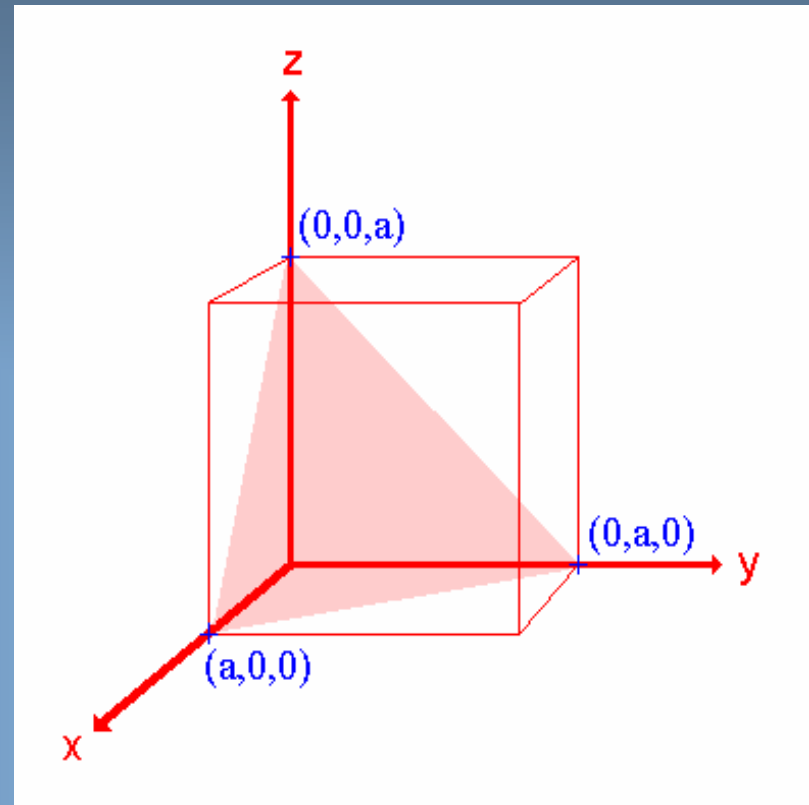(note: this is the normal vector for this plane)

Examples of Miller Indices

Intercepts: a, a,∞
Reciprocals: a/a, a/a, a/∞
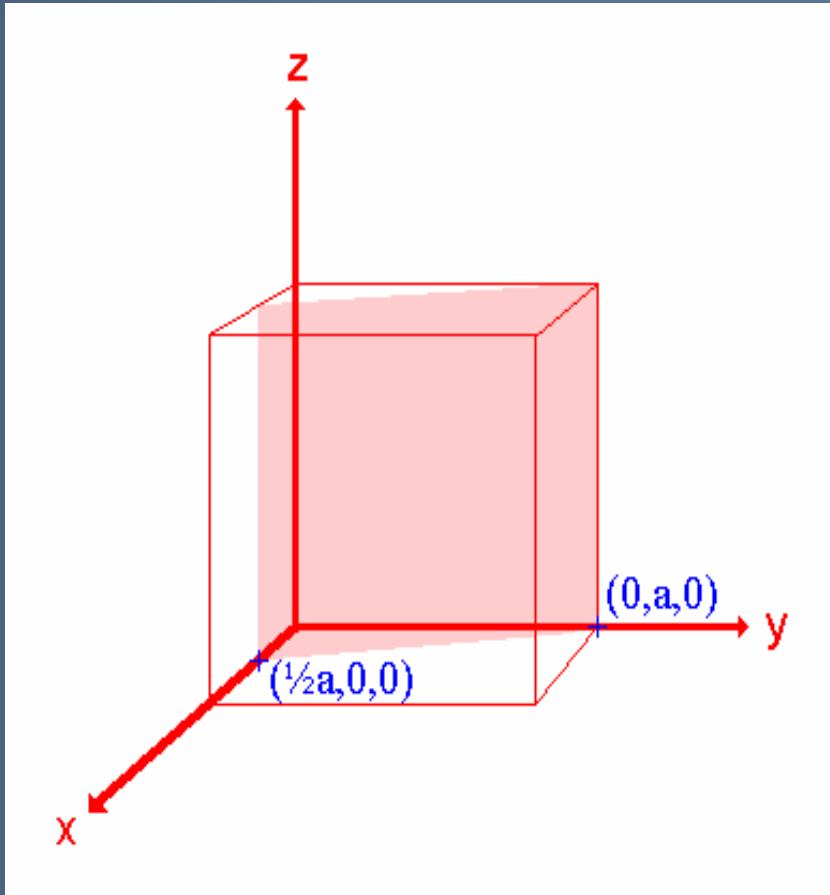   = 1, 1, 0
Miller index for this plane : (1 1 0)

Intercepts: a,a,a
Reciprocals: a/a, a/a, a/a
     = 1, 1, 1
Miller index for this plane : (1 1 1)

Examples of Miller Indices

Intercepts: 1/2a, a,∞
Reciprocals: 2a/a, a/a, a/∞
= 2, 1, 0
Miller index for this plane : (2 1 0)

Notes on notation

- (*hkl*) might mean a single plane, or a set of planes
- If a plane cuts a negative axis, we have minus signs in the (*hkl*) (ie. (*h̄kl*))
- Planes are denoted with curly brackets (*hkl*)
- A set of faces are denoted {*hkl*}
- The direction of a crystal (for example, along x for a cubic crystal) is denoted with [*uvw*] (ie. The [100] direction)
- In cubic crystals, the direction [*hkl*] is perpendicular to the plane (*hkl*) having the same indices, but this isn't necessarily true for other crystal systems

{001} face

[100] direction

[001] direction
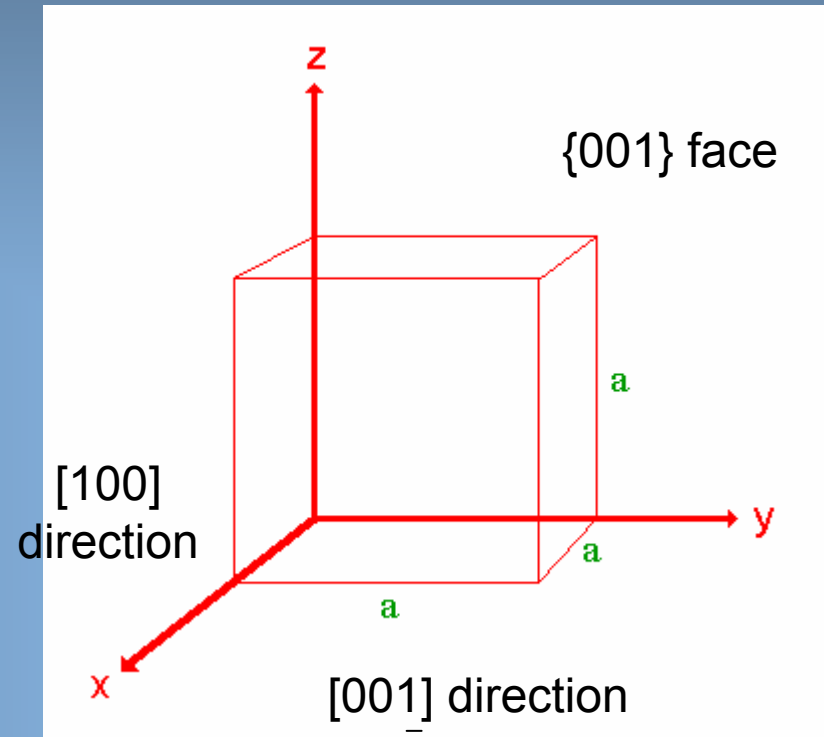
How can we look at crystals?
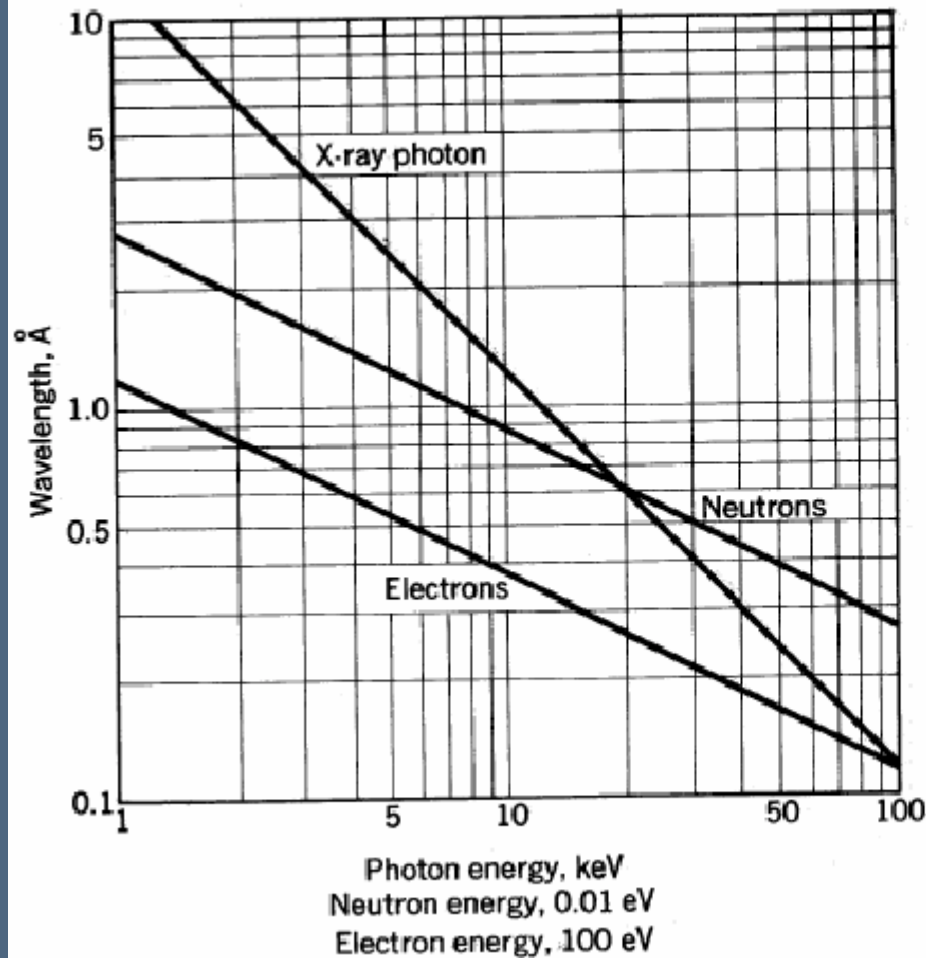
Why do we use x-rays, neutrons and electrons to investigate matter?

We need to use particles with wavelengths ~ 2 Å (remember – matter has wave-like characteristics)

Neutrons -- 20 meV

X-rays -- 6 keV

Electrons -- 0.35 eV

Wave length λ versus energy E

momentum p

Light: $\lambda = c / \nu$ $\qquad$ $h \nu = E = c\,p$

$\therefore$ $\lambda = h / p = c\,h / E$

Matter: non-relativistic, mass m

$\lambda = h / p = h / m\,v$ (de Broglie wavelength)

$E = p^2 / 2m$ $\qquad$ $p = \sqrt{(2mE)}$

$\therefore$ $\lambda = h / \sqrt{(2mE)}$

What happens during a diffraction experiment?

- X-rays (or neutrons, or electrons) of a single wavelength (and therefore, energy) are incident upon a crystal. The incoming rays are of the proper wavelength for diffraction (on the order of the interatomic spacing), and thus we see diffraction peaks at certain values of θ, the scattered beam angle. Each one of these peaks is from a plane of atoms within the crystal. This is an <u>elastic</u> process.

Diffraction peaks are observed as a function of scattered angle

Miller indices for planes of atoms
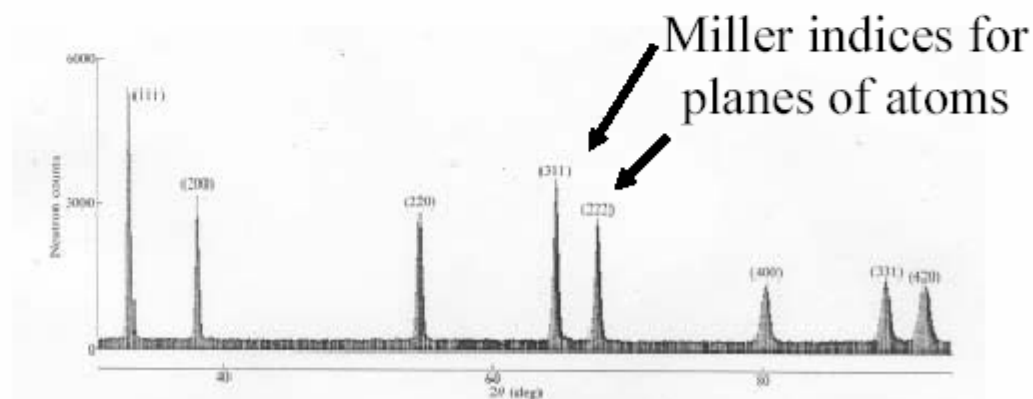
FIG. 58. A section of a powder diffraction pattern for nickel at a wavelength of 1·14 Å recorded on the PANDA diffractometer at A.E.R.E.-Harwell using a germanium monochromator. Counts are made at intervals of 0·1° of 2θ. (Courtesy of R. F. Dyer.)

Experimental setup

Because there are many different planes of atoms, we will see reflections at many different angles. The particular crystal structure of a material can be obtained by observing which reflections *cancel out* because of the arrangements of the atoms (we will talk about this later). Why do we see Bragg peaks at all?
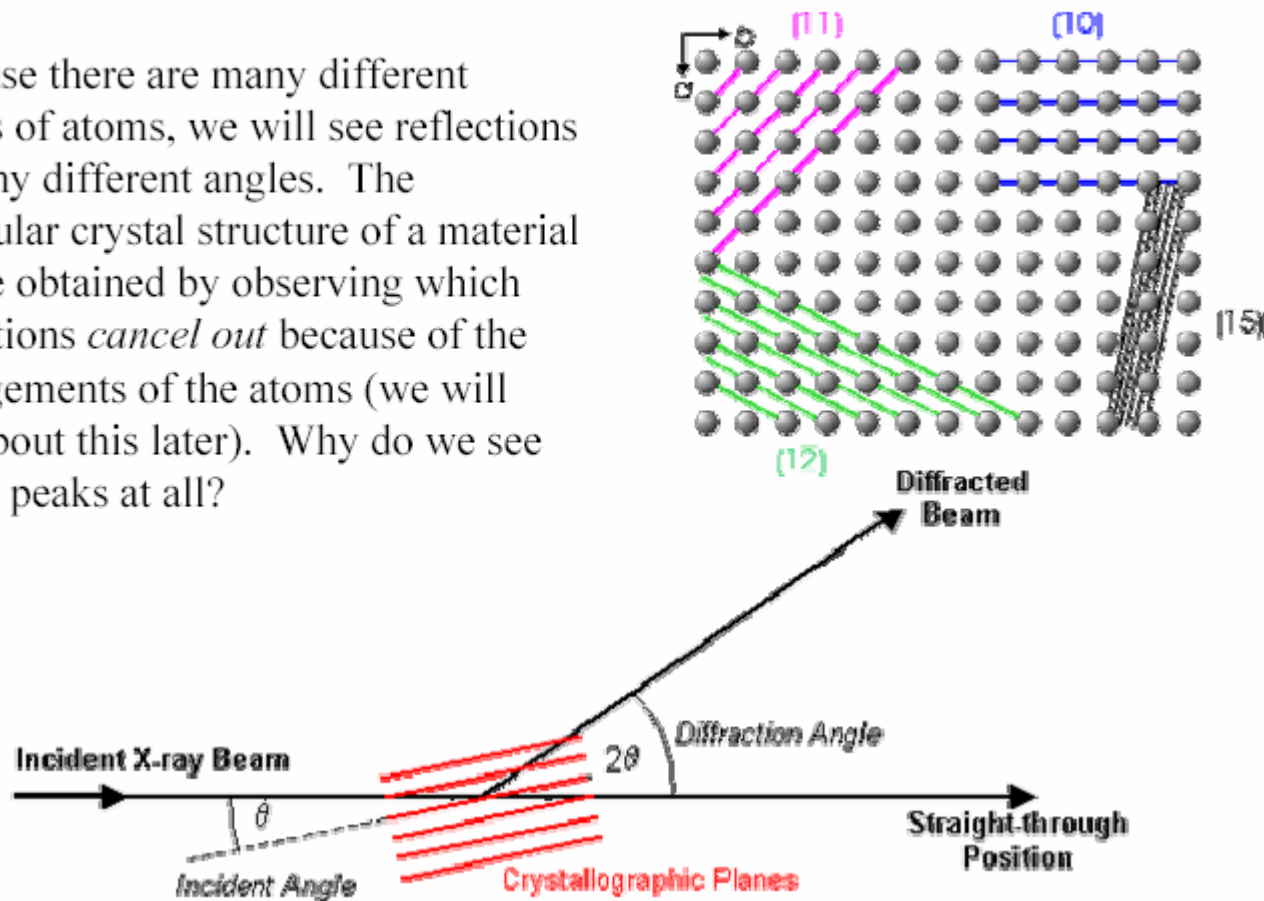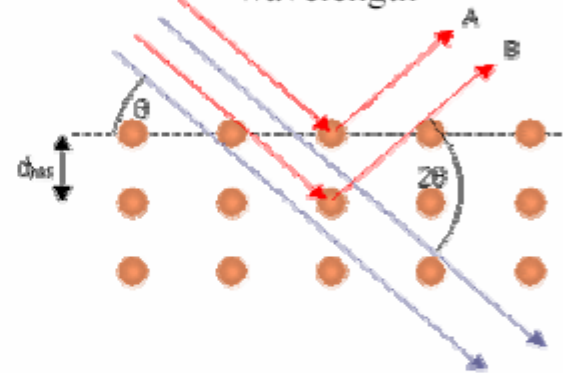
Approach to Bragg scattering

Bragg scattering occurs when reflections from parallel beams interfere constructively
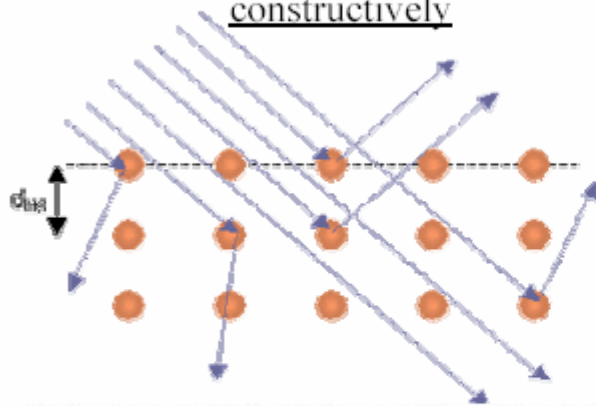
For this to happen, the extra distance travelled by light ray B must be a multiple of the wavelength

W. L. Bragg (1913) came up with this simple theory for x-ray diffraction

Bragg Condition for scattering from successive planes

$2d \sin \theta = n \lambda$: Condition for constructive interference of x-rays – Bragg peaks
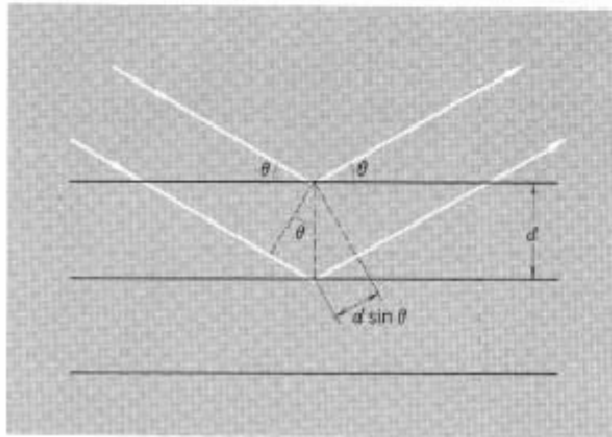
Evolution of the X-ray Powder Diffraction Pattern for spherical CdSe NCs
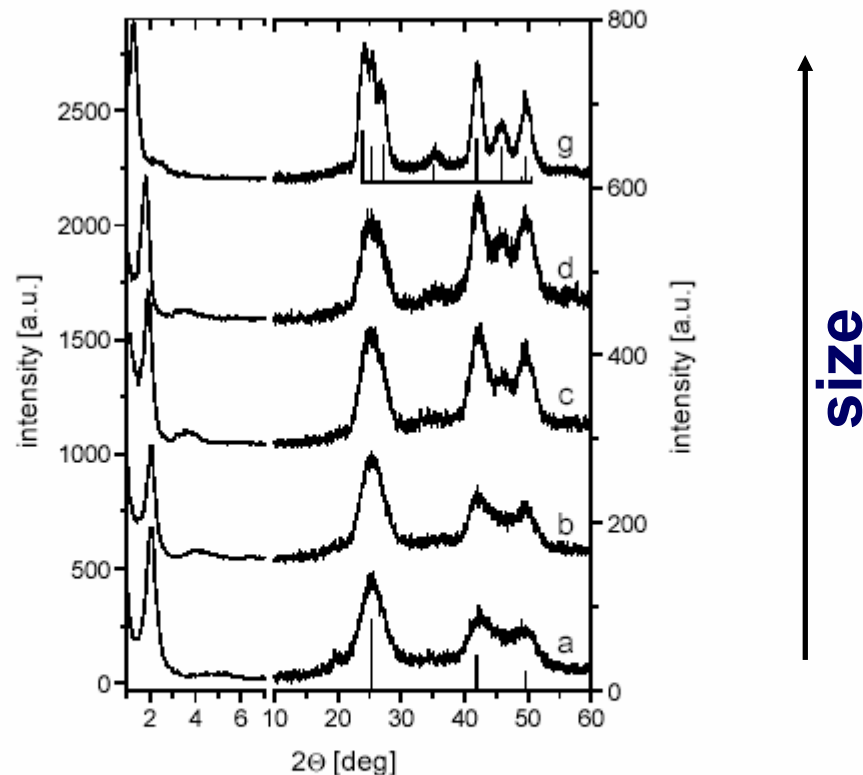
Figure 2.4. *Small-angle and wide-angle powder X-ray diffractograms of a size series of CdSe nanocrystals (samples **a-d** and **g** from Figure 2.2). Vertical lines indicate bulk CdSe reflections (top: wurtzite, hexagonal; bottom: zinc blende, cubic).*

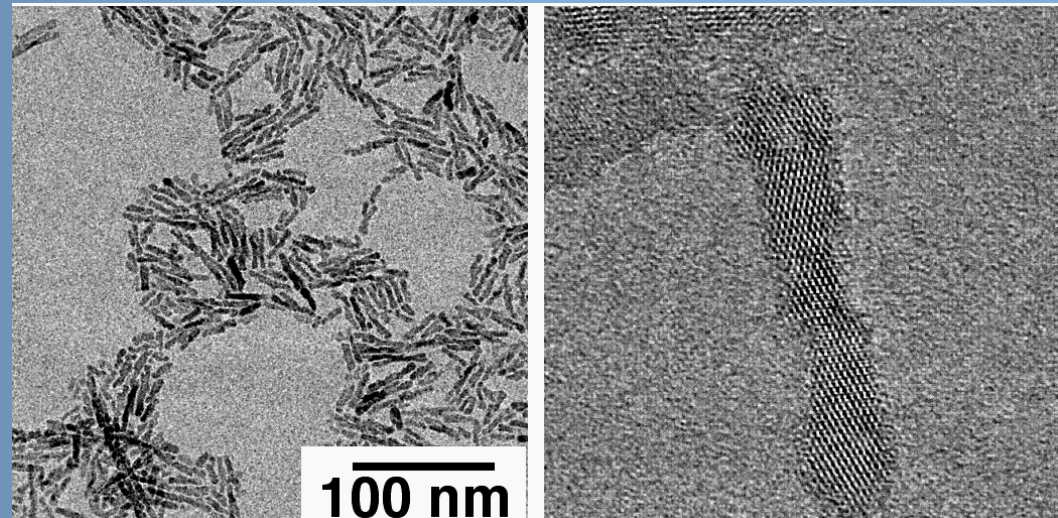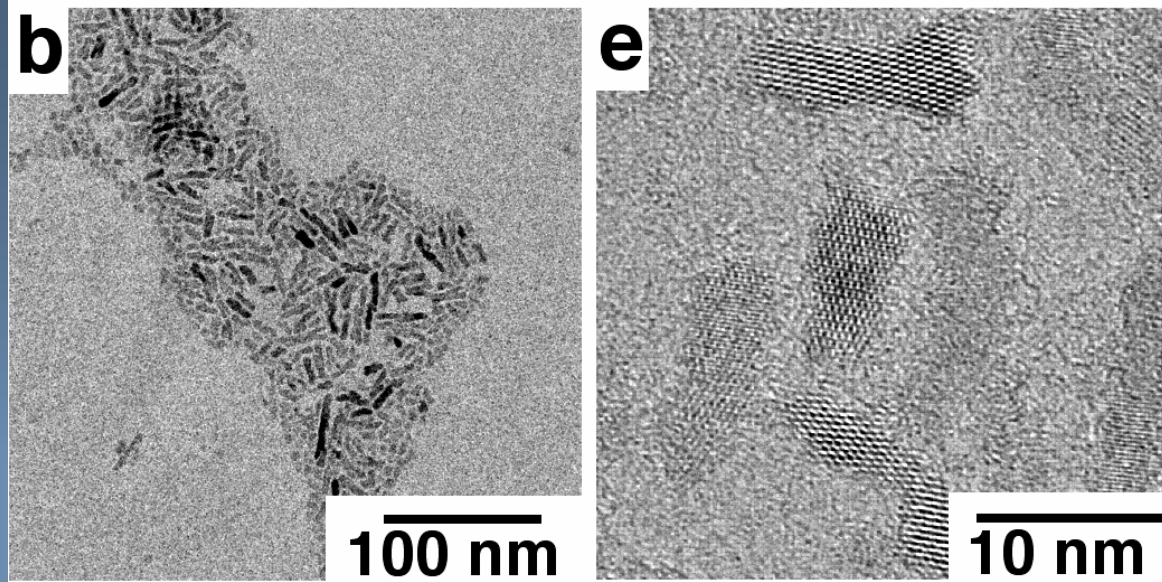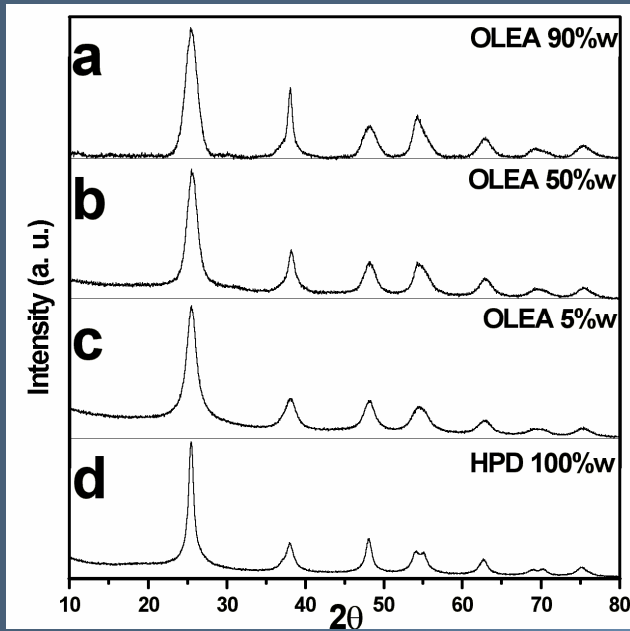**Evolution of the X-ray Powder Diffraction Pattern for spherical ZnO NCs**

WURTZITE

Intensity (a. u.)

size

Bulk ZnO

a
b
c
d

2Θ

R=0.12

40 nm   5 nm

R=0.52

40 nm   5 nm
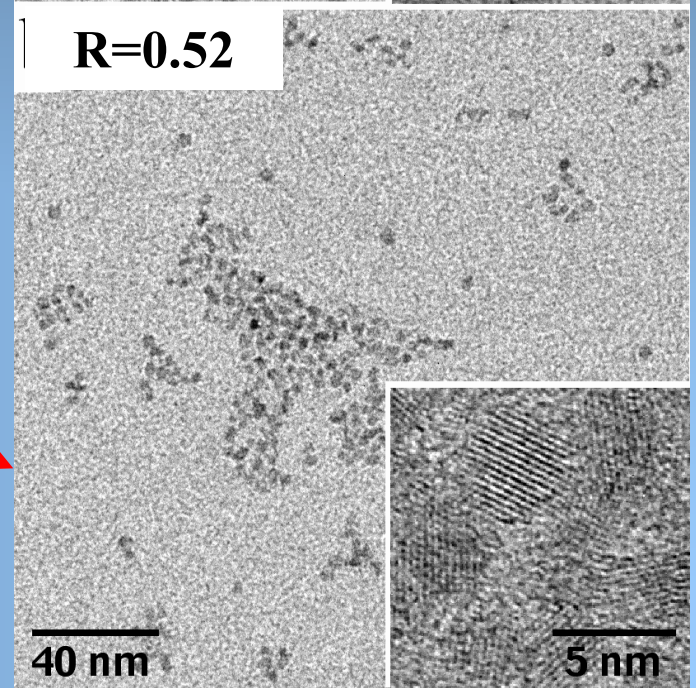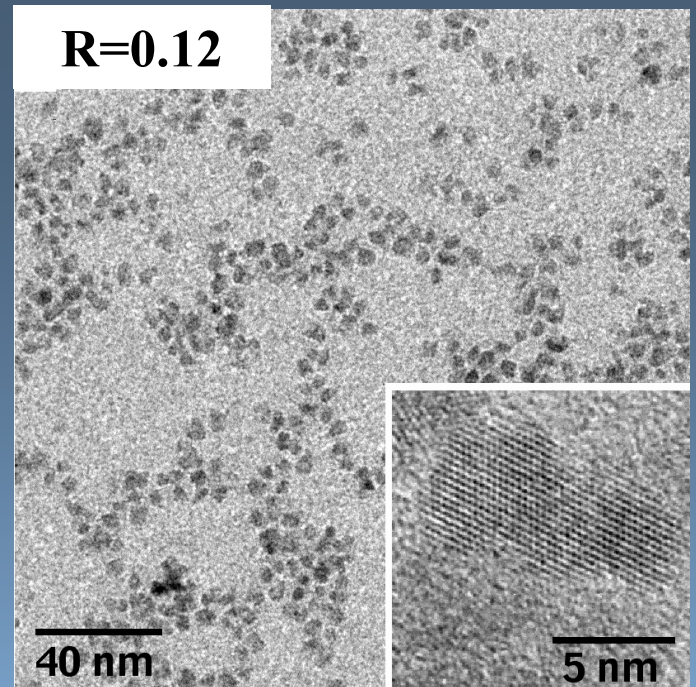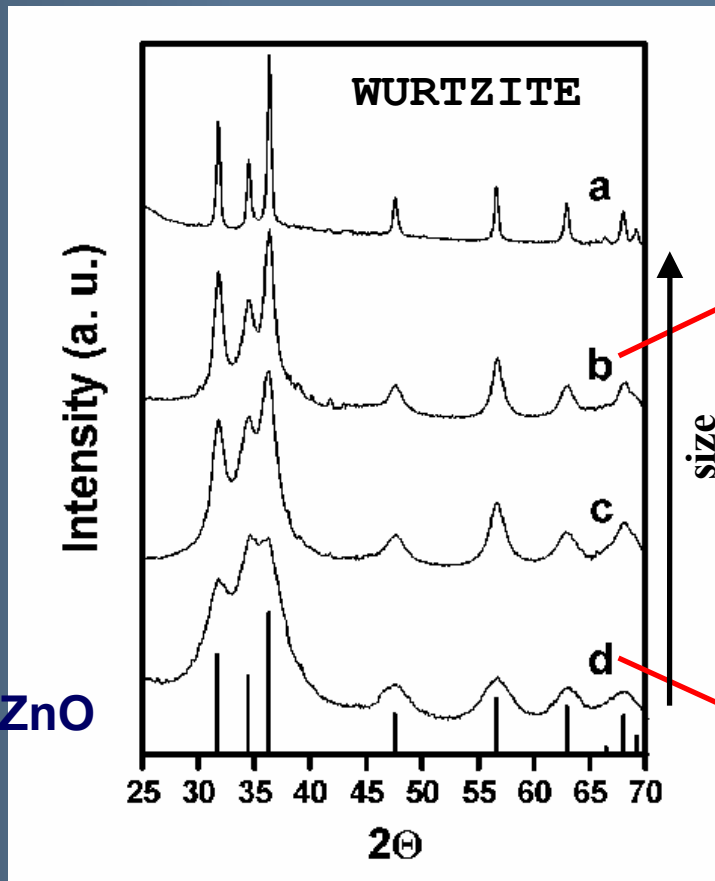
XRD and TEM data

high $[Ti(OPr^i)_4]$, TMAO catalyst
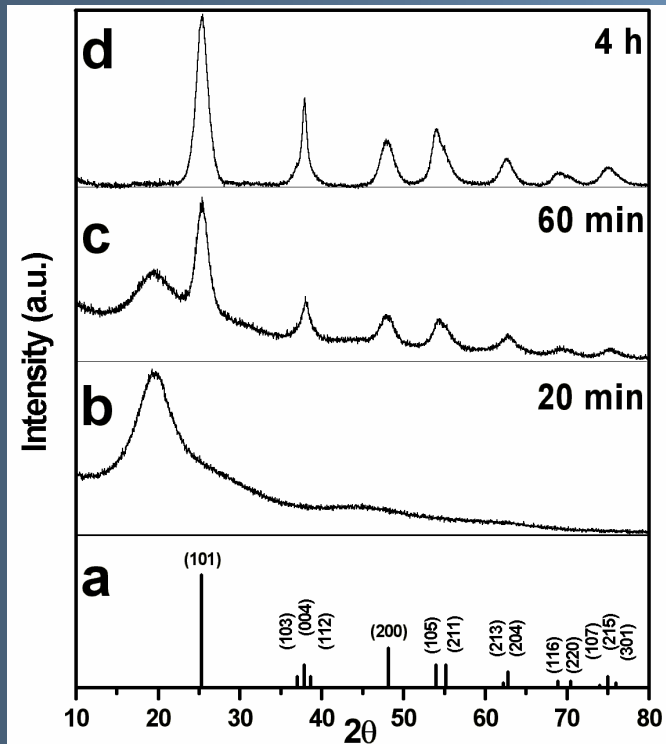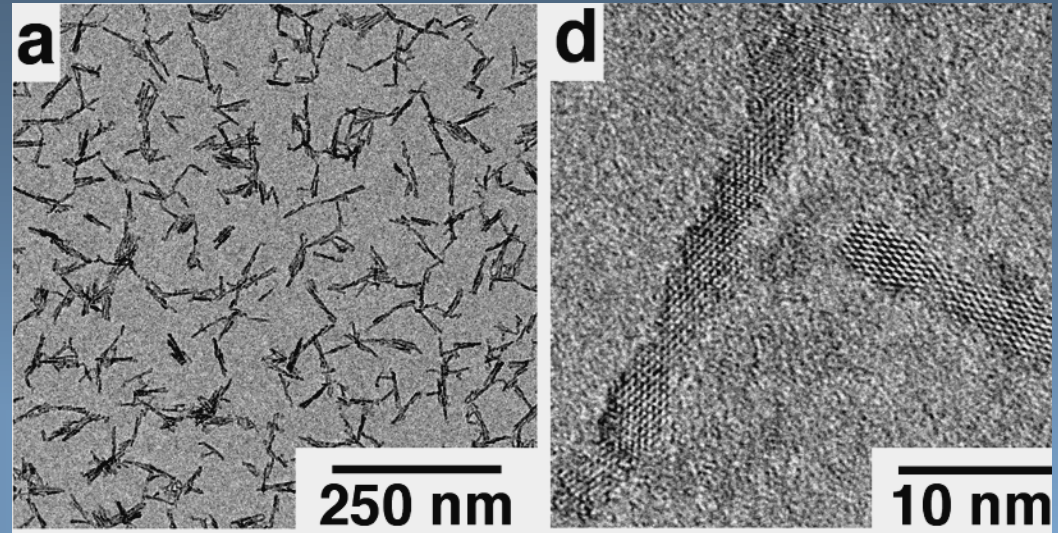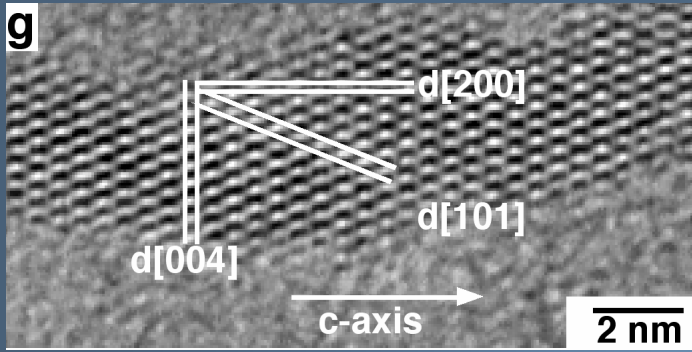
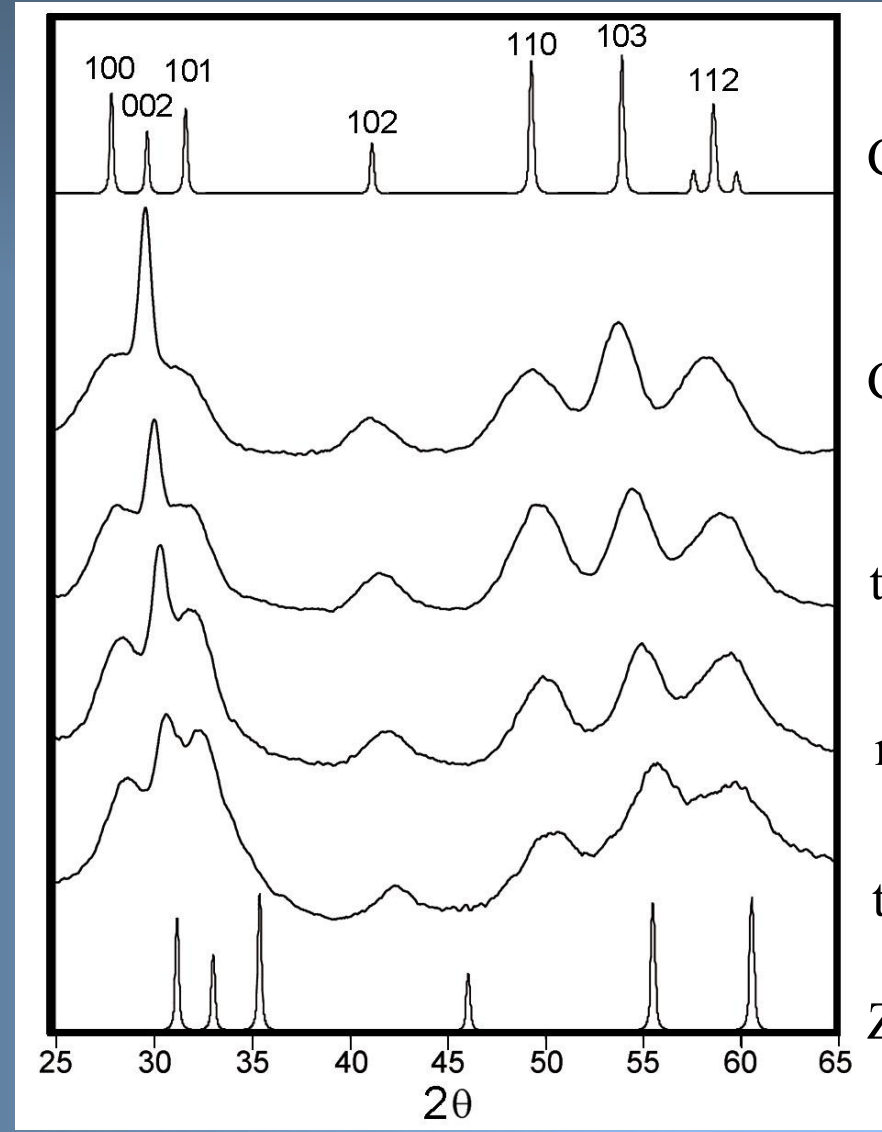low $[Ti(OPr^i)_4]$, TMAO catalyst

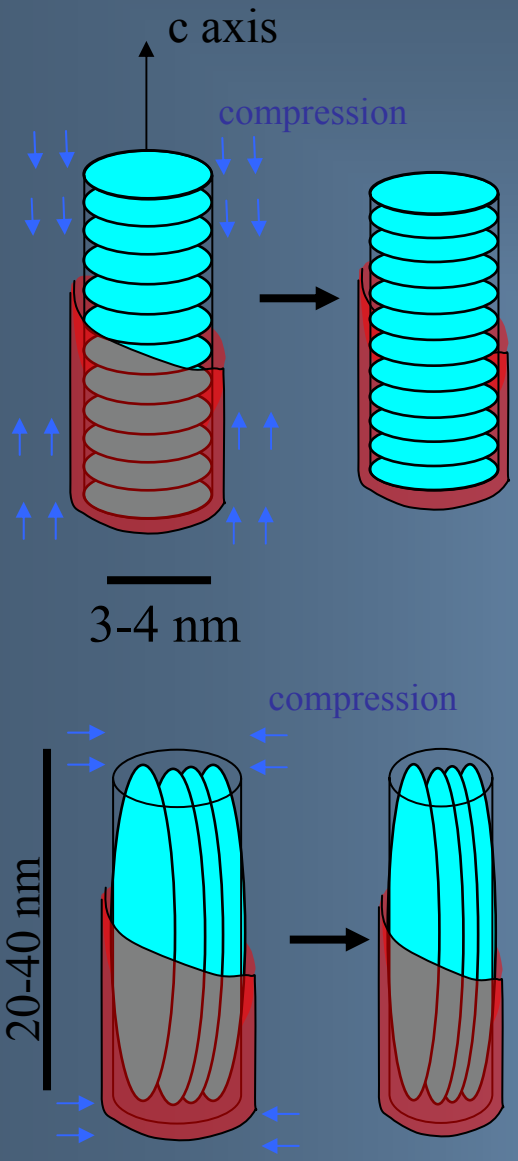OLEA 50% w/w

slow H₂O in-situ release

OLEA + Ethylenglycol

↓

ESTER + H₂O
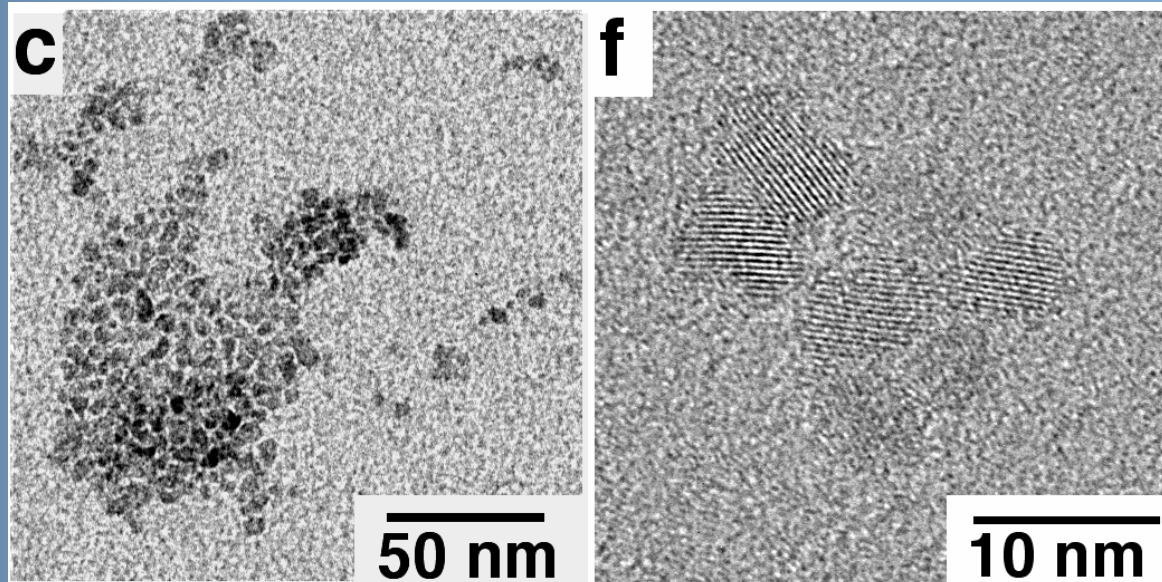
X-ray diffraction for core-shell CdSe nanorods

c axis

compression

3-4 nm

compression

20-40 nm

CdSe bulk

CdSe core

thin shell

medium shell

thick shell

ZnS bulk

100
002
101
102
110
103
112

25 30 35 40 45 50 55 60 65

2θ

Optical spectroscopy
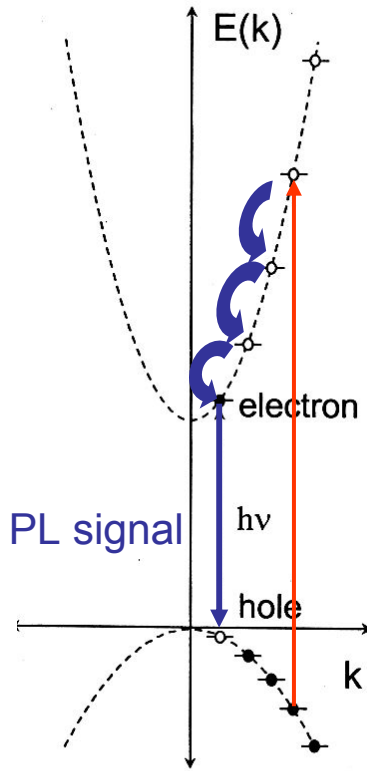## Processes occurring on a colloidal semiconductor nanocrystal following electronic excitation

e^-

h^-

hν

CB

VB

hν

+

+

+

A-

A

hν

D+

D
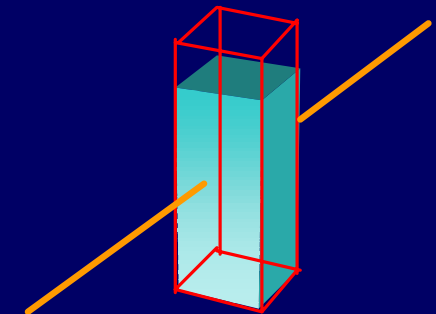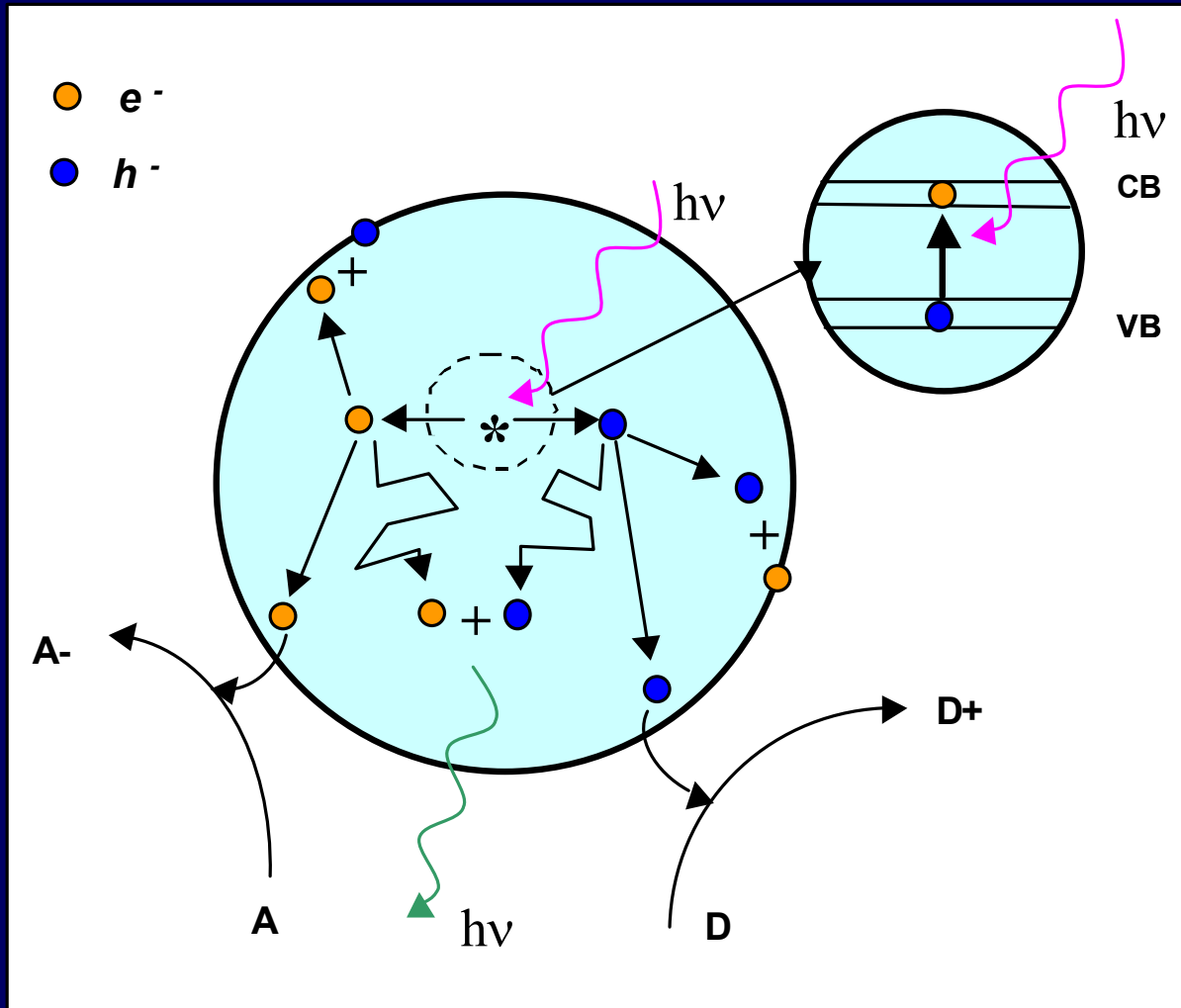
Colloidal nanocrystals dispersions
are optically clear :
Fundamental processes
can be studied

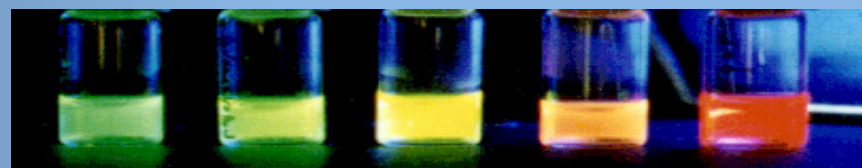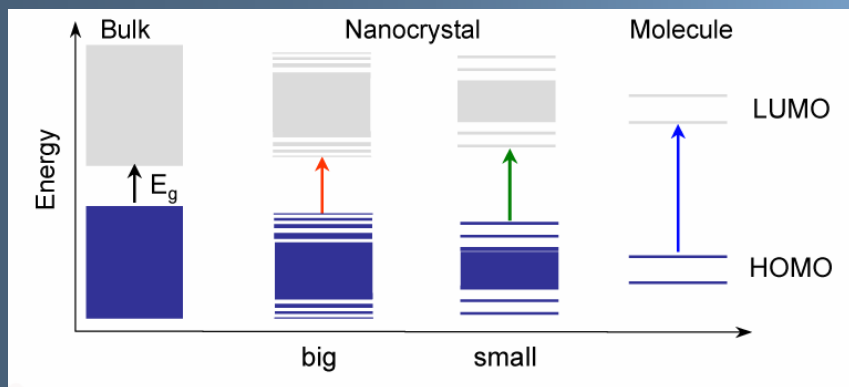# Optical transitions
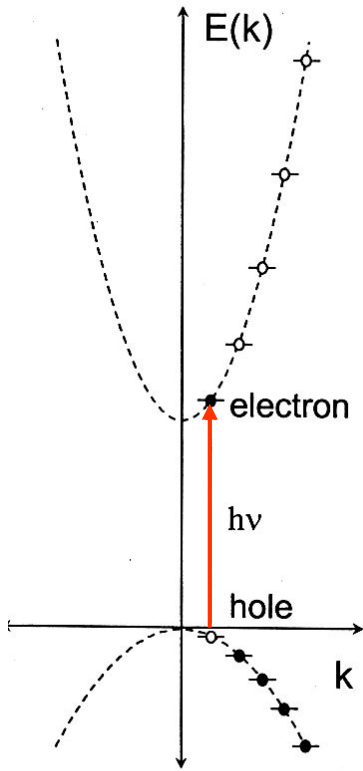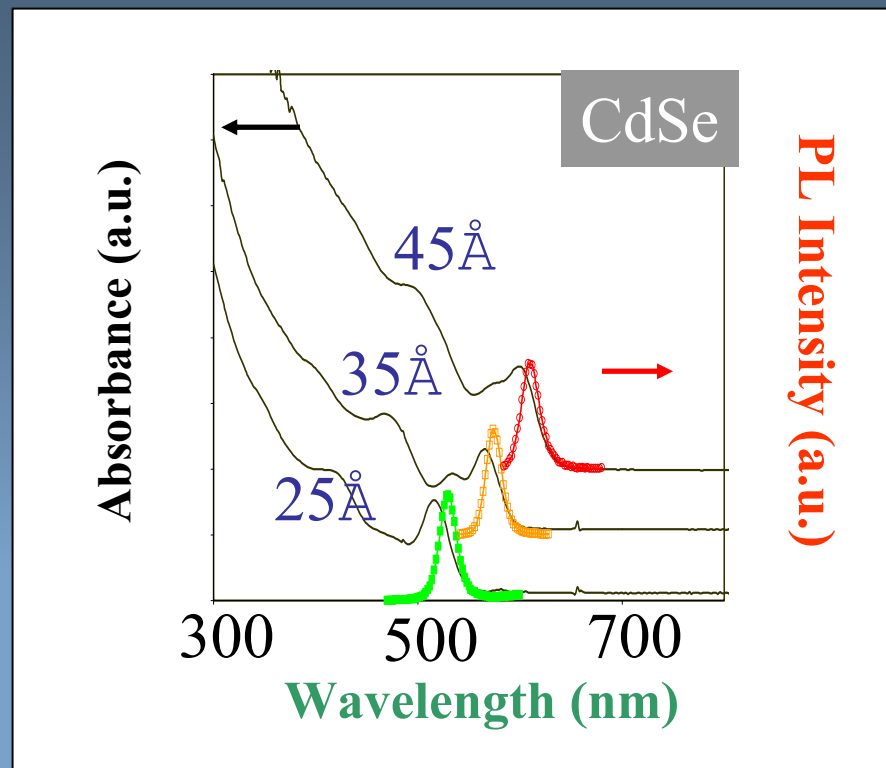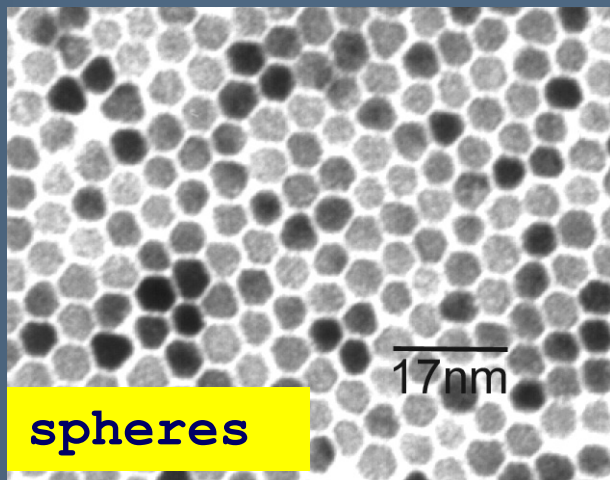

Absorption
allowed transitions

Photoluminescence
emitting transitions
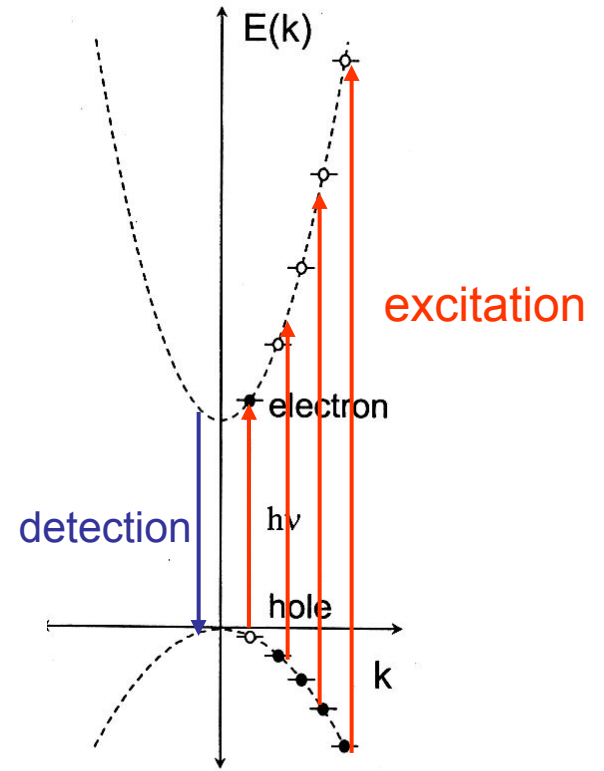
PLE
Excited states of <u>one</u> specific emitting transition

Size-Dependent Optical Properties of Semiconductor Nanocrystals

spheres

17nm

CdSe

Absorbance (a.u.)

PL Intensity (a.u.)

45Å

35Å

25Å

300   500   700

Wavelength (nm)

Bulk   Nanocrystal   Molecule

Energy

E_g

LUMO

HOMO

big   small

Size

1) the positions of both the exciton and the PL peaks are related to the mean NC size

2) the width of the peaks reflects the size-distribution
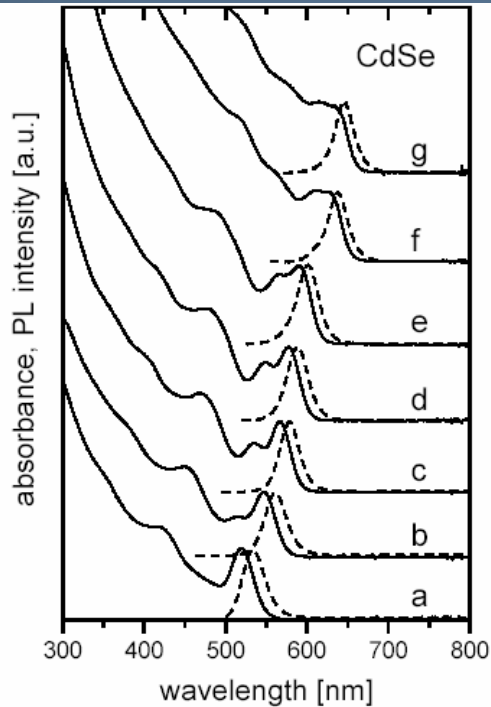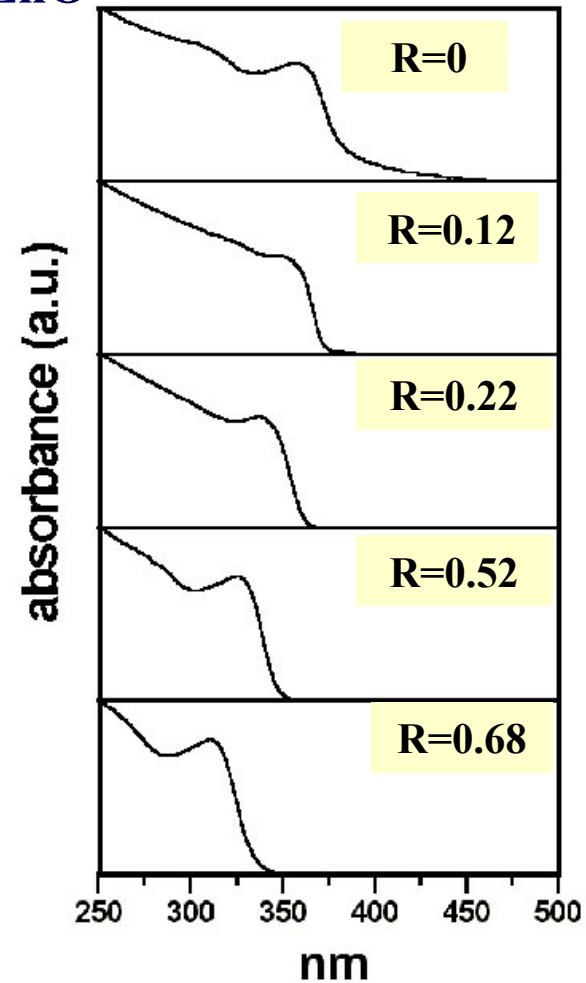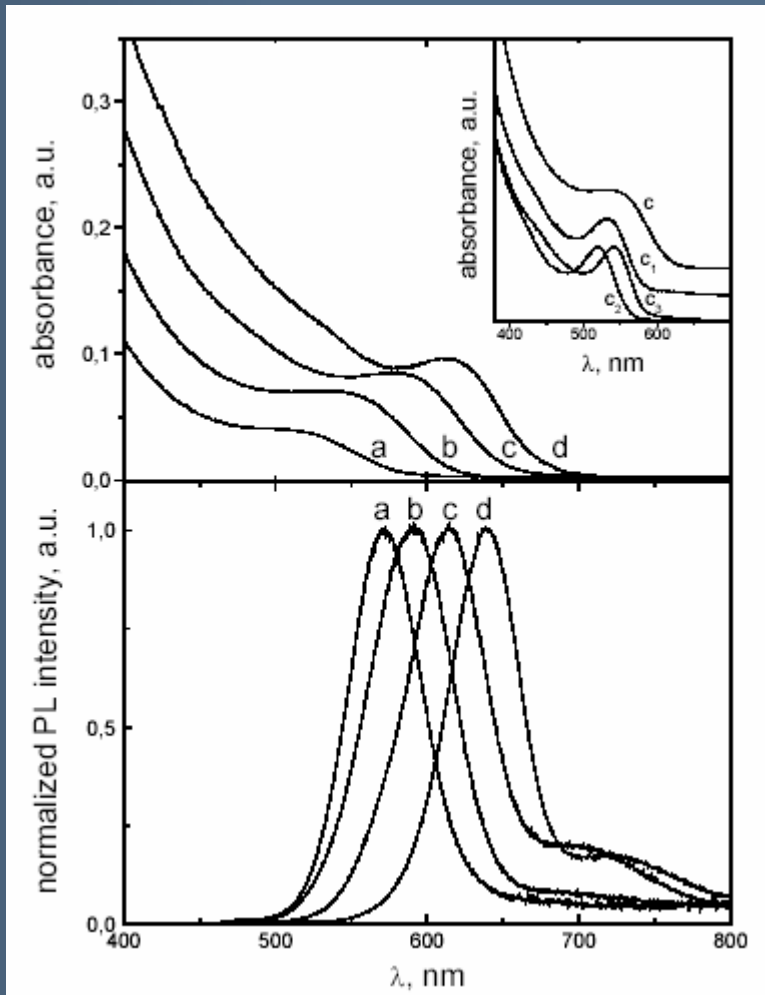
Monitoring real-time particle growth

Figure 2.2. *Room temperature absorption and emission spectra of CdSe nanocrystals monitored during the growth at 300°C.*

ZnO

R=0

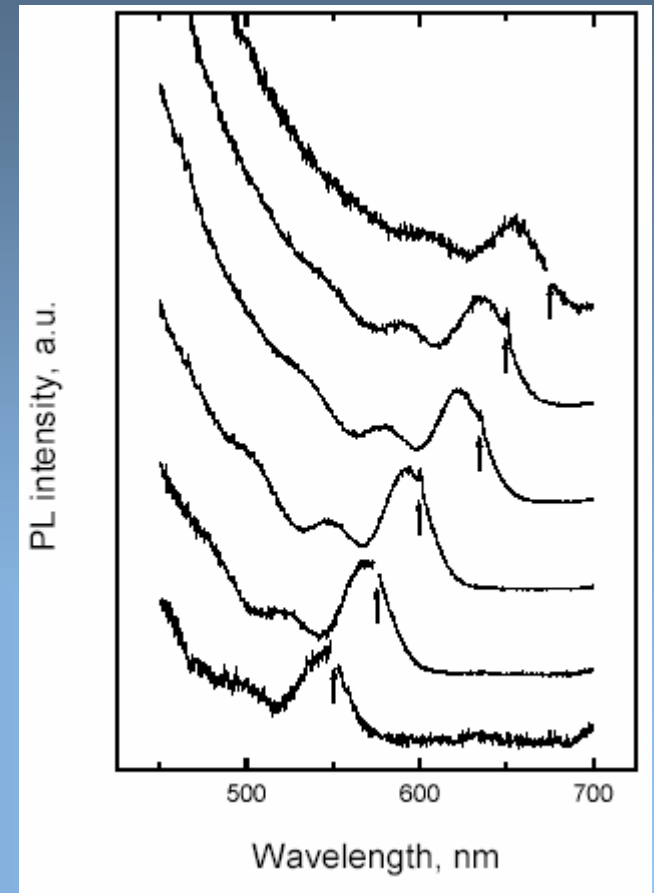R=0.12

R=0.22

R=0.52

R=0.68

size

The final NC size is related to the exciton absorption position and band width

absorption and photoluminescence (PL) spectra

PL excitation (PLE) spectra

CdTe nanocrystlas

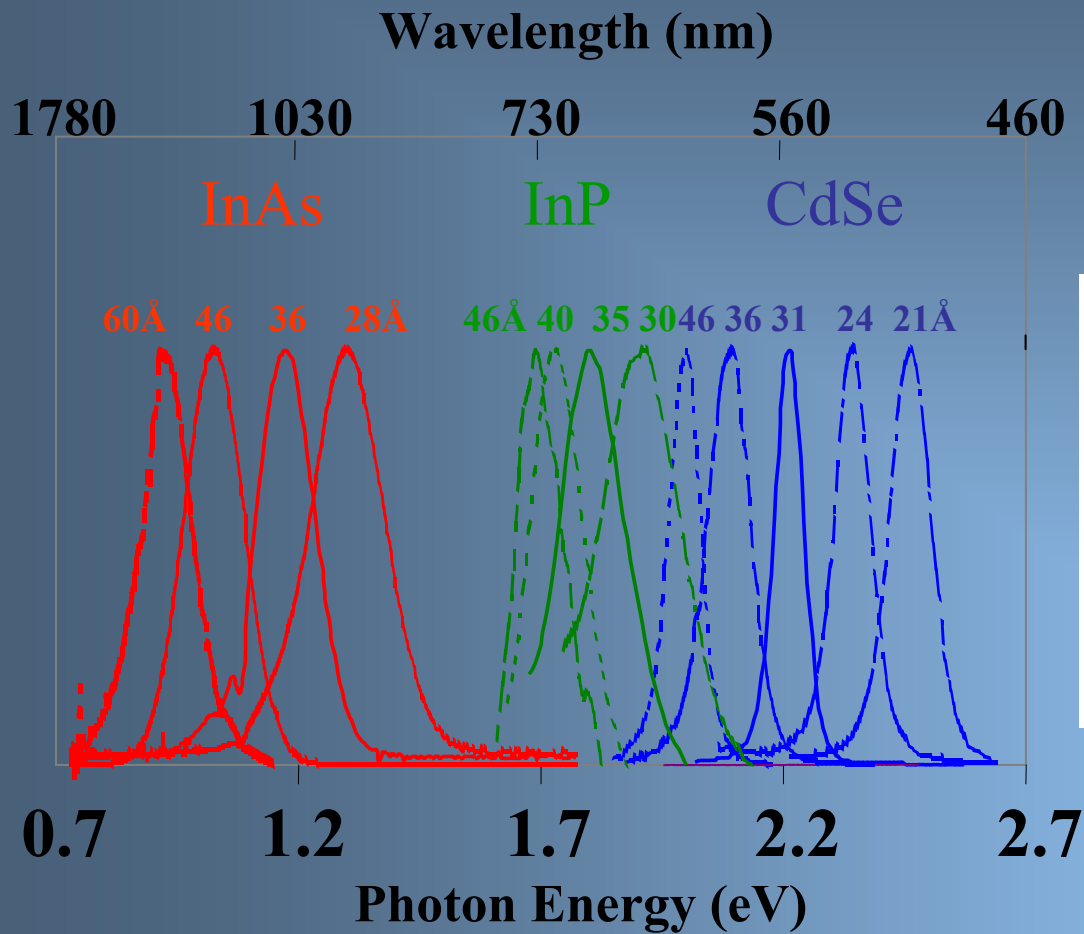# Size Dependent Photoluminescence (PL) of Semiconductor Nanocrystals

Wavelength (nm)

1780   1030   730   560   460

InAs   InP   CdSe

60Å 46 36 28Å   46Å 40 35 30 46 36 31 24 21Å

0.7   1.2   1.7   2.2   2.7

Photon Energy (eV)

Figure 1.1. *Size-dependent change of the photoluminescence color of colloidal solutions of CdSe nanocrystals passivated with a ZnS shell. The smallest (~1.7 nm) CdSe particles emit blue, the largest (~5 nm) – red.*

Rods vs. dots

hn

hν

A−

D+

A

D

e⁻ / h⁺ recombination increases for smaller size due to:
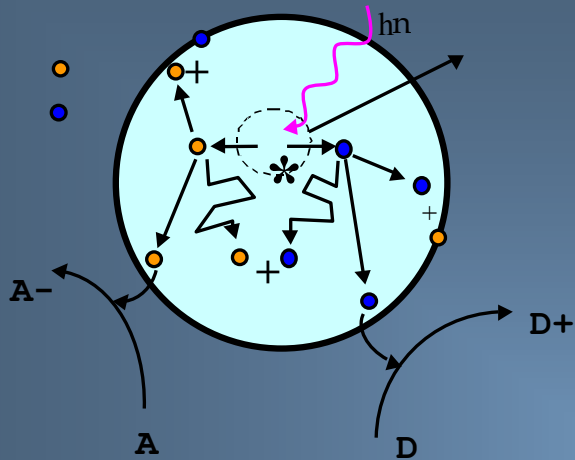
e^- / h^+ recombination increases for smaller size due to:

➢ surface trapping sites

➢ lower carrier delocalization
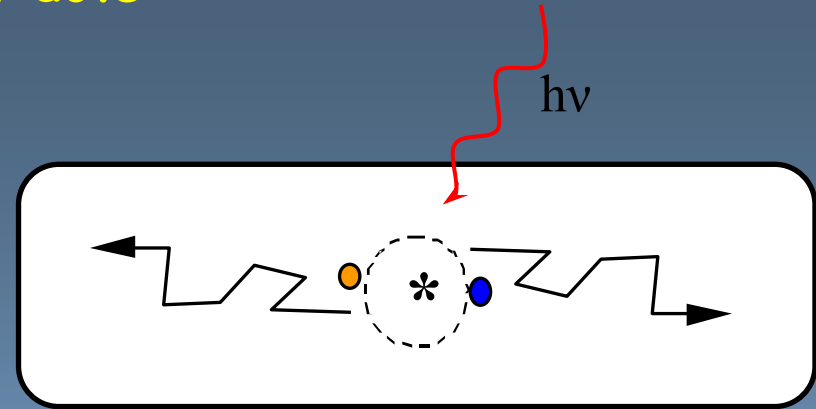
**e^- / h^+ recombination can decrease:**

➢ Higher SURFACE DENSITY of active sites for reactions at the interface

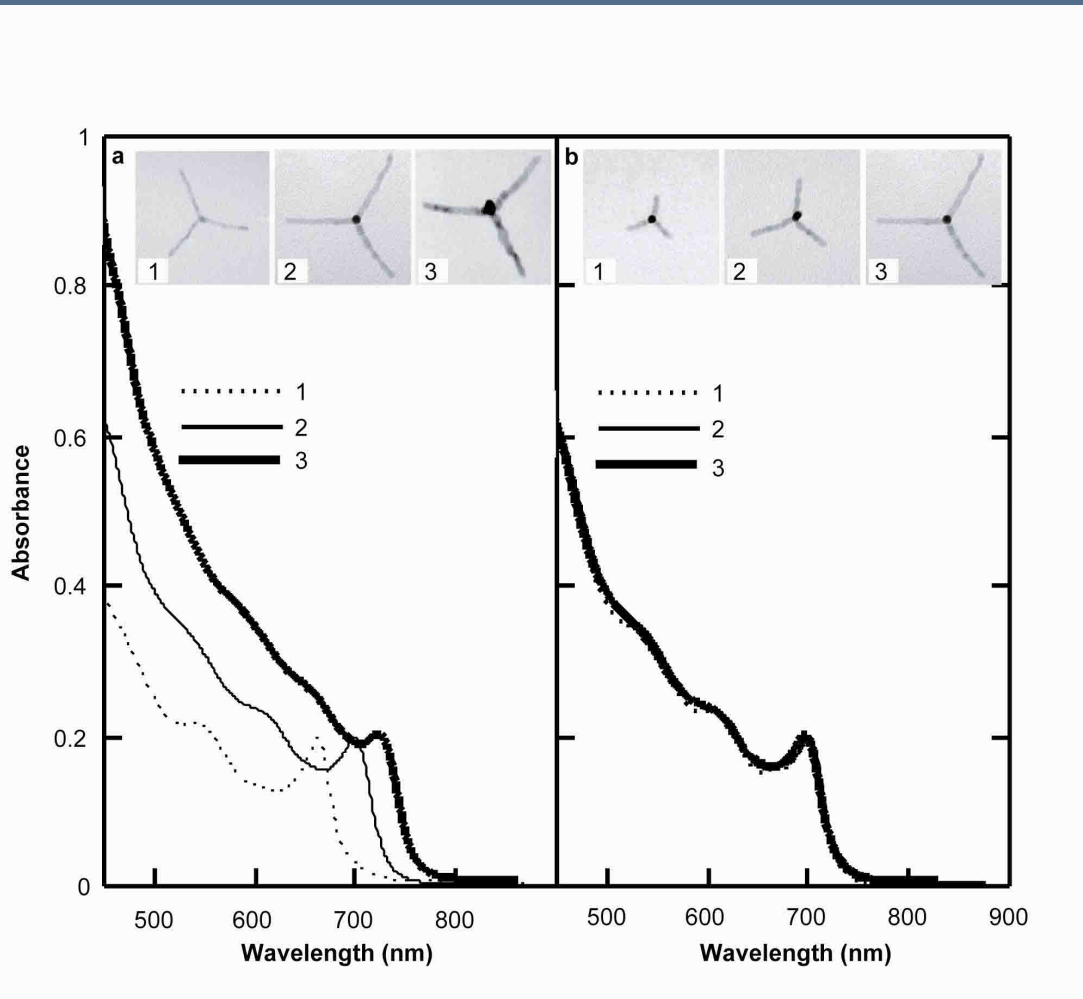➢ Increased DELOCALIZATION of carriers may compensate for surface trap states

Interaction

Weak   Strong
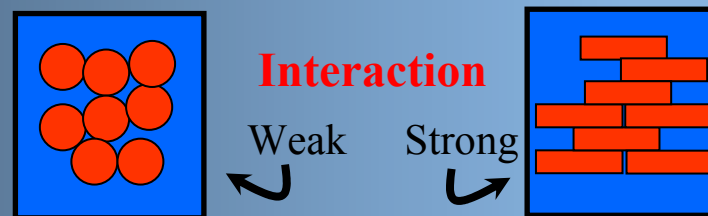
• Van der Waals attraction scale as the volume

• Forces increase with contact area

• Rod aggregation more effective than spheres

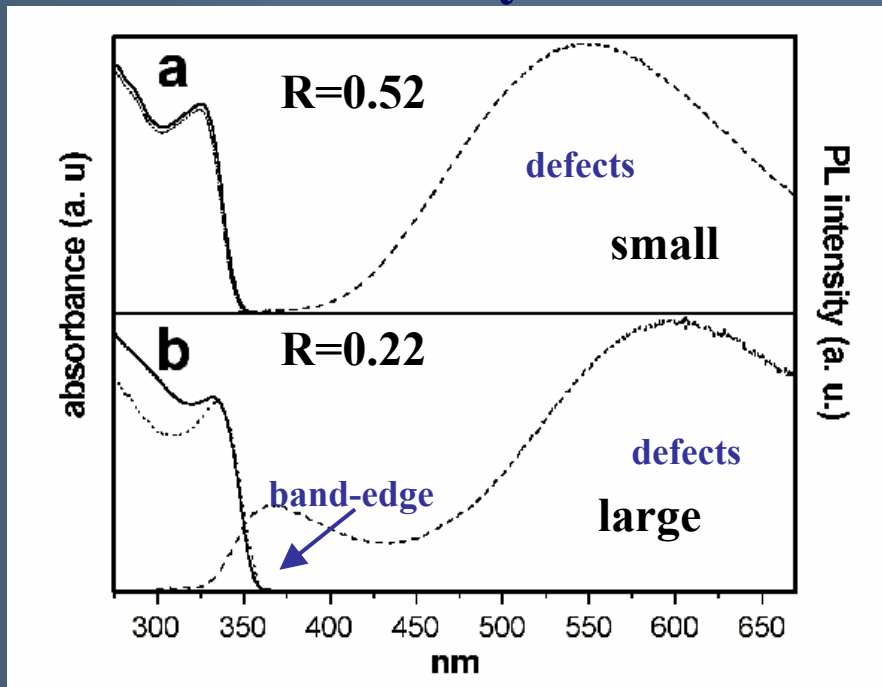# Shape-Dependent Optical Properties of Semiconductor Nanocrystals
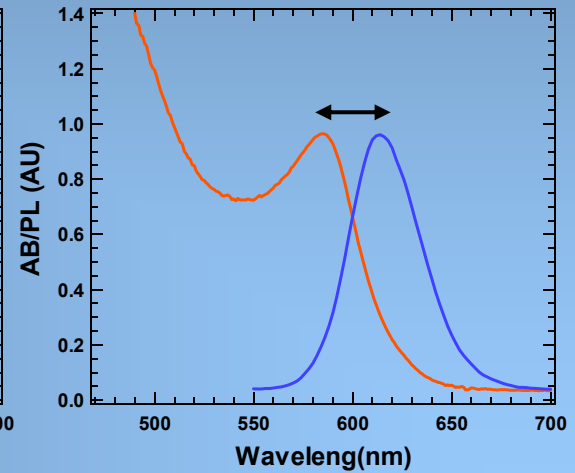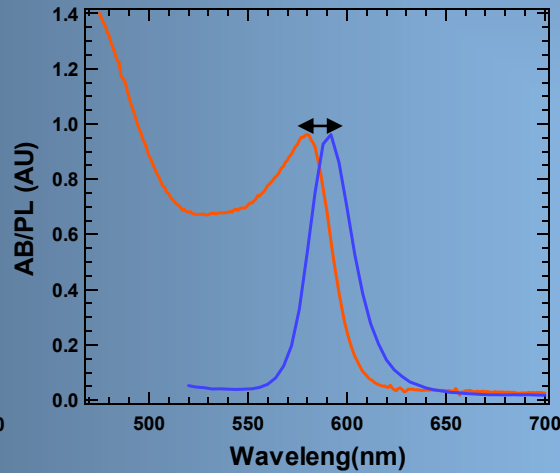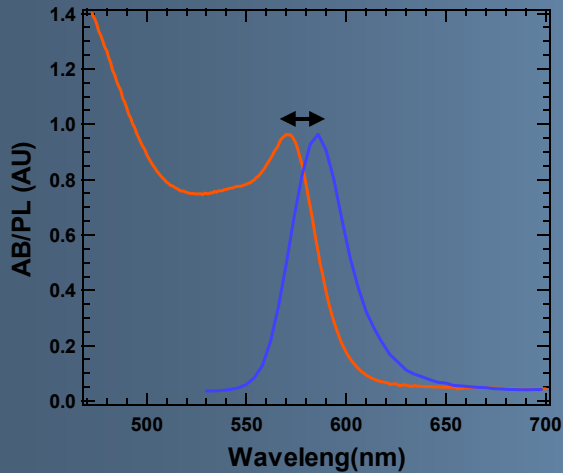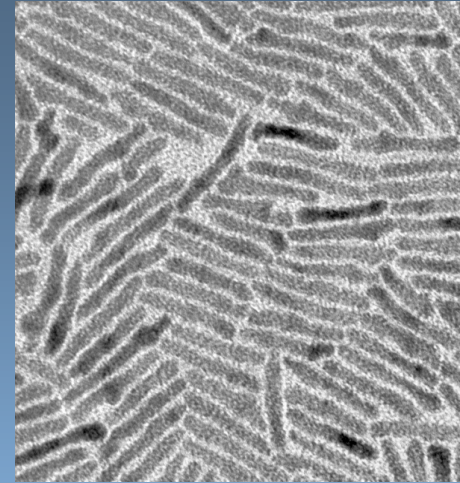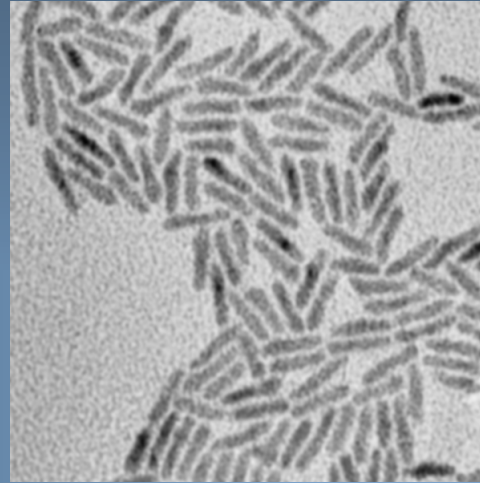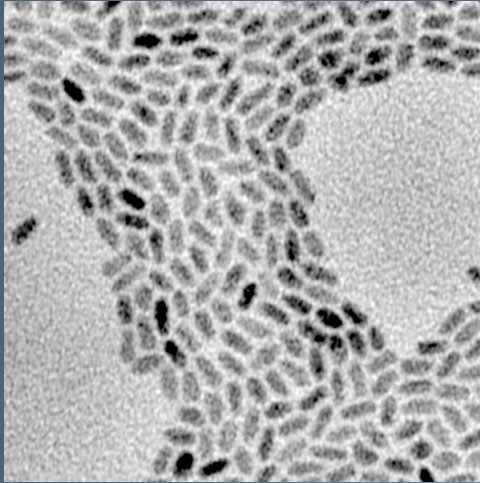
Larger Stockes Shift (less overlapping between absorbing and emitting states)
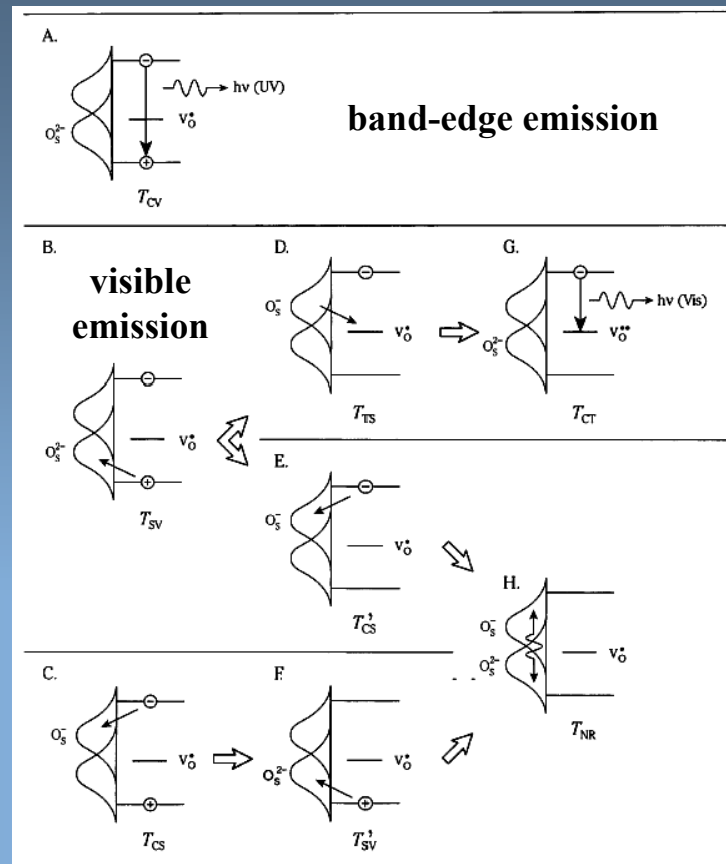
The band gap depends on the arm's diameter

Trap-State Photoluminescence

ZnO nanocrystals

R=0.52

defects

small

R=0.22

defects

large

band-edge

λ_{ex}=280 nm

Mechanism of Fluorescence

band-edge emission

visible emission
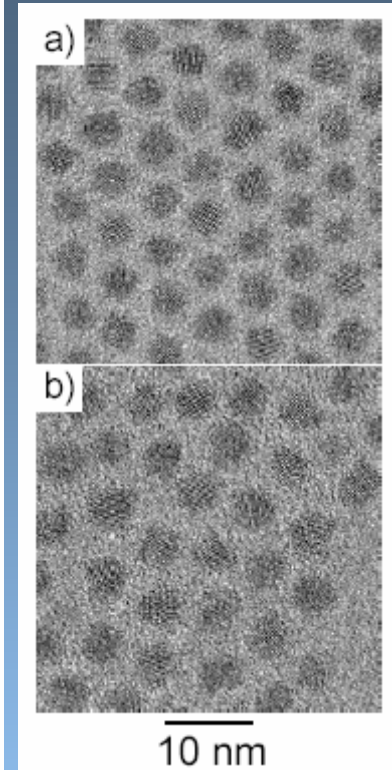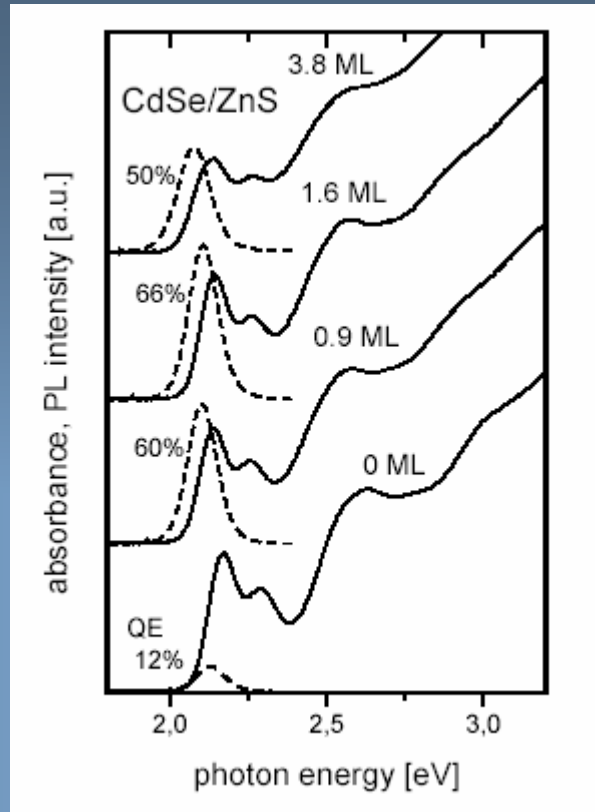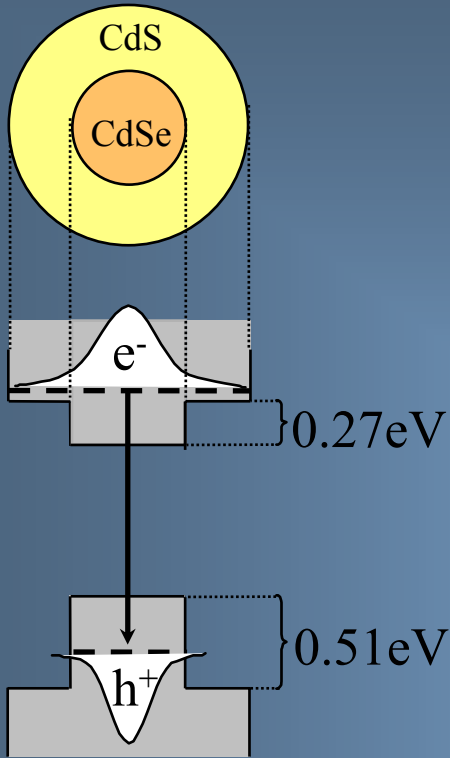
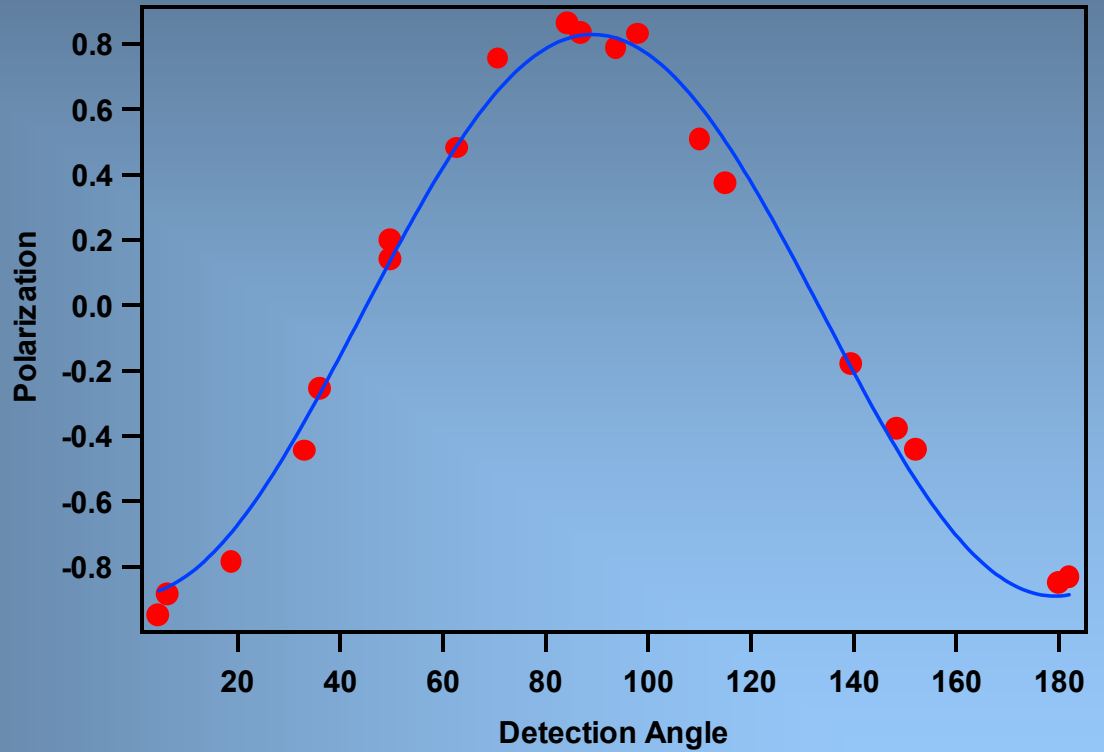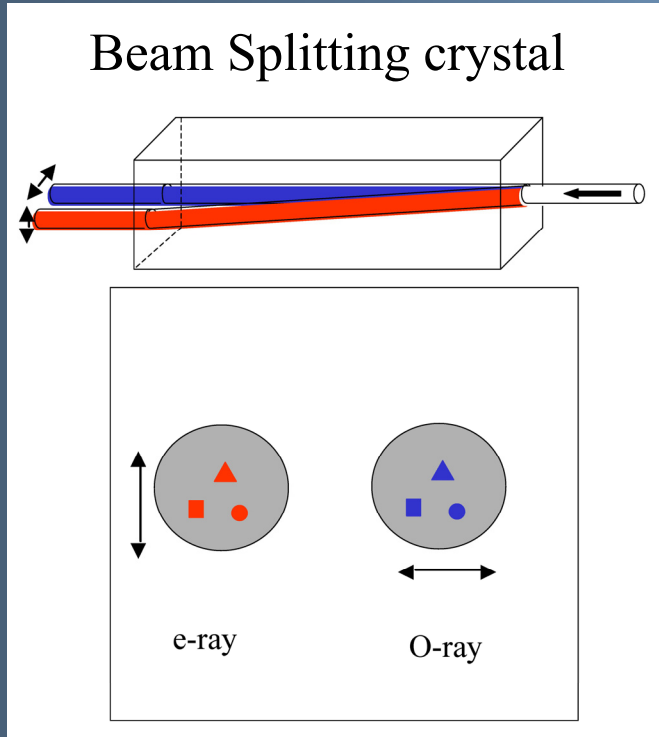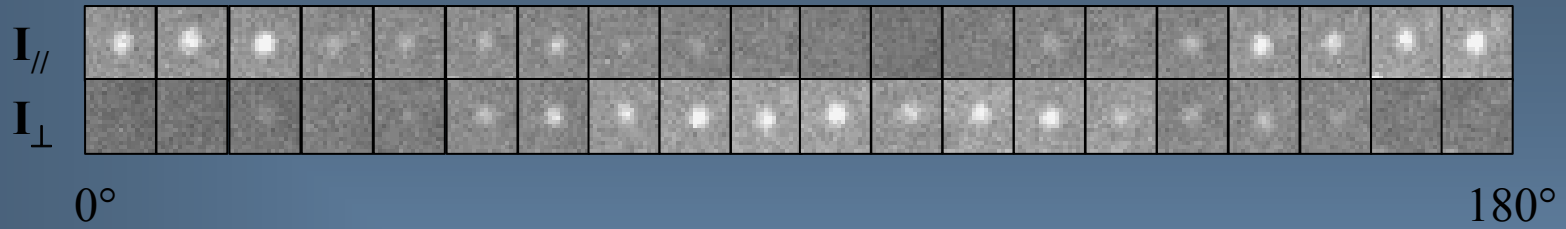Generally, defect-related PL is not correlated with the particle size

Unpassivated sites may be available for catalysis!

Epitaxial growth of stable, highly luminescent core/shell nanocrystals
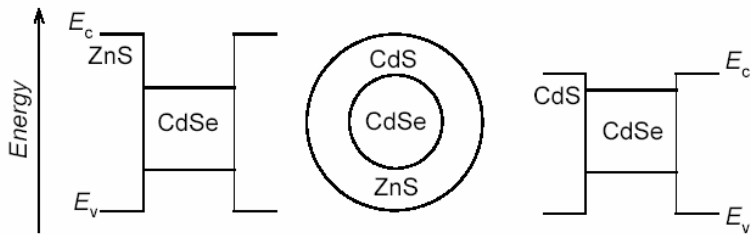
Scheme 2.1. *Schematic representation of band structure of core shell CdSe/ZnS and CdSe/CdS nanocrystals*

Polarized Emission from Single Nanorods

$I_{//}$

$I_{\perp}$

0°   180°

Beam Splitting crystal

e-ray

O-ray

Polarization

Detection Angle

$p = (I_{\perp} - I_{//}) / (I_{\perp} + I_{//})$