Chapter 3 Properties and Characterization of Nanoparticles

3.1 General properties of Nanoparticles

General

**Finite size effect*

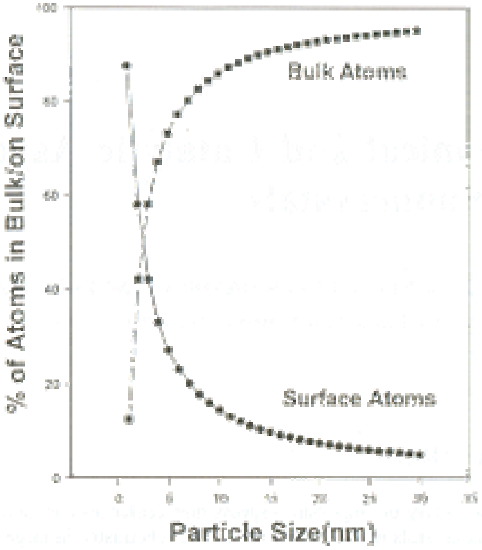
- *Small number of atoms*
- *quantum confinement (size) effect*

  "particle-in-a box"

  - *discrete electron energy levels*
- *perfect crystalline*

**Surface/interface effect*

- *Large fraction of surface atoms*
- *symmetry breaking at surface*
  - *large surface energy*
  - *changes in bond structure, atom coordination and lattice constant*

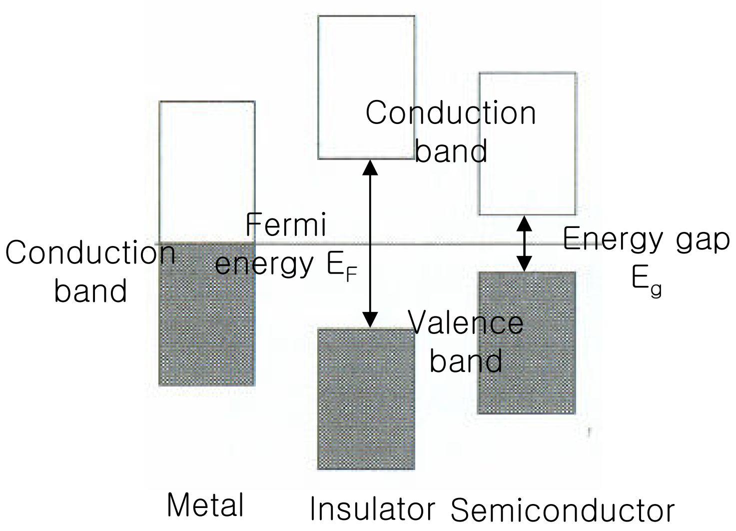


Calculated values form spherical iron nanoparticles

3.2 Quantum size (confinement) effects

- Energy levels of atoms vs. energy band in bulk

- Conductor, semiconductor, insulator



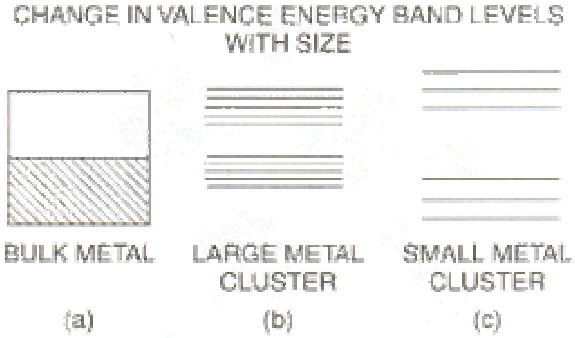
As size decreases(<de Broglie wavelength)*

electrons (and holes) are confined → "particle in a box"

→ *electrons: discrete energy level or level spacing* $> k_BT$

∴

Metals



- *Energy level spacing for metal*

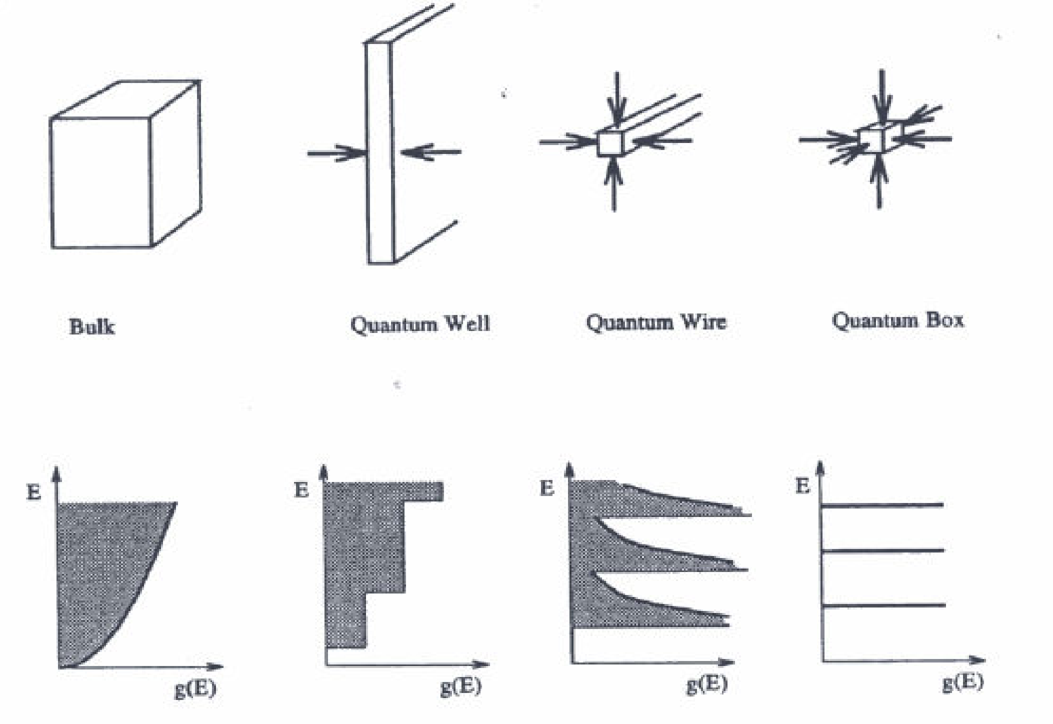
$$\delta = \frac{4E_F}{3N}$$

where E_F: Fermi energy

N: number of electrons in the particles

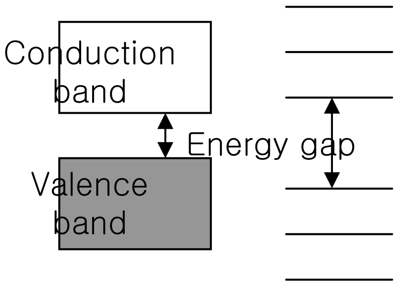
- *level spacing: relatively very small*
- *quantum size effect on electronic and optical properties: not significant even when N = tens, hundreds…*

* Energy states of electrons for bulk, quantum well, wire and dots



Change in the density of states, g(E), as the number of confining dimensions is increased.

Semiconductors

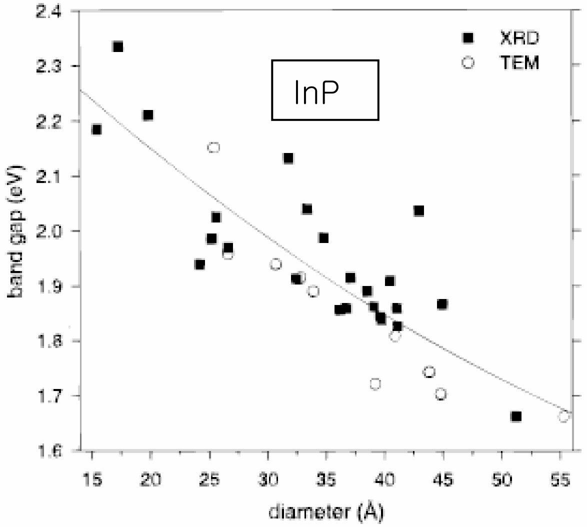


** Electron-hole pairs (excitons)*

- Due to much longer wavelength of excitons in semiconductor(1um compared to 0.5nm for metal) size confinement appears for N=10,000 atoms

- Discrete energy levels

- Increase in bad gap



Excitonic peak position from UV/vis vs nanocrystal diameter as determined by powder TEM (circles) or XRD (squares).

cf. Insulators?

3.3 Structural effect

- Mostly related with surface properties…

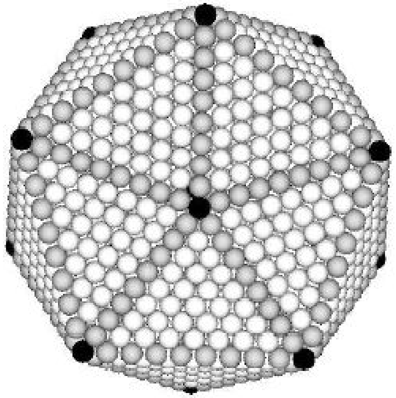


FIG. 1: An ideal Ih structure with the magic number of 2869 atoms. Atoms are shaded to indicate their local structure: fcc is white, hcp is gray, and other is black.

Au

- *<5nm: icosahedral rather than FCC (bulk)*

Al

- Al_{13}*: Icosahedral rather than FCC (bulk)*

  decrease in binding energy to 2.77eV from 3.39eV

  decrease in Al separation to 2.814A from 2.86A

In

- *<6.5nm: face-centered cubic rather than face-centered tetrahedral(>6.5nm)*

  (c/a=1) *(c/a=1.075)*

CdS

- *Lattice constants decreases linearly with* $1/d_p$
- *Surface modification: less reduction in lattice constant*

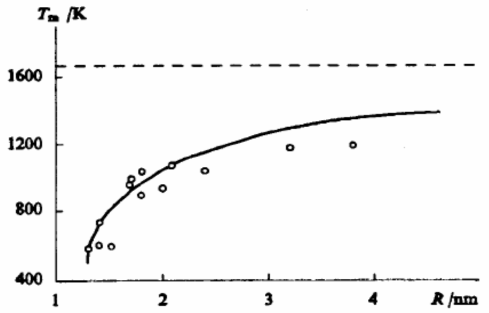
3.4 Thermodynamic effect

- due to large fraction of surface atoms

Lowering of melting point

Thermodynamic analysis

$$T_b - T_m = \left[\frac{4T_b}{\Delta H \rho_p d_p}\right]\left[\sigma_p - \sigma_l\left(\frac{\rho_p}{\rho_l}\right)^{2/3}\right]$$



Melting point of CdS particles

where T_b, T_m: *melting points of bulk and particle, respectively*

ΔH: *molar heat of fusion*

-Similarly lowers other phase transition temperatures

- lowers sintering temperatures…

Melting point and sintering temperature for nanoparticles

	Nanoparticles	Bulk
Melting point	Au(3nm):900K In(4nm):370K	1300K 430K
Sintering temperature	Ni(20nm):~200^{o}C W(22nm):~1100^{o}C	>700^{o}C >2000^{o}C

Kelvin effect

- *Vapor pressure*
- *Solubility*

  Ostwald ripening

3.5 Chemical (catalytic) properties

- *Surface activity*

  Bulk < plane surface < edge < corner

- *Catalysts: mainly depends on metal nanoparticles…*
- *Supported on alumina, silica or charcoal (highly porous materials)*
  - *Usually made by impregnation of metal salt on support surface*

    Followed by reduction
  - *Monodisperse metal nanoparticles: research issue…*
    - *Ligand protected (passivated) clusters*
    - *Reducing surface activity but tuning the activity…*

    Ex. 0.5wt% Pd NP modified with different ligands for reaction 25^{o}C

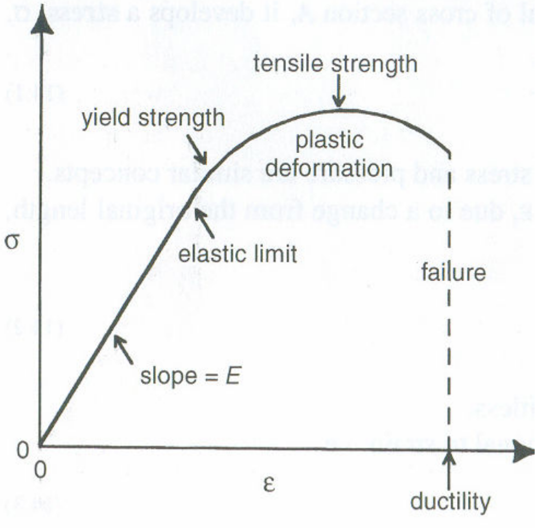
    2-hexene + H2 = cis-2 hexene

    with 1,10-phenanthroline : ultimately main product: trans-2 hexene

    with 2-nbutylphenanthroline: slow reaction to 100% cis-form

3.6 Mechanical properties

http://www.wtec.org/loyola/nano/06_02.htm



- Elastic (Young's) modulus (E), yield strength, hardness, brittleness (or ductility)

** Failure mechanism of conventional grain-sized materials*

- *Crack propagation*
- *Brittle-to-ductile transition due to dislocation*

** Nanocrystalline materials:*

- *dislocation-free or perfectness as grain diameter d deceases from 50-100nm.*
- *Some pores or flaw originated from preparation method*

** Whisker: perfectness appears for diameter <10um!*

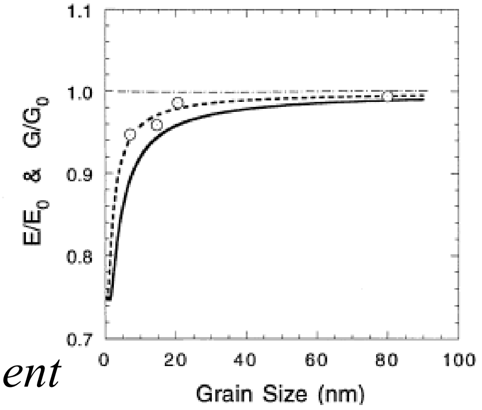
- full theoretical mechanical strength!

** Deformation and fracture mechanism of NC materials: unclear*

cf. for coarse grained materials: formation and movement of dislocation

Elastic properties

- *For grain size<5nm: decreasing E due to number of atoms associated grain boundaries becomes very large*

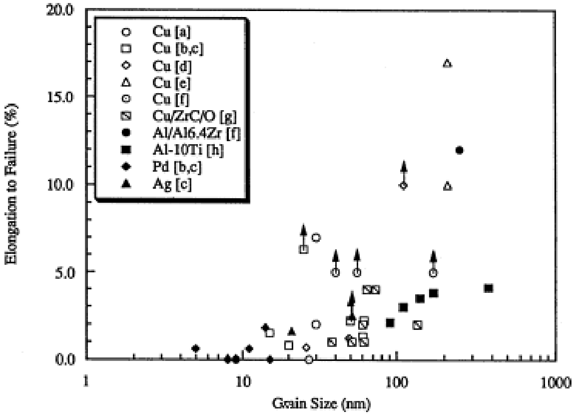


Hardness and strength

- *Increase with (grain diameter,d)$^{-1/2}$ (Hall-Petch equation) since grain boundaries: barrier against dislocation movement*
- *Some NC materials have showed deviation from H-P equation…*

Dutility and toughness

- *Increase in coarse grain size materials(d>1um), toughness and ductility increases*
- *NC materials(d<30nm): brittle*



Superplastic behavior

: elongation(tensile deformation) of 100% to >1000% without necking or fracture

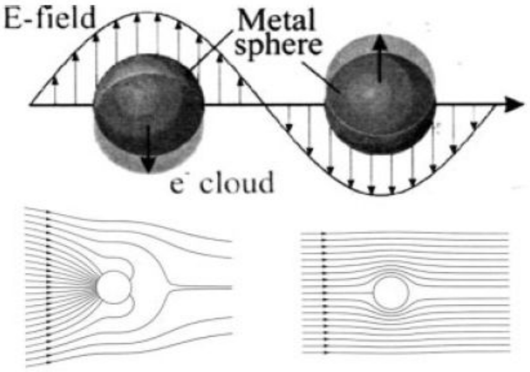
- *Some NC: superplasticity transition temperature is lowered and strain rate increased with the decrease in d, usually for T>0.5Tm*

3.7 Optical properties

-Due to surface plasmon resonance

-Due to the increased energy level spacing

http://www.materialstoday.com/pdfs_7_2/marzan.pdf#search='nanoparticles'



Surface plasmon resonance

: Coherent excitation of all the free electrons by light, leading to an in-phase oscillation for particles($d_p < \lambda_{light}$ *)*

→ *Intense SP absorption bands*

→ *Enhancement of local electromagnetic field (surface enhancement resonance)*

- SP energy determined by the dielectric property of the surrounding medium, the free electron density (size) of the particle.

- width of resonance (absorption band) related with surface scattering of electrons

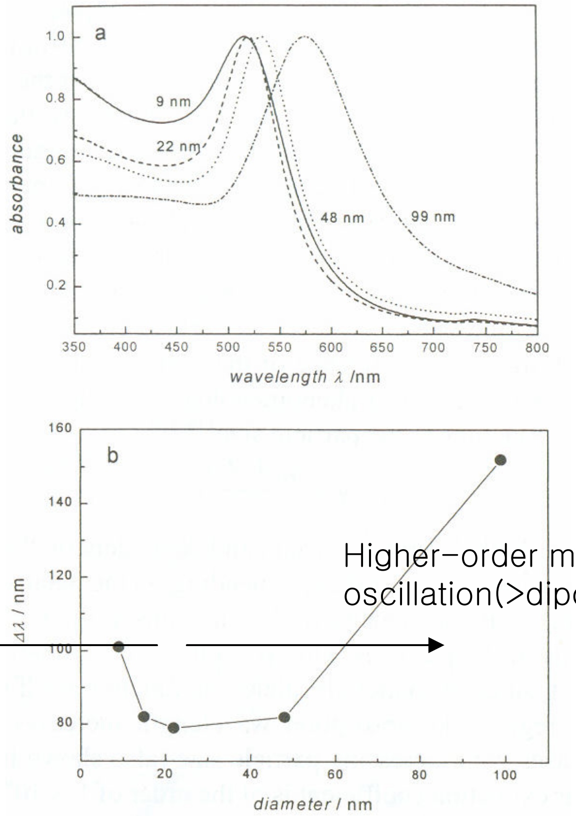
- For small nanoparticles($d_p << \lambda_{light}$*)*

$$\sigma_{ext} = \frac{9\omega_m^{3/2} v \varepsilon_2(\omega)}{c\{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2\}}$$

ω : angular frequency

V : particle volume

$\varepsilon_m, \varepsilon$: dielectric constants of medium and particle, where $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$



Higher–order mode oscillation(>dipole)

Surface scattering

SPR for gold nanoparticles in water

- *Used in waveguide; optical transmission, information storage, nanophotonic devices; switches; resonant light scatterers; sensors, biosensors; surface-enhanced Raman scattering (SERS)*

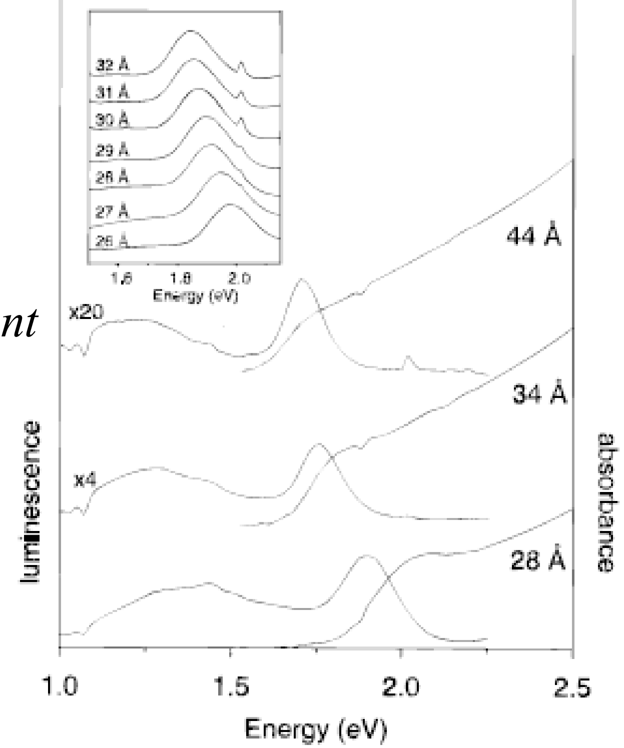
Optical properties due to size confinement effect

* *Semiconductors*

- *Rapidly increase in band gap with a decreasing size*
- *Optical absorption and photoluminescence (emission)*
  - *Blue shift*

* *Metals*

- *Observed in far infra-red absorption measurement for passivated gold nanoparticles with <2nm diameter (~100 atoms)*



Absorbance and PL spectra for several sizes of InP nanocrystal samples. The PL spectra are composed of a high-energy band edge emission band and a low-energy trapped emission band. The insert shows additional scaled PL spectra for a sequence of sample sizes exhibiting a smooth blue shift of the band edge emission feature with decreasing nanocrystal size. The samples have been treated with decylamine and were exposed to air.

3.8 Electrical conductivity

$$\rho_{total} = \rho_{thermal} + \rho_{defect}$$

Thermal: electron collision with vibrating atoms (phonons),

temperature dependent

Defect: impurities, lattice defect, grain boundary

** Surface scattering*

if the mean free path of electrons, λ_0*>particle size,* d_p

Elastic (specula) scattering

Inelastic (nonspecula, diffuse)scattering → *increase in* ρ *(resistivity)*

** Change of electronic structure*

Quantum size effect → *widening and discrete band gap*

metals → *semiconductors, semiconductors* → *insulators*

Bi nanowires: ~52nm; Sinanowires:~15nm

* *Quantum transport*

Ballistic conduction: transport without any collision

λ_0 *> length of conductor*

Resistance of a carbon nanotube (CNT) can be independent of the tube length.

Coulomb blockade:

Ohm's law $I = U / R$

E, U: Energy (voltage) required to add a single charge to the particle

$$E = \frac{e^2}{2C(d_p)} \qquad U = \frac{e}{C(d_p)} \qquad \text{and} \qquad I = \frac{U}{R} = \frac{e}{RC(d_p)}$$

$$\text{where} \quad C(d_p) = 2\pi d_p \varepsilon_0 \varepsilon_r$$

For bulk materials ($d_p \sim \infty$), E ~ 0 and V ~ 0

"I " varies linearly and continuously with" R"

Ampere: 1coulomb/s *cf. e=1.602x10^{19}coulomb*

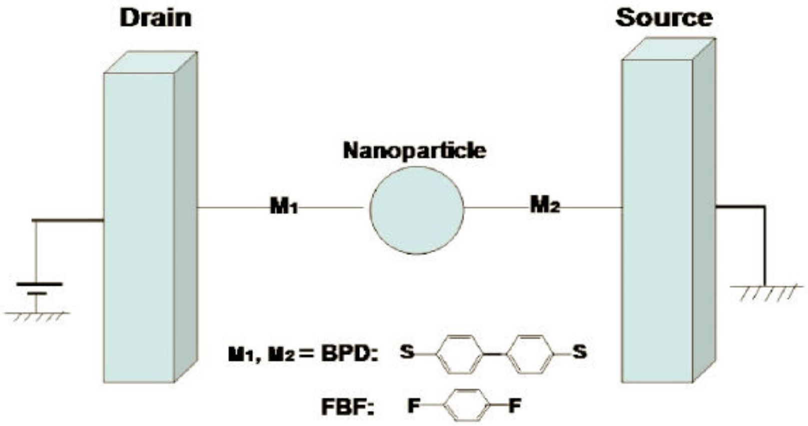
As size decreases, E ~ finite

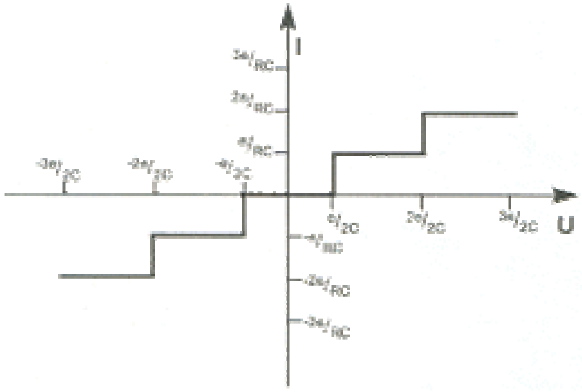
A single electron can be added to the particle when E>>kT…

"Coulomb blockade"

Two electrons ($I = \frac{2e}{RC}$) *can be added under* $U = \frac{2e}{C}$

For the configuration





“Coulombic staircase”

<u>Tunneling conduction</u>: charge transport through an insulating medium separating two conductors that are extremely closely spaced

- Overlapping of electron wave functions from two conductors

** Single electron transistor*

http://www.glue.umd.edu/~bekane/QC/QC@UMD's_LPS_Single%20Electron%20Transistor.htm

3.9 Ferromagnetic properties

** Ferromagnetic materials*

- Unpaired electrons in d-orbit : directed spin

e.g., Fe, Co, Ni

- Exchange energy: alignment of atomic spins

- Domain theory

-Lowering magnetostatic energy by forming multiple domains

- Hysteresis loop

H: magnetic field; M: magnetization (magnetic moment / volume)

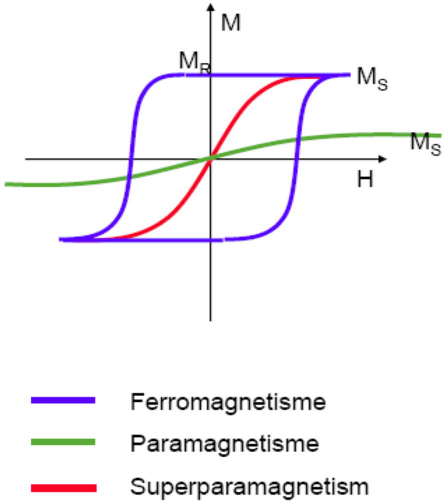
Coercivity, saturation magnetization, BH product

- Magnetic alignment

- Rotation of magnetic dipoles

- Movement of domain boundary

- Used for permanent magnet, core transformer



** Single- domain particles*

- Energy lowering by domain formation is balanced ($E_{ms} \propto d^3$ *d: domain size)*

by energy increase for boundary formation ($E_{bf} \propto d^2$*) as d decreases…*

- For small particles, single domain is in the lowest energy state…

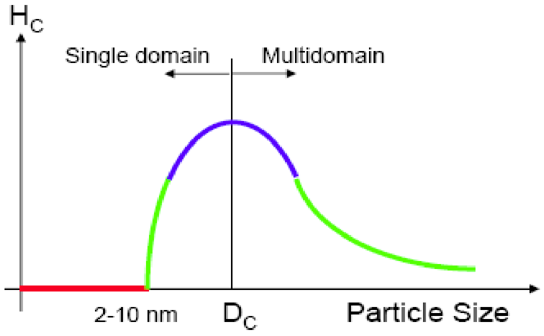
$$d_p : 10 \sim 100nm$$

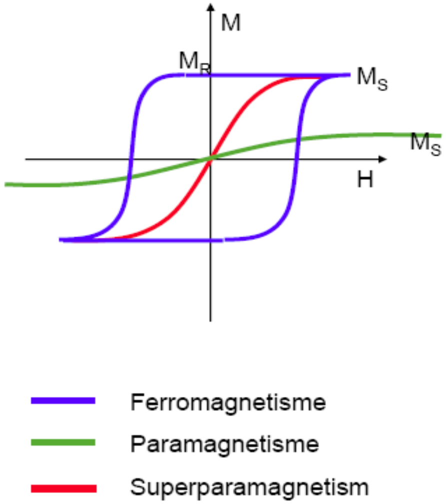
- Used for magnetic recording media

** Superparamagnetism:*

- Thermal fluctuation > magnetic alignment as the size decreases

Usually, $d_p <\sim 15nm$





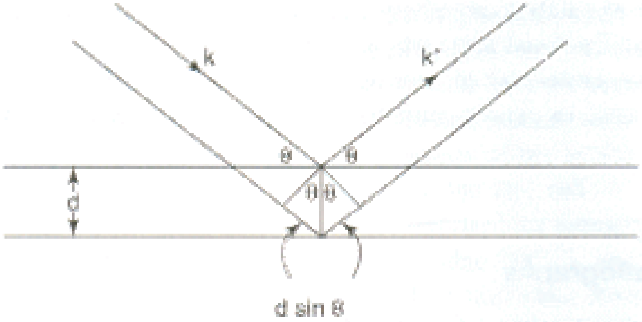
- No hysteresis loop

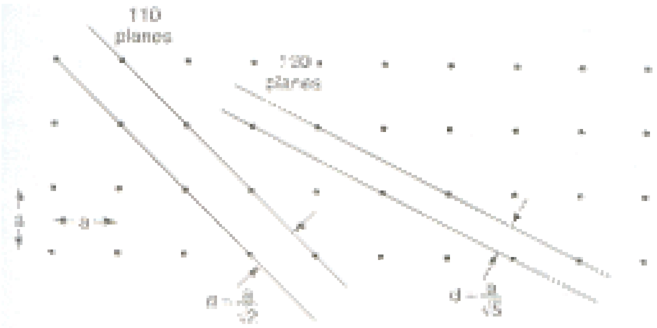
- Used in biomedical application, ferrofluids, sensors

3.10 Characterization of nanoparticles

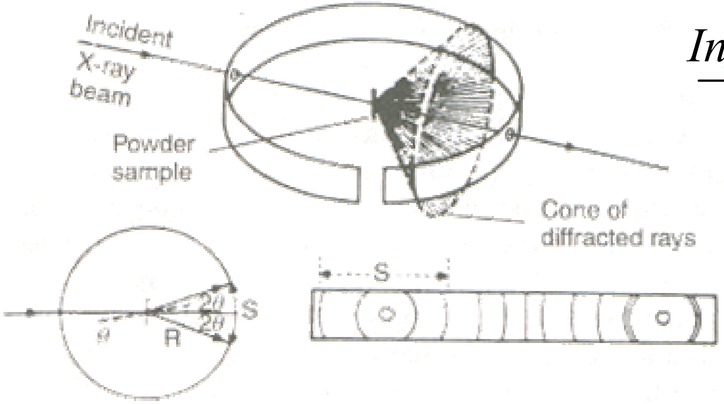
(1) X-ray diffraction

- *Bragg's law;* $2d \sin\theta = n\lambda$

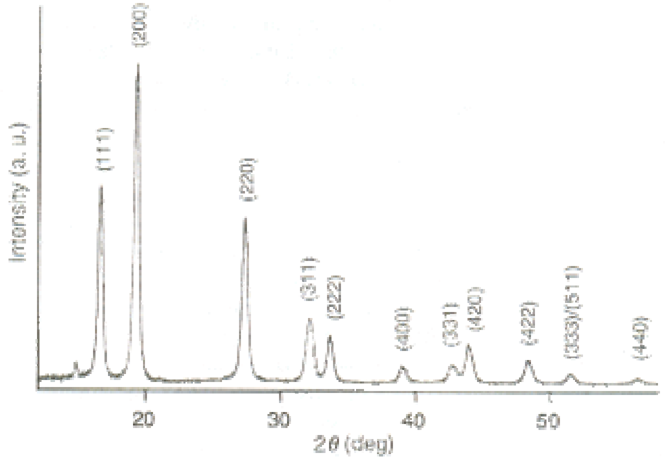




- *used to identify the specimen's crystalline phases and to measure structural properties*



Intensity vs. 2 θ $\longrightarrow$



XRD scan of nanocrystalline TiN

- *Peak broadening by inhomogeneous strains and crystallite size, d_c*

If no inhomogeneous strain,

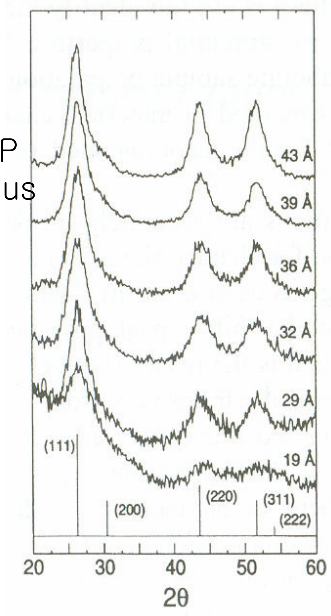
$$d_c = \frac{K\lambda}{B\cos\theta_B}$$

Scherrer equation

where K: Scherrer's constant(~1) ; λ:X-ray wavelength;

B; half width of the peak; θ_B: diffraction angle

XRD patterns of InP particles with various sizes



- *Sometimes dc is smaller than true d_p d e to twinned structure of the nanoparticles*
- *yields low intensity, suitable for high Z materials, requires large amount of materials, gives average values*

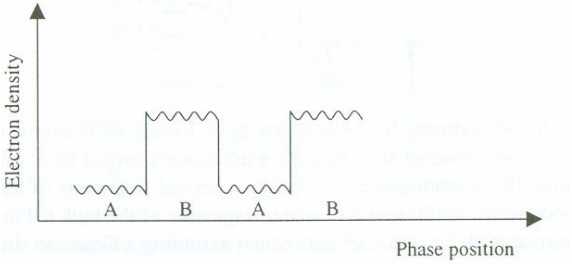
cf. Intensity for electron diffraction intensity 10^8 larger than for XRD

(2) Small angle X-ray scattering

- *X-ray intensities from fluctuation in electron density* over the length <10nm:*

  $2\theta < 5^o$

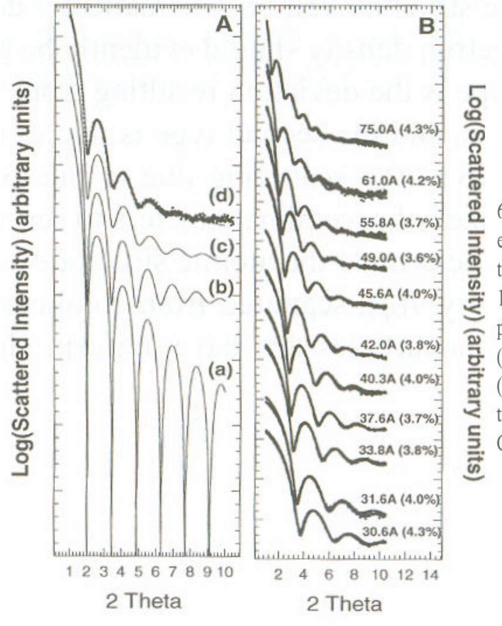
  ** Difference in density and composition*



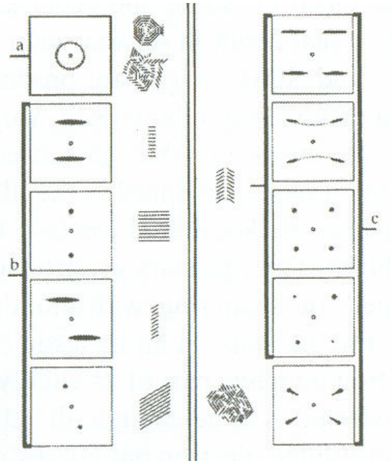
- *gives the size and shapes of small particles, their surface area per unit volume,*

  irrespective crystalline or amorphous

- *also used for determining size and ordering of mesoporous materials*



(A) SAXS patterns for model structures having 4500 atoms, comparable to a 62 Å diameter CdSe nanocrystals. The curves are models for (a) 62 Å spheres of uniform electron density, (b) monodisperse, 4500 atom spherical fragments of the bulk CdSe lattice, (c) monodisperse, 4500 atom ellipsoidal fragments of the bulk CdSe lattice, having a 1.2 aspect ratio, and (d) fit to SAXS data (dots) assuming a Gaussian distribution of ellipsoids (as in curve c), yielding the nanocrystal sample size and size distribution. (B) SAXS patterns for CdSe nanocrystal samples ranging from 30 to 75 Å in diameter (dots). Fits are used to devise the nanocrystal sample size, reported in equivalent diameters, and size distributions, ranging from 3.5 to 4.5% for the samples shown. [C.B. Murray, C.R. Kagan, and M.G. Bawendi, *Ann. Rev. Mater. Sci.* **30**, 545 (2000).]



Structures and SAXS patterns

(3) Gas adsorption

- Adsorption: reducing surface energy of the adsorbents: physical vs. chemical*

Determination of specific surface area(m^2/g)

BET adsorption isotherm

$$\frac{1}{v}\frac{x}{1-x}=\frac{c-1}{cv_m}x+\frac{1}{cv_m}$$

where v = volume of gas adsorbed per gram of sample; v_m = volume of gas adsorbed at monolayer coverage per gram of sample at standard condition; $x = P/P_o$

Adsorption of nitrogen at 77K(liquid nitrogen) → A plot of (1/V)(x/(1-x)) versus x

→ from slope and interception → v_m

Then, specific surface area(m^2/g)

$$S_g(m^2/g)=\frac{v_m N_0 A_a}{V}=4.35v_m(cm^3/g)$$ *for nitrogen at -196°C*

where N_0: Avogadro number;

A_a: area on which nitrogen molecule adsorbed (=0.162nm²)

** Single Point BET Method*

Use of v_m at $P/P_o = 0.30$ neglecting the intercept of the BET plot (small enough)

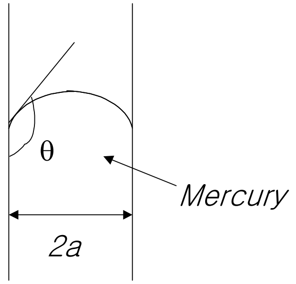
Pore volume in porous materials

* Mercury penetration

For Pore size 20-1000nm

From force balance $\pi a^2 p = -2\pi a \sigma \cos\theta$

$$\therefore d(nm) = -\frac{\sigma\cos\theta}{p} = \frac{4.36\times10^4}{p(psi)}$$ for mercury

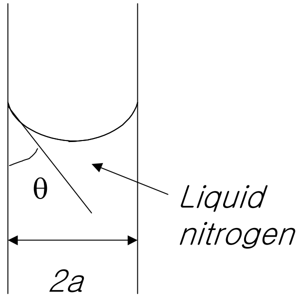


Measurement of mercury penetration volume vs. p gives pore volume vs. a

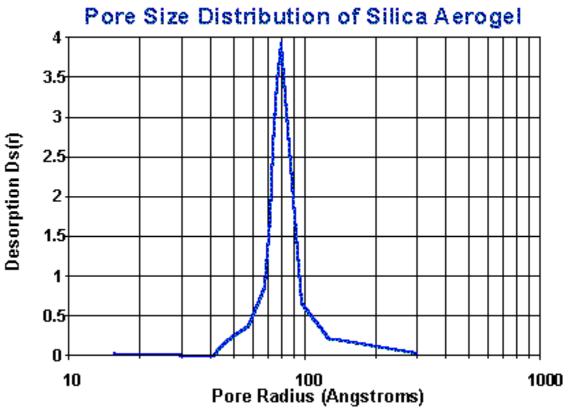
* Nitrogen adsorption-desorption

Pore size up to 20nm

Kelvin equation $$d(nm) = \frac{-4\sigma V\cos\theta}{RT\ln\left(p/p_0\right)} = 1.904\left(\log\frac{p_0}{p}\right)^{-1}$$ for nitrogen



* Measurement of desorbed nitrogen volume V vs. p gives pore volume vs. a



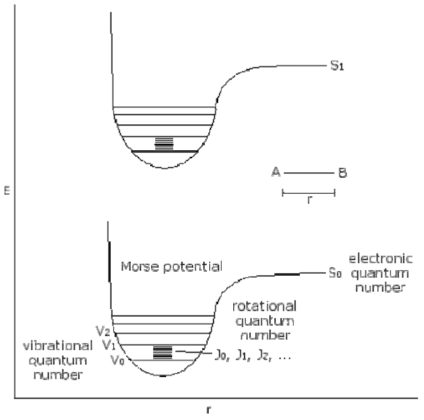
(3) Optical spectroscopy

- Absorption, emission, vibrational spectroscopy

Transition from one energy level to the another level in the electronic structure of atoms, molecules and solids

Sharpness of the peaks: atoms>molecules>solids (energy gap between CB and VB)

- Transition between electronic levels: UV/VIS and photoluminescence (PL)

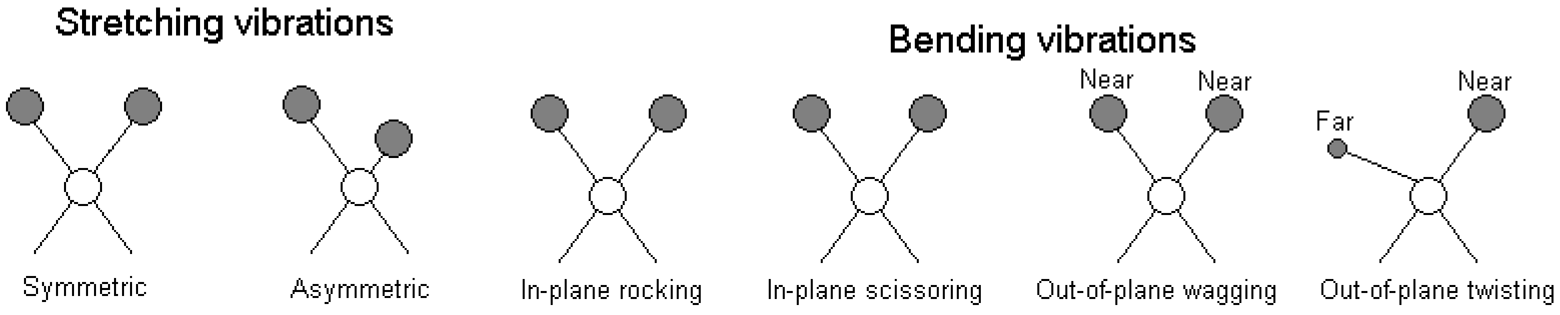


** Infra-red spectroscopy:*

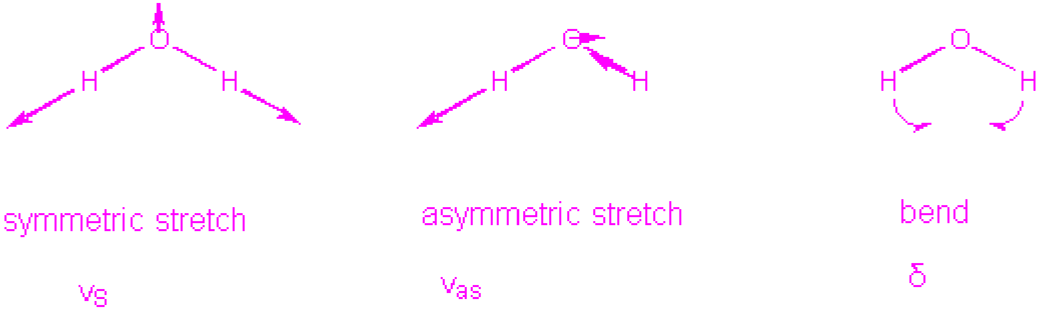
- Transition between vibrational levels(10^{12} -10^{14}Hz, or 3-300 um)

- Caused by change in dipole moment of the molecule

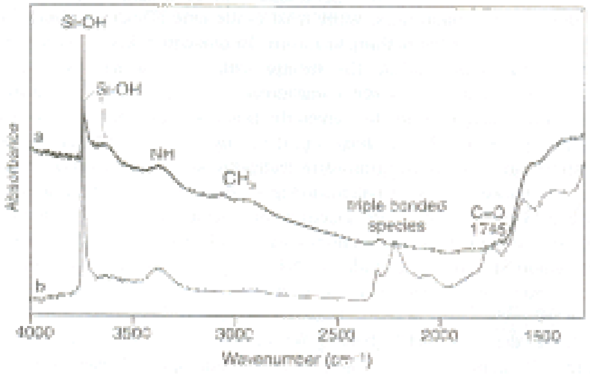
- Stretching and bending



Examples



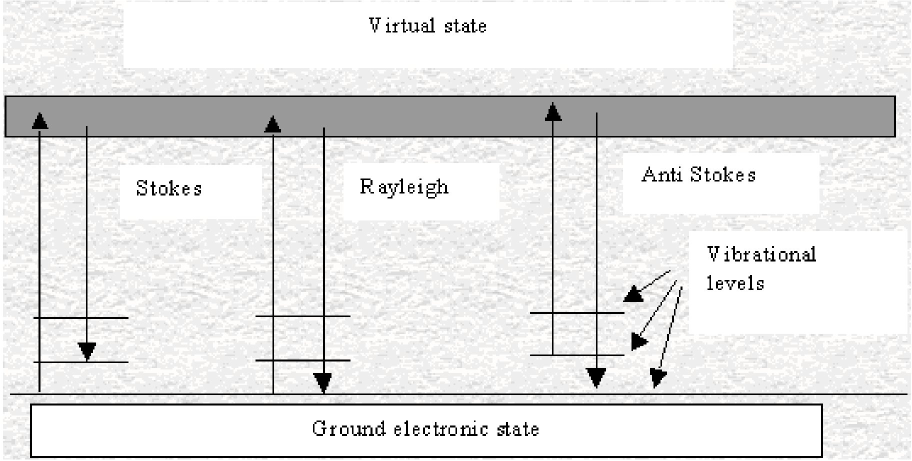
- *FT-IR: Fourier transform of intensity-time output to intensity-frequency data*
- *Determines the identities, surrounding environments or atomic arrangement, and concentrations of the chemical bond in the sample*

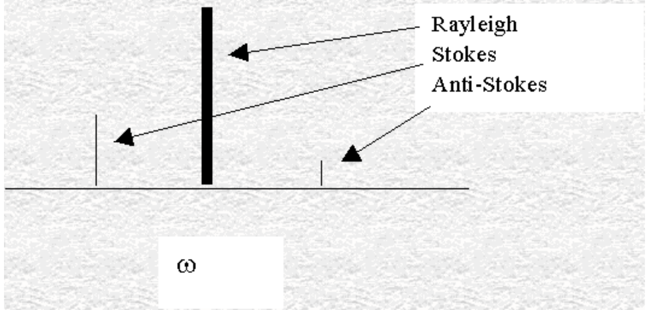


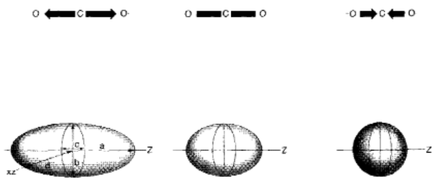
FT-IR spectra of silica particles before and after heat treatment

http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/irspec1.htm
http://www.le.ac.uk/chemistry/schools/TeachersHO.pdf
http://www.wpi.edu/Academics/Depts/Chemistry/Courses/CH2670/infrared.html

** Raman spectroscopy*



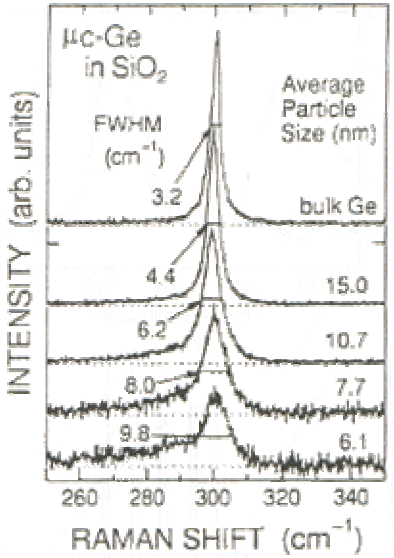




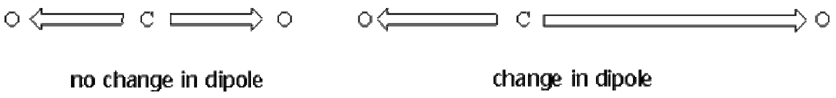
- Change in polarizability of the bond (electronic mobility)

- Used for structural characterization (sensitive to the lengths, strengths and arrangement of chemical bonds, but less sensitive to the chemical composition)

http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm



cf. In IR,

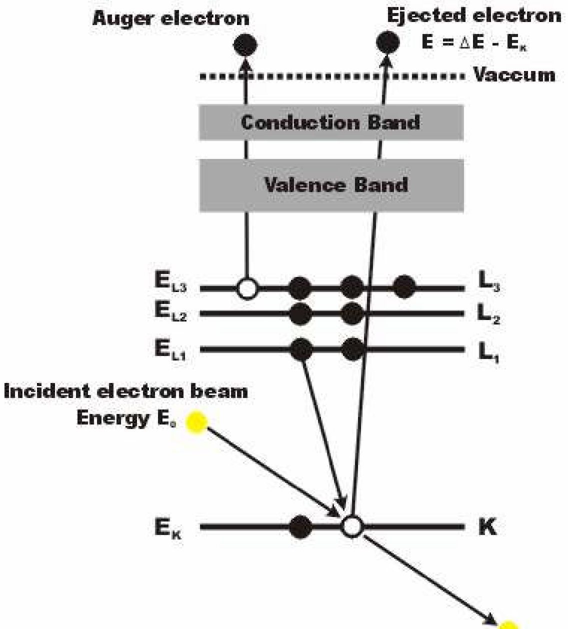


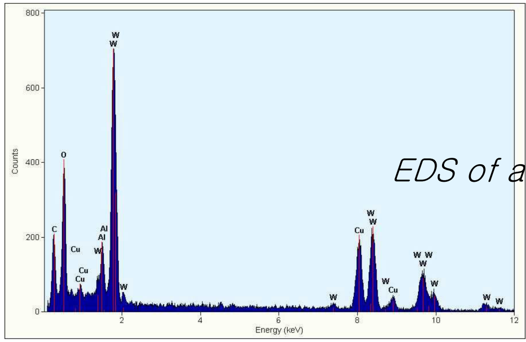
No signal in IR

(4) Electron spectroscopy

* Energy dispersive spectroscopy (EDS) and Auger electron spectroscopy (AES)

- Irradiation of X ray or gamma ray ejected an electron from an inner shell
- Measuring the energies of the X rays and Auger electrons





EDS of aluminum tungsten oxide

* X-ray photoelectron spectroscopy

- Also known as Electron Spectroscopy for Chemical Analysis (ESCA)
- Photoelectric effect by low energy X ray
- Energy of the ejected electron $E_E = h\nu - E_B$

where E_B: Energy of the bound electron state