XRD (X-ray Powder Diffraction) or PXRD

1. Wavelength of 1 Å is required to probe structure

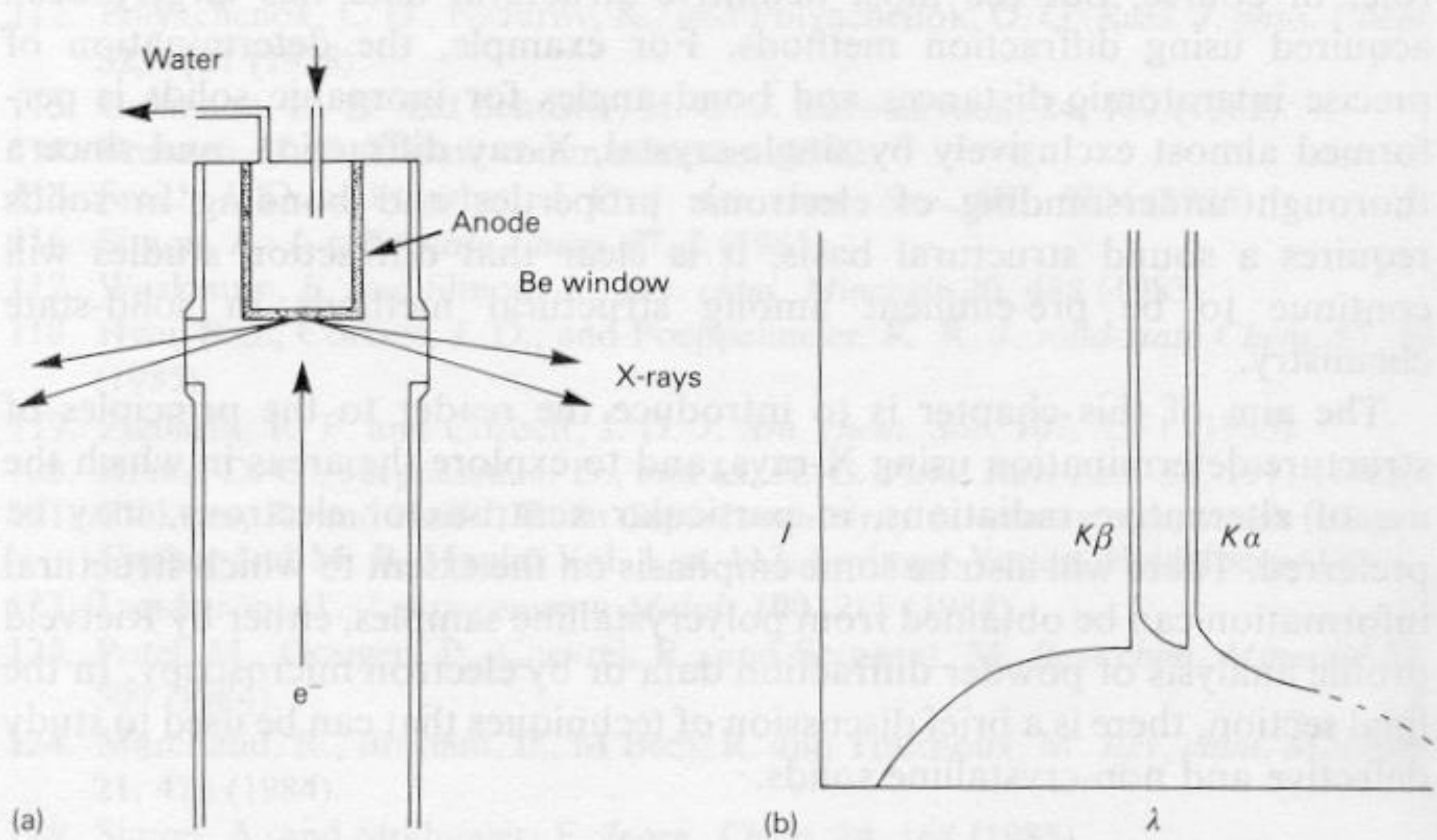
at the atomic level because the atomic radii are

in the range of ~ 1 Å

2. X-ray is generated by the bombardment of accelerated

electrons on metal target (Cu or Mo); K-shell ionization

3. Cu $K\alpha$ = 1.54178 Å and Mo $K\alpha$ = 0.71069 Å



Water
Anode
Be window
X-rays
e⁻
(a)
I
Kβ
Kα
λ
(b)

X-rays are scattered by their interaction

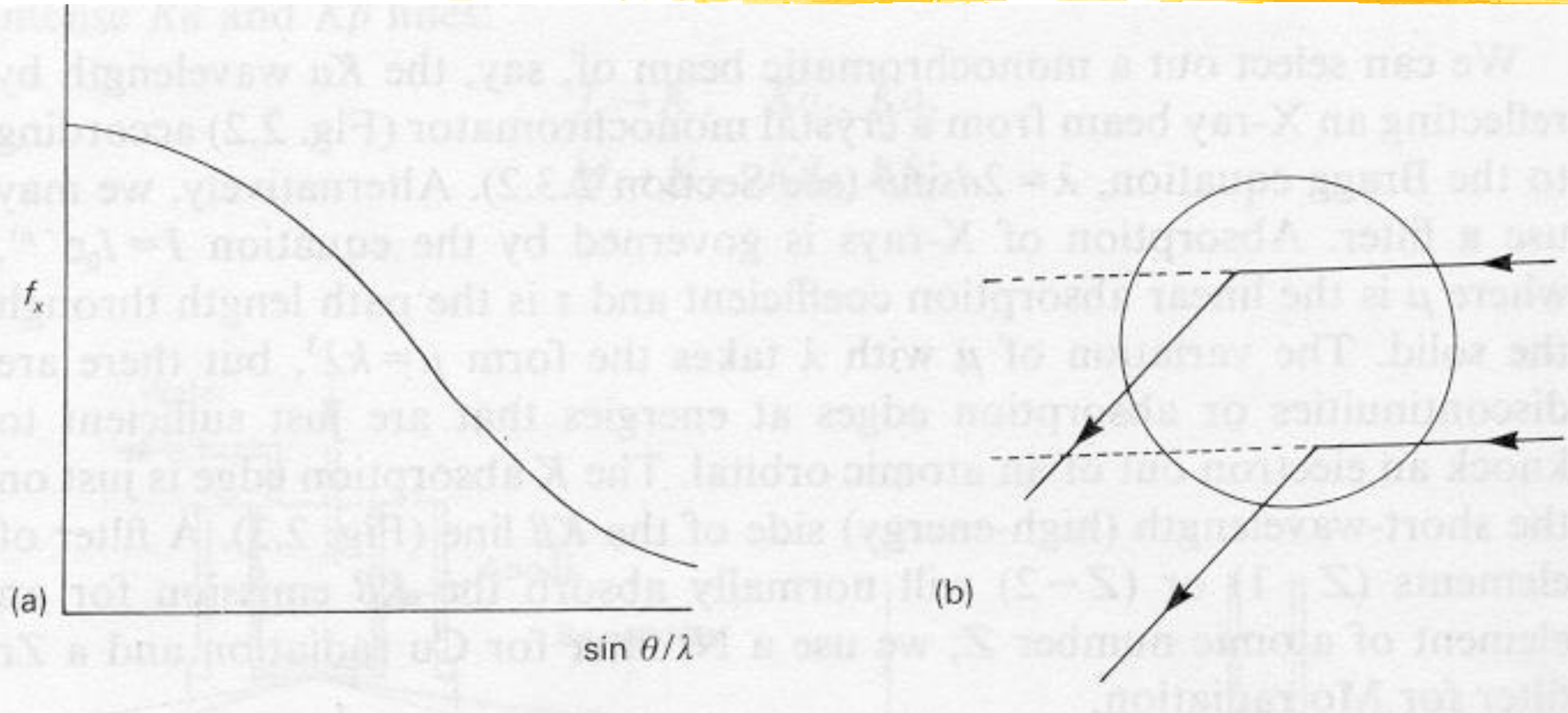
with atomic electrons and interference takes place

between X-rays scattered from different part of an atom

- Scattering factor $f_x \propto 1/2\,(1+\cos 2\theta)$

- Decrease with increasing 2θ

- $f_x \propto Z$ → H, Li very weak



Scattering factor $f_x \propto 1/2\,(1+\cos 2\theta)$

Crystals

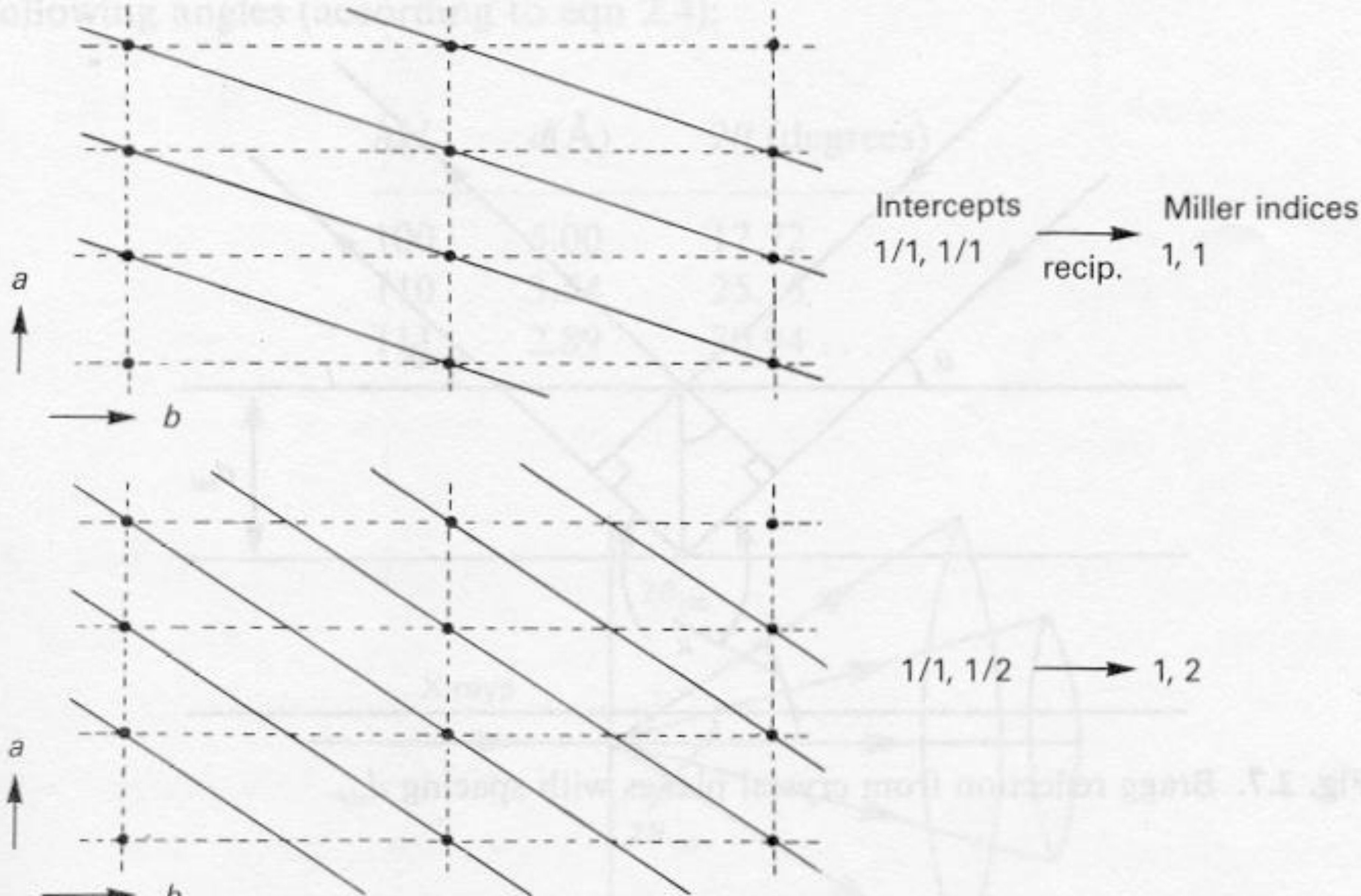
1. Unit cell: the simplest repeating unit of a crystalline Structure, defined by a, b, c and α, β, γ.

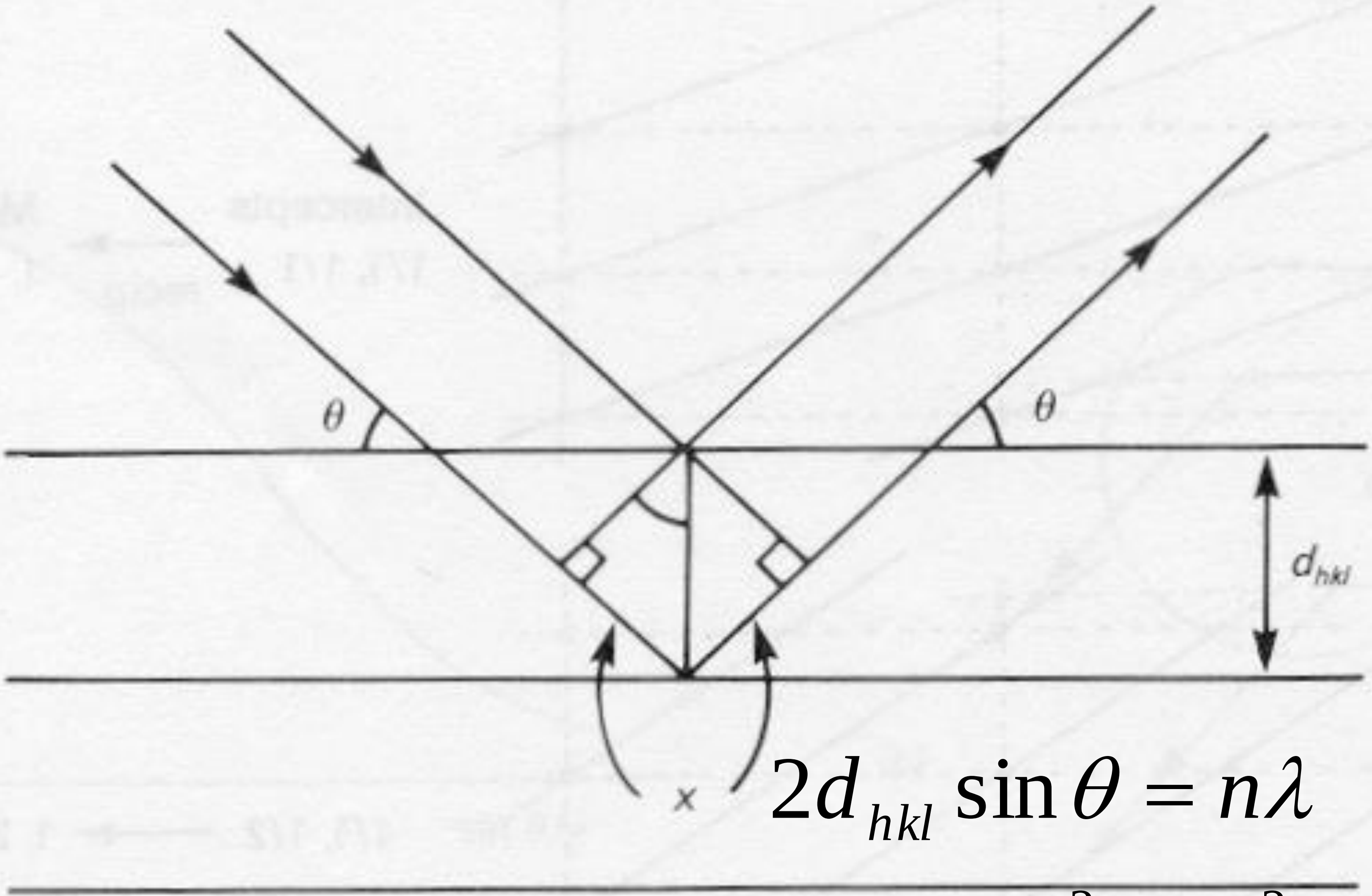
2. Lattice planes and Miller indices: parallel and equally spaced

3. Bragg equation: constructive interference

$$2d_{hkl}\sin\theta = n\lambda$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$


Intercepts
1/1, 1/1
recip.
Miller indices
1, 1
a
b
1/1, 1/2
1, 2
a
b

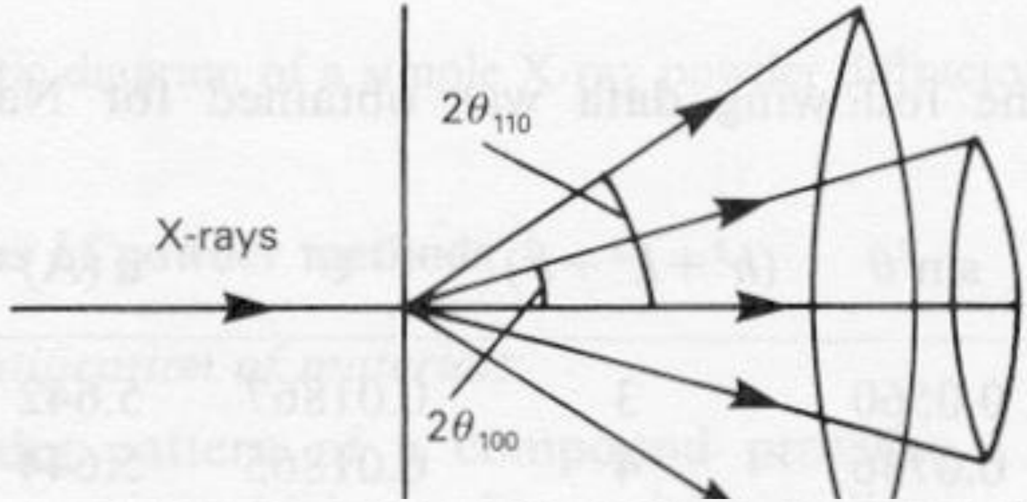


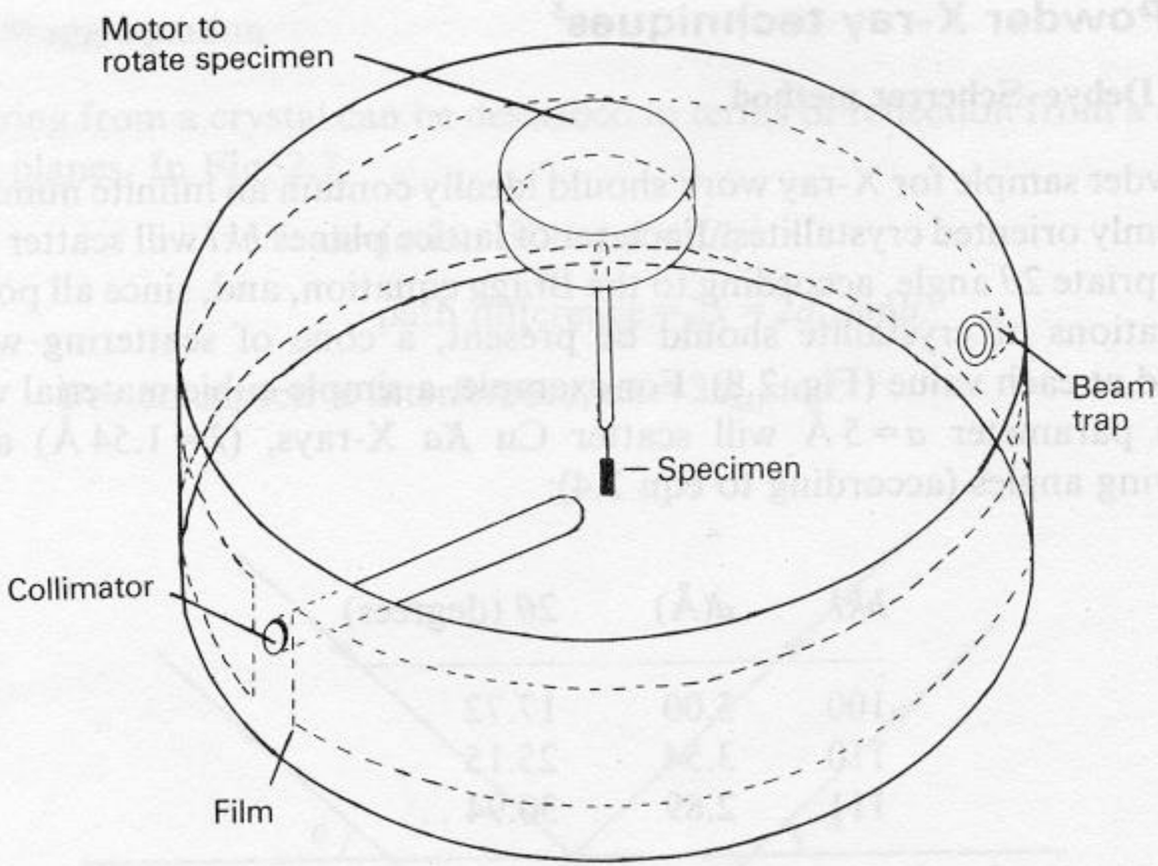
$$2d_{hkl}\sin\theta = n\lambda$$

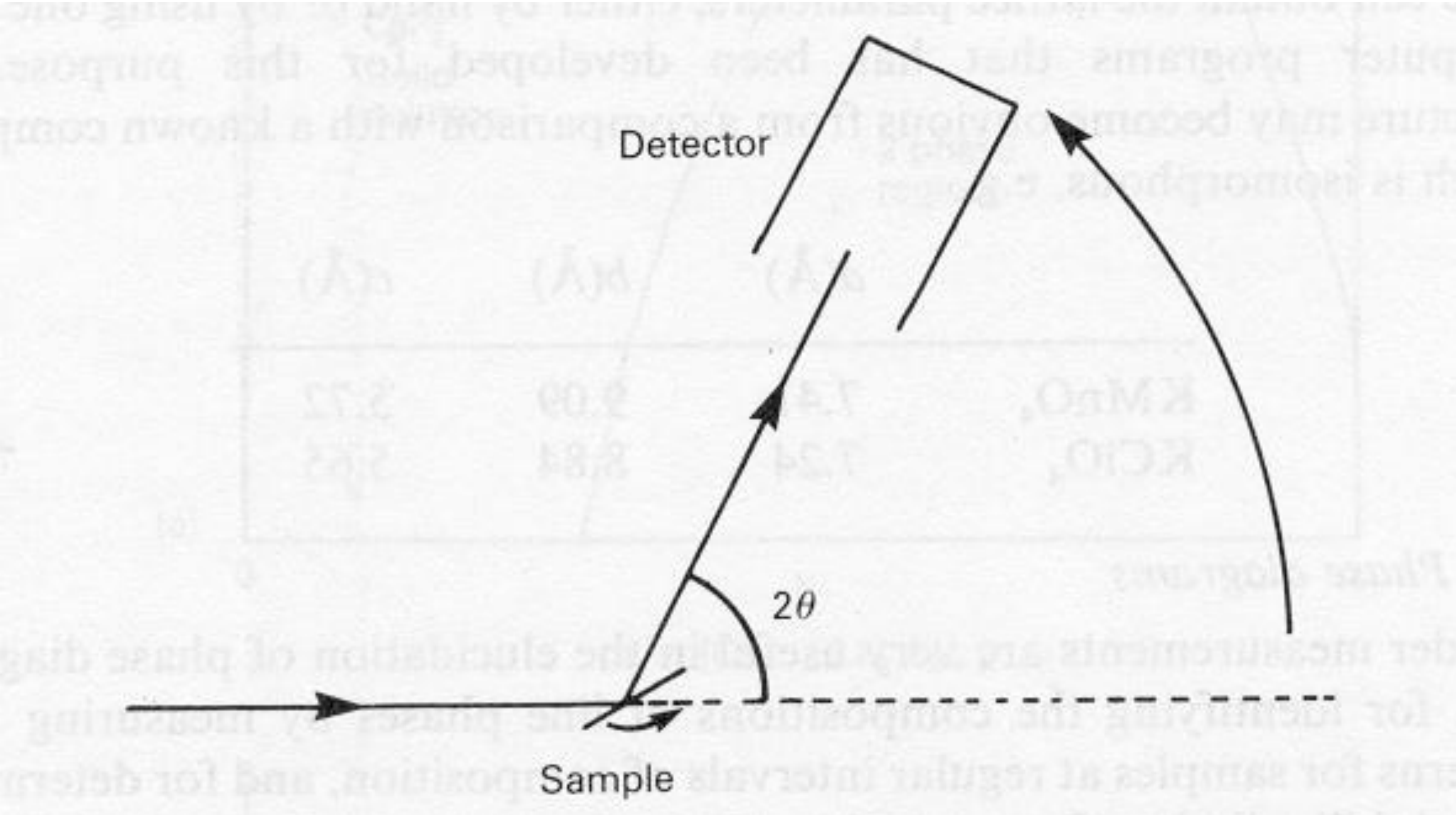
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

PXRD

1. Powder sample contains an infinite number of randomly oriented crystallites
- Each set of lattice planes *hkl* will scatter at the appropriate 2θ angle, according to the Bragg eq. Since all possible orientation of crystallite should be present, a cone of scattering will be formed at each value


2θ110
X-rays
2θ100


Motor to
rotate specimen
Beam
trap
Specimen
Collimator
Film

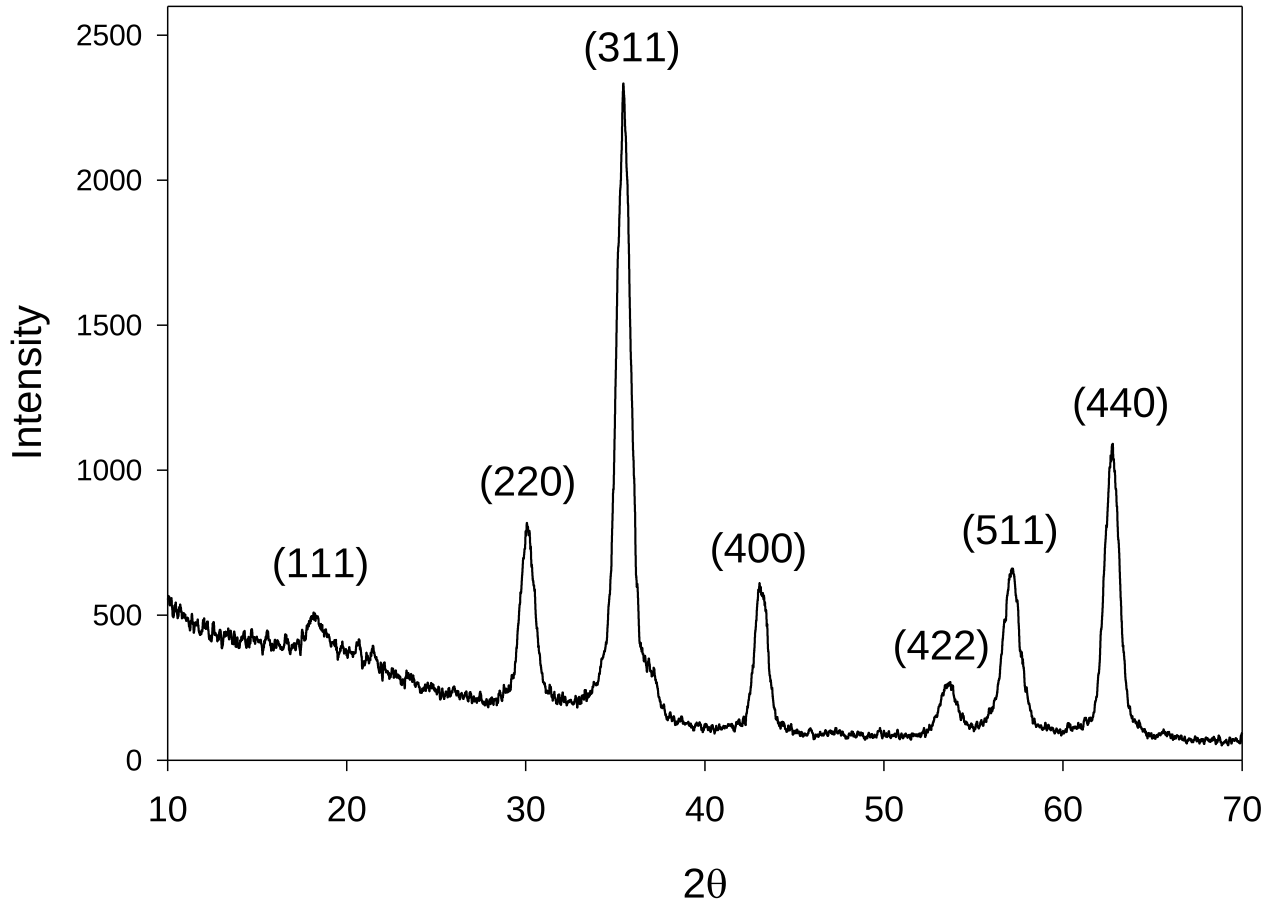

Detector
2θ
Sample

XRD applications

Reference: B. D. Cullity *Elements of X-ray Diffraction*

- Routine identification of materials→ JCPDS files

XRD of 11 nm γ-Fe_2O_3 Nanocrystallites



Comparison of d-spacing values of our sample, standard γ-Fe_2O_3 and Fe_3O_4

Our sample	γ-Fe_2O_3	Fe_3O_4
2.52	2.518	2.532
2.95	2.953	2.967
2.11	2.089	2.099
1.70	1.705	1.715
1.60	1.607	1.616
1.47	1.476	1.485
1.27	1.273	1.281

-Quantitative analysis of mixtures

→ Need standard

-Determination of lattice parameters ex) intercalation

-Particle size measurement: Debye-Scherrer eq.

$$t = \frac{0.9\lambda}{B\cos\theta} \qquad B = FWHM$$

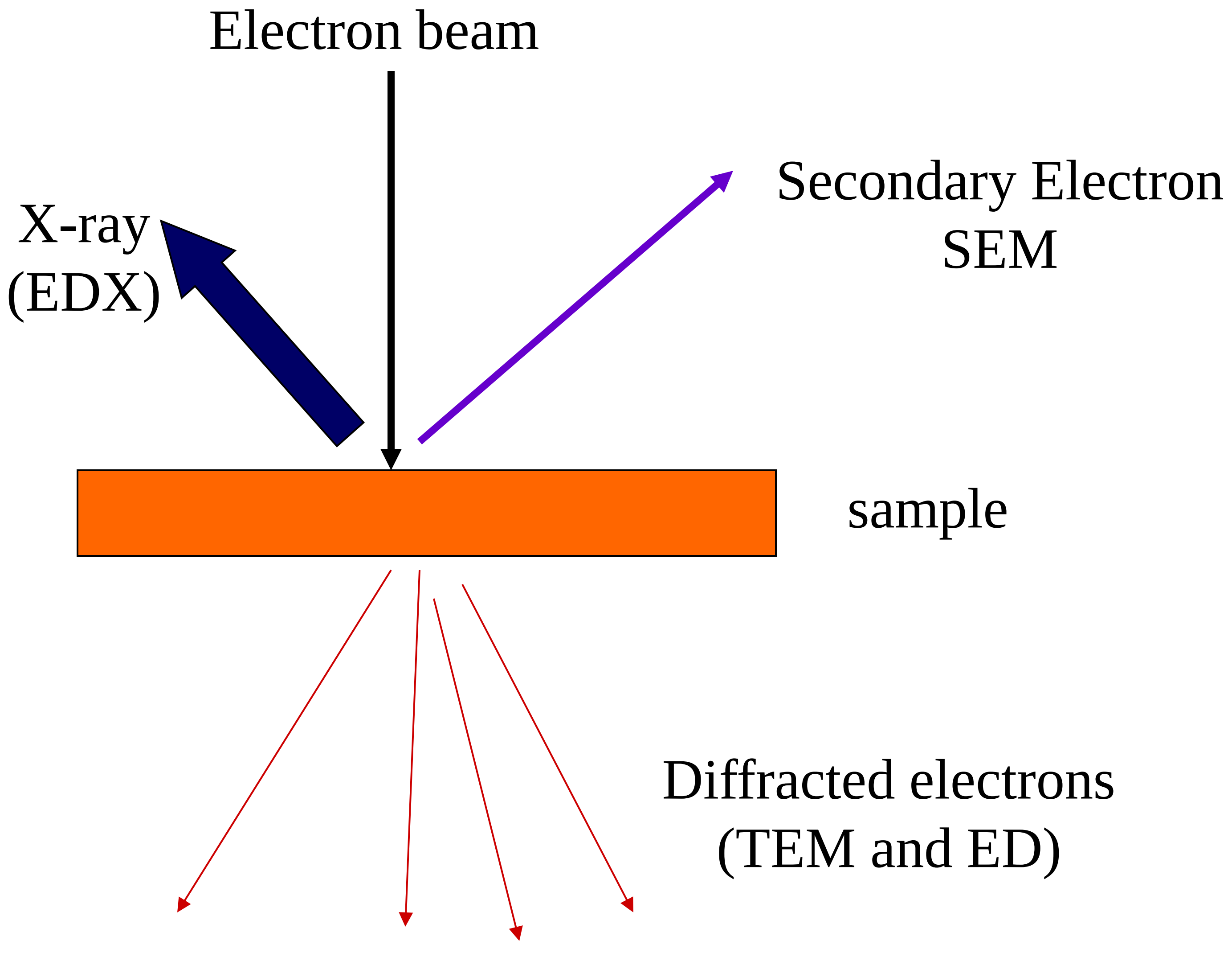
- Crystalline vs. Amorphous

Electron Microscopy (EM)

1. Electron-matter interactions

-Electrons are generated by thermionic emission from a cathode field and monochromated by acceleration through a potential E

Scattering factor fe ~ 10^4 fx very strong scattering


Electron beam
X-ray
(EDX)
Secondary Electron
SEM
sample
Diffracted electrons
(TEM and ED)

Electron Microscopy (EM)

Transmission Electron Microscopy (TEM)

-Obtain images with atomic resolution

by permitting an optimum number of diffracted beam

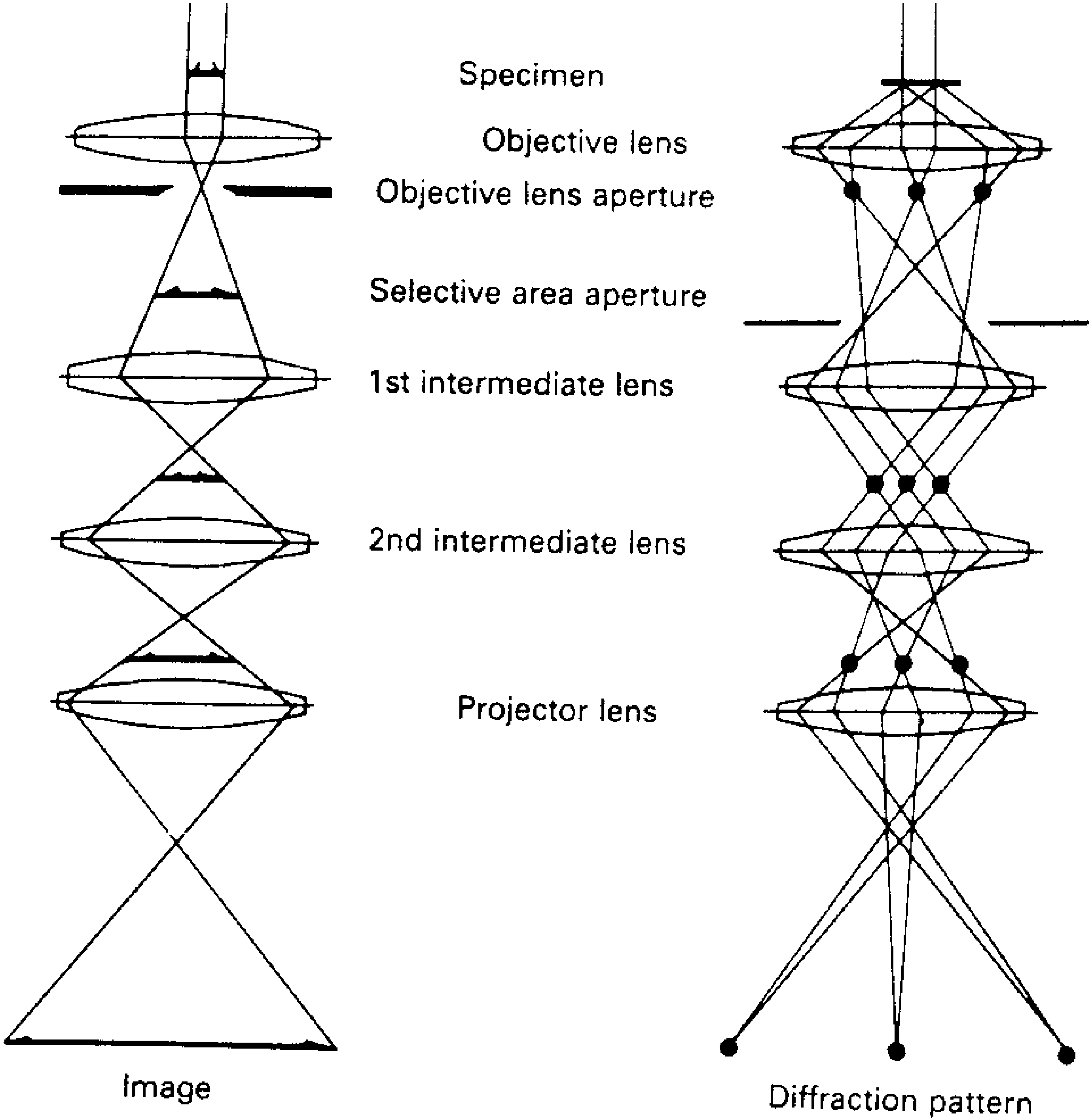
to contribute to the image

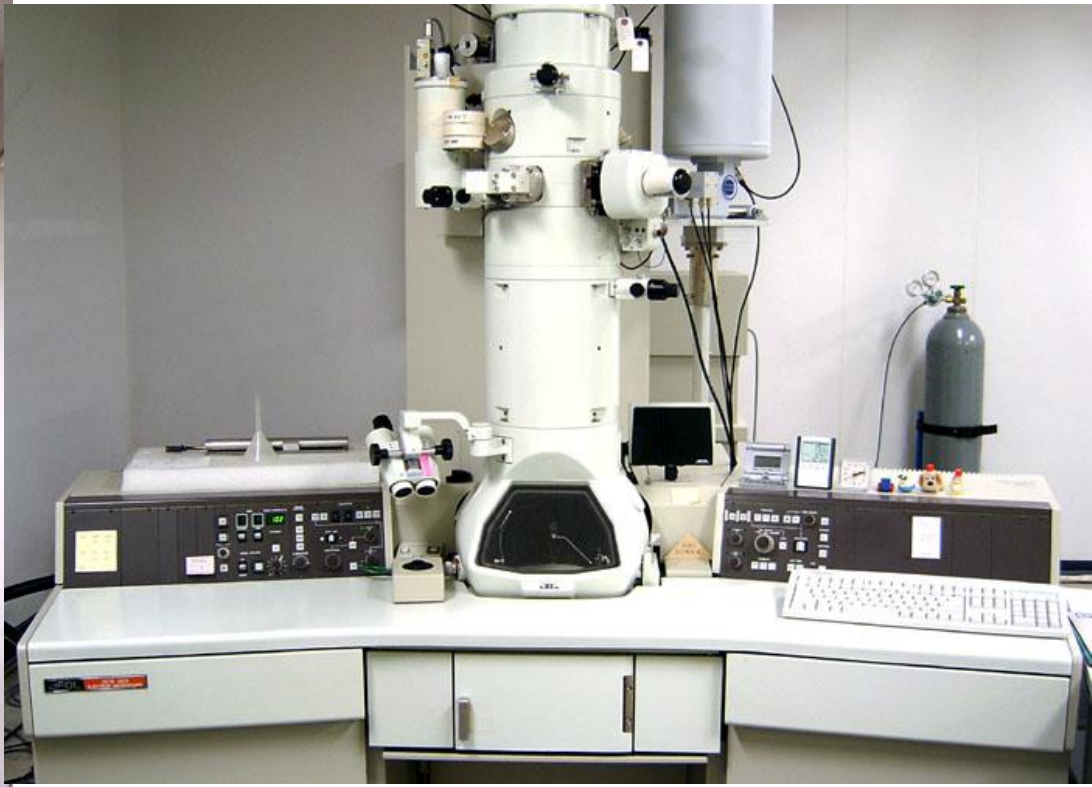
-Resolving power depends on λ

and quality of objective lens;

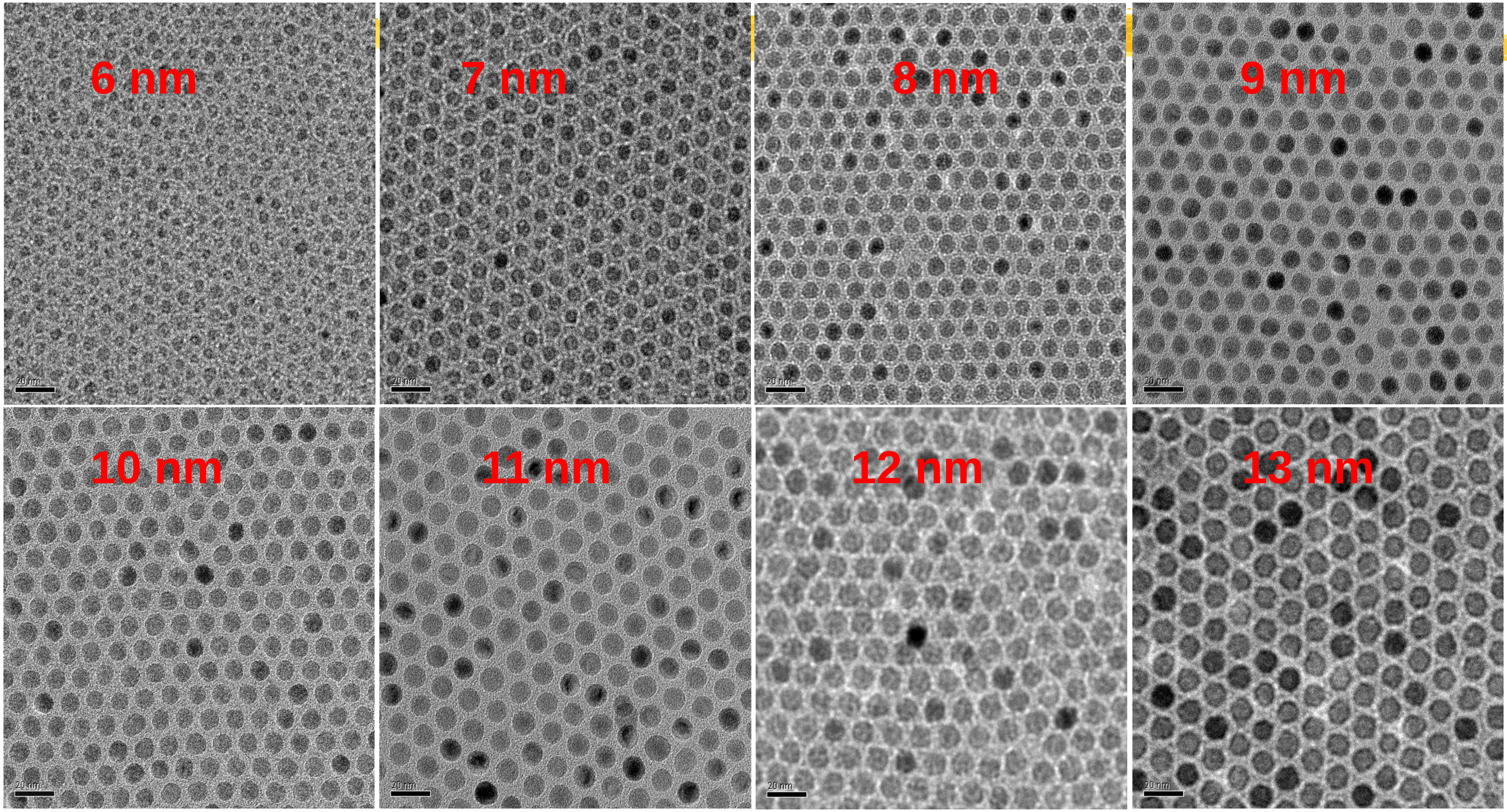
extremely thin film crystal are ideal.

-Electron diffraction (ED)

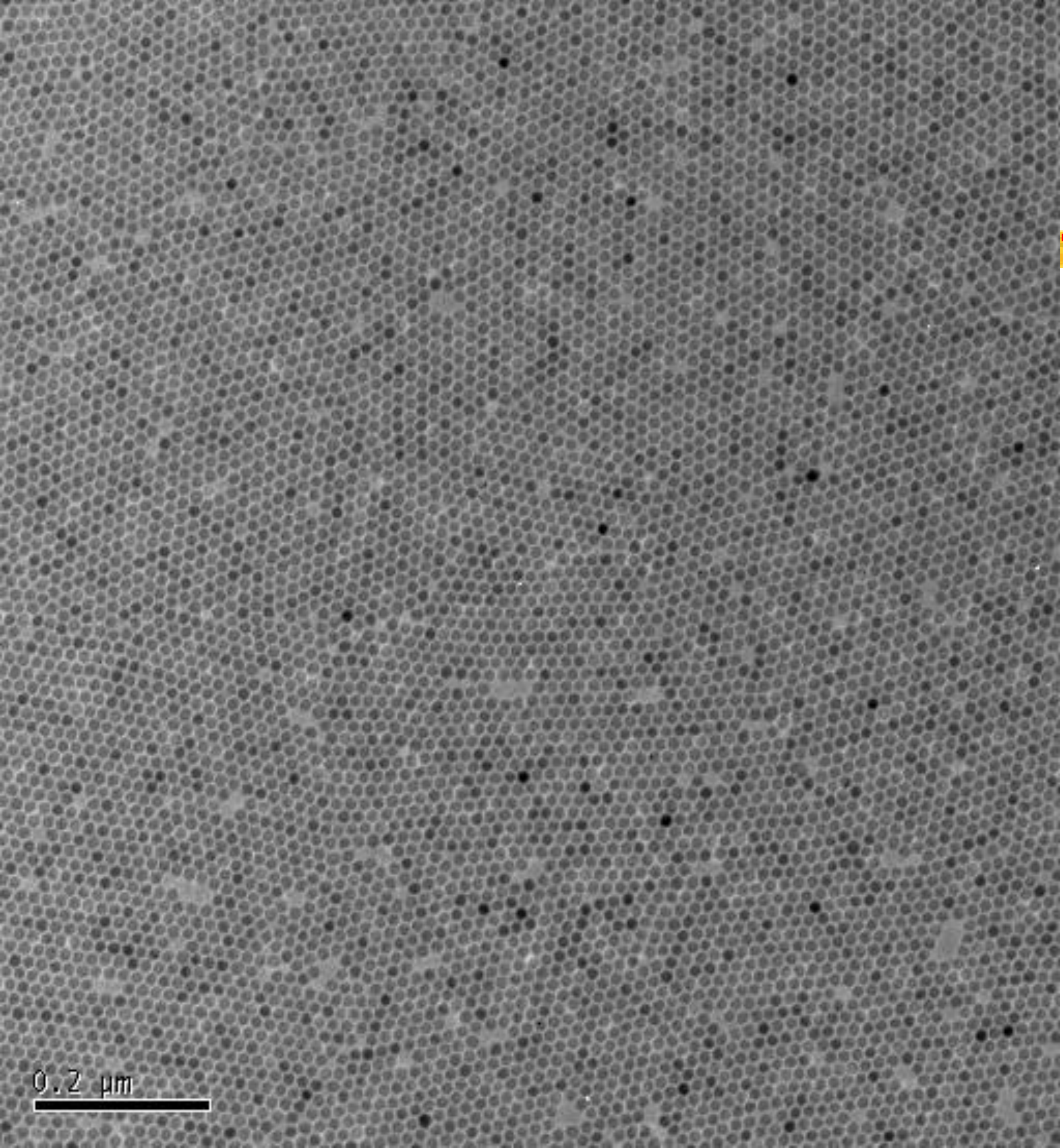

Specimen
Objective lens
Objective lens aperture
Selective area aperture
1st intermediate lens
2nd intermediate lens
Projector lens
Image
Diffraction pattern



1-nm-level size-controlled synthesis of monodisperse nanocrystals without size selection process

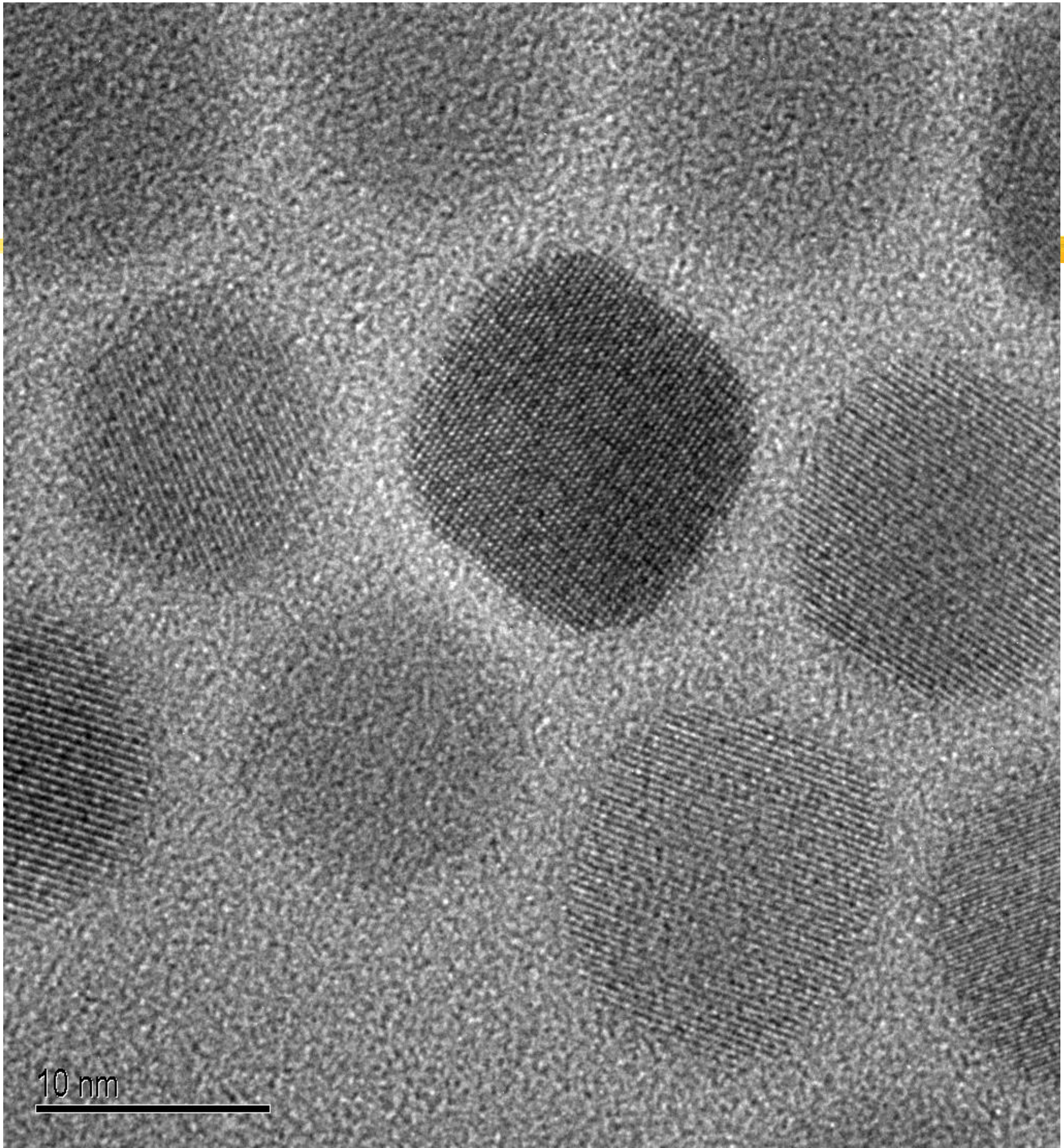


Angew. Chem. Int. Ed. (selected as a Frontispiece article) **2005**.

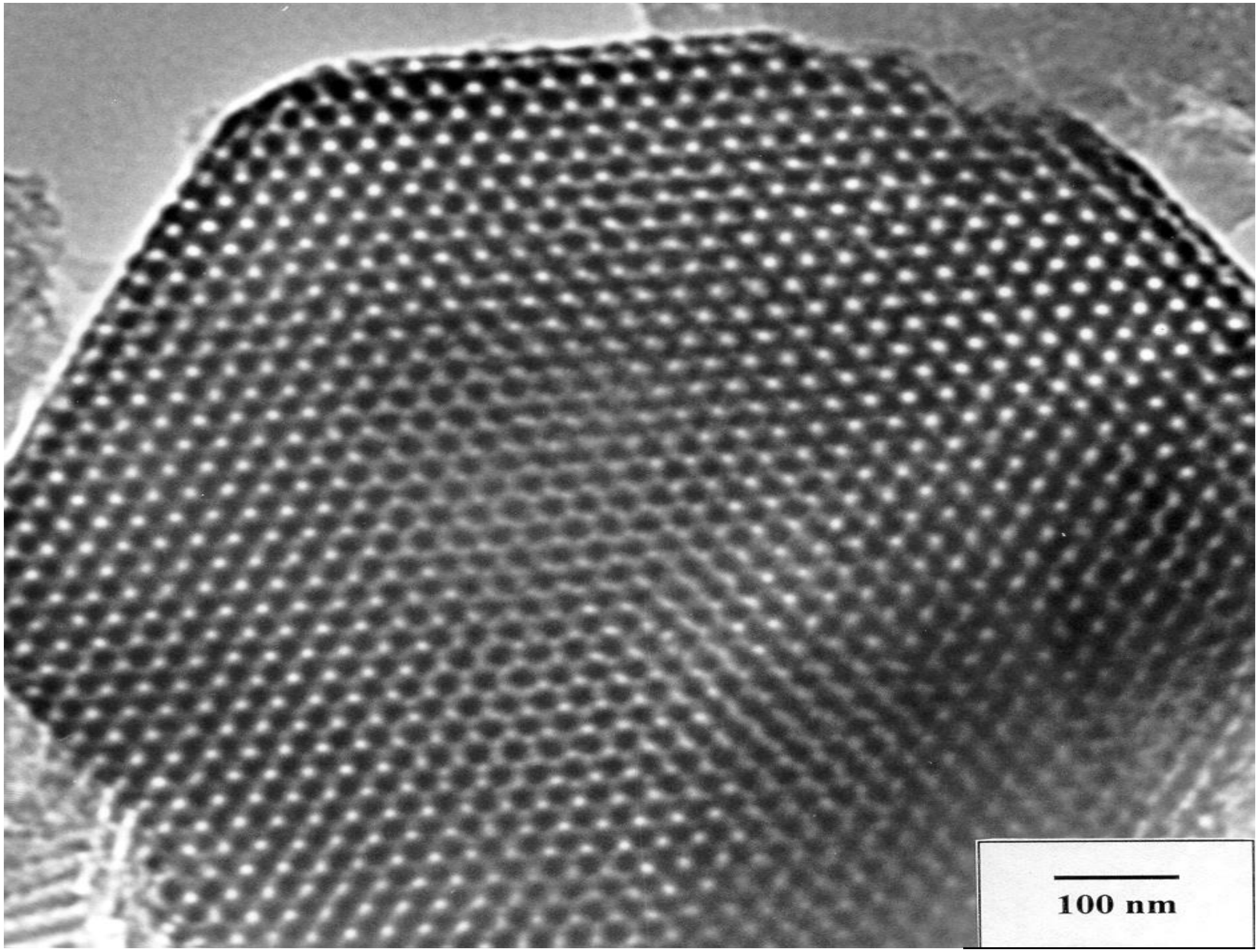


TEM image of Aligned 11 nm γ-Fe_2O_3 Nanocrystals

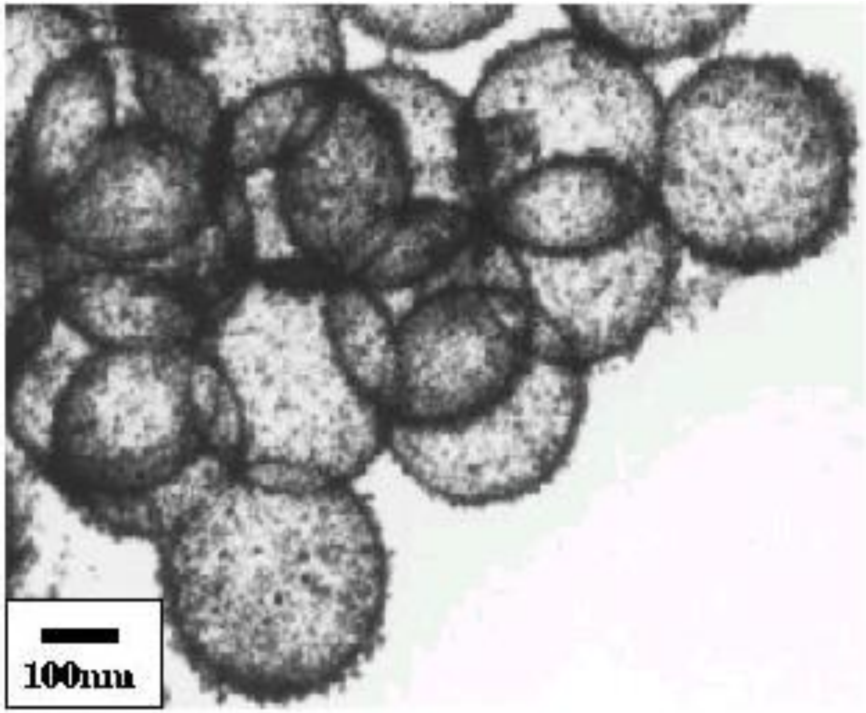
Photo by G. Markovich and Dr. P. Poddar.

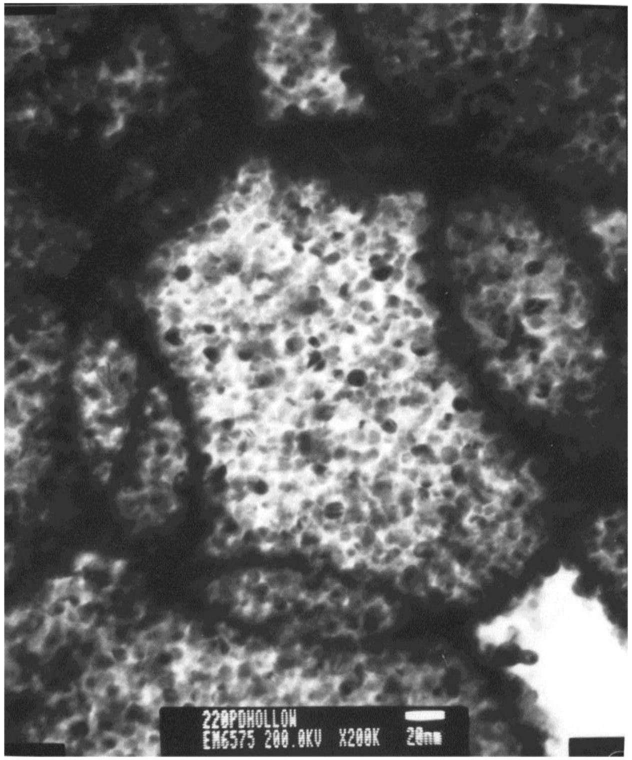

10 nm

TEM of the Proline-derivative on SBA-15



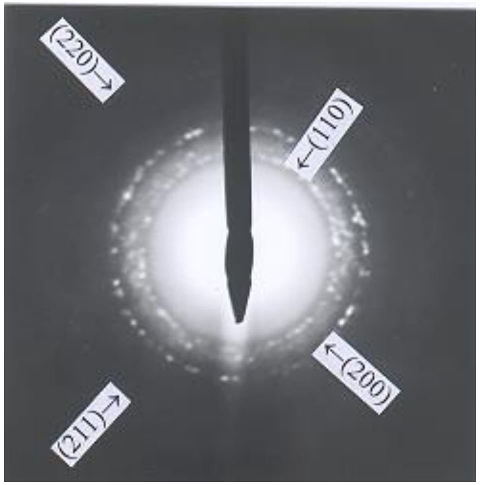
TEM image of Pd hollow spheres



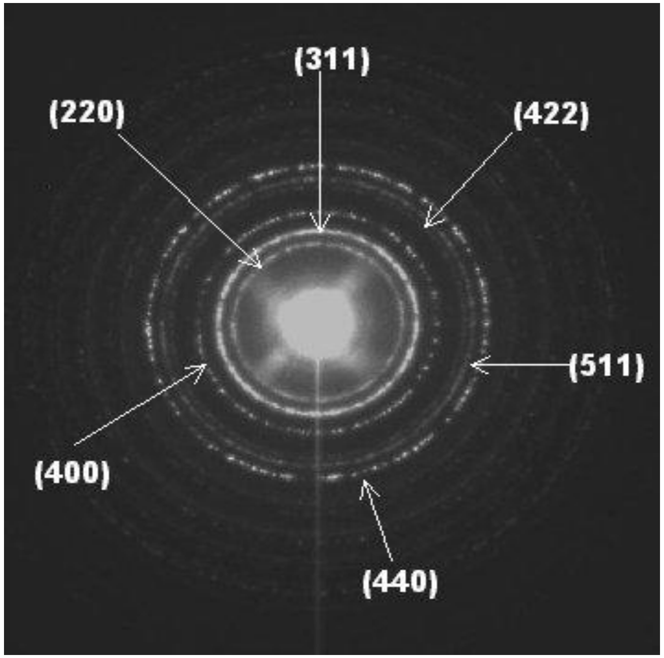


S.-W. Kim, M. Kim, W. Y. Lee, T. Hyeon *J. Am. Chem. Soc.* **2002**, 124, 7642.

Electron Diffraction



BCC Iron



γ-Fe_2O_3

d x r = instrument constant

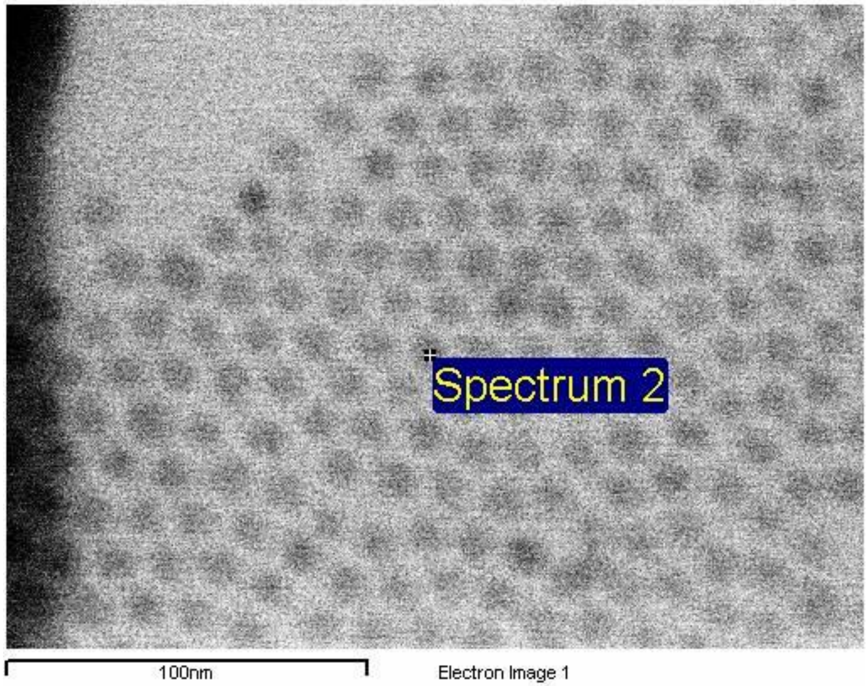
EDX or EDS

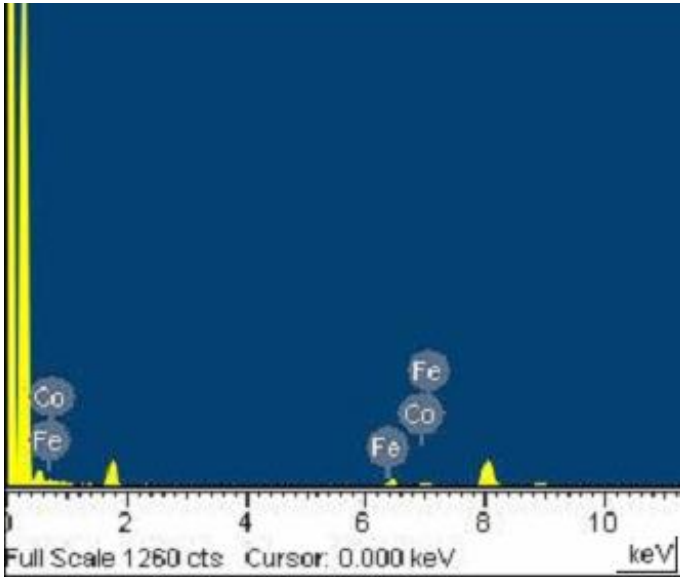
(Energy dispersive X-ray spectroscopy)

Elemental analysis in micrometer to nanometer scale

STEM (Scanning Transmission Electron Microscopy)

Elemental analysis (EDS and ICP-AES) of 9nm Cobalt Ferrite Nanocrystallites





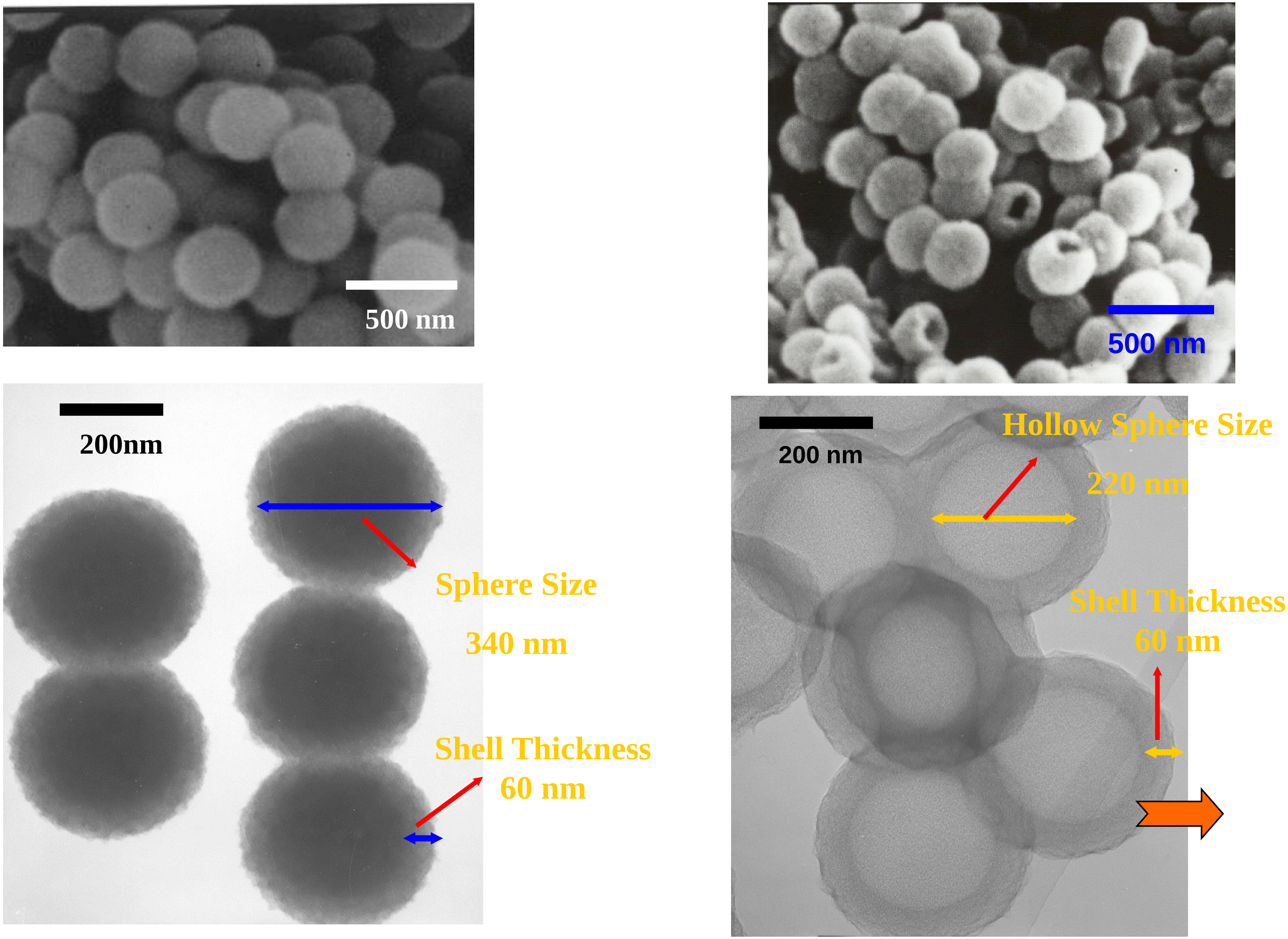
- **Co:Fe = 1:2.3** in 5nm×5nm area (averaged for 10 points)
- ICP-AES result (**Co:Fe = 1:2.2**) match with EDS data.
- Cobalt deficient cobalt ferrite : **$CoFe_{2.2}O_4$**

T. Hyeon, *et al. J. Phys. Chem. B.* 2002, 106, 6831.

Scanning Electron Microscopy (SEM)

-Low energy (< 50 eV) secondary electrons emitted from the surface of the specimen.

-The beam can be concentrated to a small probe (~20 A diameter)



S. B. Yoon, K. Sohn, J. Y. Kim, C.-H. Shin, J.-S. Yu, and T. Hyeon, *Adv. Mater*. **2002**, 14, 19.