Diffraction studies in non crystalline systems

Amitabh Das
Solid State physics Divison
Bhabha Atomic Research Centre
Mumbai

adas@barc.gov.in

Diffraction studies in non crystalline systems

- ✓X-ray
- ✓Neutron
- ✓Electron

- ✓Glasses
- ✓Nano materials
- ✓Crystalline systems – Defects, Disorder

X-ray technique   Type I users – Sample preparation
Type Ii users – Try to understand the structure

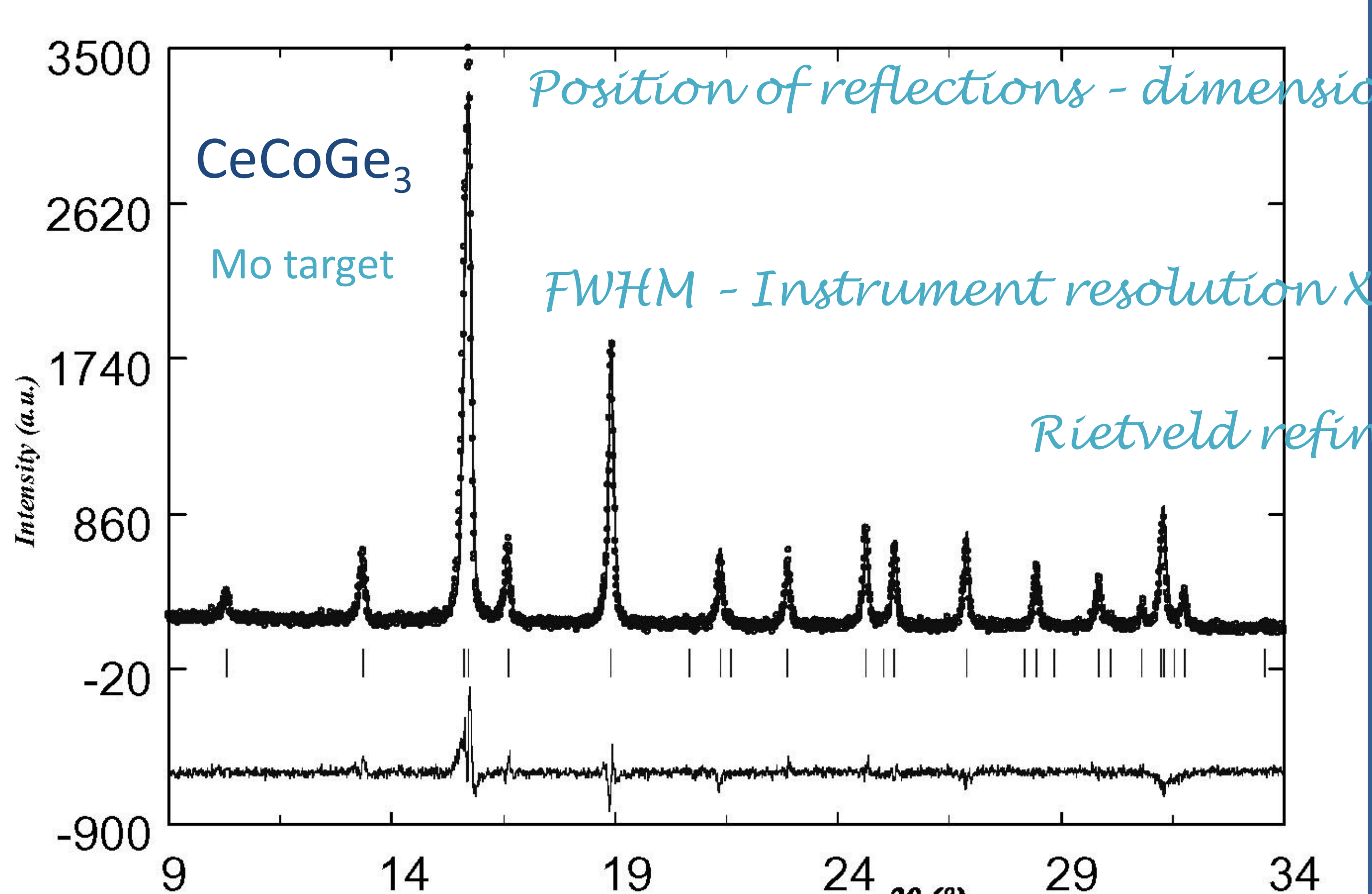
Coupling of structure with physical properties

Multiferroics
Manganites
Shape memory alloys

Popularity due to Rietveld technique

Powder pattern

Peak Intensity - Position of the atoms in the unit cell



Position of reflections - dimension of the cell

FWHM - Instrument resolution X sample

Rietveld refinement

Background Structured - TDS

Multiplicity

Elements of refinement - *Background*

Smooth

Inelastic and resonant

$$n_j = n_0 r_0^2 m_0 \Omega K t_j I_j$$

Structured

Thermal Disorder Scattering

$$\langle I_{TDS} \rangle = f^2 (1 - e^{-2M})$$

- Acoustic phonons peaks at Bragg reflections
- Optical and multiphonon processes have a smooth variation

In Debye model

$$I_{TDS} = I_{hkl} 2M_a \ln \left| \frac{g_m}{R - R_{hkl}} \right|$$

Powder Diffraction - *Advantages*

Single Crystal

•Determine Crystal Structure

•Fundamental physical properties

Powder

•Wider investigation of physical, chemical & mechanical properties

•Easier to make in large quantity

•Applications

Structure factor

$$F_K = \sum_j N_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]\exp[-M_j]$$

$$M_j = 8\pi^2 \overline{u_s^2} \frac{Sin^2\theta}{\lambda^2}$$

$\overline{u_s^2}$ is the root-mean square thermal displacement

Rietveld method- *Calculate Intensity*

Background

$$y_{ci} = s\sum_{k} L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{bi}$$

Absorption factor

Preferred orientation function

Scale factor

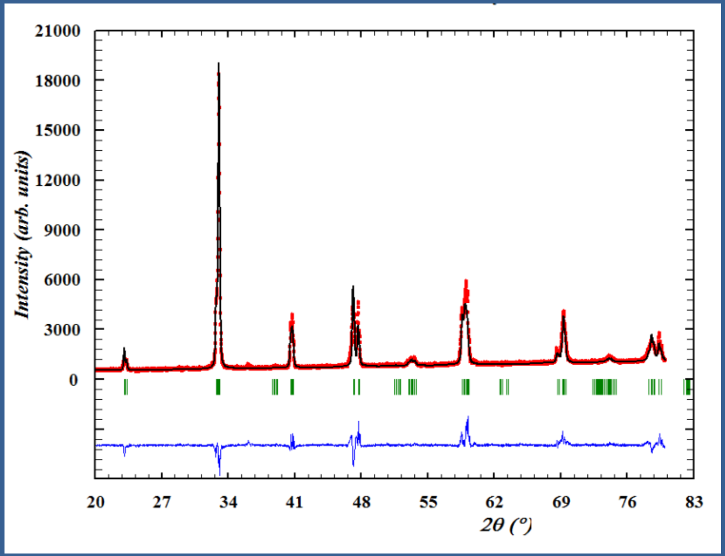
Reflection profile function

Structure factor

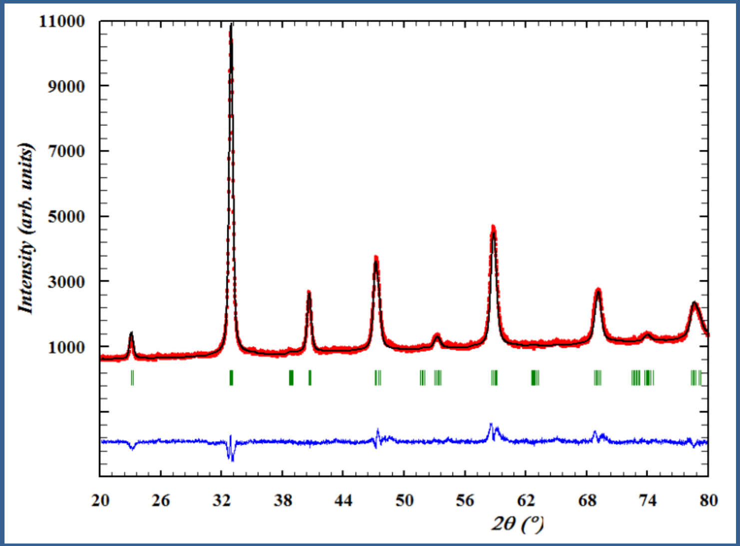
Lorentz, polarization, and multiplicity factor

Effect of reducing the particle size

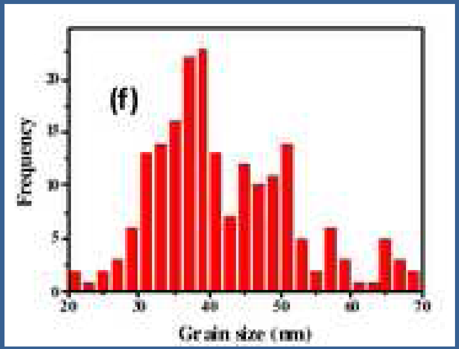
$Nd_{0.5}Sr_{0.5}MnO_3$



800 nm



40 nm



The structure factor in the case of crystalline materials

$$S_G = \sum_j f_j \exp(-i\mathbf{G} \bullet \mathbf{r}_j)$$

$$S_G = \sum_j f_j \exp[i2\pi(hx + ky + lz)]$$

In the absence of long range order -
Non crystalline solids – Glass, liquids….

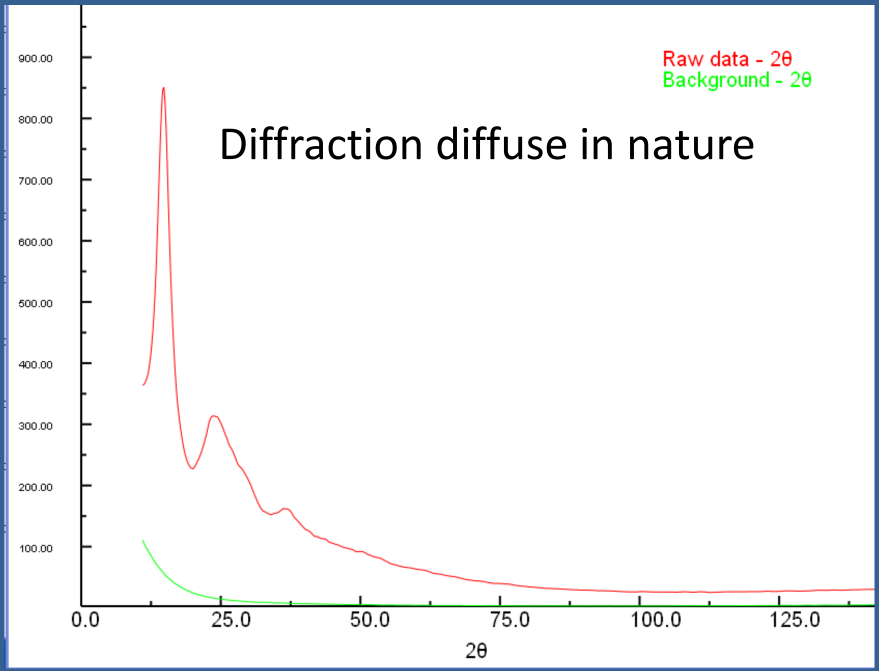
Short range order

Radial distribution function - pair correlation function

# of atoms in a spherical shell of unit thickness at a distance r from a reference atom

$G(r) = 4\pi r\rho_o\,[\rho(r)/\rho_o - 1]$

$\rho(r)$ and ρ_0 are the local and average atomic densities



Reciprocal lattice vector **G** replaced by arbitrary scattering vectors, Δ**k**=**k**’-**k**

$$S(\Delta\mathbf{k}) = \sum_m f_m \exp(-i\Delta\mathbf{k} \bullet \mathbf{r}_m)$$

$$I = S * S = \sum_m \sum_n f_m f_n \exp[-i\Delta\mathbf{k} \bullet (\mathbf{r}_m - \mathbf{r}_n)]$$

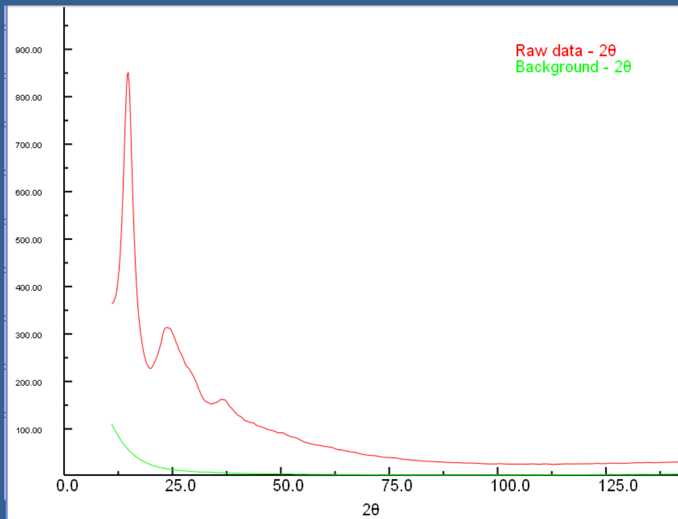
$$I = (\sum_m \sum_n f_m f_n \sin Kr_{mn}) / Kr_{mn}$$

$S(K) = I/Nf^2$

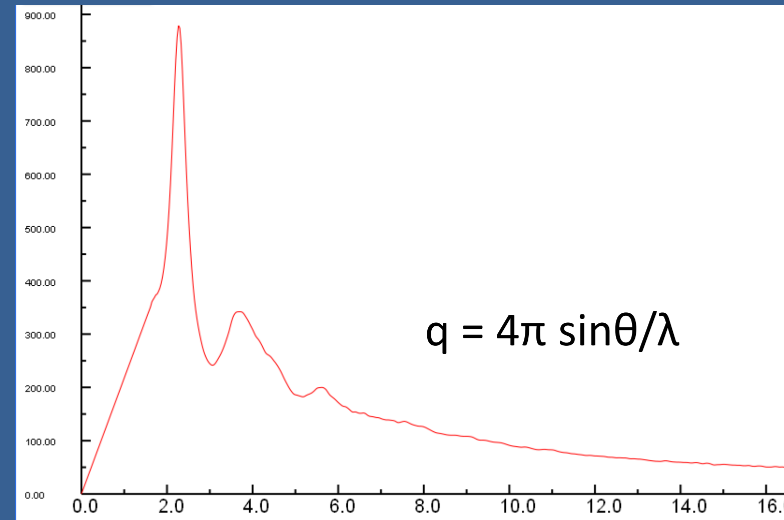
Liquid structure factor
N - # of atoms, f – Atomic form factor

Radial distribution function, g(r)

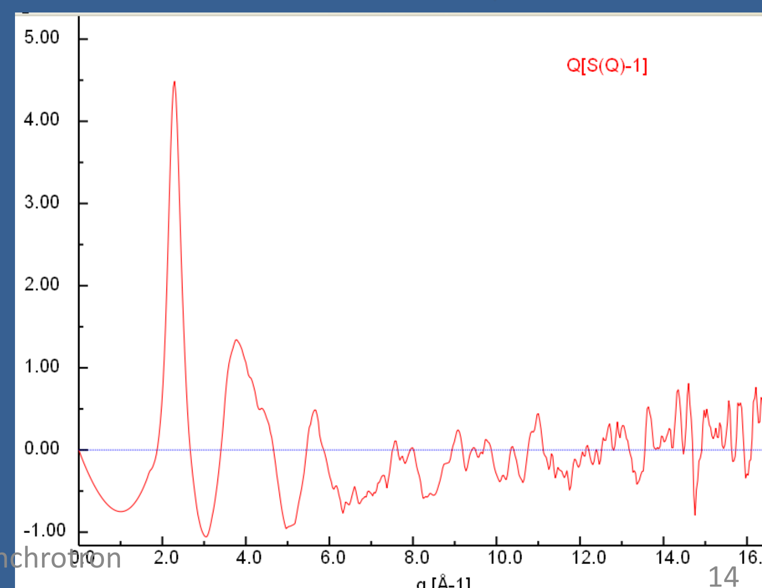
$$g(r) - 1 = \frac{1}{2\pi^2 \rho_0 r} \int d\mathbf{K}[S(\mathbf{K}) - 1]\mathbf{K} \sin \mathbf{K}r$$

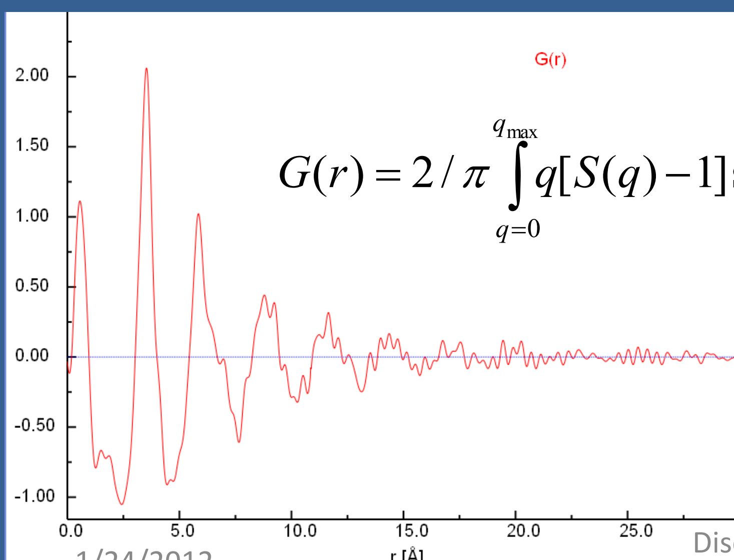


I(q)

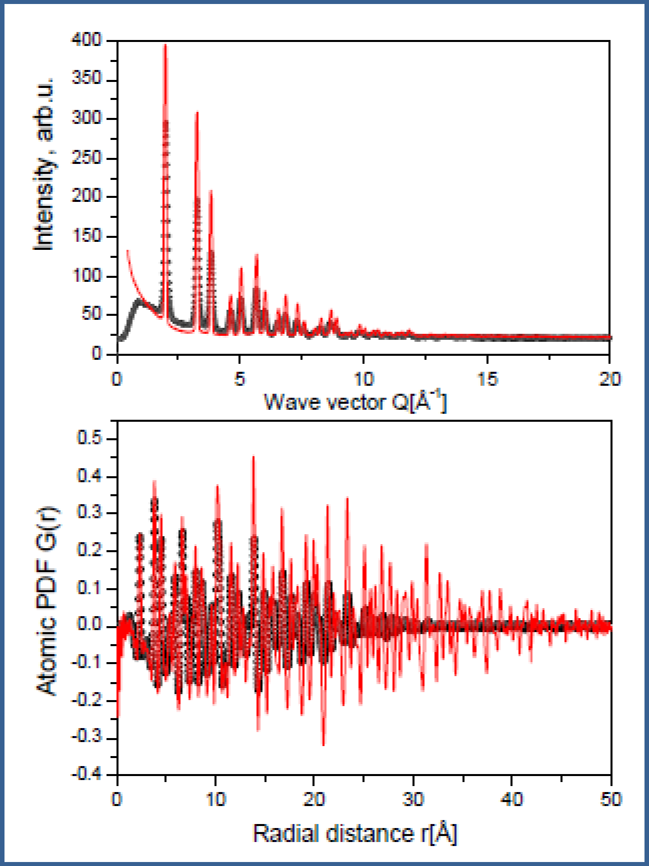


Å^{-1}





$$G(r) = 2/\pi \int_{q=0}^{q_{\max}} q[S(q)-1]\sin(qr)\,dq$$

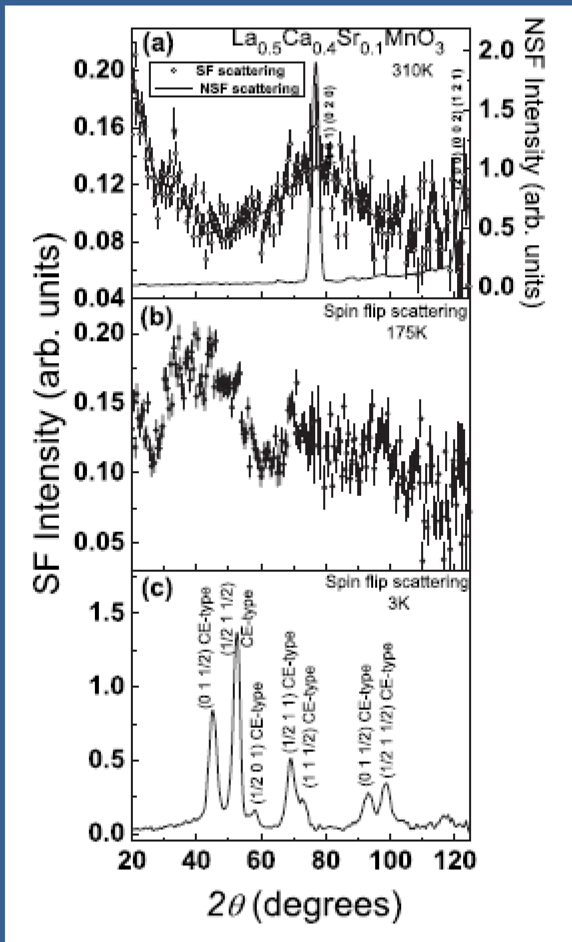

Intensity, arb.u.
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Wave vector Q[Å^{-1}]
Atomic PDF G(r)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0
10
20
30
40
50
Radial distance r[Å]

$$G(r) = 2/\pi \int_{q=0}^{q_{\max}} q[S(q)-1]\sin(qr)\,dq$$

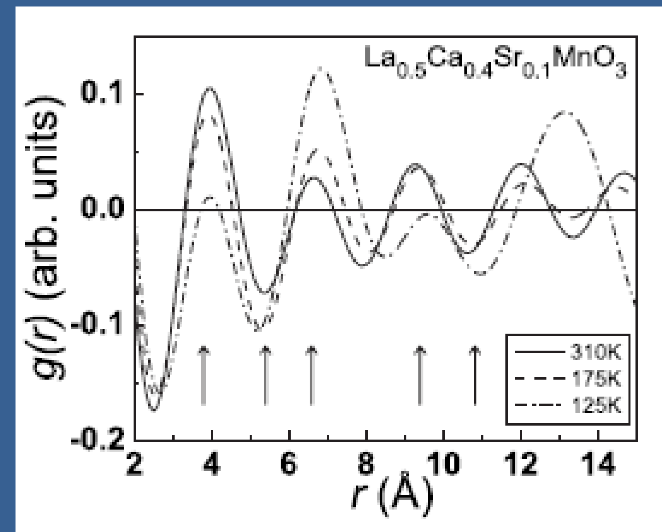
$$S(q) = 1 + \left[I^{coh}(q) - \sum c_i \left| f_i\ (q) \right|^2 \right] / \left| \sum c_i f_i (q) \right|^2$$

- ✓ q_{max} should be at least 20 Å^{-1} possible only with synchrotron or Mo
- ✓ Remove air background, sample holder, correct for absorption effects, if any
- ✓ Correct data for Compton scattering

- RAD
- PDFX
- RMCPOW



$$g(r) = \int_{Q_1}^{Q_h} I_{\mathrm{mag}}(Q) f(Q)^{-2} Q \sin(Qr) dQ,$$



$$g(r) = \frac{1}{S(S+1)} \sum_{r'} \langle S_0 \cdot S_{r'} \rangle \cdot \delta(|r| - |r'|).$$

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Diffuse neutron scattering study of magnetic correlations in half-doped $La_{0.5}Ca_{0.5-x}Sr_xMnO_3$ manganites (x=0.1, 0.3, and 0.4)

I. Dhiman,[1] A. Das,[1,*] R. Mittal,[1] Y. Su,[2] A. Kumar,[1] and A. Radulescu[2]

Neutron Scattering - *Elemantary*

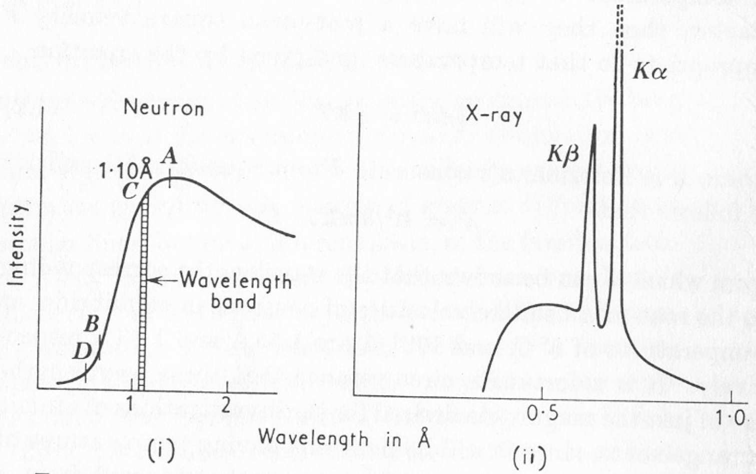


FIG. 2. The intensity versus wavelength distribution (i) for the neutron beam emerging from a reactor, indicating the band of wavelength selected by a monochromator, is contrasted with the distribution (ii) from an X-ray tube which gives intense lines of 'characteristic' radiation.

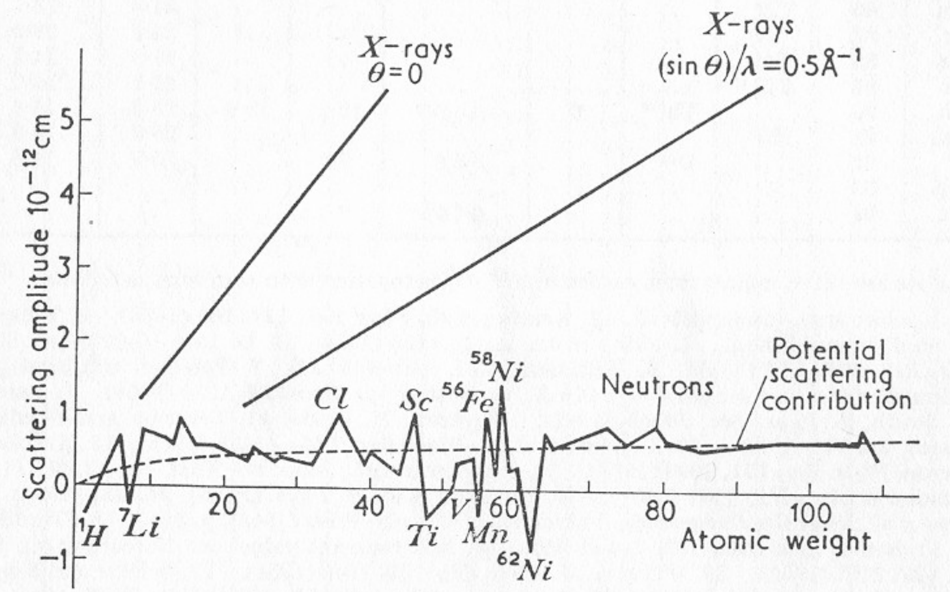
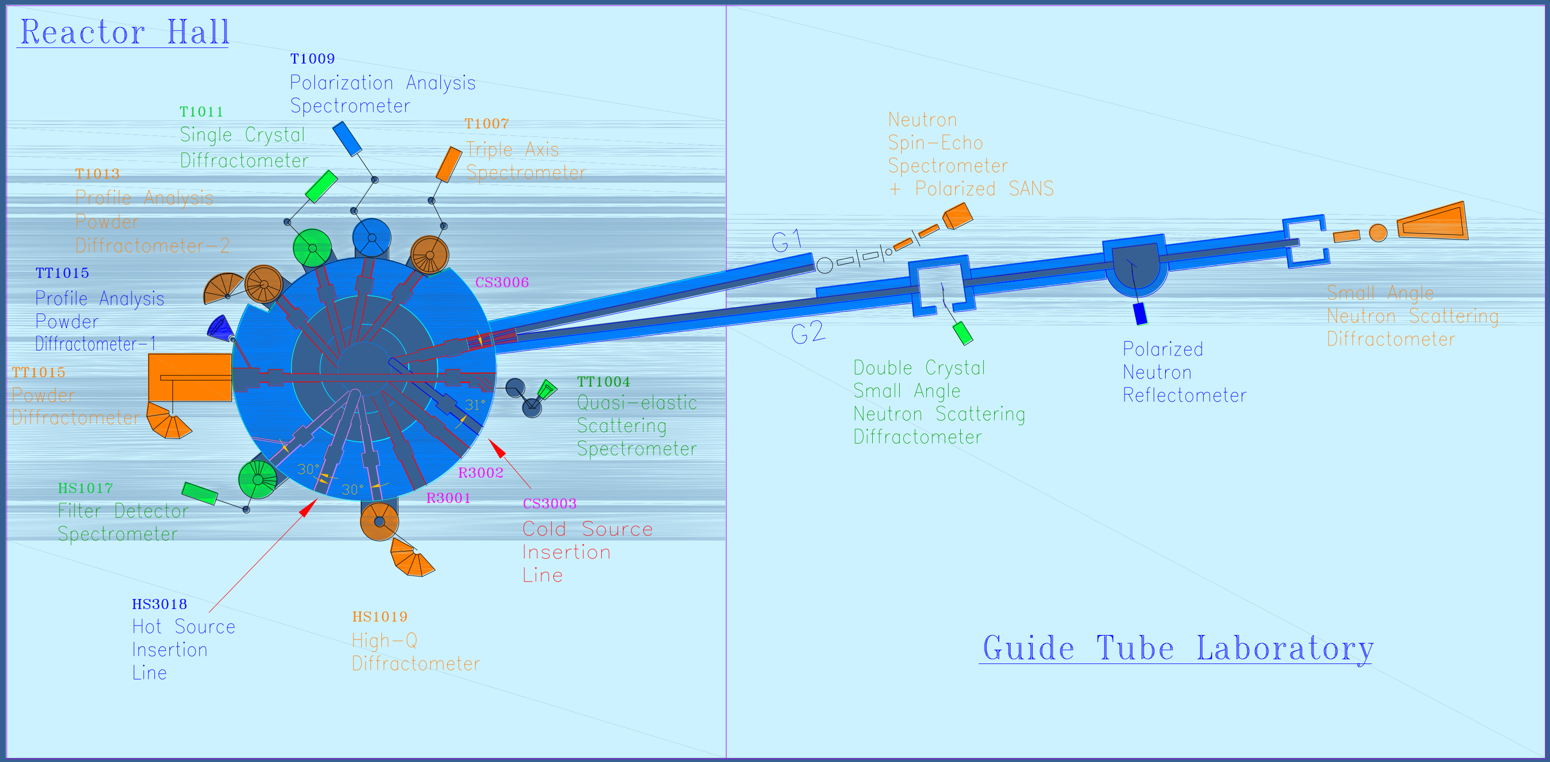


FIG. 14. Irregular variation of neutron scattering amplitude with atomic weight due to superposition of 'resonance scattering' on the slowly increasing 'potential scattering': for comparison the regular increase for X-rays is shown. (From *Research*, London, 7, 257, 1954.)

- Neutron interacts with nuclei
- It has a magnetic moment

Experimental facilities in Dhruva



The measure of the isotropic size effect

$$size(gaussian) = \frac{180 \times \lambda}{\pi \sqrt{Z}}$$

in Angstroms

$$size(lorentzian) = \frac{360 \times \lambda}{\pi^2 \times Y}$$

Anisotropic broadening of size – only lorentzian component is considered and various models are chosen through the parameter F