Scattering Amplitudes

From previous discussion on periodic function V

$$\Gamma(\mathbf{k}', \mathbf{k}) = \frac{2\pi}{\hbar} \left| \langle \mathbf{k}' | V | \mathbf{k} \rangle \right|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$$

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \left[\frac{1}{L^3} \sum_{\mathbf{R}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}} \right] \left[\int_{unit-cell} \mathbf{dx} \; e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}} \; V(\mathbf{x}) \right]$$

First term is zero unless the Laue condition is satisfied

Second term is related to the structure factor

$$S(\mathbf{G}) = \int_{unit-cell} \mathbf{dx} \; e^{i\mathbf{G}\cdot\mathbf{x}} \; V(\mathbf{x})$$

Scattering Amplitudes for X-rays

The intensity of scatter radiation is

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

X-rays scatter from electrons in a system and V is proportional to the electronic density

$$V(\mathbf{x}) \sim \sum_{\text{atom } j \text{ in unit cell}} Z_j \; g_j(\mathbf{x} - \mathbf{x_j})$$

g_j is some short-ranged function (typically of the size of an atom)

Plugging in here - $$S(\mathbf{G}) = \int_{unit-cell} \mathbf{dx} \; e^{i\mathbf{G}\cdot\mathbf{x}} \; V(\mathbf{x})$$

We get - $$S(\mathbf{G}) \sim \sum_{\text{atom } j \text{ in unit cell}} f_j \; e^{i\mathbf{G}\cdot\mathbf{x_j}}$$

Form factor ($\propto Z_j$)

Scattering Amplitudes for Neutrons

The intensity of scatter radiation is

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

Neutrons are uncharged, they scatter from nuclei (nuclear forces)

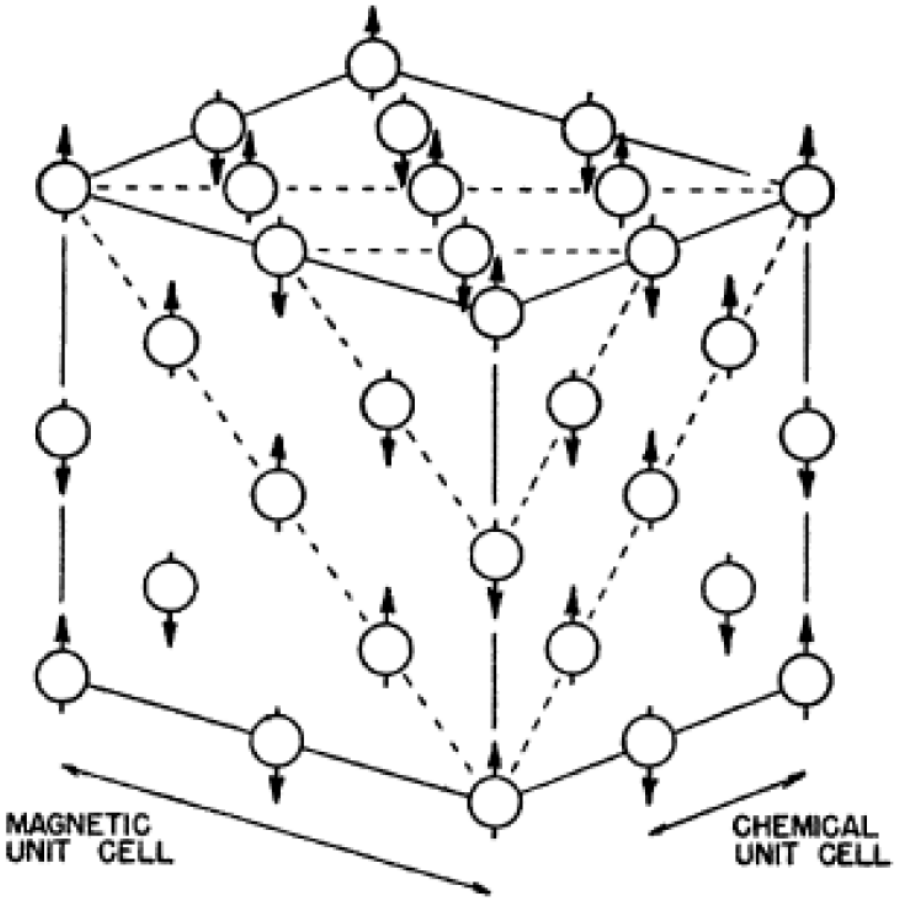
$$V(\mathbf{x}) \sim \sum_{\text{atom } j \text{ in unit cell}} b_j \; \delta(\mathbf{x} - \mathbf{x_j})$$

b_j are the nuclear-scattering-length (extremely short ranged)

X-rays and Neutron Scattering

- X-rays scatter very strongly from heavy atoms ($\propto Zj$) and hardly from light atoms. This makes it difficult to see light atoms, like Hydrogen using XRD
- Nuclear scattering length varies rather erratically with atomic number. Hydrogen turns out to be a very good neutron scatterer
- Neutrons also have spin and thus neutron diffraction signal carries additional spin information also of the scattering atoms
- Neutrons can detect whether various electrons in the unit cell have spins pointing up or down

Neutron Scattering

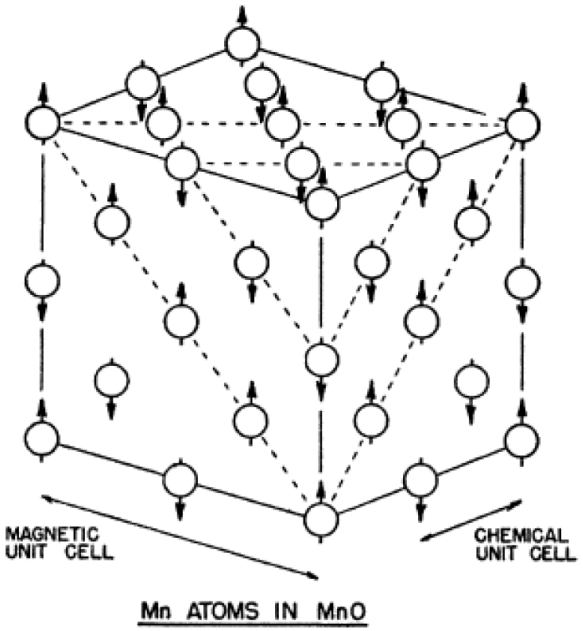


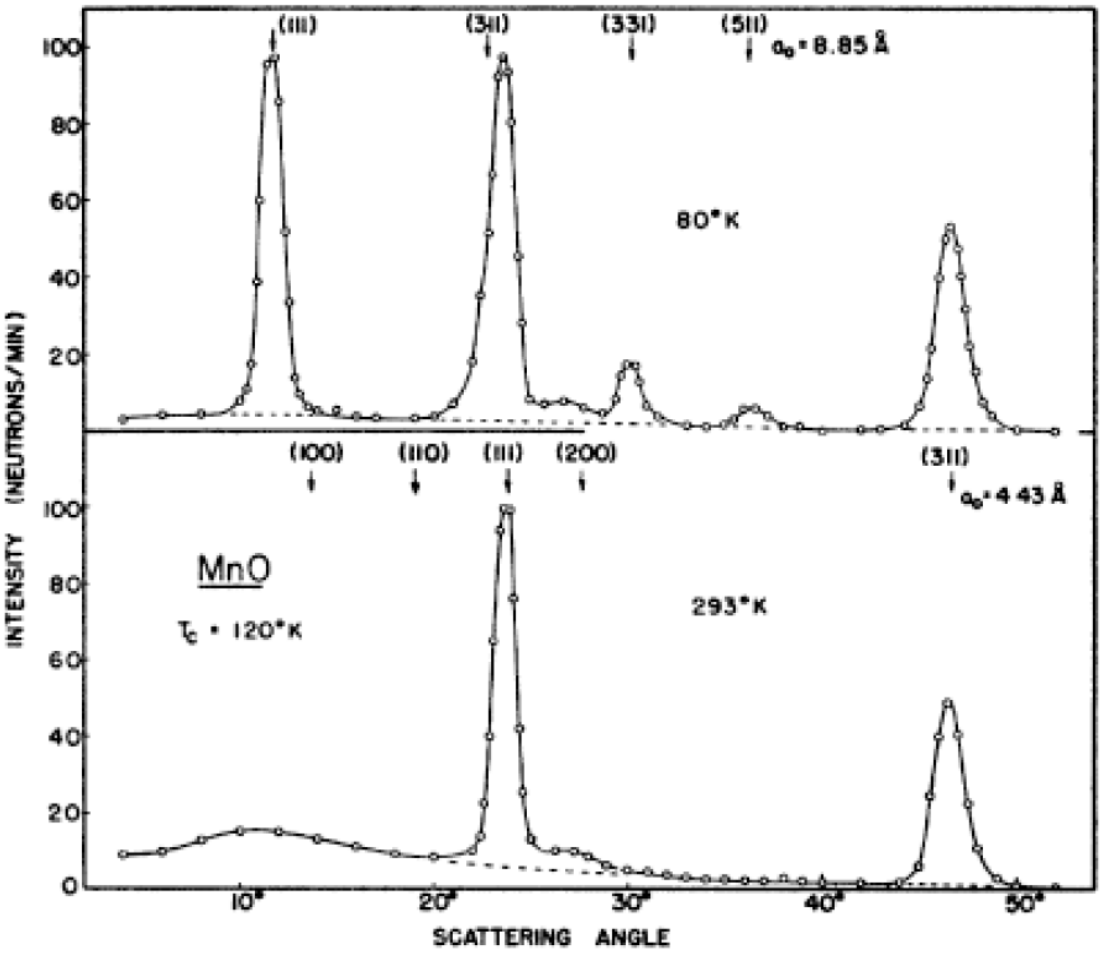
Mn ATOMS IN MnO

It crystallizes in the space group $Fm\bar{3}m$ with a lattice parameter of a = 4.446 Å

C. G. Shull *et al*. *Phys*. *Rev*. **83,** 333 (1951); W. Ratcliff *Symmetry* **14.** 1215 (2022)

Neutron Scattering





C. G. Shull *et al*. *Phys*. *Rev*. **83,** 333 (1951); W. Ratcliff *Symmetry* **14.** 1215 (2022)

Scattering of X-rays

The structure factor, as seen before, is -

$$S(\mathbf{G}) \sim \sum_{\text{atom } j \text{ in unit cell}} f_j \quad e^{i\mathbf{G}\cdot\mathbf{x_j}}$$

The reciprocal lattice vector "G" is normal to lattice planes (h k l)

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

Taking example of orthogonal primitive lattice vectors -

$$S_{(hkl)} = \sum_{\text{atom } j \text{ in unit cell}} f_j \; e^{2\pi i(hx_j + ky_j + lz_j)}$$

Here $[x_j, y_j, z_j]$ are the co-ordinates of "atom j" within unit cell in units of three primitive vectors

Example - BCC Cs

Basis		
Cs	Position=	$[0,0,0]$
Cs	Position=	$[a/2,a/2,a/2]$

$$S_{(hkl)} = f_{Cs} + f_{Cs}\, e^{2\pi i(h,k,l)\cdot[1/2,1/2,1/2]}$$

$$= f_{Cs}\left[1+(-1)^{h+k+l}\right]$$

$$\boxed{I_{(hkl)} \propto |S_{(hkl)}|^2}$$

The scattering intensity vanishes when (h+k+l) is an odd integer

This phenomenon is known as systematic absence

Example – FCC Cu

Basis given by points

$$[0,0,0], [1/2,1/2,0], [1/2,0,1/2], \text{ and } [0,1/2,1/2]$$

The Structure Factor of Cu is given by

$$S_{(hkl)} = f_{Cu}\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]$$

The scattering intensity vanishes unless h,k,l are all odd or all even

Selection rules for Bravais lattice types

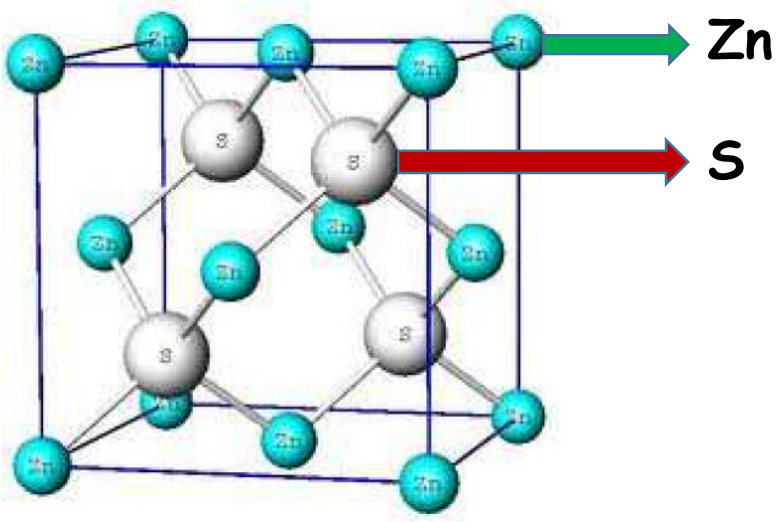
Systematic Absences of Scattering	
Simple Cubic	all h, k, l allowed
bcc	$h + k + l$ must be even
fcc	h, k, l must be all odd or all even

Selection rules for Bravais lattice types

Systematic Absences of Scattering	
Simple Cubic	all h, k, l allowed
bcc	$h + k + l$ must be even
fcc	h, k, l must be all odd or all even

- These absences, or selection rules, occur for any structure with a given Bravais Lattice type
- Even if the material is bcc with five different atoms per primitive unit cell, it will show the same selection rules as the bcc lattice with a single atom per primitive unit cell

Example – ZnS (FCC with a basis)



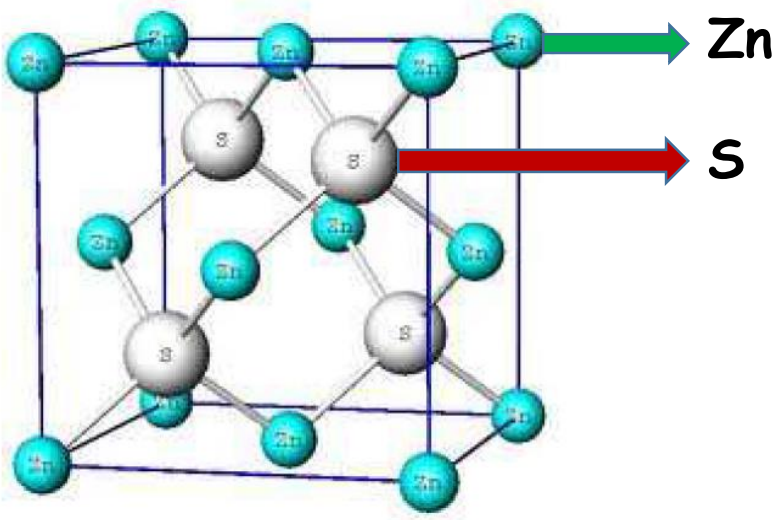
Zn atom at [0,0,0] and S atom at $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$

Basis for ZnS						
Zn	Positions=	$[0,0,0]$,	$[1/2,1/2,0]$,	$[1/2,0,1/2]$,	and	$[0,1/2,1/2]$
S	Positions=	$[1/4,1/4,1/4]$,	$[3/4,3/4,1/4]$,	$[3/4,1/4,3/4]$,	and	$[1/4,3/4,3/4]$

$$S_{(hkl)} = f_{Zn}\left[1 + e^{2\pi i(hkl)\cdot[1/2,1/2,0]} + \ldots\right] +$$

$$f_S\left[e^{2\pi i(hkl)\cdot[1/4,1/4,1/4]} + e^{2\pi i(hkl)\cdot[3/4,3/4,1/4]} + \ldots\right]$$

Example – ZnS (FCC with a basis)



$$S_{(hkl)} = f_{Zn}\left[1 + e^{2\pi i(hkl)\cdot[1/2,1/2,0]} + \ldots\right] +$$

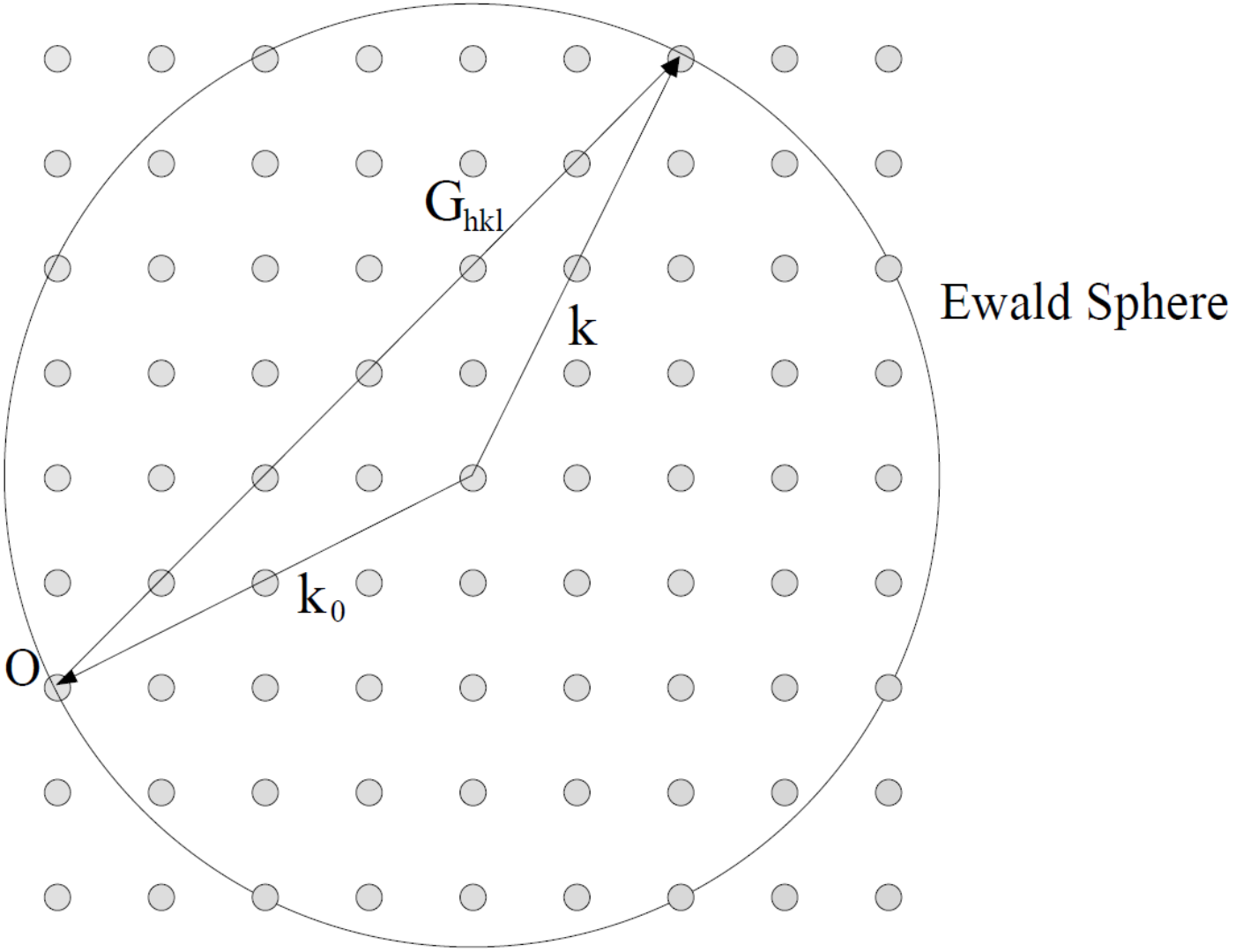
$$f_S\left[e^{2\pi i(hkl)\cdot[1/4,1/4,1/4]} + e^{2\pi i(hkl)\cdot[3/4,3/4,1/4]} + \ldots\right]$$

$$S_{(hkl)} = \left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]\left[f_{Zn} + f_S\, e^{i(\pi/2)(h+k+l)}\right]$$

$$S_{(hkl)} = S_{(hkl)}^{Lattice} \times S_{(hkl)}^{basis}$$

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

Condition for observation of XRD peak



Incident wave-vector k_0 and diffracted wave-vector k

XRD measurement techniques

Laue Method

Take a single crystal, shine X-rays on it from one direction and keep detector in some direction. Vary the wavelength of the incoming wave. This allows to satisfy the Bragg condition at some wavelength.

Rotating Crystal Method

Instead of varying wavelength of incoming X-rays, here the crystal is rotated continuously to achieve the Bragg condition

Powder Diffraction Method or Debye-Scherrer Method

Sample in the form of powders, or a group of small crystallites which are oriented in all possible directions. Incoming wave can get scattered from any of the many small crystallites. Similar in sense to rotating crystal method