

Structure of Solids - X-ray diffraction Studies (Examples)

Lecture 7

CHM 637

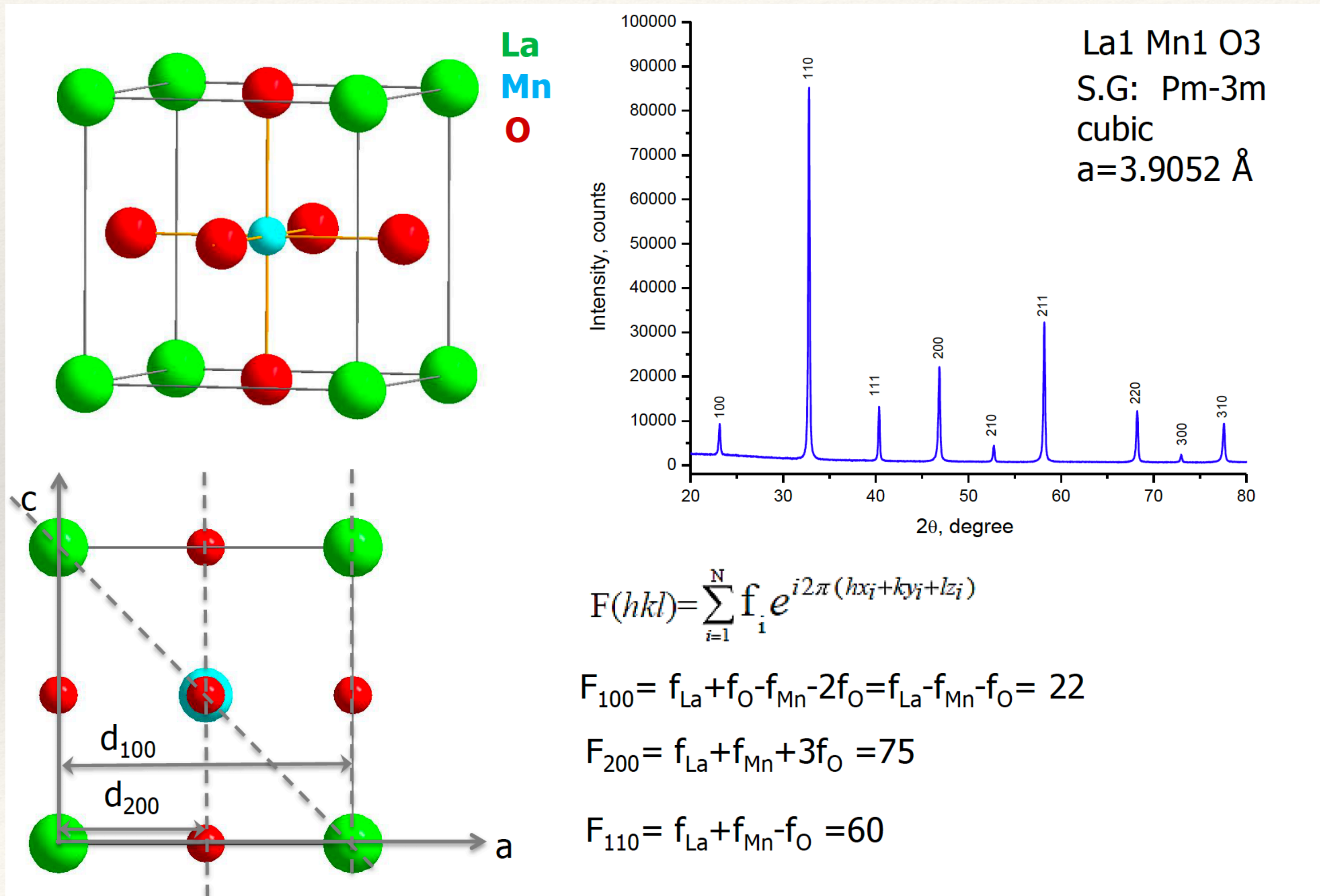
Chemistry & Physics of Materials

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Lecture Plan

- X-ray diffraction by compound crystals - an example
- XRD of powder samples
- XRD for amorphous solids

Intensities for a compound crystal



Powder patterns

Single crystals are hard to grow and most often we have poly crystalline or powder samples to analyse.

Consider such a sample with randomly oriented and randomly spaced crystallites of finite size, each located by the vector \vec{U}

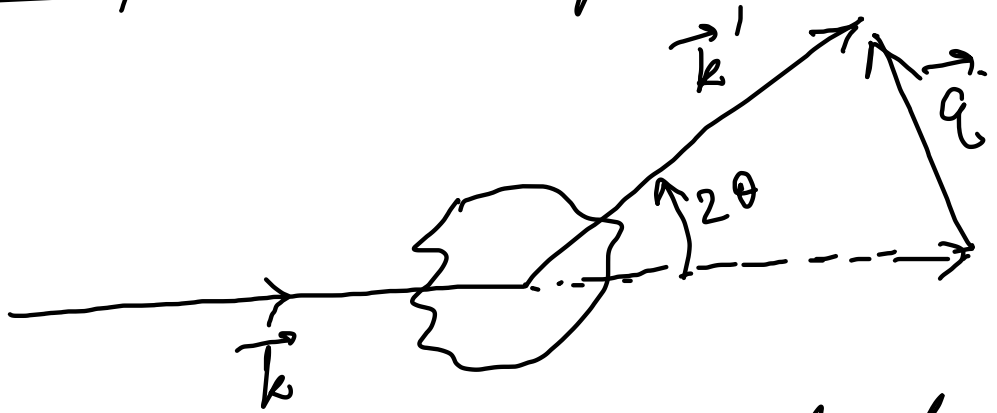
The scattered intensity at a scattering vector q from such a sample can be written as an incoherent sum of contributions stemming from individual crystallites

$$I \sim N_c^2 \sum_{\vec{U}} |\Phi(\vec{q})|^2 \sum_{\vec{G}_U} \delta_{\vec{q}, \vec{G}_U}$$

\vec{G}_U Reciprocal Lattice Vectors
of the crystallite U

N_c Average number of unit
cells in each crystallite

Scattering intensity in a polycrystalline sample



Assume that the sample has randomly oriented crystallites (finite size)

Position of j^{th} atom \vec{r}_j of the unit cell at \vec{R} in the crystallite U is:

$$\vec{A}_j(\vec{R}, \vec{U}) = \vec{U} + \vec{R}_U + \vec{S}_U^j$$

— (1)

$$I(\vec{q}) \sim |F(\vec{q})|^2$$

$$F(\vec{q}) = \sum_{\vec{R}} \sum_j f_j(\vec{q}) e^{-i\vec{q} \cdot \vec{R} + \vec{\delta}_j}$$

For our case,

$$F(\vec{q}) = \sum_{\vec{u}} \sum_{\vec{R}_u} \sum_j f_j(\vec{q}) e^{-i\vec{q} \cdot (\vec{u} + \vec{R}_u + \vec{\delta}_u^j)}$$

$$I(\vec{q}) \sim \left| \sum_{\vec{u}} \sum_{\vec{R}_u} \sum_j f_j(\vec{q}) e^{-i\vec{q} \cdot (\vec{u} + \vec{R}_u + \vec{\delta}_u^j)} \right|^2$$

Sum over all the \vec{R}_n first

For each crystallite: $\sum_{\vec{R}} e^{-i\vec{q} \cdot \vec{R}}$

$$\sum_{n=0}^{N-1} e^{-iqa n} = \frac{(1 - e^{-iqa N})}{(1 - e^{-iqa})}$$

$$= \frac{\sin\left(\frac{qaN}{2}\right) e^{-\frac{iqa(N-1)}{2}}}{\sin\left(\frac{qa}{2}\right)} \rightarrow (4) \quad e^{-\frac{iqaN}{2}} \cdot \frac{(e^{\frac{iqaN}{2}} - e^{-\frac{iqaN}{2}})}{(e^{\frac{iqa}{2}} - e^{-\frac{iqa}{2}})}$$

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = \prod_{j=1}^3 \frac{\sin\left[\left(J_j + \frac{1}{2}\right)\vec{q}\cdot\vec{a}_j\right]}{\sin\left(\vec{q}\cdot\vec{a}_j/2\right)} \quad (\text{ph}) \quad (5)$$

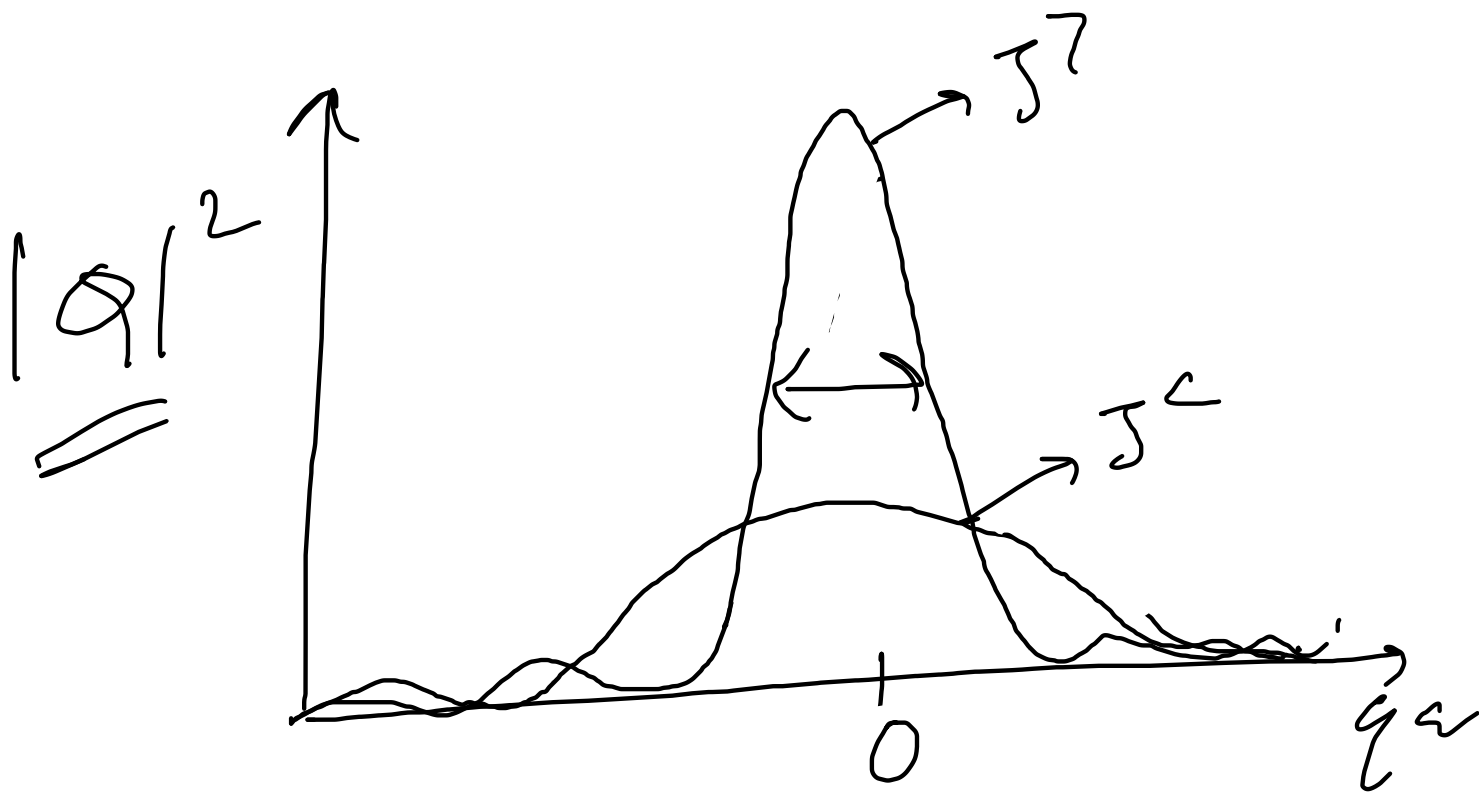
$\{\vec{a}_j\} \rightarrow$ primitive lattice vectors

Each crystallite has unit cells

running from $-J_j$ to $+J_j$ in the j^{th} direction

for $J \rightarrow \infty$

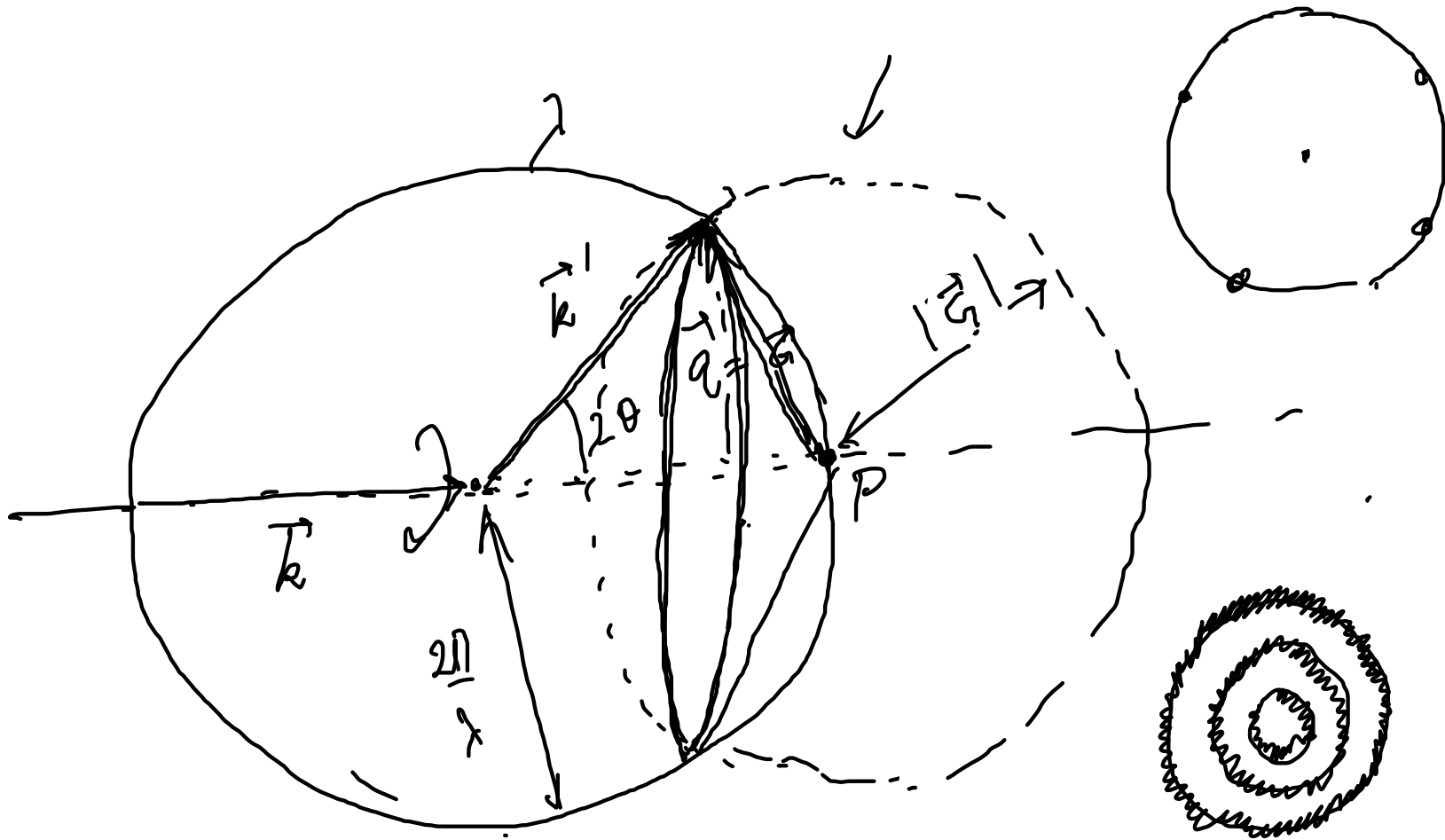
$$Q(\vec{q}a; J) \approx \frac{\sin\left(\left(J + \frac{1}{2}\right) \vec{q} \cdot \vec{a}\right)}{\sin\left(\frac{\vec{q} \cdot \vec{a}}{2}\right)}$$



$$\approx N_c^2 \sum_{\vec{u}} \sum_{\vec{s}} \sum_{\vec{s}'} f_s(\vec{q}) f_{s'}^*(\vec{q}) \sum_{\vec{u}} \delta_{\vec{q}, \vec{u}}$$

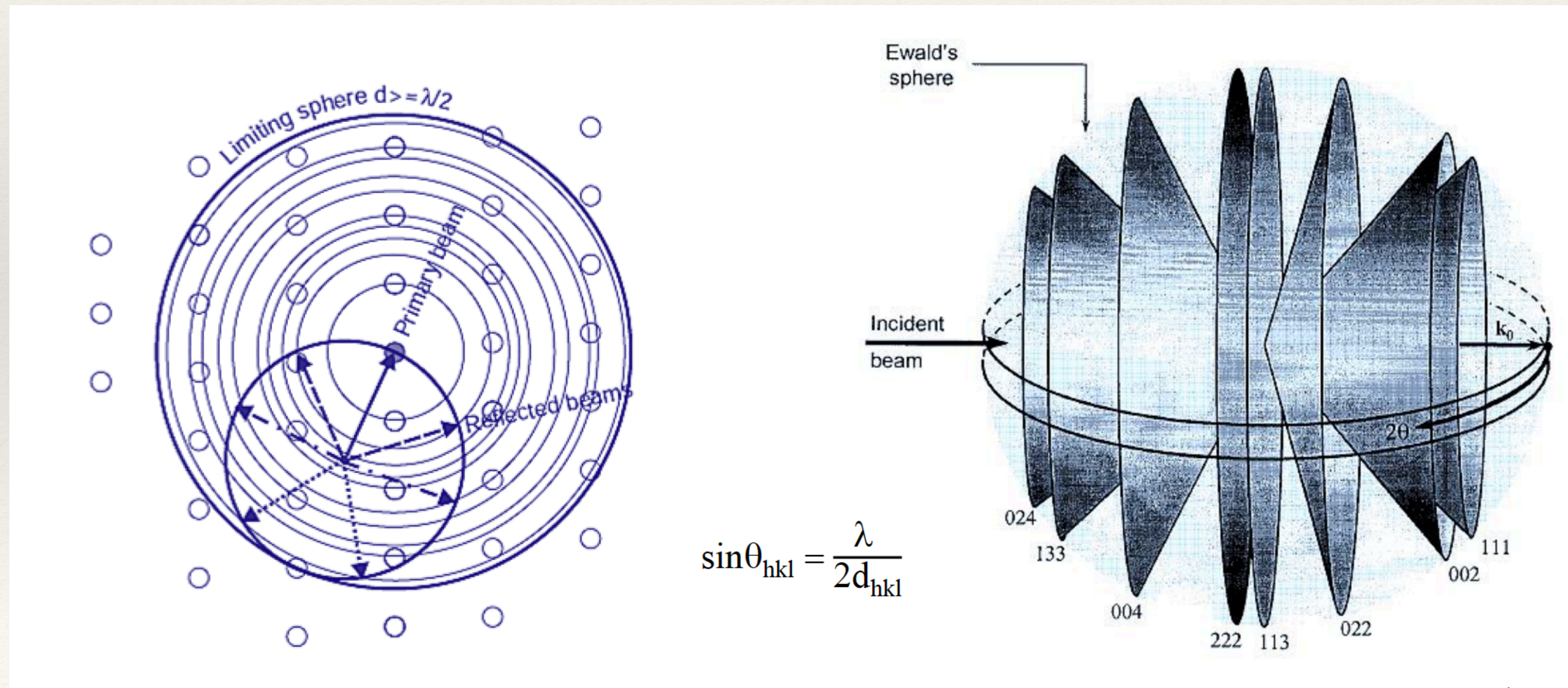
$$= N_c^2 \sum_{\vec{u}} \left[\underbrace{|\Phi(\vec{q})|^2}_{\substack{\text{---} \\ \text{---}}} \left(\sum_{\vec{u}} \delta_{\vec{q}, \vec{u}} \right) \right]$$

— (8)



Powder Samples: Ewald Sphere

The resultant diffraction pattern is a set of concentric rings on the detector. This structure arises since we have allowed for all orientations of crystallites to be present. It can be explained by the Ewald Sphere construction below.



Amorphous solids

Amorphous solids lack long-range order (periodicity) that crystals have. Instead they have short-range order.

In such samples, the XRD data can be used to infer the short-range structure.

The scattered intensity can be related to the so-called radial distribution function $g(r)$ as follows:

$$I(\vec{q}) \sim N_A |f(\vec{q})|^2 \left[1 + \rho_0 \int d^3r (g(r) - 1) e^{-i\vec{q}\cdot\vec{r}} \right]$$

Amorphous solids

$$F(\vec{q}) = \sum_{n=1}^{N_a} e^{-i\vec{q} \cdot \vec{r}_n} f_n(\vec{q}) \quad - \textcircled{9}$$

$$I(\vec{q}) \sim |F(\vec{q})|^2$$

$\vec{r}_n \rightarrow$ location of n th atom in the solid

$$= \sum_m \sum_n f_m^*(\vec{q}) f_n(\vec{q}) e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \quad - \textcircled{10}$$

Pair density: concentration (probability density)
of atoms at \vec{r} given that
there is an atom at the origin

$$P^{(2)}(\vec{r}) = \rho_0 (g(\vec{r}) - 1) \equiv \frac{1}{N_A} \sum_{n \neq m} \delta(\vec{r} - (\vec{r}_n - \vec{r}_m))$$

\uparrow
 average density
 of atoms

 \downarrow
 pair distribution function

 — (10)

In amorphous solids, it is expected that $g(\vec{r})$ is isotropic.

$\therefore g(\vec{r}) \equiv g(r) \rightarrow$ radial distribution fun.

$$\begin{aligned}
 I &\sim \sum_{n=m} + \sum_{n \neq m} \\
 &= \sum_{n=1}^{N_A} |f_n(\vec{q})|^2 + \sum_{n \neq m} f_m^*(\vec{q}) f_n(\vec{q}) e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \\
 &= |f(\vec{q})|^2 \left[N_A + N_A^* \frac{1}{N_A} \sum_{n \neq m} e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \right] \\
 &= |f(\vec{q})|^2 \left\{ N_A + N_A \int d^3r \left(\frac{1}{N_A} \sum_{n \neq m} \delta(\vec{r} - |\vec{r}_n - \vec{r}_m|) \right) e^{-i\vec{q} \cdot \vec{r}} \right\}
 \end{aligned}$$

$$= |f(q)|^2 \times N_A \left\{ 1 + \rho_0 \int \frac{d^3r}{V} (g(r) - 1) e^{-i\vec{q} \cdot \vec{r}} \right\}$$

$$= I(\vec{q}) = I(q) \longrightarrow \textcircled{11}$$

By inverse F.T.

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty dq \sin(qr) \times \left\{ \frac{I(q)}{N_A |f(q)|^2} - 1 \right\}$$

— $\textcircled{12}$

$$G(r) = 4\pi\rho_0 r (g(r) - 1) - (12)$$

reduced radial distribution

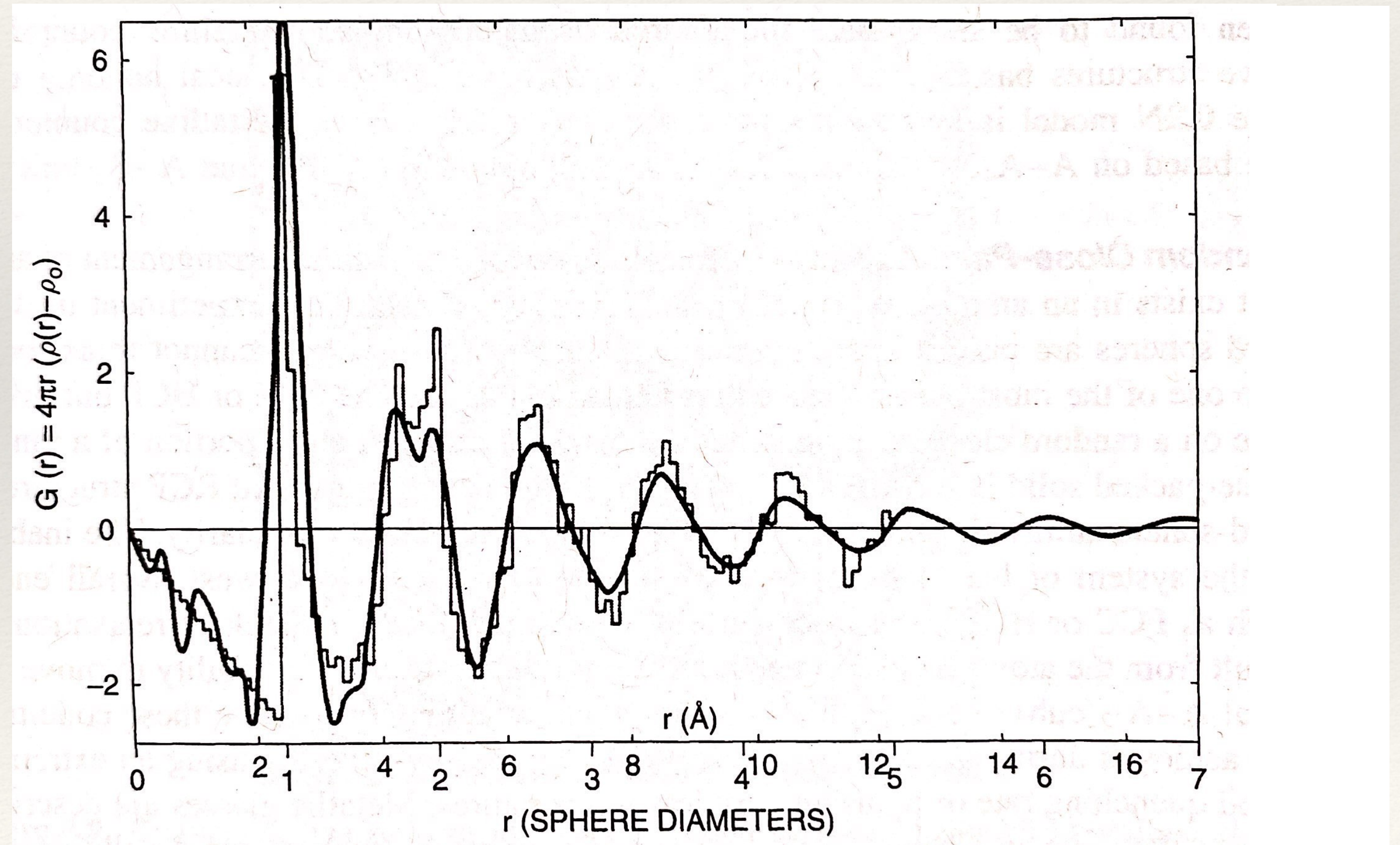
Peaks in $g(r) \Rightarrow$ favorable interatomic distances

$g(r) = 1 \Rightarrow G(r) = 0 \Rightarrow$ continuum

Amorphous solids

The radial distribution function can then be obtained by inverse Fourier transform of the intensity.

Example, $\text{Ni}_{0.76}\text{P}_{0.24}$ - a metallic glass



Source: Gersten and Smith