TongJi Materials Science and Engineering
"X-ray Diffraction" April 2015 (Prof. Ian Robinson)

Lecture 1: Kinematic Diffraction

Als-Nielsen & McMorrow "Elements of Modern X-ray Physics", Wiley (2011), sections 1.1, 1.2, 5.1;
B. E. Warren "X-ray Diffraction", Dover (1990) chapters 1-2

1. Classical electron scattering.
   Radiation accelerates electron; electron radiates.
   $I = I_0 (e^4/m^2c^4R^2) \frac{1}{2}(1+\cos^2\phi)$ where
   $(e^4/m^2c^4)^{1/2} = 2.8\times10^{-15}$m = Thomson (classical) electron radius
   Depends on polarization with respect to scattering angle ϕ

2. Scattering by an atom.
   Complex sum of amplitudes from all electrons in atom.
   $f = \Sigma_n \int 4\pi r^2 \rho_n(r) \sin(Qr)/(Qr)\, dr$
   Defines *form factor* of atom f(Q) where $Q = (4\pi/\lambda) \sin\theta$

3. Compton scattering (called `modified' scattering in Warren)
   The difference between the intensity scattered by an electron bound in atomic orbital and a classical electron at a point.
   Scattering is *incoherent* because it has a different frequency.

4. Crystal lattice.
   Crystal = Lattice * Basis (convolution)
   Lattice is the repeating part with ideal points.
   Basis is the contents of each cell, atoms or electron density
   Translational symmetry is property that defines a lattice.
   Lattice may have other symmetry, eg rotation, reflection that distinguishes one crystal *system* from another.

5. Bravais Lattice
   14 possible ways to make (3D) space translationally invariant. 2 definitions:
   (a) Infinite array of discrete points, which appears identical in both position and orientation, when viewed from any of the points.
   (b) $\mathbf{R} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$ with $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ non-coplanar.

6. Reciprocal lattice.
   The set of all plane wave wavevectors **G** that possess the periodicity of a given Bravais lattice, $\mathbf{R} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$
   $\exp(i\mathbf{G}\cdot\mathbf{R}) = 1$ hence $\mathbf{G}\cdot\mathbf{R} = 2\pi$ (integer)
   General Solution: $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$
   with $\mathbf{b}_1 = (2\pi/V_{cell})\, \mathbf{a}_2\times\mathbf{a}_3$ etc $V_{cell} = \mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3$.

7. Important properties
   i) **G** is a Bravais lattice itself.
   ii) Reciprocal lattice of **G** is **R** again.
   iii) If the $\mathbf{a}_i$'s are primitive, then so are the $\mathbf{b}_i$'s.

iv) Orthogonality: $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$

v) hkl are `Miller indices' of lattice planes in real space
with $|\mathbf{G}_{hkl}| = 2\pi / d_{hkl}$ d_{hkl} = `d-spacing' of planes.

Lecture 2: Integrated Intensity

Als-Nielsen & McMorrow sections 5.1, 5.5, 5.6.1; Warren chapters 3-4

1. Diffraction by a crystal
Intensity distribution diffracted by a small crystal of dimension $N_1\mathbf{a}_1 \times N_2\mathbf{a}_2 \times N_3\mathbf{a}_3$
$I(\mathbf{Q}) = I_0 (e^4/m^2c^4R^2)\ ½(1+\cos^2 2\theta)\ |F(\mathbf{Q})|^2\ S_1(\mathbf{Q})\ S_2(\mathbf{Q})\ S_3(\mathbf{Q})$
where the first two terms are the electronic cross-section we saw last time,
$F(\mathbf{Q}) = \Sigma_n f_n(Q) \exp(i\mathbf{Q}\cdot \mathbf{r}_n)$ is the Structure Factor
The summation is over all the atoms of the unit cell, defined by $\mathbf{a}_1$ $\mathbf{a}_2$ and $\mathbf{a}_3$.
$S_j(\mathbf{Q}) = \sin^2(N_j\mathbf{Q}\cdot \mathbf{a}_j) / \sin^2(\mathbf{Q}\cdot \mathbf{a}_j)$ is the slit function
$S_1(\mathbf{Q})\ S_2(\mathbf{Q})\ S_3(\mathbf{Q})$ is strongly peaked at the nodes of the reciprocal lattice.

2. Examples of Structure Factor
The evaluation may be carried out with different choices of unit cell:
FCC evaluated with cubic unit cell:
$F = f(Q)\ [1 + \exp(\pi i(h+k)) + \exp(\pi i(k+l)) + \exp(\pi i(l+h))]$
$= 4\ f(Q)$ when hkl unmixed (all even or all odd), $= 0$ when hkl mixed
Other examples: NaCl and Zn

3. Naming of crystal structures.
Correct convention is to name after the parent compound:
`Rocksalt' for any cubic structure AB with the NaCl arrangement
`Zincblende' for any cubic structure AB with the ZnS arrangement
`Diamond', `Copper', `Tungsten', `Magnesium' etc
Strictly incorrect, but common, to name the lattice for elements: FCC, BCC, HCP

4. Integrated Intensity.
Desire accurate measurements of structure factors to learn about crystal structure.
Peak value of $S_j(\mathbf{Q})$ is difficult to define because of practical limitations, collimation, crystal mosaic, inhomogeneities, etc
$\int S_1(\mathbf{Q})\ S_2(\mathbf{Q})\ S_3(\mathbf{Q})\ d^3\mathbf{Q}$ is well defined, hence $\int I(\mathbf{Q})\ d^3\mathbf{Q}$ is good measure of $|F(\mathbf{Q})|^2$
Integrated intensity measurement corresponds to rotation of crystal (at constant rate ω) and collection of entire diffracted beam (open detector).
$E = I_0/\omega\ (e^4/m^2c^4R^2)\ \lambda^3 V/v_a^2\ (1+\cos^2 2\theta)/2\sin 2\theta\ |F(\mathbf{Q})|^2$
new terms are: $\sin 2\theta$ = Lorentz factor,
V = crystal volume, and v_a = unit-cell volume.

5. Powder sample with extended face.
Integration over angle is now done by a random distribution of mosaic orientations.
Need to consider absorption length of beam in crystal = μ^{-1} and the incident power, $P_0 = I_0 A_0$ instead of intensity, I_0 (A_0 = area of incident beam).
Finally, m = *multiplicity* of the reflection = number of equivalents over 4π.
$P' = P_0/16\pi^2 R\ (e^4/m^2c^4R^2)\ \lambda^3 m/2\mu v_a^2\ (1+\cos^2 2\theta)/(\sin\theta \sin 2\theta)\ |F(\mathbf{Q})|^2$

Lecture 3: Crystallographic Experimental Methods

Als-Nielsen & McMorrow sections 5.1, 5.6.1; Warren chapters 5-7

1. Ewald construction
   Draw sphere of radius $|\mathbf{k}|$ tangential to the origin of reciprocal space.
   $\mathbf{k}_i$ is vector from origin to center of sphere.
   Any reciprocal lattice node touching sphere will be an allowed value of $\mathbf{k}_f$
   In general there is *no diffraction*. Need to move something to hit diffraction condition.

2. Laue method.
   Continuous spectrum of wavelengths gives range of Ewald spheres.
   Region of reciprocal space between limiting spheres contains active reflections.
   Back-reflection version good for crystal cutting.
   Transmission method no longer obsolete; now used for `single shot' crystallography.

3. Zone axis.
   $\mathbf{A}(uvw) = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$ is a low-index *real-space* direction defining zone uvw.
   This is perpendicular to a plane of lattice points in reciprocal space.
   Construct Laue pattern as set of intersecting rings (ellipses on flat film) passing through origin of pattern. Very obvious for large-unit-cell crystal.

4. Rotation method.
   Rotate about zone axis; entire reciprocal space plane will pass through reflection.
   Generates a line of points on detector or film, called `layer 0'.
   Other layers are parallel to this, with n'th layer satisfying uh + vk + wl = n

5. Powder Method.
   All orientations present in sample; gives `Debye-Scherrer' rings.
   Focussing geometry allows divergent beam and large ample to be used efficiently.
   Energy dispersive method with single incident and exit beam direction.
   Simple example: analysis of NaCl

6. Integrated intensity for powder sample with extended face.
   Integration over angle is now done by a random distribution of mosaic orientations.
   Need to consider absorption length of beam in crystal = μ^{-1} and the incident power, $P_0 = I_0 A_0$ instead of intensity, I_0 (A_0 = area of incident beam).
   Finally, m = *multiplicity* of the reflection = number of equivalents over 4π.
   $P' = P_0/16\pi^2 R\,(e^4/m^2c^4R^2)\,\lambda^3 m/2\mu v_a^2\,(1+\cos^2 2\theta)/(\sin\theta \sin 2\theta)\,|F(\mathbf{Q})|^2$

7. X-ray detectors.
   Ionization chamber: not photon-counting
   Proportional (Geiger) counter: counting, 10% energy resolution.
   Solid-state detector: 1% energy resolution.
   Scintillation counter: faster counting, <10% energy resolution.