

Crystal Physics - Revision Notes

Andrew Winter

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1 The Crystalline State

1.1 The Crystal Lattice

- Choose an atom to be the origin.
- Identify all positions within the crystal that are identical in all respects to the origin, assuming an infinite crystal.
- This set of identical points is called the **crystal lattice**. Lattice is not in general the same as the structure.
- A crystal lattice is independent of the choice of origin.
- The coordinate axis is obtained by joining the lattice at the origin to its neighbours (two in 2D, three in 3D).
- Conventionally choose coordinates which reflect the symmetry of the lattice. Label **a, b, c**.
- The lattice is completely specified by giving the lengths of **a, b, c** and the angles between them α, β, γ . All points in the lattice can be reached by vectors of the form:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \text{ where } u, v, w \in \mathbb{Z} \quad (1)$$

α	$0, 2\pi$	$\frac{\pi}{3}$	$\frac{\pi}{2}$	$\frac{2\pi}{3}$	π
n	1	6	4	3	2
Shape					

Table 1: Table of symmetry representations.

- Lattice vectors also define a **unit cell**, a shape defined so that the entire crystal can be formed by stacking such cells.
- Volume of a unit cell in a 3D lattice can be found by $V_c = |\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}|$
- A **Bravais lattice** is one of 14 possible lattices defined in 1 containing one, two, three, four and six fold rotation axes.
- The smallest possible unit cell is said to be a **primitive unit cell**.
- A **basis** of the structure is found by identifying the group of atoms which, when associated with each lattice point, completely generates the structure. If the basis vector is $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$ then the position of an extra atom included in the basis is said to be (x, y, z) .

1.2 Point Symmetry

Point symmetry is the symmetry of an object as observed from a point. It is defined by a symmetry operation which translates an object onto itself. Here it is used to describe the local symmetry of the unit cell within a lattice. Different points in the lattice will have different point symmetry.

These are basic point symmetry operations

- Rotation about an axis by an angle $\alpha = \frac{2\pi}{n}$, where n gives the degree of symmetry. The degree of symmetry is denoted by a shape on the point in question as defined in table 1.
- Inversion through a point $(x, y, z) \longleftrightarrow (\bar{x}, \bar{y}, \bar{z})$.
- Reflection, which in 2D is like roto inversion.

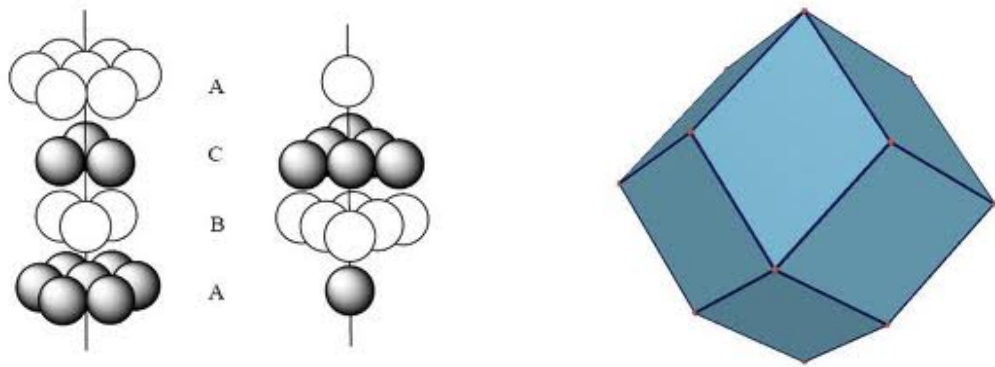
The point symmetry of the basis must be compatible with the underlying symmetry of the lattice to form a crystal. It is clear that only some point groups can be placed on high symmetry lattices. Tetrads can only be placed on a square lattice and triads and hexads can only be placed on a hexagonal lattice.

1.3 Crystal Planes and Miller Indices

- We can identify sets of equally spaced parallel planes in a lattice. A plane is defined by the Miller indices $(h \ k \ l)$ where the plane that passes closest to the origin has intercepts at $a/h, b/k$, and c/l . Negative intercepts are denoted with a bar. The set of $(\bar{h} \ \bar{k} \ \bar{l})$ planes is of course equivalent to the set of $(h \ k \ l)$ planes.
- For a crystal with an orthogonal crystal axis, adjacent lattice planes are separated by

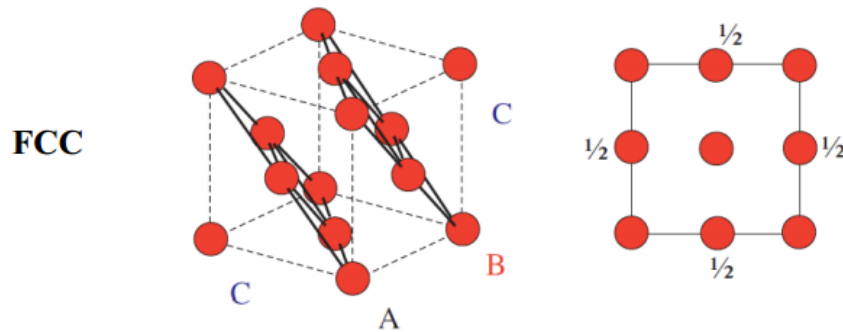
$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \quad (2)$$

- Note if \mathbf{a}, \mathbf{b} , and \mathbf{c} define a primitive unit cell then Miller indices do not have a common factor.
- For crystals with high level of symmetries we can define sets of planes related by symmetry, being equivalent from an atomic point of view. For example, for crystals with cubic symmetry, the three sets of planes $(100), (010)$ and (001) are related and belong to the **form** $\{100\}$, where curly brackets mean all planes equivalent by symmetry to the given plane.
- A direction in a lattice $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ is written $[u \ v \ w]$. This is not a Miller index, but in the cubic case will be perpendicular to the plane $(u \ v \ w)$.



(a) The construction of a FCC structure from stacking spheres.

(b) Rhombic dodecahedron, an atomic sphere of influence in a FCC structure.



(c) The conventional unit cell which shows the symmetry of a FCC structure. Four times bigger than the primitive cell.

Figure 1: FCC structure

1.4 Close-Packing Spheres

Spheres can be packed with varying closeness depending on the structure of the material they form. The closeness of the packing, or the **packing ratio** (see below), is dependent on the forces between atoms, and the closer it is to 'ideal' for a particular structure, the more well behaved the material will be. To understand the packing ratio, we must first understand some crystal structures.

Packing Structures

- We can consider packing in terms of a 2D cross section. After circles are closely packed, the next layer will fit into half the interstices in the same arrangement of the first. This can be repeated for the set of interstices that have no atom centred on them to give an ABCABC... stacking sequence (Figure 1). This is **face-centred cubic** (FCC) or **cubic close-packed** (CCP). Examples of elements which crystallise into FCC structure are aluminium, calcium, nickel, copper, silver, gold, lead, neon, argon, krypton and xenon.
- The **atomic coordination polyhedron** is a way to visualise the environment of an atom in a FCC structure. It is formed from planes which are perpendicular bisectors of lines joining an atom to its neighbours. It represents a 'sphere of influence' of an atom, and in this case is a rhombic dodecahedron (Figure 1b), with 12 faces corresponding to its 12 nearest neighbours; hence each atom is said to have a **coordination number** of 12. This is also a type of unit cell known as the **Wigner-Seitz cell**.
- **Hexagonal close-packing** (HCP) (Figure 2) is similar to FCC except that we remove the C layer from Figure 1a to get an ABAB... structure. In this case all the A- plane atoms have an identical environment and can be considered lattice points (see section 1.1). The unit cell contains a basis of an A atom at $(0, 0, 0)$ and a B atom at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. The close-packed A planes are the (001) planes with B planes between them.
- Due to the different environments of A and B atoms, their coordination polyhedra have the same shape but different orientations.

- For a HCP structure we can now define the **packing ratio** as c/a where c is the distance between an A plane to the next A plane, and a is the length of the base of the cell. The ‘ideal’ ratio can be found by geometry to be $(8/3)^{1/2} \approx 1.633$.
- In reality, because atoms are not hard spheres, packing ratios deviate from this value. Some examples of some ratios in HCP structures: magnesium (1.623), titanium (1.586), zinc (1.861), cadmium (1.886) and helium (1.633).

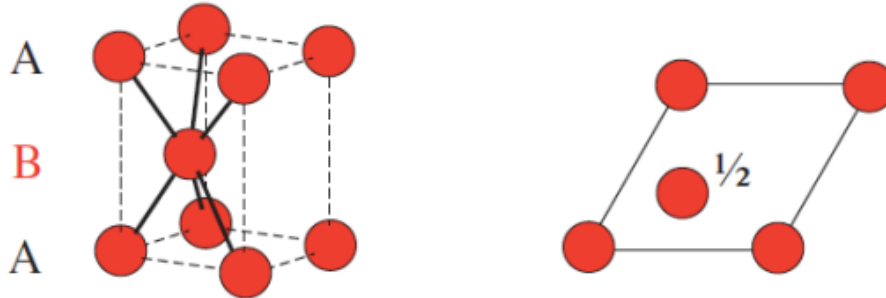


Figure 2: Hexagonal close-packing, in 3D on the left and on the right as seen from above.

- In a **body-centred cubic** (BCC) structure the environments are the same for all atoms, hence the lattice is equivalent to the structure. It is only slightly less closely packed than a FCC structure.
- The non-primitive cubic unit cell is the conventional choice for BCC, and contains two lattice points.
- The BCC coordination polyhedra has 8 hexagonal faces indicating ‘contact’ with 8 nearest neighbours of each atom. Thus the coordination number is 8. This is smaller than the 12 for FCC and HCP structures, however, in BCC we find 6 smaller square faces, indicating neighbours not much further away than the nearest.
- The metallic elements lithium, sodium, potassium, chromium, barium and tungsten crystallise into the BCC structure.

Note the three types of cubic lattice considered, and the notation used to refer to them:

- **Primitive** (P): lattice points on the cell corners only.
- **Body** (I): one additional lattice point at the center of the cell.
- **Face** (F): one additional lattice point at the center of each of the faces of the cell.

1.5 Order and Disorder in Solids

Not all solids are crystals. The table below outline order and disorder in different kinds of solids.

Crystalline Solids	Noncrystalline Solids
Single crystals	Amorphous materials (liquids and glasses)
Polycrystalline materials	Polymers
	Liquid Crystals (nematic, smectic, cholesteric)
Artificial nanostructures	
Fractals	
Quasi-crystals	

The physical properties of solids can also be anisotropic. For example:

- Electrical conductivity
- Elastic properties
- Magnetic response
- Refraction indices

Such anisotropies can lead to behaviour such as biased growth in a particular direction or plane.

2 Bonding in Solids

- **Ionic bonding** is the transfer of one or more electrons from one atom to another resulting in positive and negative ions with filled atomic orbitals. Ionic bonding is not directional and solids bonded in this way are hard, crystalline materials. Ionic crystalline structures are principally determined by the Coulomb energy:

$$\phi^{\text{Coulomb}}(r_{ij}) = \frac{Q_i Q_j}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

- **Covalent bonding** involves the ‘sharing’ of unpaired electrons. Atomic wavefunction mix (hybridize) and lower total energy. It is strong and highly directional.
- **Metallic bonding** is the extreme limit of covalent bonding. Outermost electrons become free to move around the crystal creating a ‘sea’ of negative charge binding together positive ions. Metallic bonding is not directional and is generally weaker which explains why metals tend to be softer and more ductile.
- **Hydrogen bonding** is a covalent bond between different atomic species in which there is a partial separation of charge. This charge distribution results in attraction to opposite ends of the covalent bond. The effect is particularly strong in hydrogen (one electron leads to greater change in charge distribution). The effect is much weaker than ionic, covalent or metallic bonds. Examples include water molecules in ice and the two strands of the double helix in DNA.
- **Van der Waals bonding** is due to quantum fluctuations of electric dipole moments in atoms. The force between an electric dipole moment on one atom and the moment this induces in another is attractive. This is described by the Lennard-Jones potential:

$$\phi_{ij}(r_{ij}) = -4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{ij}} \right)^{12} \right] \quad (4)$$

Here σ is the finite distance at which the inter-particle potential is zero, ϵ is the maximum potential energy (or depth of the potential well), and r_{ij} is the spacing between particles i and j . The force is very weak and is usually secondary to other bonding types, but it is important in organic molecules, polymers, noble gases and liquids at low temperature.

3 X-ray Diffraction

3.1 The Bragg Law

For x-rays the wavelength λ is typically 1\AA , comparable to the interatomic spacing of solids. This means a crystal acts as a three dimensional diffraction grating. This is important for the analysis of crystal structures because it is possible to deduce the size of a unit cell from the separation of diffraction maxima (like line spacing in a diffraction grating), and relative intensities of different orders allows for analysis of the arrangement of atoms in the cell.

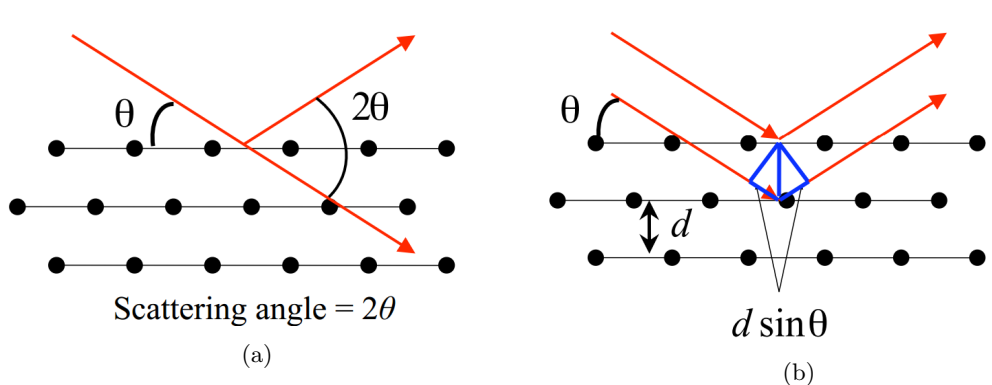
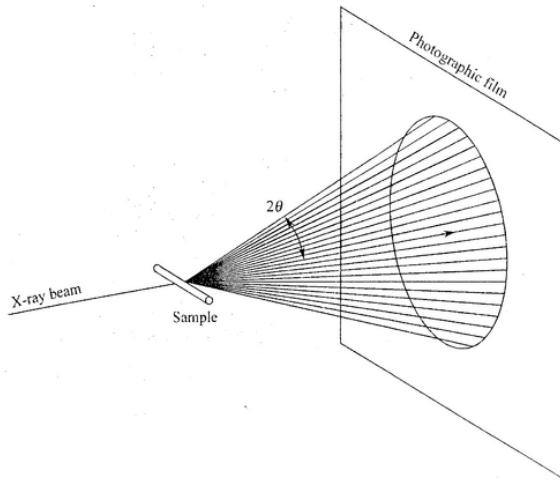
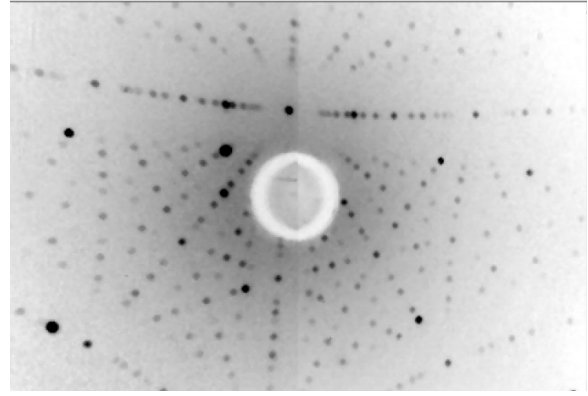


Figure 3: Ray diagrams for x-ray diffracting in a crystal structure.

- The glancing angle θ is used in crystallography rather than the incidence angle. The reflection condition implies that the x-ray beam is deflected by angle 2θ (Figure 5). Note also that we consider scattering concerned with lattice points, not atoms, because it is the basis of atoms associated with each atom that



(a) The experimental set up for a Laue photograph.



(b) The photographic result of polychromatic diffraction.

Figure 4: The Laue method.

is the true repeat crystal; the lattice point is the analogue of the line on an optical diffraction grating, the basis represents the structure of the line.

- In order to achieve a diffraction maximum, successive planes should scatter in phase. This will be the case if the path difference for scattering of two adjacent planes is an integral number of wavelengths, and from Figure 3a we see that:

$$2d \sin \theta = n\lambda \quad n \in \mathbb{Z} \quad (5)$$

where d is the plane spacing defined in equation 2. This is **Bragg's law**.

- Rewriting this law as in equation 6 demonstrates that the n th order diffraction off (hkl) planes of spacing d look like first order diffraction of spacing d/n . Planes of this reduced spacing would have Miller indices $(nh \ nk \ nl)$.

$$2(d/n) \sin \theta = \lambda \quad (6)$$

- Bragg used an arrangement like an ordinary spectrometer and measured intensity in reflection from the cleaved face of a crystal, finding six values of θ for which sharp peaks of intensity occurred, corresponding to three characteristic wavelengths (K, L and M x-rays) in first and second order. By repeating such an experiment for different faces, ratios can be found between planar spacings, and the symmetry of a crystal can be confirmed.

3.2 Experimental Arrangements

- Most experiments involve accelerating electrons through a potential difference of order 30keV and colliding them with a metal target to produce x-rays. The x-ray emission is then a mix of the characteristic lines (K, L, M etc.) of the metal and a background which varies with wavelength. By changing the voltage almost monochromatic or a broadened white spectrum can be achieved.
- If a higher intensity source is required, charged particles can be accelerated (so that they become a source of electromagnetic radiation) in a synchrotron. Synchrotrons are used for the determination of structure in very small crystals and crystals containing biological molecules where unit cells are complex.
- One common type of measurement of diffraction in a crystal is a **Laue photograph**, in which a single crystal is illuminated with collimated beam of 'white' x-rays (Figure 4a). Each set of crystal planes will satisfy the Bragg condition (equation 5) for some wavelength. The resulting diffracted beam creates a pattern of spots on a photographic film (Figure 4b). The symmetry of the spot pattern reflects the symmetry of the crystal when crystal when viewed along the direction of the incident beam. The Laue method is often used to determine the orientation of single crystals that do not have well developed external faces.

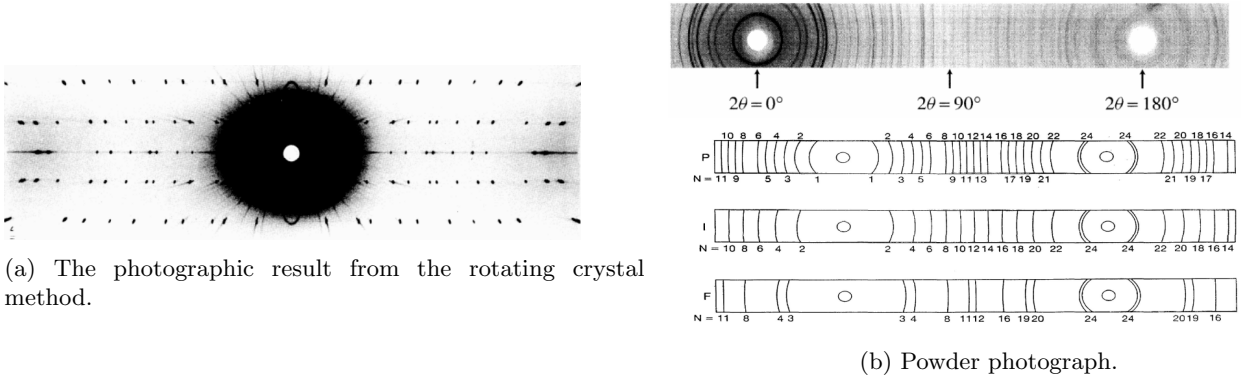


Figure 5: Diffraction from monochromatic beams.

- When a single crystal is exposed to a collimated *monochromatic* beam, as in the **rotating crystal method**, there is generally no diffraction as no set of lattice planes satisfy Bragg's law. When the crystal is rotated around a fixed axis perpendicular to the x-ray beam, the glancing angle θ varies for sets of planes that are not perpendicular to the rotation axis. A set of such planes is likely to satisfy the Bragg condition for some θ . The crystal is surrounded by a photographic film and the resulting pattern of diffraction spots (Figure 5a) can be analysed to obtain structure.
- Instead of rotating the crystal, a **powder photograph** (Figure 5b), in which many randomly oriented grains are glued together to form a sample, can be taken. This works because some grains will be oriented with Bragg angle θ to the incident rays. Structure can be determined from the measured values of θ and the relative intensities.

3.3 Selection Rules

To analyse the structure of crystals we note that the Bragg law can only be applied to a lattice when the plane is correctly oriented with respect to the x-ray beam. In the cubic case, while for the primitive case the Bragg law is simple, in other lattice structures extra atoms cause out of phase scattering at particular angles giving rise to selection rules. We can see this by writing the distance between planes in a cubic lattice of side length a as:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (7)$$

and combining this with Bragg's law (equation 5) to get:

$$\left(\frac{\lambda}{2a}\right)^2 = \frac{\sin^2 \theta}{h^2 + k^2 + l^2} \quad (8)$$

Equation 8 can be used to derive the selection rules for h , k , and l in P, I, F cubic lattices. These are as follows:

- SC (P): no constraint (simple)
- BCC (I): $(h + k + l)$ is even (body centred)
- FCC (F): h, k, l are all even or all odd (face centred)

3.4 The Reciprocal Lattice

For this section, we denote wave number of an incident x-ray \mathbf{k} and the wavenumber of the diffracted ray \mathbf{k}' . In diffraction we assume elastic scattering so that $|\mathbf{k}| = |\mathbf{k}'| = 2\pi/\lambda$ where λ does not change (for spectroscopy λ changes). We denote $\hbar\mathbf{Q} = \hbar(\mathbf{k}' - \mathbf{k})$ the change in momentum of incident particles. For a maximum amplitude we can find $|\mathbf{Q}| = Q$ in terms of the planar separation d :

$$Q^2 = |\mathbf{k}' - \mathbf{k}|^2 = \mathbf{k}'^2 + \mathbf{k}^2 - 2\mathbf{k}' \cdot \mathbf{k} \quad (9)$$

Which we can rewrite with the magnitudes of \mathbf{k} and \mathbf{k}' :

$$Q^2 = 2\left(\frac{2\pi}{\lambda}\right)^2 - 2\left(\frac{2\pi}{\lambda}\right)^2 \cos 2\theta \quad (10)$$

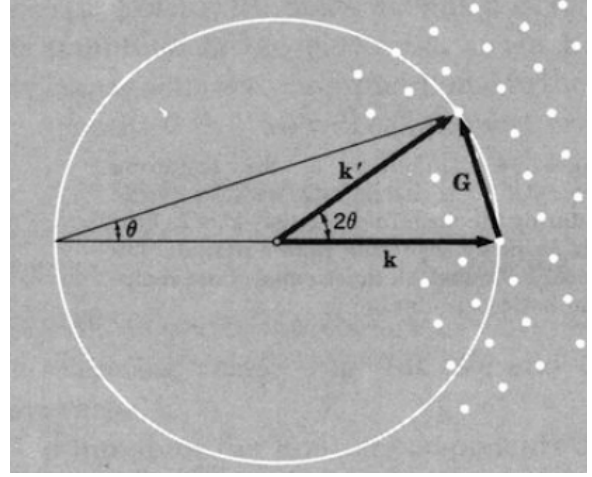
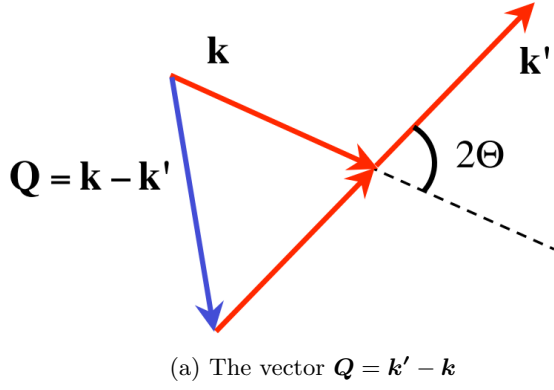


Figure 6: Vectors involved in the diffraction of beams.

And simplify to:

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d} \quad (11)$$

Furthermore, defining the lattice points as in equation 1 it can be shown that the directions of diffracted beams are given by a set of vectors \mathbf{Q} which satisfy the conditions:

$$\mathbf{Q} \cdot \mathbf{a} = 2\pi h \quad \mathbf{Q} \cdot \mathbf{b} = 2\pi k \quad \mathbf{Q} \cdot \mathbf{c} = 2\pi l \quad (12)$$

which are known as the **Laue conditions**.

These can be expressed neatly by developing the concept of a **reciprocal lattice** on which the vectors \mathbf{Q} which satisfy the Laue conditions lie on the lattice points. All points on the reciprocal lattice are generated from the primitive vectors \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* by:

$$\mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (13)$$

and linking reciprocal primitive vectors to the originals with the following transformation:

$$\mathbf{a}^* = \frac{2\pi}{V_c} \mathbf{b} \times \mathbf{c} \quad \mathbf{b}^* = \frac{2\pi}{V_c} \mathbf{c} \times \mathbf{a} \quad \mathbf{c}^* = \frac{2\pi}{V_c} \mathbf{a} \times \mathbf{b} \quad (14)$$

where $V_c = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the cell volume.

Note that in crystals with orthogonal axes the reciprocal lattice vectors are parallel to the corresponding lattice vectors:

$$a^* = \frac{2\pi}{a} \quad b^* = \frac{2\pi}{b} \quad c^* = \frac{2\pi}{c} \quad V_c = abc \quad (15)$$

With the reciprocal lattice defined, it can be shown that the Laue conditions now become:

$$\mathbf{Q} = \mathbf{G}_{hkl} \quad (16)$$

from which it also follows that:

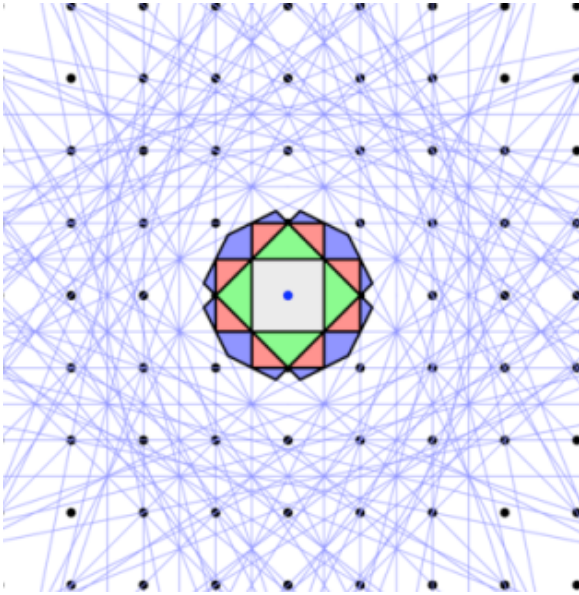
$$\mathbf{G}_{hkl} \cdot \mathbf{k} = \frac{1}{2} G_{hkl}^2 \quad (17)$$

3.5 Diffraction Intensity

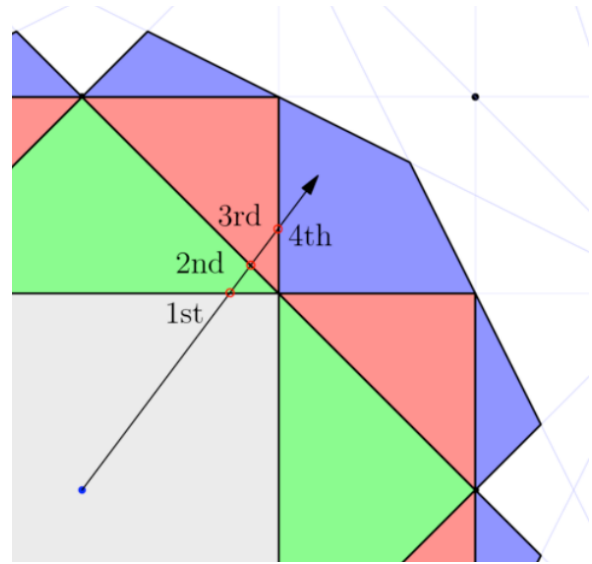
The total intensity of a diffracted beam at any point is a product of the Fourier transforms of contributions due to lattice points (as addressed in the reciprocal lattice), and due to atoms in the basis. This latter term incorporates the structure of the unit cell, the atomic form factor (dependent on electrons in the atoms), and thermal motivation which is the Debye-Walker factor.

- Intensity I of diffraction from the lattice plane with Miller indices $(h \ k \ l)$ is:

$$I_{hkl} = |S_{hkl}|^2 \delta(\mathbf{Q} - \mathbf{G}_{hkl}) \quad (18)$$



(a) The construction of Brillouin zones by bisecting distances between points in a reciprocal lattice.



(b) A vector which travels across three bisecting lines, and hence reaches the fourth Brillouin zone.

Figure 7: Brillouin zones.

- The **structure factor** is

$$S_{hkl} = \sum_j f_j(\mathbf{G}_{hkl}) e^{2\pi i(hx_j + ky_j + lz_j)} \quad (19)$$

for which $f_j(\mathbf{G}_{hkl})$ is the atomic form factor of atom j . The delta function reflects the Laue conditions. The sum runs over all atoms in the unit cell, and (x_j, y_j, z_j) are the fractional coordinates of the j^{th} atom in the cell.

3.6 Brillouin Zones

Brillouin zones arise from the natural splitting of regions in a lattice by the effect of a periodic potential on electron states.

- They are the Wigner-Seitz unit cells in reciprocal space.
- Their boundaries represent Bragg planes which diffract waves having particular wave vectors.
- Each zone has the same volume (or area in 2D).
- The first Brillouin zone is the set of points closer to the origin in reciprocal space than any other reciprocal lattice point.
- All the physics of a system is contained within a Brillouin zone. For any point outside the first zone there exists a unique reciprocal lattice vector that will translate that point back inside the first zone.
- Some examples for cubic lattices: consider the reciprocal lattice of a SC (still a SC), then the first Brillouin zone is also a cube. For a BCC structure, the reciprocal lattice is FCC and therefore has a rhombic dodecahedron as its first Brillouin zone. FCC has a BCC reciprocal and therefore a truncated octahedron is its first zone.

4 Crystal Dynamics

The idea of a crystal as a regular arrangement of *stationary* atoms cannot be correct as it violates Heisenberg uncertainty principle. Therefore at a temperature of absolute zero atoms must vibrate around their equilibrium positions with **zero point energy**. We now consider the nature of atomic motions in crystals, known as **lattice vibrations**.

4.1 Lattice Vibrations of 1D Crystals

Consider a longitudinal (e.g. sound) wave propagating in a one dimensional crystal.

- In the **linear chain model** we consider identical atoms, mass m , separation distance a , oscillating in a chain. In this case the dispersion relation is

$$\omega = 2\sqrt{\frac{C}{m}} \left| \sin \frac{ka}{2} \right| \quad (20)$$

with k wavenumber, C force constant. From this we see that in the long wave limit wave sound velocity is independent of frequency. The group velocity is:

$$\frac{\partial \omega}{\partial k}(k \rightarrow 0) = a\sqrt{\frac{C}{M}} \quad (21)$$

At the boundaries of a Brillouin zone ($k = \pm\pi/a$) the solution to the equation of motion gives a standing wave (i.e. group velocity is zero).

- If we consider similar lattice vibrations with atoms of two different masses M and m in the **diatomic chain model** we find a new dispersion relation:

$$\omega^2 = C \frac{M+m}{Mm} \pm \left\{ \left(\frac{M+m}{Mm} \right)^2 - \frac{4}{Mm} \sin^2 \left(\frac{ka}{2} \right) \right\}^{1/2} \quad (22)$$

which has two solutions for each k , the acoustic (-) and the optic (+) branches. The two masses will also oscillate with different amplitudes, the ratio between them is:

$$\alpha = \frac{2C - \omega^2 M}{2C \cos \left(\frac{ka}{2} \right)} \quad (23)$$

This is the simplest model for (for example) an ionic crystal.

- The **number of branches** in solutions to the dispersion relation is given by the number of atoms in a primitive cell times the number of dimensions they are free to oscillate in. For example, a 3D crystal made of N primitive cells each containing p atoms will have $3pN$ degrees of freedom and $3p$ branches. Each individual branch will have N allowed k -values. There will be one acoustic branch for each dimension, and the rest will be optic branches. For acoustic branches, frequency goes to zero with wavevector.

4.2 Phonons

- We now consider the vibrational system quantum mechanically by supposing the lattice vibration mode of frequency ω will behave like a simple harmonic oscillator, and will thus be restricted to energy values:

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad (24)$$

- The energy of a normal vibrational mode can be written:

$$E(\mathbf{k}) = \left(n(\mathbf{k}) + \frac{1}{2} \right) \hbar \omega(\mathbf{k}) \quad (25)$$

where $n(\mathbf{k})$ is the number of quanta in the mode with wavevector \mathbf{k} .

- A **phonon** is a quanta of vibrational energy, and adding more phonons is equivalent to increasing the amplitude of atomic vibrations.
- The number of phonons $n(\mathbf{k})$ with a particular frequency is determined by the temperature T when a solid is in thermal equilibrium:

$$n(\mathbf{k}) = (e^{\frac{\hbar \omega}{k_B T}} - 1)^{-1} \quad (26)$$

- Phonons distribution, the Plank distribution law, is a special form of the Bose-Einstein distribution function. **Phonons are boson quasiparticles.**
- Phonons act as if they have a momentum $\mathbf{p} = \hbar \mathbf{k}$, but this is not a true kinematic momentum because:

- for all k -values (except $k = 0$) the centre of mass of a crystal does not move when a phonon is excited.
- the phonon wavevector is not single-valued; $\mathbf{k}' = \mathbf{G}_{hkl} + \mathbf{k}$ represents the vibrational mode equally well.
- The **density of states** $g(\omega)$ is defined such that $g(\omega) d\omega = pg(k) dk$ is the number of vibrational modes between ω and $\omega + d\omega$. Here p is the number of degenerate modes per k -state.
- In 1D, applying periodic boundary conditions gives the allowed wavenumbers:

$$k = \frac{2\pi m}{Na} = \frac{2\pi m}{L} \quad (27)$$

where m is an integer and L is the length of the lattice. The allowed states are uniformly distributed in k -space and are separated in each direction by $2\pi/L$.

- In 1D $g(k) dk = (L/2\pi) dk$
- In 2D $g(k) dk = (L/2\pi)^2 2\pi k dk$
- In 3D $g(k) dk = (L/2\pi)^3 4\pi k^2 dk$

4.3 Lattice Heat Capacity

- **Lattice heat capacity** is defined by $C_{\text{lat}} = \frac{\partial U_{\text{lat}}}{\partial T}$ where U_{lat} is the thermal average lattice vibrational energy.
- In the **Einstein model** all modes have the same frequency ω . The heat capacity is then given by:

$$C = \frac{2Nk_B T \exp(\theta/T)}{(\exp(\theta/T) - 1)^2} \left(\frac{\theta}{T} \right)^2 \quad (28)$$

where $\theta = \hbar\omega/k_B$. This gives a high temperature limit $C \approx 3Nk_B$ and low temperature limit $C \rightarrow 0$ (exponentially).

- In the **Debye model** dispersion is isotropic, linear, and extends up to the Debye frequency ω_D , determined by the condition

$$3N = \int_0^{\omega_D} g(\omega) d\omega. \quad (29)$$

The heat capacity is then given by:

$$C = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{y^4 e^y}{(e^y - 1)^2} dy \quad (30)$$

where $y = \hbar\omega/k_B$ and θ_D is the **Debye temperature**:

$$\theta_D = \frac{\hbar\omega_D}{k_B} \quad (31)$$

In the high temperature limit, for $(T \gg \theta_D)$, then again $C \approx 3Nk_B$. However in the low temperature limit $(T \ll \theta_D)$, the upper limit of the integral tends towards infinity and the integral evaluates to a constant. We are left with a cube law: $C \approx \frac{12}{5} Nk_B \pi^4 \left(\frac{T}{\theta_D} \right)^3$.

5 Introduction to Neutron Scattering

Properties of neutrons:

- Mass: $1.67 \times 10^{-27} \text{kg}$
- Charge: 0
- Spin: 1/2
- Magnetic Moment: $-1.9\mu_N$

5.1 Motivation for Using Neutrons

- Their wavelength is similar to atomic spacing, so diffraction measurements can be obtained.
- Energy is the same order of magnitude to the diffuse motion in solids/liquids and the coherent waves in crystals, so spectroscopy measurements can be obtained.
- Highly penetrating, bulk samples can be analysed.
- Non-destructive, so delicate samples can be studied.
- The magnetic scattering cross section is similar in magnitude to the nuclear cross section, so magnetic diffraction measurements can be made, and inelastic magnetic scattering probes magnetic dynamics.
- Polarized neutrons can distinguish magnetic and nuclear scattering and a specific spin component.

5.2 Neutron Sources

Neutron sources include nuclear reactors, in which fission is just nuclear decay induced by collisions with neutrons. During decay, large nuclei emit more neutrons etc.

Another source is spallation in which negatively charged hydrogen ions are accelerated to very high energies. It is then passed through a foil, which strips off each ion's two electrons, converting it to a proton. The protons pass into a ring where they accumulate in bunches. Each bunch of protons is released from the ring as a pulse. The high energy proton pulses strike a heavy-metal target, which is a container of liquid mercury. Corresponding pulses of neutrons freed by the spallation process are slowed down in a moderator and guided through beam lines to areas containing highly specialized instruments for conducting experiments. Once there, neutrons of different energies are used in a wide variety of experiments.

6 Exercises

1. Find the ideal packing fraction for SCC, HCP, BCC, FCC structures.
2. Consider a cubic lattice with a conventional choice of unit cell.
 - Sketch the lattice planes $(1\ 1\ 1)$, $(1\ 0\ 2)$, and $(1\ 1\ 0)$
 - Calculate plane spacing for planes listed above if the lattice parameter $a = 2.87\text{\AA}$
 - What direction is the line of intersection of $(1\ 1\ 1)$ and $(1\ 0\ 2)$
3. Explain the significance of different quantities for Van der Waals bonding, both on the potential graph and in the equation.
4. Calculate S_{hkl} for BCC and FCC lattices. Hint: use selection rules.