PY3P03: Crystal Structure

David Whyte dawhyte@tcd.ie

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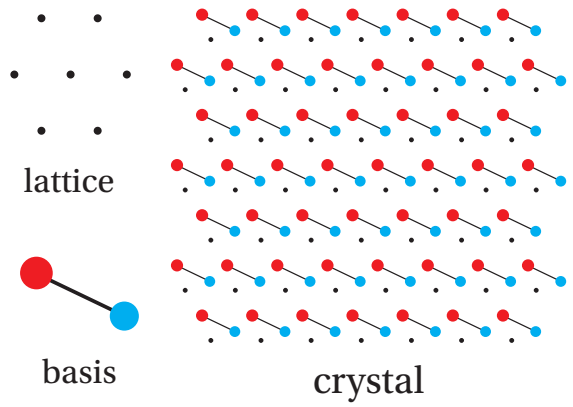
Basics

A **crystal** is a solid in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating pattern extending in all three spatial dimensions.

A **lattice** is a regular, periodic array of points throughout an area (2D) or a space (3D).

All crystal structures consist of identical copies of the same physical unit, called the **basis**, assigned to all the points of the lattice. There is no unique choice of basis.



If a basis is symmetric with respect to some axis, crystal properties are independent of the direction of measurement along that axis.

A **Bravais lattice** is a discrete set of vectors, not all in the same plane, closed under vector addition or subtraction. Equivalently, it is the set of points with position vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ (the **primitive vectors**) are not coplanar, and n_1, n_2 and n_3 are integers. There is no unique choice of primitive vectors.

All non-Bravais lattices can be created from a Bravais lattice and a basis.

The **coordination number** of a Bravais lattice is the number of nearest neighbours to each point in the lattice.

The **primitive unit cell** is the set of all points:

$$\mathbf{R} = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are primitive vectors, and x_1, x_2 and x_3 range from 0 to 1.

Each primitive unit cell contains exactly one point of the Bravais lattice. Its volume V is given by $V = \frac{1}{n}$ where n is the density of points.

There is no unique choice of primitive unit cell. Two common choices are:

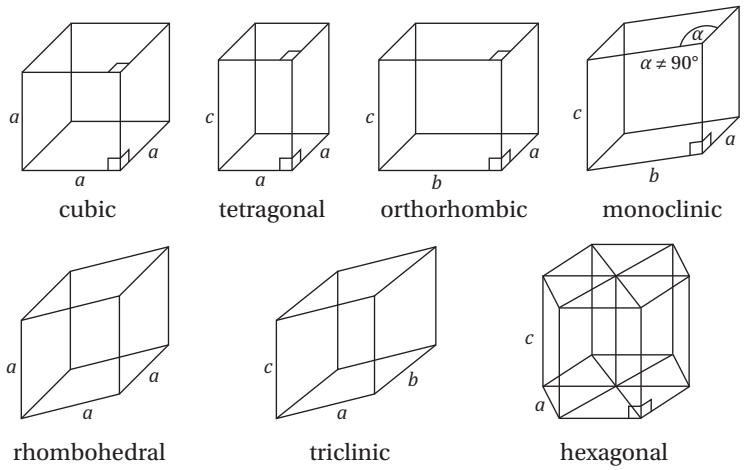
- The **Wigner–Seitz cell**: the region of space about a lattice point which is closer to that point than to any other. It is constructed by bisecting the lines which join each point to its nearest neighbours.
- The **conventional unit cell** is chosen to display the symmetry of the lattice. It fills up all the space without any overlap when translated through some subset of the vectors of the Bravais lattice. It is generally bigger than a primitive cell.

Symmetry & groups

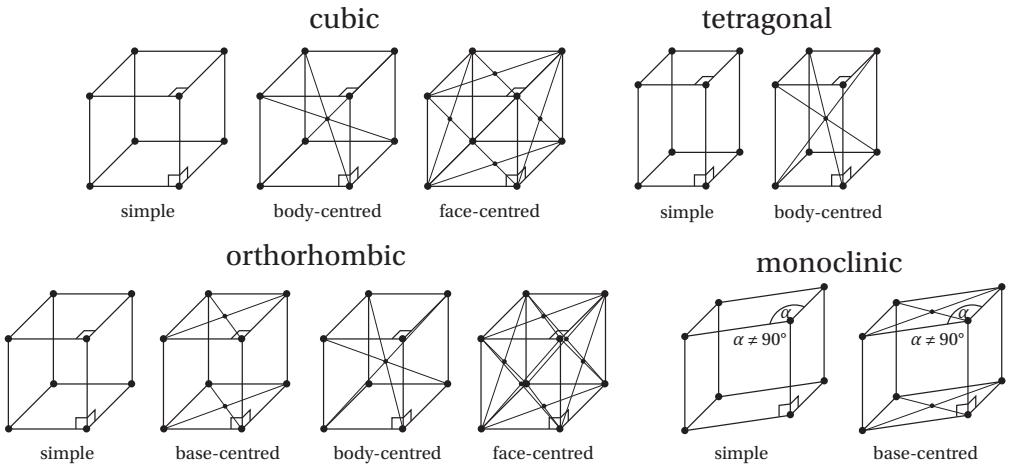
The **symmetry group** of a lattice is the set of operations which map the lattice onto itself.

The **point group** of a lattice is the set of symmetry operations which hold one point of the lattice in place and map each remaining point to a point in the lattice: the point group operations are rotations, reflections and inversions. Every symmetry operation can be expressed as a translation through a lattice vector combined with a point group operation.

There are seven **crystal systems** into which any crystal structure can be categorised based on the point group of its underlying Bravais lattice:

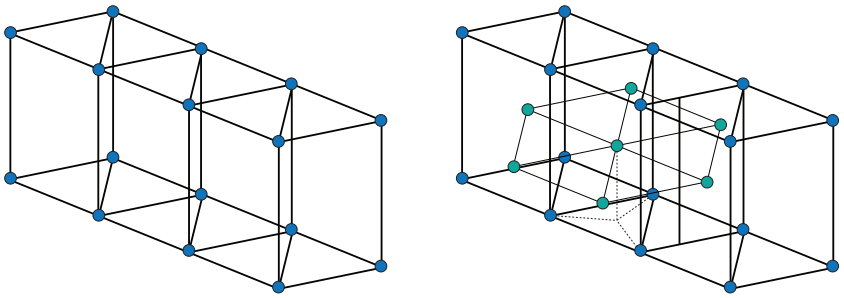


When considering the full symmetry group, not just the point groups, some crystal groups can be subcategorised, giving fourteen distinct types of Bravais lattice:



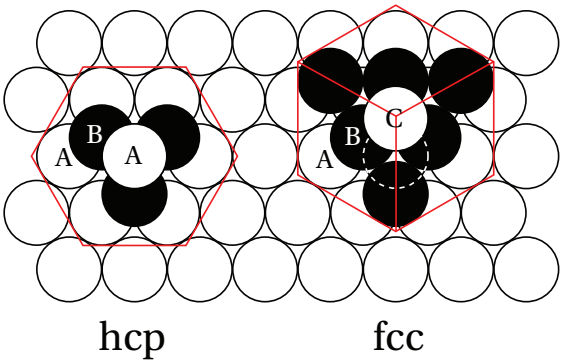
Packing

The **hexagonal close-packed** (hcp) structure can be viewed as two interpenetrating simple hexagonal lattices.



Simple hexagonal Hexagonal close-packed

hcp and fcc are the two most efficient ways of packing spheres. In hcp, the third layer



is identical to the first (giving *ABAB*... alternance) and in fcc the fourth is identical to the first (*ABCABC*... alternance).

Reciprocal lattice

Consider a 1D crystal lattice described by a function $n(x)$. The Fourier series of $n(x)$ is:

$$n(x) = \sum_p n_p \, e^{i2\pi px/a}$$

We say that $\frac{2\pi p}{a}$ forms a set of points in the **reciprocal lattice** of the crystal. This is a set of points which tell us the allowed terms in the Fourier series.

Reciprocal space or k-space is the space in which the Fourier transform of a spatial function is represented. It is useful in making certain observations about crystals.

In 3D, reciprocal lattice points are now three-dimensional vectors, called **wavevectors** which yield plane waves with the same periodicity as the Bravais lattice. It can be defined as the set of all $\mathbf{k}$ which satisfy

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 1$$

for all $\mathbf{R}$ in the Bravais lattice.

The primitive vectors of the reciprocal lattice are:

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

where $\mathbf{a}_i$ are the primitive vectors of the Bravais lattice.

The reciprocal lattice is also a Bravais lattice: If $e^{i\mathbf{k}_1\cdot\mathbf{R}} = 1$ and $e^{i\mathbf{k}_2\cdot\mathbf{R}} = 1$, then $e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} = 1$, i.e. the set $\{\mathbf{k}\}$ is closed under vector addition, a sufficient condition for a Bravais lattice.

The reciprocal of the reciprocal is the original lattice. This is due to the fact that the definition of a reciprocal lattice is symmetric in $\mathbf{R} \leftrightarrow \mathbf{k}$.

The Wigner–Seitz primitive cell of the reciprocal lattice is called the **first Brillouin zone**. It has volume $\frac{2\pi}{V}$, where V is the volume of of the primitive cell in the direct lattice.

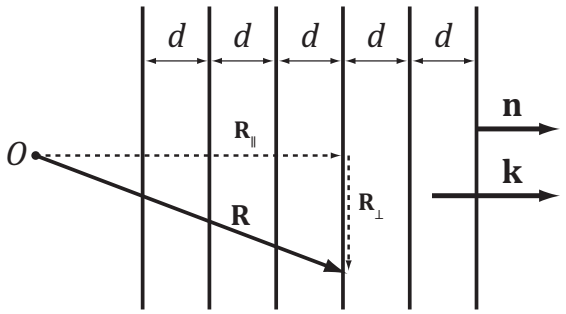
Lattice planes and reciprocal lattice vectors

A **lattice plane** is any plane which contains at least three non-collinear points of a Bravais lattice. A **family** of lattice planes is a set of parallel lattice planes which contain *all* the points of the Bravais lattice. Any lattice plane is a member of one such family. Remember that a plane can be defined by the set of points $\mathbf{r}$ for which $\mathbf{r} \cdot \mathbf{n} = A$.

For any family of lattice planes separated by a distance d, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which has length $\frac{2\pi}{d}$.

Conversely, for any reciprocal lattice $\mathbf{k}$, there is a family of lattice planes normal to $\mathbf{k}$ and separated by a distance d, where $\frac{2\pi}{d}$ is the length of the shortest reciprocal lattice vector parallel to $\mathbf{k}$.

Proof 1



Let $\mathbf{k} = \frac{2\pi \mathbf{n}}{d}$. Then,

$$\begin{aligned} e^{i\mathbf{k}\cdot\mathbf{R}} &= e^{i\mathbf{k}\cdot\mathbf{R}_\perp} e^{i\mathbf{k}\cdot\mathbf{R}_\parallel} \\ &= \text{const.} \times 1 \end{aligned}$$

So $e^{i\mathbf{k}\cdot\mathbf{R}}$ is constant in any plane.

Furthermore, for two planes 1 and 2 separated by d, $e^{i\mathbf{k}\cdot\mathbf{R}_2} = e^{i\mathbf{k}\cdot\mathbf{R}_1} e^{i|\mathbf{k}|d}$, so $e^{i\mathbf{k}\cdot\mathbf{R}}$ has the same value on planes separated by d if:

$$\mathbf{k} = \frac{2\pi m}{d}.$$

Putting the origin in a plane gives the result that $e^{i\mathbf{k}\cdot\mathbf{R}} = 1$ where $\mathbf{R}$ is any point on any plane. In other words, $\mathbf{k}$ is a reciprocal lattice vector.

If $|\mathbf{k}'| < |\mathbf{k}|$, then the wavelength of $\mathbf{k}'$ is $\frac{2\pi}{|\mathbf{k}'|} > d$, so it cannot take the same value of any plane, therefore it is not a reciprocal lattice vector. This means that $\mathbf{k}$ is indeed the shortest reciprocal lattice vector.

□

Proof 2

Suppose $\mathbf{k}$ is the shortest in a set of parallel reciprocal lattice vectors. Look at the set of real space planes for which $e^{i\mathbf{k}\cdot\mathbf{S}} = 1$.

For Bravais lattice planes, $e^{i\mathbf{k}\cdot\mathbf{R}} = 1$, so they are a subset of these real space planes.

If any of the real space planes are *not* Bravais lattice planes, then they must have separation less than that of Bravais lattice planes, i.e. $\frac{2\pi}{|\mathbf{k}|} < d$. But this would mean that $\mathbf{k}$ is not the shortest reciprocal lattice vector.

□

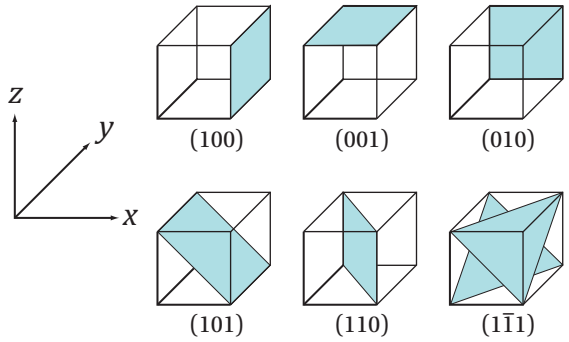
Miller indices

The **Miller indices** of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to the plane, with respect to a specified set of primitive reciprocal lattice vectors. The most 'obvious' choice of $\mathbf{a}_i$ and $\mathbf{b}_i$ is used.

A plane with Miller indices $(hk\ell)$ is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$. h, k and ℓ are integers.

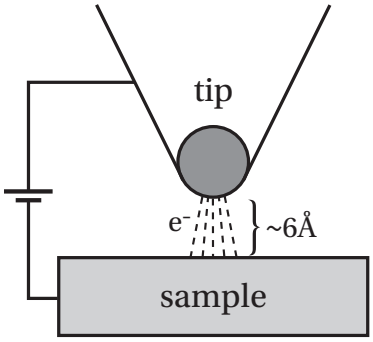
The Miller indices of a plane are inversely proportional to its intercepts with the axes. For example, a plane with intercept points $\frac{1}{2}$, 1, $\frac{1}{2}$ has Miller indices (212).

For a negative index, a bar over the index is used, e.g. $(1\bar{1}1)$

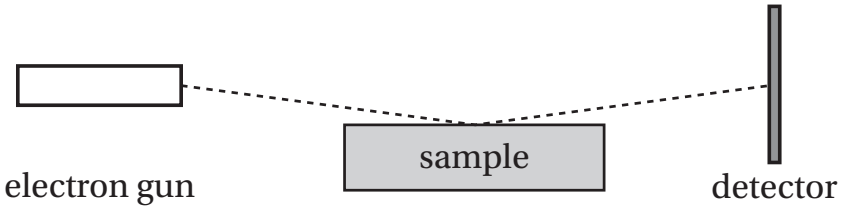


For directions written in terms of the lattice vectors, square brackets are used: $[UVW]$. For a set of symmetrically equivalent directions, angle brackets are used: $\langle UVW \rangle$.

Imaging



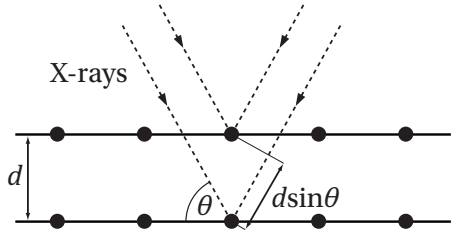
In a **scanning tunneling microscope** (STM), a tip is brought very near a metallic or semiconductive surface, and the bias between the two causes electrons to tunnel through the vacuum between them.



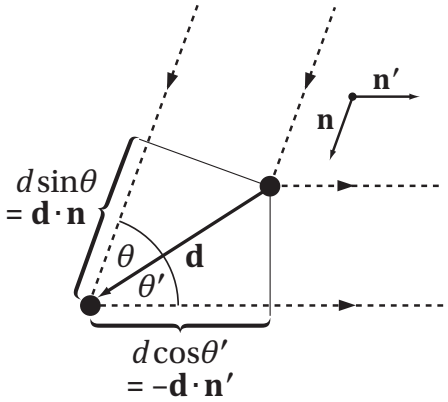
In **reflection high-energy electron diffraction** (RHEED), incident electrons are diffracted by the surface of the sample, and intefere constructively on a screen.

The structure of a crystal can be determined using **X-ray diffraction.** X-rays are used because they have a wavelength of the same order of magnitude as typical interatomic distances.

Diffraction



The **Bragg condition** for constructive interference is $n\lambda = 2d\sin\theta$.



The **Laue condition** for constructive interference is $\mathbf{d}\cdot(\mathbf{n}-\mathbf{n}') = m\lambda$ locally. For a lattice, this becomes $\mathbf{R}\cdot(\mathbf{k}-\mathbf{k}') = 2\pi m$, where $\mathbf{R}$ is any Bravais lattice vector.

Rewriting this as $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = 1$ shows that constructive interference occurs when $\mathbf{K} = \mathbf{k}-\mathbf{k}'$ is a reciprocal lattice vector.

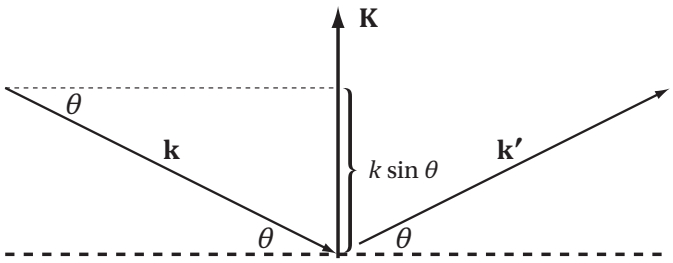
Since $\mathbf{k}$ and $\mathbf{k}'$ have the same length, this is equivalent to saying that the tip of the incident wavevector $\mathbf{k}$ must lie in a **Bragg plane**, i.e. one which bisects a reciprocal lattice vector $\mathbf{K}$.

The Bragg and Laue conditions are equivalent.

Proof

Start with the Laue condition. Because of elastic scattering, $|\mathbf{k}| = |\mathbf{k}'|$, so $\mathbf{K} = \mathbf{k}'-\mathbf{k}$ bisects the angle between $\mathbf{k}$ and $\mathbf{k}'$. $\mathbf{k}$ and $\mathbf{k}'$ make the same angle θ with the lattice plane perpendicular to $\mathbf{K}$. Can view the scattering as being from a family of lattice planes which are perpendicular to $\mathbf{K}$.

Write $\mathbf{K} = n\mathbf{K}_0$, where $\mathbf{K}_0$ is the shortest reciprocal lattice vector in that direction.



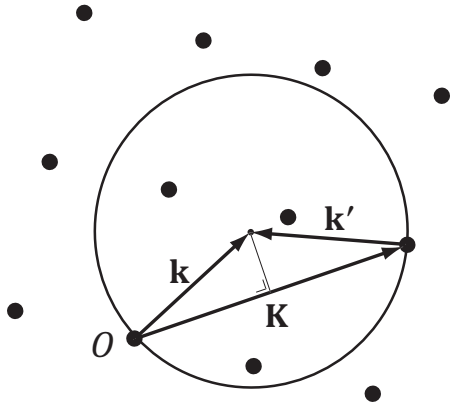
Since $|\mathbf{K}_0| = \frac{2\pi}{d}$, $|\mathbf{K}| = \frac{2\pi n}{d}$. But $\mathbf{K} = 2k\sin\theta$, as can be seen on the diagram.

So $\frac{2\pi n}{d} = 2k\sin\theta$, i.e. $n\lambda = 2d\sin\theta$, the Bragg condition.

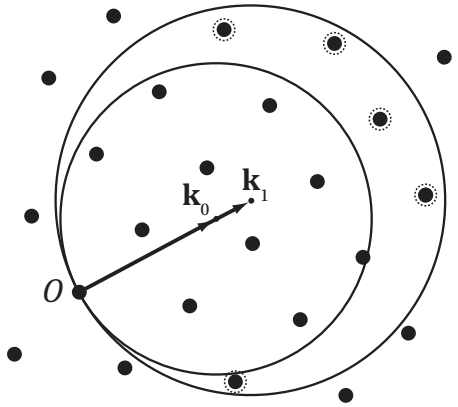
□

Ewald's sphere

This is a sphere of radius $|\mathbf{k}|$ drawn around the tip of the incident wavevector $\mathbf{k}$. Constructive interference occurs only if the sphere intersects a reciprocal lattice vector.



If a non-monochromatic X-ray beam is used, there will be a range of wavevectors, and peaks will be observed for any reciprocal vector which lies between the spheres of the extreme wavevectors.



In practise, monochromatic X-rays are used, and the sample is rotated (changing $\mathbf{k}$) until peaks are found.

Structure factors

In a monoatomic crystal with an n-atom basis ($n > 1$), the amplitude of a scattered ray with wavevector change $\mathbf{K}$ contains the **geometrical structure factor**:

$$S_{\mathbf{K}} = \sum_{j=1}^{n} e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

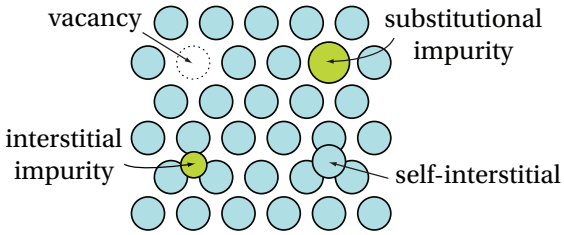
If the ions in the basis are *not* identical, the structure factor is:

$$S_{\mathbf{K}} = \sum_{j=1}^{n} f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

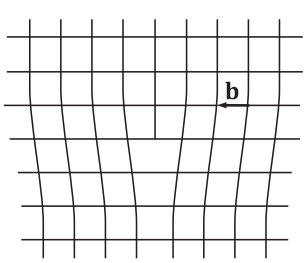
where f_j is the **atomic form factor**, which depends on the structure of the ion at position $\mathbf{d}_j$.

Defects

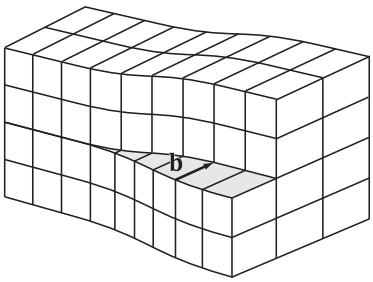
Point defects do not extend in any direction in space.



In **line defects**, the **Burgers vector** $\mathbf{b}$ indicates the size and direction of the distortion. Line defects often occur on **grain boundaries**; boundaries between unaligned crystals.



edge dislocation



screw dislocation

Crystal twinning occurs when two separate crystals share some of the same lattice points in a symmetrical manner.