

# Lecture 1.4

## Reciprocal lattice

See A&M Chapter 5

Last time, found  $\Delta\mathbf{k} \cdot \mathbf{d}$  for two points separated by  $\mathbf{d}$ .

If  $\mathbf{d}$  is a lattice vector, then there is a large number of points. For scatter from each of these to add up constructively, we require  $\Delta\mathbf{k} \cdot \mathbf{d} = 2\pi \times p$  where  $p \in \mathbb{Z}$ .

Find the set of vectors  $\mathbf{G} = \Delta\mathbf{k}$  for which  $\Delta\phi = 2\pi \times p$  when  $\mathbf{d} = \mathbf{R}_n$ .

Recall that  $\mathbf{R}_n = \sum_i n_i \mathbf{a}_i$ .

The condition above should be true for any lattice vector. Therefore, consider the following:

- $\mathbf{G} \cdot \mathbf{R}_{100} = \mathbf{G} \cdot \mathbf{a}_1$
- $\mathbf{G} \cdot \mathbf{R}_{010} = \mathbf{G} \cdot \mathbf{a}_2$
- $\mathbf{G} \cdot \mathbf{R}_{001} = \mathbf{G} \cdot \mathbf{a}_3$

We are going to state the solution and show that it works:

Let  $\mathbf{G}_m = \sum_i m_i \mathbf{b}_i$  and  $\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$  and *cyclic permutations*

By construction, we have  $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$  (the Kroneker delta). (Other choices are possible, but this most convenient.)

The term  $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$  is the volume of the parallelepiped, which we know is a valid primitive unit cell, all of which have the same volume.

The lattice spacing has units of **inverse length**. It exists in **momentum space**, just like  $k = 2\pi/\lambda$  has units of inverse length and  $\hbar k$  is a momentum.

Reciprocal lattice is a Bravais lattice (possibly different from the corresponding real-space lattice).

**Interpretation:** Crystal can only impart discrete chunks of momentum to diffracted x-rays.

This comes from the infinite periodic nature of crystal.

General reciprocal lattice vector written as  $\mathbf{G}_m = \mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ . The use of  $(hkl)$  is convention; sometimes annoying because  $k$  also used for wavenumber.

## Reciprocal lattice: simple cubic example

For simple cubic unit lattice vectors  $\mathbf{a}_1 = a\hat{x}$ ,  $\mathbf{a}_2 = a\hat{y}$ ,  $\mathbf{a}_3 = a\hat{z}$ , we find

$$\mathbf{b}_1 = \frac{2\pi}{V} a\hat{y} \times a\hat{z} = \frac{2\pi}{a^3} a^2 \hat{y} \times \hat{z} = \frac{2\pi}{a} \hat{x}$$

We have used the volume  $V = a^3$  i.e. we don't need to do  $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$  because we know this is a volume. **Use this trick** especially when working with an FCC or a BCC where  $V = a^3/n$  where  $n$  is the number of points in the conventional unit cell.

Similarly,  $\mathbf{b}_2 = \hat{y}2\pi/a$  and  $\mathbf{b}_3 = \hat{z}2\pi/a$ .

The reciprocal lattice of SC is hence another SC, now with lattice constant  $2\pi/a$ .

It is straightforward to show that FCC and BCC lattices are reciprocals of each other.

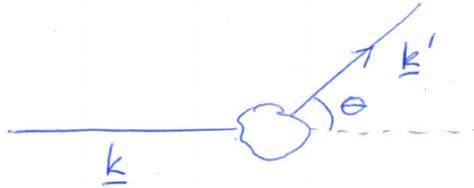
Rotating the real-space lattice also rotates the reciprocal lattice.

## Powder X-ray camera

Cleanest experimental method would be to illuminate with plane wave monochromatic x-rays and measure diffraction around the full solid angle for a pure crystal.

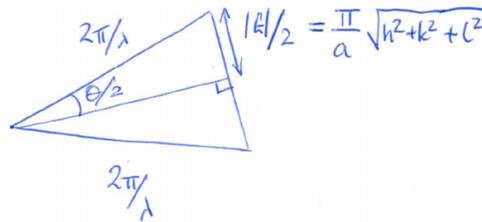
It's much easier to obtain a powdered sample, made of lots of small grains of the crystal. The signal is (incoherent) sum of diffraction from each grain. (These grains are still huge on the atomic scale.)

Define  $\theta$  as angle between incident  $\mathbf{k}$  and scattered  $\mathbf{k}'$  x-rays.



Powder x-ray camera schematic

Consider only **elastic scattering**, where  $\|\mathbf{k}\| = \|\mathbf{k}'\|$  i.e. no change in energy and hence in the **magnitude** of the momentum.



Powder x-ray camera geometry

Work with **conventional** unit vectors which is a simple cubic, for which the reciprocal is also a simple cubic.

$$\mathbf{k}' - \mathbf{k} = \Delta\mathbf{k} = \mathbf{G}_{hkl} = \frac{2\pi}{a} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Hence  $\|\mathbf{G}_{hkl}\| = (2\pi/a)\sqrt{h^2 + k^2 + l^2}$  and, for elastic scattering,  $\|\mathbf{k}'\| = \|\mathbf{k}\| = 2\pi/\lambda$ .

Find

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

This gives us a link between the observable wavelength  $\lambda$  and angles  $\theta$  and the microscopic properties  $hkl$  and lattice constant  $a$ .

We can apply this to **all** cubic crystals (SC, FCC, BCC, diamond) with one more ingredient: the Geometric Structure Factor.

In the Workshop on Friday we will use this to deduce the crystal structure of a sample from measurements.

## Diffraction and the Structure Factor

The crystal is the basis copied to every lattice point.

Treat the scattered wave (e.g. electric field) as proportional to some density  $\rho(\mathbf{r})$  (e.g. electron cloud).

The incident wave is  $E = E_0 e^{i\mathbf{k}\cdot\mathbf{r}}$ .

The outgoing wave is  $E' = E'_0 e^{i\mathbf{k}'\cdot\mathbf{r}}$ .

Integrating over the density of the crystal and accounting for the phase delay for each point:  $E'_0 \propto \int_{\text{Crystal}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} dV$

We now exploit translational symmetry  $\rho(\mathbf{r} + \mathbf{R}_n) = \rho(\mathbf{r})$

Hence,  $E'_0 \propto (\sum_n e^{i\Delta\mathbf{k}\cdot\mathbf{R}_n}) \int_{\text{Unit cell}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} dV$

For the whole thing to be non-zero, we require that  $\Delta\mathbf{k} = \mathbf{G}_m$  where  $\mathbf{m} = (m_1, m_2, m_3)$ .

Hence,  $E'_0 \propto (\sum_n e^{i\mathbf{G}_m\cdot\mathbf{R}_n}) \int_{\text{Unit cell}} \rho(\mathbf{r}) e^{i\mathbf{G}_m\cdot\mathbf{r}} dV$

The first term is to do with the lattice.

The second term is to do with the basis and is called the **structure factor**.

The integral above, with the phase factor, is a **Fourier transform**.

A "convolution" (thing copied to every point in another thing) becomes a multiplication after a Fourier transform.

This is why we can consider basis and lattice separately.

## Geometrical structure factor

We have chosen to describe some crystals as a convenient lattice with more than one point copied to each lattice point.

In effect, our basis is a collection of points. We can chain this sort of description, if we like, and copy an atom to each of these points.

For now, consider a collection of points at each lattice point.

We can use the structure factor (above) by representing these points as a collection of Dirac delta functions i.e.

$$\rho(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{d}_n)$$

i.e. there is a point (perhaps with an atom centred on it) at each point  $\mathbf{d}_n$ .

The integral thus becomes

$$\text{GSF} = \int_{\text{Unit cell}} \rho(\mathbf{r}) e^{i\mathbf{G}_m\cdot\mathbf{r}} dV = \sum_n e^{i\mathbf{G}_m\cdot\mathbf{d}_n}$$

For example, suppose we chose to describe a BCC lattice with conventional lattice vectors. The lattice part is trivial (the reciprocal of a SC is another SC) and we have two points in the conventional unit cell. These points are at  $\mathbf{d}_0 = 0$  and  $\mathbf{d}_1 = (a, a, a)/2$ . Hence, the Geometrical Structure Factor is

$$\text{GSF} = e^{i0} + e^{i\mathbf{G}_{hkl}\cdot(a,a,a)/2} = 1 + e^{i\pi(h+k+l)}$$

where we have expanded  $\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$  and used  $\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$  when computing the dot product.

This expression tells us that there will be **missing orders** (as compared with what we expect for the simple cubic) when  $h + k + l$  is odd.