Reciprocal lattice

This lecture will introduce the concept of a 'reciprocal lattice', which is a formalism that takes into account the regularity of a crystal lattice introduces redundancy when viewed in real space, because each unit cell contains the same information. There are two concepts you might have seen from earlier courses that we will touch on:

- A periodic structure is most naturally described by its Fourier transform (e.g. if you have a function which is a sine wave in the time domain, $f(x) = \sin(\omega t)$, the essential information about this function is captured by its frequency ω)
- Light is diffracted by a periodic structure, and this can be described by Bragg's law: $2d\sin\theta = n\lambda$, where λ is a wavelength, n is an integer, and d is the period of the periodic structure. This equation applies equally to a diffraction grating (typically using visible light) or to a crystalline solid (typically using x-ray light)

Definition of reciprocal lattice vectors

The primitive translation vectors $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3}$ represent the direct lattice.

The reciprocal lattice vectors, $\boldsymbol{b_1}, \boldsymbol{b_2}, \boldsymbol{b_3}$, are defined as follows:

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3}$$

$$b_3 = 2\pi \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}$$

- The denominator of all three is a scalar which gives the **volume** of the primitive cell: $V_c = |a_1 \cdot a_2 \times a_3|$
- If a primitive lattice vector is mutually orthogonal to the other two, its reciprocal lattice vector will point in the same direction. If all three primitive lattice vectors of the direct lattice are mutually orthogonal, the reciprocal lattice vectors will all point in the same direction as the direct lattice vectors.
  if $\boldsymbol{a_i} \cdot \mathbf{a_j} = \delta_{i,j}$ for both values of j, $\boldsymbol{a_i} || \boldsymbol{b_i}$
- If primitive lattice vectors are all mutually orthogonal, the reciprocal lattice vectors point in the same direction at the direct lattice vectors but have a magnitude $2\pi/|a_i|$
- Generalization of the previous two statements: $\boxed{b_i \cdot a_j = 2\pi\delta_{i,j}}$ where $\delta_{i,j} = 1$ if i=j and $\delta_{i,j} = 0$ if $i \neq j$

Example: orthorhombic lattice system

An **orthorhombic** lattice is comprised of rectangular prism cells with all edges of unequal length. The direct lattice vectors are:

$$a_1 = a\hat{x}$$

$$a_2 = b\hat{y}$$

$$a_3 = c\hat{z}$$

Where $a \neq b \neq c$

- $a_1 \cdot a_2 \times a_3 = abc$
- $a_2 \times a_3 = bc\hat{x}$
- $a_3 \times a_1 = ac\hat{y}$
- $a_1 \times a_2 = ab\hat{z}$

$$b_1 = \frac{2\pi}{a}\hat{x}$$

$$b_2 = \frac{2\pi}{b}\hat{y}$$

$$b_3 = \frac{2\pi}{c}\hat{z}$$

For cubic, tetragonal, and orthorhombic primitive lattices, reciprocal lattice vectors are straightforward to compute—they are in the same direction as the corresponding direct lattice vector with a magnitude given by $2\pi/|a_i|$. This is **not true** for crystal lattice systems in which the primitive lattices are not mutually orthogonal. When in doubt, just calculate using the full equations from earlier.

The reciprocal lattice is also a lattice (and if the direct lattice is primitive, then so is the reciprocal), and points in reciprocal space are mapped out by the set of vectors:

$$G = v_1 b_1 + v_2 b_2 + v_3 b_3$$

Where v_1, v_2, v_3 are integers
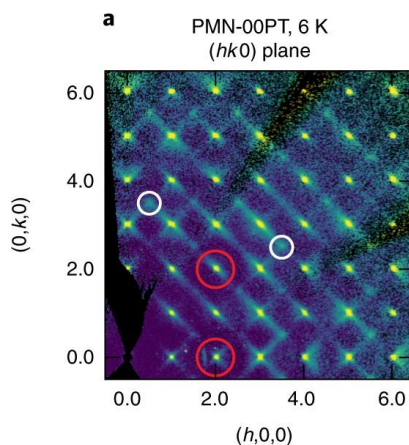

Figure 1. Image source: https://www.nature.com/articles/s41563-018-0112-7

Students often wonder whether a reciprocal lattice is a 'real' object or a conceptual object. While reciprocal lattices might not be encountered in everyday life, many experiments for measuring the structure of materials indeed measure the reciprocal lattice not the direct lattice (analogy: when you listen to music, each note is distinguished by its frequency).

The image to the left shows neutron scattering measurements on a ferroelectric material, where the yellow dots indicate regions of maximal signal. In data like these, (h,k,l) correspond to the x,y,z directions in reciprocal space (l is fixed to be zero for this image), and the units are such that the reciprocal lattice vectors have unit length. The bright dots on the grid of integers is precisely what you would expect from the equation for **G** above. For an ideal crystal, these bright dots would only be broadened by instrument resolution and temperature, but the additional structure in this image (e.g. diagonal streaks) indicates deviations from perfect crystallinity, which this paper explores.

Reciprocal lattice and fourier series

Now that we know what the reciprocal lattice vectors are, lets get some physical intuition behind them. A crystal is composed of infinitely repeating unit cells (unit cell = basis of one or more atoms attached to a lattice point). A crystal is invariant under translation of the form $T = u_1 a_1 + u_2 a_2 + u_3 a_3$ where u_1, u_2, u_3 are integers and a_1, a_2, a_3 are the lattice vectors. This is another way of saying that every unit cell is identical to every other unit cell.

When we think of a periodic structure, whether it be a sine wave, a square wave, or some other more complicated shape which repeats with period a, we should immediately think of a fourier transform or a fourier series.

Let's consider the **lattice** (no basis), which mathematically is represented by a series of delta functions.

Only consider a one dimensional lattice at first, with spacing a between lattice points.

<div align="center">Direct Lattice</div>
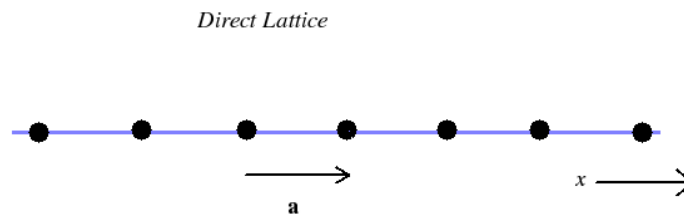
This structure can be written as: $L(x) = \sum_{u_1} \delta(x - u_1 a)$, where u1 is an integer

The Fourier transform of this is given by:

$$R(q) = \int_{-\infty}^{\infty} e^{iqx} L(x) dx$$

$$= \sum_{u_1} \int_{-\infty}^{\infty} e^{iqx} \delta(x - u_1 a) dx$$

Aside: generally, the FT of a delta function is given by $\int_{-\infty}^{\infty} e^{iqx} \delta(x - x_0) dx = e^{iqx_0}$

Also, the FT is often expressed with a factor of 2pi in the exponent, but we will account for that later

$$= \sum_{u_1} e^{iqu_1 a} = \sum_{u_1} \cos(qu_1 a) + isin(qu_1 a)$$

Simplification: we only need to keep the cosine term because the sum goes over positive and negative values of u1 and $\sin(-x) = -\sin(x)$
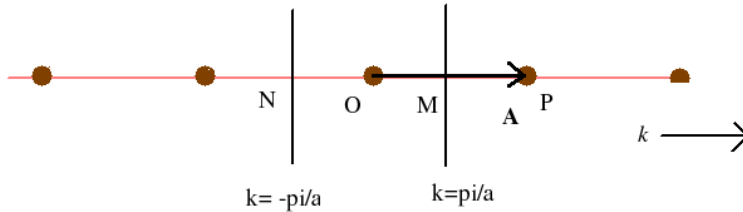
$$R(q) = \sum_{u_1} \cos(qu_1 a)$$

For arbitrary values of q, this sum will tend to zero as the number of terms goes to infinity. This can only be avoided if specific values of q are chosen:

$$q = \text{integer} \times \frac{2\pi}{a}$$

This gives a 1 dimensional lattice with points separated by $2\pi/a$. This is the reciprocal lattice.

Reciprocal Lattice

This can be generalized to three dimensions:

$$L(\vec{r}) = \sum_{u_1, u_2, u_3} \delta\big(r - (u_1 \boldsymbol{a_1} + u_2 \boldsymbol{a_2} + u_3 \boldsymbol{a_3})\big)$$

Where u_1, u_2, u_3 are integers and $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3}$ are lattice vectors which span 3D space

Take the Fourier transform again same as in 1D:

$R(\boldsymbol{k}) = \sum_{u_1, u_2, u_3} cos\big(\boldsymbol{k} \cdot (u_1 \boldsymbol{a_1} + u_2 \boldsymbol{a_2} + u_1 \boldsymbol{a_1})\big)$

Again, the sum will generally be non-zero only if **k** is a reciprocal lattice vector R(**k**)

$$\boldsymbol{k} = k_1 \boldsymbol{b_1} + k_2 \boldsymbol{b_2} + k_3 \boldsymbol{b_3}$$

Thus, one physical interpretation of the reciprocal lattice is that it is the Fourier transform of the direct lattice, a mathematical operation which takes into account the repetition of the crystal lattice

2nd intuition: reciprocal lattice vectors as specific plane wave states

Consider a set of points **R** constituting a bravais lattice and a generic plane wave $e^{i\boldsymbol{k} \cdot \boldsymbol{r}}$

For a general value of k, such a plane wave will not have the periodicity of the lattice, but for a certain choice of k, it will:

The set of all wavevectors **K** which yields plane waves with the periodicity of the lattice is known as the reciprocal lattice

The way to state this mathematically, is that the following expression applies for all spatial coordinates **r** (why? Because the **R** vector is defined as a translation operation which leaves the lattice invariant)**:**
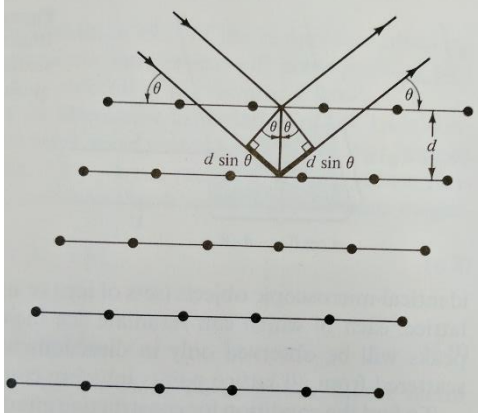
$$e^{i\boldsymbol{K} \cdot (\boldsymbol{r} + \boldsymbol{R})} = e^{i\boldsymbol{K} \cdot \boldsymbol{r}}$$

$$e^{i\boldsymbol{K} \cdot \boldsymbol{R}} = 1$$

This expression holds if $K \cdot R$ is an integer multiple of 2π, which we showed in the exercise above

Scattering: application of reciprocal lattice

Old way:

Ray 1 travels a distance $2d\sin\theta$ longer than ray 2

For them to **constructively interfere,** this path length difference, must be an integer multiple of the wavelength of light, $n\lambda$

This gives the usual formulation of Bragg's law, $2d\sin\theta = n\lambda$

Bragg's law can be reformulated using the reciprocal lattice

Theorem: the set of reciprocal lattice vectors **G** determines the possible x-ray reflections
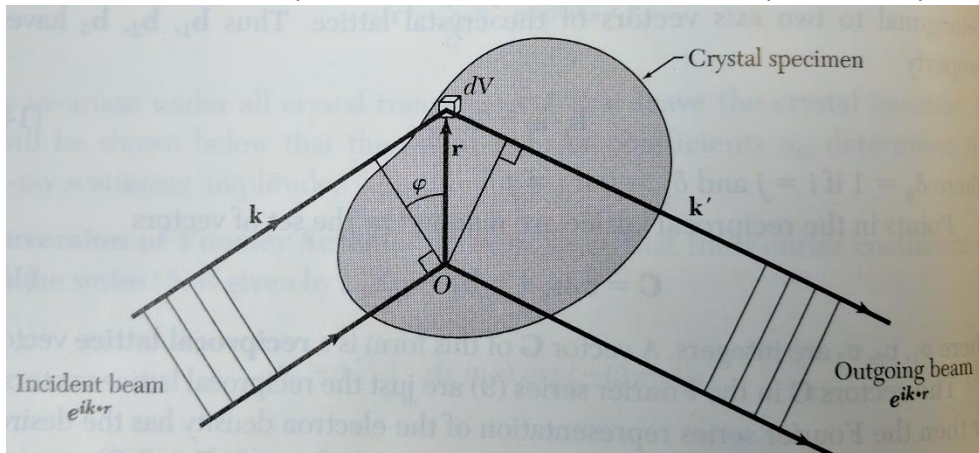
In the figure above, the incident beam is a plane wave given by $e^{ik \cdot r}$. We consider the wave scattered from two different positions in the solid: the origin (given by O) and a volume element **r** away, called dV. The wavevector **k** encodes the wavelength of the light $k = 2\pi/\lambda$ and also its propagation direction.

Step 1: find **phase** difference of the **incoming** beams as they travel to O as compared to dV (confusing point in figure: k and r have different units)

The **path length** difference is given by $r\sin\phi$

Lets express that path length difference as a phase difference (what fraction of 2pi?)

In words, the phase difference is given by $\frac{\text{path length difference}}{\text{wavelength}} * 2\pi$. The first term gives the number of wavelengths which fit in the path length difference (not necessarily an integer) and the factor of 2π tells you what fraction of a full wave cycle this path length difference corresponds to. This gives a phase difference of $2\pi r \, \sin\phi/\lambda$

Remember, $k = \frac{2\pi}{\lambda}$ (definition of wave number)

Thus, the **phase difference** of the incoming beam going to O vs going to dV is $\mathbf{k} \cdot \mathbf{r}$ (check graphically that the segment we are talking about indeed represents the component of **r** that is along **k**)

Step 2: find phase difference of diffracted beam from O vs dV

For the diffracted beam, if we go through the same exercise, we will get $-\mathbf{k}' \cdot \mathbf{r}$ (the negative factor comes because **k'** points in the opposite direction relative to **r**; also, there is a typo in your textbook in labeling the outgoing beam, it should be $e^{ik' \cdot r}$)

Thus the total phase angle difference is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$

The wave scattered from dV has a phase factor of $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}$ relative to the wave scattered from the origin located distance **r** away.

Define $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$
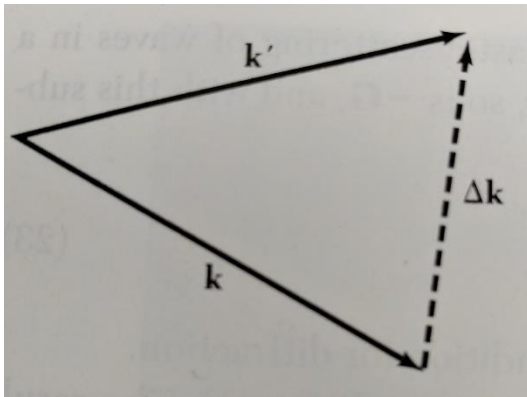
Now, we have to account for the fact that we are not just considering two scatterers, but we are considering an array of scatterers. The relative positions of all of these scatters are given by the lattice vectors: $\mathbf{R} = u_1\mathbf{a_1} + u_2\mathbf{a_2} + u_3\mathbf{a_3}$

The total phase factor from this array of scatterers is given by:

$$F(\Delta\mathbf{k}) = \sum_j e^{i\Delta k \cdot r_j}$$

The **intensity** of the scattered beam:

$$|F(\Delta \boldsymbol{k})|^2 = \sum_{i,j} e^{i\Delta \boldsymbol{k} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)}$$

The separation between any two scatterers in a bravais lattice is given by a translation vector of the lattice:

$$|F(\Delta \boldsymbol{k})|^2 = \sum_{i,j} e^{i\Delta \boldsymbol{k} \cdot (u_1 a_1 + u_2 a_2 + u_3 a_3)}$$

Each of the exponential terms will be equal to 1 if $\boxed{\Delta \boldsymbol{k} = \boldsymbol{G}}$ where **G** is a vector of the **reciprocal lattice**. This is called the **Laue condition**.

Most scattering experiments used to determine crystal structure are **elastic** experiments, meaning the energy (and wavelength) of the incoming and outgoing beam are the same. This also means that the magnitudes of the wavevectors are equal:

$|\boldsymbol{k}| = |\boldsymbol{k}'|$ and $k^2 = k'^2$

With this, the diffraction condition can be re-written as:

$$\boldsymbol{G} = \boldsymbol{k}' - \boldsymbol{k}$$

$$(\boldsymbol{k} + \boldsymbol{G})^2 = k'^2 = k^2$$

$$(k^2 + 2\boldsymbol{k} \cdot \boldsymbol{G} + G^2) = k^2$$

$$2\boldsymbol{k} \cdot \boldsymbol{G} + G^2 = 0$$

$2\boldsymbol{k} \cdot \boldsymbol{G} = G^2$ (we can do this because if **G** is a vector of the reciprocal lattice, so is **–G**)

Detour: Miller indices

The process of finding miller indices:

1. Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3; Integer or fractional intercepts are fine
2. Take the reciprocals of these numbers and reduce to 3 smallest integers
3. Express result as 3 numbers in parentheses, usually no commas (hkl)

Below: examples for cubic lattice
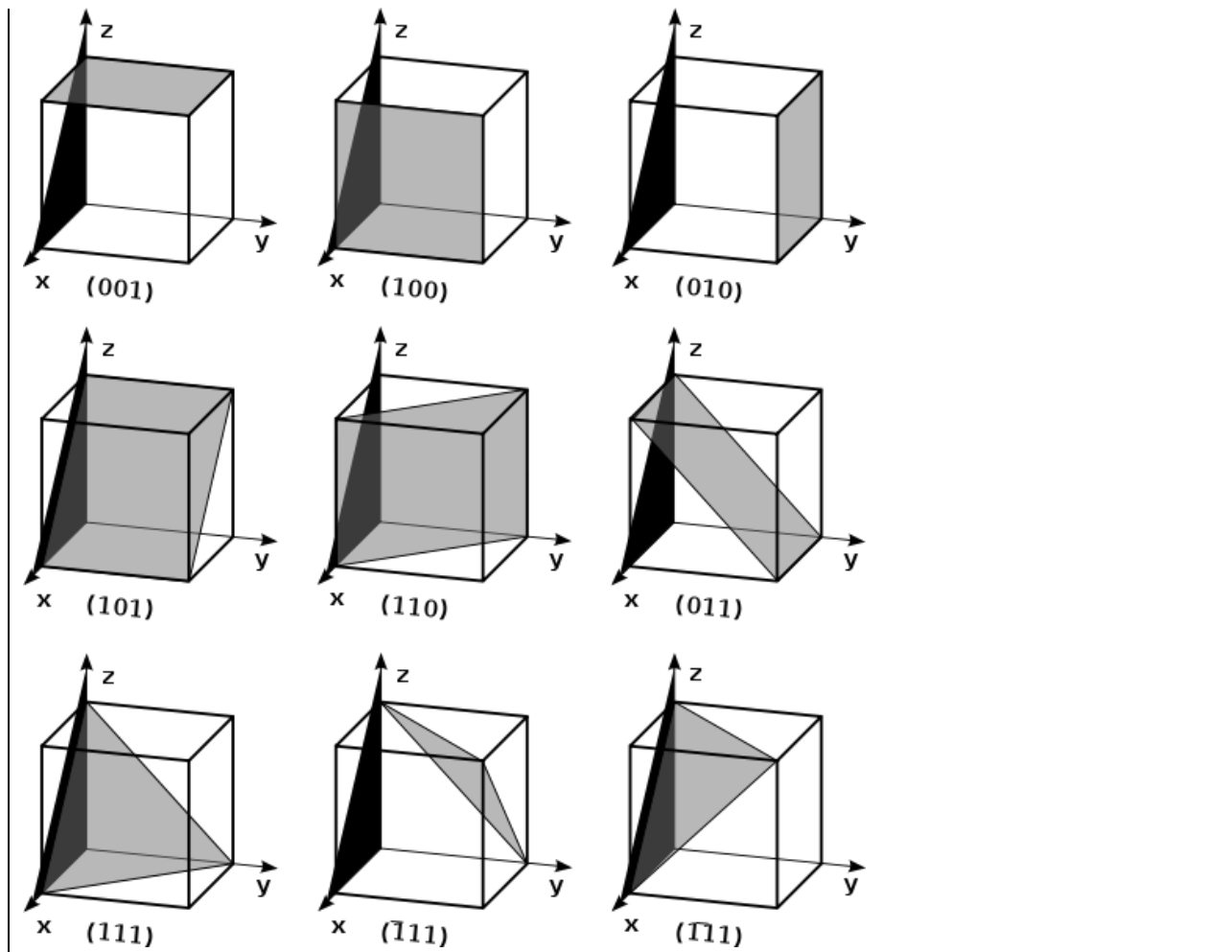
Remember, a crystal lattice can be divided up into equivalent **planes**, a concept which is formalized via miller indices in Ch 1 of your textbook. The spacing between adjacent planes with a specific miller index is called d(hkl).

It turns out that $d(hkl) = 2\pi/|G|$ where $G = hb_1 + kb_2 + lb_3$ is **normal** to the plane of interest (we will show this for specific examples shortly).
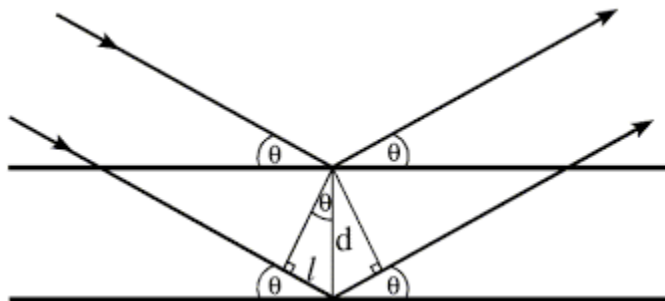
Plugging this result back in to $2k \cdot G = G^2$ we get

$$2\left(\frac{2\pi}{\lambda}\right)(sin\theta)\frac{2\pi}{d(hkl)} = \left(\frac{2\pi}{d(hkl)}\right)^2$$

(θ is the angle of the incident beam relative to the planes. The sine comes in because **G** is normal to the plane of interest, and the dot product takes the component of one vector along the direction of the other)

Simplifying the expression above:

$$\frac{4\pi sin\theta}{\lambda} = \frac{2\pi}{d(hkl)}$$

$$2d(hkl)sin\theta = \lambda$$

This is basically the Bragg condition, sans a factor of integer n in front of . This is missing because the definition of miller indices we use explicitly removes common integer divisors. E.g. (h/n,k/n,l/n) would be reduced to just the (hkl) plane by the definition.

Thus, we have shown the equivalency of Bragg's law and a scattering formalism using the reciprocal lattice.

Methods for measuring crystal structures in reciprocal space

Bragg's law will work if d is of similar magnitude to λ

| Object	Source of diffracted wave
Diffraction grating in class ($d\sim1\mu m$)	Laser pointer, $\lambda = 532\ nm$
Planes of crystal ($d\sim1-10\text{Å}$)	x-rays, $\lambda\sim0.1-10\text{Å}$
Planes of crystal ($d\sim1-10\text{Å}$)	Neutrons, $\lambda = \frac{h}{p}\sim0.3-2\text{Å}$
Planes of crystal ($d\sim1-10\text{Å}$)	Electrons, $\lambda = \frac{h}{p}\sim0.1-1\text{Å}$

Cl⁻
Na⁺
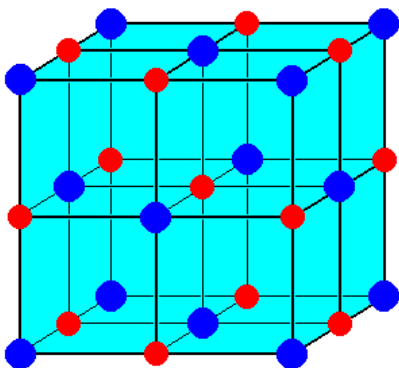
NaCl

Earlier in this lecture, there was a picture of neutron scattering data. Below are some other common methods for using x-rays and wave-like particles to learn about structure. I will not give too much background about measurements, as the intent is just to get used to seeing them and understand what information is extracted from them.

The first two experiments deal use x-rays to measure rock salt (NaCl). This material has a cubic crystal structure, based on the FCC lattice, where each lattice point has one Na and one Cl atom.

Method 1: Laue uses white' (multicolor) x-rays light, and is typically used to learn about rotational symmetries of a crystal or orient a crystal by finding a symmetric orientation. It shines a broad spectrum x-ray light on the sample in order to meet the Bragg condition for many reciprocal lattice points simultaneously. The image below shows a 4-fold pattern because the NaCl is oriented with one of its 4-fold symmetric axes facing the beam.
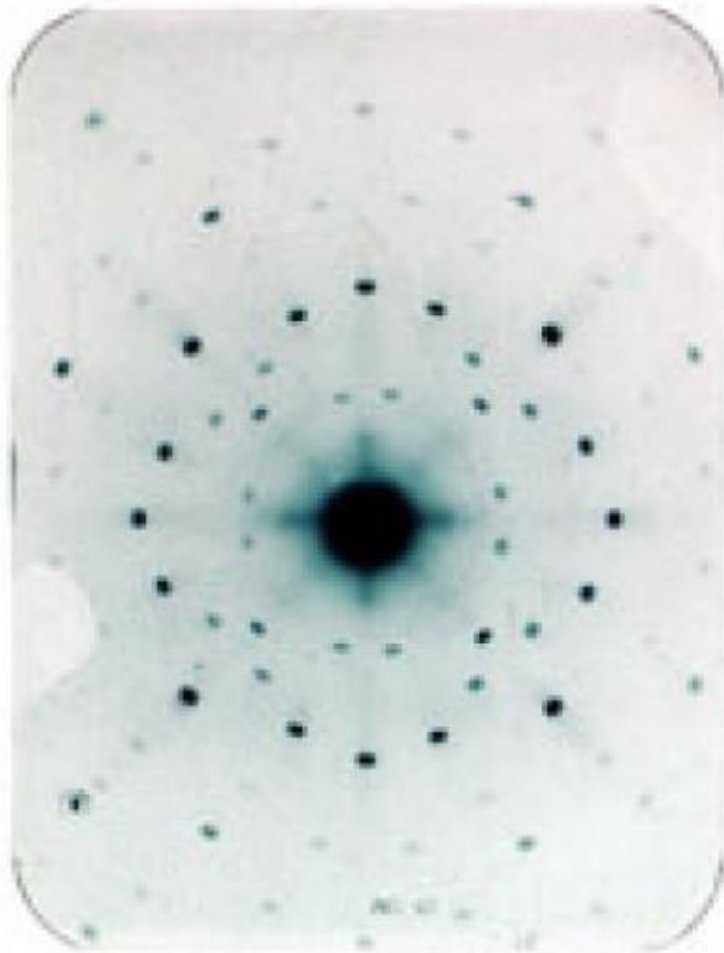
Method 2: 'Powder' x-ray diffraction (XRD) uses monochromatic x-ray light. Reciprocal lattice points are accessed either by rotating the sample (for a single crystal) or by using a 'powder' sample which has crystallites of all possible orientation. This is by far the most common technique for characterizing crystal structures with x-rays. This graph should be read in terms of the Bragg formula: $2dsin\theta = n\lambda$ where the x-axis is plotted as 2θ because that is the angle difference between the incoming and outgoing beam. The labels above the peaks are the Miller indices. When the Bragg formula is applied to this experiment, λ is fixed and known, while the material has a fixed number of ways to divide it into planes. Thus only select angles θ correspond to those select planar spacings, d.
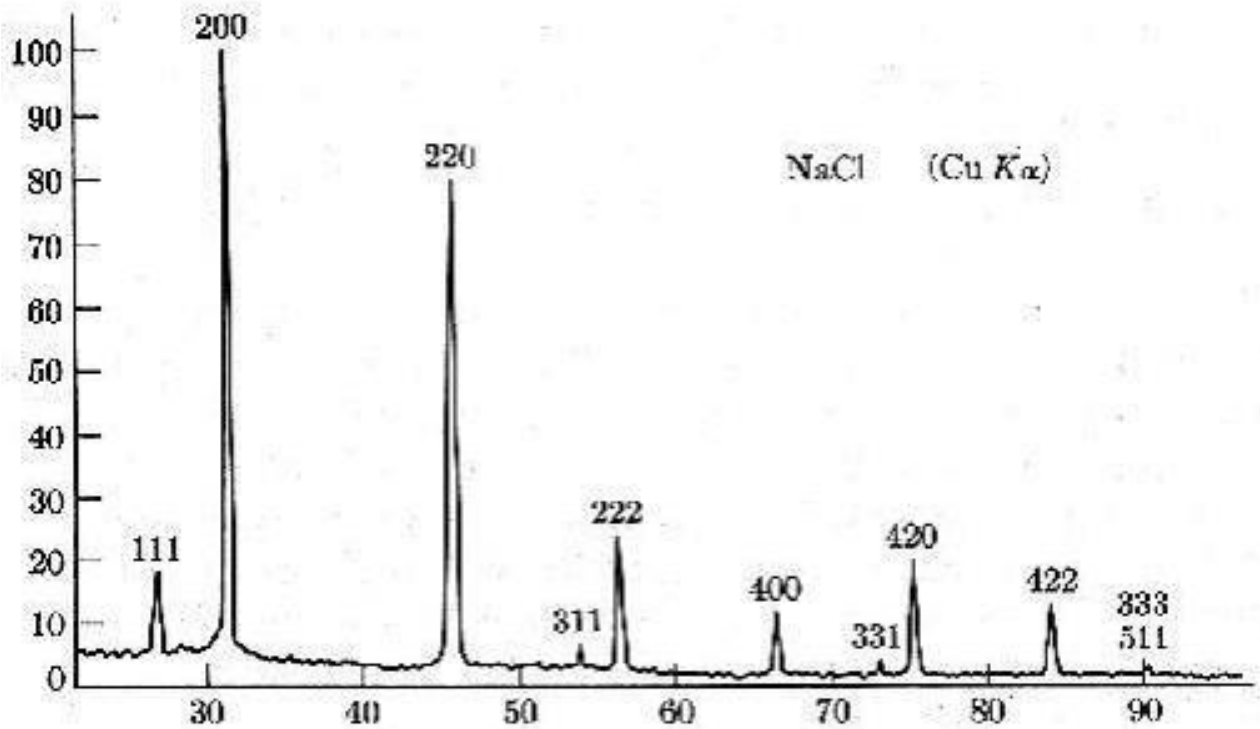
The image below shows Low Energy Electron Diffraction (LEED) data for NaCl. The electron gun shadowing the image is a giveaway that this is some sort of electron diffraction technique. Different reciprocal lattice points (bright dots) correspond to different reflection angles of electrons and hence different positions on the detector. Electron diffraction techniques are extremely surface sensitive (an atomic layer or two), x-rays have slightly deeper penetration depth (a micron or so), and neutrons are truly bulk sensitive.
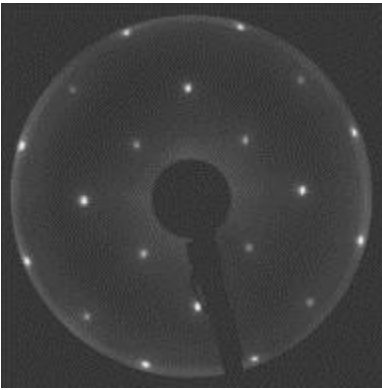

Figure 2. Image source: https://doi.org/10.1016/S0039-6028(01)01391-7