Part IV: Measuring crystals structures

So, how does one go about measuring what the crystal structure is, for a given material? The answer is: look at it! The problem, of course, is that looking with visible light (i.e., the narrow part of the em spectrum, with wavelengths between $\sim 400-800$nm, that can be detected by the photoreceptors in our eyes) is not doing much good. I'm sure you've all seen crystals, and many of them are very beautiful, and some are really expensive because of that beauty, like diamonds and rubies, but we don't see the atoms and how they are ordered. We'll actually discuss in the second part of the course what is it that we see, i.e. why do various crystals have various colors.

But why can't we see the atoms directly?

The answer is that in order to see something, it must be inhomogeneous on a lengthscale comparable with the wavelength of the wave that we use to "look" at it (which, of course, doesn't have to be in the visible part of the spectrum). For example, consider the air around us. It's full of atoms and molecules, of course, but we can't see it. This is because it is homogeneous on the lengthscale of micrometers, i.e. the scale typical for the light in the visible spectrum. Because of this, there is nothing (no region that is more dense, or less dense) for the visible light to scatter on more, or less, so it travels straight and we "see" nothing. We can see, however, clouds in the sky or fog – what happens then is that tiny water or ice droplets form, on the scale of $\sim 0.5\mu m$, which is in the right ballpark. Visible light scatters off of it and then we see that something is there. (Actually, visible light does scatter off of atoms – all light does. In fact, that's the very reason why our sky is blue, because of light scattering off of the atoms in the atmosphere. But that is a low probability event, not likely to happen much on the short distances accessible to my eyes).

Ok, so the point is, if we want to "see" something, we have to "look" at it with waves whose wavelength is comparable to the typical scale for density fluctuations for this object. For a crystal, this means that the wavelength must be in the few $\mathring{A}$ neighbourhood – this is the typical size of lattice constants, so this is the lengthscale for variations in density and other properties.

For light (i.e., em waves) this means that we must use Xrays – they are energetic enough to have such small wavelengths. But of course, we could (and people do) look with other waves. For example, neutrons. We know that particles with momentum p have a de Broglie wavelength $\lambda = h/p$. So, given the mass of the neutron, you can calculate what the energy $E = p^2/2m$ should be so that its wavelength is $\lambda \sim 1\mathring{A}$. The answer is around $0.08eV$, I think – in any event, quite comparable to average thermal energy at room temperature, since $k_B T_R = 25meV$ – this is why these are called thermal neutrons. We could (and people do) look with electrons as well. These are much lighter so they will need to have much larger energy, but that can be easily arranged. The problem is that electrons are charged and therefore interact very strongly with the atoms so they can't penetrate very deep inside a material. Neutrons are neutral, thus much better suited for this purpose.

There are some variations on what one sees depending on what one uses to "look" at the crystal. For simplicity, let's consider Xrays. Again, if you go on to study cond-mat at a more advanced level, you'll learn all about neutron scattering. The main result (seeing the Bragg peaks, see below) is the same, but there are differences in details, as you'd expect.

So, suppose we have a point-source of Xrays, with some chosen wavelength λ and some amplitude A_0. Let's place it at point S, and let's ask what is the light's amplitude at some distance $\vec{R}$. This is a spherical wave, so the answer is:

$$A(\vec{R}) = A_0 \frac{e^{ikR}}{R}$$

where $k = 2\pi/\lambda = \omega/c$ is the wavenumber. The corresponding intensity is $I(\vec{R}) = |A(\vec{R})|^2 = I_0/R^2$;

hopefully this makes perfect sense to you. It only depends on the distance R from the source, but not on the direction from which we look, and it decreases like R^2 because the same amount of energy per unit time goes through each spherical shell. The further we are, the larger the area $4\pi R^2$ is, so the intensity (which is energy per unit time per unit area) must decrease accordingly.

Now suppose that we have the set-up as shown below. The source is at S, the crystal is around O and the detector is at D. We'll assume that the crystal is much smaller than the SO and OD distances (which is reasonable, most crystals are a few mm or so big, while those distances are on the scale of meters).

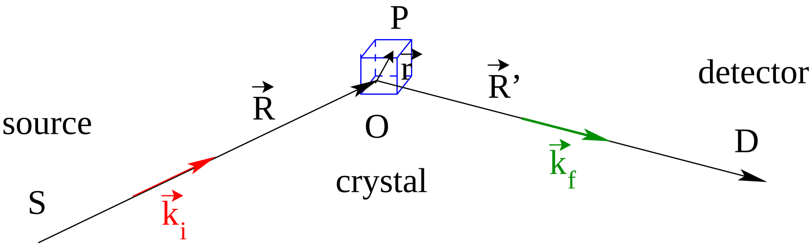

Figure 1: Set-up for a Xray scattering measurement.

As we just said, the amplitude of the light arriving at a point P located at a distance $\vec{r}$ (as measured from O) inside the crystal is:

$$A(\vec{r}) = A_0 \frac{e^{ik|\vec{R}+\vec{r}|}}{|\vec{R}+\vec{r}|}$$

since the total distance to the source is $\vec{R}+\vec{r}$. If $|r| \ll |R|$, we can Taylor expand and keep the largest term, to find:

$$A(\vec{r}) = A_0 \frac{e^{i\vec{k}_i\cdot(\vec{R}+\vec{r})}}{R}$$

where $\vec{k}_i$ is parallel to $\vec{R}$ (see figure). You might recognize this as the formula for a planewave with momentum $\vec{k}_i$, which is precisely what it is. All it says is that very far from the source, on a short lengthscale of order r, the curvature rate of the spherical wave is so small that it looks planar.

The probability of this wave of amplitude $A(\vec{r})$ to scatter is proportional to the density $\rho(\vec{r})$ of the electrons at that location – they feel the electric field associated with the wave, can absorb it and re-emit it in any other direction (electrons act like little antennae). In any event, if there are no electrons at some point, there is nothing to scatter the light there. Once the light is absorbed by the electrons at $\vec{r}$, they act as a new point source, scattering light in all directions equally. So, after scattering, its amplitude at the detector, which is located at $\vec{R}'-\vec{r}$, will be:

$$A_D = \int_{crystal} d\vec{r} A_0 \frac{e^{i\vec{k}_i\cdot(\vec{R}+\vec{r})}}{R} \cdot \rho(\vec{r}) \cdot \frac{e^{ik|\vec{R}'-\vec{r}|}}{|\vec{R}'-\vec{r}|}$$

The integral is simply because we must sum all the waves that scatter to D, to find the total amplitude in the detector. If $R' \gg r$, we can also simplify the last bit just like we did for the incident wave, so we get:

$$A_D = \int_{crystal} d\vec{r} A_0 \frac{e^{i\vec{k}_i\cdot(\vec{R}+\vec{r})}}{R} \cdot \rho(\vec{r}) \frac{e^{i\vec{k}_f\cdot(\vec{R}'-\vec{r})}}{R'} = f(R,R',k) \int_{crystal} d\vec{r} e^{i(\vec{k}_i-\vec{k}_f)\vec{r}} \rho(\vec{r})$$

where $\vec{k}_f$ is parallel to $\vec{R}'$. Of course, $|\vec{k}_i| = |\vec{k}_f| = 2\pi/\lambda$, i.e. the wave is simply re-directioned but its energy is not changed (this is known as elastic scattering). In the second equality, I pulled out all the terms that depend only on the general geometry out of the integral. This will contribute an overall (boring) constant, which I'll ignore from now on. The important part is the remaining integral, since this is what depends on the crystal structure, through the density of the electrons. The only external quantity it depends on is the difference $\vec{k}_i - \vec{k}_f$, i.e. the wavelength used, which determines the size of these vectors, and the angle between them.

For the integral, let's remember that the density is periodic inside each unit cell. So we can split it as a sum of integrals over individual unit cells. Let n index the unit cells, let $\vec{R}_n$ be their lattice vector, so that when inside unit cell n, $\vec{r} = \vec{R}_n + \vec{\xi}$, where $\vec{\xi}$ explores the volume of the unit cell. Then, $\rho(\vec{R}_n + \vec{\xi}) = \rho(\vec{\xi})$, and we have:

$$A_D(\vec{k}_i - \vec{k}_f) \propto \sum_n \int_{\text{unit cell}} d\vec{\xi} \rho(\vec{\xi}) e^{i(\vec{k}_i - \vec{k}_f)(\vec{R}_n + \vec{\xi})} = \sum_n e^{i(\vec{k}_i - \vec{k}_f)\vec{R}_n} \int_{\text{unit cell}} d\vec{\xi} \rho(\vec{\xi}) e^{i(\vec{k}_i - \vec{k}_f)\vec{\xi}}$$

Let's consider separately the two parts:

(i) The sum over unit cells:

$$\sum_n e^{i(\vec{k}_i - \vec{k}_f)\vec{R}_n} = N \sum_{\vec{G}} \delta_{\vec{k}_i - \vec{k}_f, \vec{G}}$$

where N is the number of unit cells in the sample, proportional to its volume. $\vec{G}$ are our good friends, the reciprocal lattice vectors.

What this equality means, is that if there is a reciprocal lattice vector $\vec{G}$ so that $\vec{k}_i - \vec{k}_f = \vec{G}$, then the sum is maximum (each term contributes 1, so the total is N). If not, the sum is zero.

The first part is easy to check. We know that lattice vectors are of the general form $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, while reciprocal lattice vectors are of the general form: $\hat{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$, where $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{i,j}$. As a result, $\vec{R}_n \cdot \vec{G} = 2\pi(n_1 m_1 + n_2 m_2 + n_3 m_3)$, i.e. a multiple integer of 2π, and therefore $e^{i\vec{G}\cdot\hat{R}_n} = 1$. So indeed, if $\vec{k}_i - \vec{k}_f = \vec{G}$ all the scattered waves interfere constructively since they are all in phase, and we get a peak. If not, the waves interfere destructively and we get nothing (try this at home; maybe I'll give it as a homework problem, it's just a bit of math. You should prove it in 1D first, to simplify things).

Conclusion: It is only possible to see light scattered off the crystal at angles such that $\vec{k}_i - \vec{k}_f = \vec{G}$. This is known as **Laue's condition**.

If this condition is satisfied, the intensity of light scattered in this direction is:

$$I(\hat{G}) = |A_D(\vec{k}_i - \vec{k}_f = \vec{G})|^2 \propto |\int_{\text{unit cell}} d\vec{\xi} \rho(\vec{\xi}) e^{i(\vec{k}_i - \vec{k}_f)\vec{\xi}}|^2 = |S(\vec{G})|^2,$$

where

$$S(\vec{G}) = \int_{\text{unit cell}} d\vec{\xi} \rho(\vec{\xi}) e^{i\vec{G}\vec{\xi}}$$

is known as the **structure factor**. At all other angles, the intensity of light is zero.

Let's see how this works in practice. For simplicity, let's consider a 2D rectangular lattice with lattice vectors $\vec{a}_1 = a_1\hat{x}, \vec{a}_2 = a_2\hat{y}$, see figure below. The reciprocal lattice vectors are, then, $\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2$, where $\vec{b}_1 = \frac{2\pi}{a_1}\hat{x}, \vec{b}_2 = \frac{2\pi}{a_2}\hat{y}$.

Let's now draw all the reciprocal lattice vectors, as I showed in the figure below. Each point in that lattice corresponds to some $\vec{G}$. We also know $\vec{k}_i$ – after all, we decide where to place the sample. I drew a particular choice, from the origin. Remember that the length of this vector is controlled by the wavelength of the Xrays – so we can vary, at will, both its orientation and its length.

For the choice shown below, we now draw a circle of radius $|k_i|$, centered at the tip of $\vec{k}_i$. If a reciprocal lattice point falls on this circle, that means that there is a $\vec{k}_f$ pointed in that direction, where if we place the detector we see a peak. This is known as a **Bragg peak**. Of course that the origin itself always works – but here $\vec{k}_f = \vec{k}_i$ so this is light that is not scattered at all. We're interested in finding other solutions, if they exist.

Depending on how we choose $\vec{k}_i$ and what the lattice is, we might see none or one or many Braggs peaks for it (my example shows only one non-trivial possible solution, but clearly things would change is I adjusted either the length of k_i, and/or its orientation).

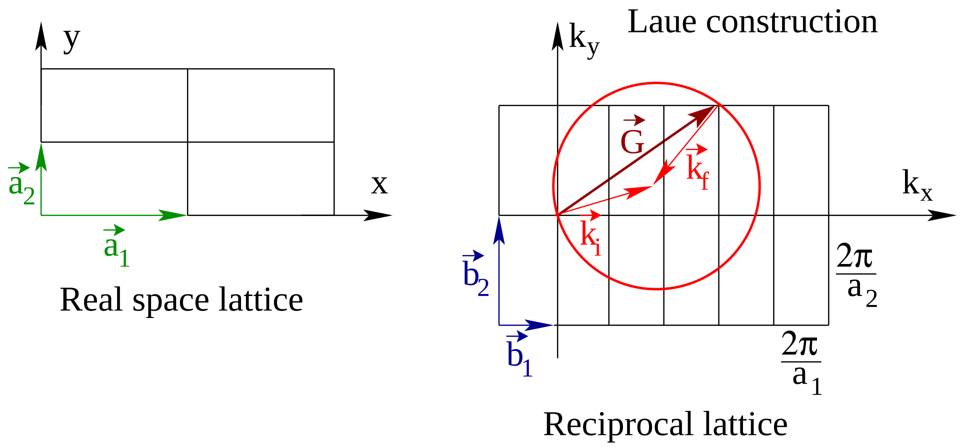

Figure 2: Laue construction: how to find for what $\vec{k}_f$ (i.e., in what directions) we can see Bragg peaks, if we know the lattice structure and $\vec{k}_i$.

Of course, in practice things are the other way around. We choose a $\vec{k}_i$ and then rotate the detector around (thus varying the value of $\vec{k}_f$), and we see a picture sort of like below:

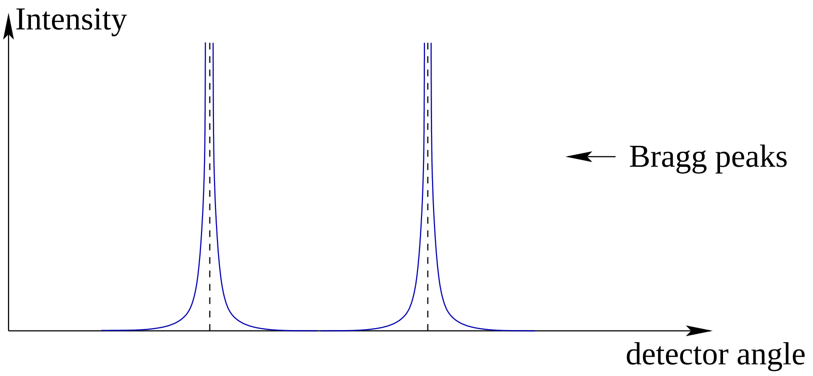

Figure 3: Sketch of the intensity measured as function of detector angle.

Every time we find a peak, we know that that $\vec{k}_i - \vec{k}_f = \hat{G}$, so we found a vector in the reciprocal lattice. Once we have enough of those, we should be able to identify the crystal (if we know several $\hat{G}$, we can infer what the reciprocal lattice vectors are, and from those find the values of a_1, a_2 etc., i.e. figure out the lattice in real space.) The tricky part is to try all possible crystal structures, and see which one has peaks where the experiment finds them

At this point, you might ask: but how can we distinguish between a simple rectangular cell, and a centered one? After all, they have the same unit cell and the same reciprocal lattice, so the Bragg peaks will have the same locations! This can actually done quite easily. It is true that both predict the same Bragg peaks, but remember that we have the structure factor that tells us the intensity of each Bragg peak, so there is more information to be used.

Let's calculate the structure factor first for a simple rectangular cell, and then for a centered one. For the simple cell, there is a single atom in the unit cell (suppose, for instance, that we choose the Wigner-Seitz unit cell, to make this easier). Let me make a pretty drastic approximation, and assume that all Z electrons of that atoms are very close to it, not spread around through all the unit cell. Then, the density $\rho(\vec{\xi})$ is like a delta-function located where the atom is, let's say at location $\vec{d}$ (in most cases, we would choose $\vec{d} = 0$, but as you'll see in a second, it doesn't make any difference). So then:

$$S(\vec{G}) \approx e^{i\vec{G}\vec{d}} \int_{\text{unit cell}} d\vec{\xi} \rho(\vec{\xi}) = Z e^{i\vec{G}\vec{d}}$$

and so the intensity of the peak is $\propto |S(\vec{G})|^2 = Z^2$. In other words, all peaks have the same intensity, which moreover will identify for us the atom we're looking at (if we can properly account for all the other factors).

If we have two atoms in the unit cell, like in the centered case, let $\vec{d}_1, \vec{d}_2$ be their locations in the unit cell. Then, with the same rather drastic approximation, we could split the integral into two parts – one close to atom 1, where all its electrons are closely bunched near $\vec{d}_1$ and one close to atom 2. There is no contribution from anywhere else, so we find:

$$S(\vec{G}) \approx Z_1 e^{i\vec{G}\vec{d}_1} + Z_2 e^{i\vec{G}\vec{d}_2}$$

and the intensity of the peaks is, now:

$$|S(\vec{G})|^2 = Z_1^2 + Z_2^2 + 2Z_1 Z_2 \cos(\vec{G}(\vec{d}_1 - \vec{d}_2))$$

So now different peaks have different intensities, which will allow us to figure not only what are the two atoms, i.e. Z_1 and Z_2, but also the distance between them inside the unit cell (we can always choose one in the origin, so only the relative location is needed).

For example, suppose we have the centered unit cell and both atoms are identical, $Z_1 = Z_2 = Z$. Then $\vec{d}_1 - \vec{d}_2 = (\vec{a}_1 + \vec{a}_2)/2$, and we can see that if $\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2$, then:

$$\cos(\vec{G}(\vec{d}_1 - \vec{d}_2)) = \begin{cases} 1 & \text{, if } m_1 + m_2 = \text{ even} \\ -1 & \text{, if } m_1 + m_2 = \text{ odd} \end{cases}$$

In other words:

$$|S(\vec{G})|^2 = \begin{cases} 4Z^2 & \text{, if } m_1 + m_2 = \text{ even} \\ 0 & \text{, if } m_1 + m_2 = \text{ odd} \end{cases}$$

so precisely half of the Bragg peaks that would be there for a simple rectangular lattice will disappear for the centred rectangular lattice. This is because even though light scattered by each unit cell interferes constructively, in the latter case the light scattered off the two atoms inside the unit cell interferes destructively, so nothing comes out.

If the two atoms are not identical, then the "odd" peaks will have intensity proportional to $(Z_1 - Z_2)^2$, while the even ones are proportional to $(Z_1 + Z_2)^2$. So we can still see easily that it's a centered lattice, and figure out what the two atoms are.

This should give you an idea of how things work. Of course, in practice one has good software to sort out through all the possibilities and figure out what crystal works for a given pattern of Bragg peaks, with their associated intensities. In practice, one also does a better job to calculate the structure factors, since the densities are not necessarily quite so peaked as we assumed here, so there are some corrections to this. But the general idea is correct, i.e. the bigger atoms, with larger Z, scatter the light more, and with some care you can figure precisely what is the unit cell, and how many atoms it has in the basis, and what are they.

Just to (try to) impress you, let me say that people now routinely use Xrays scattering to figure out the folded structure of proteins, such as DNA. As you hopefully know, these proteins are very complicated "molecules", with thousand and thousand of atoms placed wherever they happen to want to stay. Of course, one is shown the beautiful double helix, but in reality the proteins are bundled up, else they wouldn't fit inside the cells. It turns out that under appropriate conditions, one can make a crystal of such proteins, i.e. these complicated "bundles" order spatially in a crystal. One can use Xrays to find not only the crystal structure, but also the basis, i.e. where is each atom inside the protein. That is quite amazing, and should tell you that there certainly isn't much difficulty in figuring out what's the structure of the much simpler crystals we're interested in.

Since I have a bit more space on this page, let me say that oftentimes, this condition for Bragg peaks is presented as coming from scattering off of parallel planes of atoms inside the crystal, leading to constructive/destructive interference, as I sketched below. It is quite easy to check that in this case, the maxima correspond to angles θ for which $2d\sin\theta = n\lambda$ – this is known as **Bragg's condition**. With a bit of goodwill, one can show that this is precisely equivalent to the Laue condition that we just discussed. It turns out that the distance d between parallel layers is related to length of reciprocal lattice vectors which are perpendicular to the layers' orientation, by $G = 2\pi/d$. So, considering various ways to choose layers (I only showed one, but of course there are infinitely many ways to group the atoms in parallel layers), you can find all the Bragg peaks.

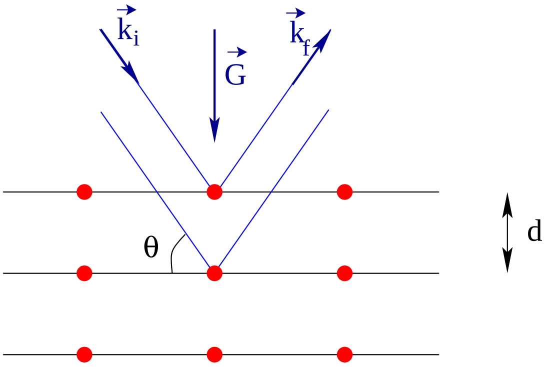

Figure 4: Sketch of the scattering off "planes" of atoms, leading to Bragg's condition.

I prefer Laue's formulation because it is more general, for instance it's easier to understand what happens if not all atoms are identical, or if the unit cell is not a nice symmetric one, and to find the Bragg peaks more easily (in my opinion). In any event, if you want to learn more about Bragg's formulation, any elementary solid state book will go through all its details.